

# Hazards Associated with Molten Salt Reactor Systems

Oak Ridge National Laboratory

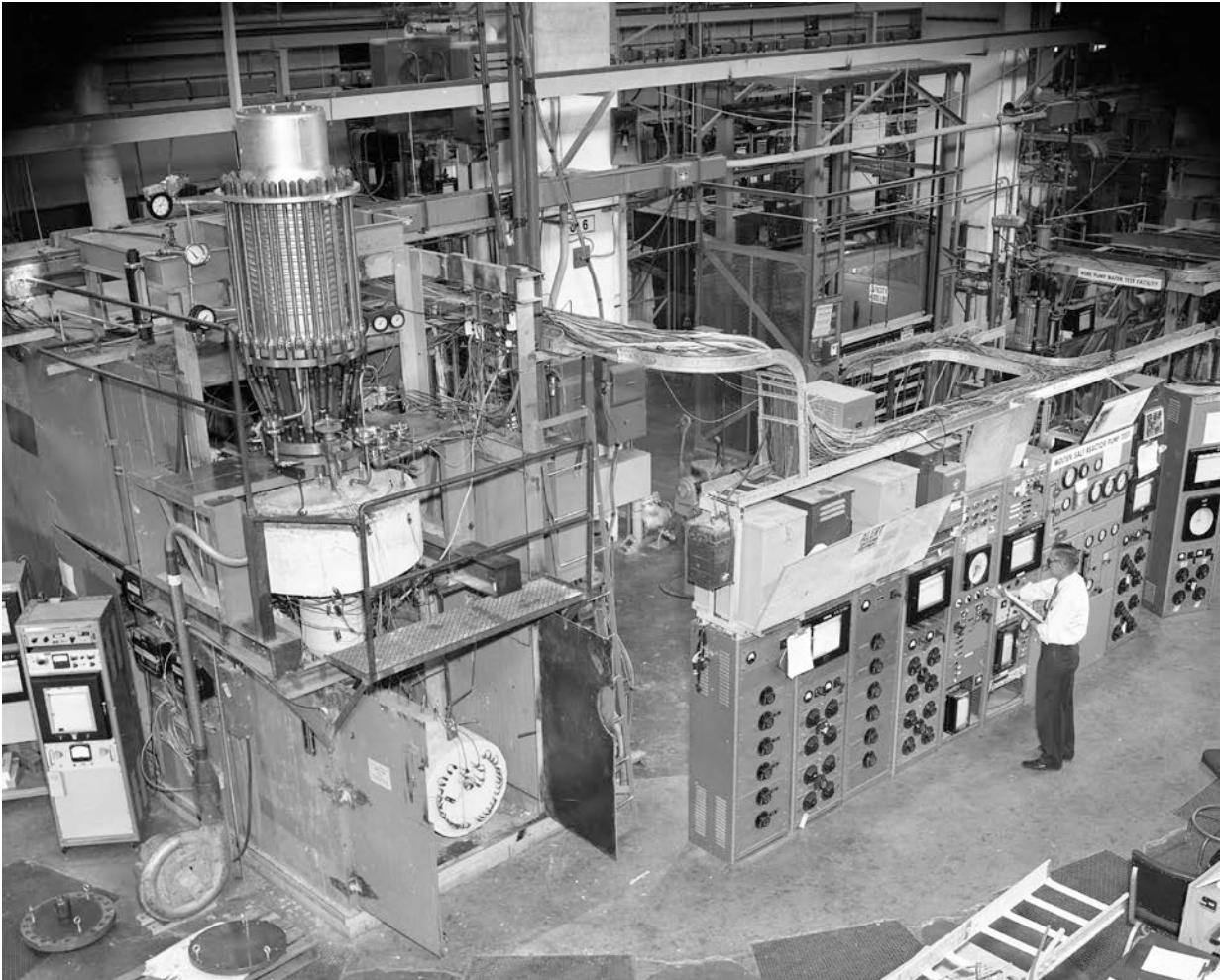
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A molten salt reactor uses a high temperature inorganic salt in the primary circuit for heat transfer.



A liquid-salt fueled reactor carries the fissile material, either flowing or in natural circulation.

**Molten Salt Reactor Experiment, MSRE pump test stand, April 1964**

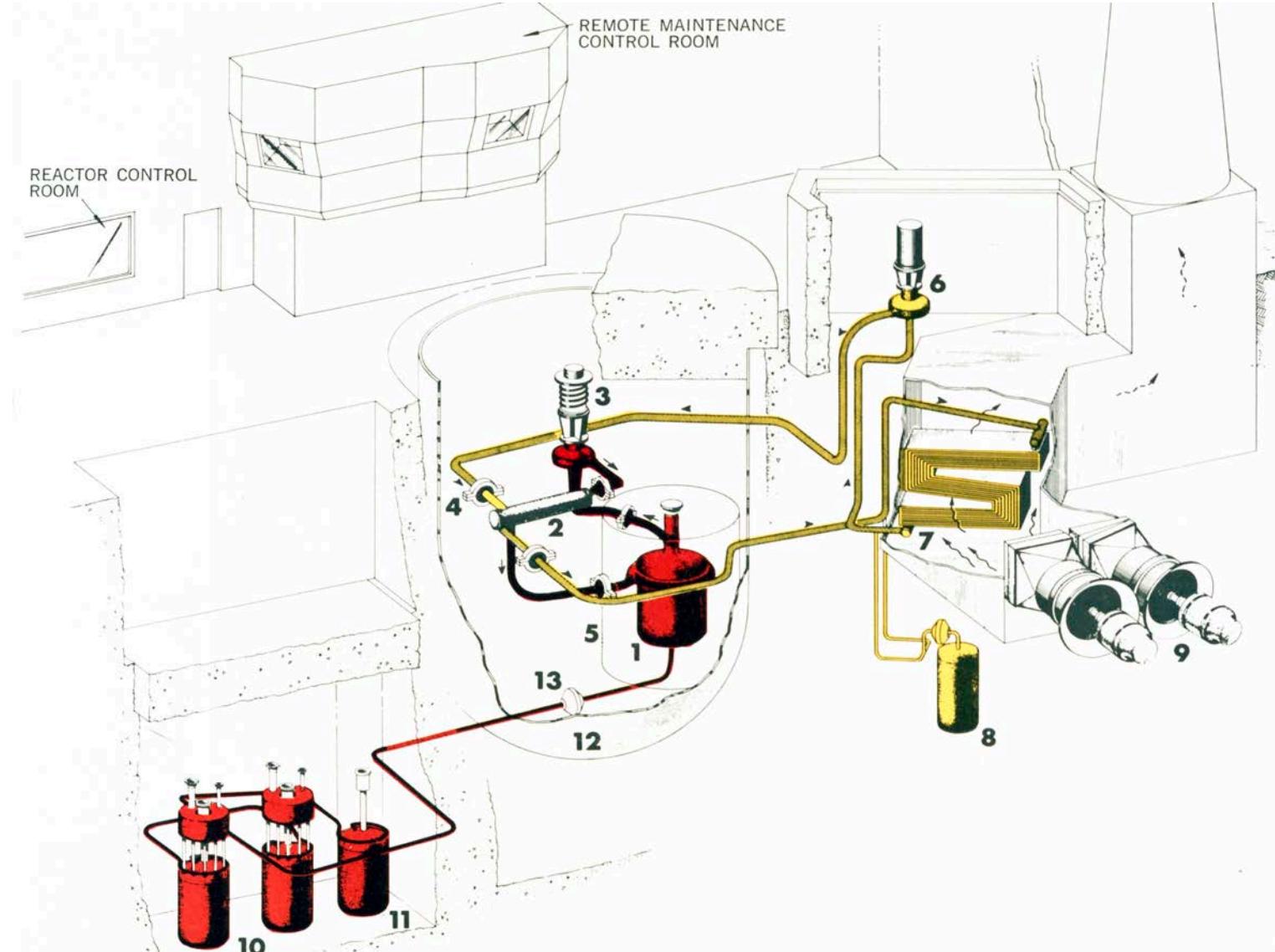
This image is approved for public release, November 5, 2020.

