^{99}Mo Production Technology Development at LANL

Steven K. Klein
Los Alamos National Laboratory
Advanced Nuclear Technology Group

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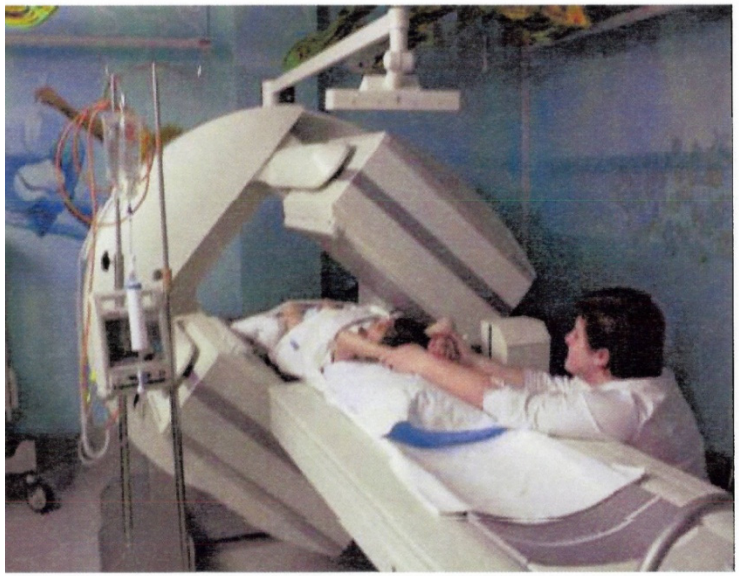
Nuclear Medicine

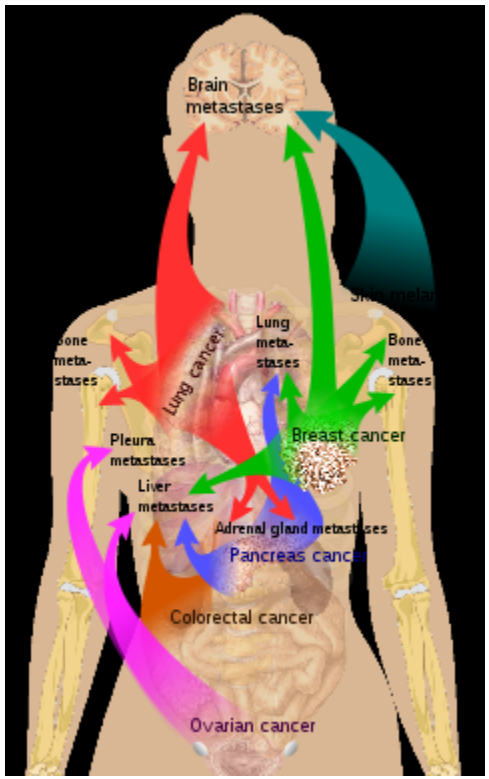
Diagnostic Medical Imaging



Dual Head Gamma Camera

- Single photon imaging remains the workhorse of imaging worldwide. The US performs 18 million procedures annually for its patients; ^{99m}Tc is used in 16 million of them
- LANL produced PET isotope ^{82}Sr used in approximately 23,000 cardiac patients each month

Treatment



^{225}Ac

Leukemia

Prostate

Bladder

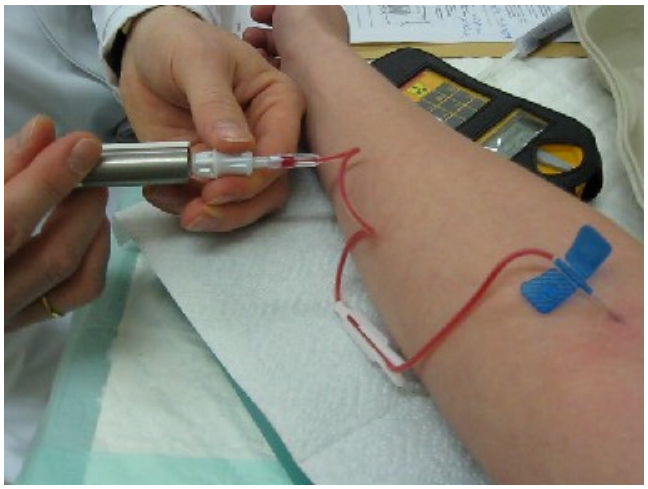
Ovarian

Pancreatic

Melanoma

- LANL is a principal supplier of accelerator produced ^{225}Ac
- ^{131}I will be produced in fissile solutions along with ^{99}Mo

Medical Imaging Using ^{99m}Tc

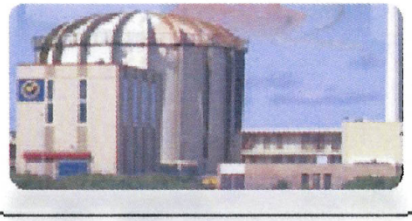
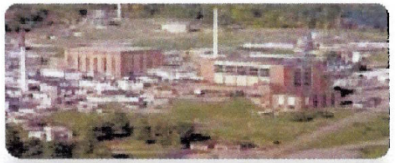
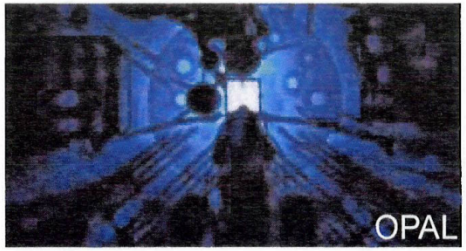


$^{99}Mo \rightarrow {}^{99m}Tc + \beta^- + \nu_e$ (half life ~66 hours)

$^{99m}Tc \rightarrow {}^{99}Tc + \gamma$ (~6 hours half life)

- Bone
- Cardiac
- Lung
- Thyroid
- Brain
- Liver
- Gastrointestinal
- Biliary System
- Lymphatics
- Renal
- CSF
- Labeled Cells
- Oncology

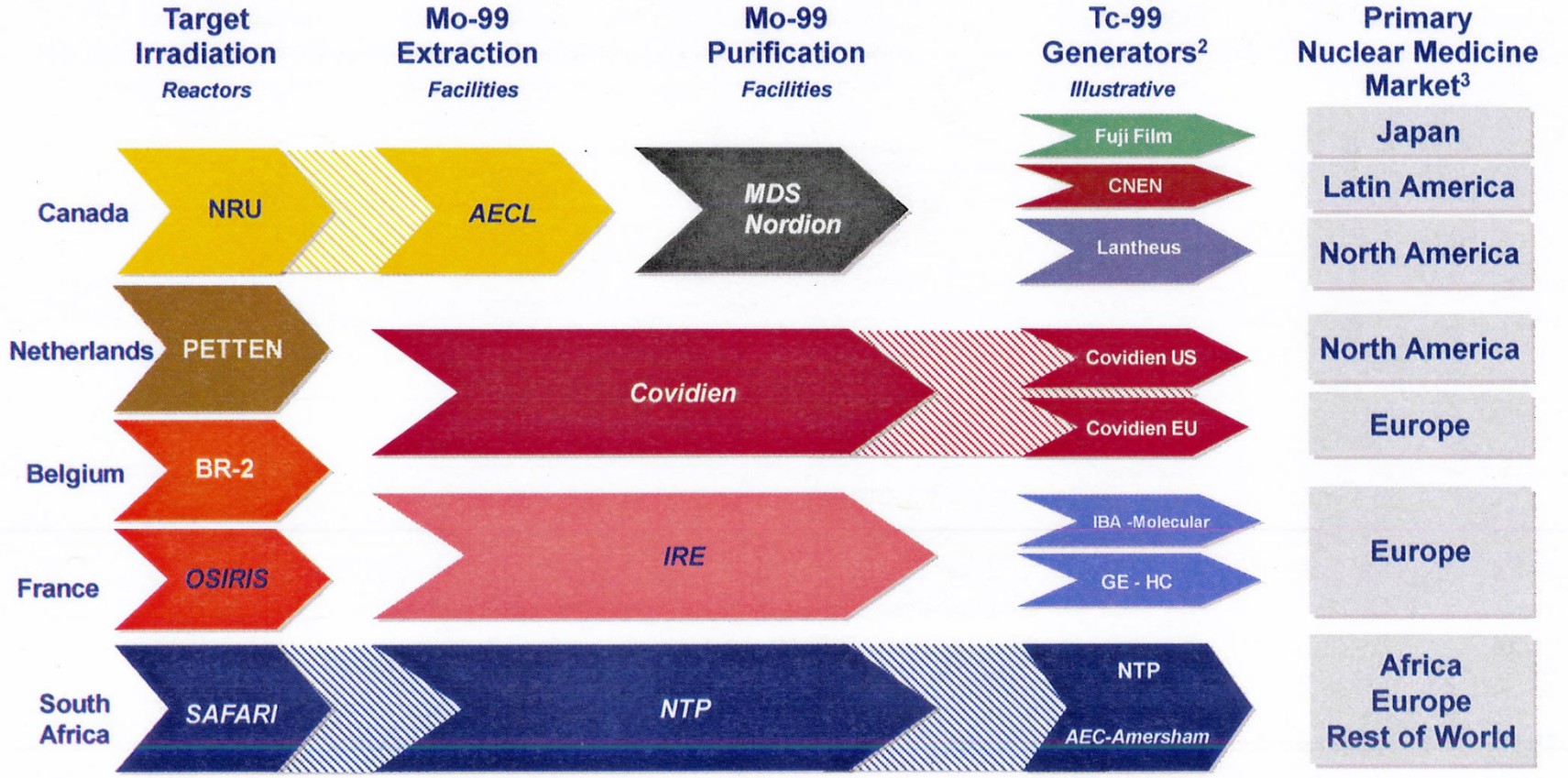
Profile of Current Producers

High Flux Reactor Petten, Netherlands	National Research Universal Reactor Chalk River, Canada	Other Mo-99 Reactors
		
