

# Nuclear Waste Management Strategy for Molten Salt Reactor Systems

Dr. Brian Riley and Dr. John Vienna

Pacific Northwest National Laboratory, USA

15 June 2022



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## Meet the Presenters

**Dr. Brian Riley** has a PhD in Materials Science and Engineering from Washington State University. He is a Senior Materials Scientist in the Radiological Materials Group at PNNL and is a Technical Team Leader for the Waste Form Development Team. His research primarily focuses on salt waste form development and salt waste partitioning methods with funding from DOE Office of Nuclear Energy. Recently, Dr. Riley has been performing and leading research on various projects in these areas as well as looking at methods for treating salt wastes from molten salt reactor, as well as developing and testing sorbents for capturing volatile radionuclides such as iodine gas.

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**Dr. John Vienna** is a Laboratory Fellow in Materials Science at the Pacific Northwest National Laboratory (PNNL). He earned B.S. and M.S. degrees in Ceramics Engineering from Alfred University and a Ph.D. degree in Materials Science from Washington State University. Dr. Vienna joined PNNL in 1993. Throughout his career, has served in numerous technical leadership roles in nuclear waste management, including serving the U.S. Department of Energy's Office of Nuclear Energy as a technical lead for nuclear waste treatment.

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# Past and Current Collaborators

## Funding – US Department of Energy (US DOE)

- DOE Office of Nuclear Energy (USA); K. Gray, S. Kung, B. Robinson
- National Technical Directors (USA) from Nat'l Labs:
  - Patricia Paviet (@PNNL – MSR Campaign)
  - Ken Marsden (@INL – MRWFD and JFCS)

## Collaborations

- **Pacific Northwest National Laboratory (USA)** – S. Chong, J. Crum, W. Lepry, C. Lonergan, A. Lines, S. Bryan (et al.)
- **Oak Ridge National Laboratory (USA)** – J. McFarlane, G. DelCul, C. Contescu, K. Myhre, H. Andrews
- **Idaho National Laboratory (USA)** – S. Frank, K. Marsden, T. Todd
- **Argonne National Laboratory (USA)** – W. Ebert, S. Stariha
- **Rensselaer Polytechnic Institute (USA)** – J. Lian
- **University of Utah (USA)** – M. Simpson



- **University of Reno – Nevada (USA)** – K. Carlson
- **Washington State University (USA)** – J. McCloy
- **Clemson University (USA)** – M. Tang
- **Korea Atomic Energy Research Institute (KAERI)** (South Korea) – H.S. Park, K. Lee, Y.-Z. Cho
- **Australian Nuclear Science and Technology Organisation (Australia)** – L. Vance, D. Gregg
- **National Nuclear Laboratory (UK)** – J. Turner, M. Harrison
- **University of Sheffield (UK)** – N. Hyatt

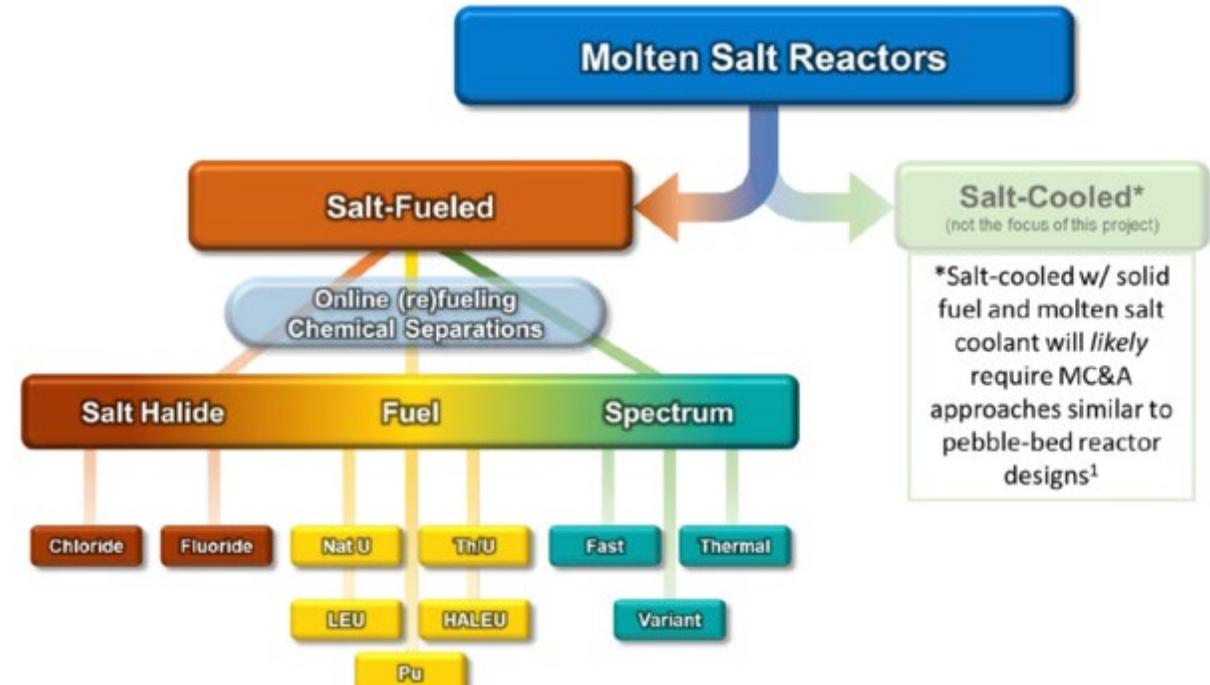
# Overview of Presentation

- 1) MSR Overview (High Level)
- 2) Waste types from MSRs
- 3) Off-Gas Treatment and Monitoring Examples
- 4) Waste Form Examples
- 5) Other Considerations
- 6) Summary and Conclusions

# MSR OVERVIEW (HIGH LEVEL)

# Examples of Salt Compositions for Two-Salt Concepts

- **Types**
  - Burner reactors vs breeder reactors
  - Thermal spectrum vs fast spectrum
- **Salt compositions**
  - Fluorides or chlorides are most often discussed but other options exist
- **Common abbreviations** you might see in the literature
  - FLiBe =  ${}^7\text{LiF}-\text{BeF}_2$
  - FLiNaK =  $\text{LiF}-\text{NaF}-\text{KF}$



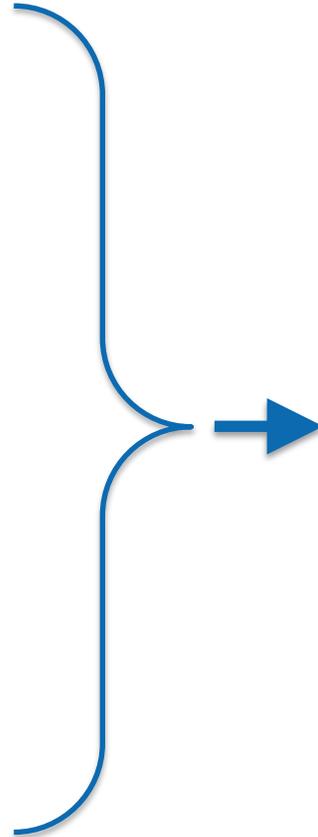
**Salt-Cooled\***  
(not the focus of this project)

\*Salt-cooled w/ solid fuel and molten salt coolant will likely require MC&A approaches similar to pebble-bed reactor designs<sup>1</sup>

Reactor Type	Neutron Spectrum	Molten Salt Application	Reference Salt Systems
Molten Salt Breeder Reactor	Thermal	Fuel	${}^7\text{LiF}-\text{BeF}_2-\text{AnF}_4$
	Fast	Secondary coolant	$\text{NaF}-\text{NaBF}_4$
		Fuel	${}^7\text{LiF}-\text{AnF}_4$
			$\text{NaCl}-\text{MgCl}_2-\text{UCl}_3-\text{PuCl}_3$
		$\text{LiF}-\text{NaF}-\text{BeF}_2-\text{AnF}_3$	
Advanced High Temperature Reactor	Thermal	Primary coolant	${}^7\text{LiF}-\text{BeF}_2$
Very High Temperature Reactor	Thermal	Heat transfer coolant	$\text{LiF}-\text{NaF}-\text{KF}$
Liquid Salt Cooled Fast Reactor	Fast	Primary coolant	$\text{LiCl}-\text{NaCl}-\text{MgCl}_2$
		Intermediate coolant	$\text{NaNO}_3-\text{KNO}_3$

# MSR Salt Processing

- Fluorination/chlorination
- UF<sub>6</sub> purification/reduction
- Vacuum distillation
- Reductive extraction (Pa/Bi)
- Hydrofluorination
- Metal transfer process
- Electrolytic oxidation/reduction
- Oxide precipitation
- Selective crystallization
- Electrochemical separations



- Prepare fuel salt
- Separate Pa-233
- Remove fission products
- Remove corrosion products
- Recycle Cl-37
- Recycle Li-7
- Reduce waste volume
- Promote waste form production

Fredrickson et al. 2018, *Molten Salt Reactor Salt Processing – Technology Status*, INL/EXT-18-51033,  
<https://www.osti.gov/biblio/1484689-molten-salt-reactor-salt-processing-technology-status>

# WASTE TYPES FROM MSR<sub>s</sub>

## Questions that Require Answers

- What streams should be considered?
- What do we know about the streams?
  - Do we know enough to determine treatment route?
  - Any challenges?
- Are there disposition pathways?
  - Restrictions on stream management (e.g., storage, treatment, packaging, disposal environment)?
- How would effluents be treated and disposed?
- Which streams require research?
  - Determine or estimate characteristics
  - Develop method or treatment of waste form
  - Identify potential restrictions or trade-offs with salt chemistry and processes
  - Generate data for MSR process models

# Some of our Work Aimed to Help in These Areas

## *Identification of Potential Waste Processing and Waste Form Options for Molten Salt Reactors*

Nuclear Technology  
Research and Development

Prepared for  
U.S. Department of Energy  
MSR Campaign  
B.J. Riley,<sup>(a)</sup> J. McFarlane,<sup>(b)</sup>  
G.D. DelCul,<sup>(b)</sup> J.D. Vienna,<sup>(a)</sup>  
C.I. Contescu,<sup>(b)</sup> L.M. Hay,<sup>(a)</sup> A.V. Savino,<sup>(a)</sup>  
H.E. Adkins,<sup>(a)</sup>  
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<sup>(b)</sup>Oak Ridge National Laboratory  
August 15, 2018  
NTRD-MSR-2018-000379, PNNL-27723



Source: <https://info.ornl.gov/sites/publications/Files/Pub114284.pdf>

**I&EC**  
research  
Industrial & Engineering Chemistry Research  
pubs.acs.org/IECR Review

**Electrochemical Salt Wasteform Development: A Review of Salt Treatment and Immobilization Options**  
Brian J. Riley\*

Cite This: *Ind. Eng. Chem. Res.* 2020, 59, 9760–9774 Read Online

Source: <https://pubs.acs.org/doi/10.1021/acs.iecr.0c01357?ref=pdf>

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**Nuclear Engineering and Design**  
journal homepage: [www.elsevier.com/locate/nucengdes](http://www.elsevier.com/locate/nucengdes)

**Molten salt reactor waste and effluent management strategies: A review**  
Brian J. Riley<sup>a,\*</sup>, Joanna McFarlane<sup>b</sup>, Guillermo D. DelCul<sup>b</sup>, John D. Vienna<sup>a</sup>,  
Cristian I. Contescu<sup>b</sup>, Charles W. Forsberg<sup>c</sup>

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Source: <https://doi.org/10.1016/j.nucengdes.2019.02.002>

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2021, VOL. 66, NO. 5, 339–363  
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FULL CRITICAL REVIEW  Check for updates

