OAK RIDGE National Laboratory

Isotope program at Oak Ridge National Laboratory for target material for superheavy element research

Presented by:

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Oak Ridge National Laboratory

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

U.S. DEPARTMENT OF ENERGY

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Outline

- Historical perspective
- Oak Ridge National Laboratory facilities
- Processing descriptions
- New developments

Isotope production and research has been a mission of ORNL from the beginning

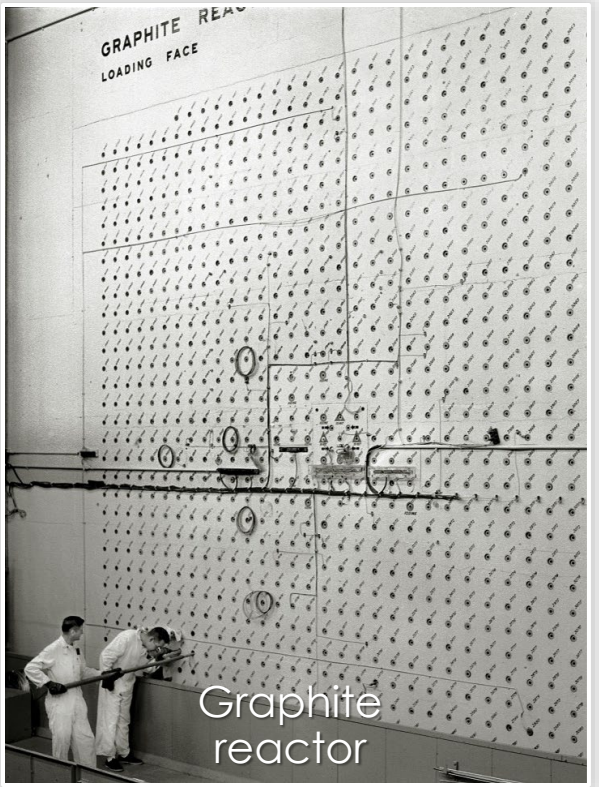
1946 First shipment of a radioisotope to a hospital for cancer research

1960s >100,000 radioisotope shipments annually with applications in research, medicine, and industry

Today ORNL focuses on isotopes not available in the private sector

Manhattan Project facilities were repurposed for early isotope research and production


Calutron mass separators



Graphite reactor

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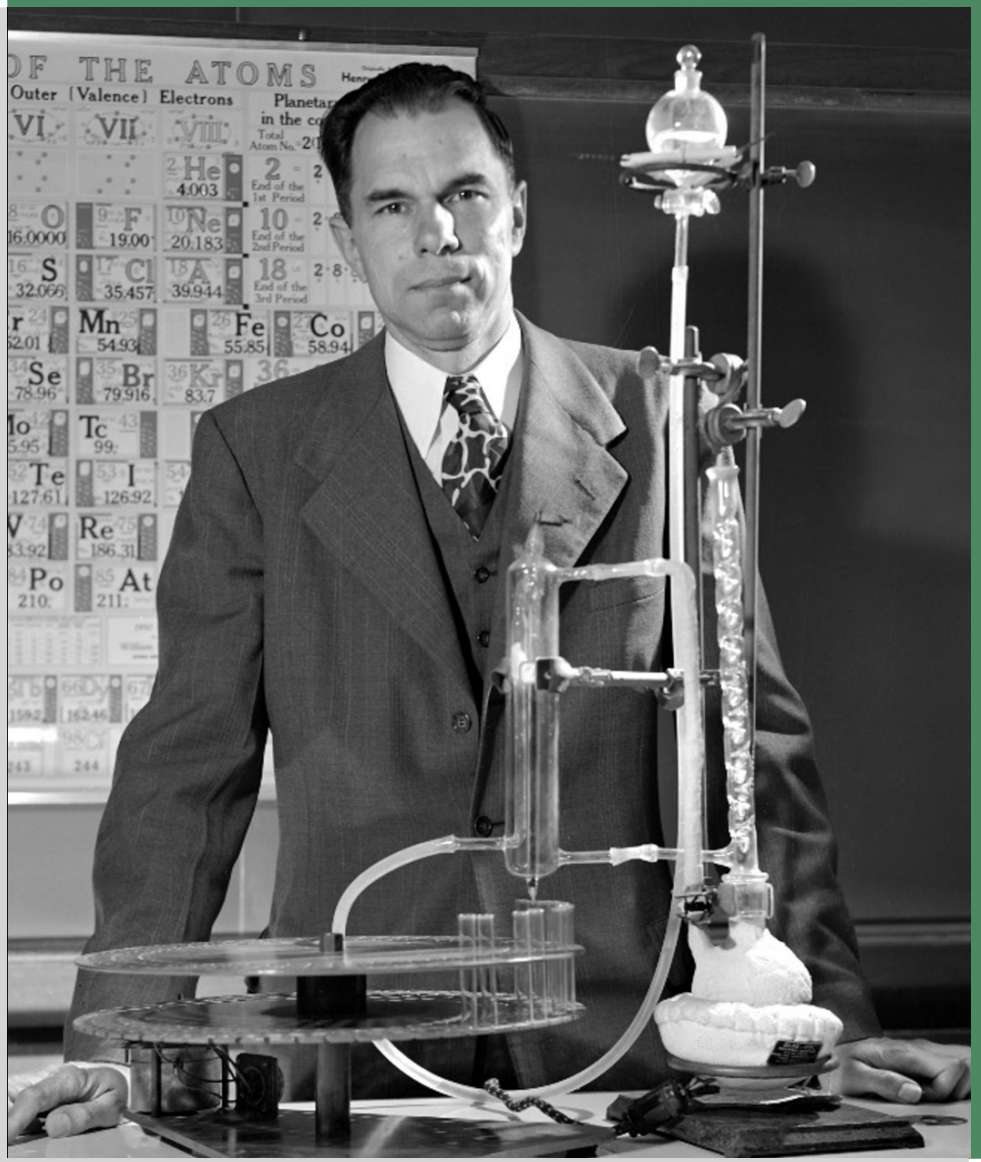
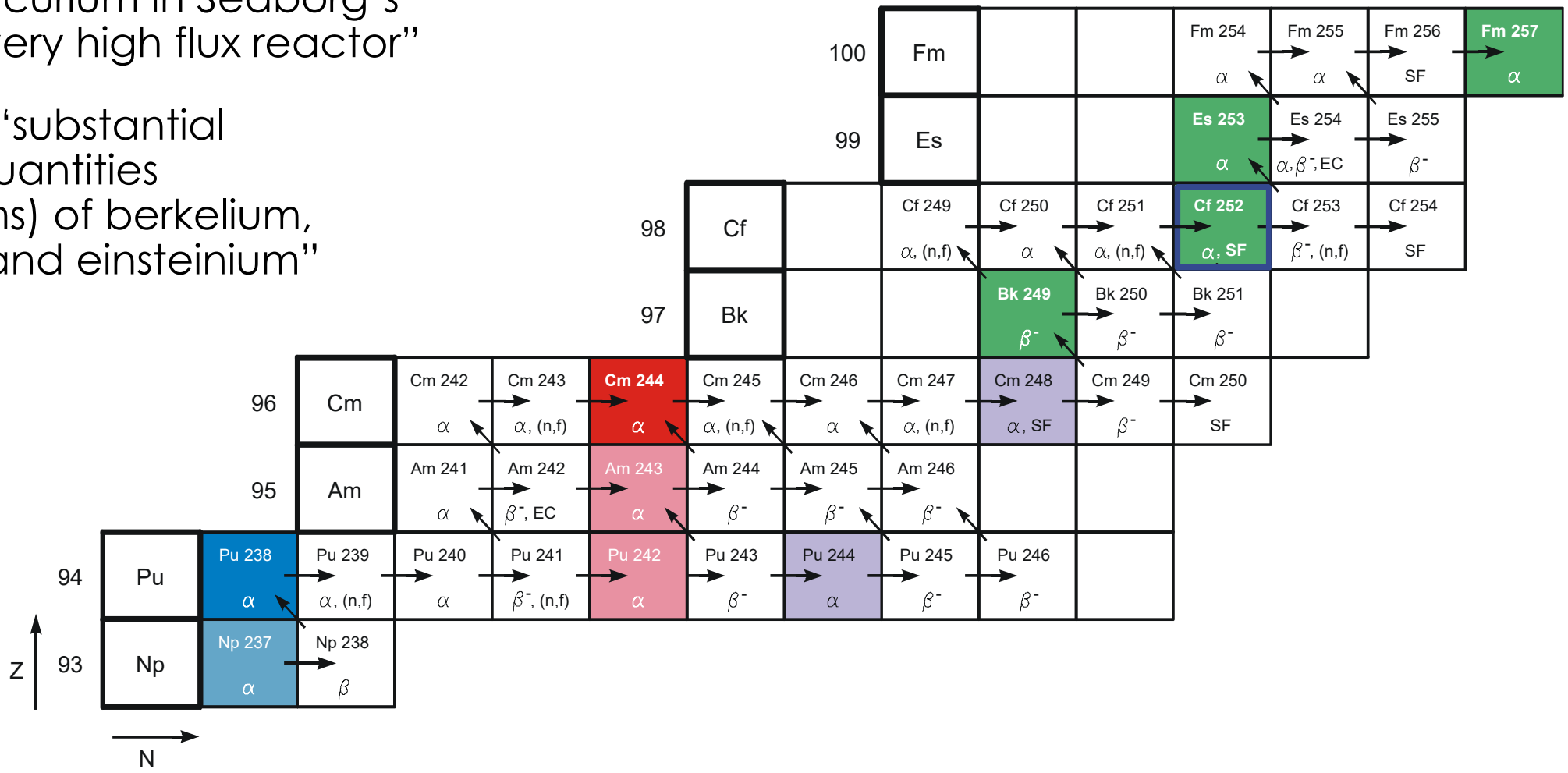
Realizing Seaborg's vision:
A "very high flux reactor" for heavy element production