• 48 years old, multi-purpose reactor • 30 - 40% of world Mo-99 supply • Owned by European Commission, operated by Nuclear Research and Consultancy Group • HEU targets • Covidien facilities nearby • "Deformations" in primary system, ingress of bubbles • Minimum three month repair started in March 2010. Restart in August • Final shutdown planned for 2015 • New reactor (Pallas) planned by 2016, cost €300M?	• 52 years old, multi-purpose reactor • 30 - 40% of world Mo-99 supply • Owned and operated by Atomic Energy of Canada, Ltd. • HEU targets • Safety and legislative crisis in 2008 • Heavy water leaks found, out of service since May 2009 • C$72M repair to be finished by "May 2010" (now late July with C$11M per month)	• BR2, Belgium • Osiris, France • Safari-1, South Africa • Three above plus HFR and NRU produce ~95% of world supply; all are 40 or more years old; all HEU targets and/or fuel • New OPAL reactor in Australia producing small amounts • Interim supplies from Polish and Czech reactors

Tc-99 Global Distribution Channels

Five nuclear reactors serve global demand through four distribution channels[1]

Wholesale Processor of Bulk Mo-99



1. Distribution channels illustrate markets where majority of sales occur
2. Most Bulk Mo-99 processors also cross-sell to some other generator companies
3. Indicates markets where majority of sales occur; distributors also serve other markets

Source: SECOR Analysis

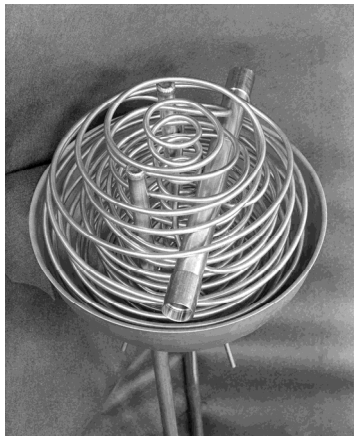
Non-HEU ^{99}Mo Production Options

- Reactor Based
  - ***Aqueous homogenous reactors***
  - LEU reactor fuel and production targets for conventional reactors
- Accelerator Based
  - ***^{100}Mo(γ,n)^{99}Mo***
  - ^{98}Mo(n, γ)^{99}Mo
  - ***^{235}U(n, fission)^{99}Mo (~6% yield)***
  - ***^{238}U(γ,fission)^{99}Mo (~6% yield)***

  Bold Italics: LANL Supports Development

Leveraging LANL History

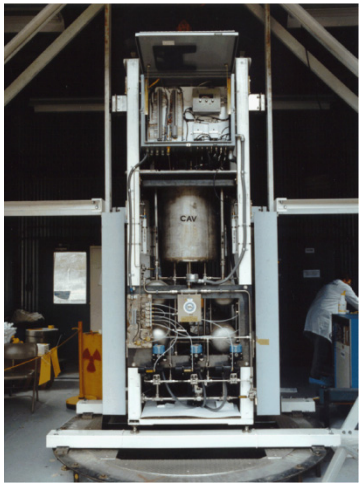
65 Years of AHR Development



LOPO
HYPO
SUPO

SHEBA I
SHEBA II

LANL Demonstrated Separation of ^{99}Mo from SHEBA II



Accelerator Development & Isotope Production

Isotopes Produced:
^{82}Sr, ^{68}Ge, ^{26}Al, ^{32}Si

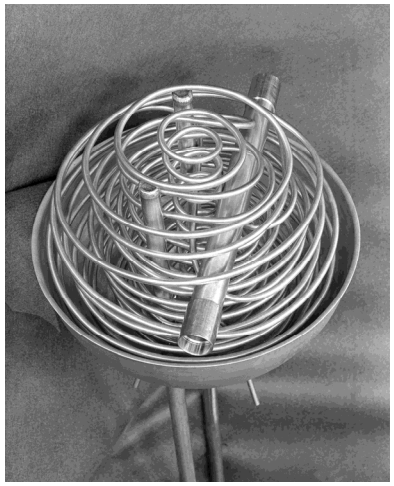
Fissile Solutions and ^{99}Mo Production

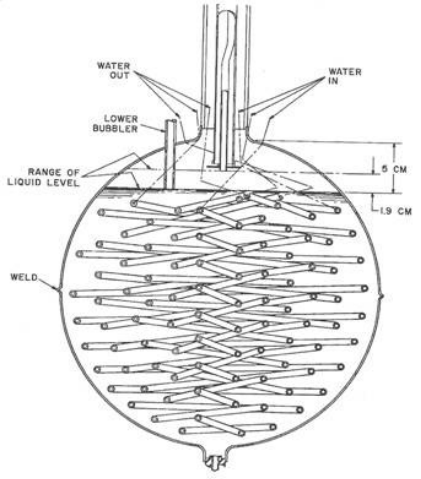
- Solution Fueled Reactors
  - In 1944 the third reactor ever built began operation at Los Alamos with Enrico Fermi at the controls; it was a solution fueled reactor called “LOPO” for Low Power
  - Since 1944 – 2005 a series of solution reactors operated nearly continuously at LANL; one SUPO for Super Power operated from 1951 – 1974, is considered prototypical of a Medical Isotope Production Reactor
- Advantages of Solution Fueled Systems
  - Inherent stability and safety
  - Relative ease of reactivity control
- ^{99}Mo Production
  - Approximately 6.3% of fission products from ^{235}U is ^{99}Mo
  - No neutron source required as fissile solution is it’s own source
  - No target processing required; ^{99}Mo already in solution

SUPO: Prototypical AHR – Most Relevant for B&W Design

Characteristics

- Operated at LANL from 1951-1974
- Spherical, Graphite Reflected, Cadmium & Boron Control Rods, Actively Cooled-30 cm dia.; SS347
- Accumulated ~600,000 kW/h of operation; typically 25kW (1.7 kW/liter) @ 60° C
- HEU Uranyl Nitrate fuel-12.6L; 75gU/L
- Produced ~11 liters/min radiolytic gas @ 25 kW; 2kW/L



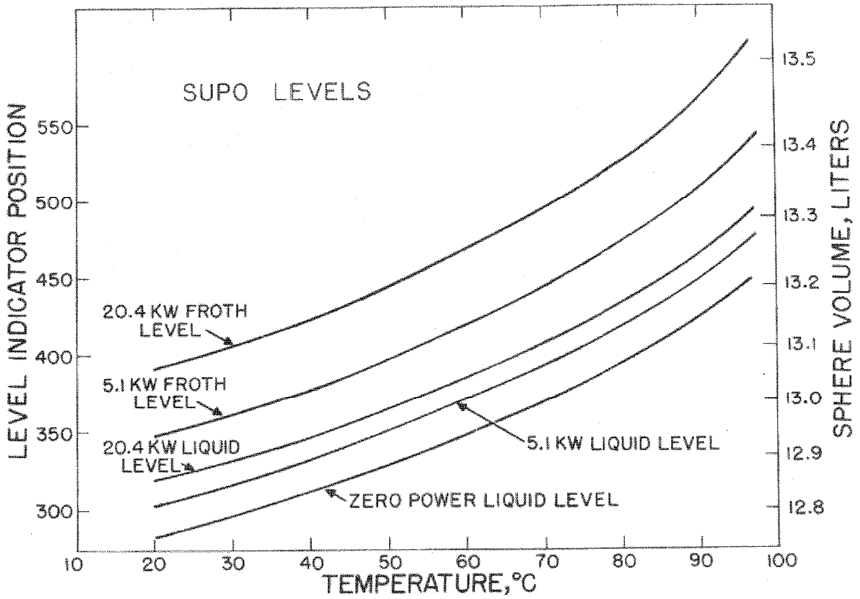


Observations

- **Essentially all data on transient behavior of "cold-unsaturated" core; little on steady-state operation of a "hot-saturated" core**
- **Standard theoretical treatment of transient excursions does not match data**

HYPO/SUPO – At least as many questions as answers

- Data
  - On the surface, these curves seem to indicate the bubble void fraction as a function of temperature.
  - However: How many points were used to generate the curves? The level as a function of temperature is purely an analytic function.
  - Nevertheless, these curves provide the only reference to void fraction as a function of temperature!
- Observations
  - "After the HYPO had been run for several hundred kilowatt hours it was observed that its reactivity had increased remarkably."
  - "After some investigation, it was found that the uranyl nitrate was gradually being converted into basic nitrate and that the free nitrate was presumably being carried away by the flushing air." "Chemical tests indicated that about 30% of the nitrogen had disappeared."