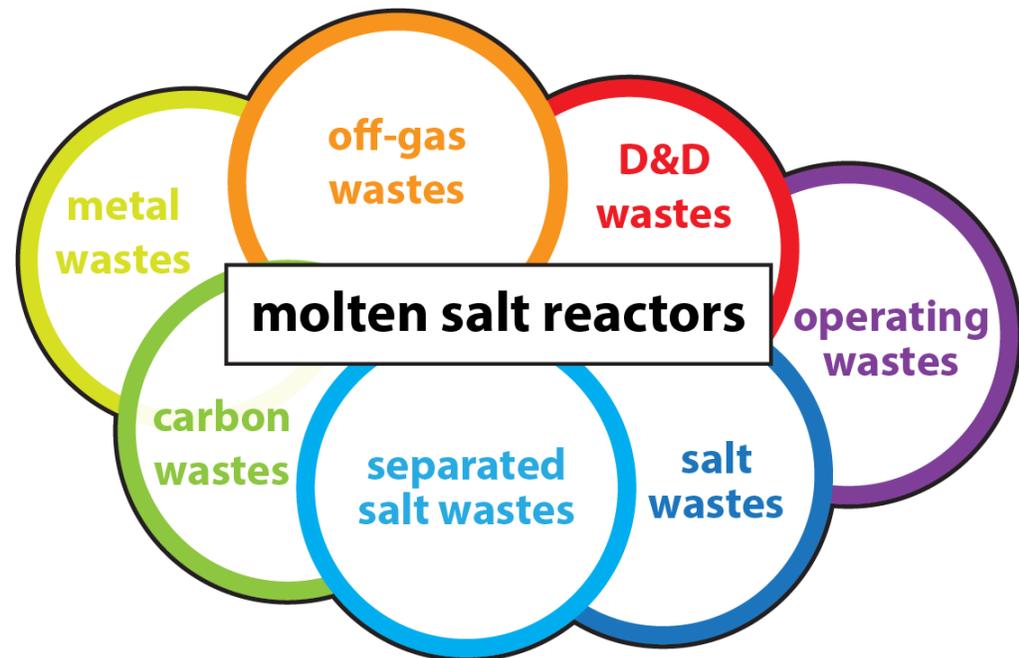
**Molten salt reactors and electrochemical reprocessing: synthesis and chemical durability of potential waste forms for metal and salt waste streams**  
Krista Carlson<sup>a</sup>, Levi Gardner<sup>a</sup>, Jeremy Moon<sup>b</sup>, Brian Riley<sup>c</sup>, Jake Amoroso<sup>d</sup> and Dev Chidambaram<sup>b</sup>

<sup>a</sup>Department of Materials Science and Engineering, University of Utah, Salt Lake City, UT, USA; <sup>b</sup>Department of Chemical and Materials Engineering, University of Nevada Reno, Reno, NV, USA; <sup>c</sup>Pacific Northwest National Laboratory, Richland, WA, USA; <sup>d</sup>Savannah River National Laboratory, Jackson, SC, USA

Source: <https://doi.org/10.1080/09506608.2020.1801229>

# General Streams – Output from PNNL/ORNL Report

- Decommissioning and Decontamination (D&D)
- Metal
- Off-gas
- Operating
- Carbon
- Spent salt
- Separated salt

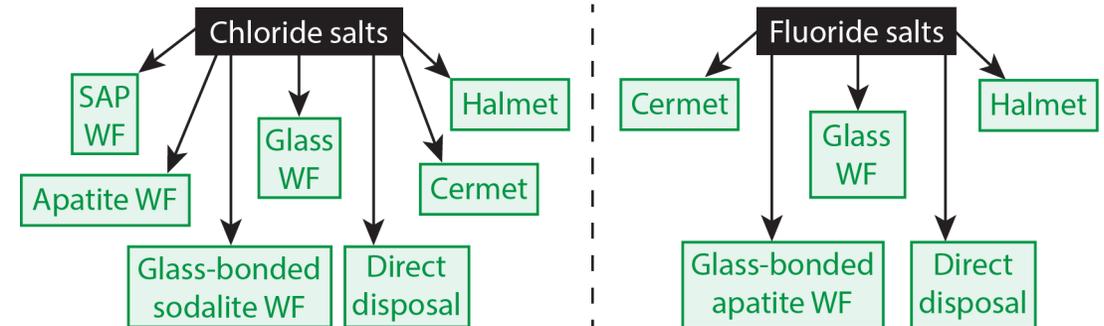


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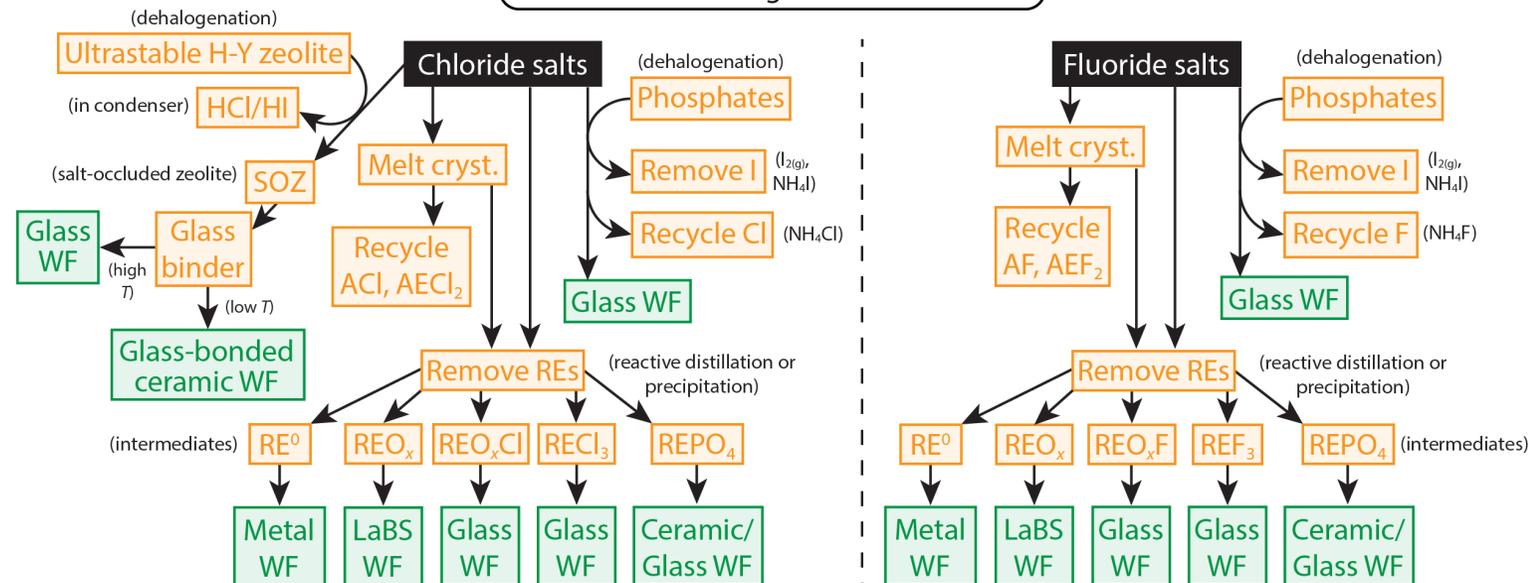
# Salt Streams: Challenges & Questions

- Halide immobilization is complicated
- $^{36}\text{Cl}$  and  $^{129}\text{I}$  dose drivers for repository (require fractional release rates of ppm/year)
- Halogen impact on disposal site
- High doses from insanely short cooling
- Salt storage/transportation (radiolysis, dispersibility)
- Uncertain stream compositions and characteristics
- Isotopically enriched  $^{37}\text{Cl}$  and  $^7\text{Li}$ 
  - Methods for enrichment
  - Costs of enrichment (favor recycle)
  - Methods for capture/recycle
  - Additional wastes produced?

Direct Immobilization of Waste Salt

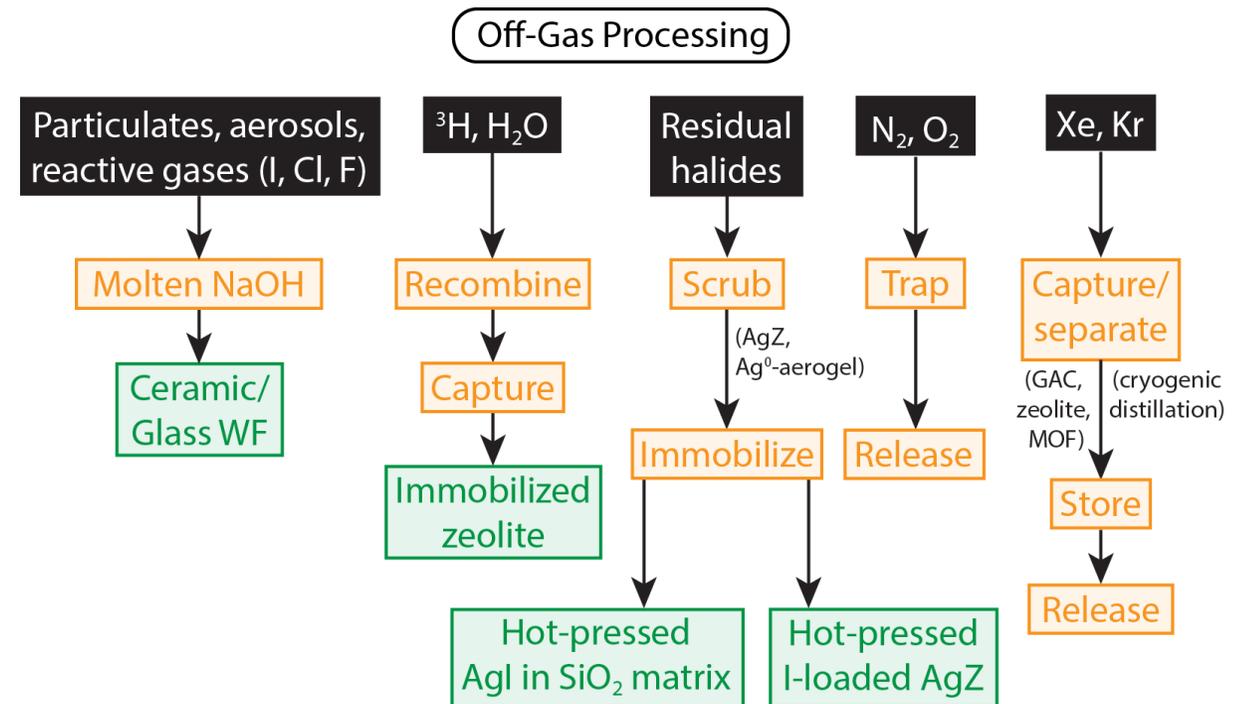


Waste Salt Processing and Immobilization



# Reactor Off-Gas Streams: Challenges/Questions

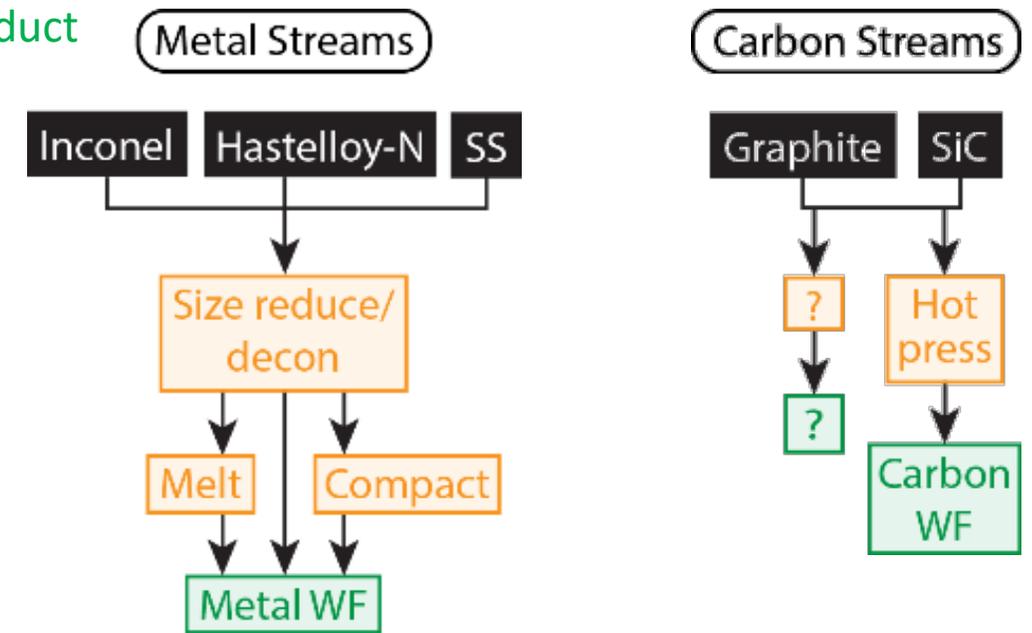
- Current U.S. regulations require  $^{85}\text{Kr}$  capture and storage
  - $^{85}\text{Kr}$  gas storage is point source, high rad, high pressure, corrosive daughters
  - $^{85}\text{Kr}$  immobilization is expensive, low loading
- Acid gas capture in inert gas
- Salt mist/entrainment
- High-dose streams require holdup for decay (e.g., Xe)
- Recycle He back into the reactor
- Need to deal with  $^3\text{H}$  partitioning and transportation (permeation through metallic reactor components)



