DEVELOPMENT OF FRONTEND PROCESSING TO ALLOW USE OF HIGH-DENSITY LEU FOIL TARGETS IN CURRENT Mo-99 PRODUCTION FACILITIES

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June 29, 2014
Mo-99 Topical, Washington, D.C

URANIUM ENRICHMENT

> 90% U-235

Nuclear

< 20% U-235

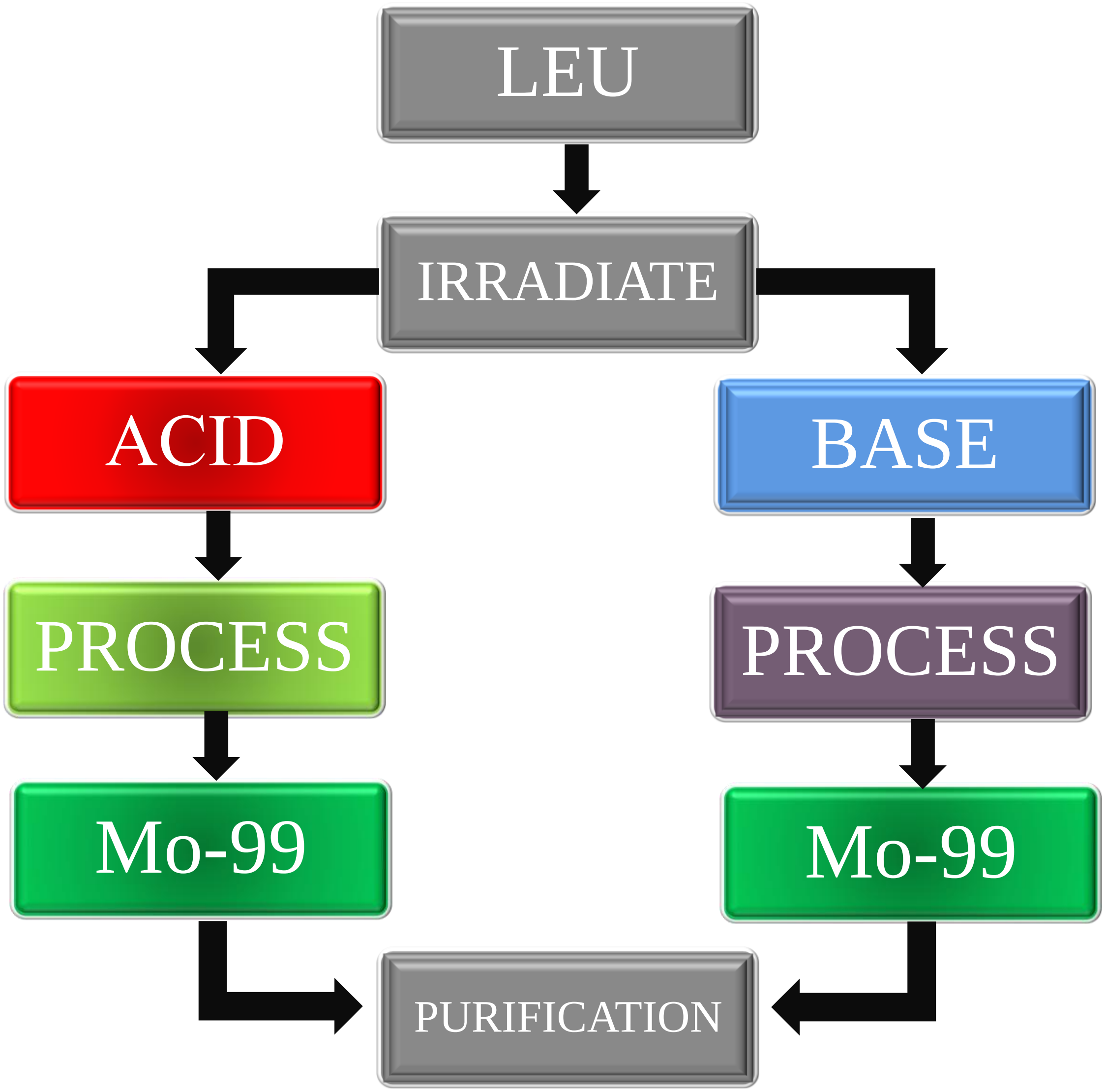
U-Foil

Chemical

UAl_x- Target

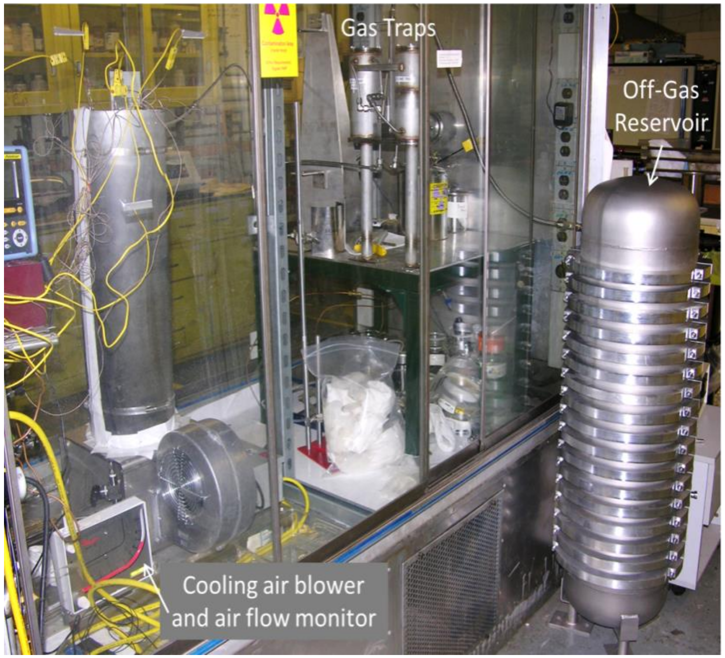
National Nuclear Security Administration

ARGONNE HD-TARGET FRONTEND PROCESSES

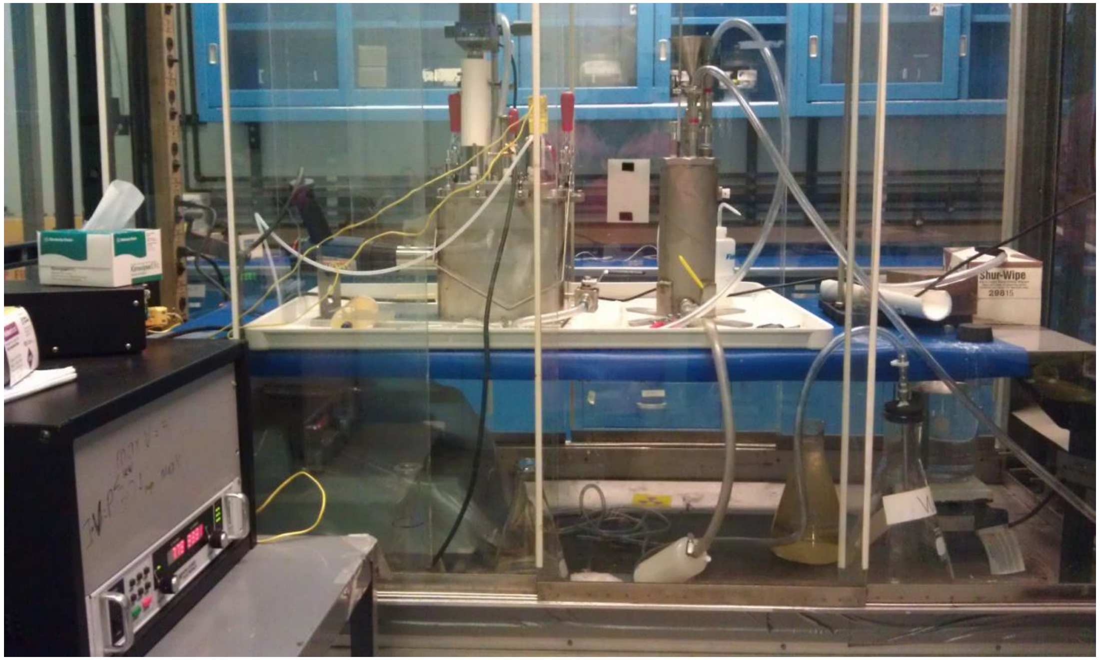


ARGONNE HD-TARGET FRONTEND PROCESSES

ACID PROCESS

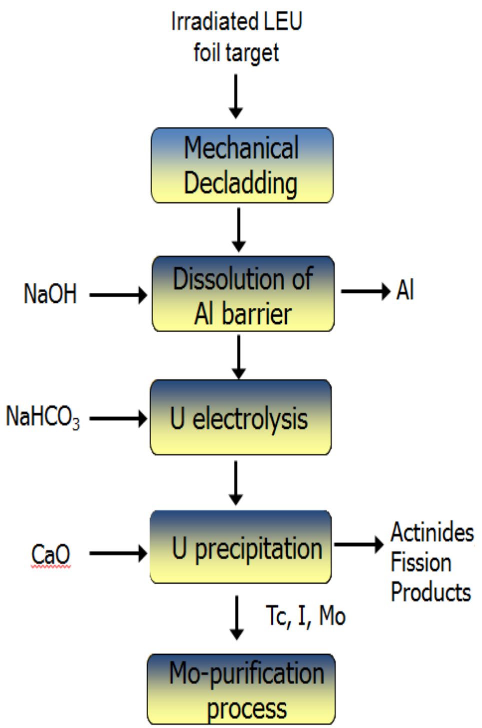


ELECTROCHEMICAL PROCESS



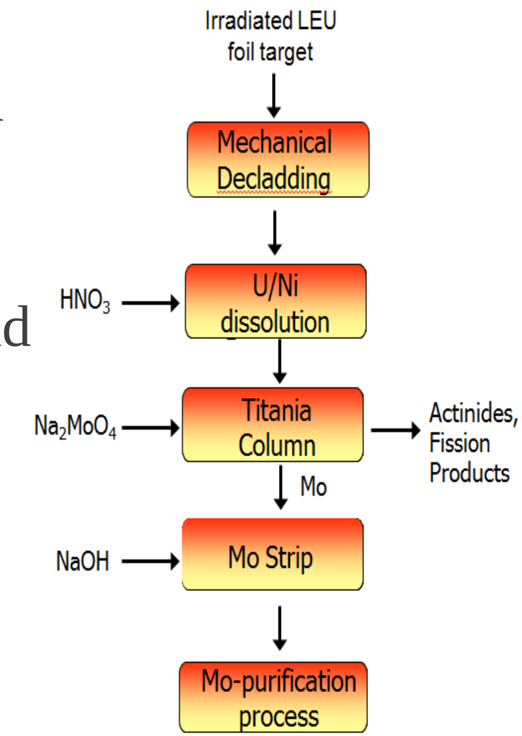
ARGONNE HD-TARGET FRONTEND PROCESSES

ELECTROCHEMICAL PROCESS



- Prototype that can be scaled up
- 20-g U/batch
- Resistant to radiation, corrosion, and hot-cell compatible
- Warm test (DU)
- Hot test (irradiated LEU)

ACID PROCESS



- Full-scale design
- 250-g U/batch
- Resistant to radiation, corrosion, and hot-cell compatible
- Cold test (Ni)
- Warm test (DU)
- Hot test (irradiated LEU)

LEU IRRADIATIONS AT ARGONNE

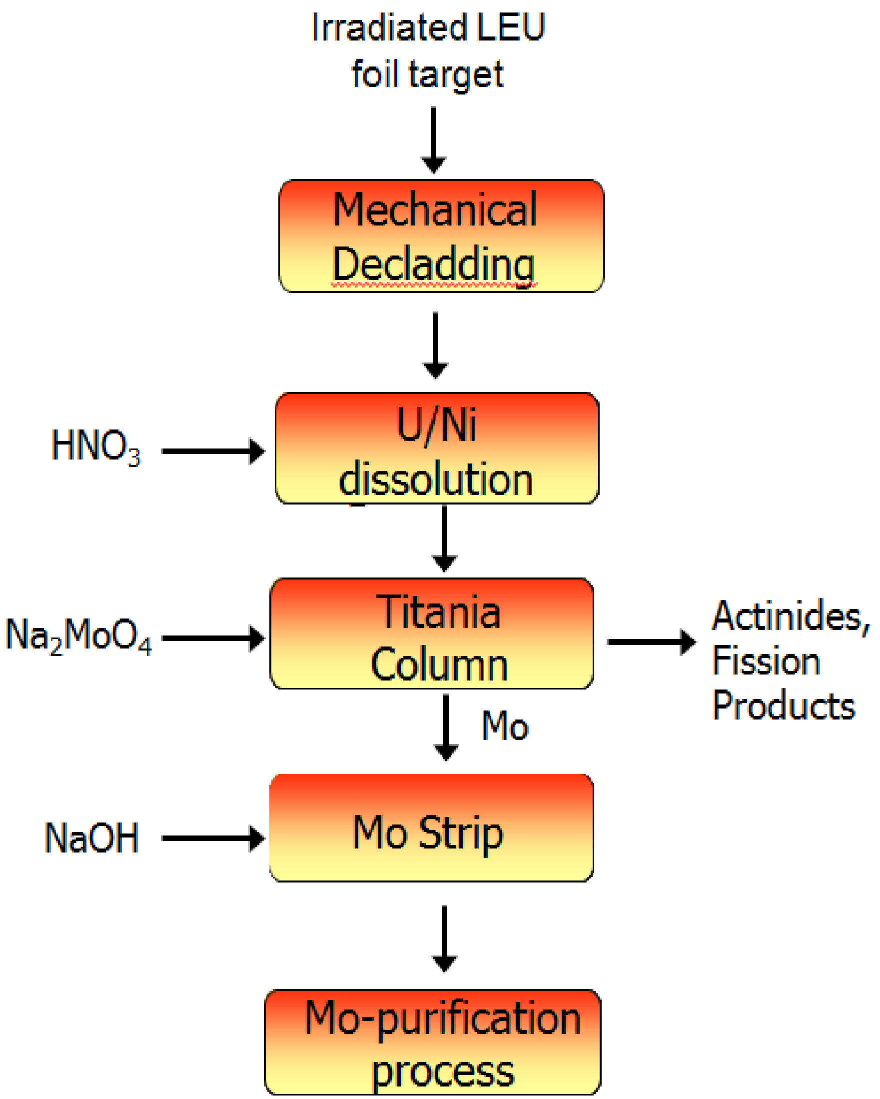
- LEU foils: 6 – 15 grams
- Mimic fission recoil barriers: Al (electrochemical) / Ni (acid)
- Thermal neutron flux: $\sim 10^{11}\ n \times cm^{-2} \times s^{-1}$
- 10 minute irradiation
- Over-night cooling
- Calculations: 50-100 µCi ^{99}Mo