- Fuel-carrying salts are fluorides or chlorides. Other salts can be used as moderators/secondary coolants.
- Reactors operate  $\sim 650^{\circ}\text{C}$ , well above the salt melting point.
- Historic fuel salt operations
  - Aircraft Reactor Experiment
  - Molten Salt Reactor Experiment (MSRE)
  - Stripping of uranium from MSRE fuel and flush salts
  - Salt processing at INL (electrorefining in chloride salt)

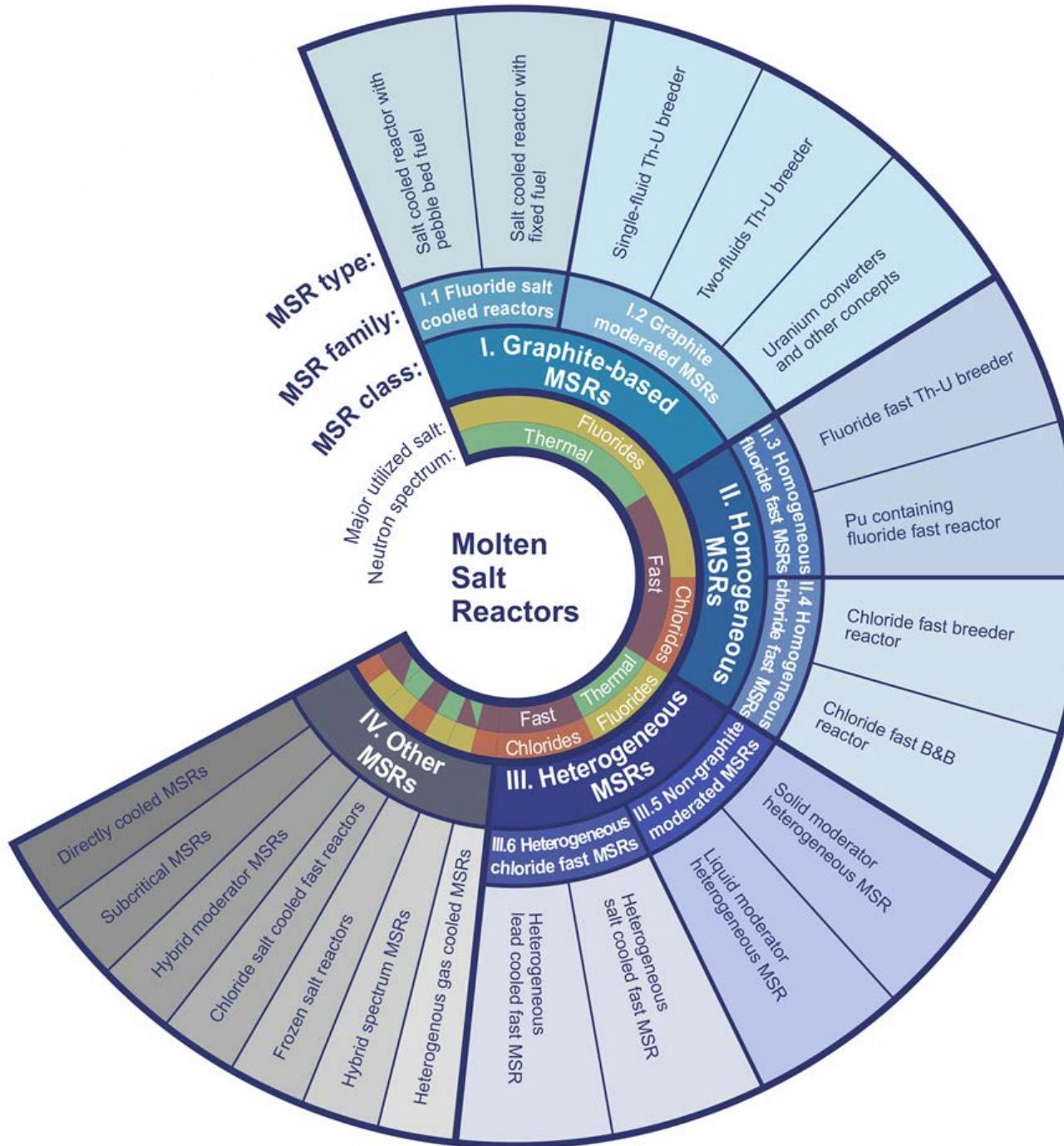


# Primary drawing of the Molten Salt Reactor Experiment plant layout

This drawing (63-1209R) is  
approved for public release.