- Letter to Atomic Energy Commission Chairman Lewis Strauss, October 24, 1957
  - Future progress in "the field of new transuranium elements" requires production of "substantial weighable quantities (say milligrams) of berkelium, californium, and einsteinium"
- Response: With support from Seaborg, ORNL designed and constructed the High Flux Isotope Reactor (HFIR) and the Radiochemical Engineering Development Center (REDC) to produce these elements

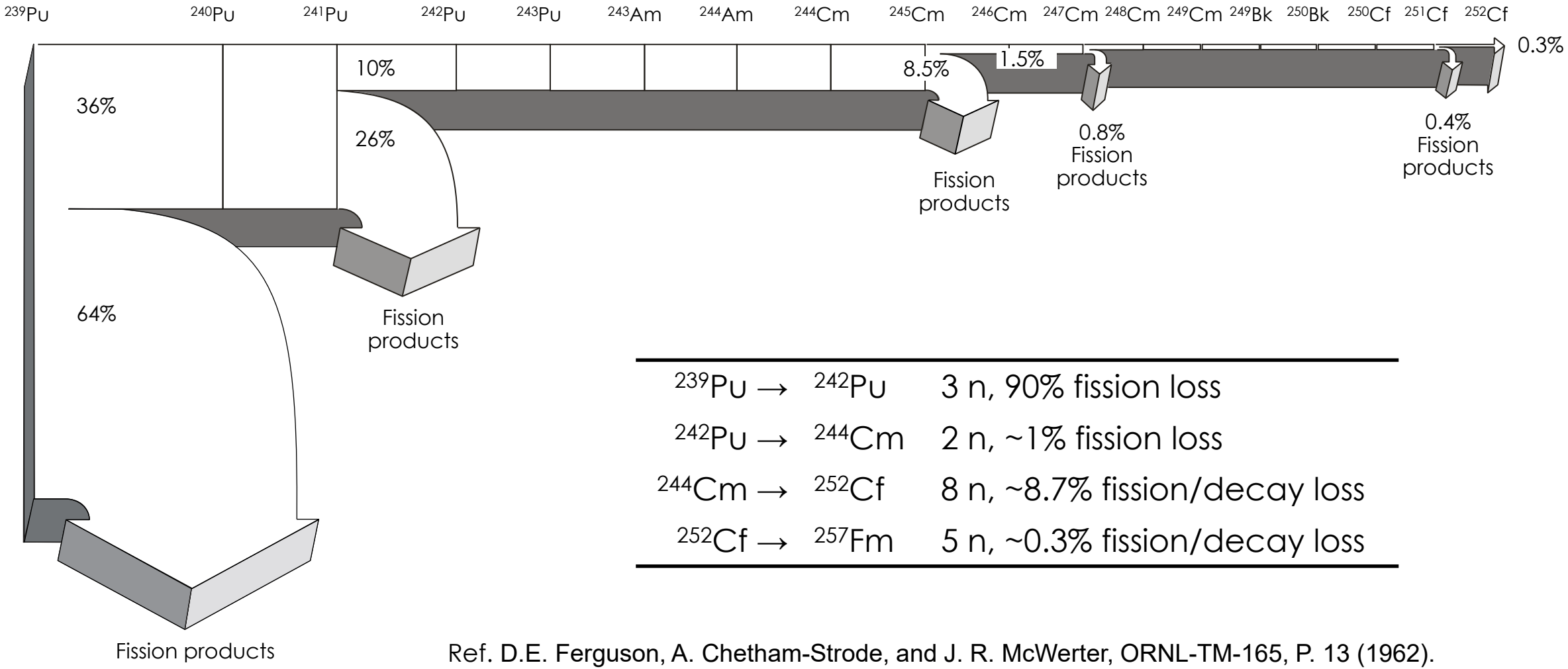


Heavy element production program at ORNL

- Irradiation of curium in Seaborg's suggested "very high flux reactor"
- Recovery of "substantial weighable quantities (say milligrams) of berkelium, californium, and einsteinium"



Transplutonium-element yield and fission loss during thermal neutron irradiation of plutonium



$^{239}Pu \rightarrow$	^{242}Pu	3 n, 90% fission loss
$^{242}Pu \rightarrow$	^{244}Cm	2 n, ~1% fission loss
$^{244}Cm \rightarrow$	^{252}Cf	8 n, ~8.7% fission/decay loss
$^{252}Cf \rightarrow$	^{257}Fm	5 n, ~0.3% fission/decay loss

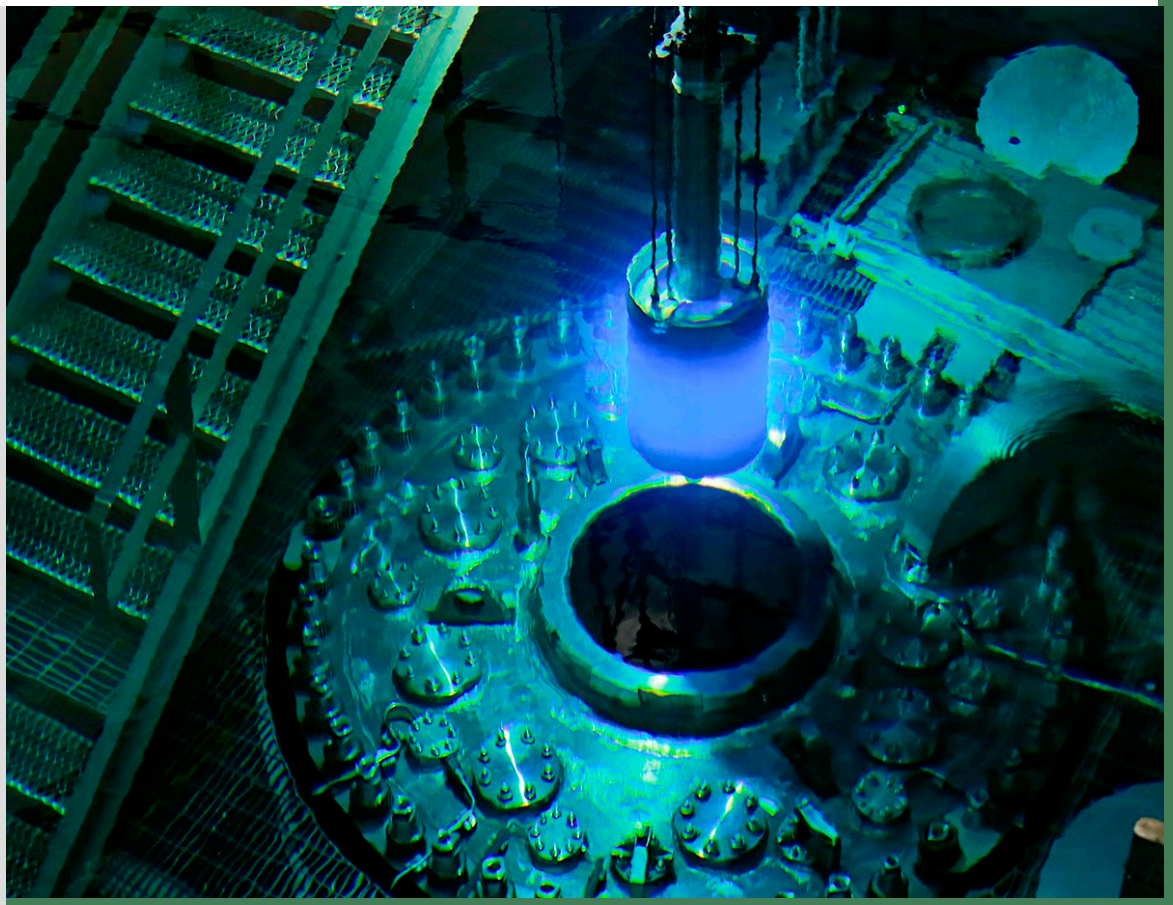
Ref. D.E. Ferguson, A. Chetham-Strode, and J. R. McWerter, ORNL-TM-165, P. 13 (1962).

