# SRNL Tritium Development Activities for Accelerator Mo-99 Production

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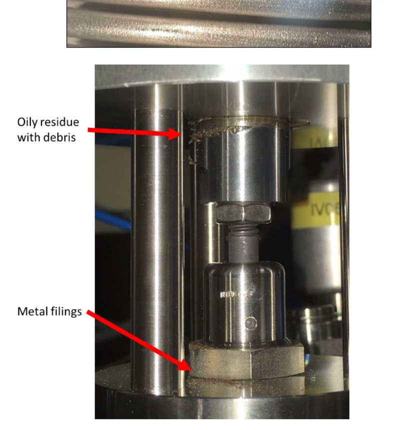
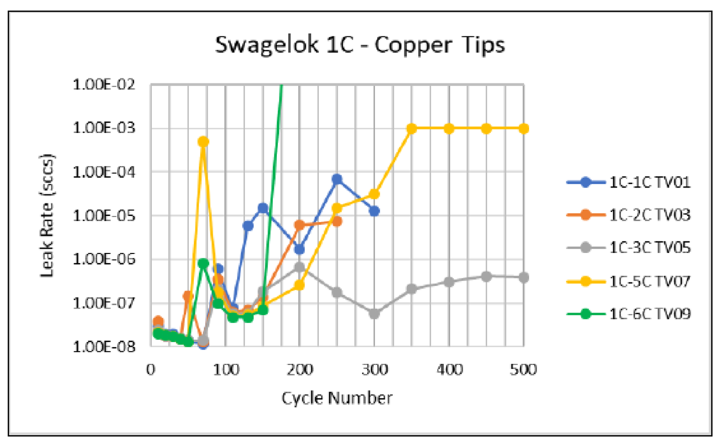
**Abstract:** SRNL has support accelerator production of Mo-99 since 2012. Use of deuterium accelerators using a tritium target require additional study and development for gas handling, processing, storage, confinement, and waste disposal. A brief description of some SRNL tritium-related studies to support Mo-99 production are presented here.

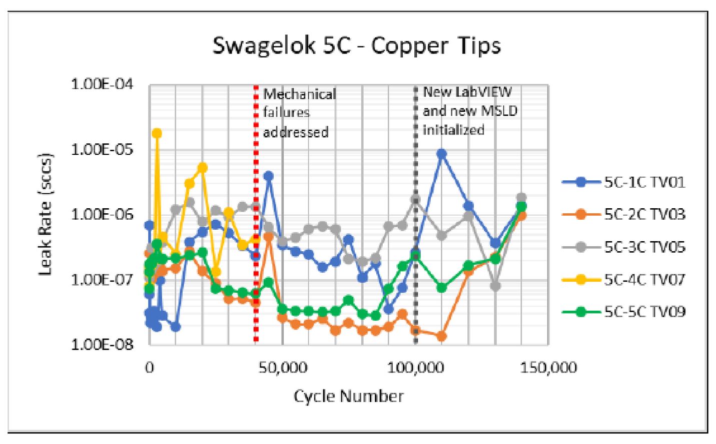
**Future Work:** SRNL continues to evaluate tritium removal from $SF_6$ in FY23. In addition to current SRNL work, future Mo-99 support work will focus on actinide processing, radiological facility issues, and waste disposition activities.

## Bellows Sealed Valve Cycle Testing

- ¼" Nupro B-series bellows sealed valve for tritium service
- 3 normally closed pneumatic actuator sizes: 1C, 3C, and 5C
- Three tip seals for tritium (no Kel-F® for tritium service):
- Vespel® (polyimide) Copper, and Stellite™ (cobalt alloy)
- What is smallest actuator to give reliable valve closure: 150k cycles
- 3 failure mechanisms: Stem tip wear, bellows failure, actuator failure
- Copper tests shown here (1C dual actuated)

