SEPTEMBER 10-13, 2017
MONTREAL MARRIOTT CHATEAU CHAMPLAIN
MONTREAL, QC CANADA

ARGONNE EXPERTISE AND CAPABILITIES

AMANDA YOUKER

Chemist –
Nuclear Engineering Division

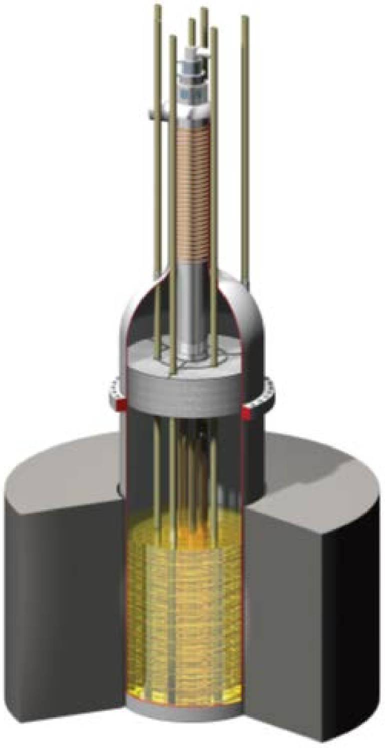
Sergey Chemerisov, Peter Tkac, David Rotsch, Alex Brown, Thomas Brossard, Jerry Nolen, David Ehst, Michael Kalensky, John Krebs, Kurt Alford, James Byrnes, William Ebert, Roman Gromov, Charles Jonah, Kevin Quigley, Kenneth Wesolowski, Nick Smith, John Greene, Walter Henning, Joengsoeg Song, Candido Pereira, Artem Gelis, Mark Williamson, David Chamberlain, Megan Bennett, and George F. Vandegrift

ARGONNE'S ROLE IN MO-99 PROGRAM

- Assisted multiple potential US Mo-99 producers
  1. BWXT – Aqueous Homogeneous Reactor
  2. NorthStar – Neutron Capture
  3. NorthStar - Accelerator
  4. SHINE – Accelerator-driven process for fission Mo-99
  5. Niowave – Accelerator-driven process for fission Mo-99 (SPP)
- Provided foreign Mo-99 producers with possible front-end processes to allow use of high density LEU-foil targets
  1. Low-pressure system for acidic dissolution
  2. Electrochemical dissolver
- Cooperated with Necsa and NTP in developing
  - Recycling and downblending of spent HEU from Mo-99 production
  - Potential waste forms for irradiated LEU
- Cooperated with Indonesian BATAN and Argentine CNEA to develop and demonstrate the annular LEU foil target
- Cooperated with BATAN to develop and demonstrate the LEU-Modified Cintichem Process currently being used for their production of Mo-99
- Played a major part in many IAEA CRPs on conversion of Mo-99 production to LEU

BWXT – MIPS (MEDICAL ISOTOPE PRODUCTION SYSTEM)

- Developed separation, recovery, and purification processes for Mo-99 from a uranyl nitrate solution
- Designed flowsheet for target solution recycle
- Performed a series of uranyl-nitrate solution irradiations at AFRRI (Armed Forces Radiobiology Research Institute)
    1. Gas generation
    2. Fission product partitioning on titania
    3. Mo-99 separation, recovery, & purification
- Utilized 3 MeV Van de Graaff accelerator to examine the effects of a high radiation field on titania, reagents in purification process, and small-scale column experiments with tracers



Argonne NATIONAL LABORATORY

NORTHSTAR MEDICAL RADIOISOTOPES

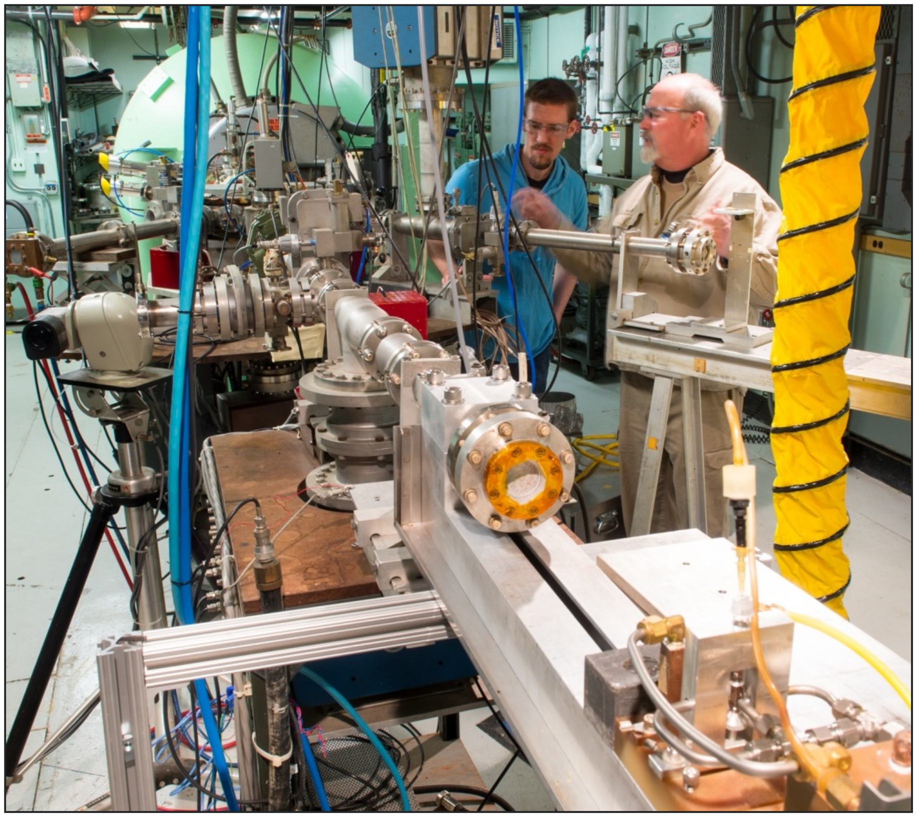
Near Term Solution – Neutron Capture

- University of Missouri Research Reactor (MURR)
  - Mo-98(n,γ)Mo-99

- Argonne R&D Activities
  - Assessing radiation stability of components and materials
  - Developing and demonstrating irradiated disk processing
  - Developing and demonstrating full-scale hot-cell dissolver
  - Developing and demonstrating process for recycle of enriched Mo

RADIATION STABILITY TESTS

Van de Graaff (VDG) Accelerator



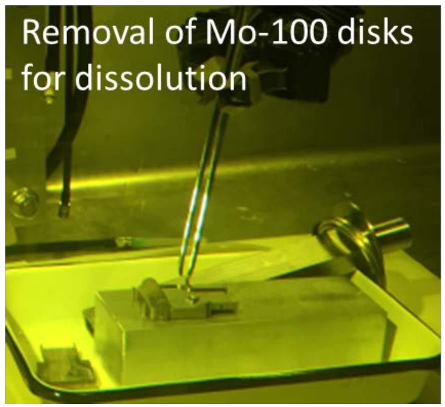
- One example of a radiation damage tests using the VDG
  - Effects of photon radiation on HDPE bottles containing K_2MoO_4 in 6 M KOH
  - Zero to 6.5 MRad shown (up to twice calculated dose expected)

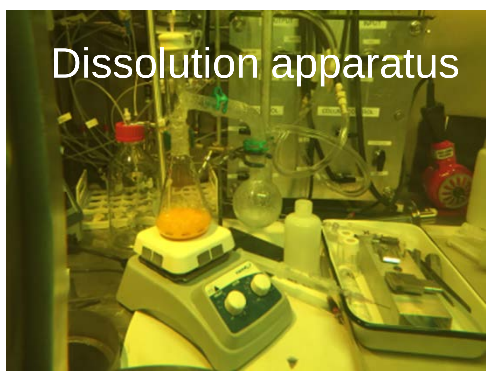
- Syringes, tubing, controllers, pressure gauges, etc. also tested