HFIR and REDC enable heavy element production at ORNL

- HFIR and REDC began operation in 1965 and 1966
- Operation is expected to continue at least until 2040
- High-end aspects of isotope production (heavy actinides, specialty medical isotopes), neutron scattering, and materials irradiation
- Unique capabilities for radioisotope separations (>400 isotope shipments annually to universities, hospitals, industry, and other research institutions)

HFIR: Unique capabilities

- Highest steady state thermal flux
  - 2.1×10^{15} n/cm^2-s thermal
  - 1×10^{14} n/cm^2-s epithermal (< 1 MeV)
  - 4.7×10^{14} n/cm^2-s fast (> 1 MeV)
- Brightest cold neutron source in world
- Delivers 6–7 cycles per year
- Missions:
  - Neutron scattering research
  - **Isotope production**
  - Materials irradiation
  - Neutron activation analyses

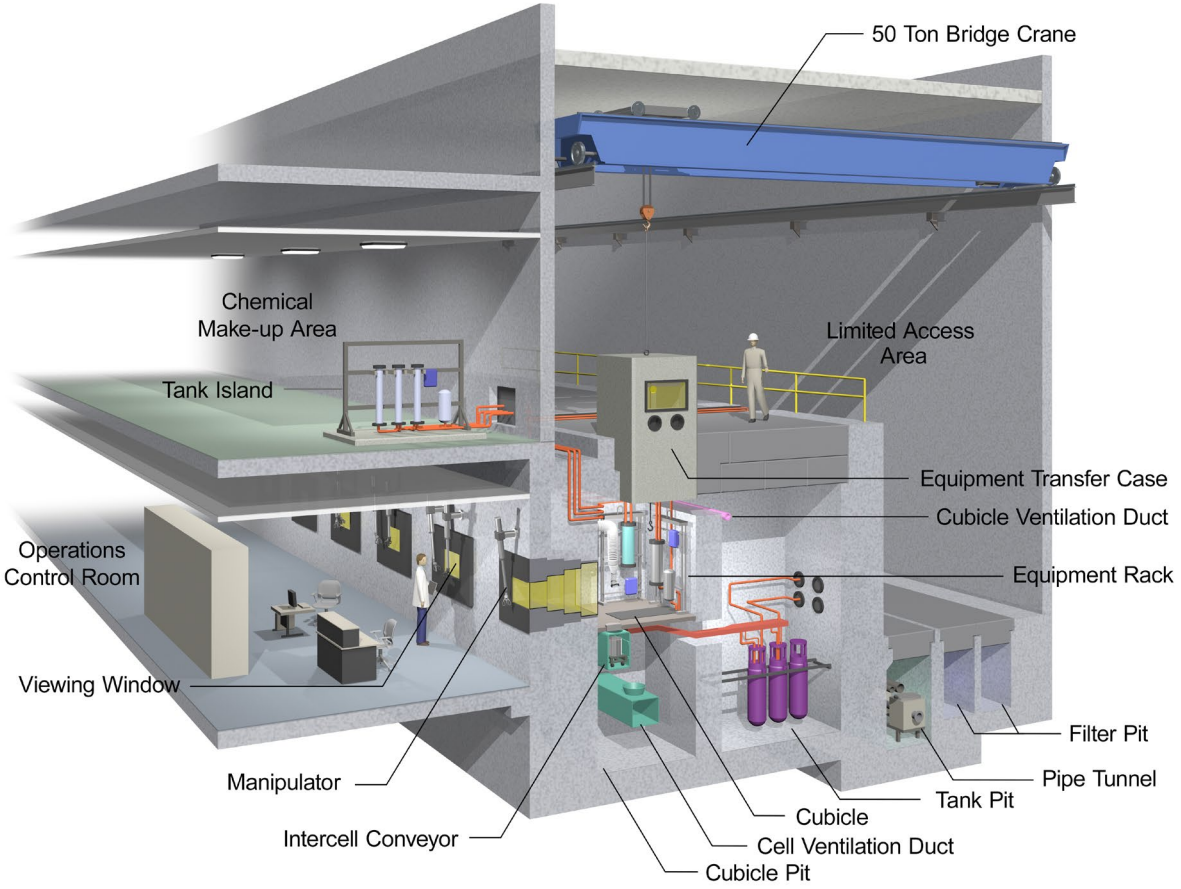


HFIR operations are supported by the Office of Basic Energy Sciences in DOE's Office of Science

Radiochemical Engineering Development Center

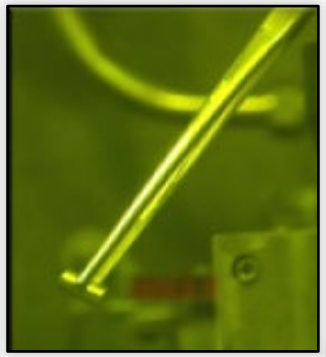
Unique capabilities for radiochemical processing and related R&D

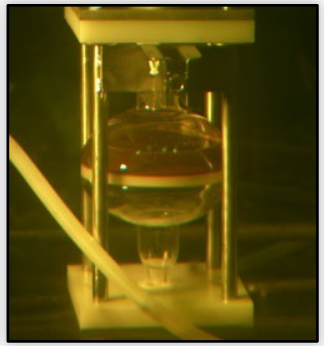
- Heavily shielded hot cells for radiation control and alpha containment
- Shielded caves for radiochemical processing and R&D
- Glove box labs for final product purification and R&D
- Radiochemical labs for sample preparation and analysis
- Cold labs for chemical make up, cold testing, and target fabrication



REDC is fully utilized for research and production for industrial, medical, and research partners

Irradiated Cm target processing at REDC

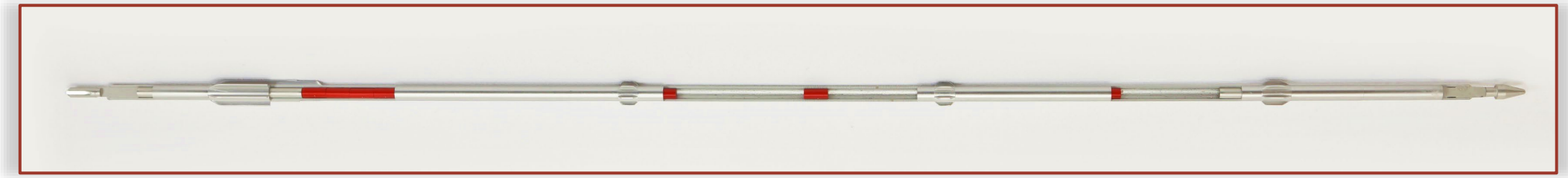




† Di(2-ethylhexyl) phosphoric acid
‡Alpha-hydroxyisobutyrate

Curium target dissolution

Target body and pellets in an Al matrix → Dissolution using caustic-nitrate and heated to ~90 °C → Dissolved aluminum and caustic soluble FPs discarded → Actinide and fission products collected on filter and dissolved with HNO_3



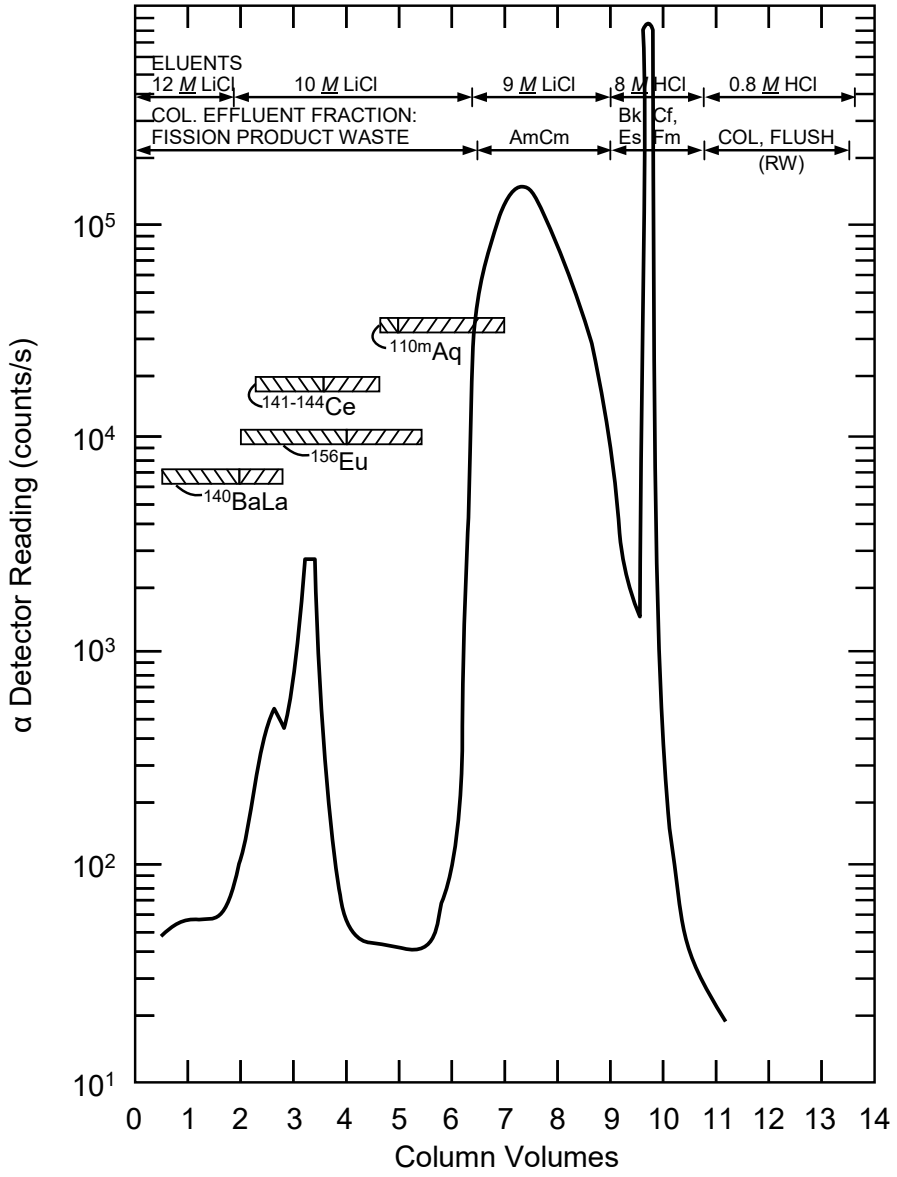
Mockup of Cm target body with Cm pellets (red)

