OAK RIDGE National Laboratory

Module 12: Waste Streams

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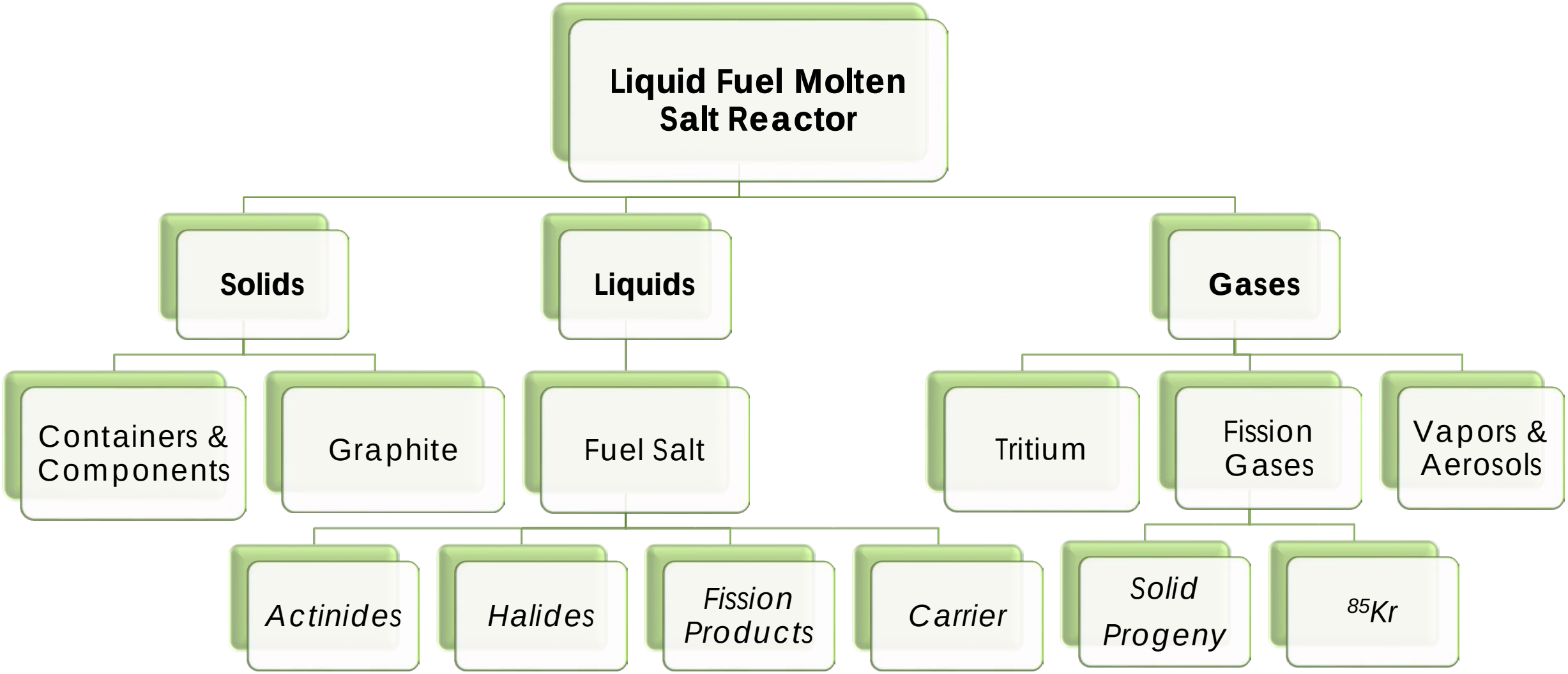
U.S. DEPARTMENT OF ENERGY

Plant Hierarchy Provides Structure For Waste Evaluation



Materials Released From Fuel Salt Include Tritium, Fission Gases, Vapors and Aerosols

- Tritium is an activation product and ternary fission product
  - Much higher amounts of tritium production from salts containing lithium or beryllium
  - Mitigation methods include trapping, blocking, and stripping
- All fissions have substantial direct and indirect noble gas yields
  - Noble gases have low solubilities in halide salts
  - Stripping ^{135}Xe and its precursor ^{135}I improve thermal spectrum MSR neutron efficiency
- High temperatures and kinetics result in vapors and aerosols
  - Some materials volatilize (e.g., UCl_4 boiling point is 791 °C)
  - CsI is has low solubility *(Beneš, 2021 - DOI: 10.1039/d0cp05794k)*