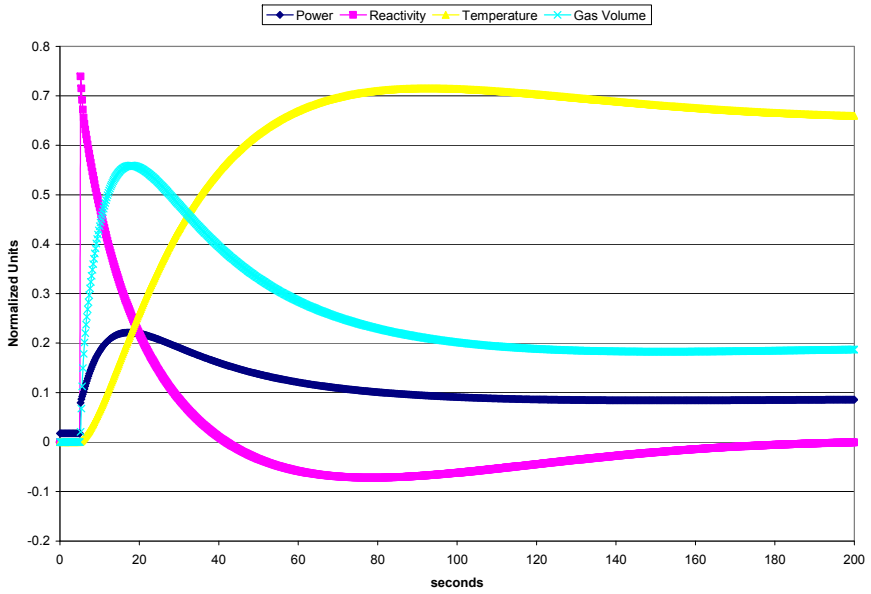
▪Source: L.D.P.King, *International Conference on the Peaceful Uses of Atomic Energy,* "DESIGN AND DESCRIPTION OF WATER BOILER REACTORS, p. 28.

"Steady-State" AHR Model

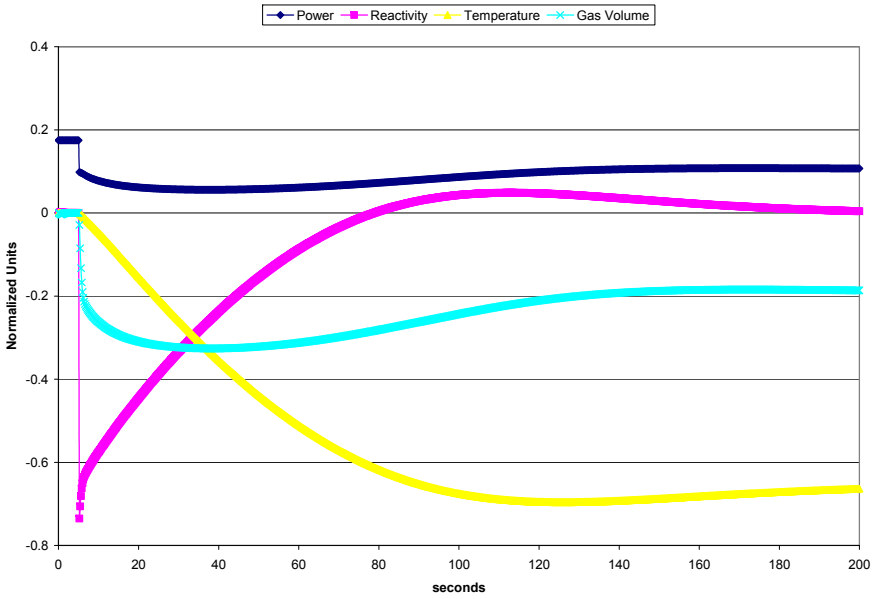
(*Documented in LA-UR-10-04318: "Stability Analysis of the SUPO Reactor"; Kimpland, Hayes, & Grove; June 2010)*

- SUPO empirical data on radiolytic gas production and dynamics could not be reproduced using "standard" theoretical treatments (*Hetrick & Kimpland*), which accurately predict core dynamics of transients from a "cold-unsaturated" core; (*AHR for ^{99}Mo production will operate steady-state with a "hot – saturated" core*)
- Developed new theoretical treatment (spatially independent), which closely matches SUPO performance
- Model is stable (stability refers to the characteristic that an AHR initially at steady state re-establishes a new steady state condition on its own following a reactivity perturbation); model response to changes very docile

Stability Predicted by New Model



Model response following a $0.75 step in the SUPO reactor with an initial steady state power of 25 kW.



Results for a $-0.75 step insertion from an initial power of 25 kW.

Model predicts for well designed cores any available step in reactor power will result in a new steady-state (no unbounded excursions)

Fuel Chemistry Effects of AHR Reactivity

(*Documented in LA-UR-10-04317: "Effects of Solution Chemistry on Aqueous Homogeneous Reactor (AHR) Klein; June 2010)*

- General mechanisms include
  - Dynamics – Indirect effect due to gas transport and heat removal (viscosity, specific heat)
  - Neutronics – Direct effect due to elemental composition over time (Water loss, Nitric acid radiolysis and nitrogen depletion, pH variation, Burn-up)
- Conclusions
  - Solution chemistry strongly affects reactivity (Hydrogen, Nitrogen & Fission Products)
  - Solution chemistry including water make-up, pH stability, and related factors must be part of any AHR control system

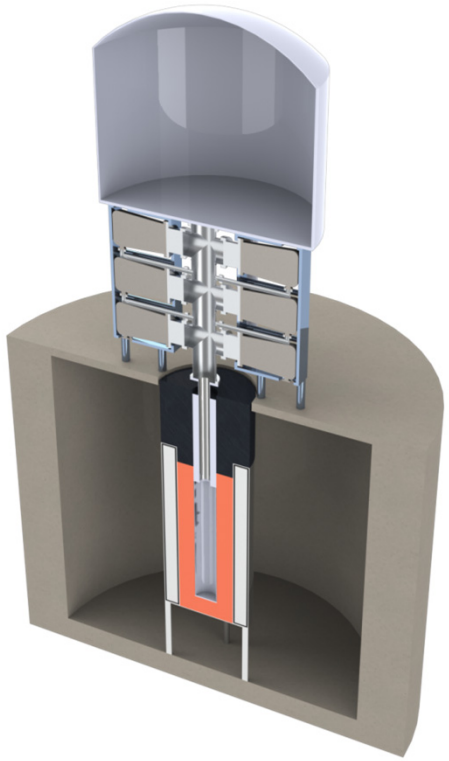
AHR Design Considerations (*State of the Art*)

- Lack of empirical data on steady-state (hot, saturated) behavior forces design dependence on general theoretical principles and anecdotal inferences from historical record of transient conditions
  - Based on theoretical computations of reactivity, considerable excess reactivity must be present to handle reactivity variations over time from radiolytic gas production and fuel chemistry changes due to pH, water content, fission product inventories
  - Off-gas handling system must be capable of handling approximately 0.44 liters/min/kw of Hydrogen + Oxygen in an approximate stochiometric mixture and approximately 2.5 cc/min/kw of mixed oxides of nitrogen (*King, 1955*)
- If cooling is provided internal to the core design of cooling tubes or coils should not impede the transport of radiolytic gas from the system (*Kimpland & Hayes, 2010*)