“Cleanex” batch solvent extraction for transplutonium purification

- Purification from non-lanthanide fission products and other metallic impurities as well as plutonium
- Convert from nitrate to chloride form
- Extractant: di-(2-ethylhexyl) phosphoric acid (HDEHP) in a diluent of Exxsol D60 to recover trivalent actinide and lanthanide elements from the dilute acid/salt solution

Actinide/lanthanide separations via LiCl-based anion exchange

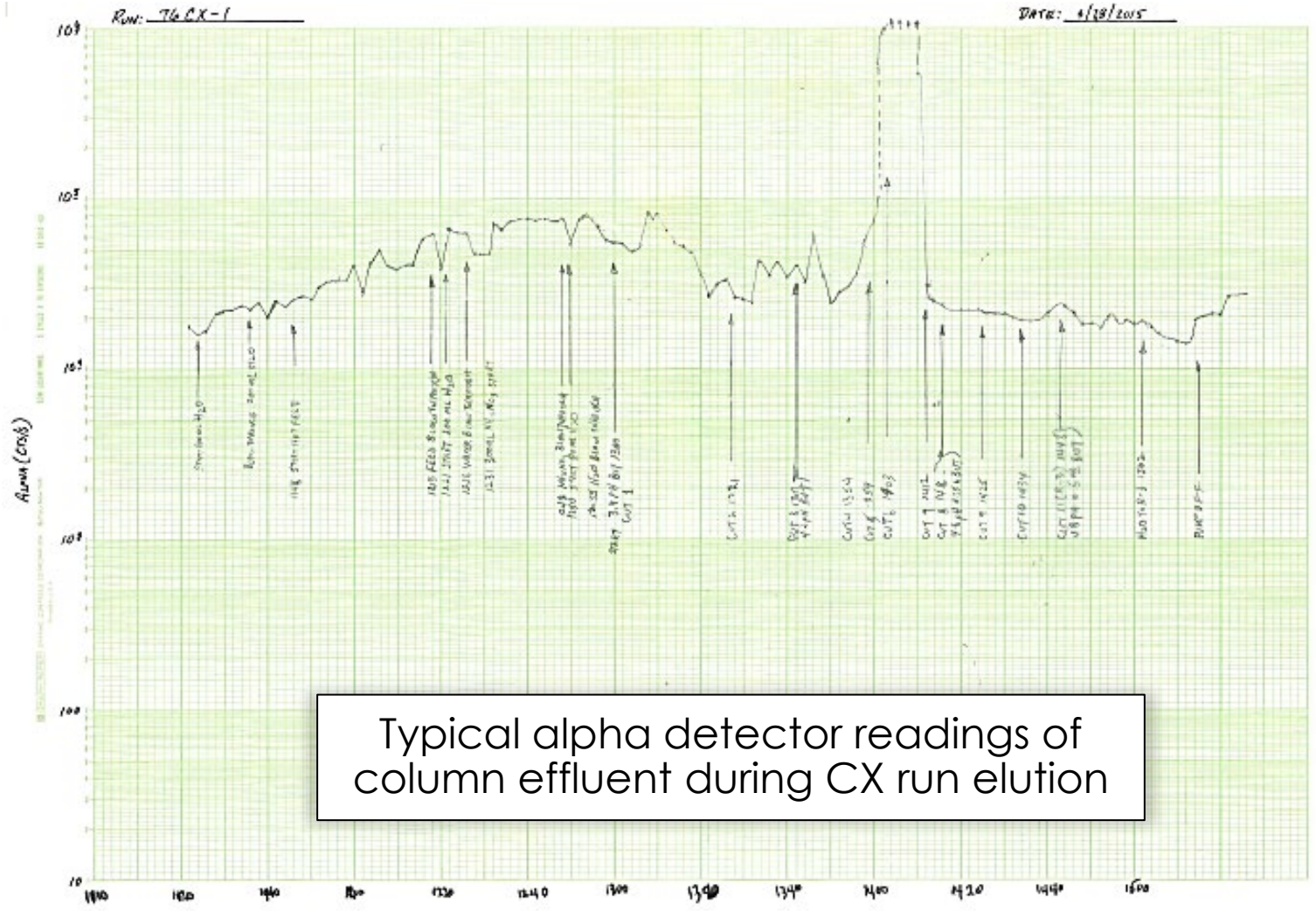
- Separation of Cm, rare earth fission products, and transcurium elements
- Uses a strong base, Dowex 1 × 10 resin, in a tantalum column
- Complexes for each element form at varying strengths, allowing for different rates of movement
- Rare earth elements are eluted nominally at 10*M* LiCl, Am/Cm at 9*M* LiCl, and transcurium elements with 8*M* HCl



Ref. E. D Collins, et. al., Multigram Group Separation of Actinide and Lanthanide Elements by LiCl-based Anion Exchange, ACS Symposium Series No. 161, Transplutonium Elements—Production and Recovery, J. D. Navratil and W. Schulz

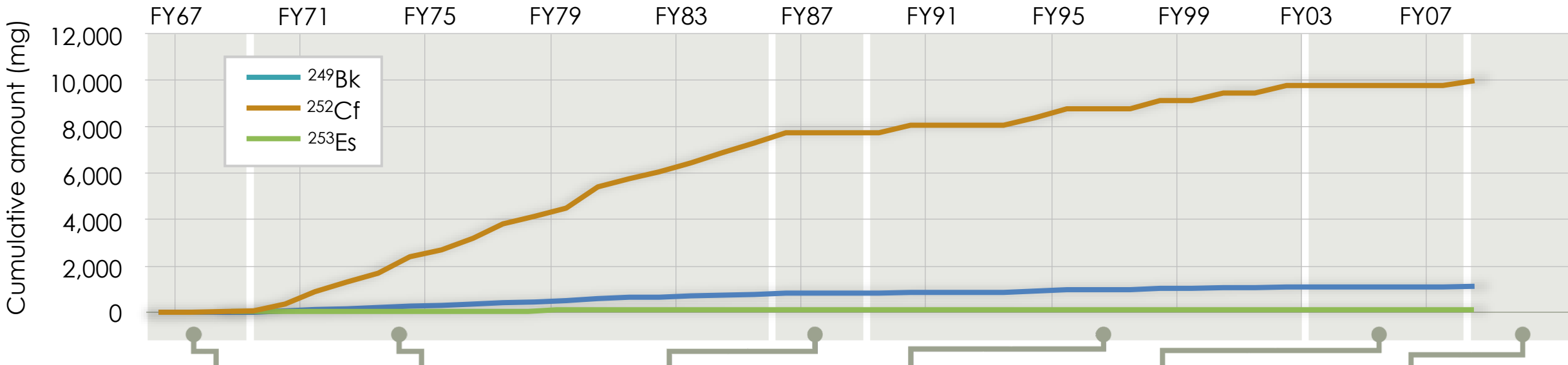
Transcurium element separations via cation exchange elution using AHIB

- Conversion from chloride form to nitrate by hydroxide precipitation, filtration, and re-dissolution in HNO_3
- Elemental separation by ammonium alpha-hydroxyisobutyrate (AHIB)at varying values of pH
- Column is heated ~70°C
- Element (band) separation followed with neutron and alpha probes