PROCESSING OF IRRADIATED MO TARGETS

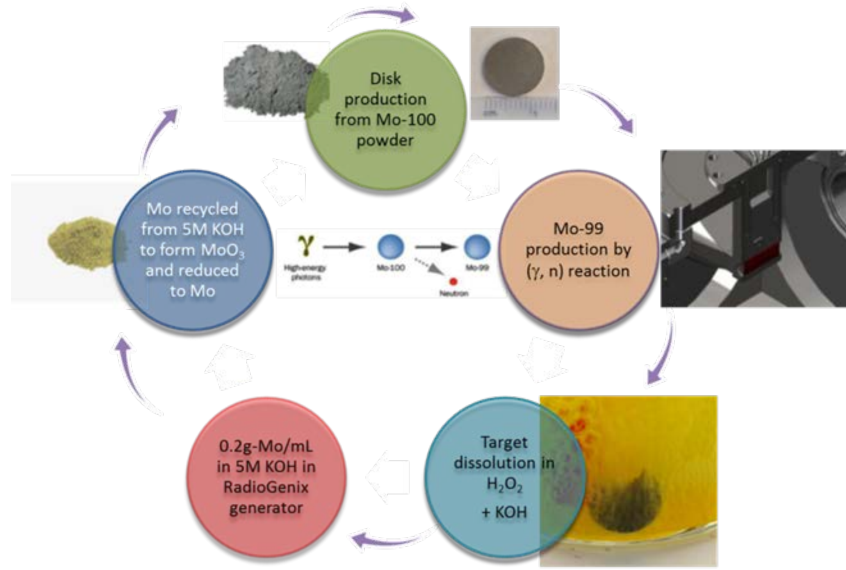
Long Term Solution – Photon Capture

- NorthStar’s accelerator methodology
- Mo-100(γ,n)Mo-99





LANL developed and fabricated target

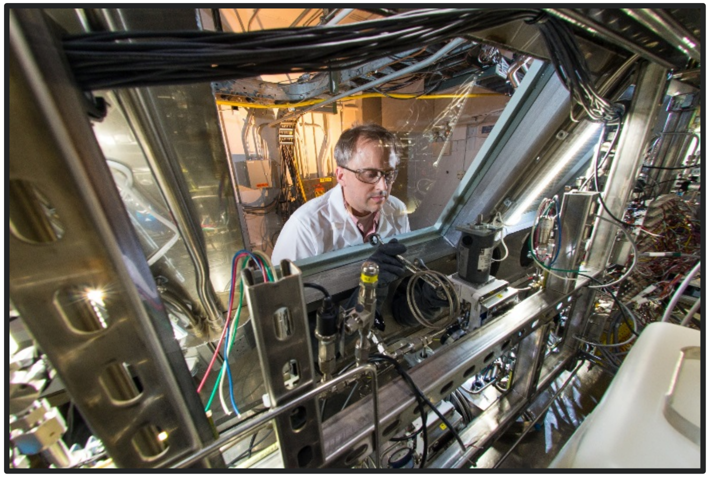


- Patent pending for the recycle process

- 7-day irradiation using electron linac
- Six 95.08% Mo-100 enriched disks
- 12.4 Ci of Mo-99 produced in 6 disks

SHINE MEDICAL TECHNOLOGIES

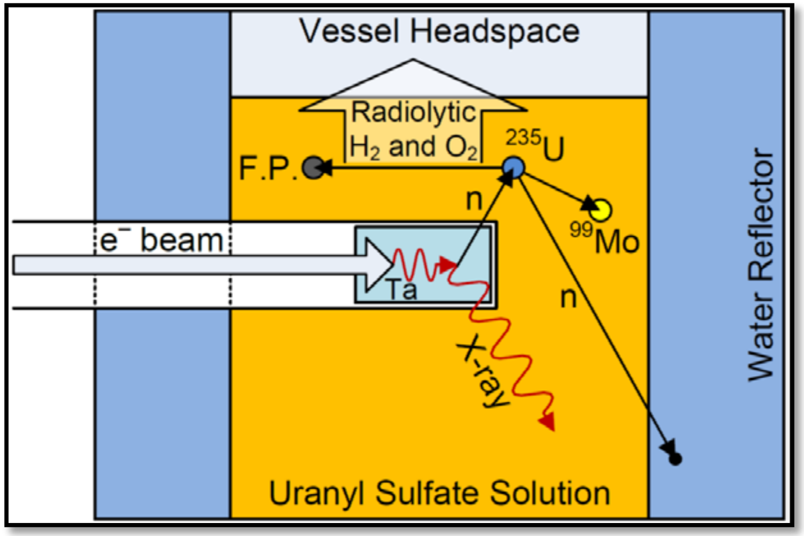
- Developed separation, recovery, and purification processes for Mo-99 from a uranyl sulfate solution
- Designed flowsheet for target solution recycle and waste
- Completed phase 1 AMORE (Argonne Molybdenum Research & Development Experiment)
    1. Gas generation
    2. Fission product partitioning on titania
    3. Mo-99 separation, recovery, & purification
- Utilized 3 MeV Van de Graaff accelerator to examine precipitation of uranyl peroxide, stability of key components in AMORE, and perform small-scale column experiments with tracers



SMALL-SCALE PILOT OPERATIONS

Phase	Status	Energy (MeV)	Beam Power (kW)	Volume and Maximum Mo-99 Produced	Peak Neutron Flux ($n/cm^2 \cdot sec$)	Neutron Flux in solution ($n/cm^2 \cdot sec$)	Neutron Flux in mini-AMORE ($n/cm^2 \cdot sec$)
I	Complete	35	10	5 L & 2 Ci	1×10^{12}	$0.1\text{-}0.2 \times 10^{11}$	0.1×10^{12}
II	Underway	35	20	20 L and 20 Ci	5×10^{12}	$0.5\text{-}1 \times 10^{11}$	$0.5\text{-}1 \times 10^{12}$

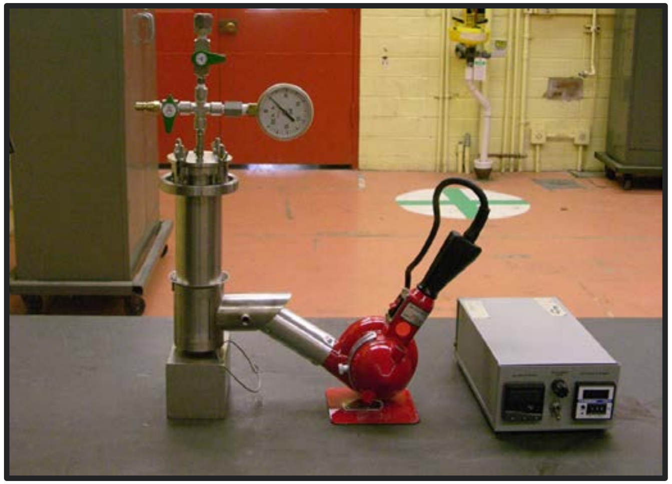
- Solutions irradiated at 35 MeV
  - Phase I target: Ta
  - Phase II target: DU
- Study the effects of fission on target-solution chemistry and radiolytic off-gas generation
- Demonstrate the recovery and purification of ^{99}Mo from an irradiated target solution
- Ship ^{99}Mo product to potential ^{99m}Tc generator manufacturer partners



A.J., Youker, S.D., Chemerisov, P., Tkac, M., Kalensky, T.A., Heltemes, D.A., Rotsch, G.F. Vandegrift, J.F., Krebs, V., Makarashvili, & D.C., Stepinski.*J. Nuc. Med.*, 2016, 116, 181040.