Concluding Remarks on AHR Development

- While technology had largely been demonstrated over decades the peculiarities of operating at steady-state (hot, gas saturated core) has not been assessed either theoretically or empirically
- Effects of full fuel cycle are only now being examined; limits on uranium concentration, core chemistry, presence of fission product inventories as related to core reactivity and separations efficiency largely unknown
- Greatest impediment to realizing an operational AHR for isotope production is the lack of empirical data

Accelerator-Driven LEU Solution Concept

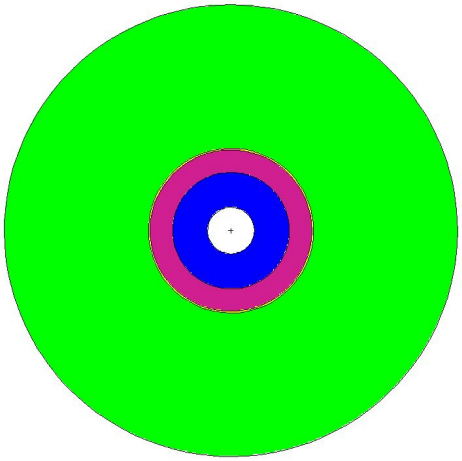


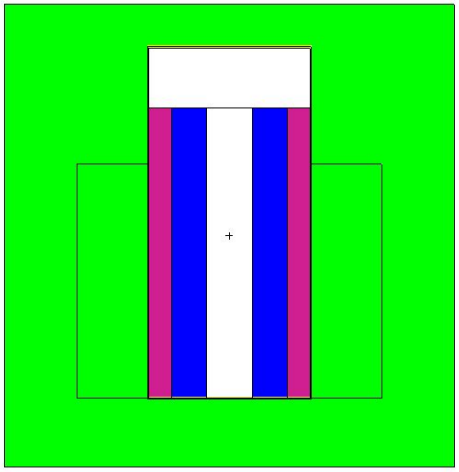
- DT Accelerator driven subcritical system
- Multiplier (Be, NU, DU)
- LEU solution target in reaction vessel
- Moderated and reflected system
- Internally Cooled

Reaction Vessel Design

- Object is to maximize fissions per source neutron (direct measure of ^{99}Mo production)
- Select candidate Low Enriched Uranium (LEU) fuel
  - Uranium concentration (gU/liter)
  - Solvent (heavy or light water)
- Select candidate vessel configuration
- Estimate critical fuel volume for candidate fuel and vessel configuration
- Reduce fuel volume by 5% ("*Kimpland Volume*")
- Estimate production for reaction vessel at room temperature and 80 ° C
- Estimate production effects of variation of fuel pH and temperature

Homogeneous Vessel Concept



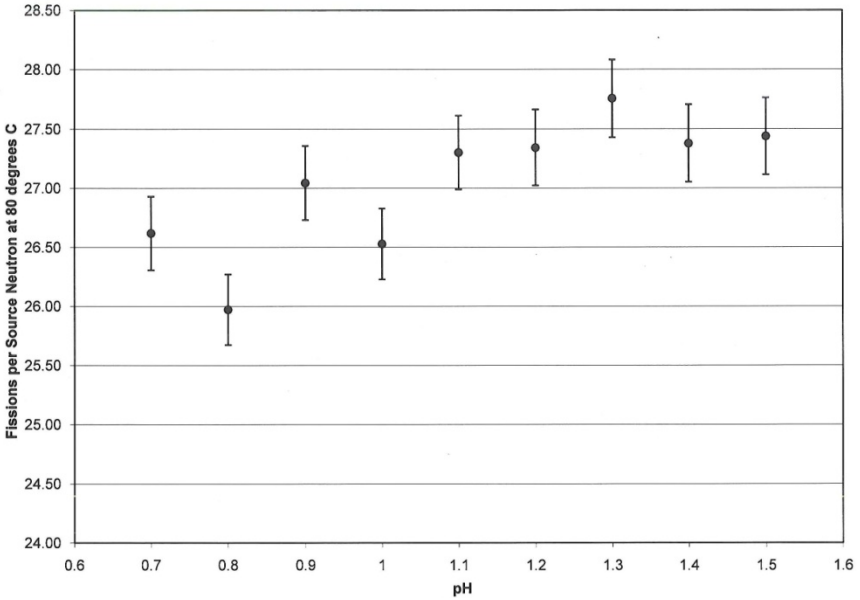


- Fuel
  - 150 gU/liter (19.75% ^{235}U) uranyl nitrate in light water
  - 272 liters critical volume
  - 258 liters Kimpland Volume
  - 7.7 kg ^{235}U
- Configuration (core outward)
  - Accelerator target (20 cm)
  - Be neutron multiplier (15 cm)
  - Fuel (10 cm)
  - Light water reflector

Homogeneous Model Results

- Kimpland Volume
  - 114 fissions/source neutron at 20° C
  - 41.8 fissions/source neutron at 60° C (2.5% density loss: 1.5% temperature effect; 1% radiolytic gas void)
  - 26.5 fissions/source neutron at 80° C (5% density loss: 3% temperature effect; 2% radiolytic gas void)
- Equivalent kW; kW/liter; ^{99}Mo production at shutdown (5 day irradiation; 16 hr cooldown)
  - 368 kW; 1.43 kW/l; 2,514 6-day Ci
  - 135 kW; 0.52kW/l; 922 6-day Ci
  - 85.5 kW; 0.33 kW/l; 584 6-day Ci

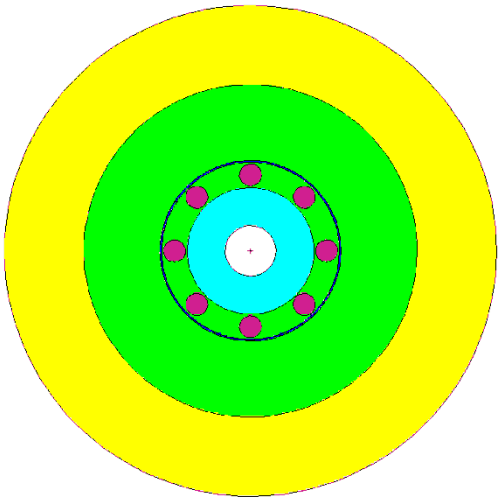
Fissions/source neutron by pH (Kimpland Volume at 80° C)

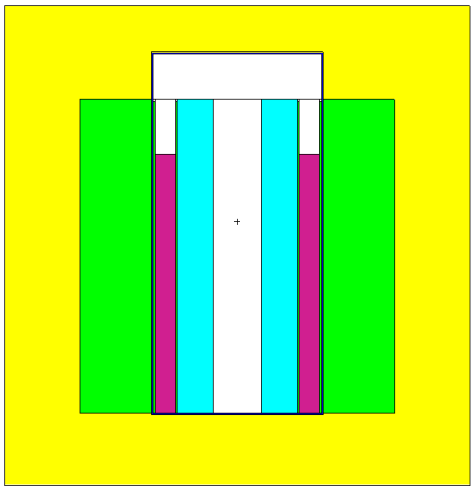


Estimated radiolytic gas volumes:

- 162 l/min H+O; 0.92 l/min N
- 59.4 l/min H+O; 0.38 l/min N
- 37.6 l/min H+O; 0.21 l/min N

Heterogeneous Vessel Concept



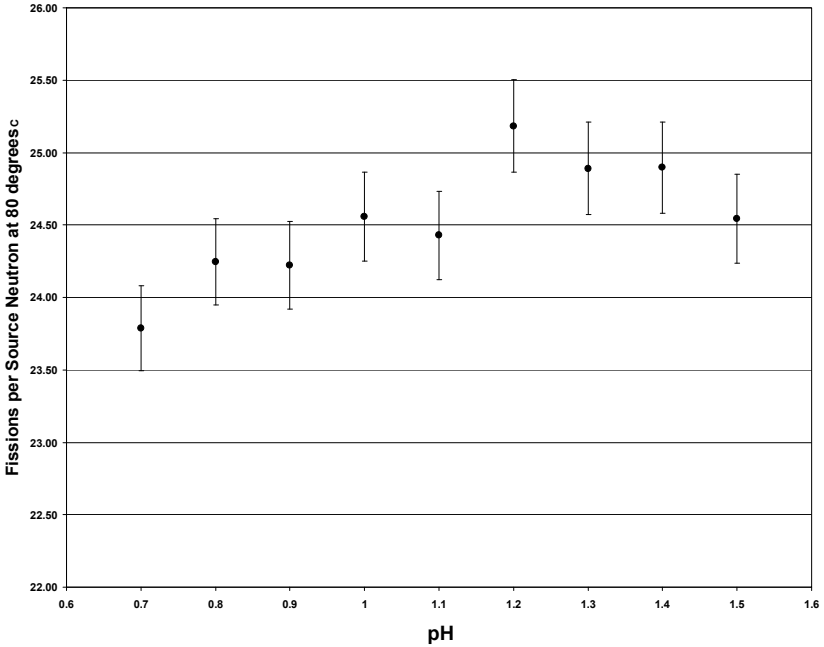


- Fuel
  - 300 gU/liter (19.75% ^{235}U) uranyl nitrate in light water
  - 57.3 liters critical volume
  - 54.4 liters Kimpland Volume
  - 3.3 kg ^{235}U
- Configuration (core outward)
  - Accelerator target (20 cm)
  - Be neutron multiplier (15 cm)
  - Fuel (8 cylinders; 8.7 cm diameter)
  - Heavy water moderator (30 cm)
  - Light water reflector