Typical alpha detector readings of column effluent during CX run elution

REDC actinide production history



1966–1970

- Feedstock primarily ^{242}Pu, some ^{243}Am–^{244}Cm
- Required 30 targets in HFIR core
- Longer irradiation period
  - W.P. Overbeck, C.H. Ice, G. Dessauer, *Production of Transplutonium Elements at Savannah River,* DP-1000, 1965

1970–1987

- HFIR at 90% capacity (100 MW)
- SRS reactor in high flux mode 1969–70, lower flux until 1979
- HFIR feedstock enhanced with curium from SRS
- ^{252}Cf produced at TRU for SC R&D and DP ^{252}Cf marketing programs
- ^{252}Cf inventory to ~1 g

1987–1990

- HFIR shut down for inspections, reviews, and changing management structure
- ^{252}Cf marketing program transferred from SRS to ORNL

1991–2004

- HFIR operating at 85 MW, 50–60% capacity
- ^{252}Cf inventory depleted, production rate = use rate (+ decay)

2004–2009

- SC/BES funding for TRU program ends
- 7 HFIR targets fabricated, put in HFIR prior to shutdown

2009–present

- SC-NP funding for ^{252}Cf production begins
- Effort to restore ^{252}Cf inventory begins
- SC-NP/HEP funding for separation and purification of ^{249}Bk, $^{253/254}$Es, and $^{255/257}$Fm
- Began ^{238}Pu production

Some major scientific impacts of the heavy element products

Discovery of new heavier elements and isotopes using heavy element radionuclides as accelerator/ cyclotron targets

^{253}Es (0.17 mg, self-illuminated)

Basic research on the physics of heavy elements

- Electron behavior in orbitals
- Nuclear properties
- Nuclear reactions

The heavy element program was endorsed twice by the National Research Council

100+ publications resulted each year from research using heavy element products

E.K. Hulet, "Bimodal Symmetric Fission Observed in the Heaviest Elements," *Phys. Rev. Lett.* 56, 313–316 (1986)

Discovery of bimodal fission in some nuclides with $Z \geq 100$

Basic research on the chemistry of heavy actinides

- Chemically stable compounds
- Crystal structure of salts
- Solution chemistry
- Spectroscopy

nature › articles › article

Article | Published: 03 February 2021

Structural and spectroscopic characterization of an einsteinium complex

Korey P. Carter, Katherine M. Shield, Kurt F. Smith, Zachary R. Jones, Jennifer N. Wacker, Leticia Arnedo-Sanchez, Tracy M. Mattox, Liane M. Moreau, Karah E. Knope, Stosh A. Kozimor, Corwin H. Booth & Rebecca J. Abergel

Nature **590**, 85–88 (2021) | Cite this article

Unique actinide isotope productions

^{249}Bk

- Essentially at equilibrium at 1 cycle of HFIR irradiation and decay (24 days up, 14 days down)
- Amounts may be increased with a lower flux
- Impacts quality of ^{252}Cf produced

^{250}Cf

- Produced from short irradiations of separated ^{249}Bk
- Multi-microgram amounts of ^{250}Cf produced; very little ^{252}Cf produced as a contaminant

^{251}Cf

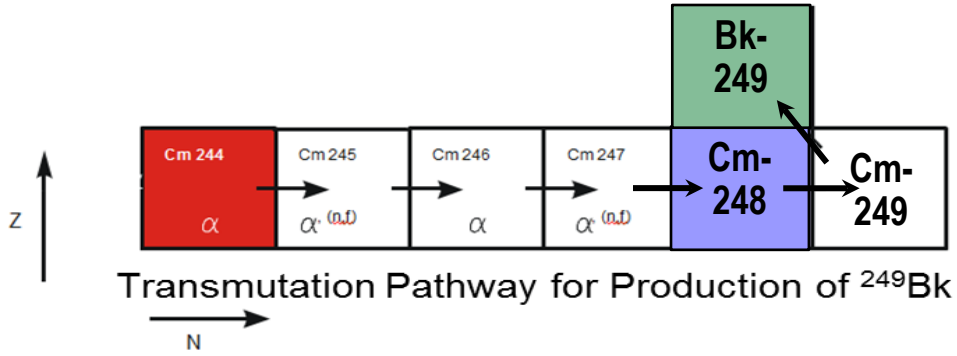
- Can be recovered in a mix of Cf isotopes from long-decayed ^{252}Cf sources
- Difficult to make directly and use, without isotope separation, because of the presence of ^{252}Cf

^{254}Es

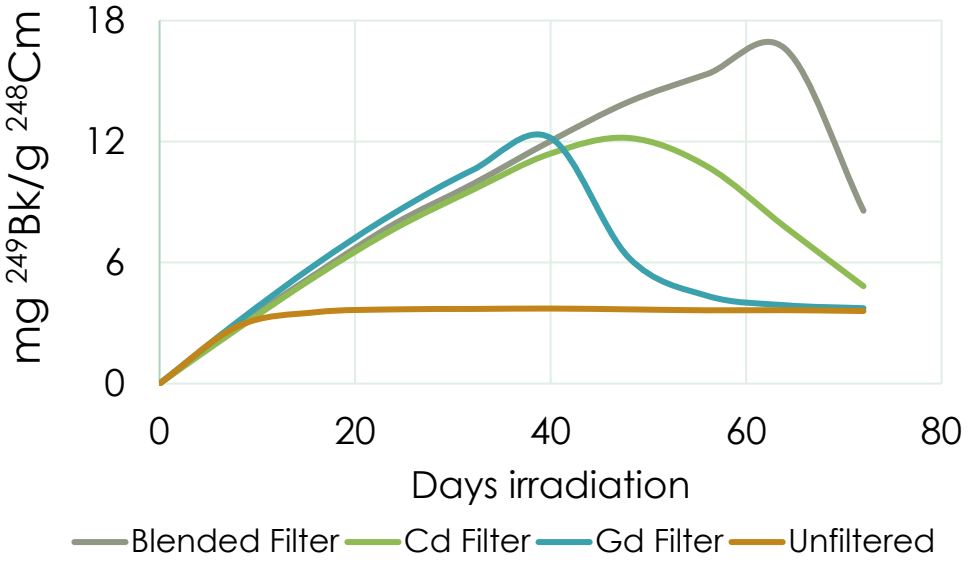
- Production is enhanced with a higher mass target such as ^{252}Cf
- Production limited to a large degree by neutron-induced fission losses on ^{253}Cf

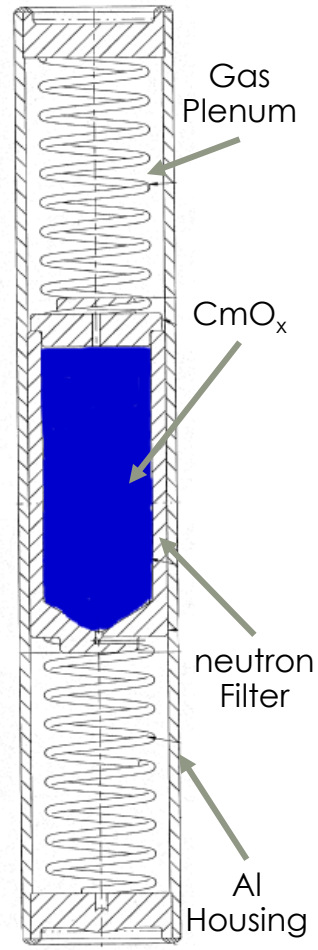
Advanced ^{249}Bk target development

- Use of optimized blended neutron filters to enhance production of ^{249}Bk from ^{248}Cm
- Possible to increase ^{249}Bk yield by ≥200% (50 mg ^{248}Cm produces 0.25 mg ^{249}Bk in 1 irradiation)
- Irradiation of a 100 mg target is planned for 2020
- Bk irradiation reaches equilibrium in ~15 days, so target can be irradiated, processed, and reirradiated in a few months



Calculated filtered and unfiltered ^{249}Bk yields





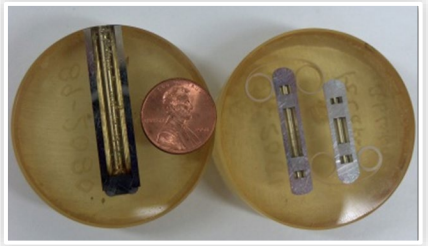
Recovering ^{251}Cf from old californium sources

- ^{251}Cf: Heaviest target material available in sufficient quantities for superheavy element (SHE) research
- Recovered from decades-old ^{252}Cf sources as a mixture of $^{249–251}$Cf (up to 70 mg potentially available)
- Mixed-Cf targets being used at JINR to synthesize heaviest nuclei to date (A = 295, 296 oganesson)

Californium recovery from aged sources		
Cf isotopes	Isotopic distribution	Quantity (mg)
Cf-249	48.10%	7.6
Cf-250	15.60%	2.5
Cf-251	36.30%	5.7
Cf-252	0.04%	0.007