Source: <https://doi.org/10.1016/j.nucengdes.2019.02.002>

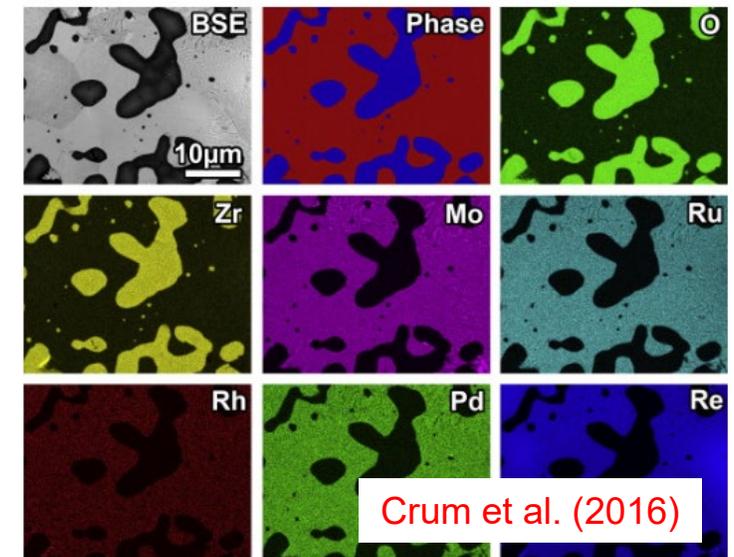
# Metal and Carbon Streams: Challenges/Questions

- Salt impregnation
- Deep penetration of radionuclides at equipment end of life
- High dose (from salt, gas penetration)
- Large portion could be GTCC\*/HLW\* due to activation products and embedded actinide salts
- Treatment options are challenging (metals) or impractical (graphite)
- Untreated durabilities questionable to poor (both graphite and many metals)
- Graphite recycle options might be plausible (next slide)



Source: <https://doi.org/10.1016/j.nucengdes.2019.02.002>

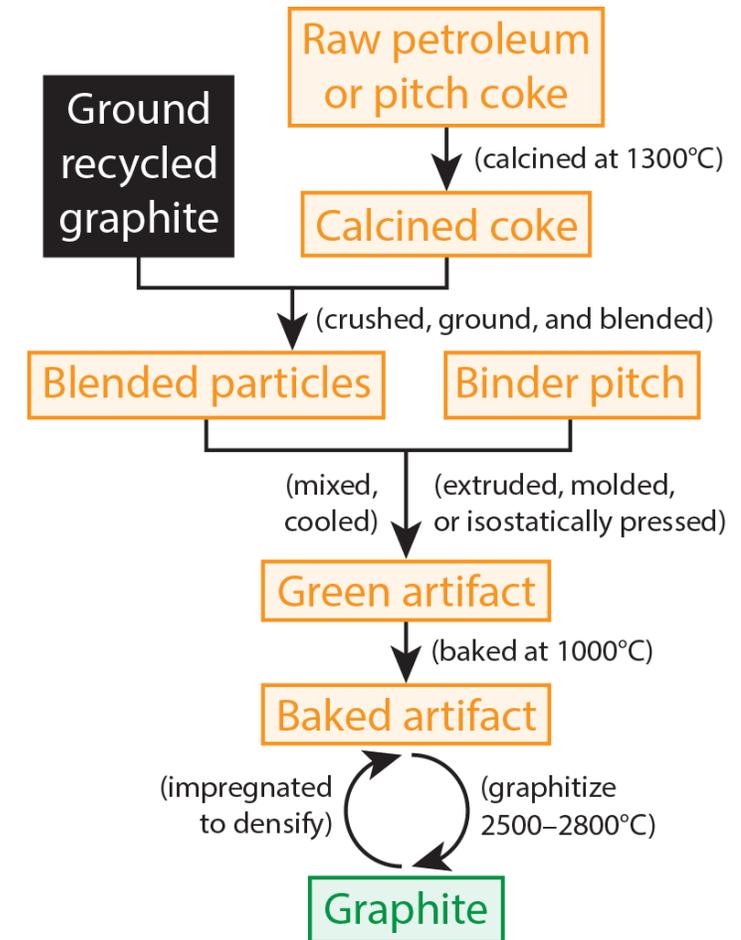
## 5-metal (Mo+Pd+Rh+Ru+Tc) epsilon phase



Source: <https://doi.org/10.1016/j.jnucmat.2013.05.043>

# Potential for Carbon Recycle

- It is possible to recycle used graphite moderators from MSR
- This could significantly reduce the carbon waste from graphite moderators
- Graphite will likely be very radioactive, complicating handling
- Eventually, at reactor end-of-life, it would have to be disposed

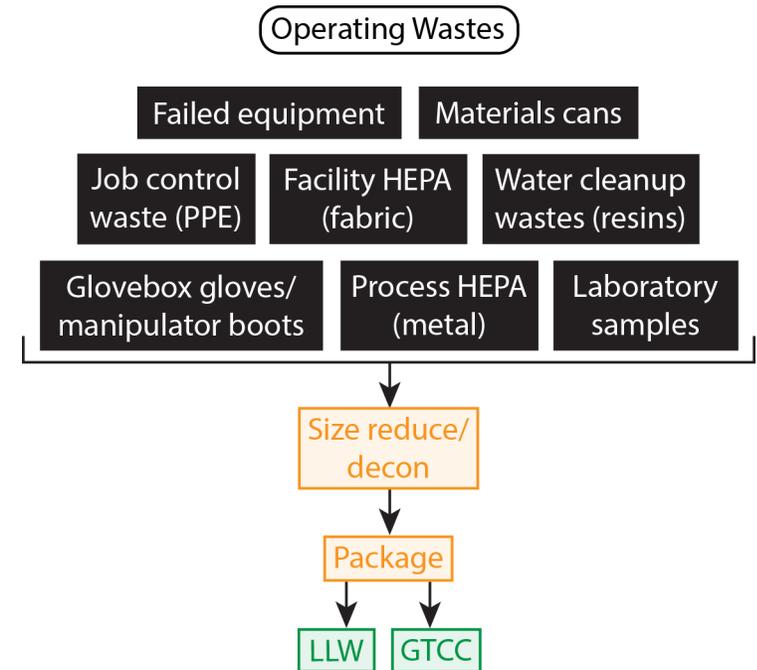
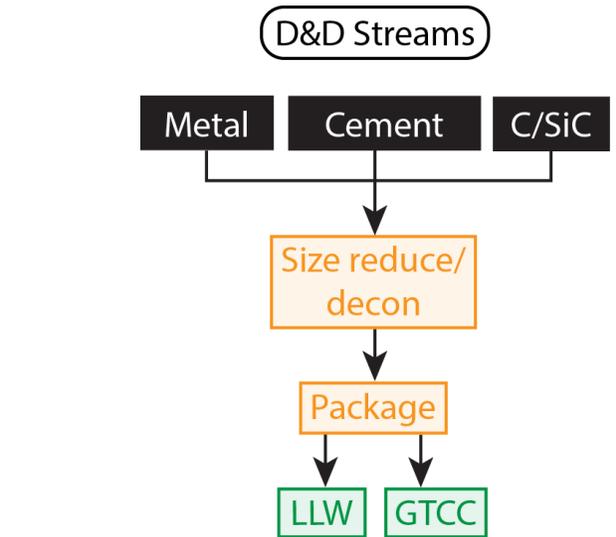


Burchell and Pappano  
(ORNL/TM-2010/00169)

Source: <https://doi.org/10.1016/j.nucengdes.2019.02.002>

# D&D and Operating Wastes: Challenges/Questions

- Potentially high doses (significant fractions GTCC)
- Potential for mixed LLW and mixed GTCC
- High volumes/masses
- Uncertain characteristics and amounts (mixed wastes?)
- Salt contaminated wastes challenge to dispose



## Primary Gaps Identified – Proposed Next Steps

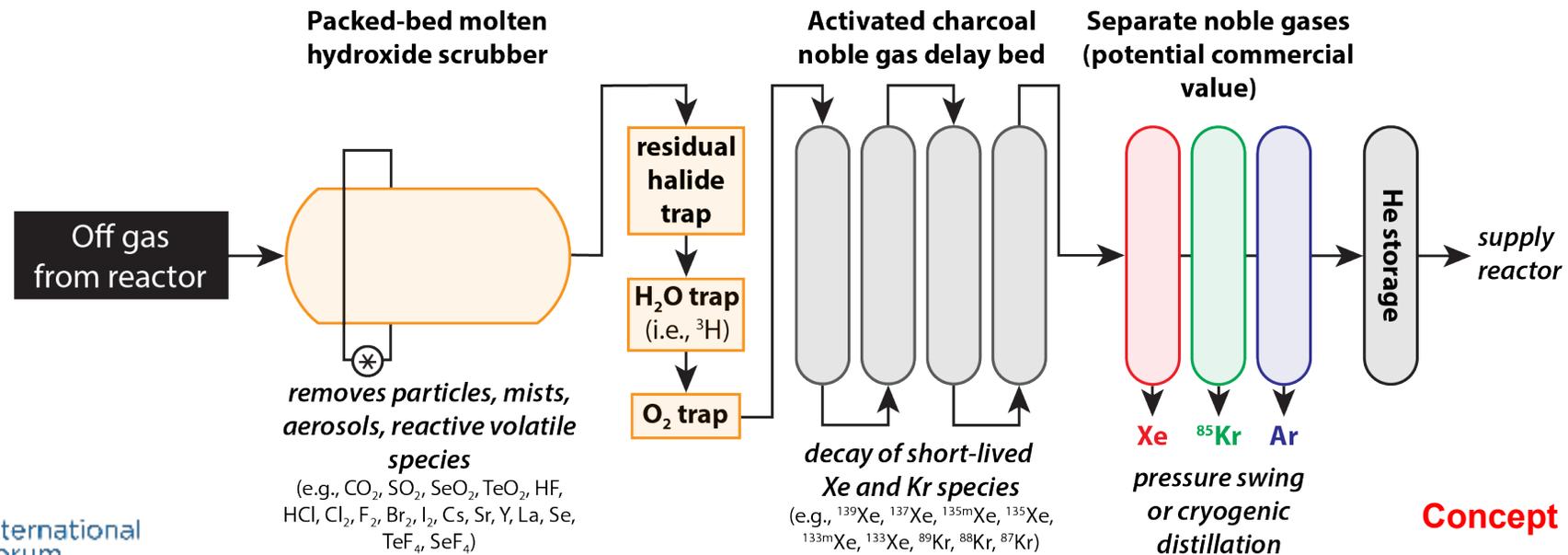
- Need more information on mass balances and compositions of expected wastes
- Need to develop initial functional and operational requirements (FOR) for MSR wastes
- Initiate off-gas treatment technology testing
- Investigate waste form options for salt-based waste streams
- Evaluate treatment options of contaminated carbon-based materials (i.e., graphite)

- 
- Some of this work is already being done through the US Department of Energy Office of Nuclear Energy (DOE-NE) Campaigns including:
    - **Material Recovery and Waste Form Development (MRWFD) (NE-4)**
    - **Molten Salt Reactor (MSR) (NE-5)**

# OFF-GAS TREATMENT & MONITORING EXAMPLES

# Molten Hydroxide Scrubber

- Potential non-aqueous scrubber option to remove halides, particulates, mists, and aerosols from process gas stream
- Would include delay bed for high-activity noble gases (e.g., neutronics poisons)
- Purge gas could be cleaned and sent back to the reactor

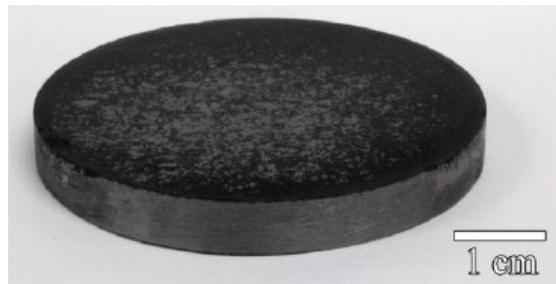


Concept by Bill Del Cul (ORNL)