Only Tritium and Krypton-85 Gases Have Half-Lives in Excess of a Few Days

- Tritium diffuses through structural alloys at high temperatures
  - Thin walled heat exchanger provides large escape surface
- Short half-life fission gases may produce longer lived progeny
  - Example ^{137}Xe ($t_{½}$ ≈ 3.82 min) decays to ^{137}Cs
- Gas stream filtered to remove suspended materials
  - Solid and liquid filters possible (carbon particle bed or liquid hydroxide scrubber)
  - Filter media becomes radioactive waste stream
- Emerging gas stream initially held to allow ^{135}Xe (and ^{135}I precursor) decay
  - Fraction of gases may be used to strip ^{135}Xe from fuel salt via sparging
  - Remainder held to allow ^{133}Xe ($t_{½}$ ≈ 5.25 days) and other short lived gases to decay
- Krypton-85 ($t_{½}$ ≈ 10.8 years) bottled and stored

Optimal Tritium Immobilization Method Depends on Reactor Design

- Key safety issue is potential for release of tritium from the plant
  - Tritium may be captured or blocked at any stage of it migration – fuel salt, structural alloy, coolant, or cover gas
  - Potential for tritium release was identified as a key issue in WASH-1222 MSR technology review
- Unbound tritium is highly mobile and readily diffuses through structural alloys at elevated temperatures
  - Chemically binding tritium can substantially decrease its mobility
- Tritium has a small diffusion coefficient in salts
  - Requires turbulent flow for tritium to effectively impinge upon materials in salt

Adequate sparging-based tritium stripping system "can be expected to increase significantly the cost and complexity of an MSBR" – Briggs et al 1970

Appropriate Tritium Binding or Blocking Technique Depends on Where Tritium is Located

- Tritium within fuel salt can be trapped by moderator material
  - Graphite will trap hydrogen at operating temperature via adsorption
    - Relationship between tritium trapping, other fission products, radiation damage to graphite, and temperature is complex
      - Potential for release at elevated temperatures (accident conditions)
      - Increase in retention with radiation damage
  - Be_2C would trap tritium as methane gas from coolant salt
    - Be_2C is not compatible with uranium fluoride – forms uranium carbide
- Tritium can be trapped within structural alloy materials – for example
  - Yttrium could be incorporated into heat exchanger tube walls
- Barrier layers have not been effective in practice due to vulnerability to imperfections and interaction with uranium in fuel salt

Tritium Can Be Chemically Trapped in Coolant, Cover Gas, or Containment Atmosphere

- Sodium fluoroborate has been demonstrated as tritium trap and coolant salt
- Nitrate “solar” salt is an effective chemical trap for tritium
  - Selected by prospective MSR vendors
  - Nitrate salts react exothermically with hot graphite
- Back diffusion of hydrogen also possible to block outward tritium diffusion
- Tritium can be effectively stripped from an inert gas stream (cover gas or containment atmosphere) by interacting with copper oxide at elevated temperature to form tritiated water

Salt Contacting Components Can Reach End-of-Useful-Life During Plant Operation

- Radiation damage, corrosion, and erosion can necessitate salt-wetted component replacement
  - Gas/vapor contacting containers likely life-of-plant structures
  - Radiation damage rate is design dependent
    - Graphite most vulnerable material - core volume can be increased to extend replacement interval
    - Interior shielding can be employed to extend container alloy lifetime
- Salt contacting materials will be highly contaminated with insoluble fission products

soluble

insoluble

sometimes soluble

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	*Zn*	*Ga*	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	*Cd*	*In*	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	*Hg*	*Tl*	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr															