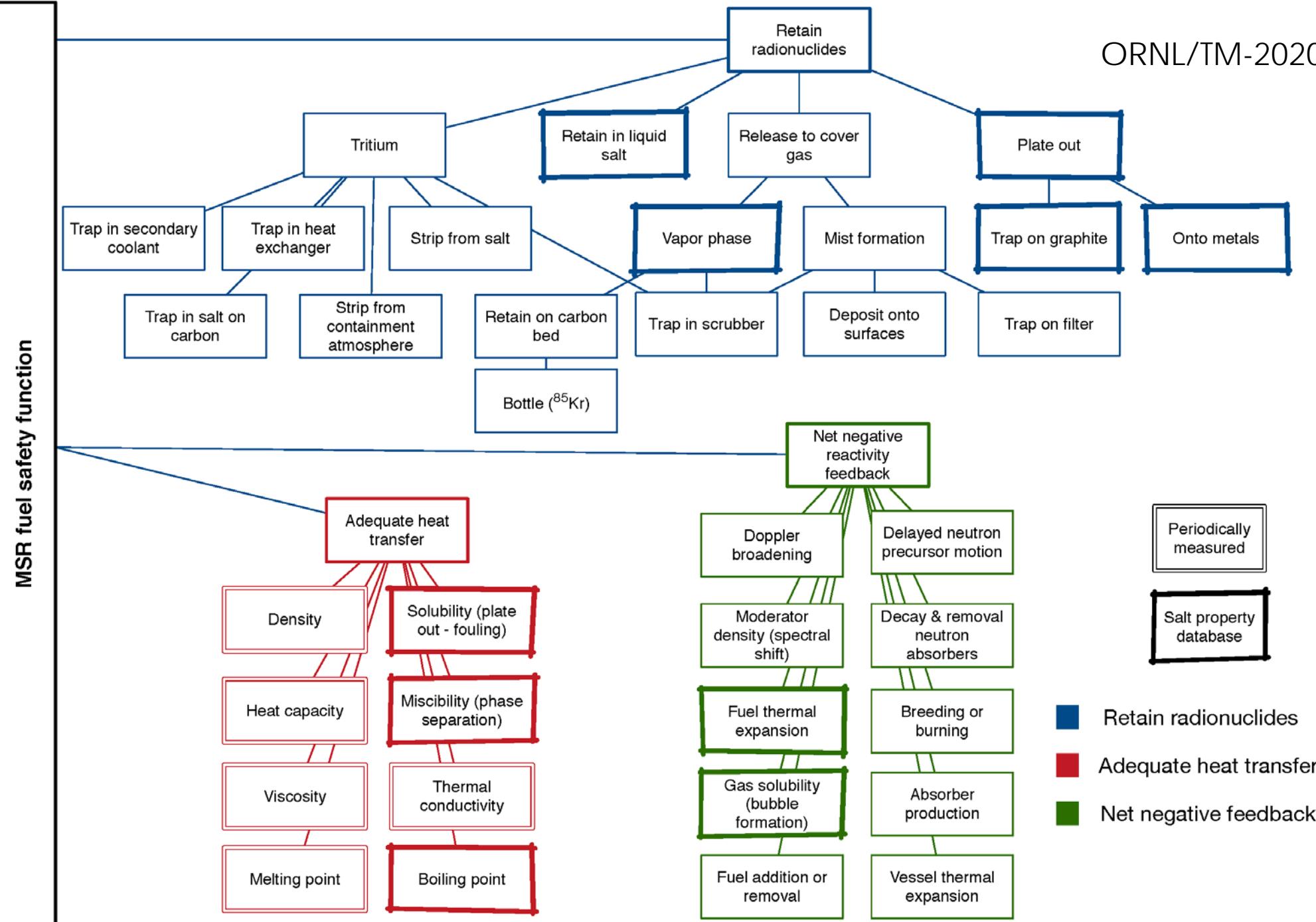
Molten salt reactors come in several varieties.



Source, IAEA, 2021  
Status of Molten  
Salt Reactor  
Technology,  
Tech Rep Series 489

# Safety features of molten salts (WASH-1222)

- Positive:
  - Salt is liquid – so core meltdown not a plausible scenario. Fast spectrum reactors that are not moderated would not become critical outside of the reactor because geometry not appropriate
  - Good solvent for most fission products, including Cs and Sr
  - Not pressurized – operated well below boiling point
  - Salt release or spill will be rapidly cooled and contained on site. Secondary criticality not an issue as spill would not be moderated
  - Activation of salt itself is minimal
  - Negative reactivity coefficient
  - As salt needs to be isolated from water/humidity, H<sub>2</sub> no release
  - Radiotoxicity of off-gas decreases rapidly
- Negative:
  - Salts are chemically reactive
  - Online maintenance, processing & refueling considerations: radioactive contamination, chemical hazards
  - Secondary containment and removal of decay heat for cover gas, decay tank systems
  - Chloride and fluoride salts not suitable waste forms
  - Tritium in some designs



# Review of Hazards Associated with Molten Salt Reactor Fuel Processing and Waste Operations

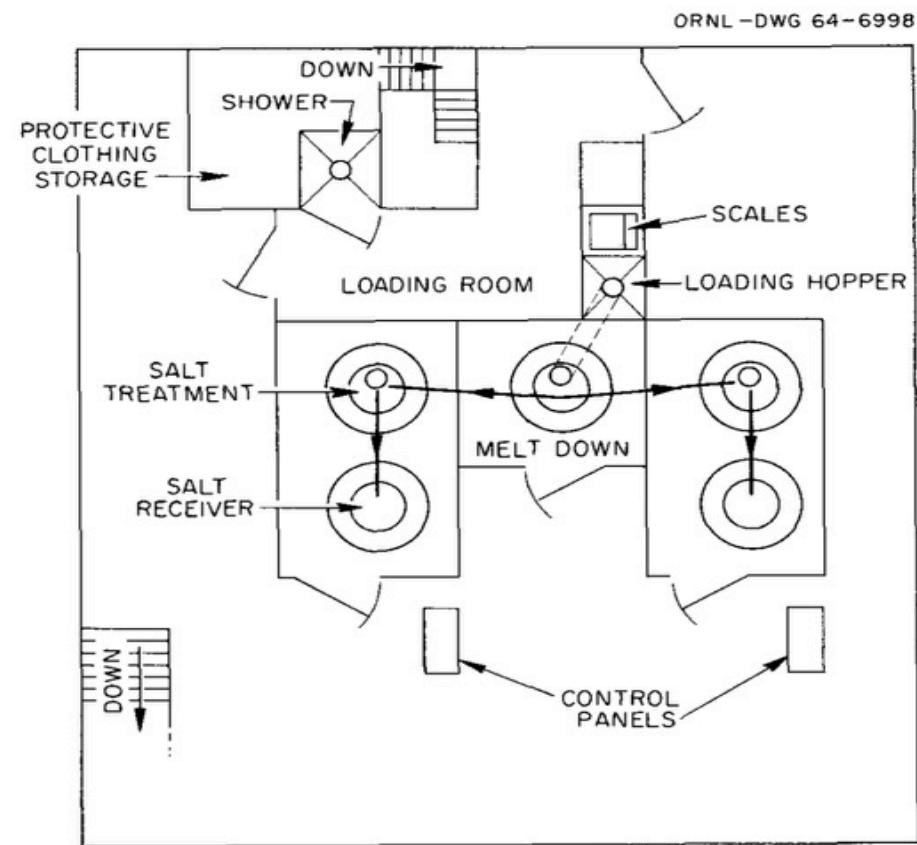
- Available on [www.osti.gov](http://www.osti.gov)
- McFarlane et al., "Review of Hazards Associated with Molten Salt Reactor Fuel Processing", ORNL/TM-2019/1195
- Riley et al. "Molten salt reactor waste and effluent management strategies: A review", Nuclear Engineering and Design 345, 94-109, 2019
- US AEC, "An evaluation of the molten salt breeder reactor", WASH-1222, 1972
- Holcomb et al., "MSR Fuel Salt Qualification", ORNL/TM-2020/1576
- National Research Council, "Evaluation of the US Department of Energy's Alternatives for the Removal and Disposition of Molten Salt Reactor Fluoride Salts", National Academy Press 1997