Heterogeneous Model Results

- Kimpland Volume
  - 90.2 fissions/source neutron at 20° C
  - 29.8 fissions/source neutron at 60° C (2.5% density loss: 1.5% temperature effect; 1% radiolytic gas void)
  - 24.2 fissions/source neutron at 80° C (5% density loss: 3% temperature effect; 2% radiolytic gas void)
- Equivalent kW; ^{99}Mo production at shutdown (5 day irradiation; 16 hr cooldown)
  - 291 kW; (5.3 kW/l); 1,356 6-day Ci
  - 96 kW; (1.8 kW/l); 908 6-day Ci
  - 78 kW; (1.4 kW/l); 736 6-day Ci

Fissions/source neutron by pH (Kimpland Volume at 80° C)



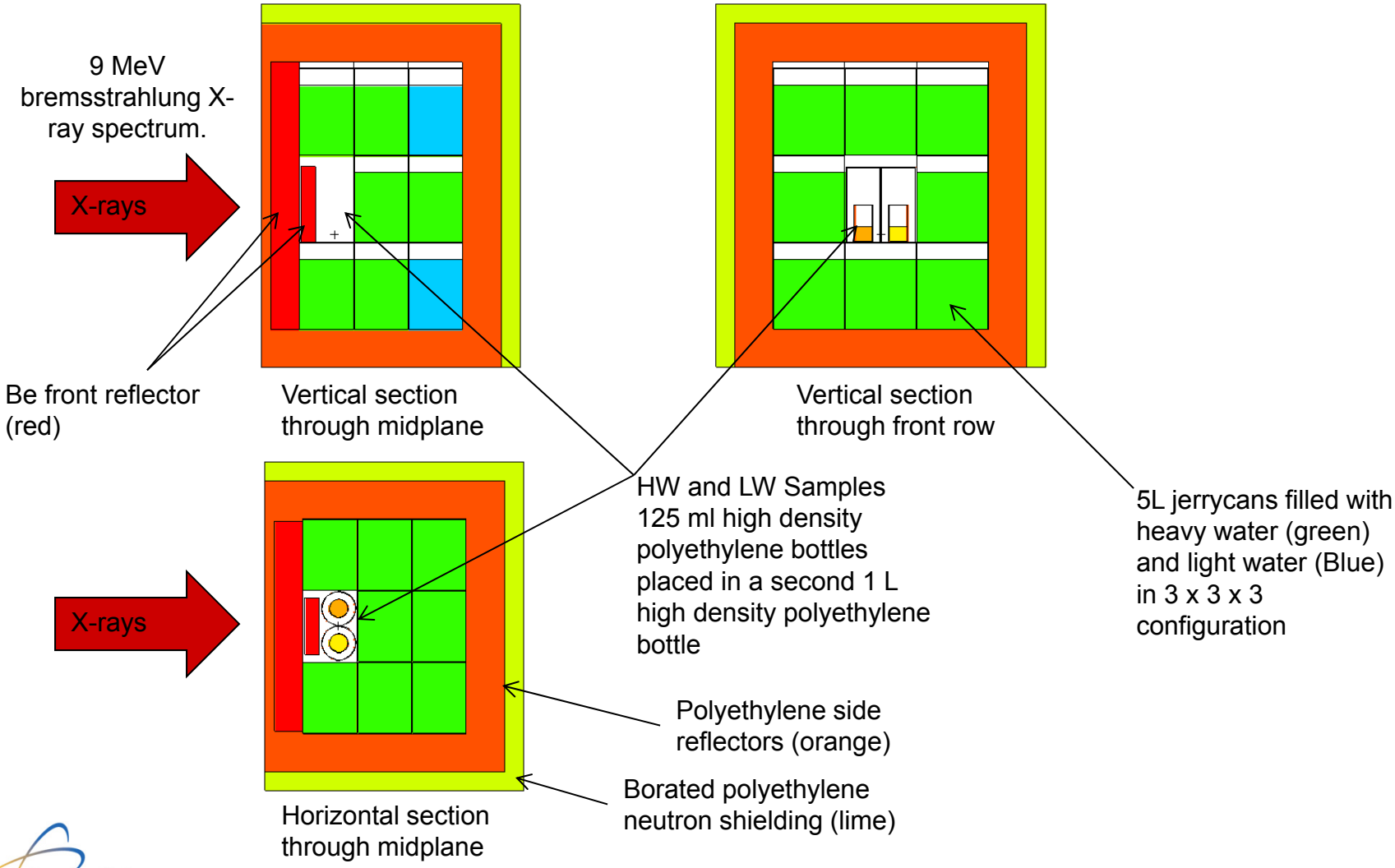
Estimated radiolytic gas volumes:

- 128.0 l/min H+O; 0.73 l/min N
- 42.2 l/min H+O; 0.24 l/min N
- 34.3 l/min H+O; 0.20 l/min N

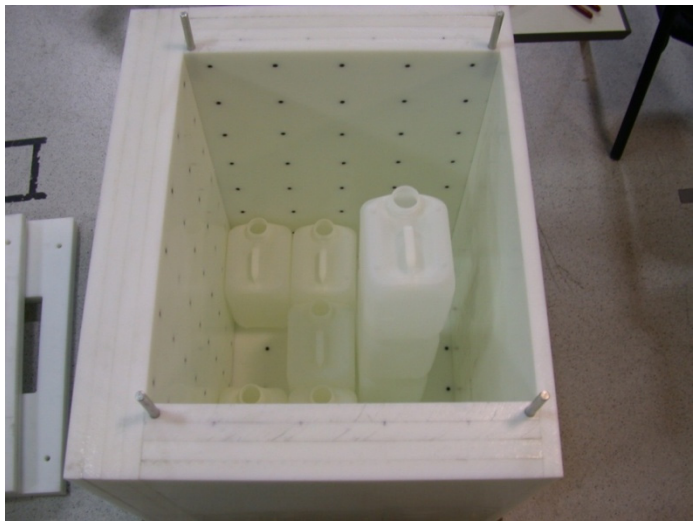
Reaction Vessel Concept Design Conclusions

- Wide Vessel Configuration Design Space
  - At 60° C ^{99}Mo production rate essentially same for heterogeneous or homogeneous systems is achievable
  - Design selection driven by chemistry not neutronics
- Heterogeneous Systems Advantages over Homogeneous Systems
  - More efficient ^{99}Mo production (Smaller fuel volume; less ^{235}U)
  - Easier to cool, handle off-gas, transport solution, control
  - Wider safety margin (from critical)
- Disadvantages
  - Higher power density
  - Higher Uranium concentration
- Uranyl Sulfate has Neutronic Advantage
  - 20% greater production at same volume (or same at 20% lower volume)
  - No pH reactivity variation; no NOx gasses