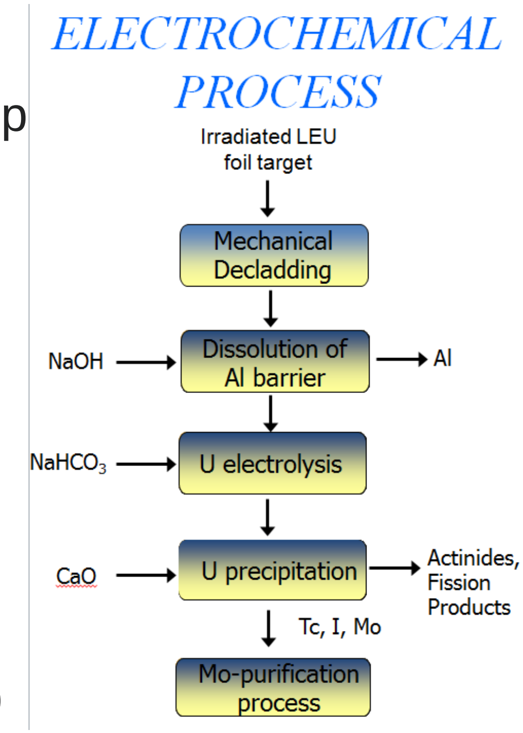
NIOWAVE

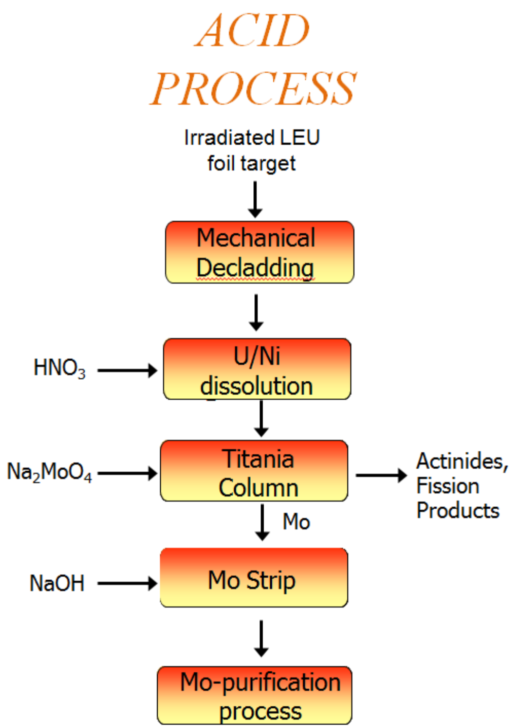
- Argonne provided Niowave with dissolver drawings
- Argonne optimized conditions for dissolving ~20 g U pellets in HNO_3
- Argonne trained Niowave staff on dissolution and LEU Modified Cintichem process for Mo-99 purification
- Argonne provided recommendations on type of cladding for Niowave targets
- Argonne gave recommendations for equipment (hoods, filters, etc) to purchase to build radiochemistry laboratories at Niowave



ARGONNE HIGH DENSITY-TARGET FRONTEND PROCESSES

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

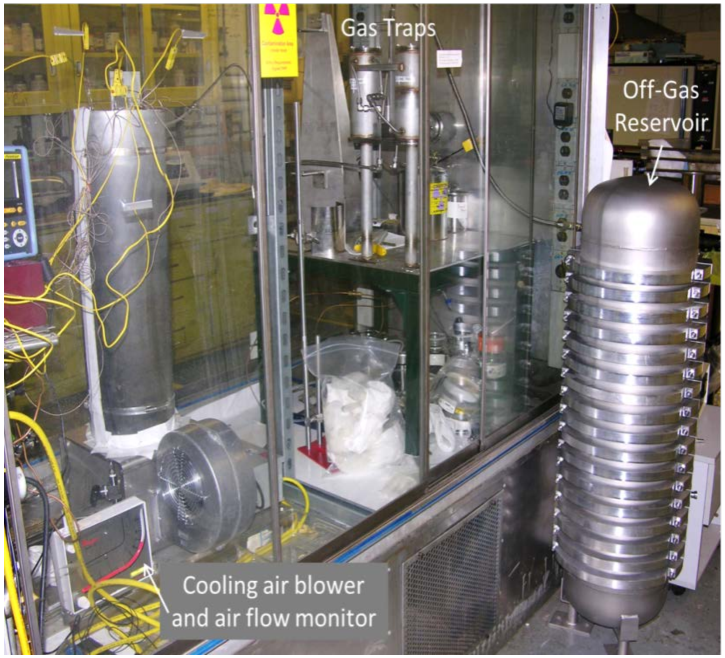




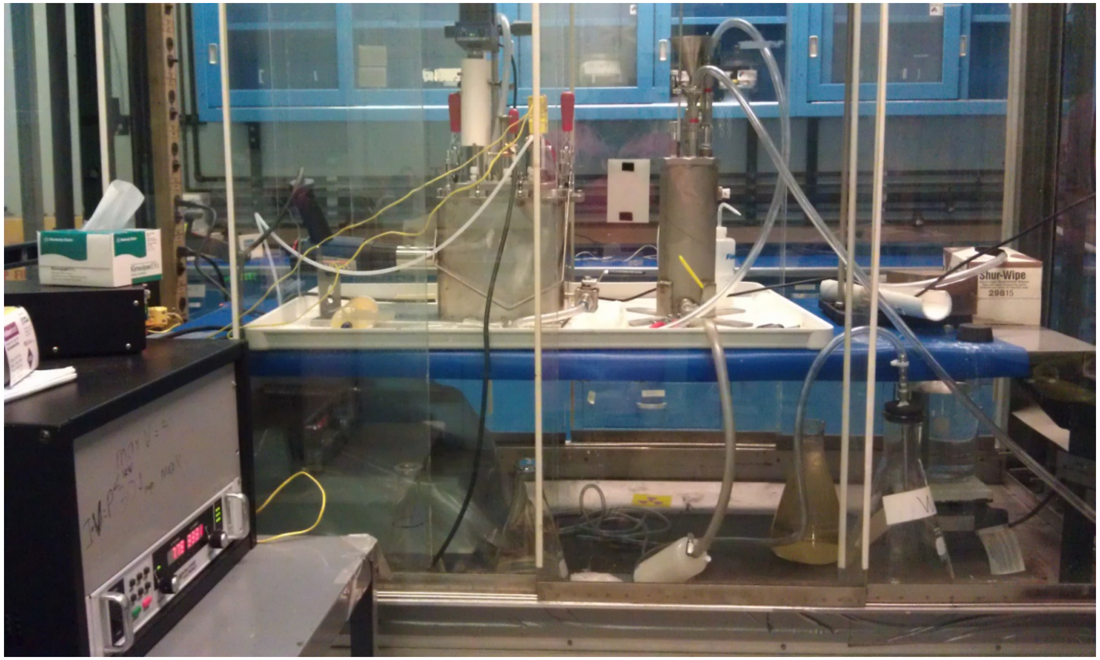
- Full-scale design
- Resistant to radiation, corrosion, and hot-cell compatible
- 250-g U/batch
- Cold test (Ni)
- Warm test (DU)
- Hot test (irradiated LEU)

ARGONNE HD-TARGET FRONTEND PROCESSES

ACID PROCESS



ELECTROCHEMICAL PROCESS

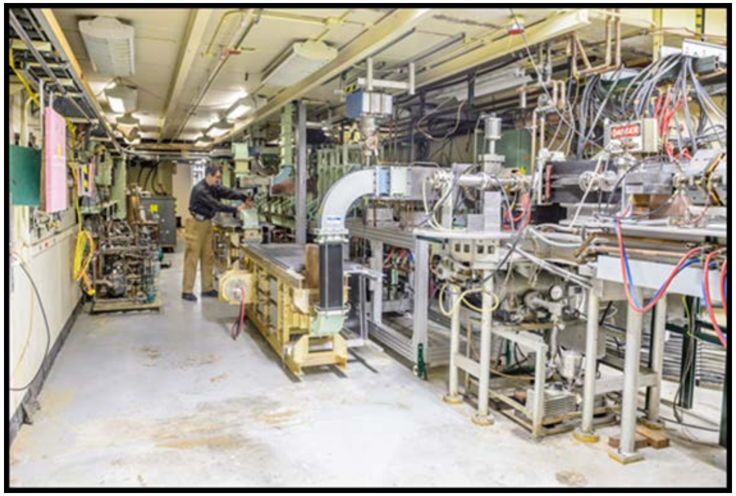


HIGH DENSITY TARGET CONCLUSIONS

- 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 frontends can be fed into current Mo-purification processes.