THE ACID PROCESS

- Uranium foil dissolved in nitric acid

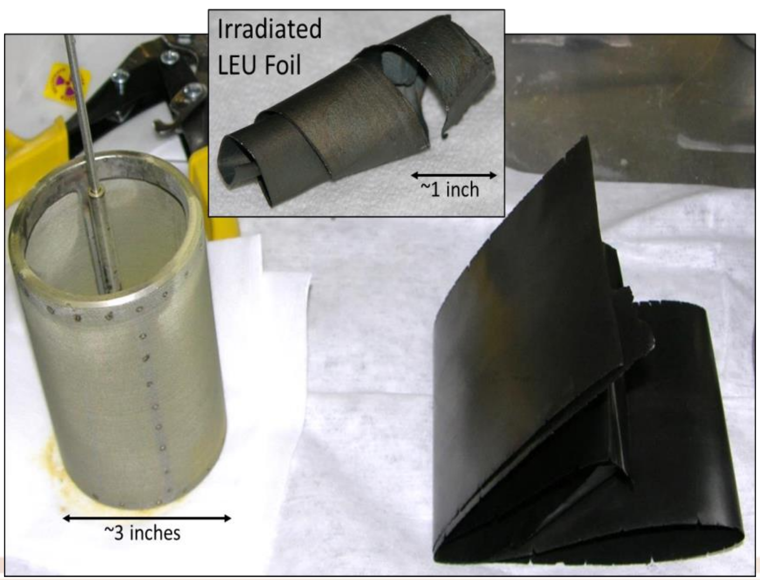
$$U + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2H_2O + 2NO$$

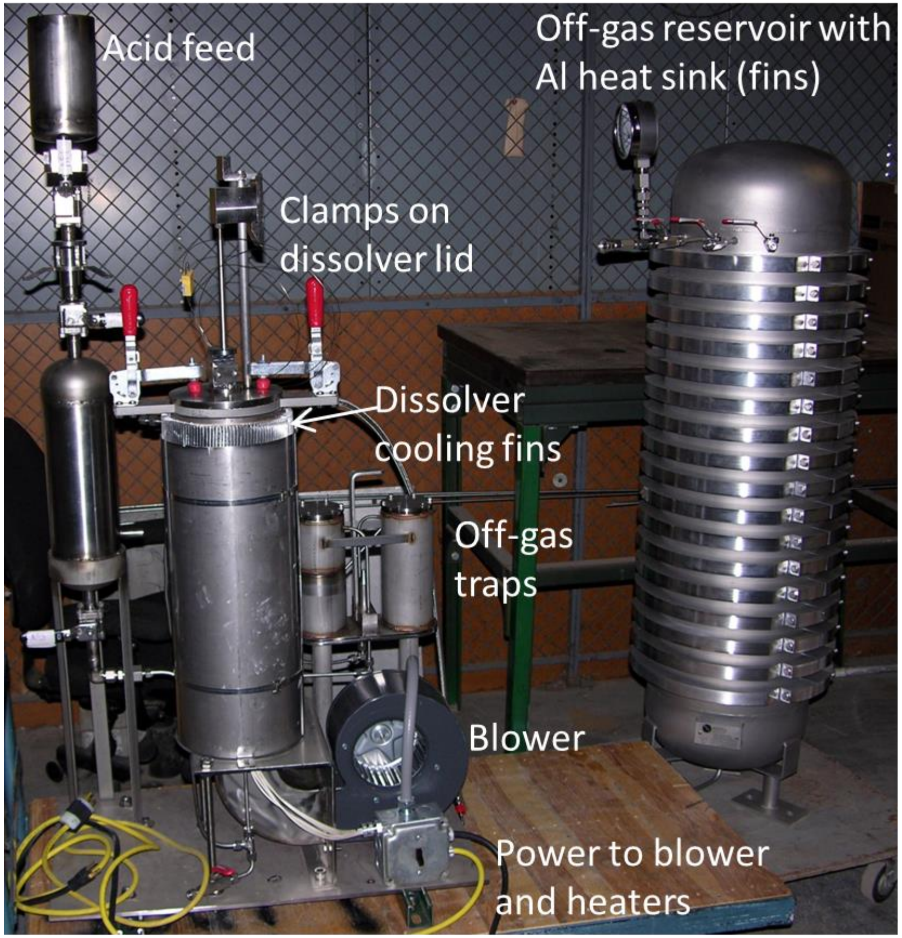
- Nickel fission-recoil barrier and all other components dissolve also
- Product fed to titania column for Mo recovery/separation and conversion to alkaline solution
- Alkaline Mo-product solution to current purification process



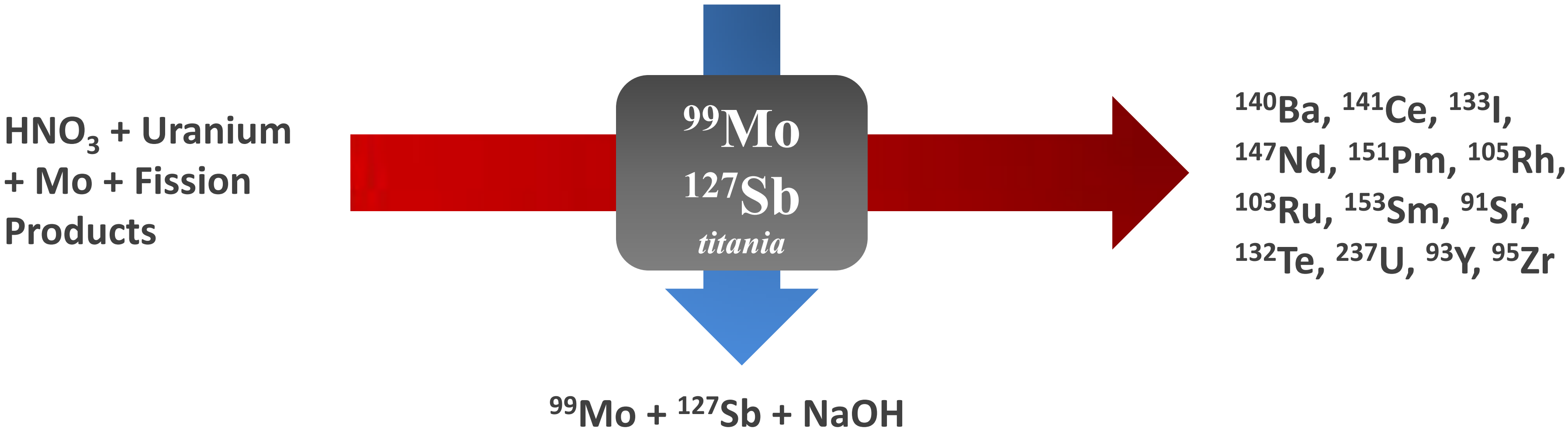
THE ACID PROCESS - DISSOLUTION

- Tested with Ni alone, DU, and finally with 242 g DU + 6 g irradiated LEU.
- All components dissolve in 500 mL of nitric acid
- 100% of Ni and U foil were dissolved in 2 hours





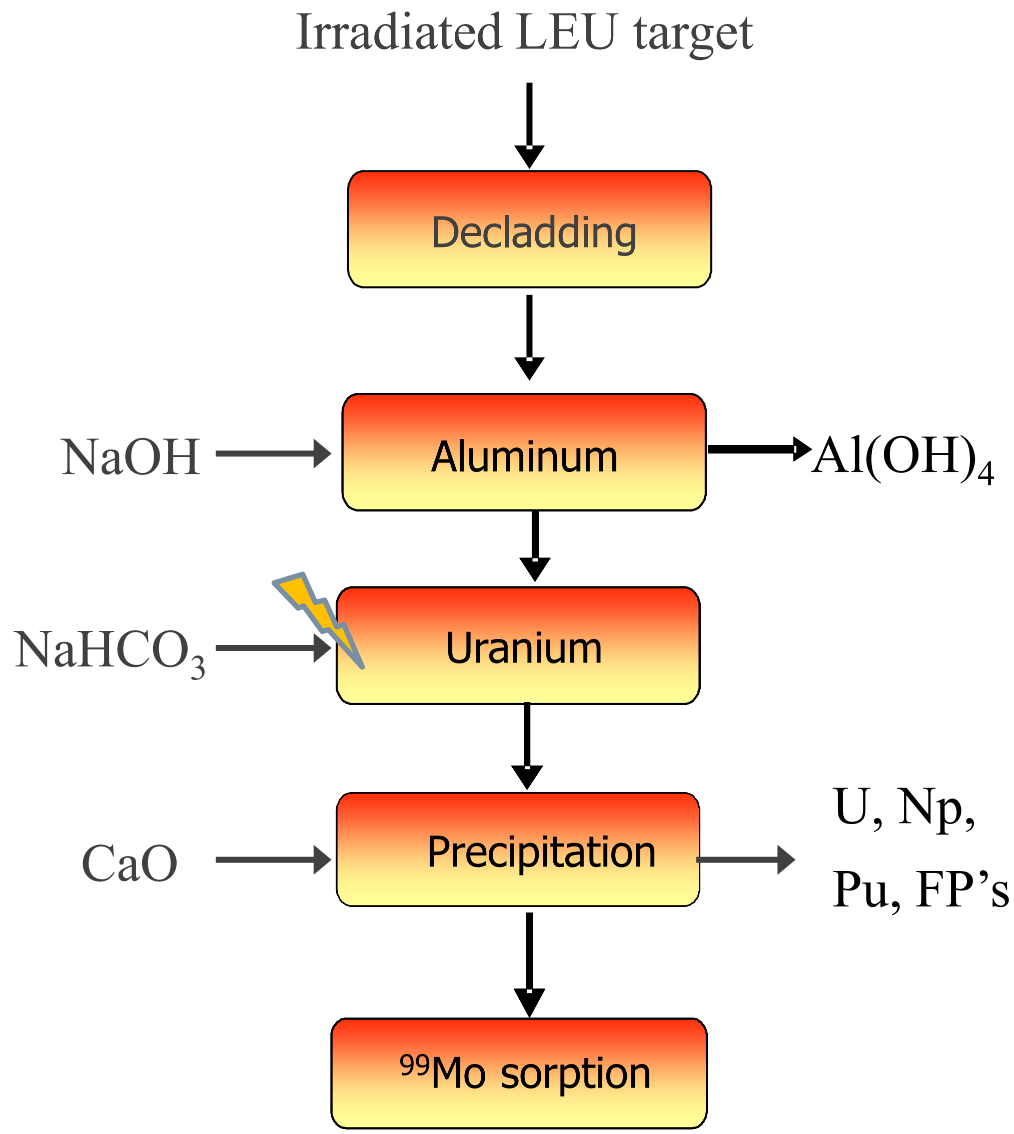
THE ACID PROCESS – Mo RECOVERY



- Mo recovered on a titania column
- Fission products
- Acid wash followed by hydroxide strip
- ~85% of fission products passed through; >90% removed after first wash
- Column step completed in < 1 hour
- *99.3% Mo loaded; 98.4% Mo stripped*

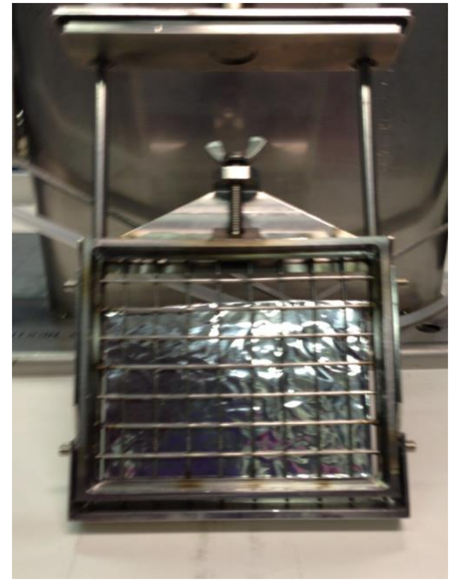
THE ELECTROCHEMICAL PROCESS

- Dissolve Al in NaOH
- Dissolve U-foil in $NaHCO_3$
- Precipitate U + FP with CaO
- Alkaline Mo-product solution to current purification process



THE ELECTROCHEMICAL DISSOLVER

- Anode / Cathode connections to a Magna-Power supply.
- SS basket with external heating
- ~2L of solution