Linatron Irradiation Experiments



Reaction Vessel Configuration

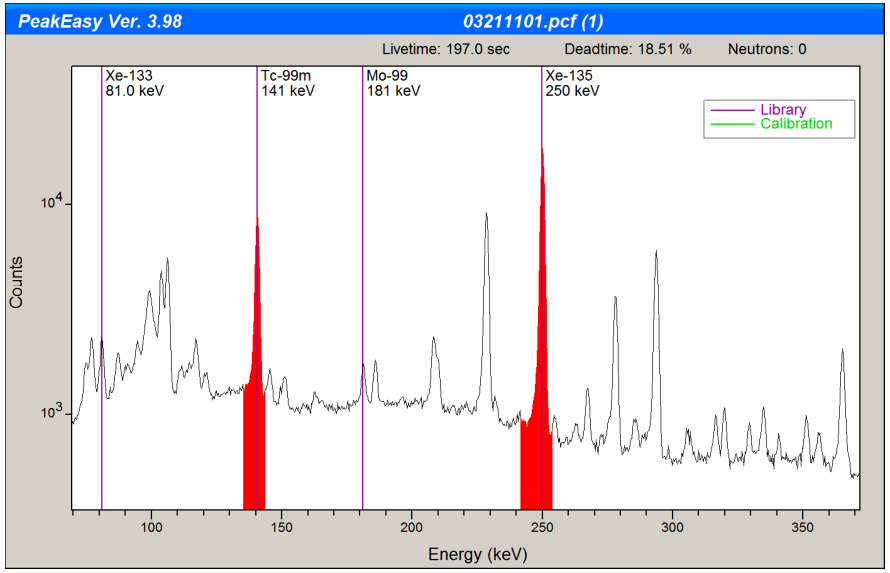


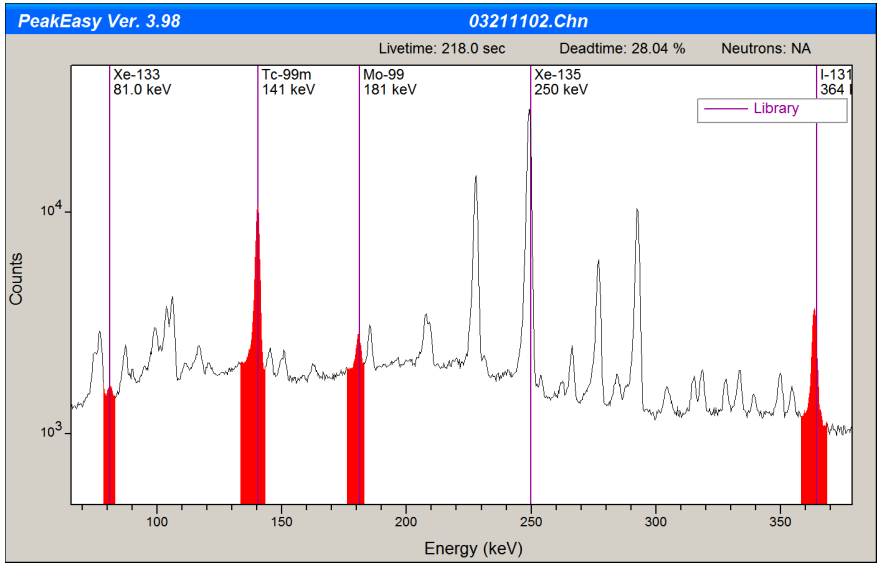
Heavy Water Reflector

LEU Samples

Beryllium Target

Gamma Spectra (18 hrs after irradiation)





Light Water Sample

- ^{135}I (~2.8 μCi)
- ^{99}Mo (~8.7 μCi)
- ^{133}Xe (~8.7 μCi)
- ^{131}I (~1.4 μCi)

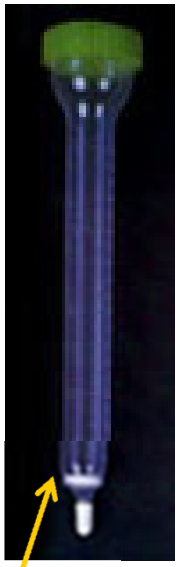
Heavy Water Sample

- ^{135}I (2.3 μCi)
- ^{99}Mo (~7.6 μCi)
- ^{133}Xe (~5.2 μCi)
- ^{131}I (~1.1 μCi)

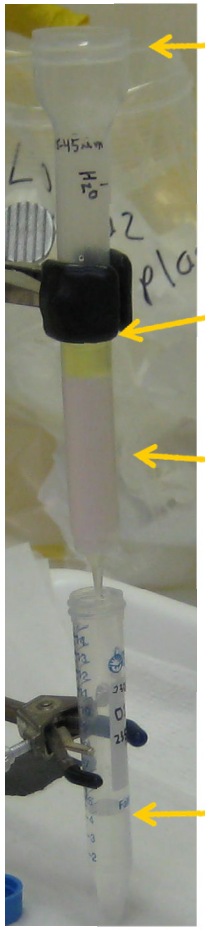
Chemical Separations – Linatron Samples

- Irradiated 70 mL 35 g/L uranium nitrate in both light (H_2O) and heavy (D_2O) water
  - 13.3 % enriched in ^{235}U
  - pH(D) 1 solutions
- Undertook alumina (Al_2O_3) column separation experiments
  - Uranium passed through the column in dilute nitric acid solution
  - ^{99}Mo stuck to the column in dilute nitric acid solution
  - ^{99}Mo could be stripped from the column in 1 M NH_4OH (base)
  - No chemistry differences between light and heavy water
- Successfully separated ^{99}Mo from uranium
  - 83 % recovery from the light water experiment
  - 81 % recovery from the heavy water experiment

The Linatron Separation Experiments



15-45 μm frit – holds the solid alumina sorbent on the column



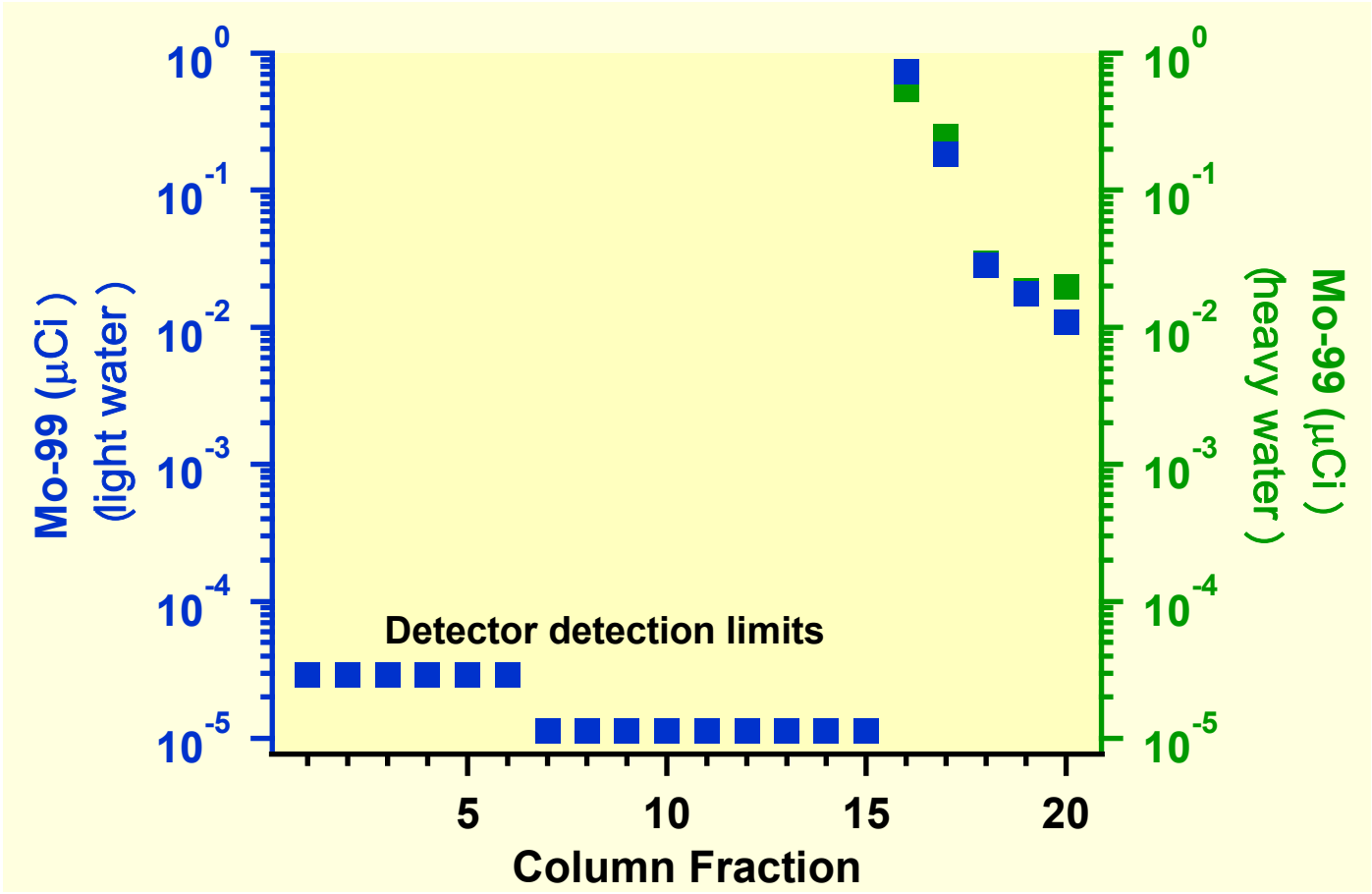
Solutions added to the top of the column in the following order: - 1) Dilute nitric acid pre-wash 2) Irradiated uranium solution (containing ^{99}Mo), 3) Dilute nitric acid 4) Water 5) Ammonium hydroxide.