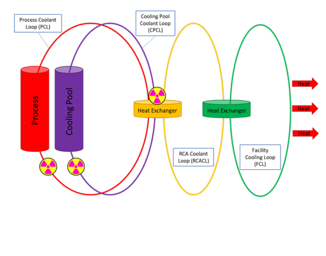



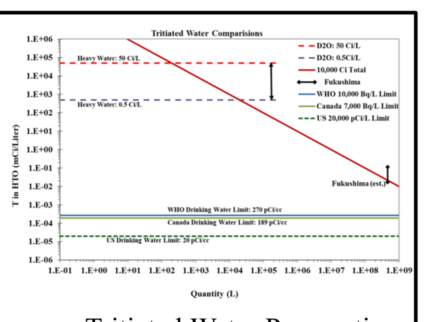

SRNL-STI-2021-00086

## Tritiated Water Disposition Strategies

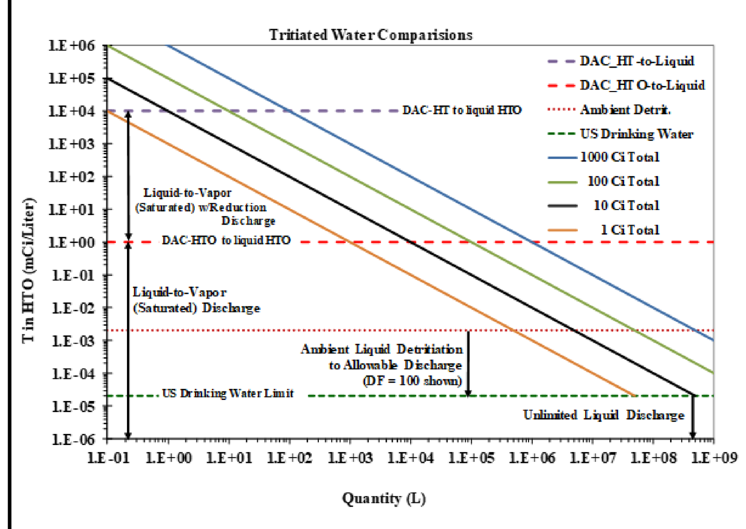
- Closed loop, recirculating cooling water systems will slowly accumulate tritium and create concentrations which exceed drinking water (or permitted discharge) concentrations
- No convenient discharge options when limits are exceeded
- Case Study: 1000 L tritiated water at 2 mCi/L
- Copper test



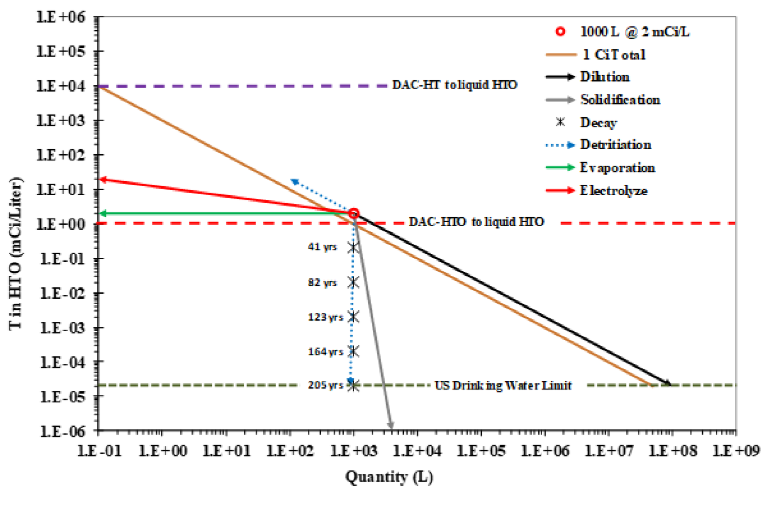
Cooling Water Loops




Tritiated Water Perspective




Tritiated Water Comparisons

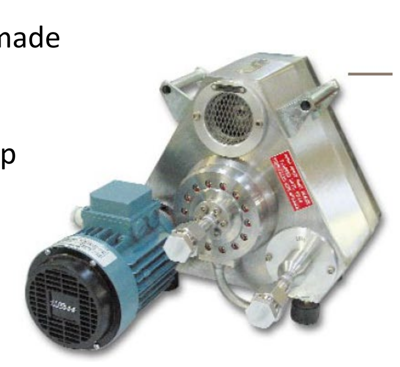


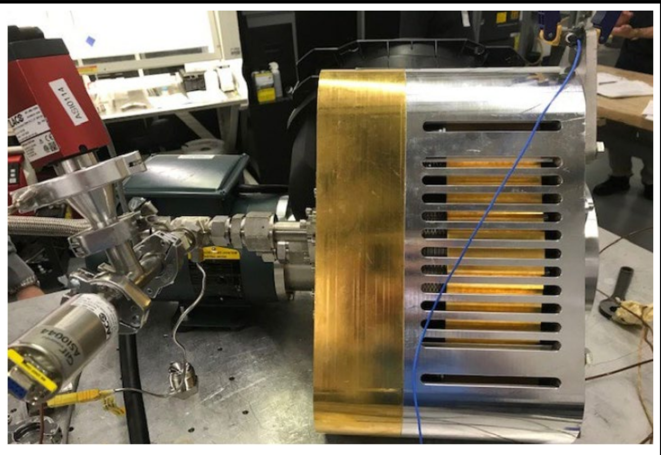

Case Study: 1000 L @ 2 mCi/L (Ci total)