# Non-reactor site fuel salt processes and hazards

- Unirradiated materials
  - Salt component synthesis
  - Synthesis of MSR fuel salt
  - Packaging and transportation of enriched  $\text{UF}_6$  and  $\text{UF}_4$
- Irradiated materials
  - Waste form preparation

# Fluoride salt purification is based on MSRE process

1. Heat powder to 300°C to remove moisture
2. Melt salt, heating to 600°C under argon
3. H<sub>2</sub>/HF sparge removes oxygen/water
  - Oxide removal
  - O<sup>2-</sup> + 2 HF → 2 F<sup>-</sup> + H<sub>2</sub>O
  - OH<sup>-</sup> + HF → F<sup>-</sup> + H<sub>2</sub>O
4. H<sub>2</sub> sparge to remove metallic fluoride impurities
  - MF<sub>2</sub> + H<sub>2</sub> → M + HF
5. Argon sweep while cooling



Fluoride salt processing facility is located in reactor building

# Excerpt from ORNL/TM-2019/1195 :

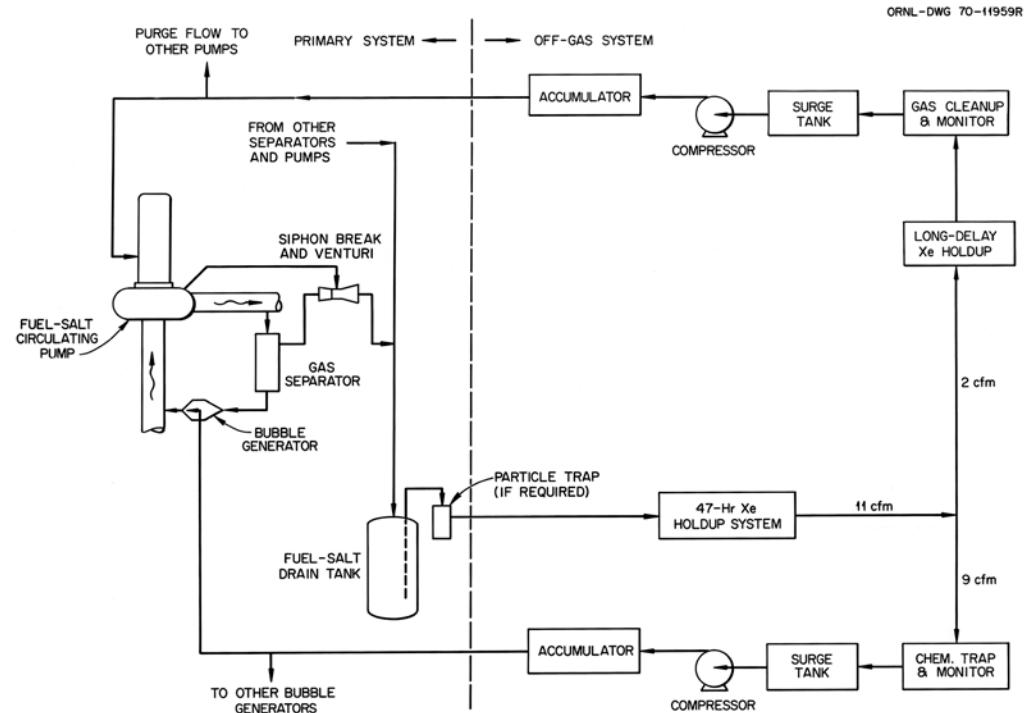
Off-site nuclear fuel preparation and handling			
Physical or chemical process	Salt type and process objective	Key hazards	Mitigation strategies
<ul style="list-style-type: none"><li>• Salt purification</li><li>• Hydrofluorination</li></ul>	Removal of oxides/hydroxides from fluoride salts	<ul style="list-style-type: none"><li>• <math>\text{H}_2/\text{HF}</math></li><li>• Be if present as the <math>\text{BeF}_2</math> salt component</li><li>• Heat (650°C)</li><li>• Contamination if actinides present</li></ul>	Standard contamination control for unirradiated materials
<ul style="list-style-type: none"><li>• Salt purification</li><li>• Chlorination</li></ul>	Removal of oxides/hydroxides from chloride salts	<ul style="list-style-type: none"><li>• <math>\text{CCl}_4</math>, <math>\text{Cl}_2</math>, <math>\text{COCl}_2</math>, <math>\text{HCl}</math></li><li>• Heat</li><li>• Contamination if actinides present</li></ul>	Standard contamination control for unirradiated materials
<ul style="list-style-type: none"><li>• Packaging and transportation</li></ul>	Actinides and non-fissile components	<ul style="list-style-type: none"><li>• Contamination if actinides present</li><li>• Air-sensitive</li><li>• Be (if present as <math>\text{BeF}_2</math>)</li></ul>	Double barrier container

# Reactor site fuel processes and hazards

- Liquid salt operations
- Fuel loading
- Fuel sampling
- Off-gas system
- Insoluble fission product filtering
- Soluble fission product separation
- Waste storage before disposal