EQUIPMENT TO SUPPORT MO-99 ACTIVITIES

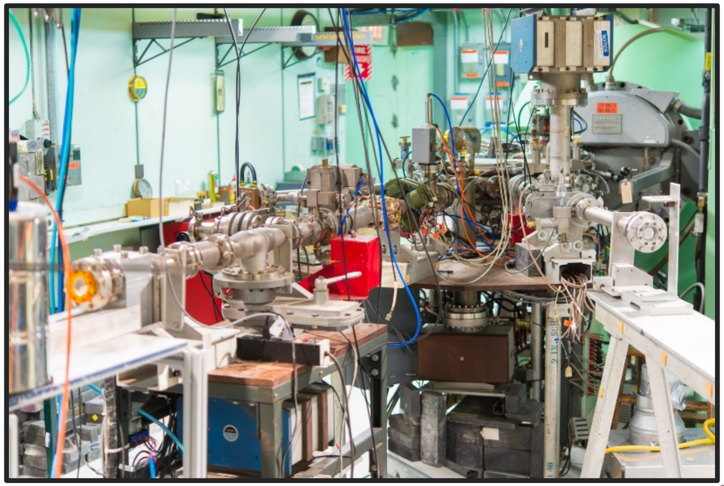
50-MeV Electron Linac



Hot Cell with Manipulators

Shielded Glovebox

3-MeV Van de Graaff accelerator

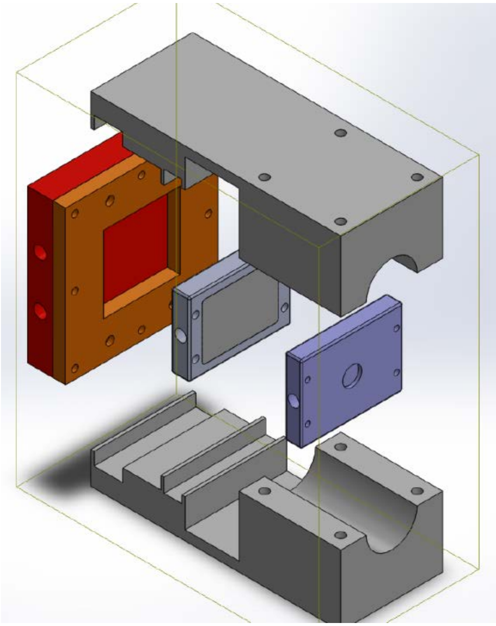


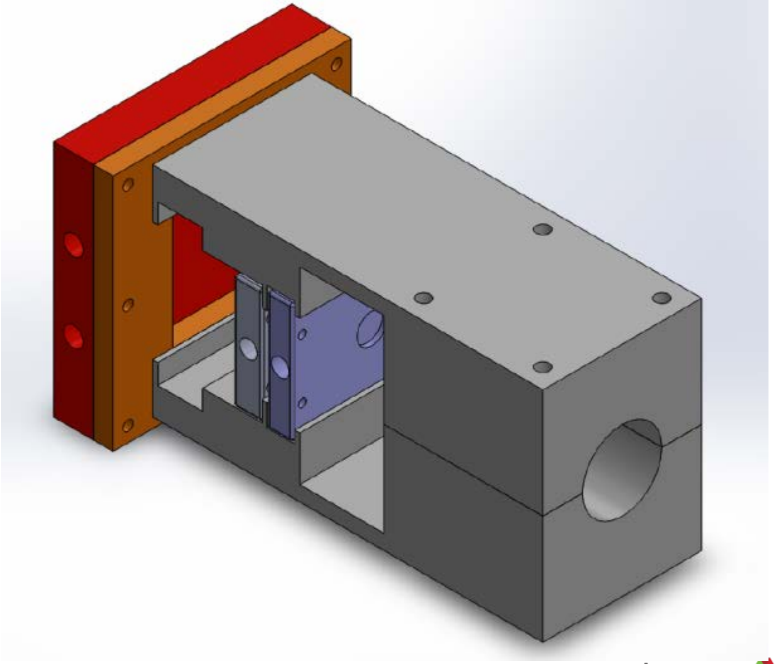
50-MEV ELECTRON LINAC

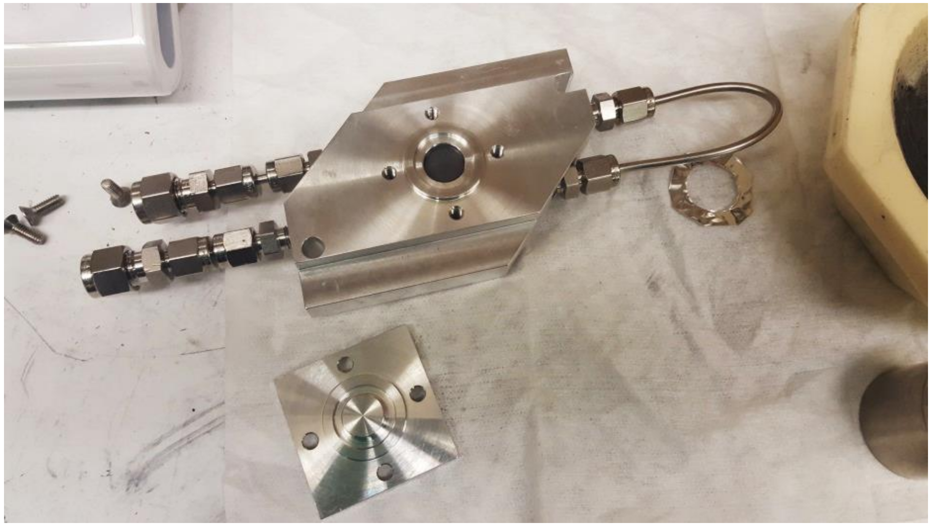
- Delivers continuous or pulsed beams with energy up to 50 MeV and average power of more than 20 kW
- Provides multiple target station locations with ample access for operations and post-run remote target transfer
- Has 3 separate beamlines
- Plays a major role in R&D for Mo-99 program and R&D and production mode for the DOE Isotope Program – Cu-67

"CLAM SHELL" RESEARCH TARGET STATION

- Modular design
  - Multiple convertors
  - Adaptable to various targets
- Small targets
- Beam power dependent on convertor design and the target material
- Low production quantities for R&D development
  - Targetry
  - Chemistry

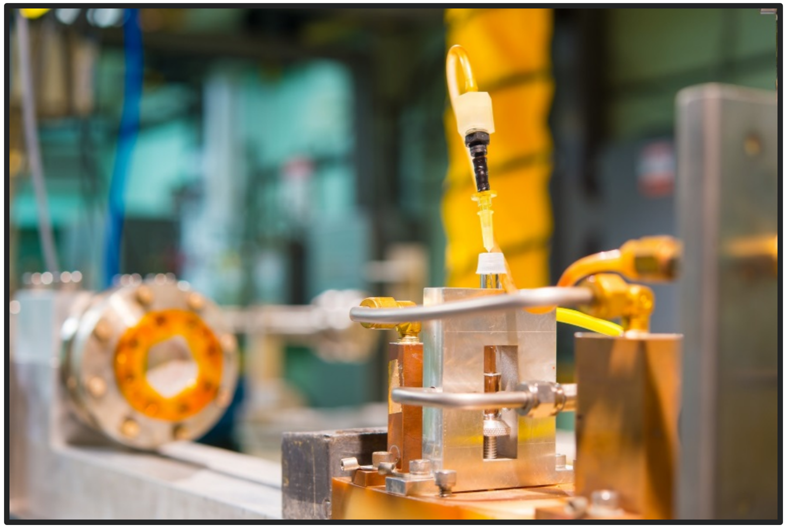


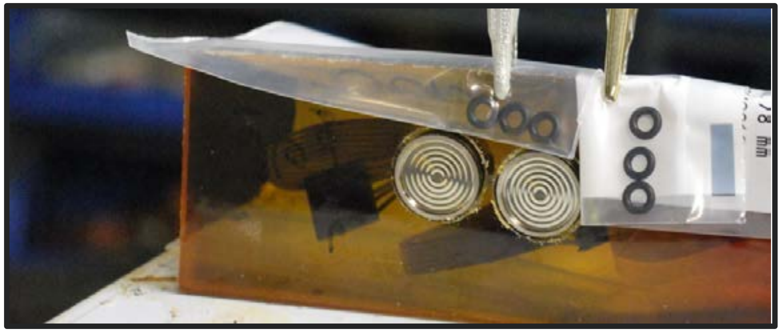




3-MEV VAN DE GRAAFF ACCELERATOR

- Used to test radiation stability of chemicals, key components, and instruments
- Operates in continuous and pulse modes
- Delivers high radiation doses without presenting activation and handling hazards of the irradiated targets
- Often used as a test bed for experiments to be conducted at linac





RELATED FACILITIES

Hot Cells

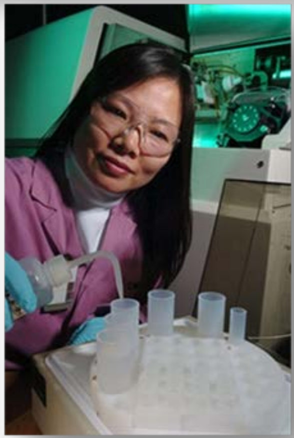
- Support for separations activities and the ability to introduce
and remove samples safely and efficiently
- Adequate shielding for hundreds of Ci of medical isotopes
- Large interior working areas
- Interior equipment within each cell, customizable as needed
- Manipulator mock-up area for pre-job testing of equipment and processes

Radiochemical Laboratories

- Available for radiochemical R&D, processing materials, final chemical processing, quality control, and quality assessment
    - Many rad hoods and gloveboxes (air and inert)

THE ANALYTICAL CHEMISTRY LABORATORY (ACL)

- Full-Cost Recovery Service Center administered by Argonne's Nuclear Engineering Division.
- Our primary mission is to provide a broad range of analytical chemistry support to Argonne scientific and engineering programs.
- The ACL also provides specialized analytical services for governmental, and industrial organizations.
  - Interagency agreement to support US EPA region 5
  - Site analysis for nuclear power plant license applications
- Quality assurance
  - The ACL maintains a graded QA program, tailored to the needs of the project.
- Site support
  - The ACL provides analysis and expertise to support the Argonne site characterization and waste management programs.