# Iodine Capture and Immobilization

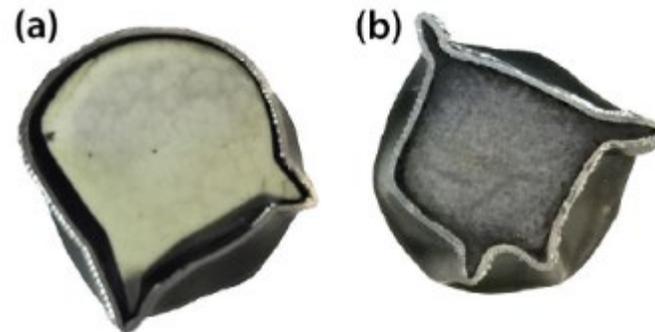
- **Solid sorbent systems utilizing chemisorption**
  - Metal-impregnated zeolites for iodine (e.g., Ag, Bi, Cu)
  - Metal-impregnated silica-based gels (e.g., Ag, Bi, Cu)
- **Fate after capture – they can be hot pressed into waste forms**

## SPS I-loaded Ag<sup>0</sup>-aerogel



**Work by:**  
Matyas, et al. (PNNL)

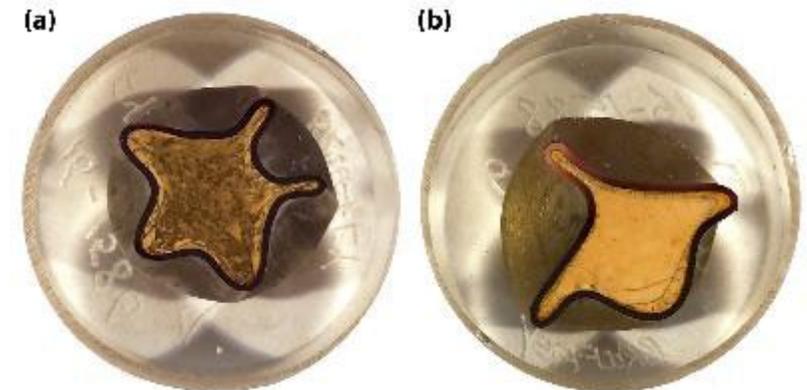
## HIPed I-loaded sodalite



**Work by:**  
Chong, et al. (PNNL) | Bruffey (ORNL)

Source: <https://doi.org/10.1016/j.jnucmat.2020.152222>

## HIPed I-loaded AgZ (mordenite)



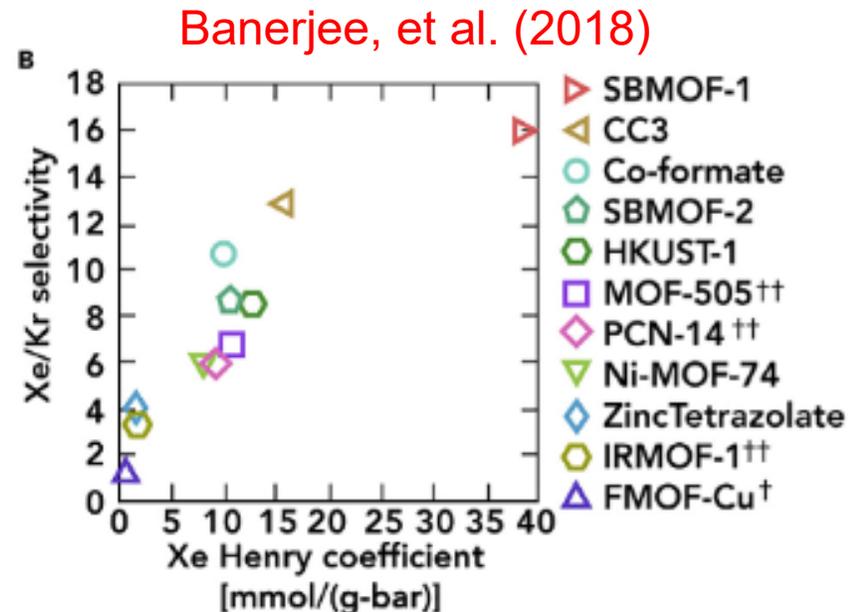
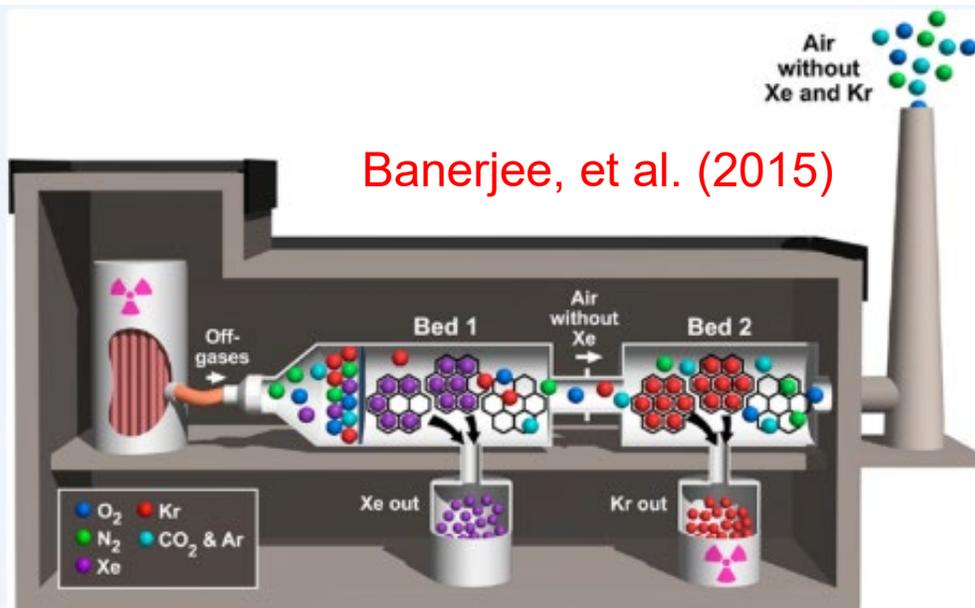
**Work by:**  
Bruffey (ORNL)

Source: ISBN: 978-1-53617-250-8 (page 259)

HIP = hot isostatic pressing; SPS = spark plasma sintering

# Noble Gas Capture

- **Metal-Organic Frameworks (MOFs) can be used to separate Xe and Kr**
  - Many MOFs have high Xe/Kr selectivities (>10×); very few have Kr/Xe selectivities
  - Separate MOFs can be used to pull out Xe in bed-1 followed by Kr in bed-2
- **Cryogenic distillation can also be used for noble gas capture**



## Engineered forms

Riley, et al. (2020)

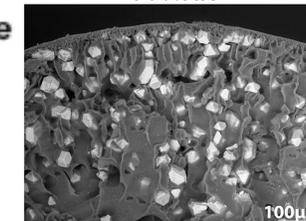
75%HK



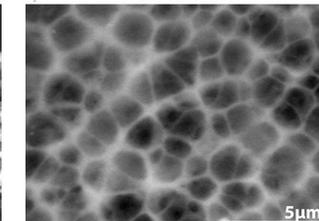
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75%HK



90%HK



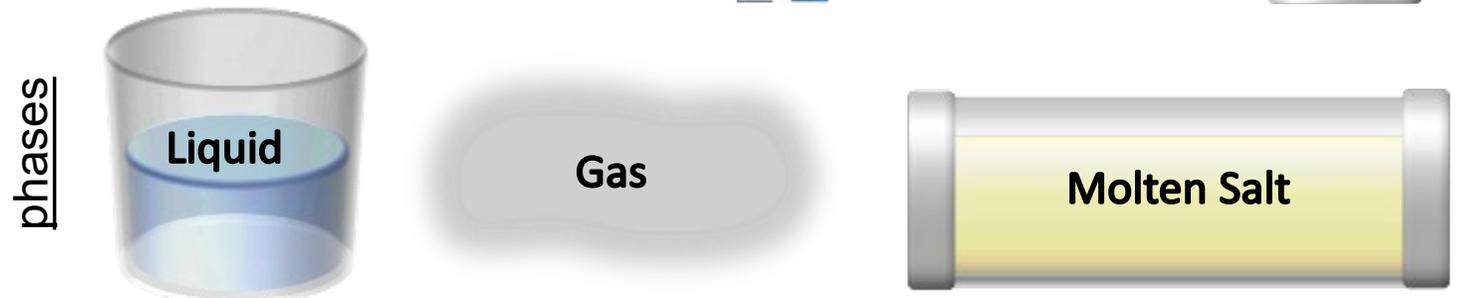
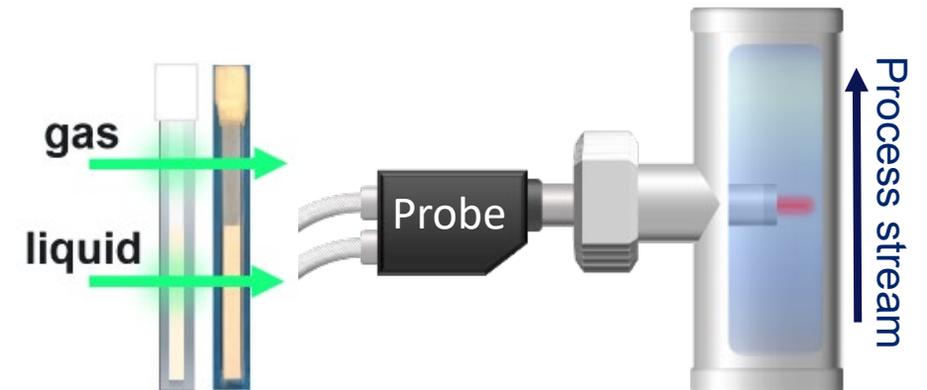
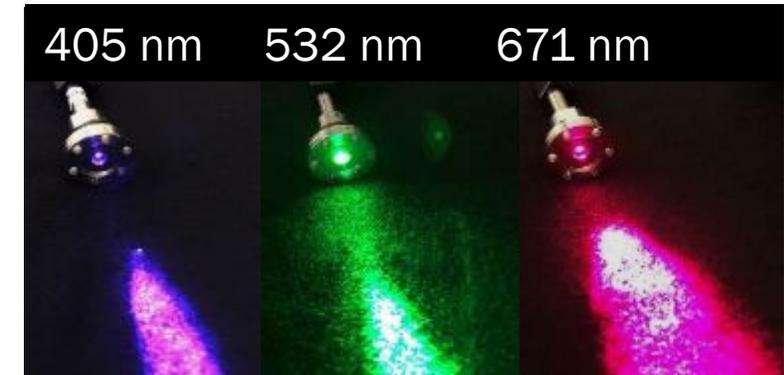
# In-Situ Off-Gas Monitoring

- Online monitoring can be used to track the species and concentrations in the off-gas streams
- Spectroscopic tools include
  - Raman
  - UV-VIS-NIR – ultraviolet-visible-near infrared
  - LIBS – laser-induced breakdown spectroscopy
- Analysis in gas phase, liquid phase, molten salt, etc.
- Species include  $I_{2(g)}$ , ICl, Xe, and hydrogen isotopes

Work led by:

Lines, Bryan, et al. (PNNL)

McFarlane, Andrews, Myhre, et al. (ORNL)



Sources:

<https://doi.org/10.1021/acs.est.0c06137>

<https://doi.org/10.1117/12.2557555>

<https://doi.org/10.1021/acs.jpca.0c07353>

# WASTE FORM EXAMPLES

# Waste Form Definitions

- Dehalogenation – halides are removed, salt cations are converted to another form (e.g., oxides, phosphates)
- Waste loading (WL) – mass fraction of waste in the waste form
  - 1) Full salt – direct immobilization of entire salt
  - 2) Salt cation loading – normalized parameter to compare waste forms on this basis despite how they are processed
  - 3) Salt cation oxide loading – mass of salt cation oxides in WF
- Storage volume – volume of final waste form required to immobilize starting salt mass
- Density – mass/volume; this affects storage volume of final waste form; effected by porosity
- Porosity – open/closed voids; some waste forms have porosity (e.g., GBS-CWF)
- Chemical durability – leach rate(s) in standardized accelerated leaching tests (e.g., PCT, C1308)