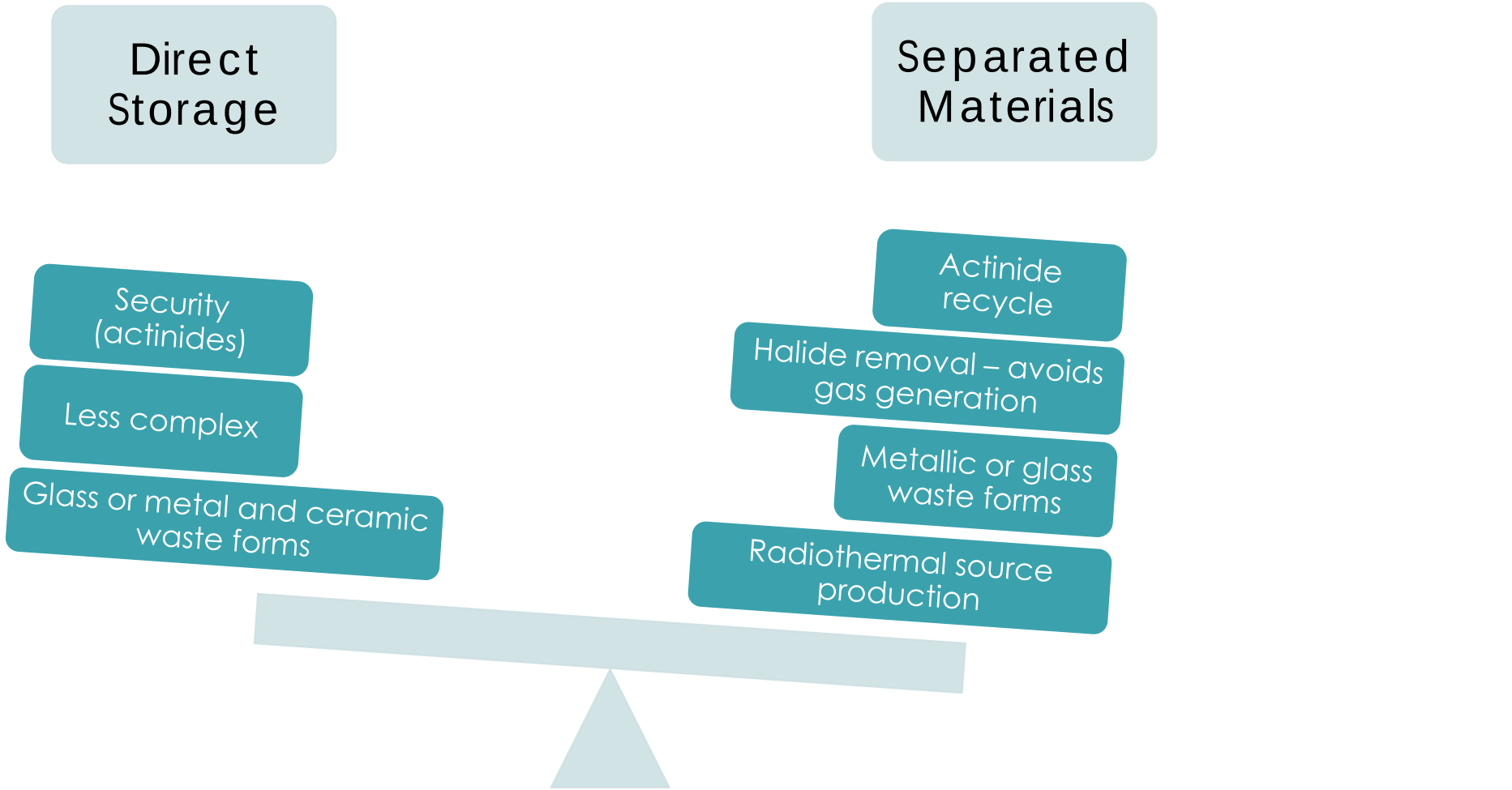
Fuel Salt-Wetted Materials Become Activated & Contaminated Waste Following End-of-Useful-Life

- Fuel salt can be drained – does not wet structural alloys or graphite
  - Unlikely to have significant residual of special nuclear materials
  - Exterior surfaces unlikely to be contaminated
  - Radiation damaged, contaminated graphite is technically difficult to handle or reprocess
- NRC is currently engaged in revising 10 CFR Part 61 to address near-surface disposal of greater than Class C and transuranic waste (SRM-SECY-20-0098 April 2022)
- MSR reactor vessels have substantial similarities to single-shell, steel waste tanks (e.g., those at Hanford and SRNL)
  - DOE has indicated that backfilling with grout can produce an adequately stable and durable waste form
- Backfilling, drained components with grout followed by near-surface disposal would have a substantial impact on both MSR operational waste streams and eventual plant decommissioning
  - Requires focused technical evaluation as well as cost evaluation to support developing plant decommissioning plan