Argonne NATIONAL LABORATORY

EXPERTISE AVAILABLE AT ARGONNE

- Separation sciences and technologies
- Nuclear and chemical engineering process development
- Radiochemistry
- Analytical chemistry
- Targetry
- Electron accelerator physics
- Theoretical simulations
- Radiation effects and dosimetry
- Radiation chemistry

- **Using the expertise and infrastructure developed under Mo-99 program to develop other important medical isotopes through the DOE Isotope Program and internal funds**

THERANOSTIC COPPER-67 AND SCANDIUM-47

- **^{67}Cu**
  - **Theranostic**
    - $t_{1/2}$ = ~2.5 days
    - Average β-: 141 keV
    - γ: 184.6 keV (49%)
    - Decays to stable Zn
  - Match pair with ^{64}Cu
    - PET
  - Uses: treatment of non-Hodgkins lymphoma, and other cancers
  - Lack of supply halted clinical trials
  - Chelation chemistry well-known due to ^{64}Cu PET-analogue

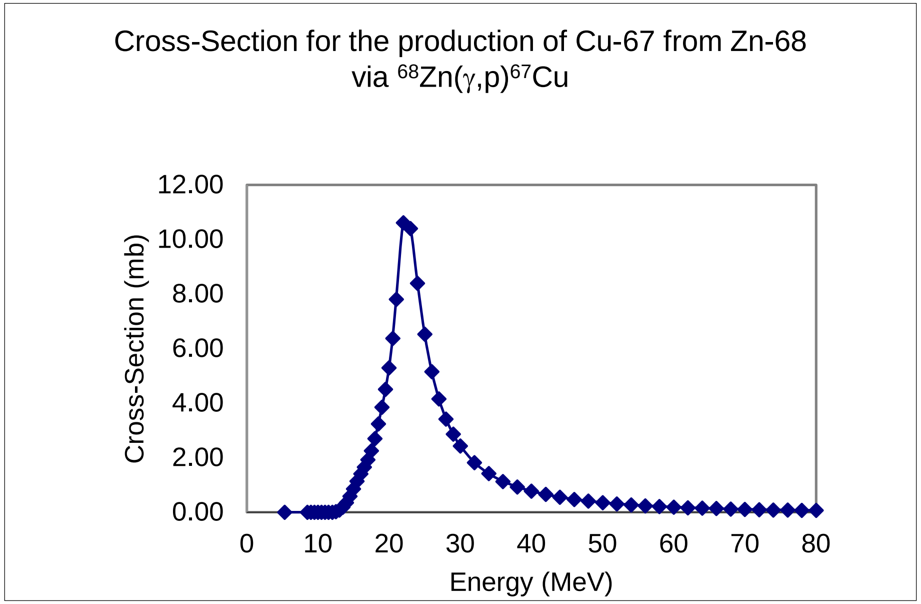
*Work supported by Office of Science Isotope Program.

- **^{47}Sc**
  - **Theranostic**
    - $t_{1/2}$ = 3.35 days
    - Average β-: 162 keV
    - γ: 159.3 keV (68.3%)
    - Decays to stable Ti
  - Match pair with ^{44}Sc
    - PET
  - Uses: promising candidate for cancer treatment
  - Chemical-cousin to lanthanides currently used in radiopharmaceuticals and (MRI-CA)
  - Synergistic with current IDPRA funded efforts to produce ^{44}Ti/^{44}Sc generator

*Work supported by Argonne National Laboratory.

^{67}Cu COPPER-67

- Bremsstrahlung: ^{68}Zn(γ,p)^{67}Cu
  – Requires a mid to high energy LINAC
  – ^{67}Cu reaction has a gamma energy threshold at ~15 MeV and a peak at ~26 MeV
  – Enriched targets will virtually eliminate co-produced isotopes
  – Simplifies separation chemistry
  – “Clean” production with enriched target
    - ^{68}Zn – 19% abundant



- Enriched ^{68}Zn ingot
  – 100 g (99.35% enrichment)
  – ~30 mm x ~35 mm (w x h) cylinder

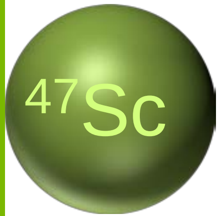
M.B. Chadwick, et al. ENDF/B-VII.1: Nuclear Data for Science and Technology: Cross Sections, Covariances, Fission Product Yields and Decay Data", Nucl. Data Sheets **112**(2011)2887

COPPER-67 PRODUCTION READINESS

- Ready for Production
  - 200 mCi batches
  - Specific Activity expected to be >30 Ci/mg
    - Individual metal content sub-μg
    - Cu-content acceptable
    - Radionuclidic purity: >99% Cu-67
  - Binds TETA effectively

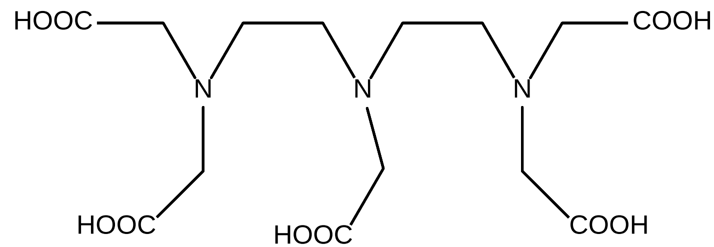
- Future plans prepare for 1 Ci batches
  - Funding required
  - Hot cell operations
  - Modify sublimation apparatus for hot cell operations
  - "Automate" as much of the wet chemical processing as possible

*Work supported by Office of Science Isotope Program.

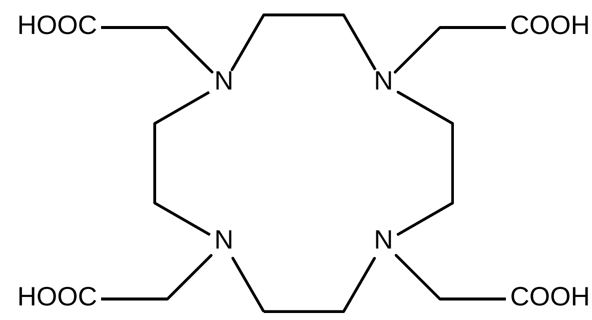


THERANOSTIC SCANDIUM-47

- Radiological Properties
  - Half life – 3.35 days
    - Decays to stable ^{47}Ti
  - Beta emitter
    - Average Beta: 162 keV
  - Gamma emission
    - 159.38 keV (68.3%)
- Match Pair with ^{43,44}Sc
- Chemical “cousin” to the lanthanides
- Well-known chelation chemistry



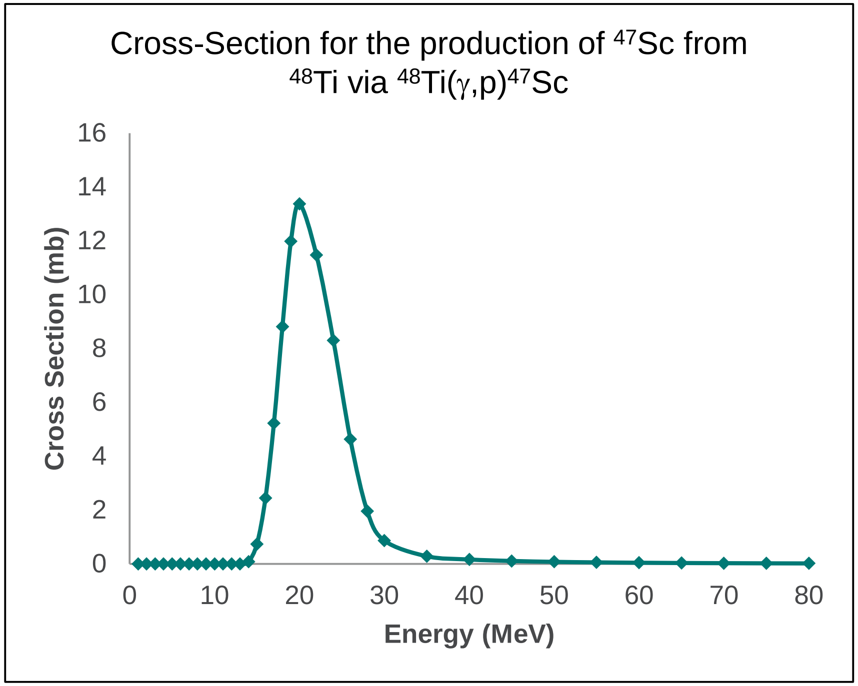
DTPA: diethylenetriaminepentaacetic acid