ORNL's Rose Boll and Shelley Van Cleve process recovered mixed-Cf material in shielded glovebox

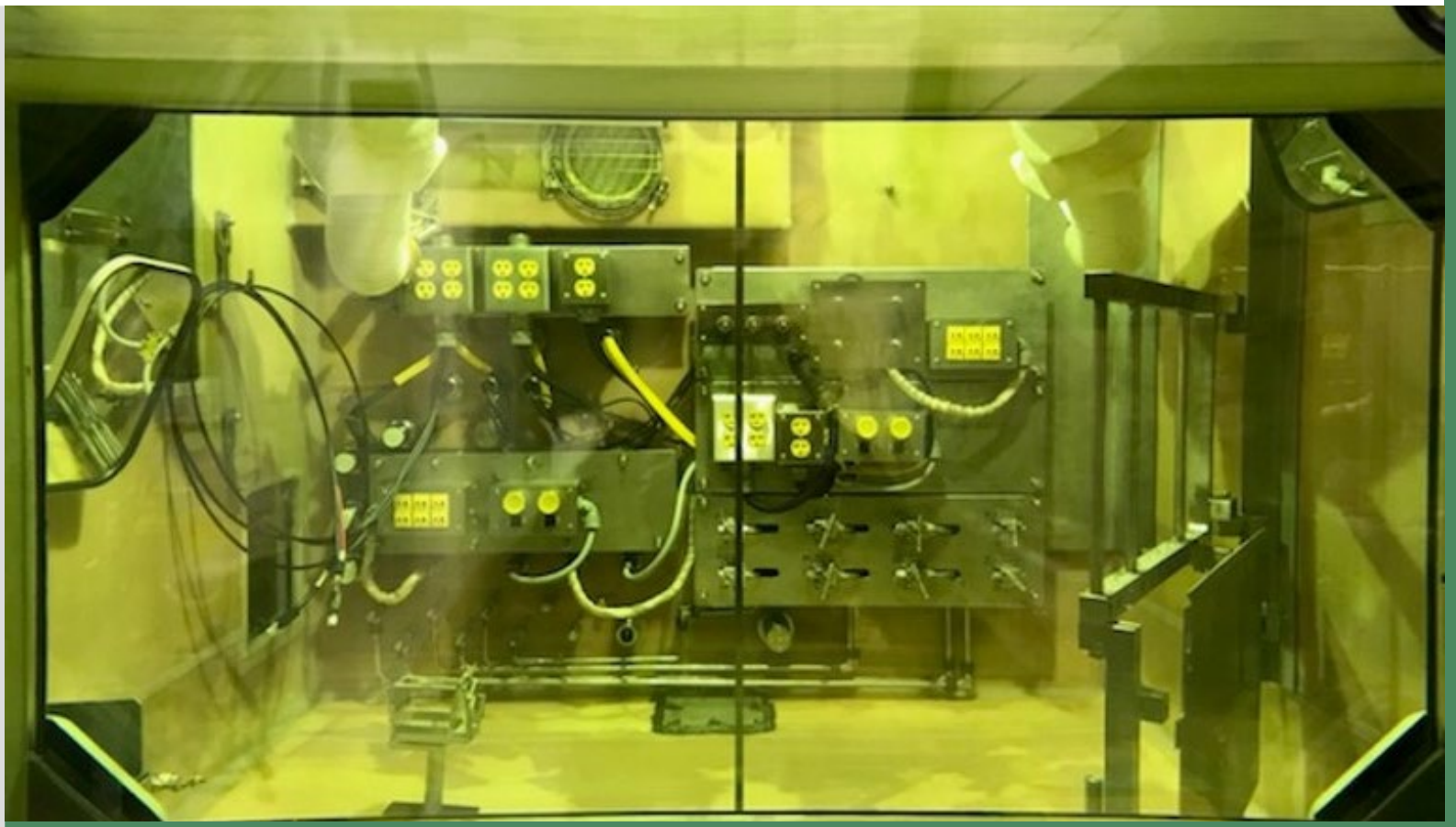
Rose Boll et al., *J. Radioanal. Nucl. Chem.* (2015); Nathan Brewer et al., *Phys. Rev. C* (2018)



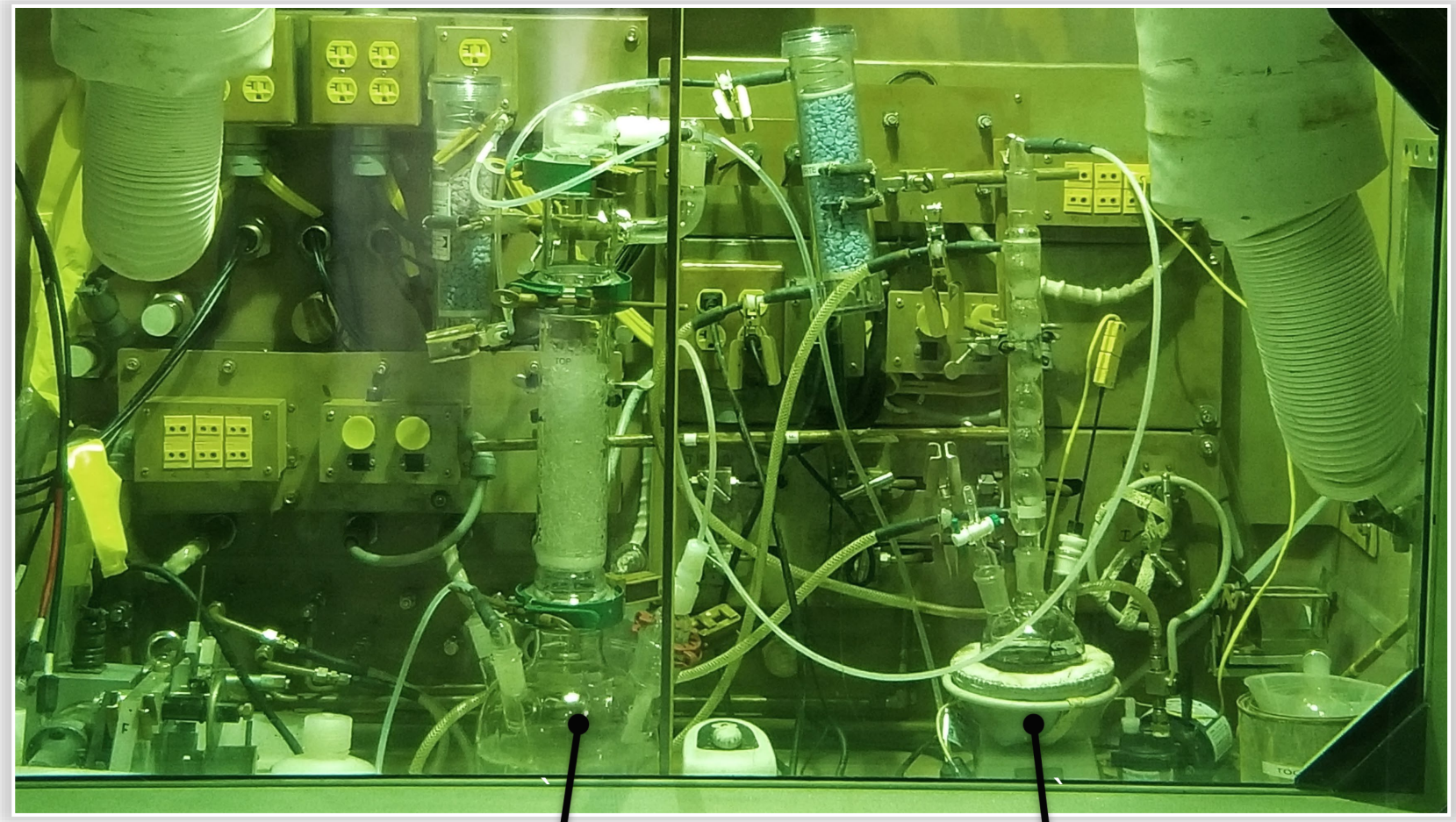
SR-Cf-100
neutron source

Shielded cave used for Cf-251 processing

- 20 in. thick concrete walls
- Leaded glass-air filled
- New liner
- All new connections