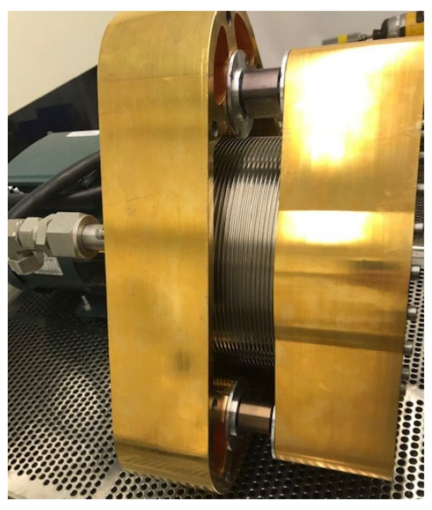
SRNL-STI-2020-00332

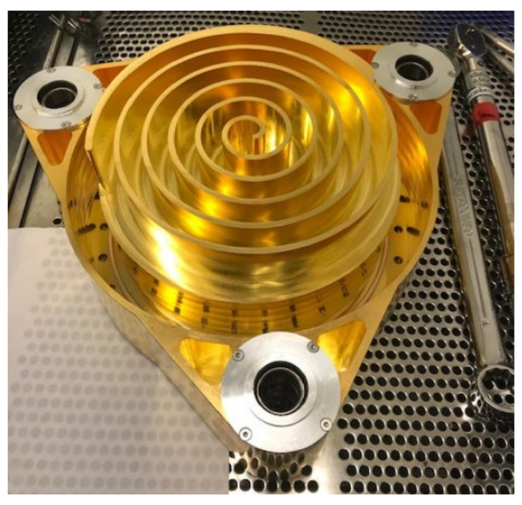
## Aluminum Scroll Pump Development

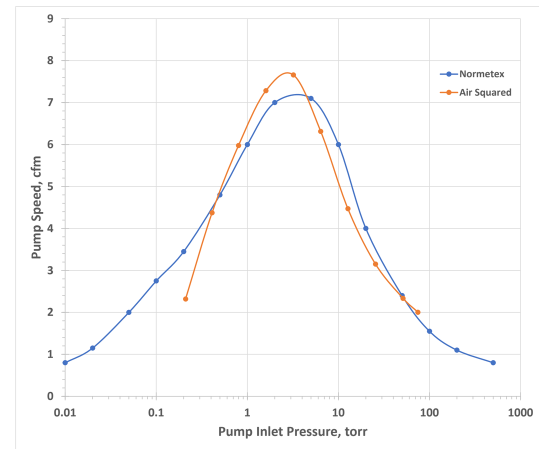
- Normetex 9 cfm all-metal pump no longer made
- Stainless steel replacement heavy, $$$
- Aluminum coated pump developed
- Pump performance similar to obsolete pump












SRNL-STI-2021-00463

## Hot Cell Tritium Stripper Sizing

- Time 0 tritium release ($Q_0$): What size stripper is needed?

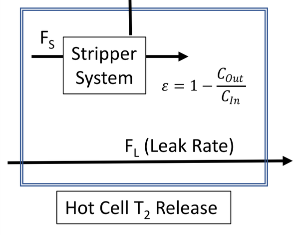
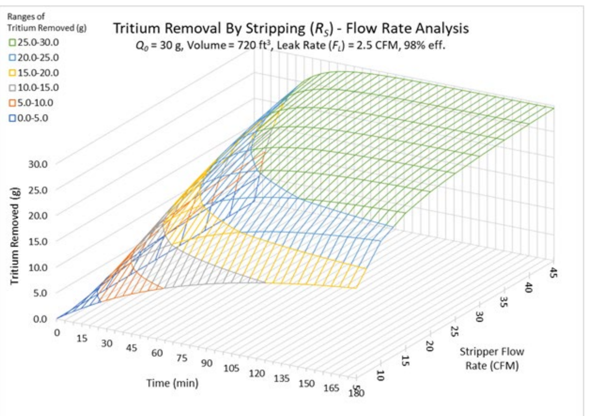



**Table** Error! No text of specified style in document.**-1 – Previous Tritium Stripping Studies**

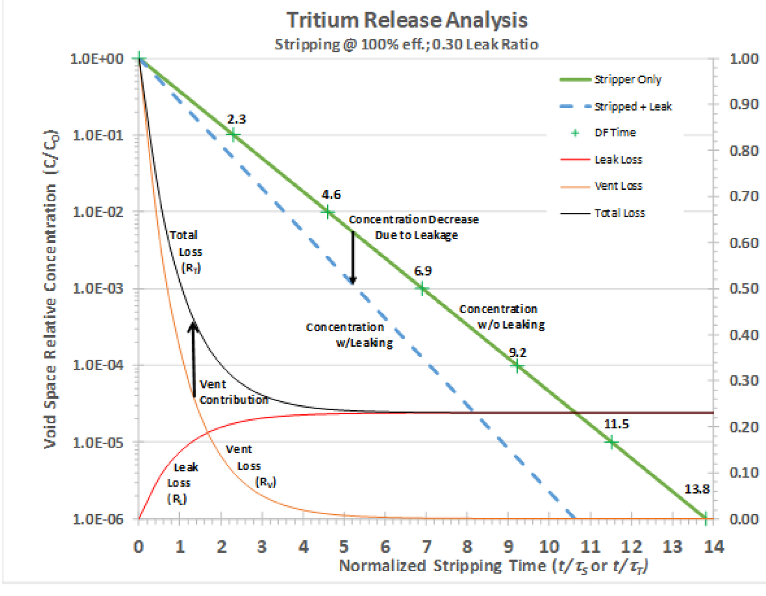
| Study | Nominal Stripped Volume (L) [ft³] | Nominal Stripper Flow (L/min) [CFM] | Initial Tritium Conc. (μCi/cc) |
|---|---|---|---|
| 1992 Shmayda et al.[2] | 14.4[a] [0.508] | 0.75 [0.026] | 1.2x10$^{-4}$ to 6.8 |
| 1995 Klein and Wermer[3] | 620 [21.9] | ~ 2 to 9 [0.071 to 0.318] | ~ 1 to 10 |
| 2001 Kobayashi et al.[4] | 11,960[b] [422.3] | 833 [29.4[c]] | 5.9x10$^{-3}$ |
| 1995 Heung[5] | 24,000 [847] | 2,833 [100[d]] | ~ 4,000 |
| This Study | 20,400 to 61,200 [720 to 2,160] | To Be Determined | 4,717 to 14,151[e] |