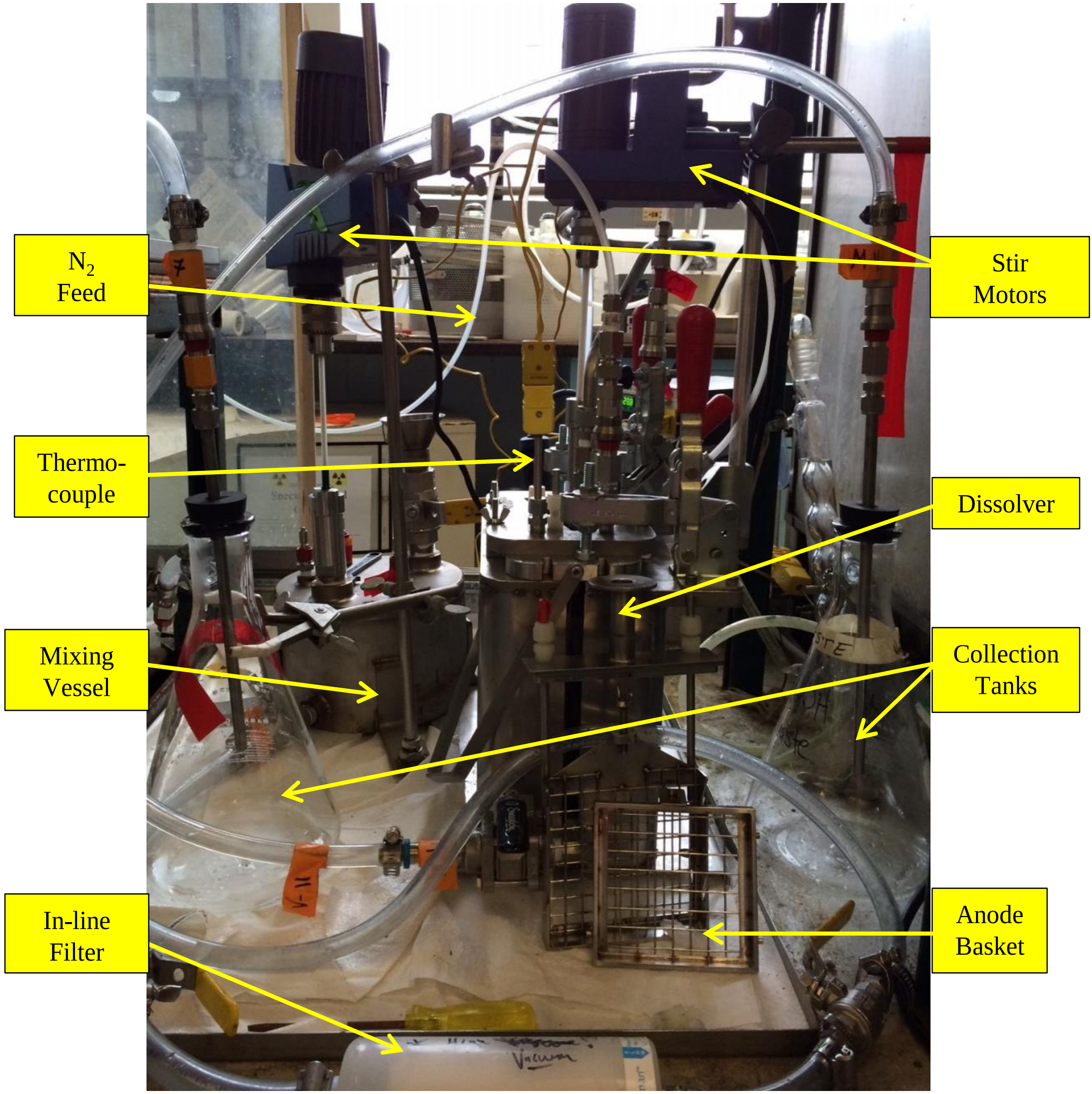


BEFORE

AFTER

THE ELECTROCHEMICAL PROCESS

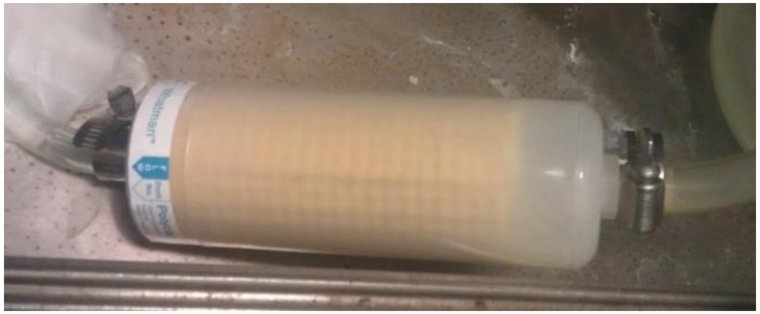
- Al dissolved in ~30 minutes
- Operated at 9 V and 40 Amps
- Gases swept with N_2
- 15 grams of LEU dissolved in 3.5 hours (98%)
- 600 mL of carbonate solution after dissolution

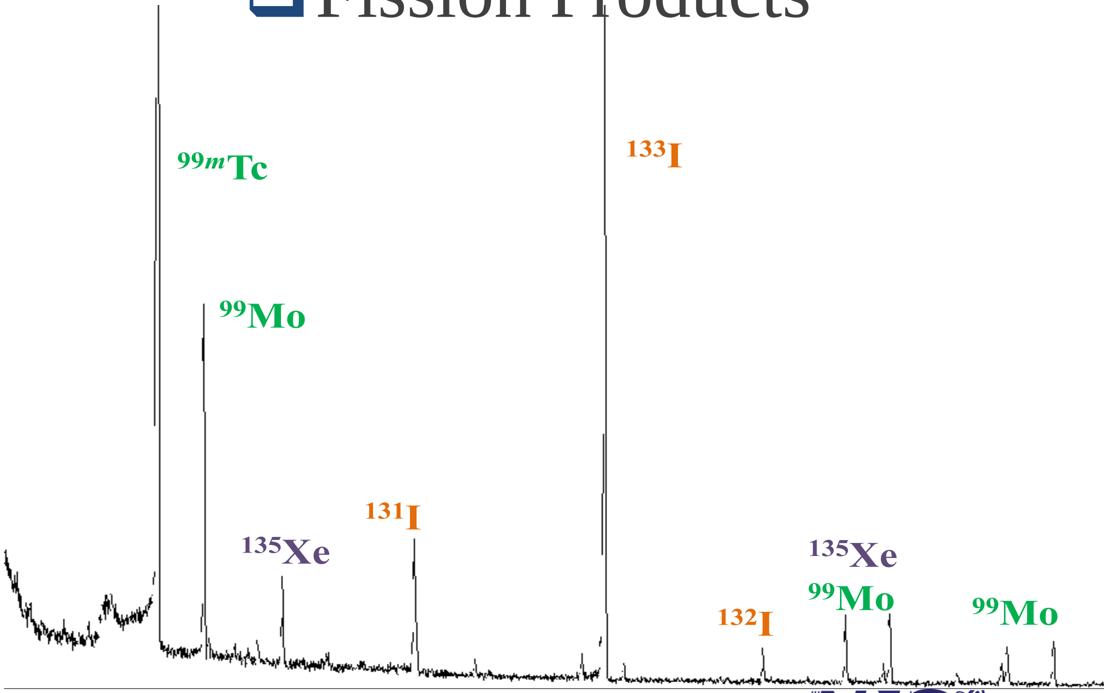


PRECIPITATION & PRODUCT

- Uranium precipitated with ~100 grams CaO
- Water rinse
- 10 µm in-line filter
- Strong signals from uranium and Fission Products

- Clear color
- pH 13.0
- Tc-99m, Mo-99, I-131
- Trace amounts of ^{237}U
- Fission Products





	Mo-99 RECOVERY	IODINE RECOVERY
Al Digest	*No Mo-99*	*Trace I-133*
U Digest	*~28 µCi Mo-99*	*~32 µCi I-133* *~1.6 µCi I-131*
Precipitation	*2 µCi Mo-99*	
Product	*26 µCi Mo-99*	*11 µCi I-133* *0.9 µCi I-131*
	92% *Mo-99 Recovered*	*30-60%* *Iodine Recovered*

CONCLUSIONS

- Two frontend processes were developed and tested at Argonne to treat irradiated LEU foil for Mo-99 production.
- An acid process used nitric acid to dissolve LEU followed by Mo-99 recovery/separation on a titania column.
- An electrochemical process utilized anodic dissolution of LEU in carbonate followed by calcium precipitation.
- Both processes demonstrated > 90% Mo-99 recovery.
- Both processes can be fed into known Mo-purification procedures.

ACKNOWLEDGMENT

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Thank you.

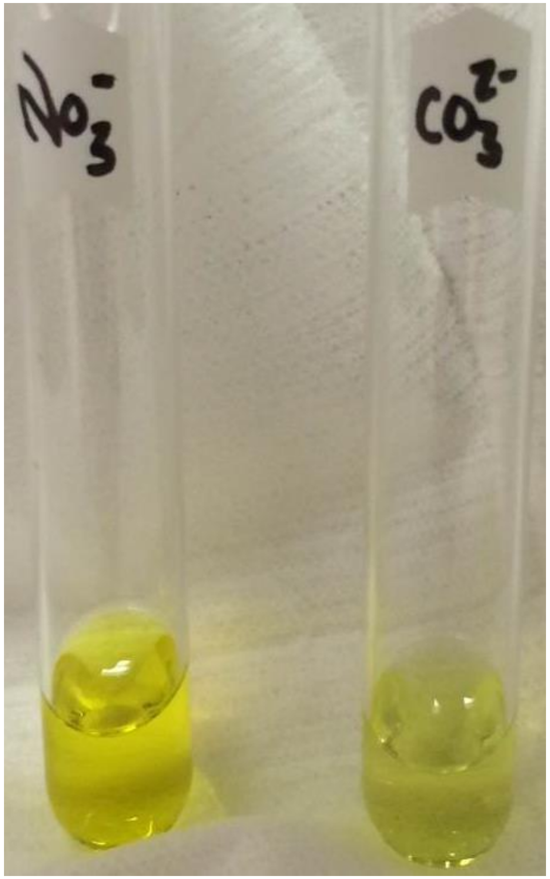
Questions?