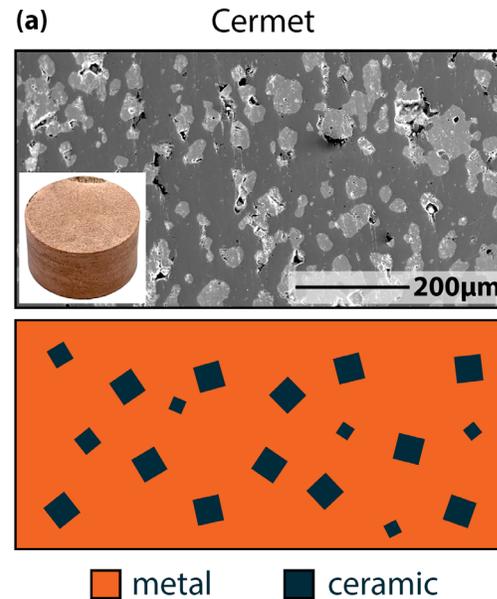
# Waste Form Types

- Single-phase waste forms – glass or crystalline material (e.g., REPO<sub>4</sub>)
- Multi-phase waste forms – cermet (ceramic-metal), halmet (halide-metal), glass-bonded ceramic (e.g., glass-bonded sodalite), glass ceramic

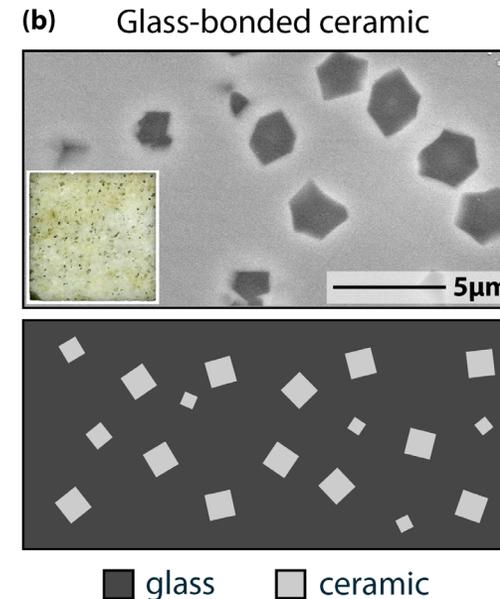


Source: <https://dx.doi.org/10.1021/acs.iecr.0c01357>

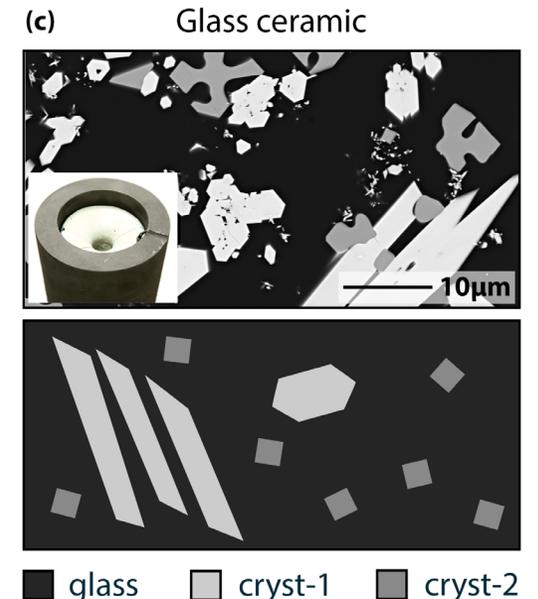
crystals in copper



sodalite



apatite/powellite



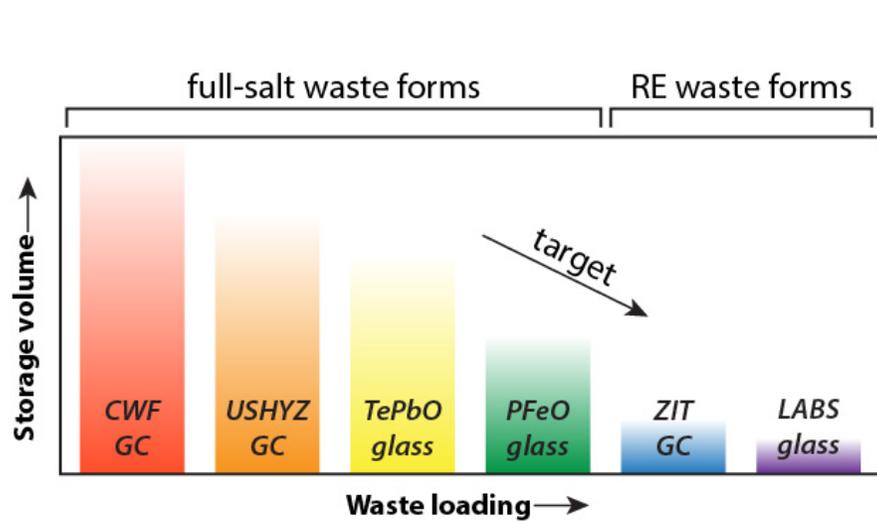
# Types of Applicable Crystalline Matrices

Mineral	Name	Halides	Alkalis	Alkaline Earths	Rare Earths	Actinides	Reference(s)
Apatite	AE-RE Apatite	F	–	Be→Ba	RE	–	Ewing (1999)
	Fluorapatite	F	–	Ca	–	–	Lu et al. (2013)
	BeF-apatite	F	Na	Be	–	–	Engel and Fischer (1990)
	LiF-BeF <sub>2</sub> apatite	F	Li	Be, Ca	–	–	Lexa (1999)
	Chlorapatite	Cl	–	Ca	–	–	Lu et al. (2013)
	Iodoapatite	I	–	Ca	–	–	Cao et al. (2017)
Perovskite	Sn-Cl perovskite	Cl	Cs	–	RE	An	Scott et al. (2018)
	Ca-Ti Perovskite	–	–	L	L	L	Vance et al. 2006)
Phosphate	Spodiosite	Cl, F	–	Ca	–	–	Donald (2010)
	RE-Monazite	–	–	–	RE	–	Boatner et al. (1980)
	An-Monazite	–	–	–	–	An	Van Emden et al. (1997)
	Xenotime	–	–	–	RE	An	Van Emden et al. (1997)
Sodalite	Chlorosodalite	Cl	Li→K	-	–	–	Riley et al. (2017)
	Wadalite	Cl	–	Ca	–	–	Mihajlovic et al. (2004)
	Iodosodalite	I	Na	-	–	–	Chong et al. (2017)
Nesosilicate	Rondorfite	Cl	–	Ca, Mg	–	–	Mihajlovic et al. (2004)
Cancrinite	Quadridavayne	Cl	Na, K	Ca	–	–	Bonaccrsi et al. (1994)
Titanate	Zirconolite	–	–	L	L	L	Vance et al. (2006)
	Perovskite	–	–	L	L	L	Vance et al. (2006)
	Hollandite	–	L	L	L	L	Vance et al. (2006)

- **“L” denotes that species could likely be incorporated (but not necessarily documented yet)**
- **“–” denotes that these species are unlikely to incorporate**
- **Primary issue is that salt must meet target stoichiometry of the crystal or additional reagents are needed**

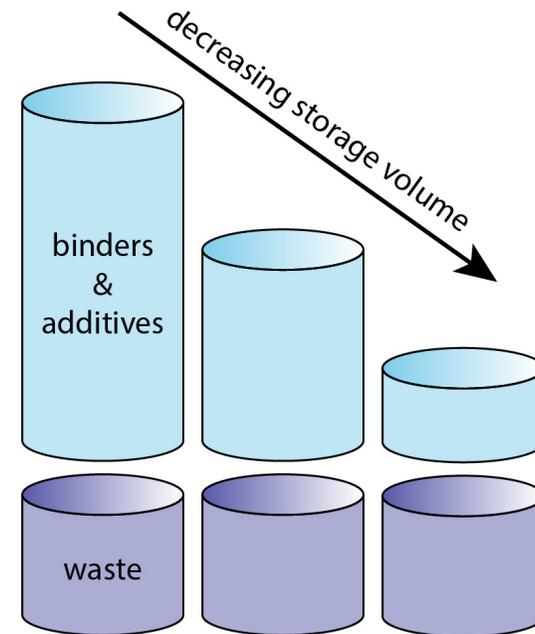
# Waste Form (WF) Graphical Representations

storage volume and waste loading



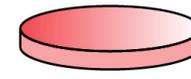
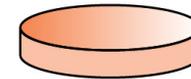
Source: <https://doi.org/10.1080/09506608.2020.1801229>

different ways to think about WL



**GBS-CWF**

**halides**  
(5.7%)

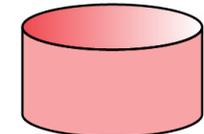
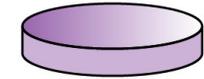


**salt cations**  
(3.8%)

salt loading:  
**9.5 mass%**

**Fe-P-O WF**

**oxygen**  
(5.5%)



**salt cations**  
(17.5%)

SCO loading:  
**23 mass%**

**Goals: maximize waste loading and minimize WF volume**

# Options for Partitioning to Remove Different Salt Components

- Full salt immobilization
- Salt partitioning options
- Immobilization of separate partitions

waste	Unpartitioned salt (e.g., LiCl+KCl+ fission products)	Partially dehalogenated salt (e.g., REOCl)	Fully dehalogenated salt (e.g., REO <sub>x</sub> )
	<i>dehalogenation</i> →		
processes	a) phosphate process b) USHYZ process c) SAP/U-SAP process	a) USHYZ process b) phosphate process c) LABS process	
wasteforms	a) GBS b) Pb-Te-O glass	a) Pb-Te-O glass b) LABS glass	a) LABS glass b) Fe-P-O glass c) SAP d) ZIT

Figure 2. Summary of ER salt processing and wasteform options for different waste streams (see text for descriptions).

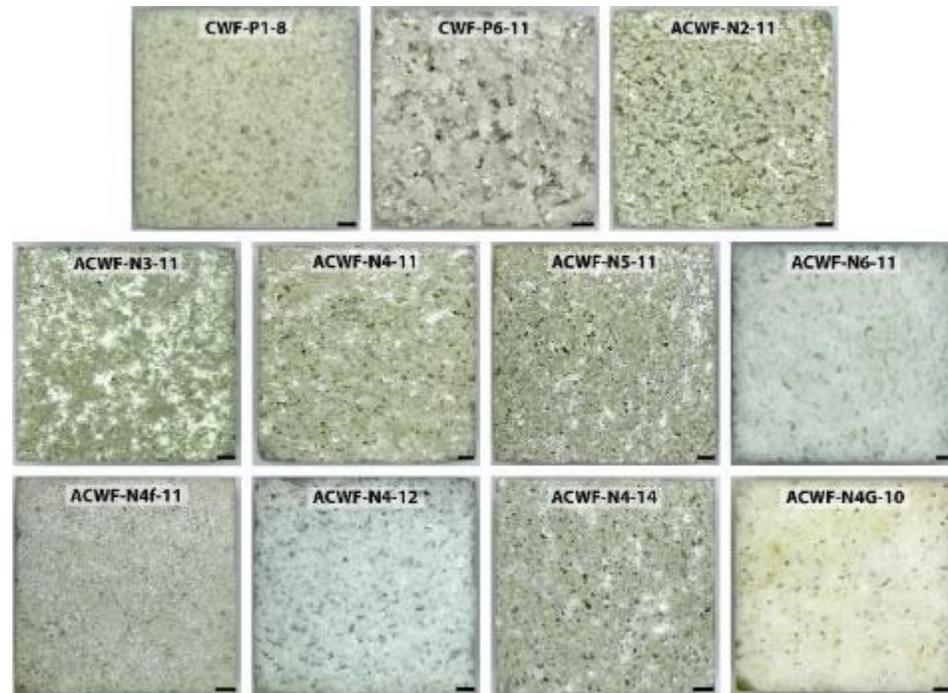
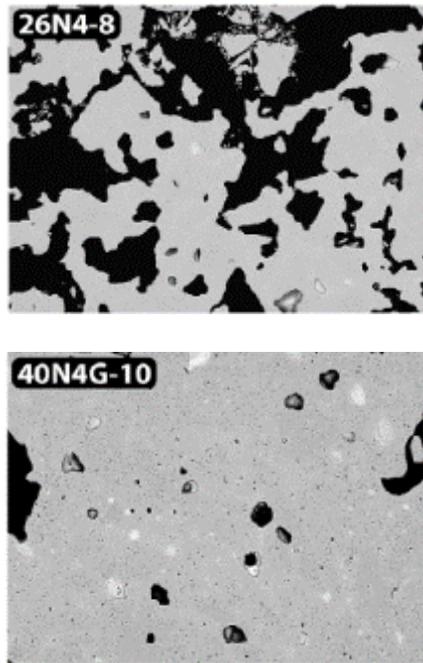
	Partitioning process	Final product(s)
A <sup>+</sup>	a) vacuum distillation b) melt crystallization c) zone freezing/refining	a) CsCl (FP) removal b) ER electrolyte (LiCl) removal c) ER electrolyte (LiCl) removal
AE <sup>2+</sup>	a) vacuum distillation b) reactive precipitation (A <sub>2</sub> CO <sub>3</sub> )	a) BaCl <sub>2</sub> remains b) (Ba,Sr)CO <sub>3</sub> precipitation
RE <sup>3+</sup>	a) oxidative precipitation (O <sub>2</sub> ) b) reactive precipitation (A <sub>2</sub> CO <sub>3</sub> ) c) reactive distillation (A <sub>3</sub> PO <sub>4</sub> )	a) REOCl/REO <sub>x</sub> mixtures b) REOCl/REO <sub>x</sub> mixtures c) REPO <sub>4</sub> mixtures
An <sup>3+</sup>	a) electrorefining b) vacuum distillation c) aqueous separations	a) An <sup>0</sup> (reduced at the cathode) b) AnCl <sub>3</sub> can be removed c) actinides dissolved in a solvent
Ha <sup>-</sup>	a) phosphate process b) USHYZ process c) SAP/U-SAP	a) dehalogenated phosphate glass b) alkali-loaded Y-zeolite c) Li <sub>3</sub> PO <sub>4</sub> droplets in silica-rich glass

Figure 1. Summary of partitioning processes and final products targeting alkalis (A<sup>+</sup>), alkaline earths (AE<sup>2+</sup>), rare earths (RE<sup>3+</sup>), actinides (An<sup>3+</sup>), and halides (Ha<sup>-</sup>) where the product(s) listed are those resulting from the partitioning process. These are described in more detail in subsequent sections.