$Q_0$ ($T_2$ release) = $T_2$ Stripped + $T_2$ Leaked + $T_2$ Vented




Total Release = Leak + Vent (at end)

$$R_T = R_L + R_V = Q_0\left[\frac{F_L}{\varepsilon F_S + F_L} + \left(\frac{\varepsilon F_S}{\varepsilon F_S + F_L}\right)e^{-\frac{t}{\tau}}\right]$$



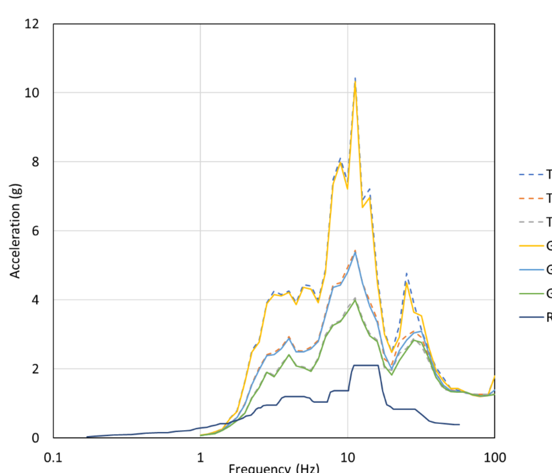

$$F_S \geq F_{S,min} = F_L\frac{(Q_0 - Q_A)}{\varepsilon Q_A} = \frac{F_L}{\varepsilon}\left(\frac{Q_0}{Q_A} - 1\right) = \frac{F_L}{\varepsilon}(DF_{min} - 1)$$

Minimum Stripper Flow ($F_S$, min.) related to Max. Allowable Release ($Q_A$)

SRNL-STI-2020-00258

## Seismic Testing of Glovebox Feedthrough Connectors and Vacuum Pumps

- Verify glovebox electrical feedthrough connectors and vacuum pumps maintain tritium confinement integrity after design basis earthquake
- Assemble simulated glovebox enclosure with feedthroughs and pumps
- Ship to test facility and run tests with pumps operating
- Components maintained leak integrity after shaker testing

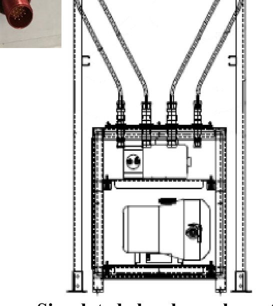



Senior Aerospace MB-602, energized during seismic test

Edwards Vacuum nXDS15iC, energized during seismic test

| Pump Model | MB-602 | nXDS15iC |
|---|---|---|
| Installed leak rate, scc/s He | 1.9E-08 | 1.1E-07 |
| Seismic tested leak rate, scc/s He | 1.9E-08 | 1.1E-08 |

| Connector Type | MS 20-27 | | MS 28-22 | | MS 28-12 | | MS 20-4 | |
|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B |
| Installed leak rate, scc/s He | 6.0E-08 | 8.3E-08 | 3.0E-7 | 9.1E-07 | 1.5E-07 | 1.4E-07 | 3.9E-08 | 1.1E-08 |
| Seismic tested leak rate, scc/s He | 1.6E-07 | 6.9E-08 | 1.4E-07 | 3.5E-07 | 1.1E-07 | 1.5E-07 | 2.5E-07 | 2.8E-07 |



Simulated glovebox schematic

Simulated glovebox mounted for seismic test

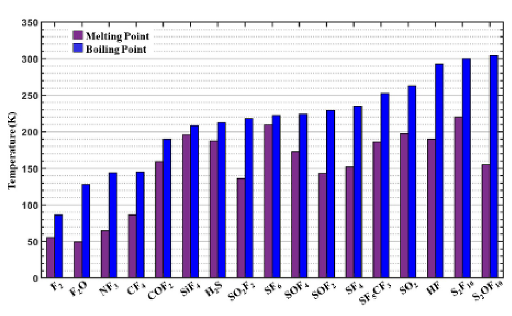
SRNL-STI-2019-00522

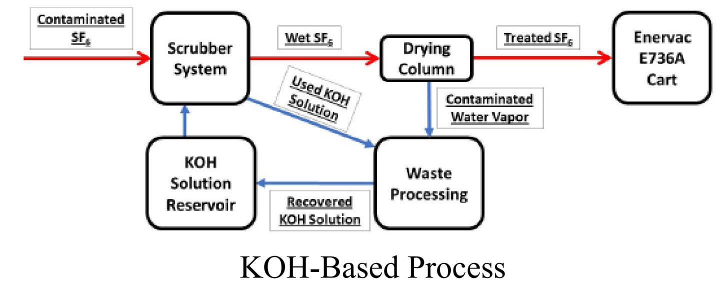
## Sulfur Hexafluoride ($SF_6$) Disposition Strategies