EXTRA SLIDES

ARGONNE HD-TARGET PROCESSES

ACID

- ✓ Dissolution
- ✗ Iodine
- ✗ NO*x* gas
- ✓ UREX
- ✓ Purification

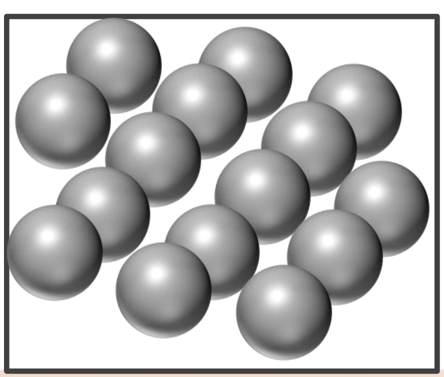


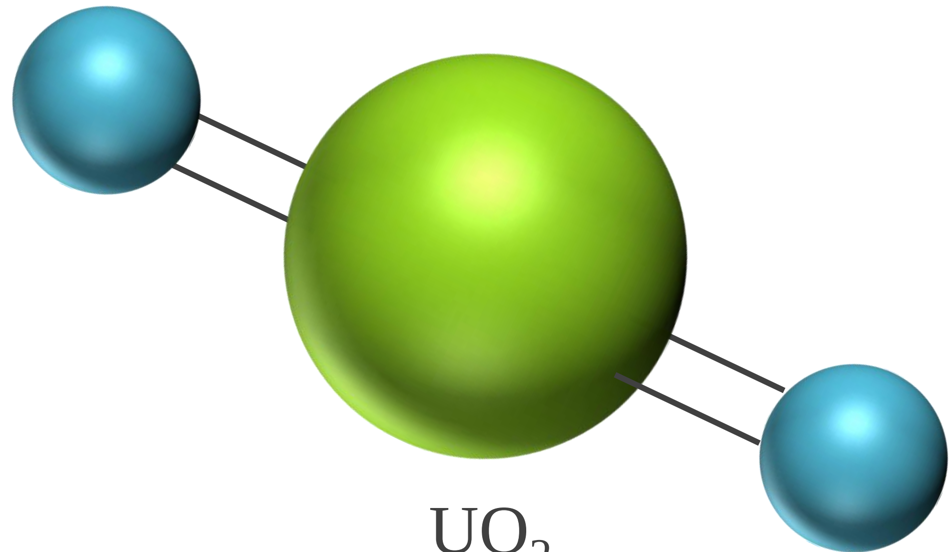
BASE

- Dissolution
- ✓ Iodine
- ✓ NO*x* gas
- ✗ UREX
- ✓ Purification

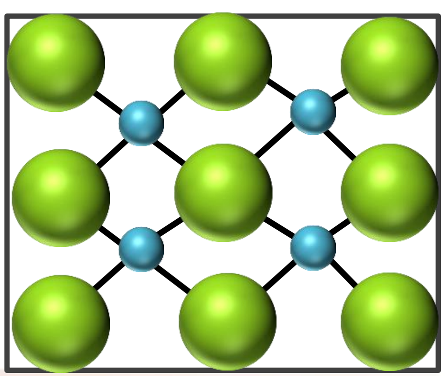
URANIUM TARGETS

U Metal
orthorhombic
$\rho = 19.1\ g/cm^3$
U-U = 2.8Å



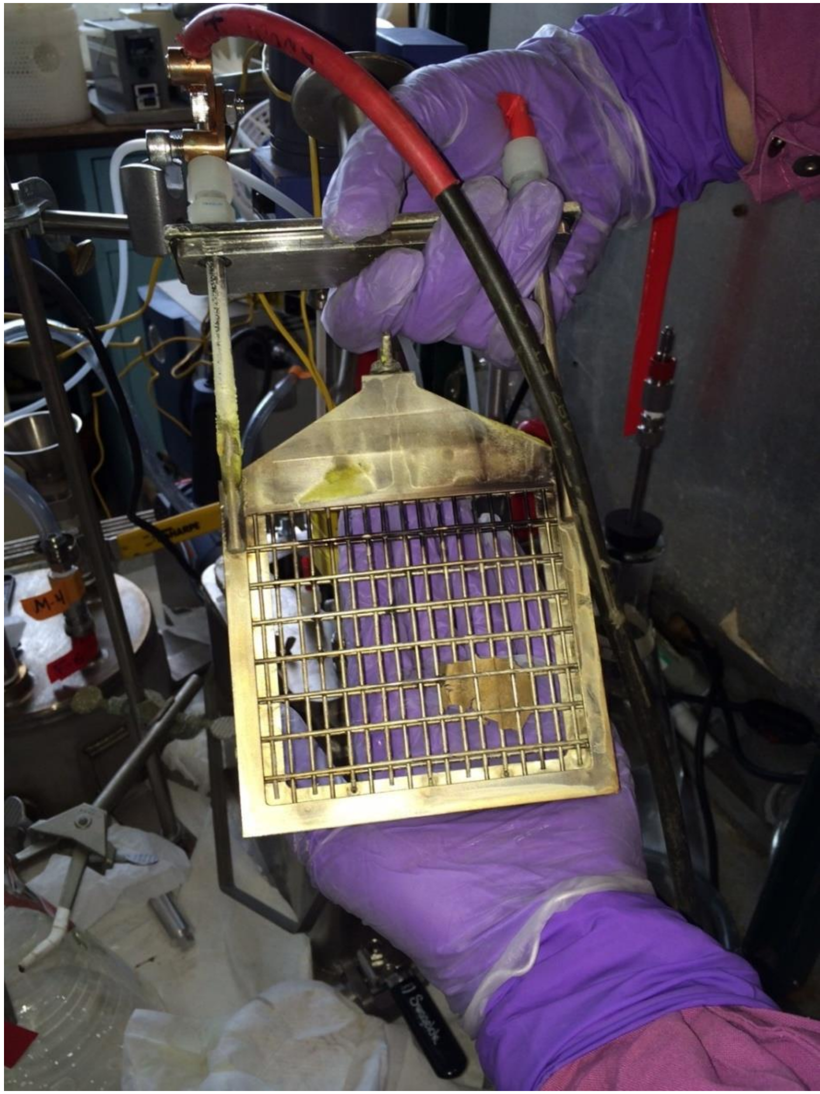


UO_2
fluorite
$\rho = 10.9\ g/cm^3$
U-O = 2.3Å



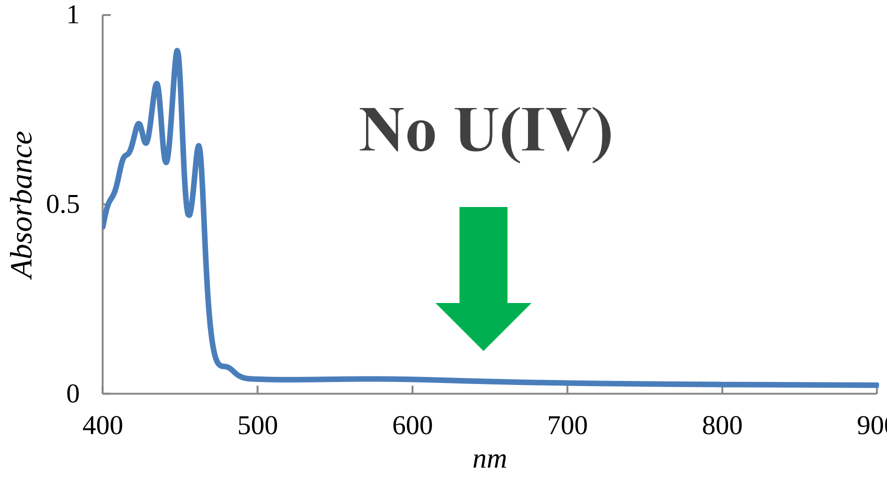
URANIUM DISSOLUTION

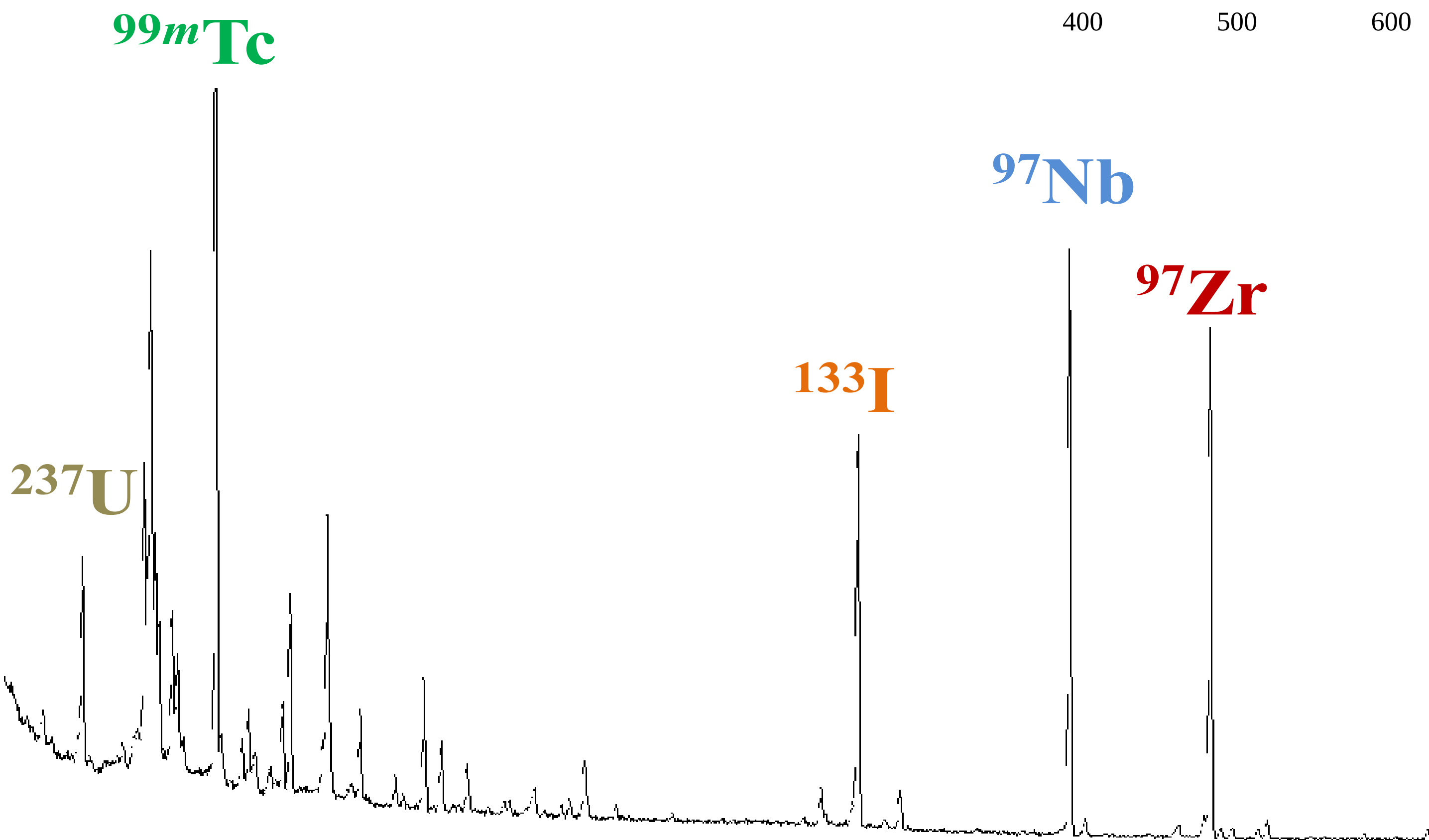
- Al dissolved in ~30 minutes
- Operated at 9 V and 40 *m*Amps
- Gases swept with N_2
- 15 grams of LEU dissolved in 3.5 hours (98%)
- 600 mL of carbonate solution after dissolution

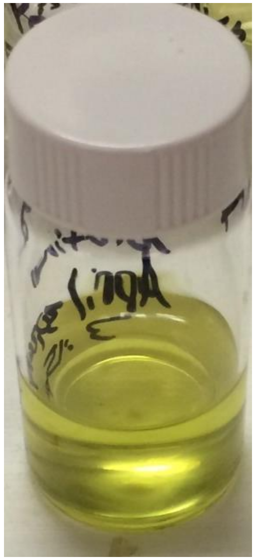


DISSOLVED URANIUM SOLUTION

- Light-green color U(VI)
- pH 10.0

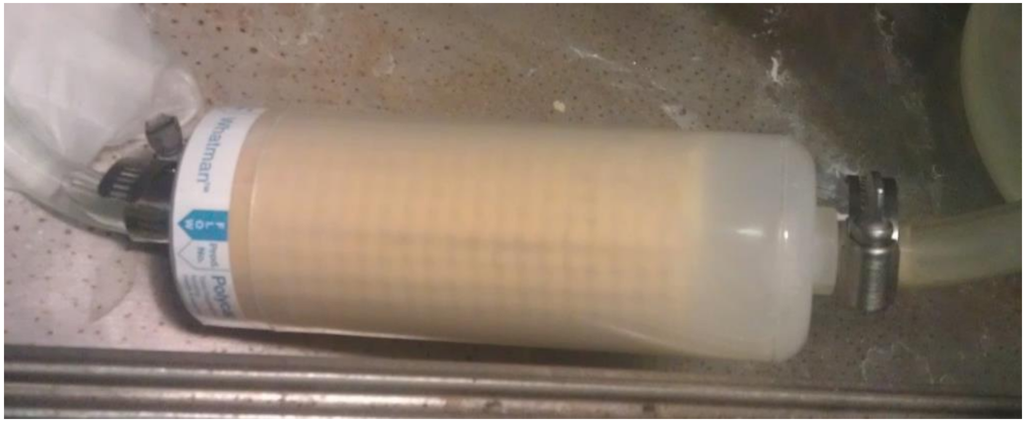






PRECIPITATION AND FILTRATION

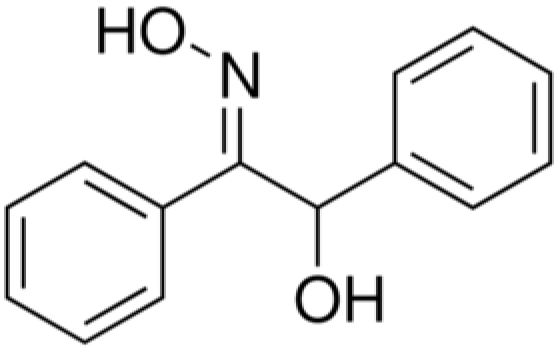
- Uranium precipitated with ~100 grams CaO
- Mixing vessel rinsed with water
- Slurry fed through 10 μm in-line filter
- ~1.2 L product solution



Mo PURIFICATION

- Product solution contacted with AG-MP-1 anion exchange resin
- Iodine and Molybdenum retained
- K_d (Mo) = ~150 mL/g
- α-Benzoin oxime precipitated Mo-carrier after acidification

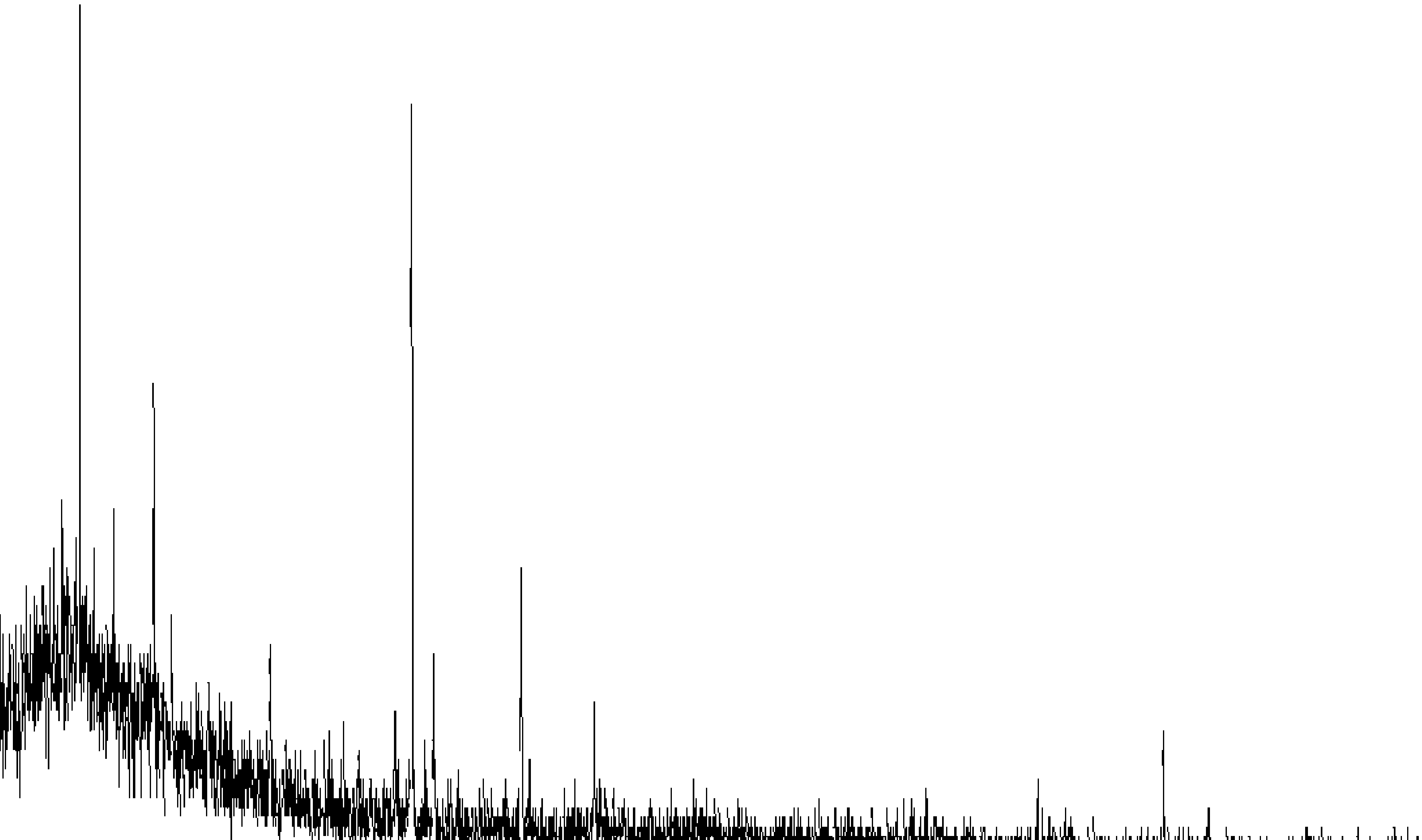
http://www.sigmaaldrich.com/catalog/product/aldrich/b8908?lang=en&region=US