# Glass-Bonded Sodalite Ceramic Waste Form (GBS-CWF)

- Made from salt (no pre-partitioning of the salt), zeolite 4A, & glass binder
- Contains some porosity due to pressureless sintering process used for synthesis

higher glass loading  
less optimal storage volume



different binders, binder loadings, and salt loadings

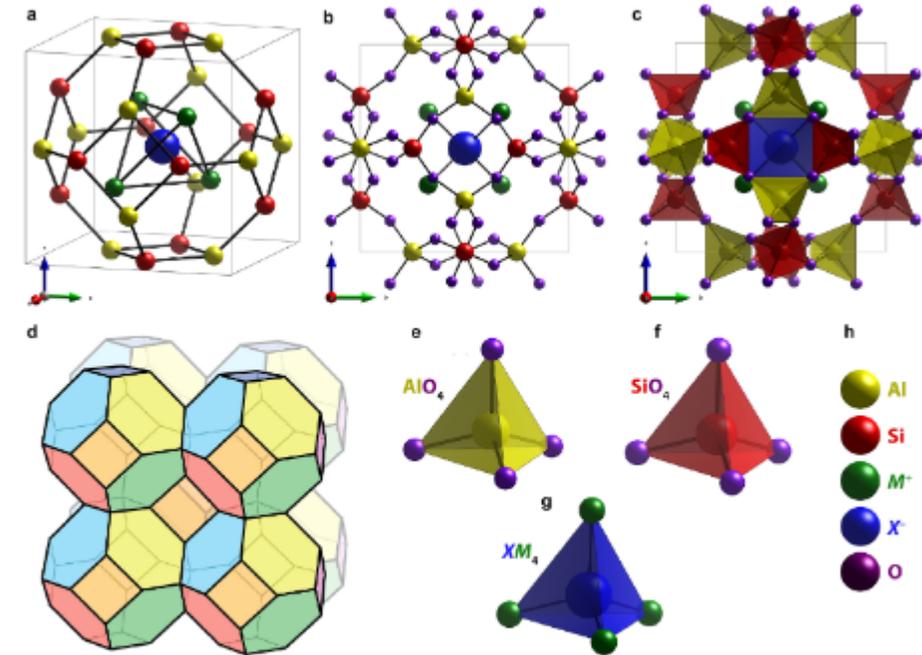
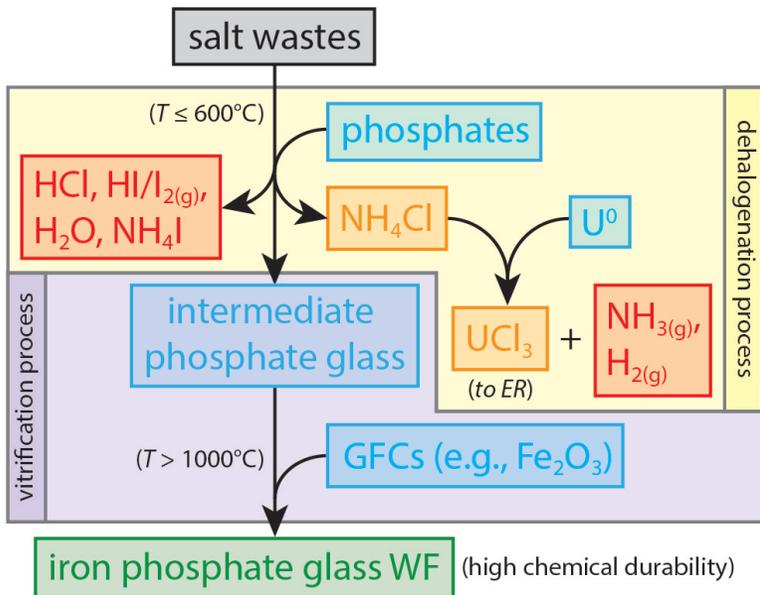


Fig.1 Sodalite  $\beta$ -cage shown in ball-stick format a without oxygen present, b with oxygen present, and c with oxygen and with space-filling polyhedra d a space-filling format with nine  $\beta$ -cages stacked together; tetrahedra including e  $AlO_4$ , f  $SiO_4$ , and g  $XM_4$ ; and h leg-

end where  $M^+$  and  $X^-$  denote metal cations and halide anions in the  $\beta$ -cage, respectively. A portion of this figure was modified from a previous figure by Riley et al. (2016b) and reprinted with permission. ©2016 Elsevier

# Iron Phosphate Waste Forms

- Salt is dehalogenated prior to WF fabrication
- Phase distribution upon slow-cooling is complex
- Low release rates during durability experiments

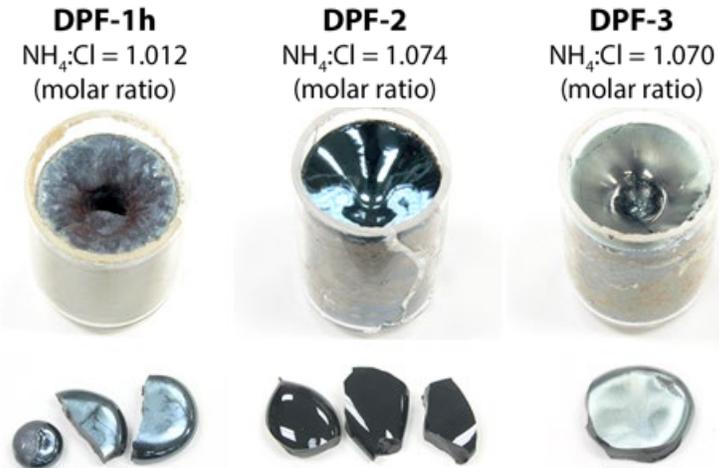


  reactant or intermediate  
   waste stream  
   reusable product  
   waste form option

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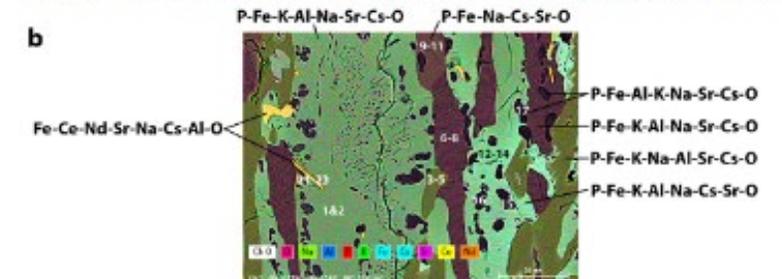
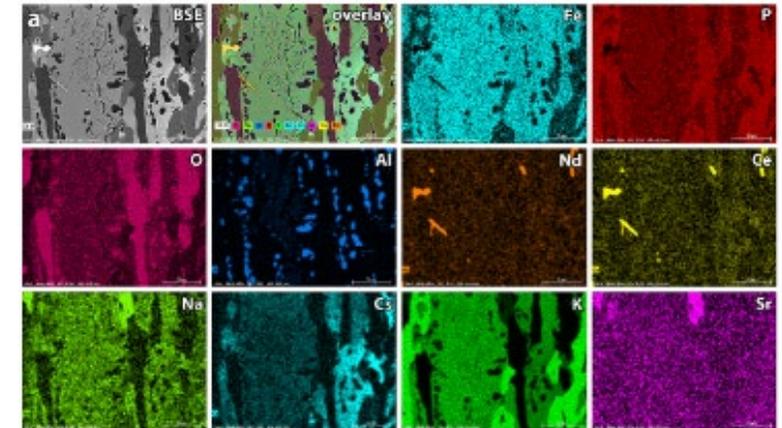
<https://doi.org/10.1016/j.inucmat.2019.151949>

## Quenched DPF WFs



Source: <https://doi.org/10.1016/j.inucmat.2019.151949>

## CCC-cooled sample with ERV2 (Echem salt simulant)

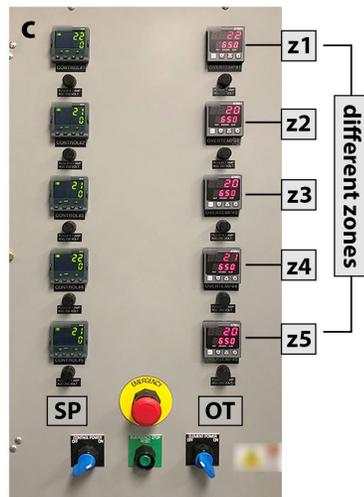
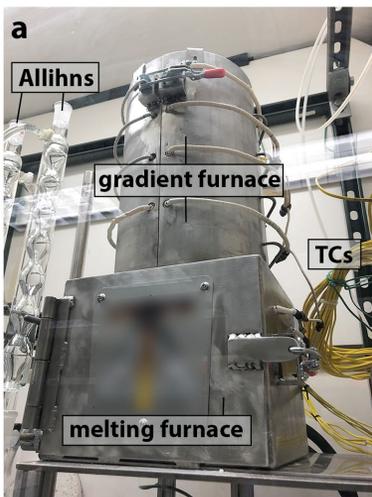
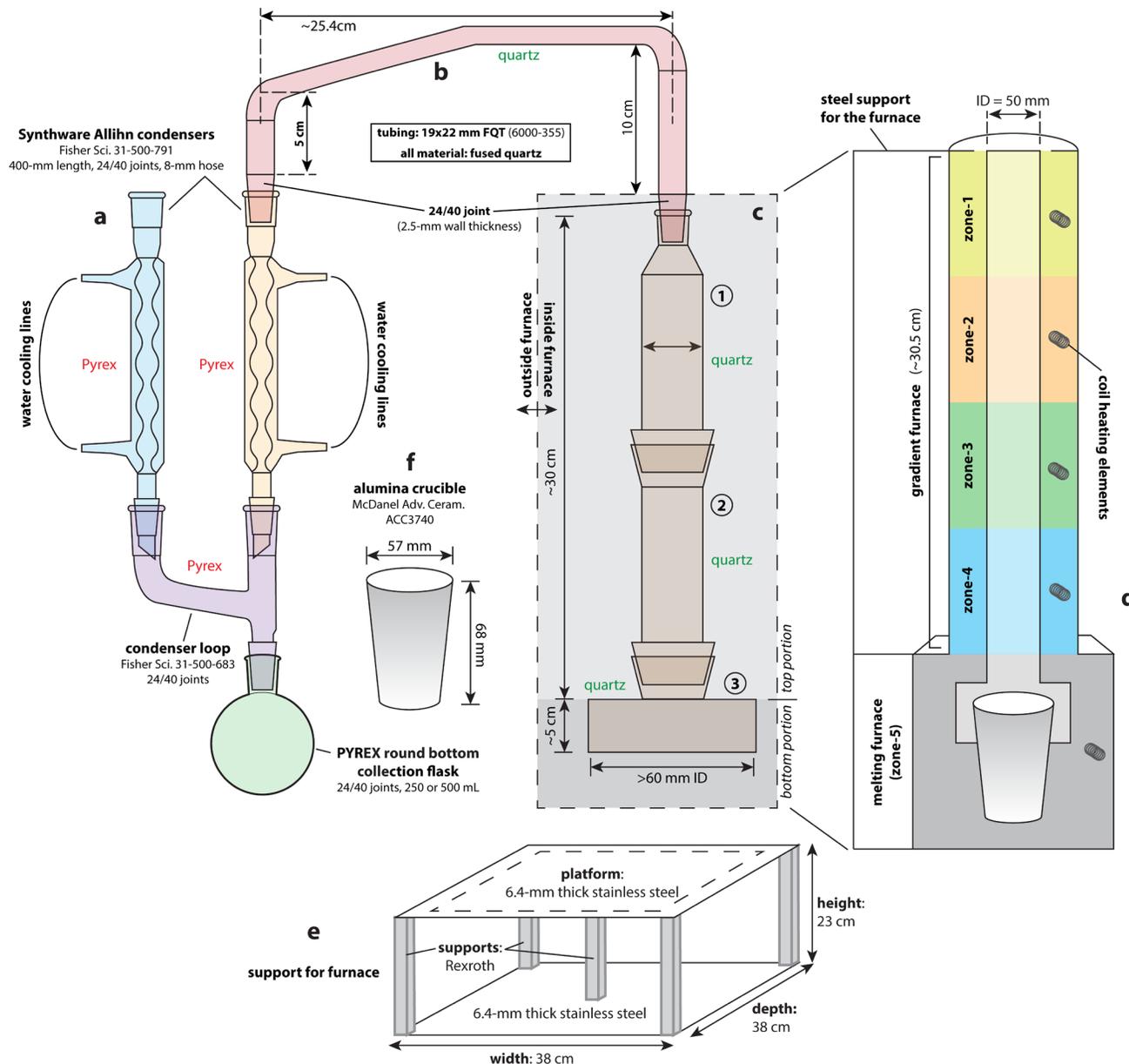