- $SF_6$ commonly used as electrical insulator for accelerators
- Electrical current dissociates $SF_6$ to S and F ions
- Most S and F ions recombine to form $SF_6$
- S & F ions react with $SF_6$ confinement materials and hold tritium
- Numerous chemical species can be formed
- Goal is to remove tritiated compounds from $SF_6$ for reuse
- Separations/clean-up method based on species present
- Data collection planned in FY23

**Table 1: Properties and references for $SF_6$ and reported $SF_6$ decomposition byproducts.**

| Chemical Formula | Chemical Name | References | M.P. (°C) | B.P. (°C) | Phase at STP |
|---|---|---|---|---|---|
| $HF$ | Hydrogen Fluoride | 5, 6 | -83.6 | 19.4 | Gas |
| $SOF_2$ | Thionyl Fluoride | 5, 7, 8, 9 | -130 | -43.7 | Gas |
| $SOF_4$ | Thionyl Tetrafluoride | 5, 7, 9, 10, 11 | -100 | -49 | Gas |
| $SF_4$ | Sulfur Tetrafluoride | 5, 12, 13, 14 | -125 | -40 | Gas |
| $S_2F_{10}$ | Disulfur Pentafluoride | 5, 12 | -92 | 29 | Gas/Liquid |
| $SO_2F_2$ | Sulfuryl Fluoride | 5, 7, 15 | -137 | -55 | Gas |
| $SO_2$ | Sulfur Dioxide | 5, 7, 16 | -10.0 | -72.7 | Gas |
| $OF_2$ | Oxygen Difluoride | 16, 17 | -224 | -145 | Gas |
| $H_2S$ | Hydrogen Sulfide | 18, 19 | -83 | -62 | Gas |
| $SF_5CF_3$ | Trifluoromethyl Sulfur Pentafluoride | 4 | -87 | -20.4 | Gas |
| $NF_3$ | Nitrogen Trifluoride | 2, 20 | -207.2 | -129.0 | Gas |
| $F_2$ | Fluorine | 6 | -220 | -188.1 | Gas |
| $COF_2$ | Carbonyl Fluoride | 21, 22, 23 | -114 | -84.6 | Gas |
| $CF_4$ | Carbon Tetrafluoride | 24 | -187 | -128 | Gas |
| $S_2OF_{10}$ | Bis(pentafluorosulfur) Oxide | 2 | -118.5 | 31 | Gas |
| $S_2O_2F_{10}$ | Bis(pentafluorosulfur) Peroxide | 2 | -95.4 | | Gas |
| $S_2O_3F_6$ | Pentafluorosulfur Fluorosulfonate | 2, 25 | -105.1 | | Gas |
| $SiF_4$ | Silicon Tetrafluoride | 3 | -97 | -65 | Gas |
| $C$ | (Amorphous) Carbon | 26 | | | Solid |
| $S_8$ | (Elemental) Sulfur | 26 | 115 | 445 | Solid |
| $Al_2S_3$ | Aluminum Sulfide | 26 | 1100 | 1500 | Solid |
| $FeS$ | Iron (II) Sulfide | 26, 27 | 1193 | | Solid |
| $Cu_2S$ | Copper (I) Sulfide | 26 | 1100 | | Solid |
| $CuF_2$ | Copper (II) Fluoride | 26 | 836 | 1676 | Solid |
| $FeF_3$ | Iron (III) Fluoride | 26, 27 | | 987 | Solid |
| $FeF_2$ | Iron (II) Fluoride | 26 | 970 | 1100 | Solid |
| $Fe_2O_3$ | Iron (III) Oxide | 27 | 1539 | | Solid |
| $AlF_3$ | Aluminum Fluoride | 26 | 1040 | | Solid |
| SiO2 | Silicon Dioxide | 26 | 1713 | 2950 | Solid |