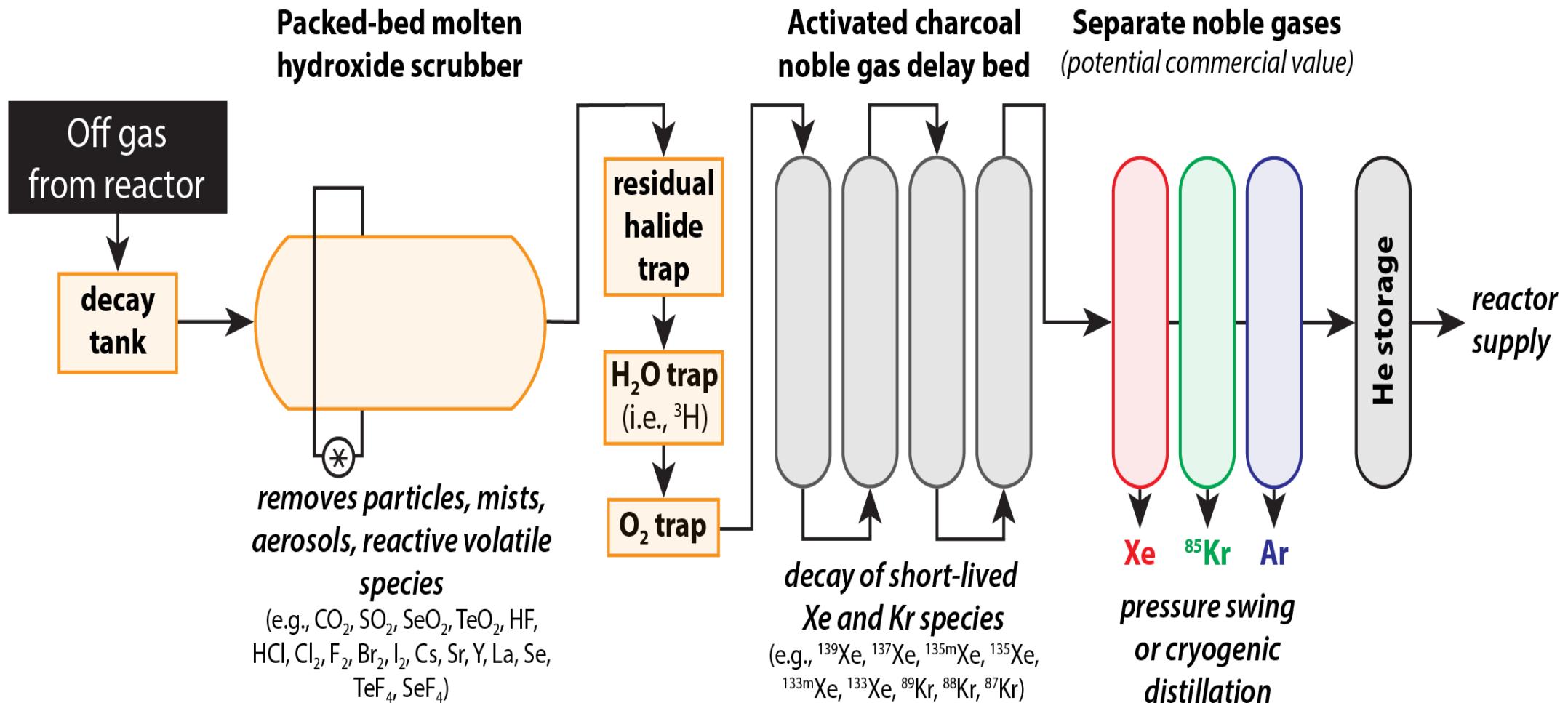
# The “pressure” boundary for fuel-salt reactors is the primary coolant system.

- Off-gas integral part of primary coolant system
  - Prevents pressurization of fuel salt circuit
  - Contain radioactive materials that escape salt
  - Strips airborne materials
  - Removes decay heat
  - Location for monitoring salt chemistry
  - Tritium removal
- Off-gas may be shared with fuel processing facility



Schematic of off-gas, MSBR.  
ORNL drawing 70-11959.  
Approved for public release.