Shielded cave set up for dissolution

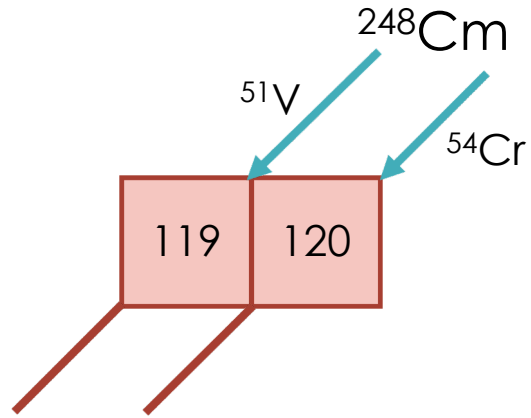


Base bath system

Round bottom flask,
heating mantle,
and reflux condenser

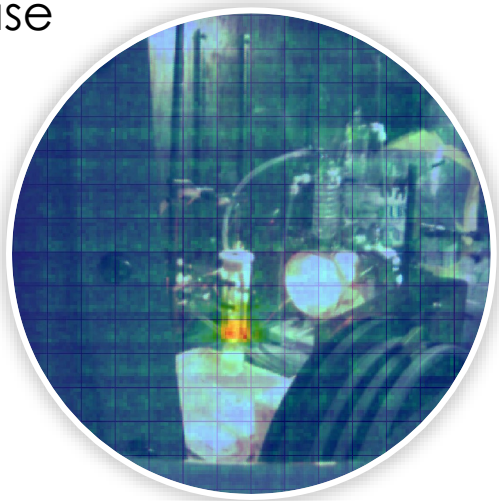
Recovery of high-weight-percent ^{248}Cm

- Projected needs for proposed SHE research ~100 mg
  - Elements 119 and 120 using ^{51}V and ^{54}Cr beams
  - p,n reactions using ^{48}Ca beams followed by electron capture, for example to reach N = 180 ^{294}Fl
- Recovery paths
  - Recover ~86 wt% ^{248}Cm from old ^{252}Cf sources (yields ~100 mg from available high-assay sources)
  - Separate Cm ingrowth from routine ^{252}Cf production (yields ~10 mg/year >90 wt% ^{248}Cm)

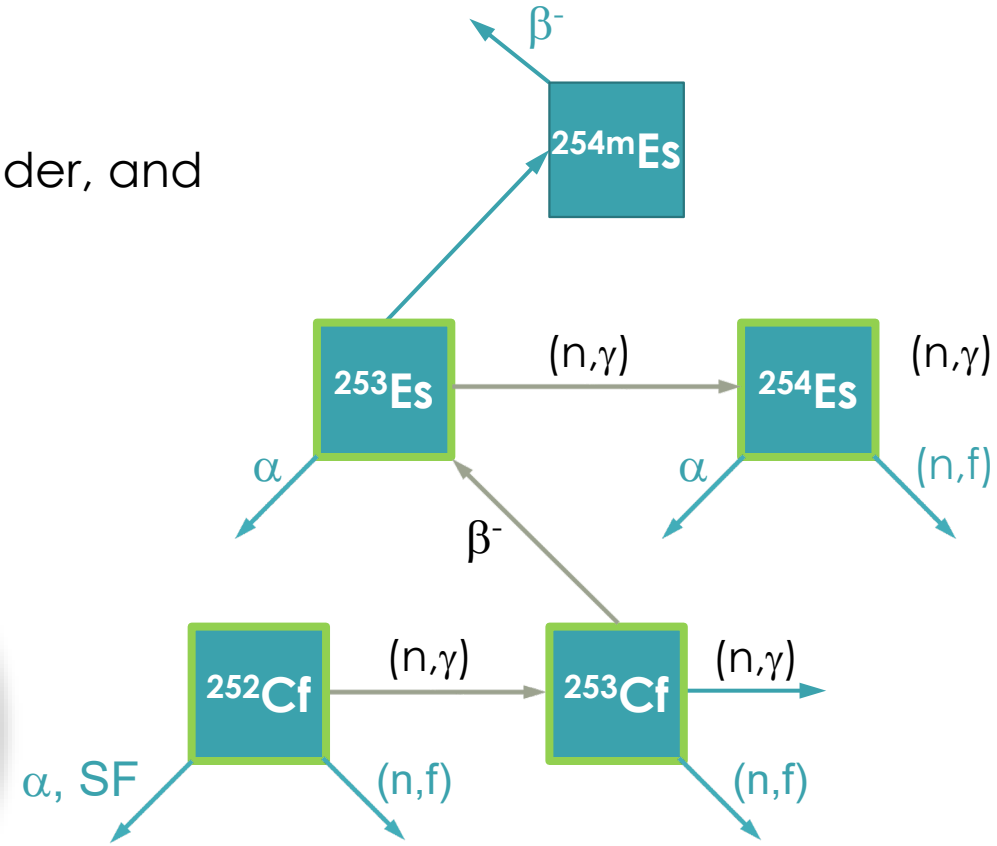


Increasing Einsteinium production
Revisiting the Large Einsteinium Activation Program (LEAP)

- Dedicated HFIR campaign proposed in the 1980s to maximize production of ^{254}Es ($T_{1/2}$ 276d) (Bigelow, Alexander, and King)
- Could yield up to 40 µg of ^{254}Es beginning with ~1g of ^{252}Cf
  - 300 times less material than the typical SHE target
- Can neutron spectrum filtering increase this yield?
- ^{254}Es attractive (if available) as path to element 119 (using ^{48}Ca beams) and 121 (^{50}Ti beams)
  - N=180 using ^{48}Ca (3n channel)
  - Significant target heating and damage challenges
  - Large-scale ^{254}Es production would be both complex and expensive

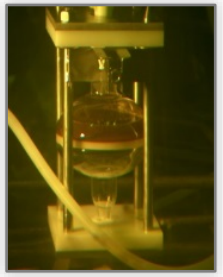


Gamma signature of Es in resin column at REDC



New processing developments

7920 hot cells and HFIR



Irradiated targets

Aluminum dissolution

HFIR irradiation

Caustic soluble FP

Nitric acid dissolution

Target fabrication

HDEHP extraction

Waste organic

Microsphere preparation

Cm

Am-Cm Separation

Am

LiCl anion exchange

Lanthanide FP

Oxalate precipitation

Am/Cm product

Hydroxide precipitation

Am/Cm product

AHIB cation exchange

Trans Cm

Hydroxide precipitation

Bk

Cf

Es

Fm

HDEHP: Di (2-ethylhexyl) phosphoric acid
AHIB: Alpha-hydroxyisobutyrate
FP: Fission products

Bk Finishing Operations in Campaign 77

In Hot Cells

Convert Bk/Cf/Impurities of low HNO_3/AHIB into a solution of 8 *M* HNO_3 by a pre-conc. CX column

Adjust Bk/Cf/Impurities of 8 *M* HNO_3 into a solution of HNO_3- $NaBrO_3$
Bk(III) → Bk(IV)

HDEHP-dodecane

HNO_3-1 *M* H_2O_2

BERKEX (SX w/HDEHP) in HNO_3-$NaBrO_3$

HNO_3- $NaBrO_3$
Raffinate/Scrub/Cf

Waste HDEHP

Repeat Above or

HNO_3-H_2O_2
Transfer to Glove-box
(Bk, Ce, impurities)

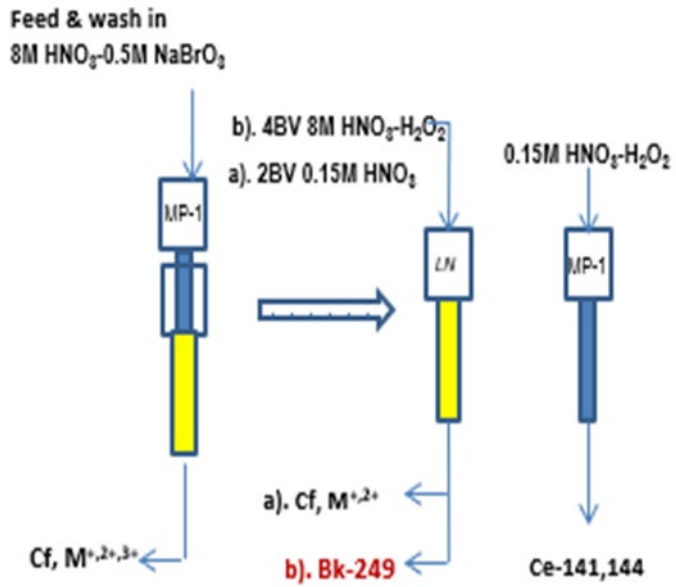
Among RE only Ce stays with Bk due to formation of Ce (IV)

By CX-AHIB in Glovebox

- 3x Organic Scrub
  1-2 days
- Volume Reduction
  to 1 mL
  2-4 days
- Initial Cation Column
  2 days
- AHIB column
  Prep 4 days
  Run 1 day
- Final Cation Column (AHIB removal)
  1-2 days