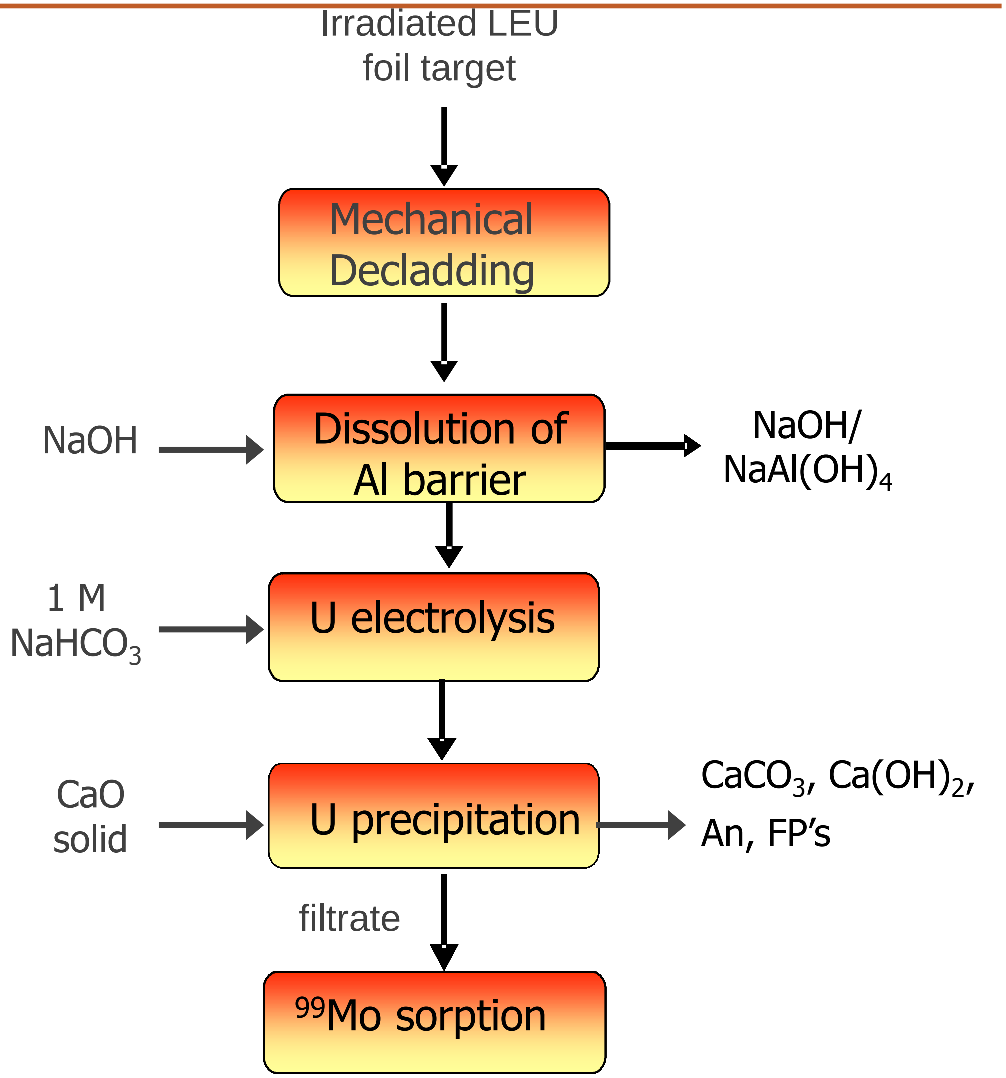
FUTURE

- More low-burnup and DU tests at ANL
- Improve hot-cell compatibility
- High-burnup tests
- More XRD studies on Na-Ca-UO_2-CO_3 precipitate

waste



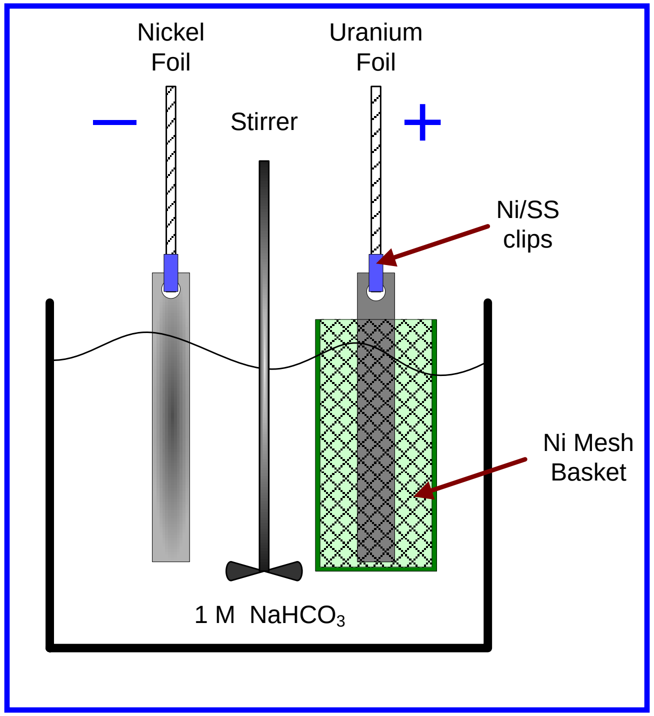
Low Temperature Low Pressure Alkaline Dissolution Process Scheme

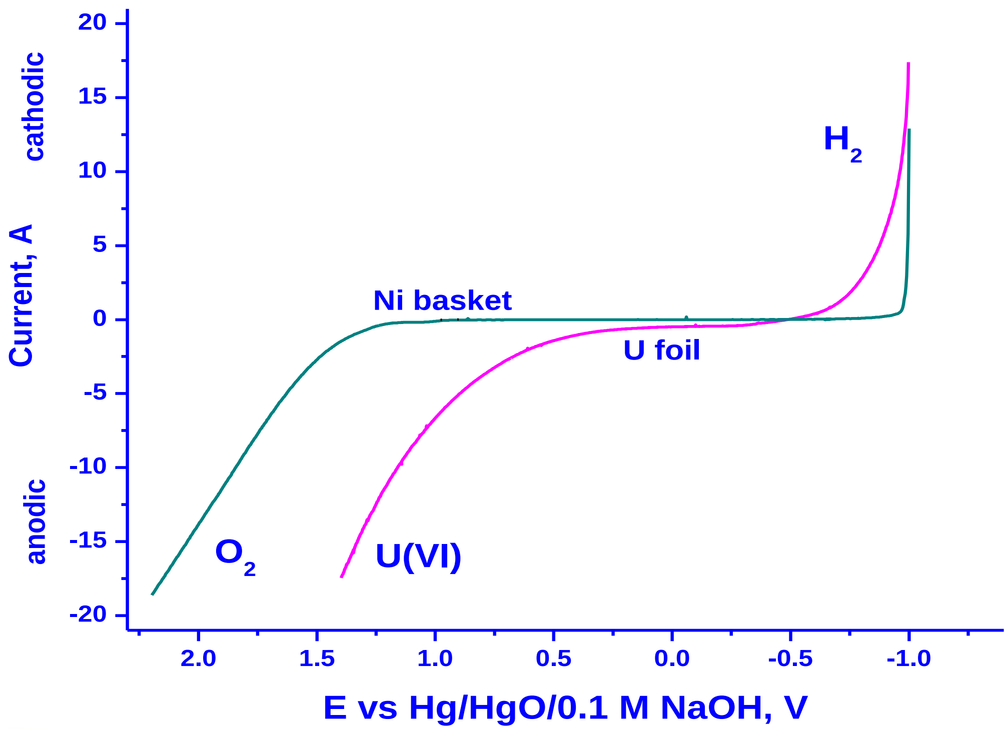


Target Dissolution

Two-step process

1. Dissolution of Al fission recoil barrier using NaOH
2. Anodic dissolution (1 M $NaHCO_3$ in a beaker with intense stirring)
    - 8.8g DU foil dissolved in 45 minutes (0.0042 g/min·cm^2)
    - 22g foil dissolved in 90 minutes





$$\underbrace{U^0 \rightarrow UO_2 \rightarrow UO_{2+x}}_{\text{fast surface reactions}} \rightarrow \underset{\substack{\uparrow \\ \text{rate-limiting step}}}{UO_2(CO_3)_n^{2-2n}}$$

Uranium Precipitation

- **Addition of CaO excess is followed by a filtration step**
- **The precipitate is very easy to filter using a paper filter under gravity**

Precipitate

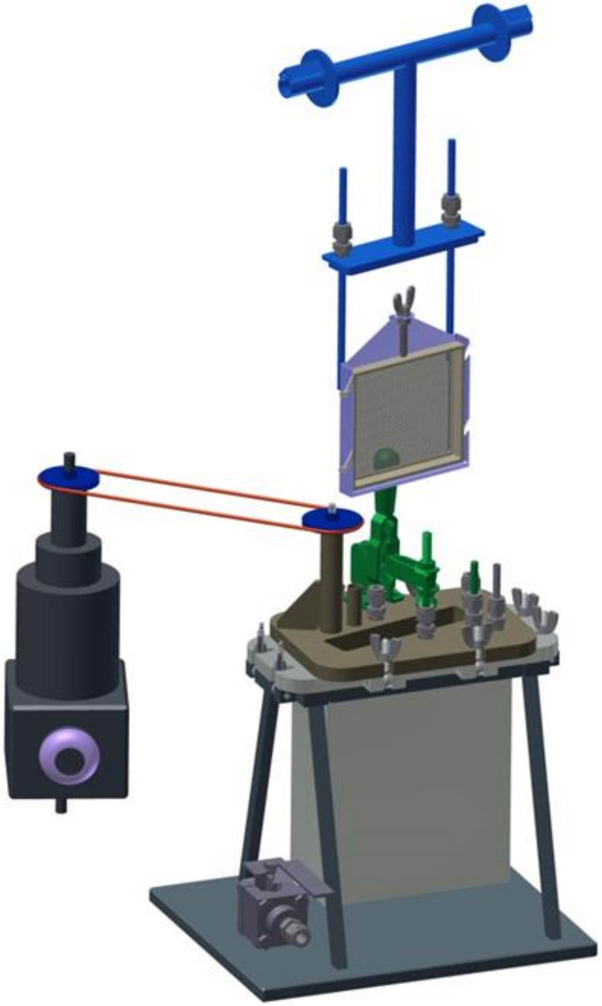
XRD of Precipitate

- $CaCO_3$
- A mixed Na-Ca-(UO_2^{2+})-(CO_3) phase
- Would also contain insoluble FPs, Pu, Np
- SEM and TEM analysis will follow

Filtrate Solution

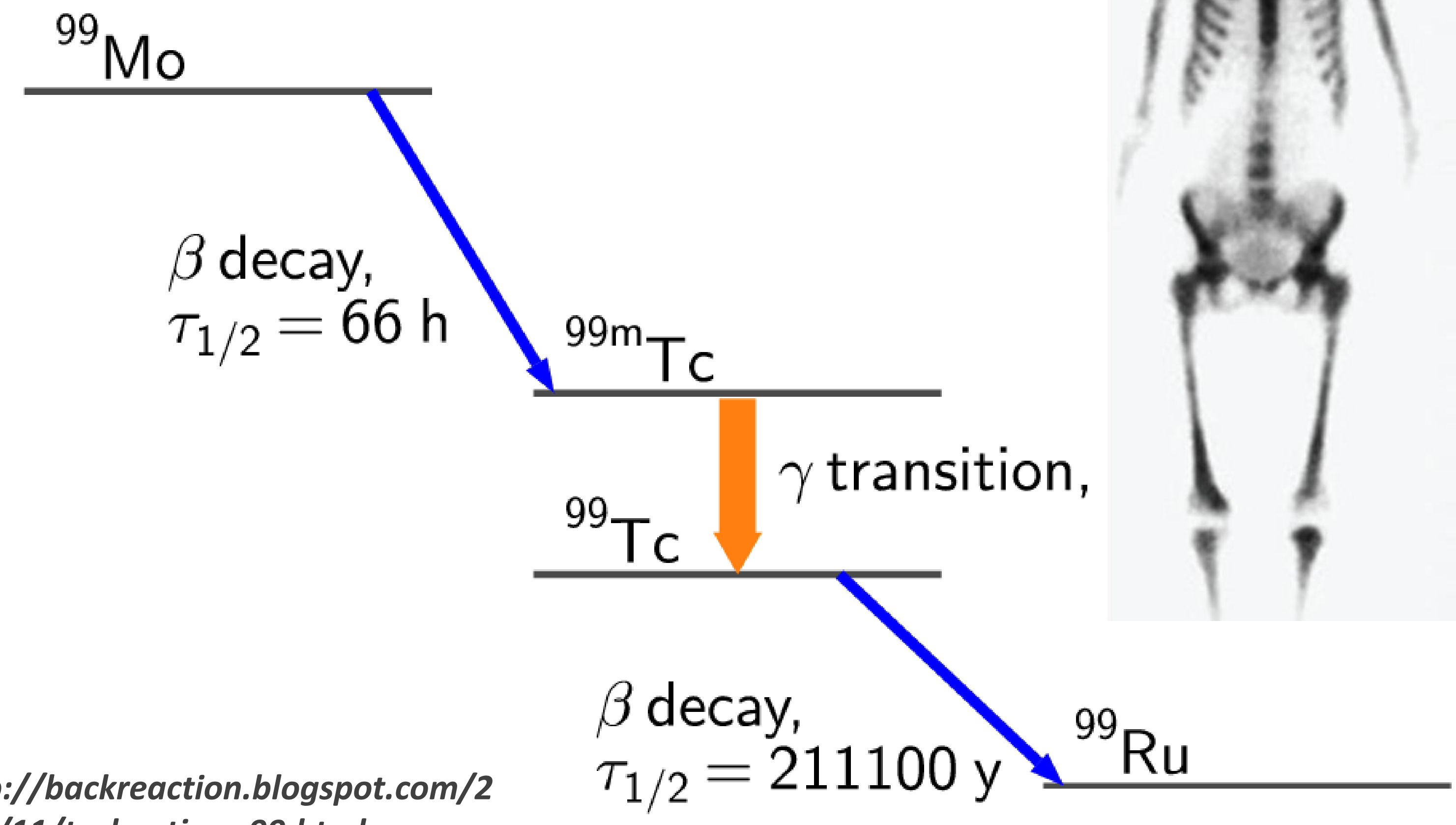
- <1 mM CO_3^{2-}
- Trace U
- Saturated $Ca(OH)_2$
- Would also contain soluble FPs
- pH 12.7
- No MoO_4^{2-} is co-precipitated !
- K_d (^{99}Mo) ~ 340 mL/g on AG-MP1