KOH-Based Process

| Reaction | Rate Constant $k_{298}$ (cm³/s) | Reference |
|---|---|---|
| $SF_5 + OH \rightarrow SOF_4 + HF$ | 1.1x10$^{-12}$ | 29 |
| $SF_5 + O \rightarrow SOF_4 + F$ | 2x10$^{-11}$ | 7 |
| $2\,SF_4 + O_2 \rightarrow 2\,SOF_4$ | n/a | |
| $2\,SF_4 + O_2 \rightarrow 2\,SOF_2 + 2\,F_2$ | n/a | |
| $2\,SF_3 + O_2 \rightarrow 2\,SOF_2 + F_2$ | n/a | |
| $2\,SF_2 + O_2 \rightarrow 2\,SOF_2$ | ≤5x10$^{-16}$ | 1 |
| $2\,SF_4 + 2\,OH \rightarrow 2\,SOF_2 + F_2 + 2\,HF$ | n/a | |
| $SF_3 + OH \rightarrow SOF_2 + HF$ | n/a | |
| $2\,SF_3 + O_2 \rightarrow 2\,SO_2F_2 + F_2$ | n/a | |
| $SF_2 + O_2 \rightarrow SO_2F_2$ | ≤5x10$^{-16}$ | 1 |
| $SF_4 + H_2O \rightarrow SOF_2 + 2\,HF$ | 1.5x10$^{-19}$ | 1 |
| $SOF_4 + H_2O \rightarrow SO_2F_2 + 2\,HF$ | 2.0 x10$^{-21}$ | 1 |
| $SOF_2 + H_2O \rightarrow SO_2 + 2\,HF$ | 1.2x10$^{-23}$ | 1 |
| $SF_5 + SF_5 \rightarrow S_2F_{10}$ | 1.8x10$^{-12}$ | 1 |
| $S_2F_{10} + H_2O \rightarrow SOF_2 + SF_6 + 2\,HF$ | n/a | 5 |
| $F + H_2O \rightarrow OH + HF$ | 9.0x10$^{-12}$ | 1 |

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# Nuclear Material Processing Development Activities at the SRNL to Support the US Production of Mo-99


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**Abstract:** The SRNL is supported by the DOE National Nuclear Security Administration to provide R&D assistance to potential new US Mo-99 producers. The assistance includes the development of flowsheets for the purification of U from dissolved targets following Mo-99 recovery and the removal of high specific activity fission products from waste streams to lower the classification (e.g., Class C to Class A or B) of the waste form. A modified PUREX process was demonstrated for nominally 90% U recovery allowing the purge of a small amount of U from the inventory each cycle to minimize the production of Pu during subsequent target irradiations. In small column tests using ammonium molybdophosphate and crystalline silicotitanate (R9120-B) with a simulated acidic sulfate waste solution containing U, Pu, Np and non-rad fission product, both ion exchange materials were highly specific for cesium. Neither material removed significant Sr or U.


## U Recovery from Mo-99 Targets

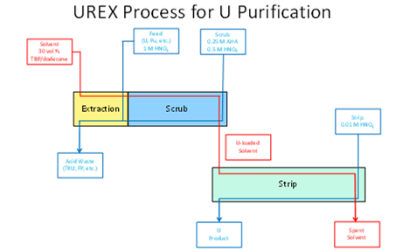
- Solvent extraction modeling combined with experimental validation to support the design of a UREX solvent extraction process for approximately 90% U recovery
  - Loss of U is desired to maintain the U-235 enrichment as high as possible during subsequent Mo-99 production cycles by blending fresh LEU during target fabrication to minimize the production of Pu
- Surrogate solution prepared for U purification experiment based on:
  - Target irradiation for 10 days at 30 kW
  - Inventory of fission and activation products calculated using Origin 2.2 following two-days of decay
  - Concentrations scaled based on 275 g/L U in the feed solution
  - Feed to solvent extraction process adjusted to 1 M $HNO_3$ following Mo-99 recovery

Concentrations of U and Selected Activation and Fission Products in Surrogate Solution

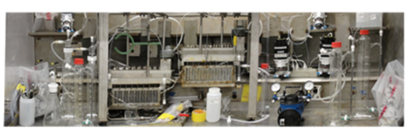
| Element | Concentration (M) |
|---|---|
| U | 1.06 |
| Np | 6.78E-05 |
| Pu | 1.34E-04 |
| Ce | 5.36E-04 |
| Cs | 2.64E-04 |
| Eu | 4.95E-06 |
| Nd | 3.76E-04 |
| Ru | 5.25E-04 |
| Sr | 4.27E-04 |
| Re(Tc) | 1.53E-04 |
| Zr | 8.74E-04 |

- Argonne Model for Universal Solvent Extraction (AMUSE) used for flowsheet design
  - Number of extraction stages and flow ratios were adjusted until the predicted U recovery was nominally 90%

UREX Process for U Purification



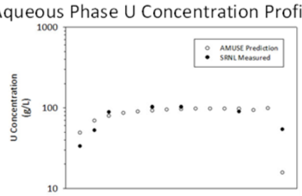

SRNL Miniature Mixer-Settlers



- UREX Process Design
  - Feed solution containing 275-300 g/L adjusted to 1 M $HNO_3$
  - 30 vol % tributyl phosphate solvent
  - 0.25 M acetohydroxamic acid (AHA) in 0.5 M $HNO_3$ used to scrub fission and activation products from loaded solvent
    - AHA complexes Pu(IV) and Np(IV) to prevent extraction
    - AHA reduces Np(VI) to Np(V) which is mostly in-extractable
  - Solvent stripped using 0.01 M $HNO_3$
- Flowsheet validation performed using two, 16 stage banks of miniature mixer-settlers
  - Mixer-settlers have a hydraulic capacity of approximately 5 mL/min
  - Approach to steady-state conditions monitored by specific gravity of U product solution