DOTA: 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid

SCANDIUM-47

- $^{48}Ti(\gamma,p)^{47}Sc$
  - Requires a high energy LINAC ~40 MeV
  - ^{47}Sc reaction has a gamma energy threshold at ~15 MeV and a peak at ~22 MeV
  - Enriched targets will virtually eliminate co-produced radioisotopes
    - "Clean" production with enriched target (^{48}Ti – 73.7% - natural abundance)
- TiO_2 – titanium dioxide
  - Density: 4.23 g/cm^3
- TiC – titanium carbide
  - Density: 4.93 g/cm^3
- Pellets pressed into cylinder
  - 12.7 mm x 12.7 mm cylindrical targets
- Custom H_2O-cooled Target Holder



Koning, A.J., et al. *TENDL-2014: TALYS-based evaluated nuclear data library*. **2014**, Available from: ftp://ftp.nrg.eu/pub/www/talys/tendl2014/gamma_html/gamma.html

CURRENT STATUS OF CU-67 AND SC-47

^{67}Cu via $^{68}Zn(\gamma,p)^{67}Cu$

- Current Production Capabilities
  - 200 mCi monthly batches
- Specific Activity acceptable for chelation chemistry
- TETA titrations show excellent binding and effective specific activities
- Funding required to increase production levels >200 mCi/batch
  - Cost/mCi drops considerably with 1 Ci batches
- Test batch recipients being located by NIDC

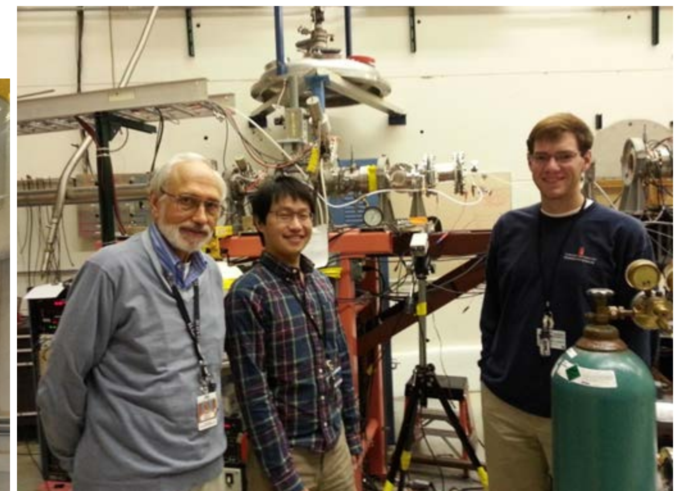
^{47}Sc via $^{48}Ti(\gamma,p)^{47}Sc$

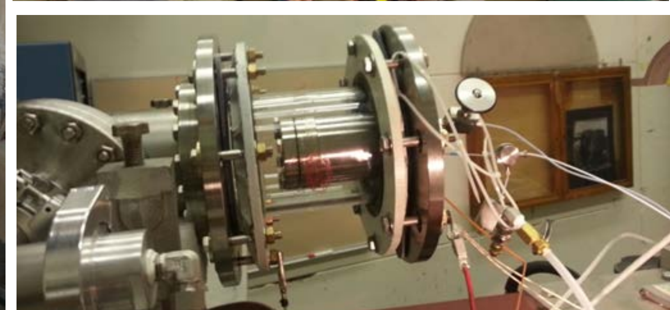
- Current Production Capabilities
  - 60 mCi ^{nat}Ti weekly batches
  - 80 mCi ^{48}Ti bi-weekly batches
- Processing chemistry completed
- Purity acceptable for chelation chemistry
- Funding required to ramp production levels
- Test batch recipient needs

R&D FOR HIGH PRIORITY ISOTOPES AT THE SUPERCONDUCTING ION BEAM LINAC ATLAS

ATLAS is a superconducting ion-beam linac at Argonne which is a National User Facility operated by the DOE Office of Nuclear Physics

- Can be used a small percentage of the time for medical isotope R&D
  - Present emphasis is on therapeutic isotopes such as the alpha emitter ^{211}At and Auger-electron emitters





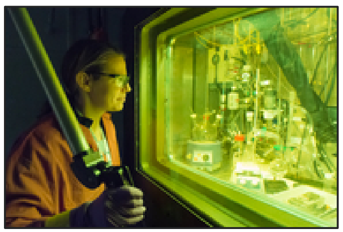
GROWTH BEYOND MO-99

Goal - become a US R&D center for small-scale production, separation, and labeling of medical radioisotopes

Medical Isotopes

^{99}Mo production with Linac

^{99}Mo from solid targets or LEU solutions



The entire chemical recovery process is evaluated

Other isotopes:

1. Isotopes particularly suited to photonuclear production:

^{67}Cu from Zn target

^{47}Sc from Ti target

Low fission yield isotopes

2. ATLAS: R&D for high priority isotopes using light ion beams

Key recovery operations:

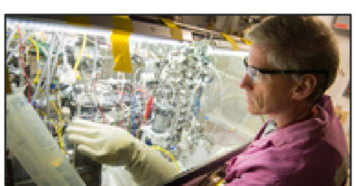
Target Fabrication

Extraction chemistries

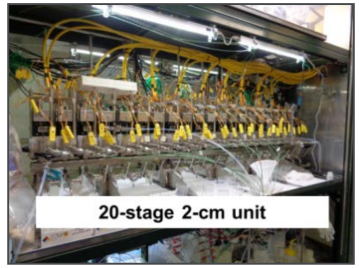
Solution clean-up

Off-gases

Waste forms



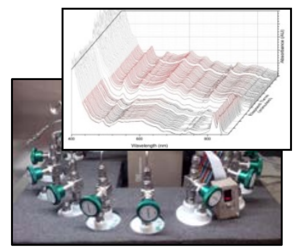
Process Monitoring



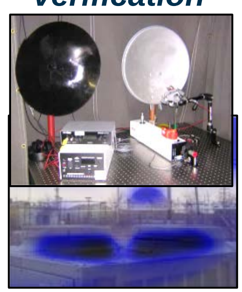
Real time accounting of material in-process

Safeguards Test Bed

Test concepts, measure actinide and FP concentrations, process status near real time



Combination of process knowledge and data collection provides verification

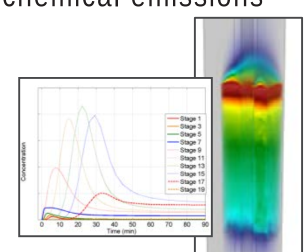


Remote sensing of processing facilities

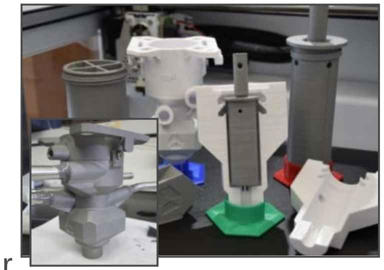
MMW and PAS for standoff & remote characterization of operations & chemical emissions

Process Modeling

Capability to evaluate observations, predict behavior



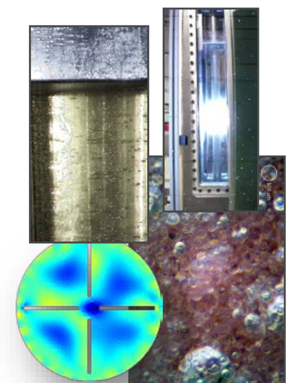
Design and Manufacture



Rapid implementation and testing of new concepts

Advanced equipment designs

3D printing in combination with advanced computation yields novel designs and flexible fabrication routes

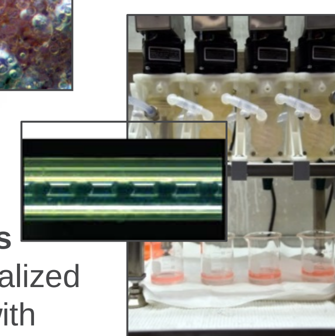


Imaging and instrumentation

Validation of code predictions, chemistry fluid behavior and design schemes

Advanced materials technologies

Enable specialized testing and with reduced cost, risk, and faster scale-up



ACKNOWLEGEMENTS

- 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
- Work supported by Office of Science, Office of Nuclear Physics Isotope Program, and Argonne National Laboratory under U.S. Department of Energy contract DE-AC02-06CH11357