Fuel Salt Will Require Stabilization to Meet Indefinite Storage Requirements

- NRC (NUREG-2157) currently requires the ability to store used fuel on-site indefinitely in the event that a repository never becomes available
- Once deeply frozen, MSR fuel becomes radiolytically unstable producing halide gases
  - Fluoride fuel salts have the potential to generate gaseous UF_6
  - Chlorine gas will include ^{36}Cl (long-lived beta emitter)
- Halide salts are water soluble necessitating additional stabilization for most proposed repositories
- Waste glasses do not dissolve large fractions of halides
  - Halide crystals can be enveloped within durable waste material
- Multiple different options have been proposed to generate a stable waste form
  - Examples provided are representative not exhaustive

Used Fuel Salt May Be Stabilized for Direct Storage or Partitioned



Both paths generate processing waste – Unprepared, used MSR fuel salt does not meet indefinite storage stability expectations

Removing Actinides is Likely First Step in Waste Stabilization

- Actinide bearing used fuel requires capability for indefinite on-site storage and eventual geologic disposal
  - Barren (SNM stripped) fuel salt residuals become byproduct materials
- Key to enabling indefinite actinide recycle
  - High resource utilization
  - MSRs are only reactor class in which thermal spectrum systems can effectively consume transuranic isotopes due to lack of fuel mechanical damage and indefinite lifetime
- French program published very promising actinide co-separation laboratory results almost 20 years ago - DOI: 10.13182/NSE06-A2611
  - Contacting fluoride fuel salt with aluminum effective separates actinides into metallic phase
    - Aluminum acts as reductant and solvent for actinides
    - 99.3% single pass separation demonstrated
    - Actinide-aluminum alloy produced – potential waste form if actinides not recycled
  - Constant current electrorefining of chloride salt onto solid aluminum cathode also demonstrated

Atomic Energy Act – 42 USC 2014 Definitions

e. The term "byproduct material" means–
(1) any radioactive material (except special nuclear material) yielded in or made radioactive by exposure to the radiation incident to the process of producing or utilizing special nuclear material;

Removing SNM From Used Fuel Salt Substantially Alters Requirements

- SNM free waste form and industrial byproduct device safety goals are identical
  - Adequately robust and durable waste forms become industrial radiothermal sources
  - Achievement of Part 61 waste form stability and durability goals simultaneously meets safety intent of requirements for industrial devices containing byproduct material
- Fission products produce useful quantities of thermal energy for decades to centuries
  - Byproduct materials can be packaged into industrial thermal and radiation sources
  - Waste forms that contain significant quantities of SNM would require costly security and different licensing
- Key issue for byproduct material waste forms is achieving adequate robustness and durability
  - ISO 2919 (1999) provides guidance on adequate robustness – incorporated in 10 CFR 71.75 *Qualification of special form radioactive material*
- Byproduct material regulations derive from Chapter 8 of the Atomic Energy Act
  - NRC establishes rules to insure appropriate management of byproduct material to protect health and safety of the public and the environment
  - 10 CFR Part 32.30 provides requirements to manufacture, process, produce, or initially transfer *industrial devices containing byproduct material*

Halides Can Also Be Stripped From Used Fuel Salt

- Durable waste glasses do not dissolve large quantities of halides
  - Waste volume is primary cost driver
  - Oxides do not occupy substantially smaller volume than halides
  - Size reduction results from increase in radionuclide solubility into waste glass
- Components from processing equipment will become contaminated waste stream upon decommissioning
- Fluorine has no radioactive isotopes
  - Potential for release for alternate uses
- Chlorine will include ^{36}Cl – long-lived beta emitter
  - Likely reincorporated into fuel salt – UCl_3
    - Series of publications over past decade on recovery of actinides via conversion to chloride salts from French program – DOI: 10.1016/j.jnucmat.2011.04.023 , 10.1016/j.jnucmat.2013.12.011, and 10.1016/j.jnucmat.2017.09.045