Source: <https://doi.org/10.1016/j.inoncrsol.2021.121319>

# Iron Phosphate Waste Forms (continued)

- Five-zone furnace
- Cl is removed and collected as  $\text{NH}_4\text{Cl}$  in the off-gas system
- It is likely that this process could be used for defluorination of fluoride-salts

## PNNL Dechlorination System



## Ultrastable H-Y Zeolite Process (Dechlorination)

- Developed by Simpson, Bagri, Wasnik (Univ. Utah) and Carlson (UNR)
- Chloride salts are reacted with H-Y zeolite, Cl reacts with H to produce HCl, resulting product is immobilized in glass-bonded waste form
- Reaction times of 120 hours at 625°C estimated to yield 99% dechlorination

USHY zeolite particulates  
(45-90  $\mu\text{m}$ )

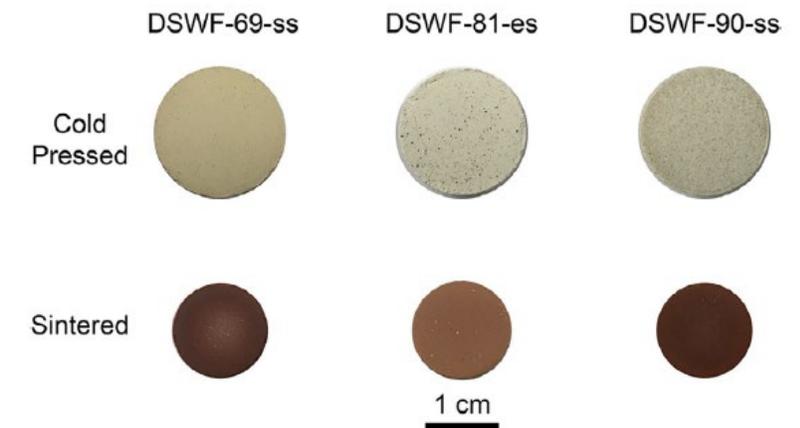


Dehalogenated particles



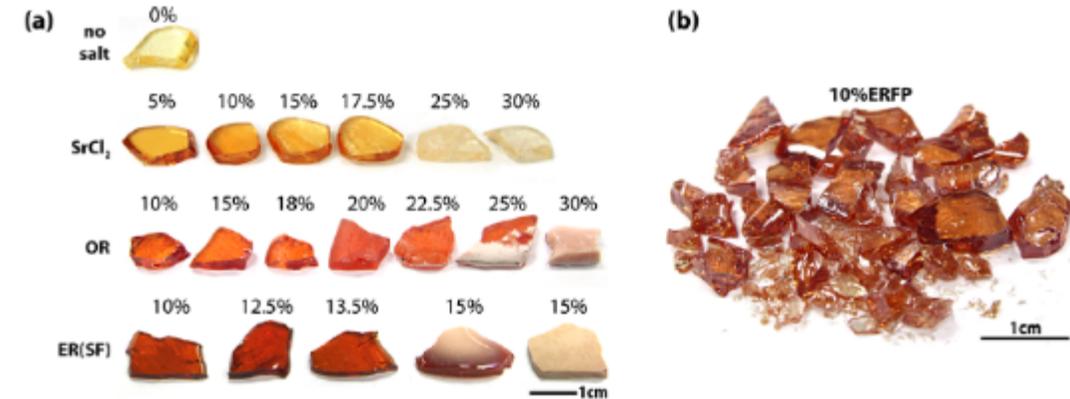
**Figure 5.** Ion-exchanged samples (45–90  $\mu\text{m}$ ) at different times of ion exchange in the increasing order of reaction time from 0 to 6 h.

Fired pellets of products



# Tellurite Glass – A Potential Full Salt Option

- Most of the work at PNNL in this area has revolved around the 78%TeO<sub>2</sub>-22%PbO (mass) glass system for different salt compositions:
  - KCl-LiCl + FPs
  - LiCl-Li<sub>2</sub>O + FPs
  - RECl<sub>3</sub>
  - REOCl
  - SrCl<sub>2</sub>
- High-LiCl glasses show poor durability
- High-RE glasses show good durability
- Glasses are expensive to make (high cost of TeO<sub>2</sub>)



**Figure 4.** (a) Pictures of 78%TeO<sub>2</sub>-22%PbO glasses (mass basis) without salt (0%) and with varying amounts of SrCl<sub>2</sub>, oxide reduction (OR), and electrorefiner [ER(SF)] salt loadings—see ref 20 for more information. (b) Picture of 78%TeO<sub>2</sub>-22%PbO glass loaded with 10 mass% RECl<sub>3</sub> salt—see ref 21 for more information. All percentages listed are in mass%. Reprinted with permission from refs 20 and 21. Copyright 2017 and 2018 Elsevier.

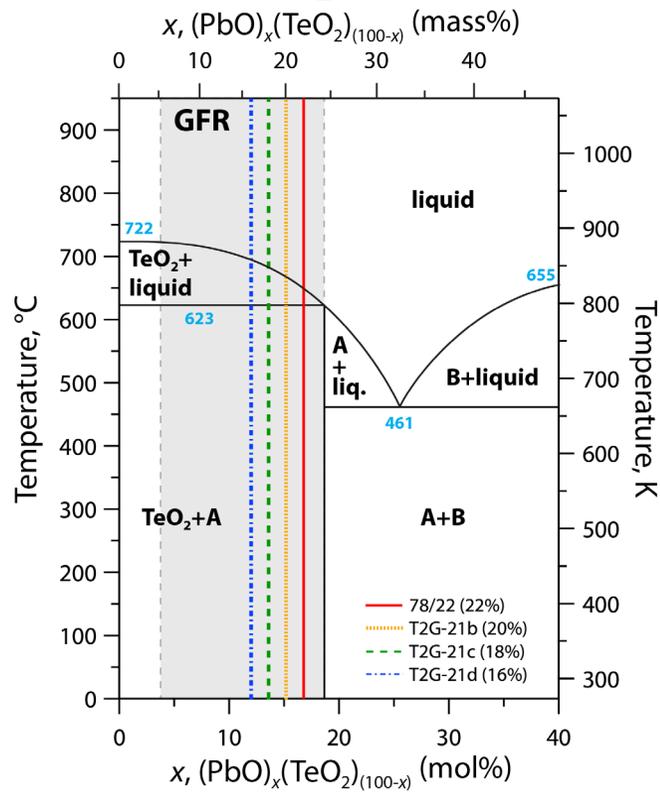
#### Sources:

<http://dx.doi.org/10.1016/j.jnucmat.2017.08.037>

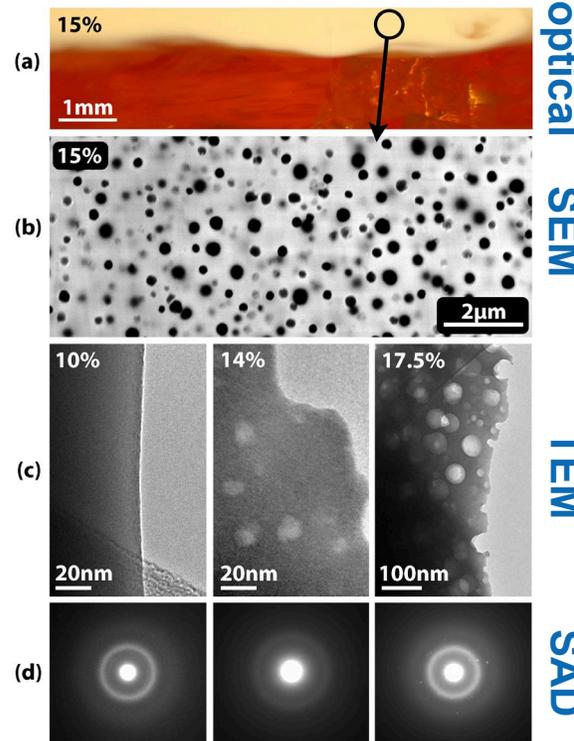
<https://dx.doi.org/10.1021/acs.iecr.0c01357>

# Tellurite Glass – Full Salt Option

Most work done at 78/22 TeO<sub>2</sub>/PbO comp.