# Cover-gas system is design specific

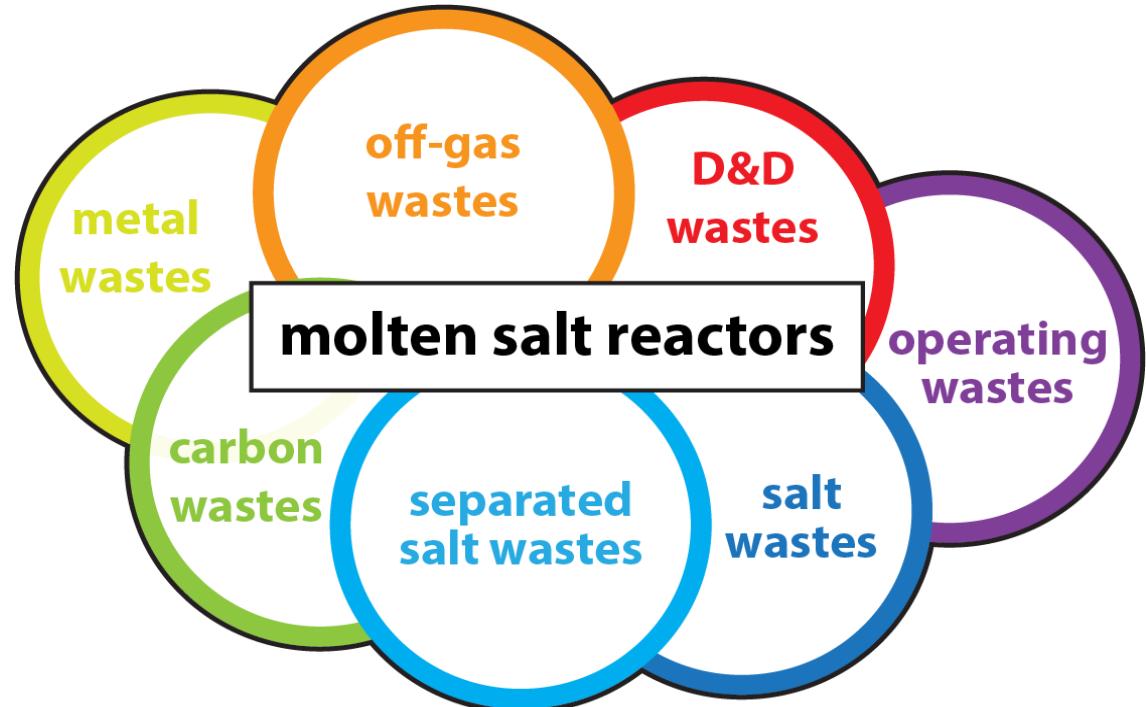


# Excerpt from ORNL/TM-2019/1195 :

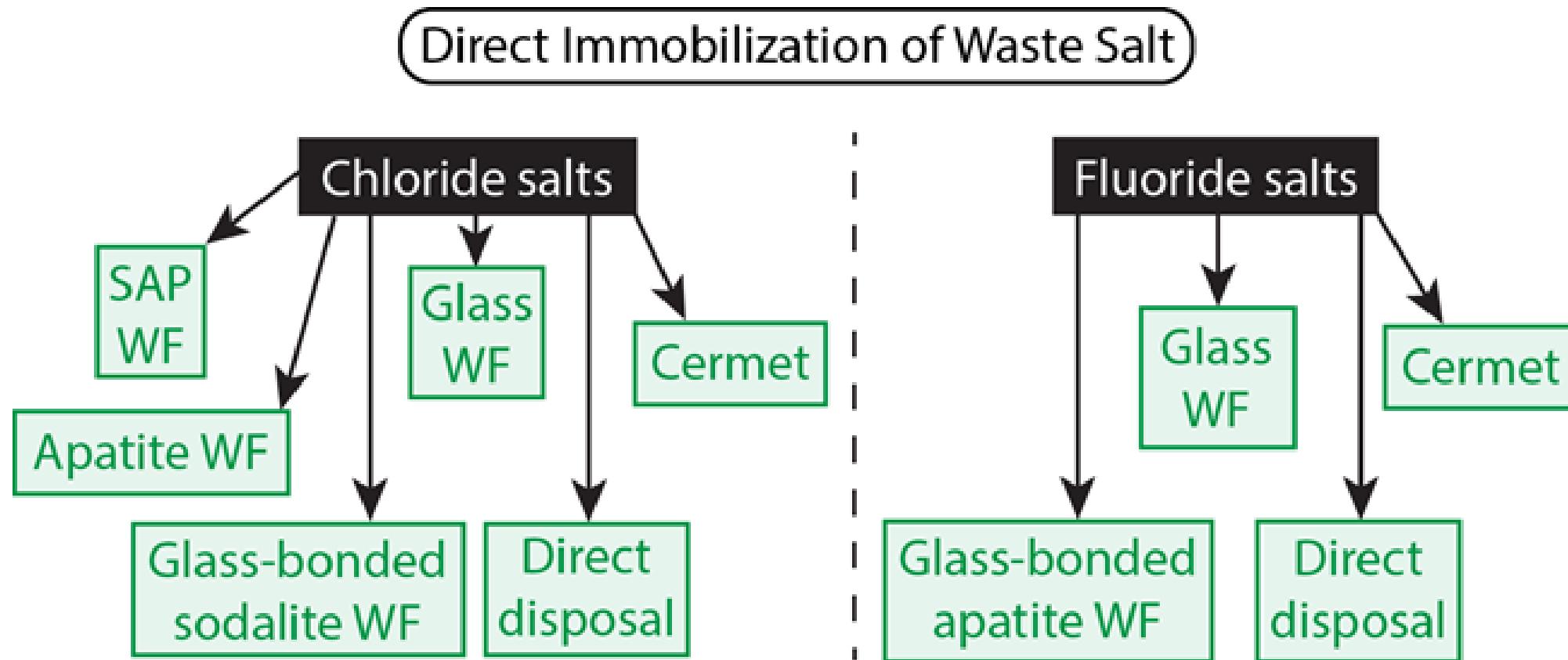
On-site fuel processing hazards during power operations			
Physical or chemical process	Salt type and process objective	Key hazards	Mitigation strategies
Online sampling of fuel salt during operation	Fluorides, chlorides to give salt composition	<ul style="list-style-type: none"> <li>• Very high radiation</li> <li>• Very high contamination (leakage of volatile FP, actinides in salt &amp; entrained aerosols)</li> <li>• Heat</li> <li>• Air sensitive</li> <li>• Be (if present as <math>\text{BeF}_2</math>)</li> </ul>	<ul style="list-style-type: none"> <li>• Remote handling</li> <li>• Inert gas flush</li> <li>• Double barrier containment</li> </ul>
Online sampling of fuel salt when loading salt during operation	Fluorides, chlorides to give salt composition	<ul style="list-style-type: none"> <li>• Flow restrictions/ pressure due to plate-out/freezing</li> <li>• Very high radiation</li> <li>• Very high contamination (leakage of volatile FP, actinides in salt &amp; entrained aerosols)</li> <li>• Criticality</li> <li>• Heat</li> <li>• Air sensitive</li> <li>• Be (if present as <math>\text{BeF}_2</math>)</li> </ul>	<ul style="list-style-type: none"> <li>• Remote handling</li> <li>• Rapid measurements (pressure, temperature, salt density)</li> <li>• Purge gas pressure relief</li> <li>• Secondary containment</li> </ul>