New Dissolver Design



Tc-99*m*

- The most important medical isotope in the world



http://backreaction.blogspot.com/2008/11/technetium-99.html

Mo-99/Tc-99*m* PRODUCTION

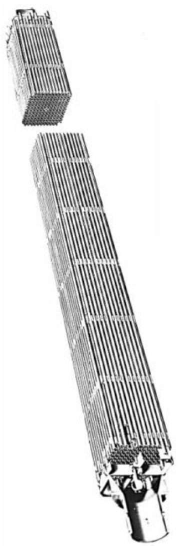
- **Fission of highly-enriched U-235 can make profitable amounts of Mo-99**
- **Canada produces *half***
- **2016 deadline**
- **A domestic supply is needed**

http://www.cins.ca/scat.html

Aecl.ca

National Nuclear Security Administration

Mo-99 PRODUCTION STEPS



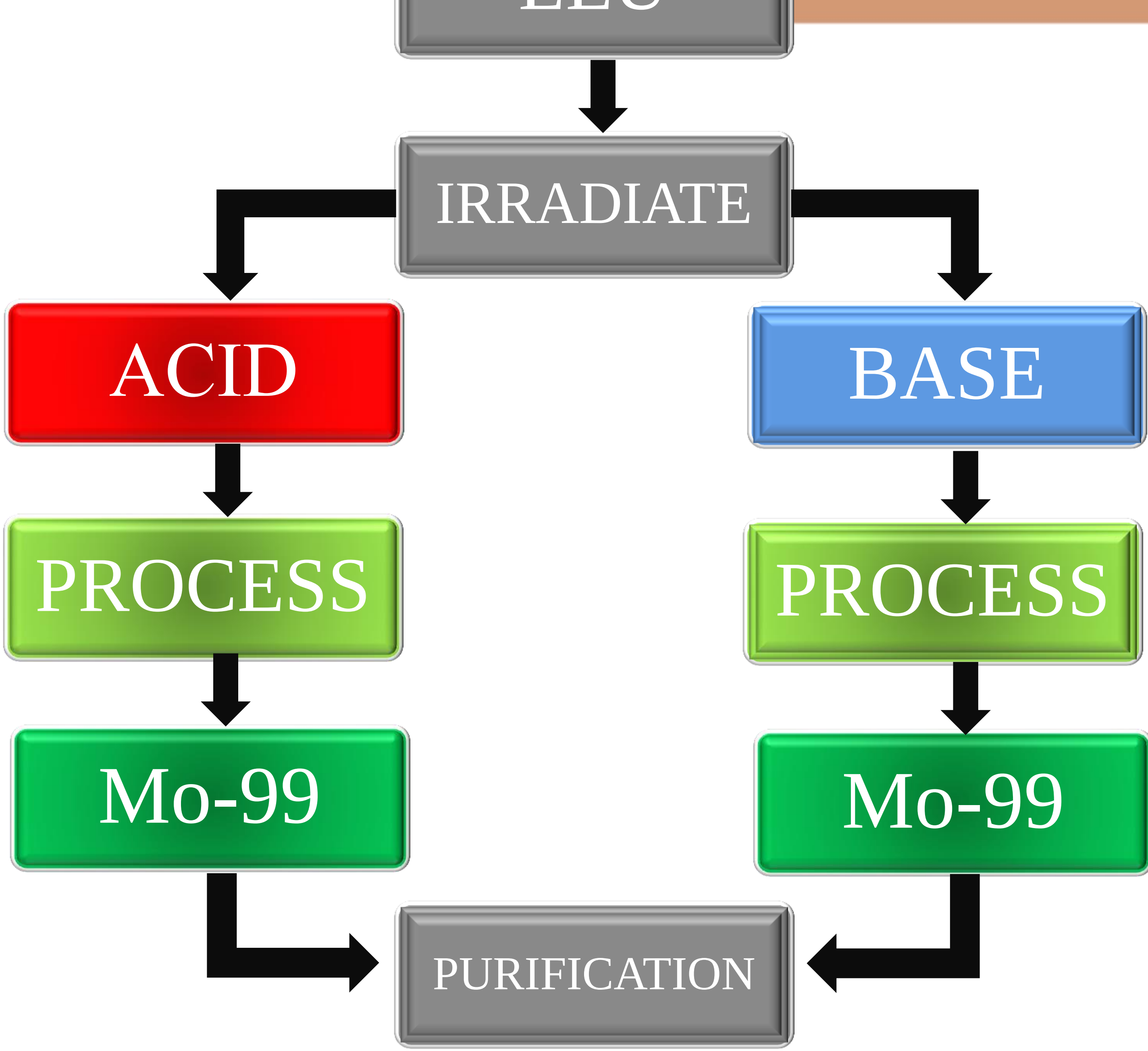
DIGEST URANIUM

CHEMICAL SEPARATIONS

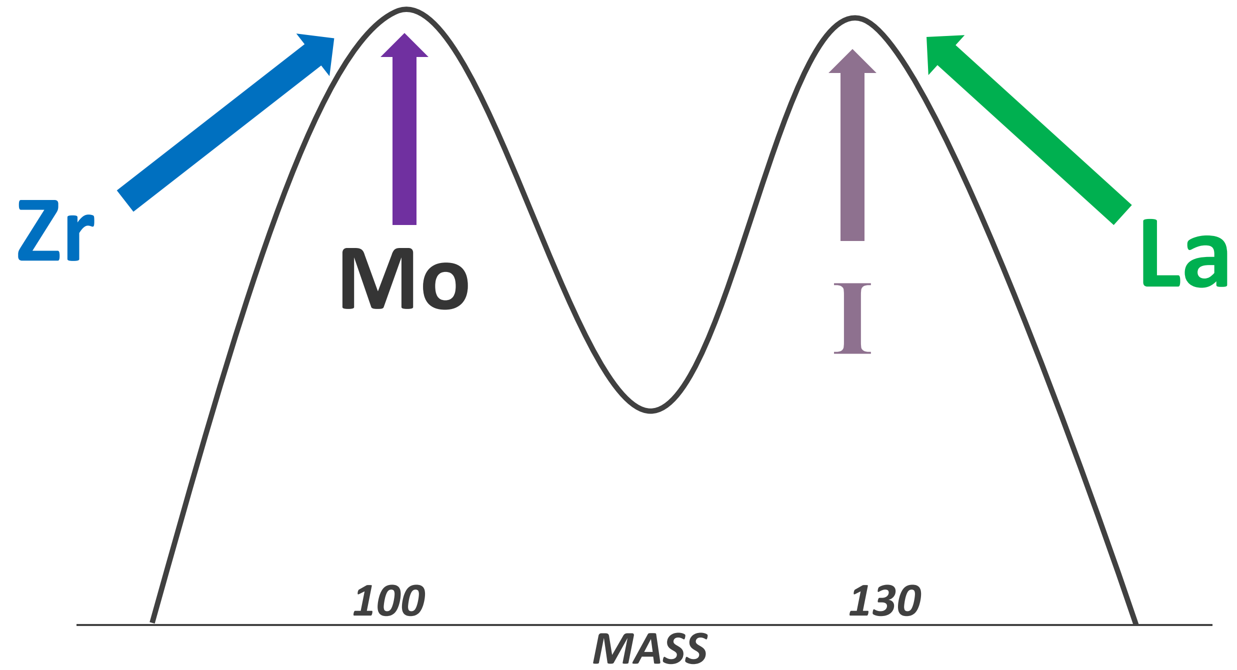
PURIFY Mo-99

Well known for acid, what about base?

Works with acid and base.


IRRADIATE
ACID
BASE
PROCESS
PROCESS
Mo-99
Mo-99
PURIFICATION

SELECTED FISSION PRODUCT H_2O CHEMISTRY



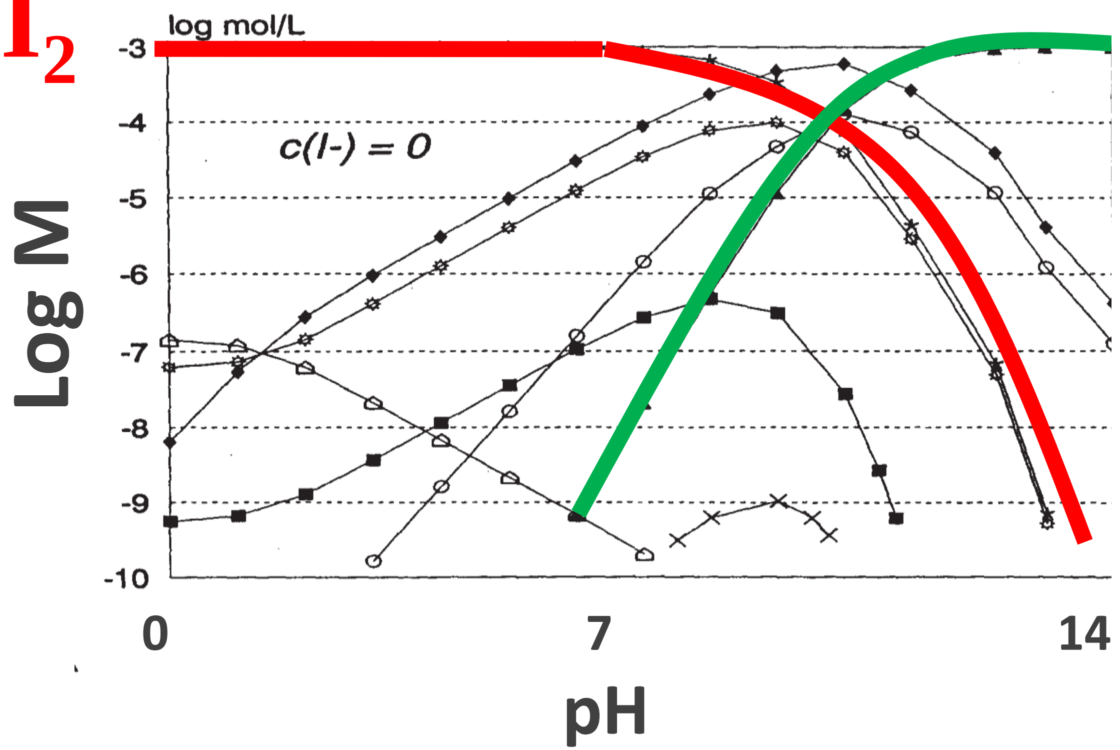
	ACID	BASE
Zirconium	Zr^{4+}, ZrO_2	$Zr(OH)_x^{4-x}$ Polymer
Molybdenum	MoO_2^{2+}	MoO_4^{2-}
Lanthanum	La^{3+}	$La(OH)_x^{3-x}$
Iodine	I_2	I^-, I_3^-, IO_3^-

National Nuclear Security Administration

IODINE

Alkali promotes anionic iodine which stays in solution!