The irradiated uranium (yellow solution) has just been added to the column – the uranium will not stick to the column.

50-200 μm solid alumina stationary phase, 9.5 mL volume. ^{99}Mo will stick to the column until the ammoniun hydroxide is added, then it will be washed off (eluted).

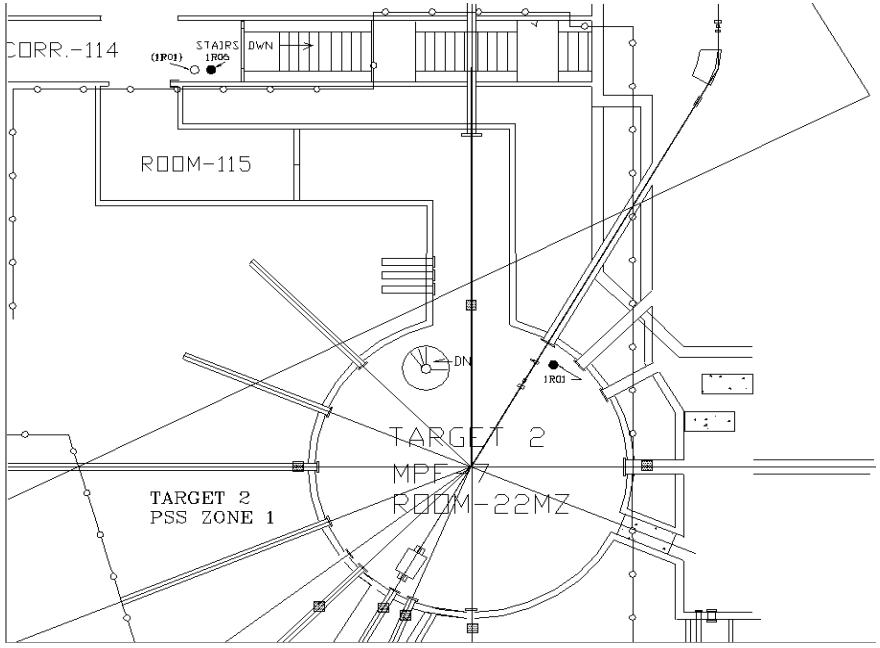
The solutions that pass through the column are collected in 10 mL fractions, 20 in total. In this case we are collecting nitric acid pre-wash.

Linatron Irradiation Separation Experiment
Mo-99 Activity at Count Time (mCi)

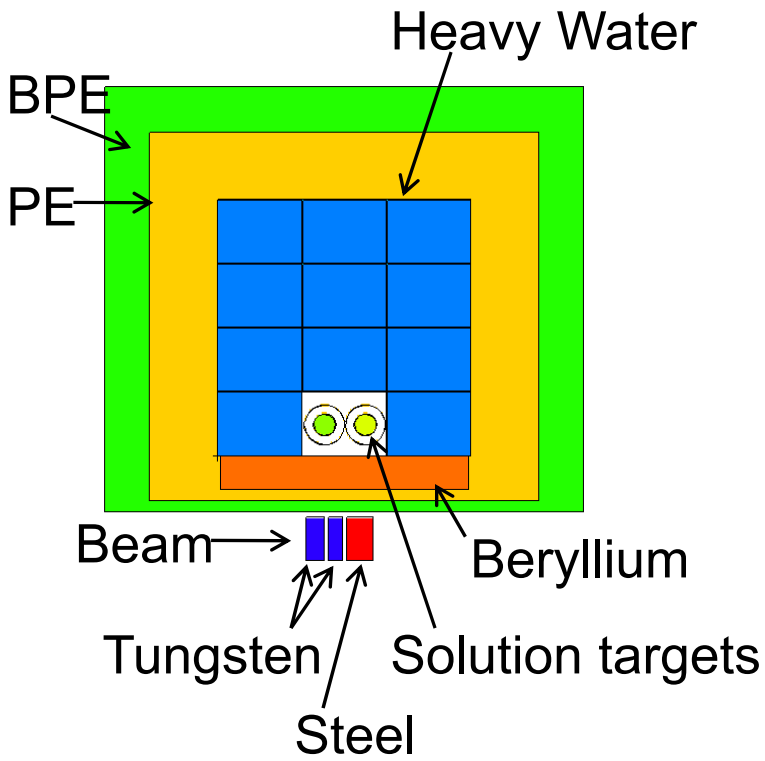


LANSCE Blue Room Experiment

Use of LANSCE Target 2 (Blue Room) to achieve longer sample irradiations with higher neutron fluxes to produce higher concentrations of ^{99}Mo for separations chemistry experiments.



Spallation Target for Blue Room Irradiations



Identical Assembly here

The Blue Room Irradiations used an existing tungsten and steel spallation target to produce neutrons from the 800 MeV proton beam from LANSCE.

Heavy water jerrycans were used as a moderator (blue) and stacked in the arrangement shown to the left.

This was surrounded by a beryllium (orange) and polyethylene reflector (yellow) and was surrounded by borated polyethylene neutron absorber.

Blue Room Separations Chemistry June 2011

- 4 target solutions – now studying higher uranium concentrations (*vs.* the Linatron experiments), and sulfate and well as nitrate
- All target solutions contain 1 ppm molybdenum as Na_2MoO_4 and 1 ppm iodine as KI (mimic production concentrations)
- Natural uranium – 0.72 % ^{235}U

Anion	U Conc. (g/L)	Volume (mL)	pH pre-irradiation	pH post-irradiation	Density (g/mL)
Nitrate	148	8.3	1.00	0.99	1.19
Nitrate	302	8.3	1.02	1.06	1.39
Sulfate	153	8.3	1.03	1.01	1.19
Sulfate	302	8.0	1.07	1.08	1.33

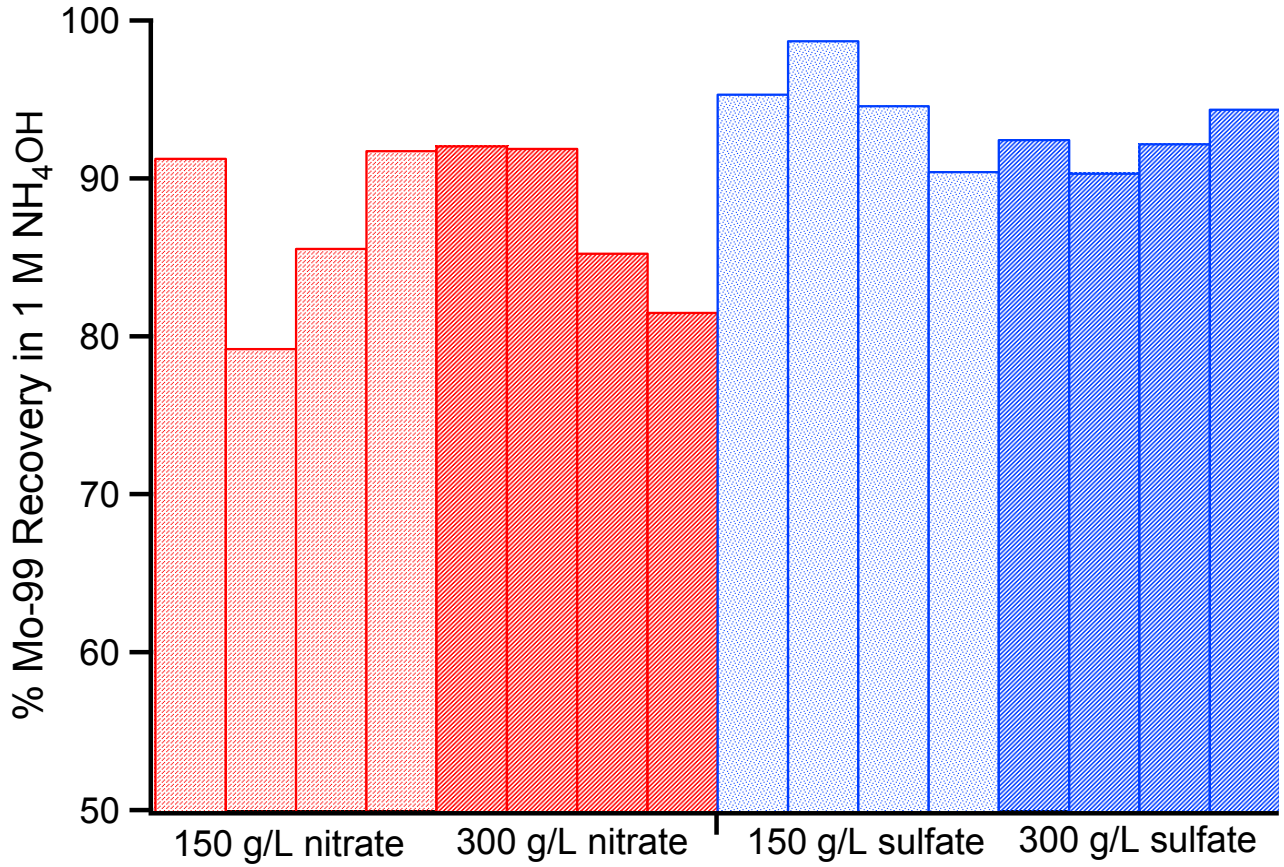
Blue Room – ^{99}Mo production (at t = 0)