Argonne NATIONAL LABORATORY

ADDITIONAL CAPABILITIES AVAILABLE AT ARGONNE

- Aqueous processing
- Pyrochemical processing
- Waste Forms
- Safeguards
- ATLAS

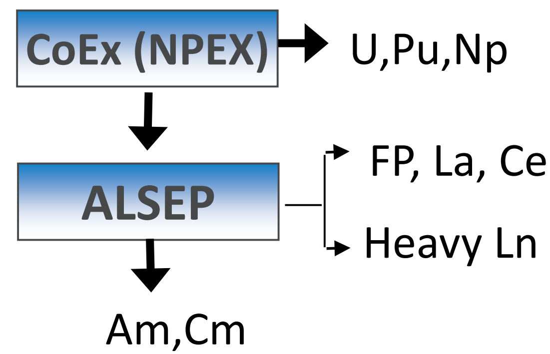
Art Gelis
gelis@anl.gov

AQUEOUS SEPARATIONS FOR MINOR ACTINIDES/LANTHANIDES, FISSION PRODUCTS, Mo/Tc

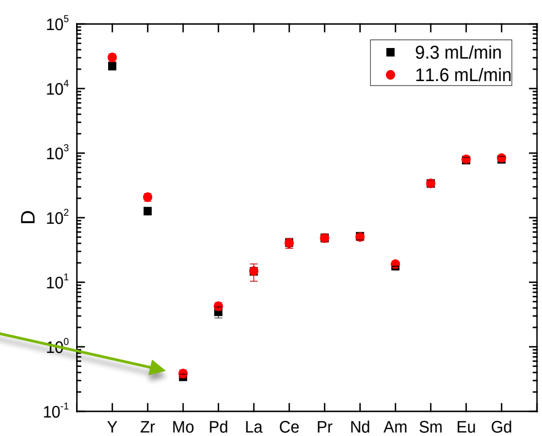
We are using microfluidics and additive manufacturing to develop and demonstrate novel solvent extraction separation processes

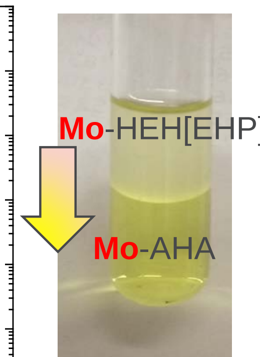
- To simplify advanced fuel cycle by minimizing the number of the process flowsheets, the Actinide Lanthanide SEParation (ALSEP) process has been developed and successfully demonstrated on a lab scale using 3D-printed multistage centrifugal contactor bank.

*Minor actinides (MA) were completely separated from the lanthanides: <**0.5 milligram/L of Ln** reported in the MA product while no actinides were detected in the Ln product.*



- A new approach has been developed to recover/separate Mo by its extraction with HEH[EHP] (aka P507) from 2-5 M **nitric acid** using stainless steel centrifugal contactors, followed by Mo-AHA strip

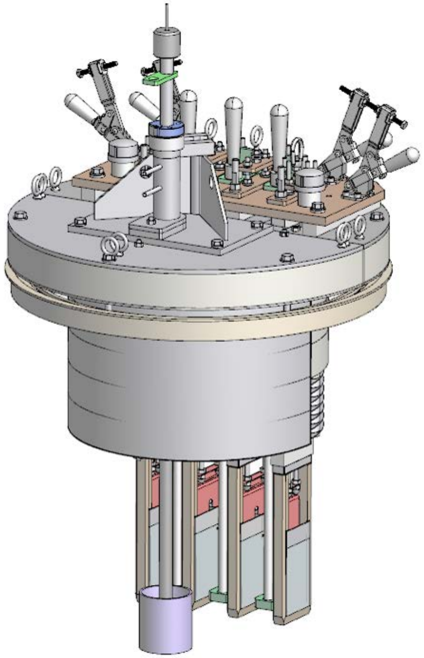




PYROCHEMICAL PROCESSING

Argonne's longstanding experience in pyrochemical processing spans the range from concept development to pilot-scale demonstration

- Argonne's capabilities include
  - Flowsheet development using the AMPYRE code specifically designed for pyroprocessing applications
  - Conceive, demonstrate and develop innovative technologies to address materials recovery and purification
  - Equipment engineering at laboratory through pilot-scale
  - Integrated demonstration of technologies to assess flowsheets
  - Facility design and evaluation



Rendering of electrorefining system for uranium and U/TRU co-deposition (left); pyroprocessing facility design concept (below)

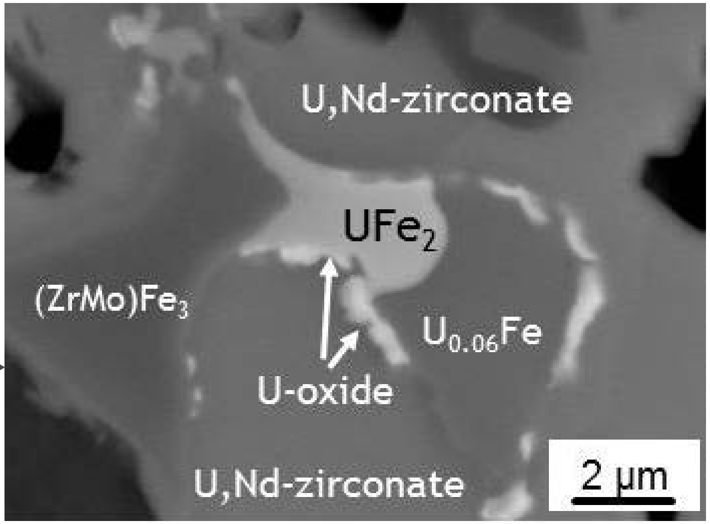
- Radiological facilities specifically designed for pyroprocess development
  - Inert atmosphere gloveboxes with integrated furnace systems (T<850 C)
  - Experimentation with U, Np, and Pu
  - Tracer studies with Am and Cm
  - Co-located suite of analytical capabilities to assess products and processes

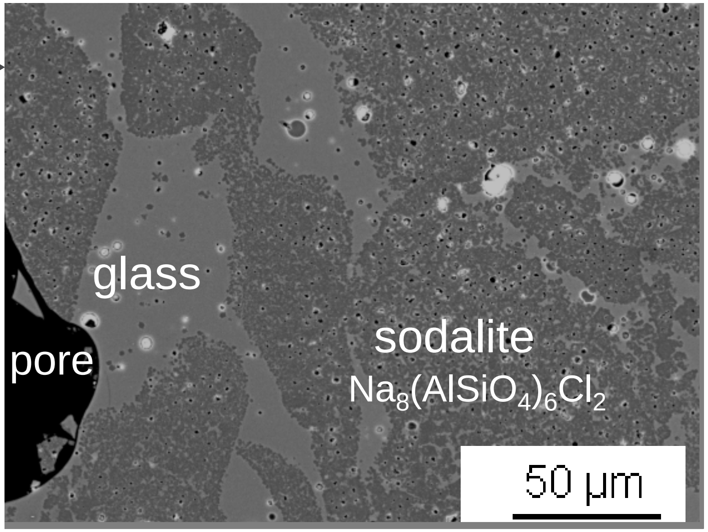
Argonne NATIONAL LABORATORY

WASTE FORM DEVELOPMENT AT ANL

Different matrices to accommodate different waste stream compositions

- **Multi-phase alloy waste forms** for steel and Zircaloy cladding combined with metallic fuel wastes
- **Multi-phase alloy/ceramic composites** for combining metallic with lanthanide and actinide oxide waste streams
- **Glass-bonded sodalite waste forms** for chloride-bearing salt wastes
- **Iron phosphate glass waste forms** for dechlorinated salt wastes (new)
- **Borosilicate glass waste forms** for oxide waste streams
- **Grout-based waste forms** for U-bearing intermediate and low-activity waste