- $^{131}I_2$



- $I_3^- + I^-$

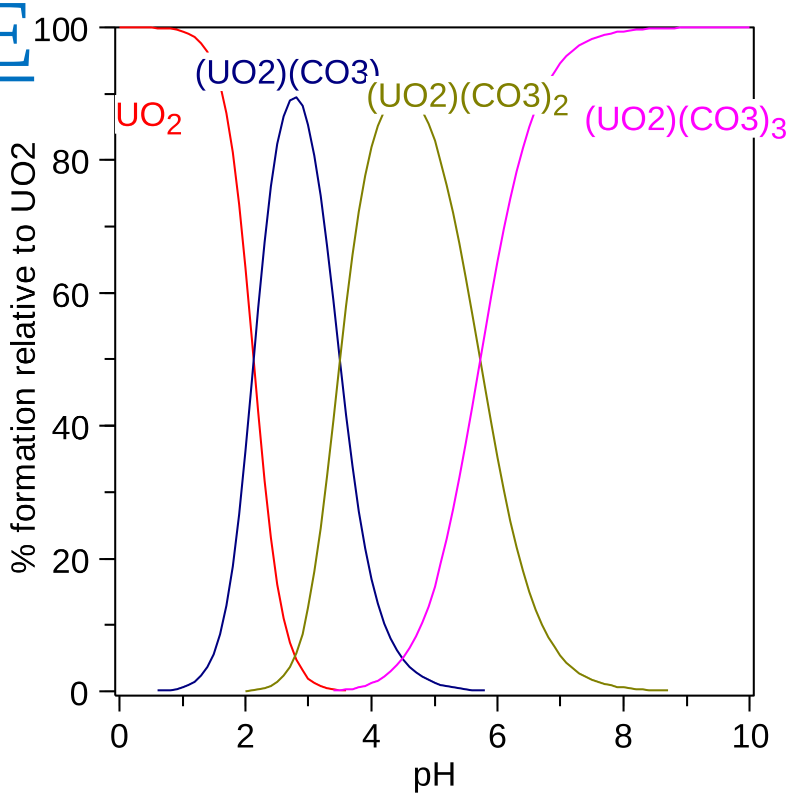
W. Gottardi, Iodine and Iodine Compounds in Disinfection, Sterilization, and Preservation S.S. Block, Lea &Febiger, Philadelphia, PA, USA, (2000).

PROCESS DESIGN

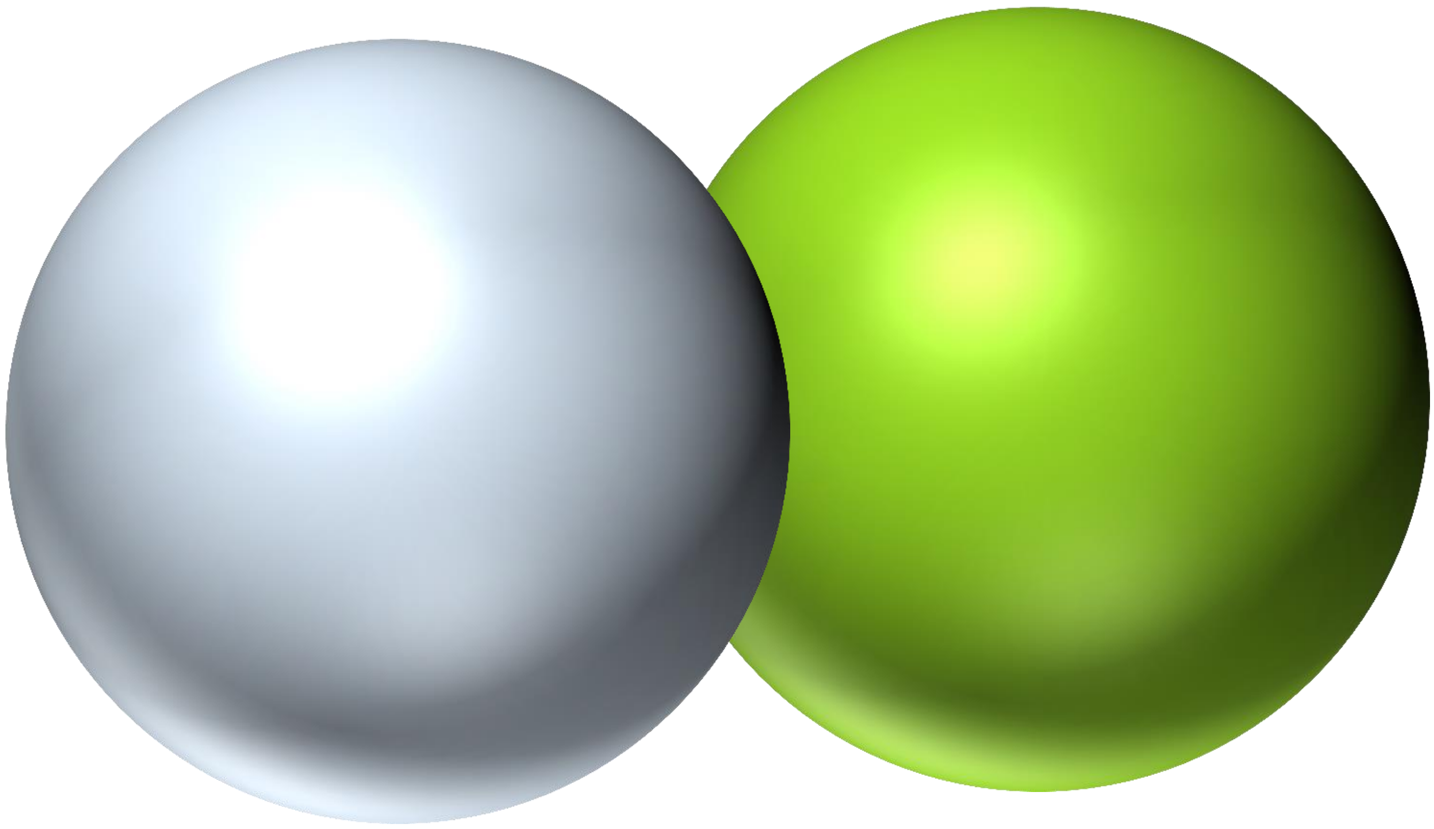
- Advantages of an **alkali** process:
  - Less I_2
  - Iodine control could mean profit
  - No NO_x gas
  - Relatively new concept
  - Mo purification fits well
- Disadvantages:
  - Uranium metal not readily digested in **base**
  - Precipitates
  - May be difficult to feed into UREX cleanup

URANIUM CARBONATE

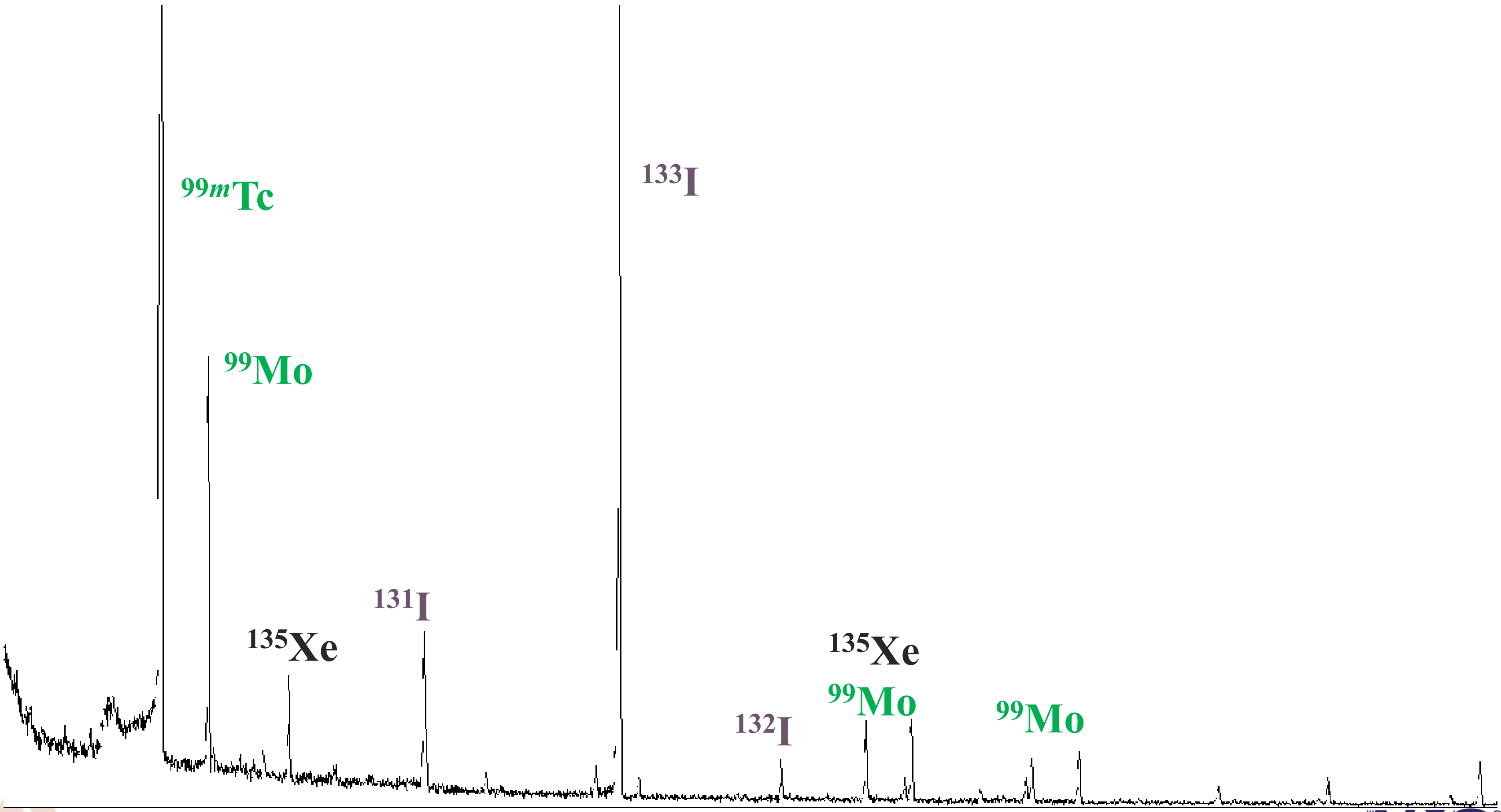
- UO_2^{2+} and carbonate
  - $UO_2(CO_3)_x^{(2x\text{-}2)-}$
- Precipitated with CaO
  - Na-Ca-(UO_2^{2+})-$(CO_3)_x$ phase
- Most fission products co-precipitate
- Mo does not precipitate!



Speciation diagram for uranium carbonate complexes.
J.J. Katz et al. The Chemistry of the Actinide Elements, 2nd ed., diagram generated by M.A. Brown using HySS



product



Less U-235 enrichment

New neutron flux

New target design

New target dissolution

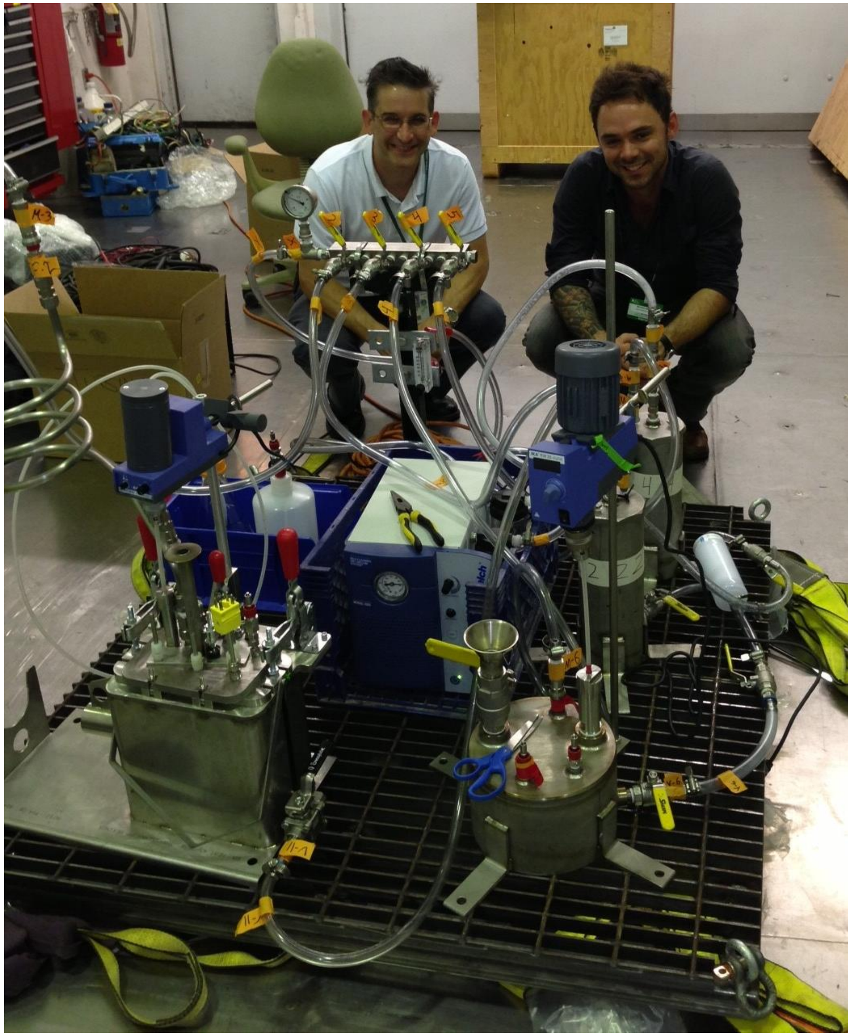
New uranium treatment

(*Same purification steps*)

Can we match the original Mo-99 yields using LEU?