- U recovery achieved was 85.7 ± 1.9%
  - Recovery predicted by AMUSE was 90.8%
  - AMUSE model was not completely optimized to match the SRNL equipment and could be adjusted to more closely predict the measured U recovery
- Measured concentration profiles were generally in good agreement with profiles predicted by AMUSE
  - Experiment demonstrated that AMUSE can be used to support the design of a UREX process to control the U recovery efficiency for recycle of U to Mo-99 targets

Aqueous Phase U Concentration Profile




Decontamination Factors (DF)

| Species | Measured | Predicted |
|---|---|---|
| Np | >4700 | 8E+18 |
| Pu | 9200 | 4E+15 |
| Ce | 47000 | 1E+19 |
| Cs | 990 | 1E+19 |
| Eu | >750 | 9E+18 |
| Nd | >22000 | 1E+19 |
| Ru | >12000 | 780 |
| Sr | >13000 | 1E+19 |
| Re(1)/Tc(2) | 6300(1) | 6(2) |
| Zr | >80000 | 2E+19 |

DF = ratio of impurity concentration in feed to product

- Predicted DF were much higher than measured values
  - Np, Eu, Nd, Ru, Sr, and Zr concentrations below minimum detection of the analysis
  - Cs DF less than expected for UREX process
  - Re DF provides bounding value for Tc

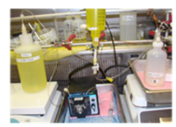
## High Specific Activity Fission Product Separation

- Waste stream from irradiated LEU sulfate solution processing, pH 1
  - Waste to be neutralized and grouted
  - Goal is to minimize amount of Class B and C waste generated by capturing and segregating limiting isotopes

| Radionuclide | Concentration, Ci/m3 | | |
|---|---|---|---|
| | Class A | Class B | Class C |
| $^{144}Ce$ (a) | 700 | (b) | (b) |
| $^{90}Sr$ | .04 | 150 | 7000 |
| $^{137}Cs$ | 1 | 44 | 4600 |

(a) Nuclides with half life < 5 years

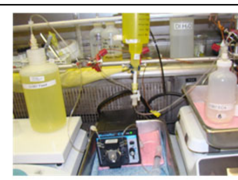
(b) No established limits, treat as Class B



- Surrogate waste solution prepared based on prior results from Mo titania column testing, $^{238}U$ primary metal ion by mass, $^{137}Cs$, $^{90}Sr$, $^{144}Ce$ limiting by regulations/activity

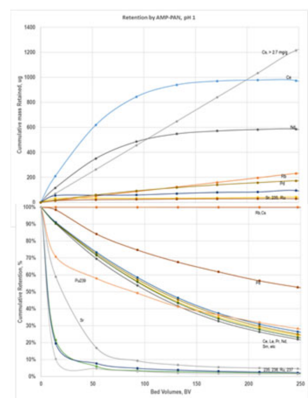
Concentrations of U and Selected Activation and Fission Products in Surrogate Solution

| Element | Concentration (mg/L) |
|---|---|
| 238 | 5816 |
| Rb | 1.3 |
| Cs | 6.6 |
| Sr | 5.1 |
| Ce | 21.7 |
| 235 | 24.0 |
| Ru | 7.1 |
| Pd | 1.8 |
| Zr | 1.0 |
| Mo | 0.1 |
| La | 1.3 |
| Pr | 2.5 |
| Nd | 12.0 |
| Sm | 1.3 |
| Eu | 1.3 |
| Gd | 2.0 |
| Re | 4.4 |
| 237 | 0.5 |
| Pu239/40 | 0.3 |
| Np237 | 0.5 |



- Absorbents tested by pumping feed solution through column and collecting raffinate
- After analysis material balance was performed
- Competition between competing species was a significant concern
  - Particularly U due to large mass
  - TRU also could affect waste classification
- AMP-PAN highly specific for Cs, Rb
- Also retained Pd, lanthanides, Pu
- Sr not retained

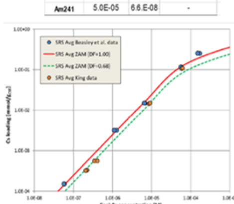
| | AMP-PAN | | |
|---|---|---|---|
| | ug | mg/g | % of Feed Mass |
| U235 | 10 | 0.02 | 0.2% |
| U238 | 2320 | 5.9 | 0.2% |
| Np237 | 0.04 | 0.0001 | 0.1% |
| Pu239/40 | 12 | 0.029 | 23% |
| Am241 | 1.6E-03 | 4.0E-06 | - |

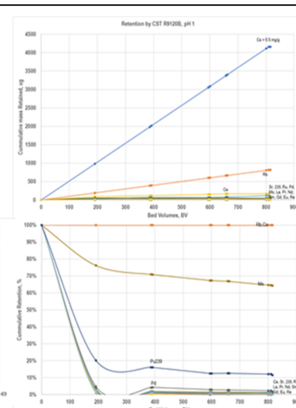



- CST R9120-B more specific for Cs, Rb from pH 1 sulfate
- Also absorbed significant Mo, little in waste
- Little retention of Sr, Ce and lanthanides
- Some retention of Pu
- Little retention of U

| | CST R9120-B | | |
|---|---|---|---|
| | ug | mg/g | % of Feed Mass |
| U235 | 6 | 10 | 0.04% |
| U238 | 1450 | 1.9 | 0.04% |
| Np237 | 0.12 | 0.0002 | 0.0% |
| Pu239/40 | 14 | 0.018 | 7% |
| Am241 | 5.0E-05 | 6.6.E-08 | - |