Argonne NATIONAL LABORATORY

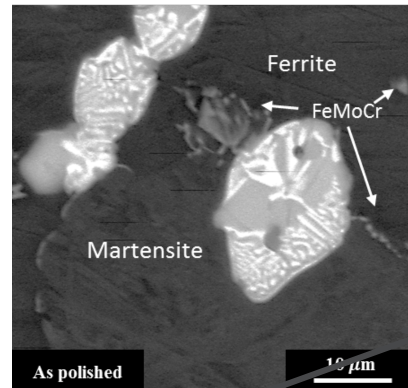
WASTE FORM TESTING APPROACH

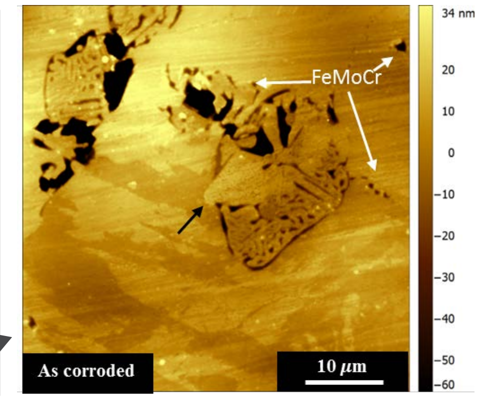
- Laboratory tests designed to support model and waste form development
  - identify process controlling material degradation and radionuclide release from homogeneous and multi-phase waste form materials
  - quantify dependencies on key material and environmental variables
  - parameterize predictive waste form degradation models for use in repository facility performance assessments
  - demonstrate regulations will be met
- Electrochemical tests address oxidative or reductive dissolution mechanisms
  - oxidative corrosion of alloy phases
  - oxidative dissolution of spent UO_2-based fuel for direct disposal
  - reductive dissolution of AgI-based composite materials
- Aqueous corrosion tests address surface dissolution and diffusion-controlled dissolution mechanisms
  - borosilicate and phosphate glass dissolution
  - crystalline phase dissolution (e.g., sodalite)
  - leaching of contaminants from grouted materials
- ANL is active in ASTM-International standards development

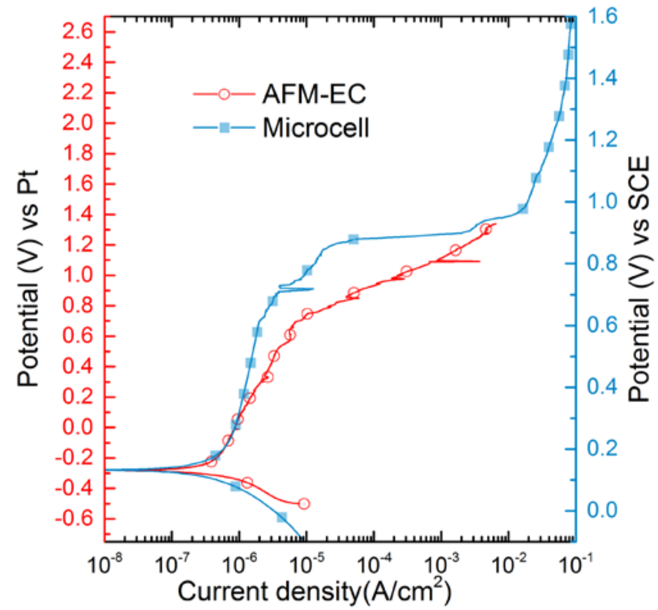
Argonne NATIONAL LABORATORY

DEDICATED ANALYTICAL FACILITIES

- Radiological and non-radiological laboratories with metallurgical specimen preparation
- **Scanning electron microscope** with associated energy dispersive X-ray spectroscopy and backscattered electron detector
- **Electrochemical systems** with microcells and environment controls
- **Atomic force microscope** with associated electrochemical cell
- **Standard corrosion** tests (immersion, flow-through, vapor hydration)
- Analytical laboratory with ICP-MS, ICP-OES, XRD
- GeoChemist's Workbench for modeling minerology, ZSimpWin for equivalent circuit modeling







WASTE FORMS FOR ^{99}MO PRODUCTION WASTE

- In the USA, waste forms for radionuclide-bearing waste streams are regulated by volume or mass limits established for individual radionuclides and sum-of-the-fractions rule given in 10 CFR Part 61.55 Waste Classification
  - Radionuclide content establishes a waste form as Class A, Class B, Class C, or Greater than Class C (GTCC) waste
- Classification of waste form produced affected by selections of processing decontamination criteria, blending of waste streams, waste loading, host matrix material, addition of stabilizing agents, etc.
- Process design should consider processing, waste form production, storage, transportation, and disposal costs

WASTE FORM TESTING

- Conduct tests supporting production
  - Optimize waste form formulation, processing conditions, and waste loading
  - Confirm effective immobilization of waste components
  - Verify compliance with chemical, physical, and radiological requirements for storage, transport, and disposal
  - Verify waste form production consistency (e.g., within Class limits)
- Conduct tests to measure performance for GTCC
  - Quantify matrix corrosion and contaminant release kinetics for relevant disposal environment
  - Determine matrix corrosion mechanism and contaminant release modes
    - Surface dissolution
    - Leaching
    - Electrochemical effects (redox-sensitive)
  - Determine dependencies on compositional and environmental variables
    - Waste stream compositions and waste loading
    - Groundwater chemistry

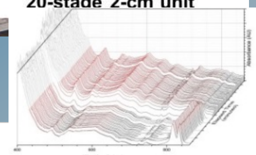
SUPPORTING SAFEGUARDS

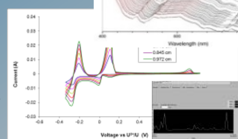
Process Monitoring

Safeguards

Safeguards Test Bed
Test concepts, measure actinide and FP concentrations, process status near real time

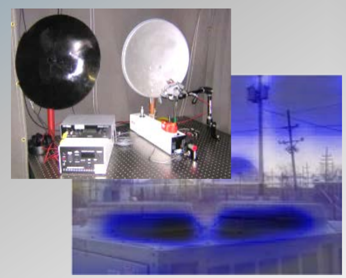
20-stage 2-cm unit





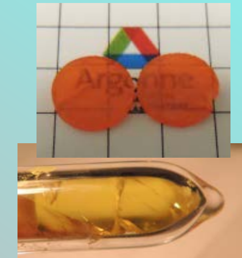
Real time accounting of material in-process
Combination of process knowledge and data provides verification

Remote sensing of processing facilities
MMW and PAS for standoff & remote characterization

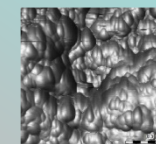


Microfluidic Sampler
Facilitates analysis of large numbers of samples to improve analysis with existing analytical equipment

Materials



Solid-state Semiconductors
Innovative design/selection, synthesis, crystal growth, and characterization for materials offering high sensitivity and operational suitability



Scanning Probe Microscopy for materials characterization

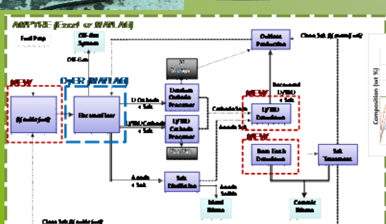
Solid Materials for UF_6 Sampling

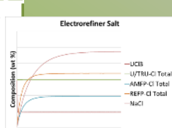
Multielectrode Array

Voltammetric techniques can be used to monitor actinide concentrations in molten salts

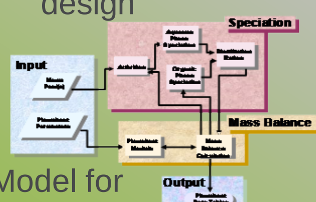
Simulations

Computational Fluid Dynamics to support design



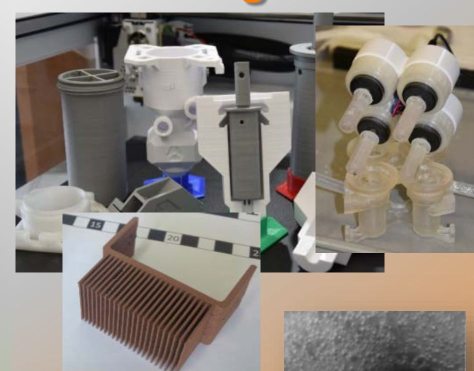


Argonne Model for Pyrochemical Recycling



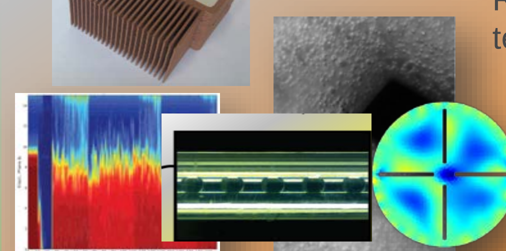
Argonne Model for Universal Solvent Extraction

Design and Manufacture



Advanced equipment designs
3D printing in combination with advanced computation yields novel designs and fabrication routes

Rapid implementation and testing of new concepts



Imaging and instrumentation
Validation of code predictions and fluid behavior in designs