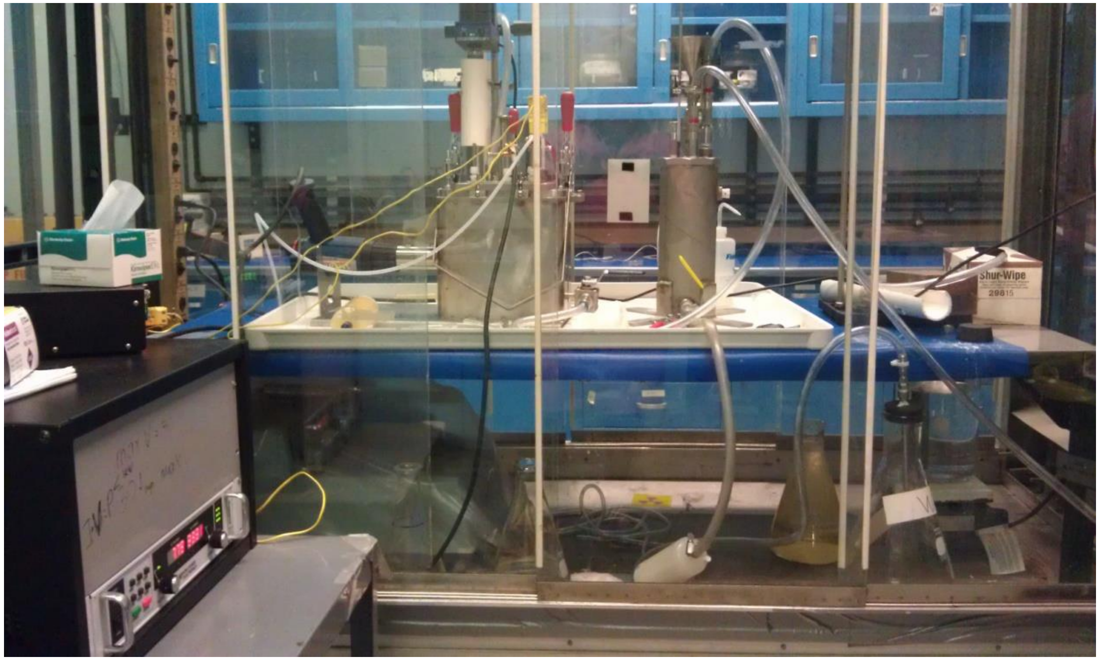
PILOT SCALE

- Test with depleted uranium at ANL
- Test low-burnup at ANL LINAC
- High-burnup



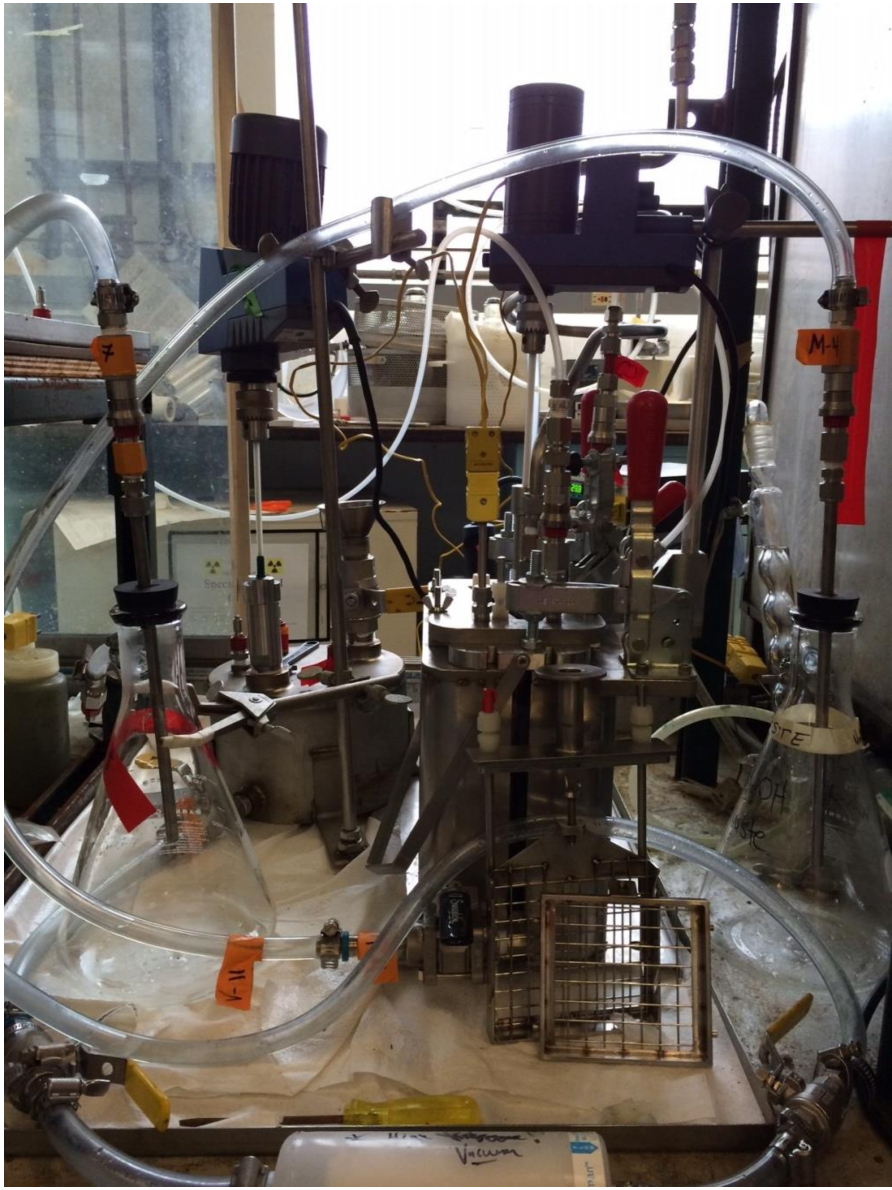
WARM TEST

- Demonstrated good electrical dissolution
- 10 grams of depleted uranium dissolved in ~ 4 hours.
- Precipitation step on a large scale.



LOW-BURNUP TEST

- ANL setup
- LINAC neutrons
- LEU foil irradiated for 10 minutes
- Cooled overnight



DISSOLUTION IN ALKALI

- Aluminum dissolves in NaOH

$$Al \longrightarrow Al(OH)_4^- \longrightarrow \textit{solution!}$$

- Uranium forms passive layer

$$U \longrightarrow U(OH)_3 \longrightarrow UO_{2+x} \longrightarrow X$$

$$U \xrightarrow{\textit{fast surface reaction}} UO_{2+x}$$

Need to manually pull electrons from U and UO_2!

http://www.gh.wits.ac.za/chemnotes/chem3028/Marques/InorgChem_Overview_2011_HMM.pdf

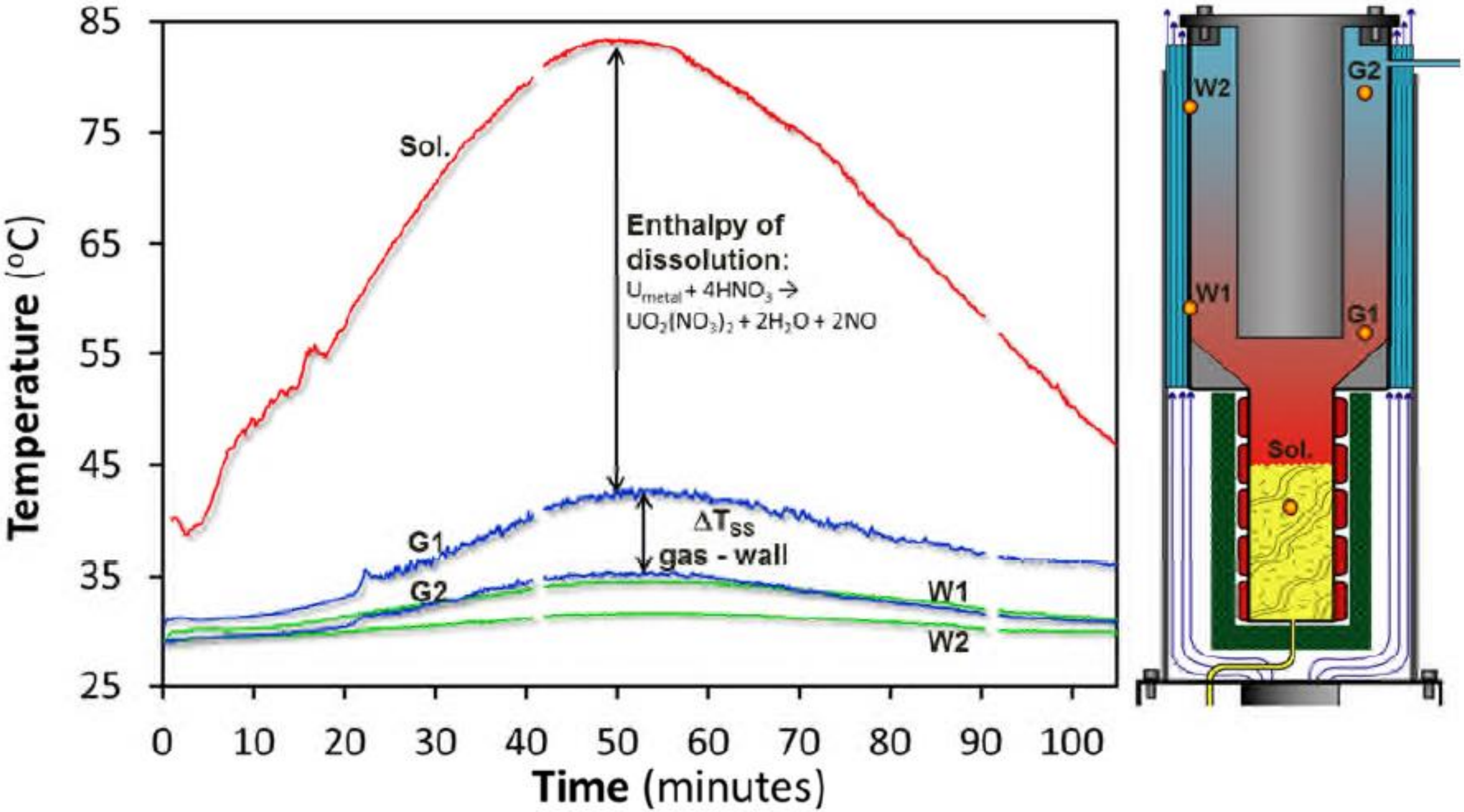


Figure 11. Thermal profiles within the dissolver and condenser sections during enthalpy of dissolution test in which a small amount of heat was added to get the dissolution reaction started and then turned off. The purpose of the test is to determine the heat output from the uranium foil dissolution reaction by itself.

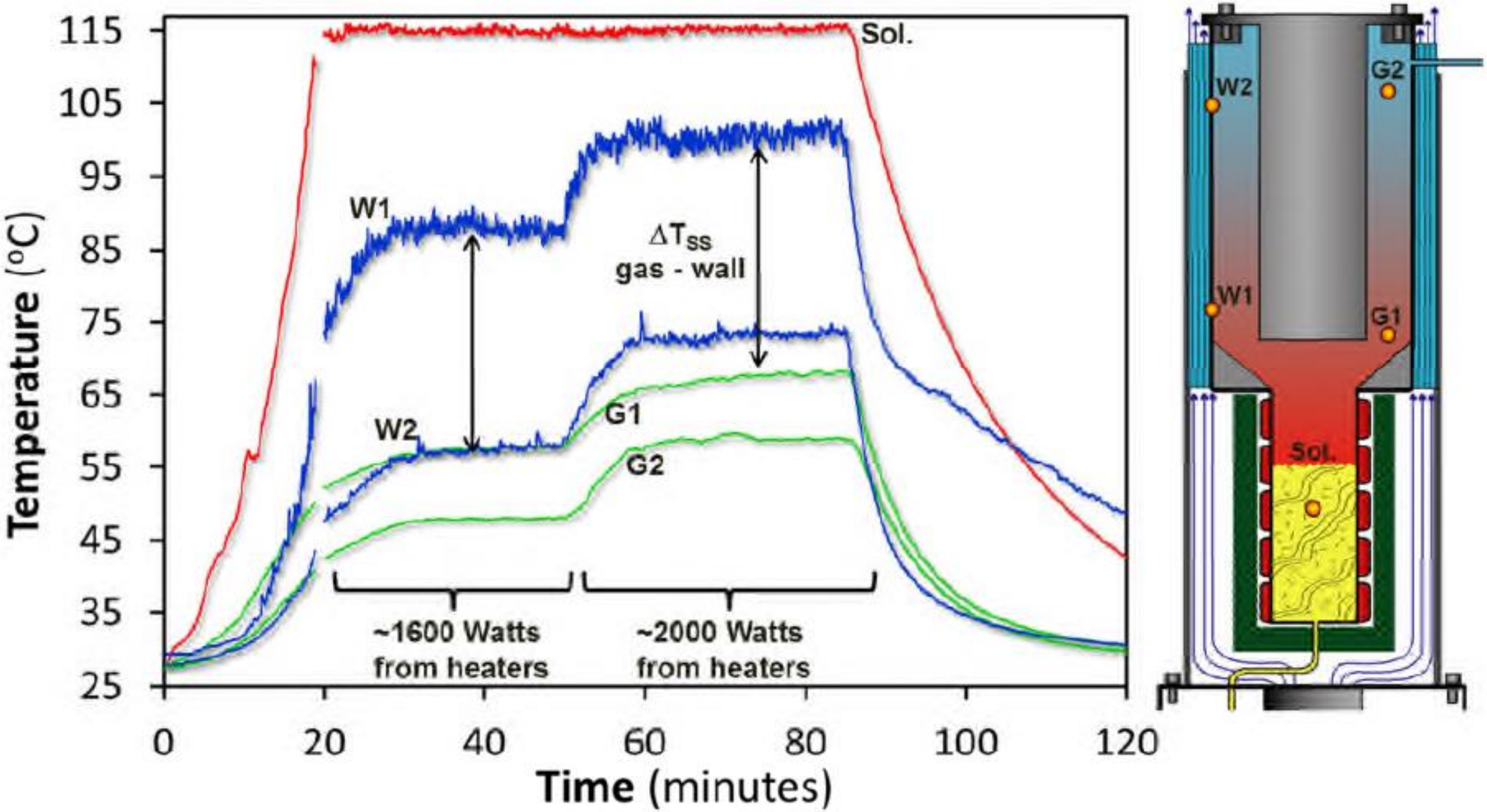


Figure 12. Thermal profiles within the dissolver and condenser sections during full scale dissolution of .242.4 grams of depleted uranium and 6.84 grams of irradiated LEU foil.