# Multiple waste streams from an MSR

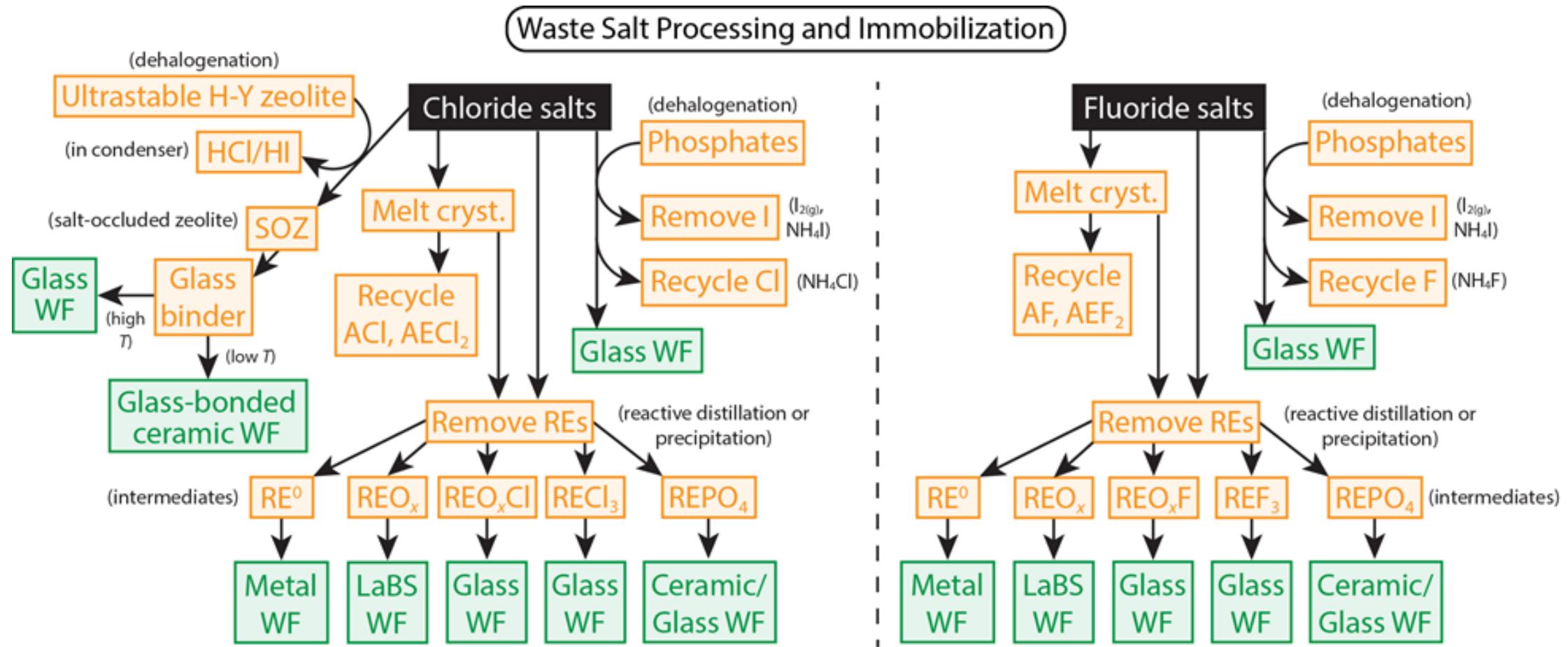
- Trapped in cover gas
- Tritium
- Metals (core components)
- Graphite
- Salts – from core, salt preparation
- Operating wastes (spent filters)
- Decommissioning and Decontamination



# Minimal processing options for salt waste



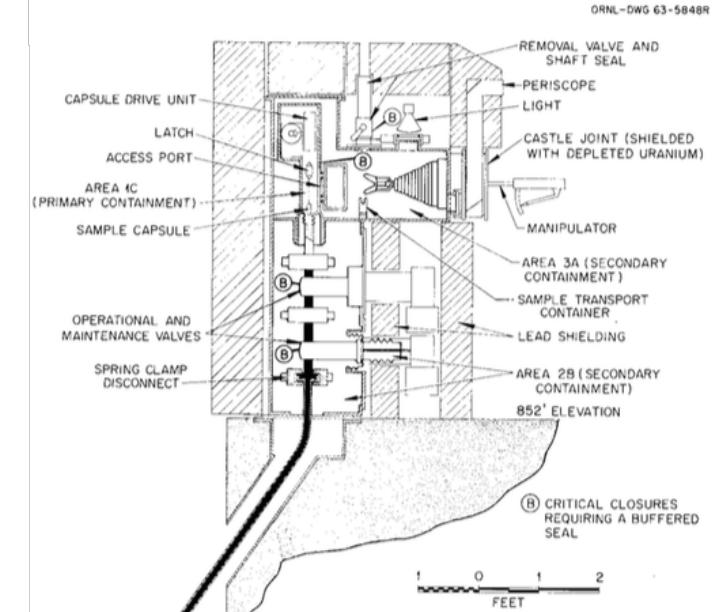
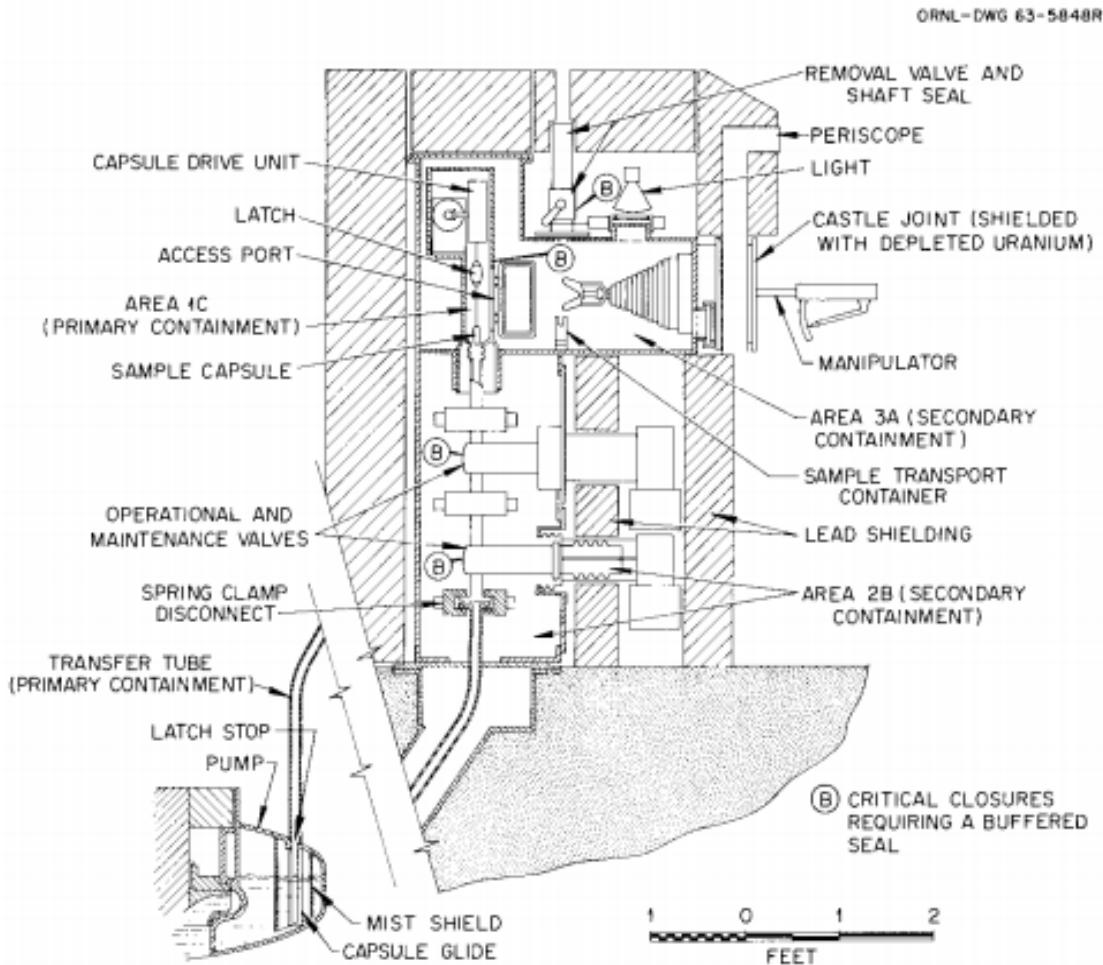
# Processing of salt waste is being evaluated.