Blue Room Experiment June 2011		
Irradiated Solution	Activity (μCi)	Activity (μCi/mL)
8.3 mL 150 g/L nitrate	56.1	6.8
8.3 mL 300 g/L nitrate	97.3	11.7
8.3 mL 150 g/L sulfate	53.0	6.4
8 mL 300g/L sulfate	88.3	11.0

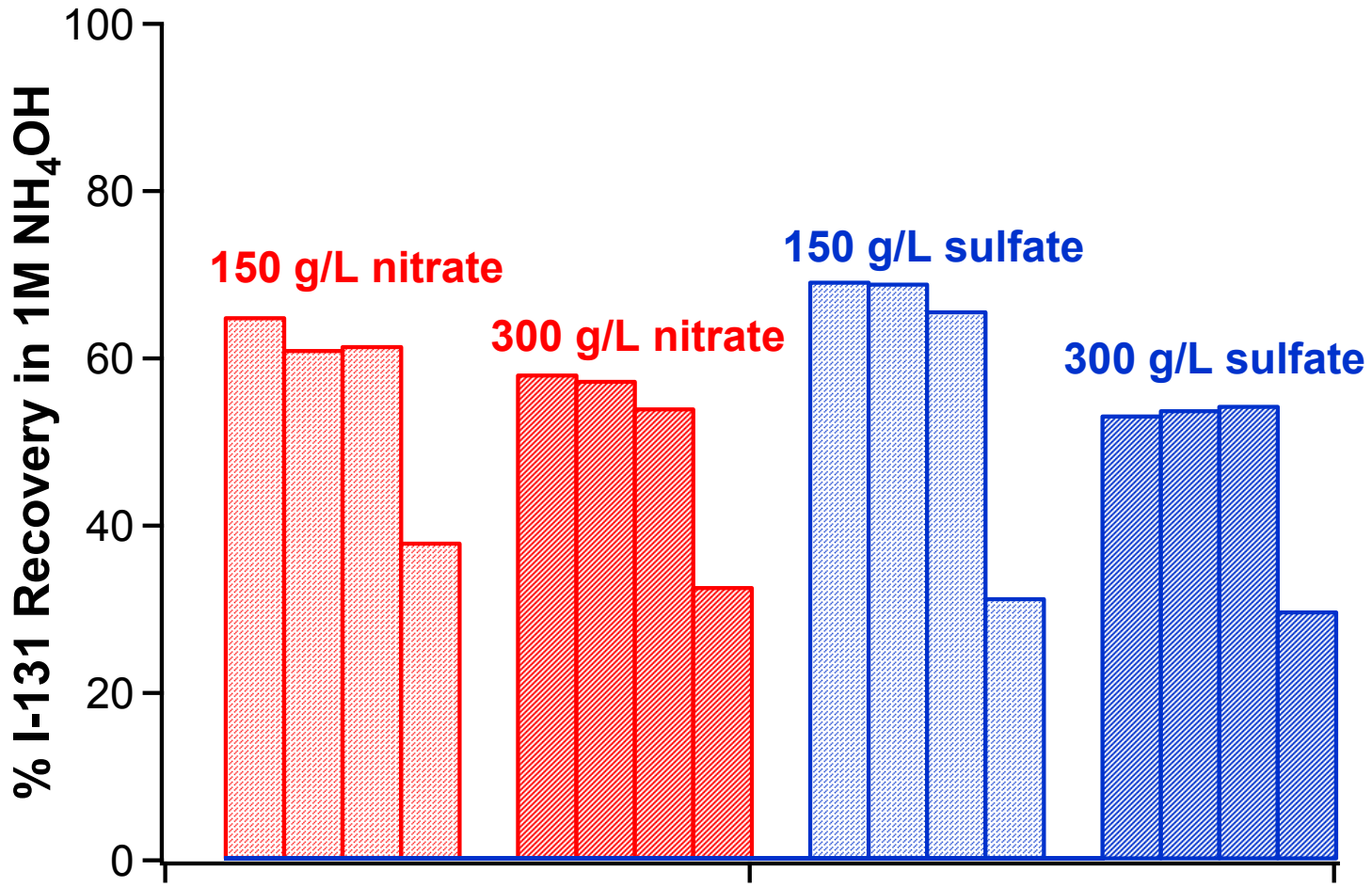
Batch Contact Separation Experiments

- Titania (TiO_2) was used as the solid sorbent. (Titania more efficient at ^{99}Mo recovery than alumina at high uranium loading)
- Contact sorbents with 1.5 mL of irradiated soln. for > 24 hrs at 60 ° C (Aim – to bind the ^{99}Mo to the titania)
- Contact sorbents with 1.5 mL 1 M NH_4OH (base) for > 24 hrs (Aim – to strip the ^{99}Mo from the titania)
- Looked at % radionuclide recovery and, where possible, quantified the extent of radionuclides binding to titania

Near Quantitative ^{99}Mo Recovery in 1M NH_4OH



A significant fraction of the ^{131}I is stripped with 1M NH_4OH

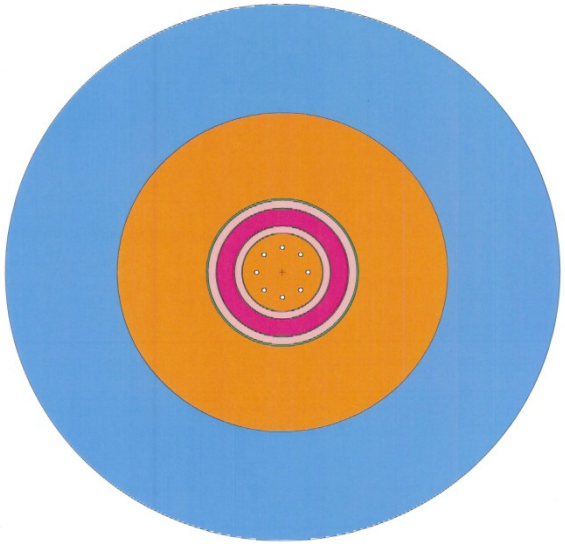


Blue Room Experiment - Conclusions

- At this extent of irradiation there is good recovery of ^{99}Mo from all four target solutions using titania as the sorbent
  - 300 g/L sulfate remains a viable option
  - Obtaining data on ^{99}Mo recovery at higher irradiations is vital
- ^{95}Zr will stick irreversibly to titania
  - Implications for reuse of sorbent material
- ^{131}I will contaminate the ^{99}Mo product (further purification required, as expected)

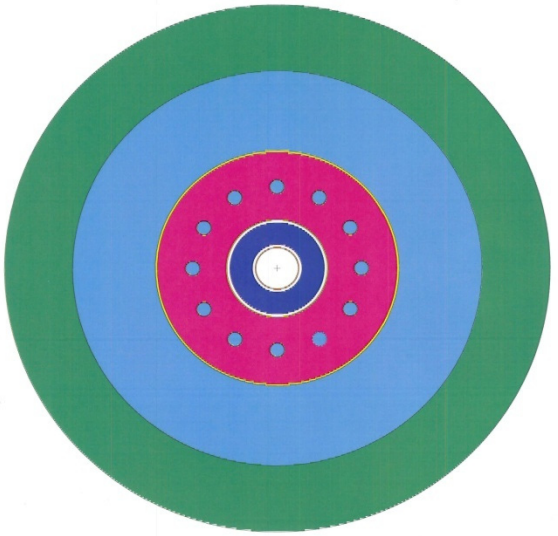
Fissile Solution Systems – State of the Art

AHR – Simpler is Better



- Central heavy water moderator with control rods
- 113 liters 165 gU/liter fuel
- 2 x 4 cm heavy water cooling channels
- Heavy water reflected

Accelerator - Driven



- Central Tritium gas target
- Natural Uranium neutron multiplier
- 420 liters 90 gU/liter fuel
- 12 heavy water in fuel cooling tubes
- Heavy water reflected

Either machine is capable of producing 25% - 30% of US ^{99}Mo need