Dehalogenation Can Increase the Stability of Waste

- Halide salts can dissolve and transport with water
  - Do not meet waste form acceptance criteria of most repositories
- Avoids potential for halide gas release and consequent waste canister pressurization
  - Fuel salt solidifies into polycrystalline mass
  - Radiolysis of deeply frozen salt yields halide gases (i.e., F_2 or Cl_2)
    - Volatile fission product compounds may also be generated (e.g., CsI)
    - Gases migrate along crystal grain boundaries and release from fuel salt mass
- Key metric is whether high waste loading of robust waste forms adequately compensates for increased processing and contaminated equipment resulting from the dehalogenation process steps
  - Remains open question
- Centralized dehalogenation facility supporting multiple reactors possible

Dehalogenation Accompanied By Oxidation is Key to Producing Robust Waste Glasses

- Dehalogenation is key element in conversion of fuel salt to either iron phosphate glass or borosilicate glass
- Multiple combined dehalogenation and oxidation methods have been demonstrated at varying TRL levels
- All require high temperatures and aggressive chemicals
  - Imperfect partitioning will result in spread of radionuclides throughout components – e.g., CsI in off-gas
- Noble metals do not readily oxidize
  - Trapped in additional metallic waste stream

Both Chlorine and Lithium Isotope Separation Likely To Be Inexpensive on Scale

- Large mass difference in isotopes
- Anion exchange based separation demonstrated for chlorine decades ago
  - Not matured or commercialized because of lack of market
  - Low-temperature, liquid phase process
  - Entering commercial market
- Lithium and/or chlorine isotope recovery from used fuel salt unlikely

Used Fuel Salt Can be Encapsulated as a Halide Salt Phase Within Durable Waste Form Matrix

- Metal or glass matrices possible
- Waste retained within a robust outer shell (e.g., extrusion billet shell or HIP canister)
  - Extrusion typically performed at lower temperature
- Waste form would be halide salt particles (likely single crystal) within robust matrix
- Limited waste loading into matrix to avoid interconnected halide particles
  - Would become vulnerability to dissolution or fission gas migration

Used Fuel Salt Can Be Encapsulated Within Sodium Aluminoborosilicate Glass

- Most technically mature option
  - Available through ANSTO
- Most of fluorine partitions to ceramic phase – CaF_2
  - Actinides, fission products, and carrier partition to glass phase
- Basic Process steps
  1. Mix (mill) salt with glass formers (e.g., H_3BO_3, $Al(NO_3)_3$, $Ca(OH)_2$, and SiO_2)
  2. Dry and calcine
  3. Mill
  4. HIP (hot isostatic press)

See DOI: 10.1111/jace.17293

Used Fuel Salt Can Be Encapsulated Into Halmet Waste Form

- Copper-tin (bronze) metal matrix composite most likely form
  - Continuous metal phase encapsulating fuel salt particles
- Technology derived from commercial halide salt metal matrix composites
  - Unproven for halide salt waste encapsulation
  - Cermets for oxide-based high-level waste have long history (ORNL/TM-6404 – 1978; DOI: 10.2172/12198598); ceramics have similar properties to halide salts
- Continuous metal phase produced by thermo-mechanically forcing metal to flow around hard fuel salt particles
  - Need to avoid remelting fuel salt during halmet formation
- Basic Process Steps
  1. Pulverize fuel salt and and mix with alloy powder
  2. Place in die, compact, and extrude (minimizes temperature required)
  3. Overlay with copper (or bronze)

Liquid Fuel MSR Waste Technology and Processes Will Be Significantly Different Than Other Reactor Classes

Future Vision

- Fuel salt wetted components (including graphite) – grouted in for shallow land disposal
  - Solid filters – grouted in for shallow land disposal
  - Hydroxide scrubber media – converted to *saltstone* followed by shallow land disposal
  - Dependent upon performance-based revision to 10 CFR Part 61currently underway
- Tritium – chemically trapped and employed for fusion
  - Complex issue with multiple options
- Krypton-85 – bottled for decay storage
- Actinides – multi-recycled
- Fission products
  - Encapsulated into robust byproduct radiothermal sources
  - Shallow burial after couple of centuries