- Retested CST at pH 9
  - Adjustment with carbonate to retain U solubility
  - Aborted due to excessive gassing
    - Caused by incomplete conversion of CST (H to Na)
- Capacity likely affected by low Cs concentration (below 4E-5 M)
  - 1 L CST likely retains 0.6 g Cs at 4E-6 M feed





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# Management and categorization of wastes resulting from Mo-99 production

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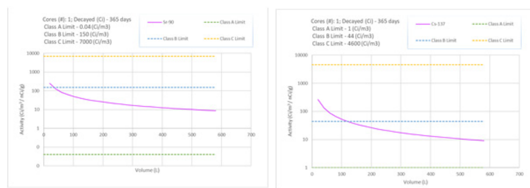
## Abstract

– Appropriate waste management strategies are critical to the production of Mo-99 using low enriched uranium (LEU). There are various Mo-99 production processes for which unique methods and strategies for treatment and disposal of the waste streams is needed. Product specifications, acceptance criteria, facility design, and process operations must all be considered as part of the overall waste management strategy.


## Waste Stream Projections

– Contact handled waste
– Process system components
– Excessed equipment & large items
– Process raffinate
  - *Compute estimated radionuclide inventory from irradiation and decay based on projected processing steps and volumes*



Normalized activity of Sr-90 and Cs-137 as a function of concentration in an example combined process raffinate. 10 CFR Part 61 waste classification limits are shown for reference

## U.S. Waste Disposal Guidelines

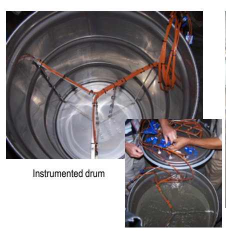
– Title 10 of the Code of Federal Regulations (10 CFR) Part 61, "Licensing Requirement for Land Disposal of Radioactive Waste" provides procedures, criteria, and terms and conditions for the licensing of facilities for the disposal of radioactive waste. Part 61.55 provides guidance on the waste classification criteria.

– 10 CFR Part 61.55, "Waste Classification" establishes criteria and limits for each of the three classes of waste (A, B, and C) that can be disposed of in near surface disposal sites. Waste that is not acceptable for near-surface disposal is waste for which form and disposal methods must be in general more stringent than those specified for Class C waste.

– Extreme measures of adding non-radioactive material or diluting the waste to circumvent stricter disposal requirements should not be used.

## Waste Solidification

– Reduce the long-term environmental burden through efficient disposal of waste materials
– Chemically bind the radioactive and hazardous components into a solid, durable material that will withstand degradation for thousands of years
– The choice of material is dependent on the application and often is a compromise between factors such as cost, performance, and suitability
  - *Crystalline ceramic*
  - *Vitrified glass*
  - *Cementitious materials*
  - *Composite*

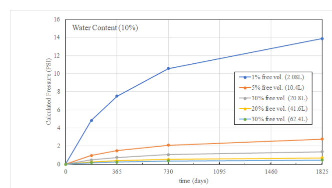


Instrumented drum

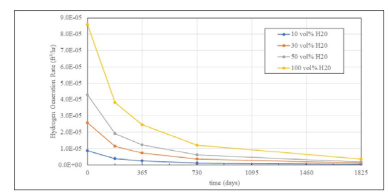
Pilot solidification test rig

## Hydrogen Generation

– Published characteristics (i. e. deposited energy (W/Ci), decay mode) and published G values (molecules $H_2$ / 100 eV) for beta/gamma and alpha irradiation of pure water were used to calculate hydrogen generation rates for various scenarios
– Incorporate best fit exponential and linear functions to integrate the hydrogen generation (moles) from most radioisotopes



Calculated pressure buildup in a sealed SHINE solid waste drum as a function of free volume (v/% of 208 L drum) and decay time.



Calculated hydrogen generation rate from projected SHINE in-drum solid waste radionuclide inventory as a function of decay time and water content.

## Future Work

– Continue to evaluate process system flowsheets to compute waste stream estimates
– Evaluate waste management strategies to ensure available disposition path
– Provide waste form design and processing experience to facilitate efficient waste disposition strategies

## Uranium Lease and Take Back (ULTB) Program

– U.S. program to use lease contracts to make LEU available for the domestic production of Mo-99 for medical uses
– U.S. program to use take-back contracts for the final disposition of spent nuclear fuel created by the irradiation, processing, or purification of leased LEU for which there is no commercial disposition path
  - *Includes radioactive waste created by the irradiation, processing, or purification of leased LEU, for which the producer does not have access to a disposal path*



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