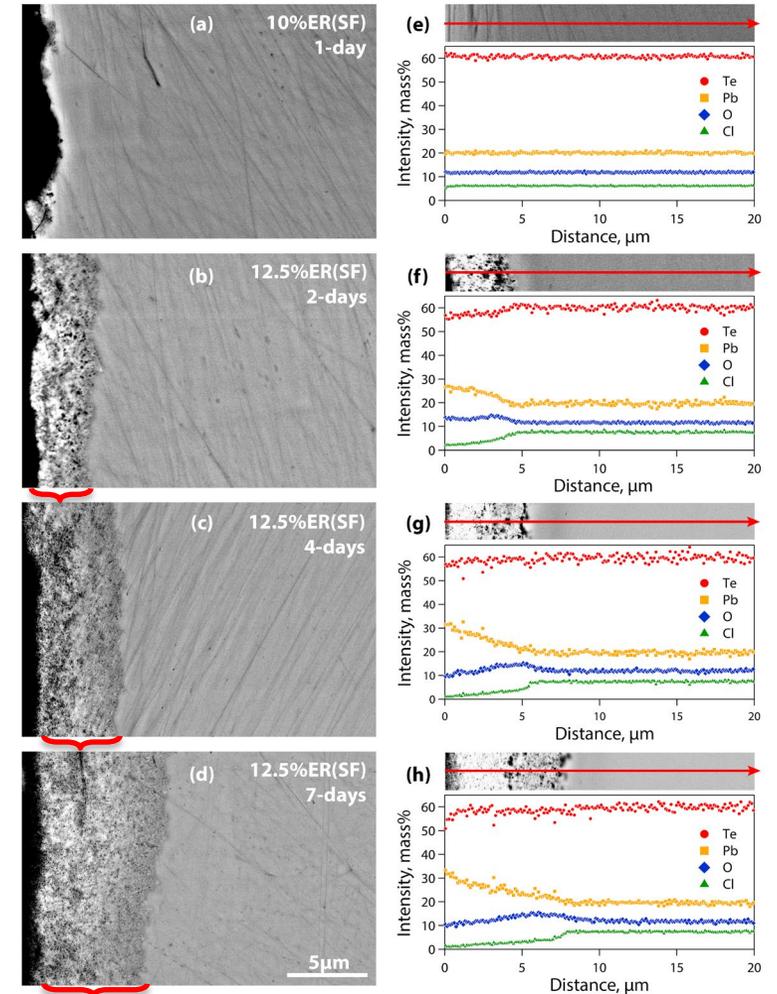


Phase separation at higher salt loadings



optical SEM TEM SAD

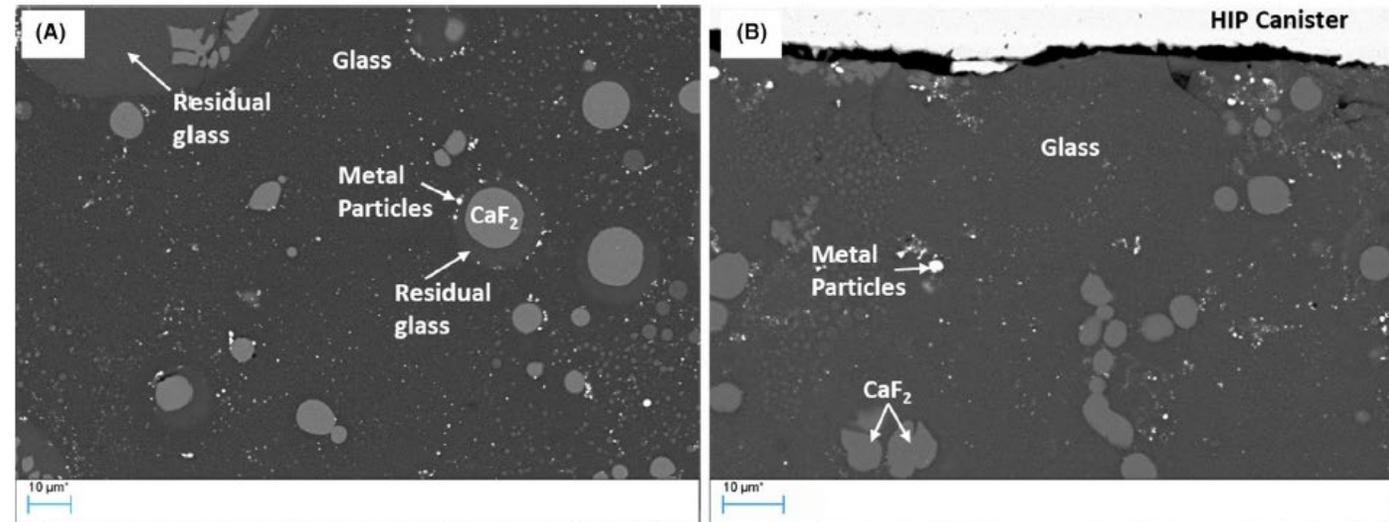
Leached layer increasing with time



## Fluoride Salt Waste Forms – Glass-Bonded $\text{CaF}_2$

- FLiNaK salt mixed with fission product simulant (alkali and alkaline earth nitrates,  $\text{Sb}_2\text{O}_3$ ,  $\text{MoO}_3$ )
- Salt added to  $\text{H}_3\text{BO}_3$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Ca}(\text{OH})_2$ , and colloidal silica
- Mixed/heated to dry at  $110^\circ\text{C}$  and dried powder was calcined at  $600^\circ\text{C}$
- Calcined powder was milled
- This product was cold pressed and sintered or processed with a hot isostatic press (HIP)
- Product has good chemical durability

HIP canister before  
and after heating



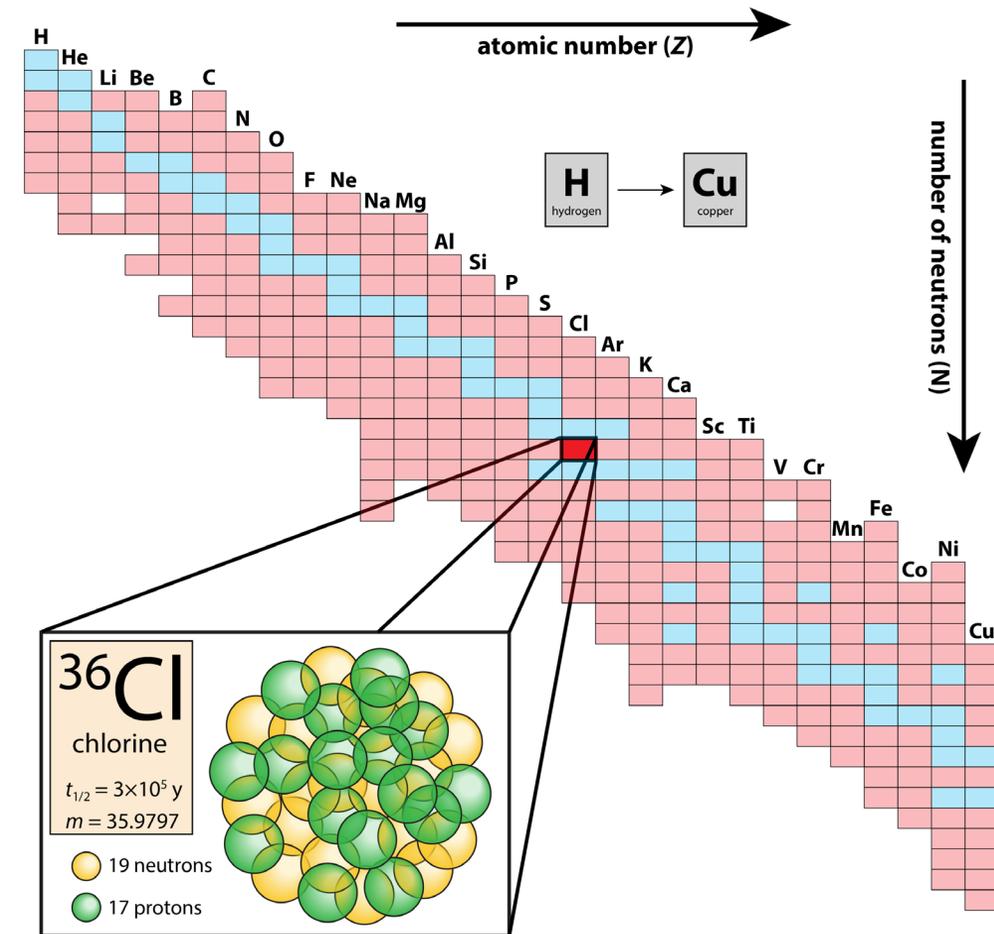
- Most of the F partitions to  $\text{CaF}_2$
- Some is left in the glass phase
- Fluoride loadings up to 7.2 mass% demonstrated
- Full waste loadings of 17-21 mass% achieved

# OTHER CONSIDERATIONS

# Options for <sup>37</sup>Cl Recycle

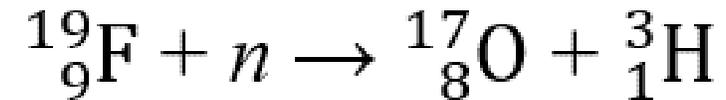
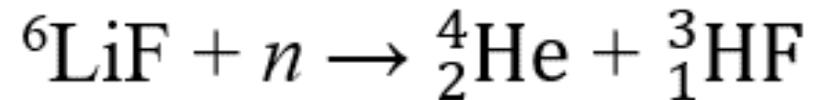
- <sup>37</sup>Cl recycle is important to prevent neutron activation of natural <sup>35</sup>Cl to <sup>36</sup>Cl ( $t_{1/2} = 3 \times 10^5$  years)
- Cl can be removed from Cl-based salts using dechlorination processes
  - Reactions with ammonium phosphates (e.g., ADP, DHP) [**↑NH<sub>4</sub>Cl**]
  - Reactions with H<sub>3</sub>PO<sub>4</sub> [**↑HCl**]
  - Reactions with USHY zeolite [**↑HCl**]

Chart of the nuclides



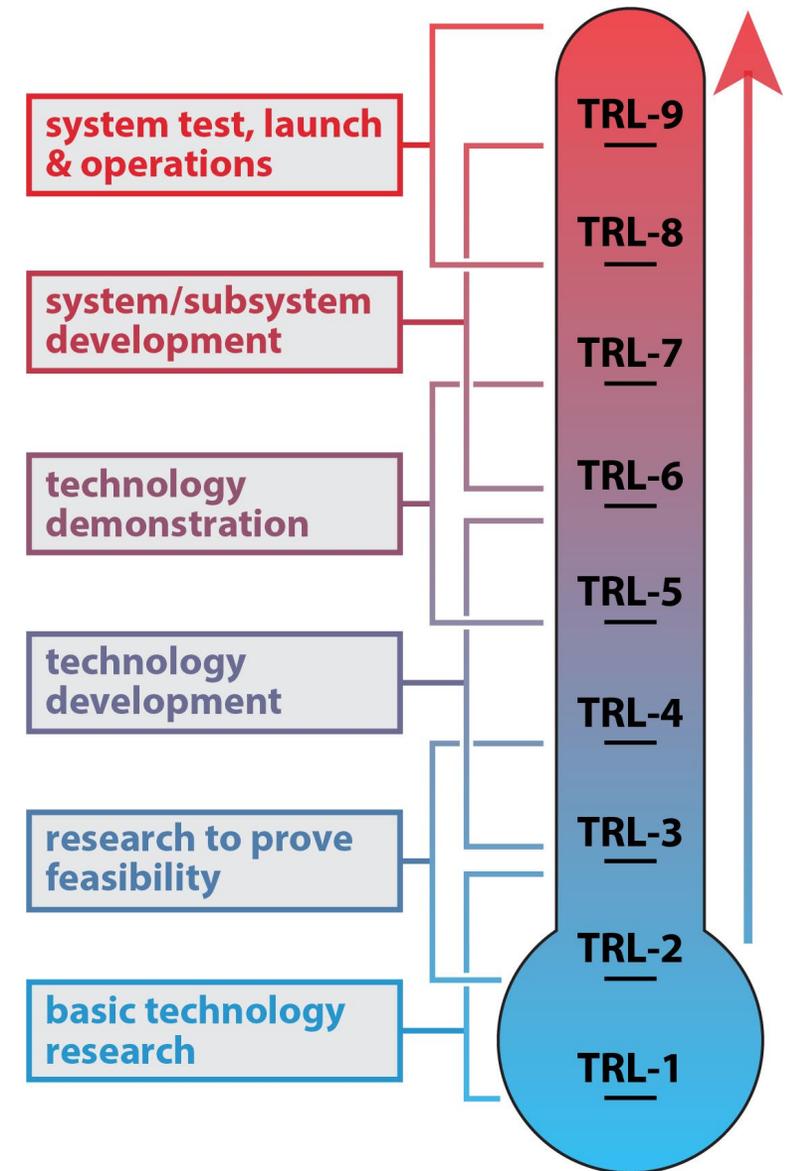
## Minimizing Tritium Production

- Tritium can be produced through activation of  ${}^6\text{Li}$  or  ${}^{19}\text{F}$
- This can be reduced by using  ${}^7\text{Li}$ -enriched salts



# Technology Readiness Levels (TRLs)

- Most waste form technologies have low TRL values
- Most are only conducted at small-scale with nonradiological salt compositions
- More work is needed to further these technologies towards higher TRLs
- Some TRL jumps are extremely expensive



# SUMMARY AND CONCLUSIONS

## Summary and Conclusions

- **High-level takeaway: the waste problem is solvable...**
- **Starting points exist** for technology development in all these topic areas
- **Several waste form options exist** for most waste streams, but most are at low TRLs
- Options demonstrated for Cl-based salts **might work for F-based salts**
- **Some WF and salt treatment options are better than others**  
(e.g., cost, waste loading, storage volume, simple vs multiple process steps)
- **Several opportunities exist** for research in development in each of these areas
- **Potential for component recycle** (e.g.,  $^{37}\text{Cl}$ ,  $^7\text{Li}$ , graphite)

# Upcoming Webinars

Date	Title	Presenter
27 July 2022	A Gas Cherenkov Muon Spectrometer for Nuclear Security Applications	Mr. Junghyun Bae, Purdue University, USA
31 August 2022	China's Multi-purpose SMR—ACP100 Design and Project Progress	Dr. Danrong Song, Nuclear Power Institute of China, China
28 September 2022	Development of In-Service Inspection Rules for Sodium-Cooled Fast Reactors Using the System Based Code Concept	Dr. Shigeru Takaya, JAEA, Japan