11-15 processing days

By Dual Column in Glovebox

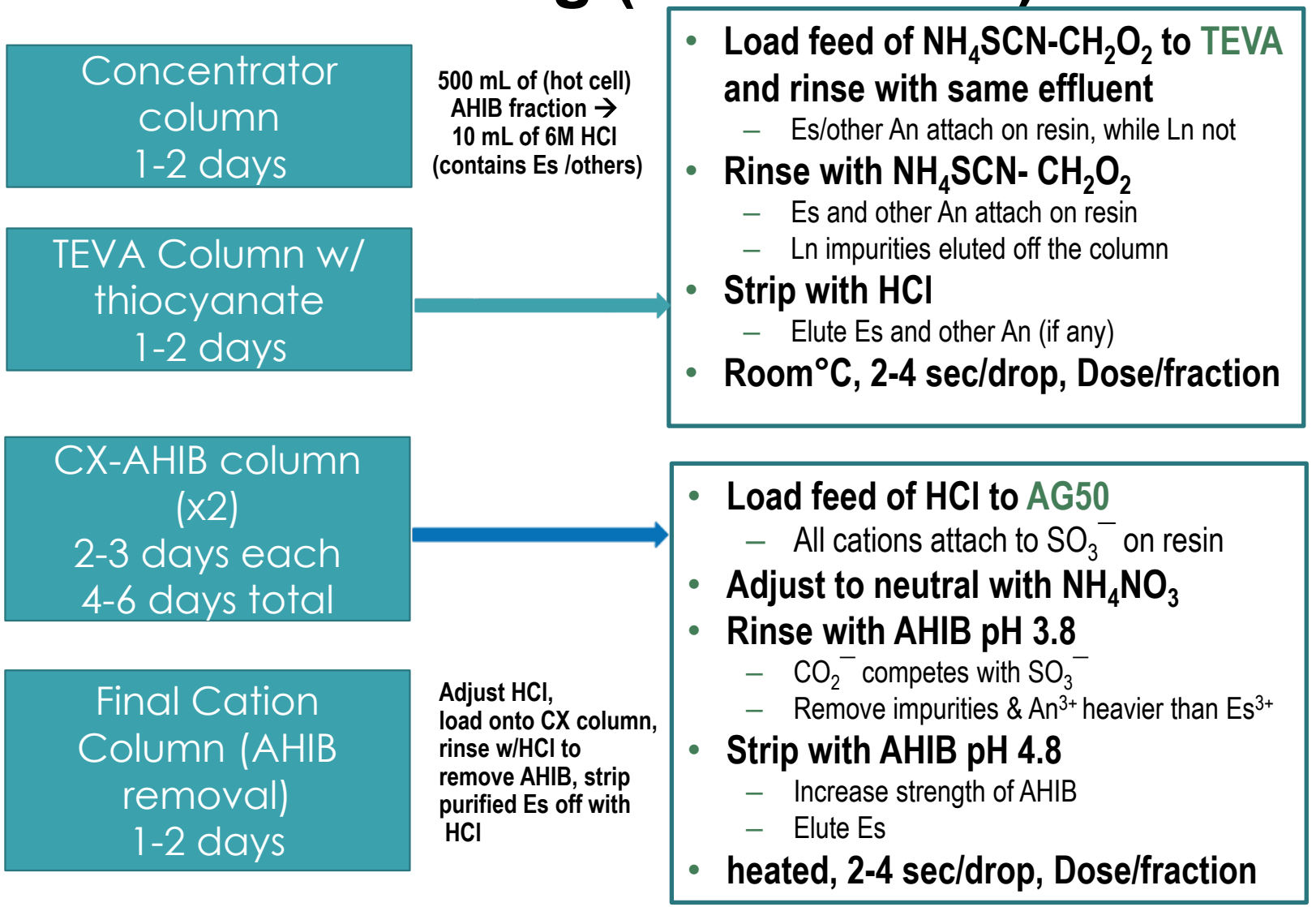


~3 processing days

CX – cation exchange resin column

Miting Du, Ryan Tan, Rose Boll, "Application of MP-1 anion exchange resin and Eichrom LN resin in berkelium-249 purification", Journal of Radioanalytical and Nuclear Chemistry, V318(1) 619-629, 2018

Es Processing (established)



Consideration of Method Options for Es Purification

- "Es" is a heavier actinide than Cf and off the column early by CX-AHIB, but requires four steps of column operations—Is possible to purify Es by fewer columns?

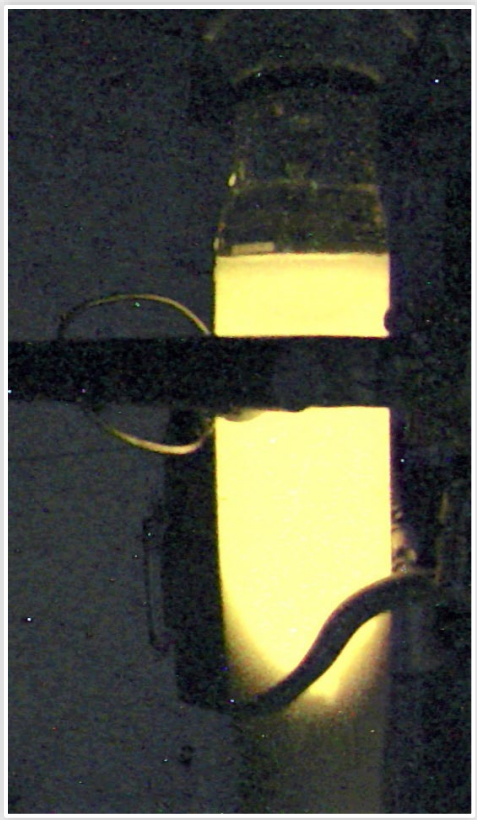
- R&D Options:

  After a concentrator column for feed prep,

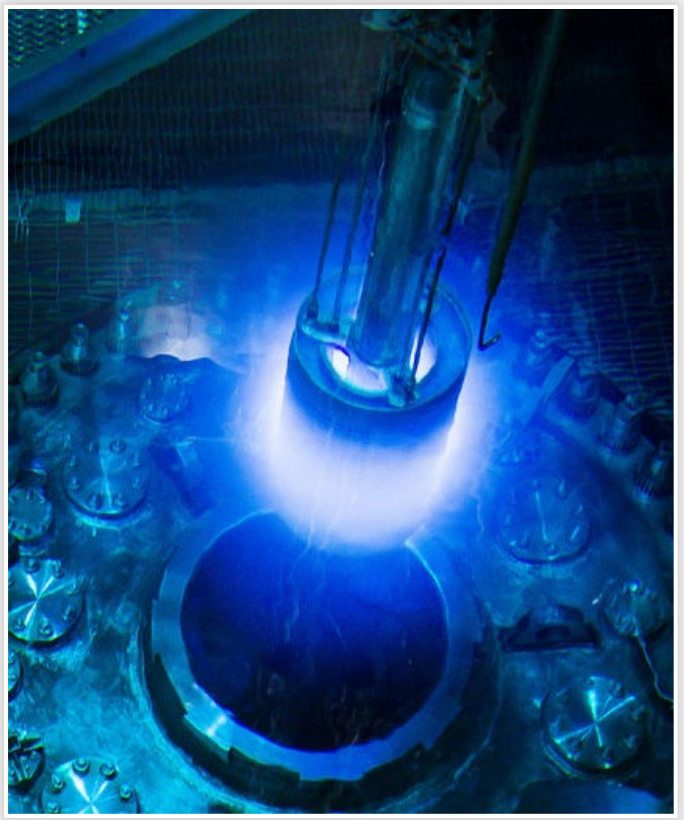
  - Run Es-Cf-Ln with a TEVA column to remove Ln. The feed solution is loaded to a CX column attach a *LN* column to CX-AHIB column in style of dual column, then elute the dual column (CX-*LN*) with AHIB pH 4.8 (Es retains on *LN*). Detach the *LN* column and elute with HCl to remove AHIB. Strip Es off with high HCl for product. (Minor changes at the end of CX-AHIB step, shortening Final Column run.)
  - Run Es-Cf-Ln in varying [HCl] through a *LN* column off in order of Ln, Cf, and Es, with a 0.5 mL DGA attached to absorb Es in HCl. Strip Es off DGA with HCl (Easy drying down for final product).
  - Run Es-Cf-Ln through TEVA column in NH_4SCN-0.1M CH_2O_2 to remove Ln, then to separate Es/Cf on same TEVA column by elution with varying [HCl].

Summary and conclusions

- REDC has conducted 78 successful radiochemical campaigns
- Campaigns have produced significant quantities of Bk-249, Cf-252, Es-253/254, and Fm-255/257
- Heavy actinides will be produced for the foreseeable future
- HFIR to be operational beyond 2040
- New production and separation methods are being explored and implemented



Loading of the Cm onto the resin column



Fuel changeout at HFIR

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Acknowledgments

- Research supported by the US Department of Energy Isotope Program, managed by the Office of Science
- This research used resources of the Oak Ridge High Flux Isotope Reactor, which is a DOE Office of Science User Facility
- ORNL is managed by UT-Battelle, LLC for the US Department of Energy under contract DE-AC05-00OR22725
- Chuck Alexander (ret.), Dennis Benker, Rose Boll (ret.), Emory Collins, Lætitia Delmau, Miting Du, Susan Hogle, Shelley Van Cleve.

Discussion