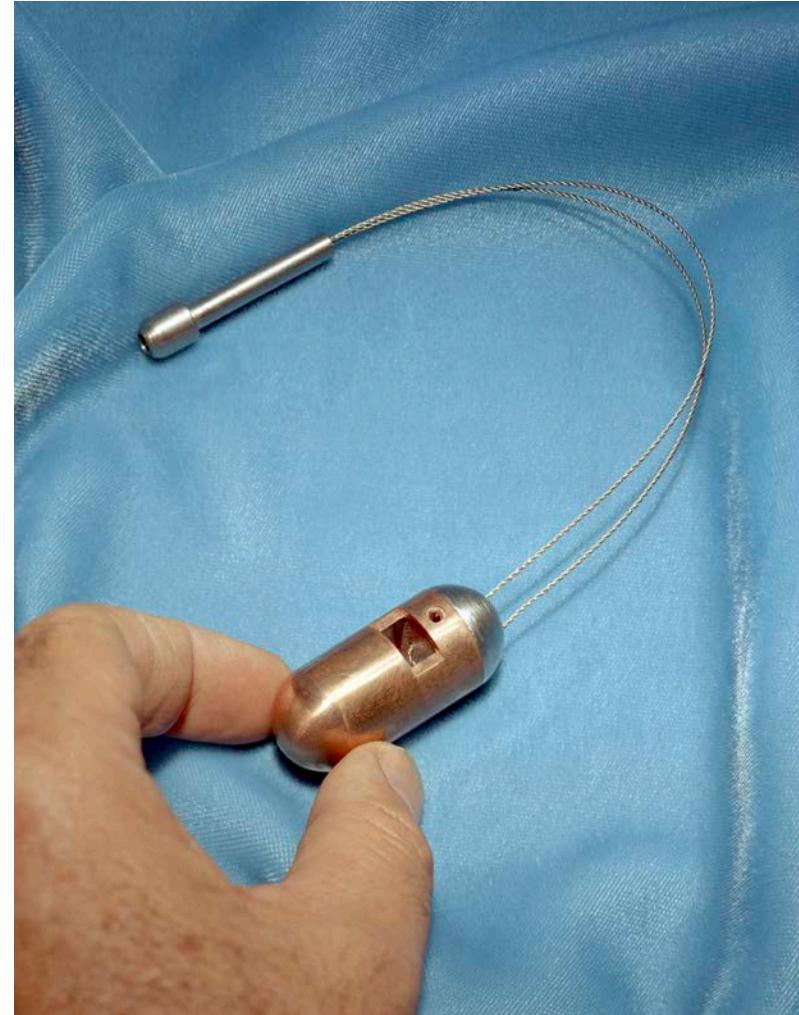
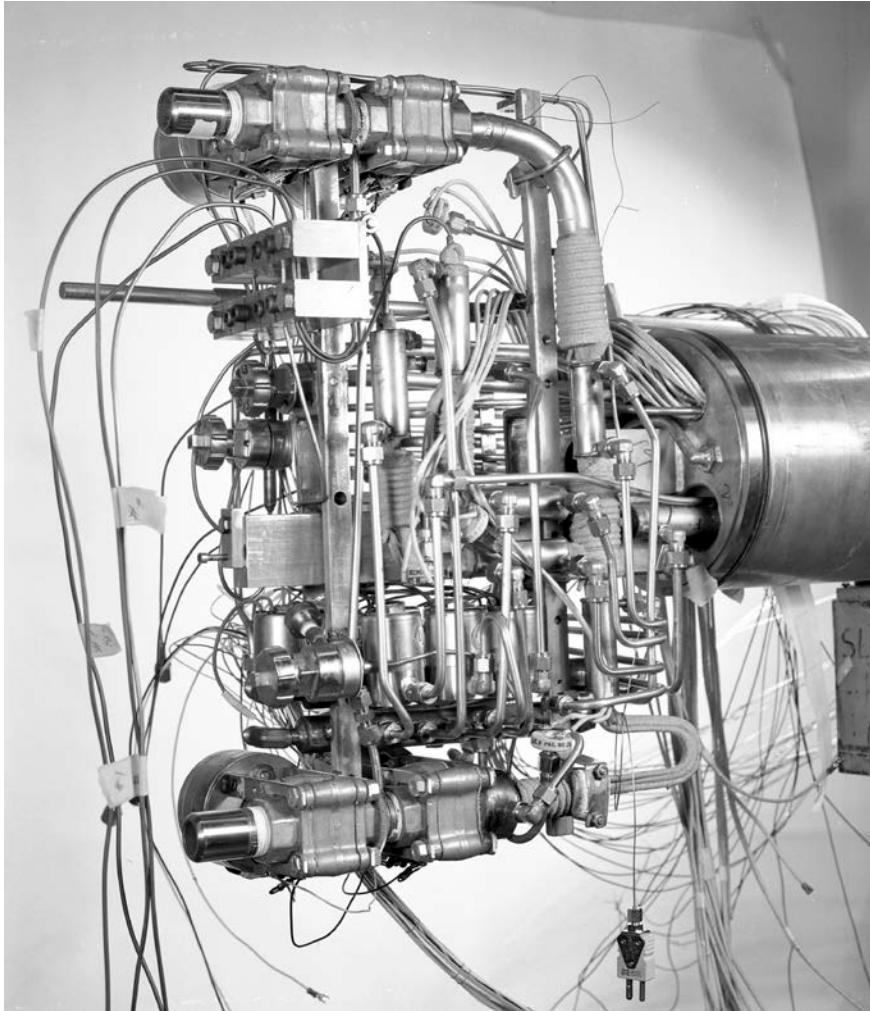
# Mitigation Strategies – Sampling during operation

- Salt samples allow us to track the chemical redox state of the salt
- Apply measures to stabilize chemistry
- Check for corrosion issues
- Monitor performance of system components

# MSRE sampler enricher



Salt samples were taken during operation and analyzed in a nearby laboratory.

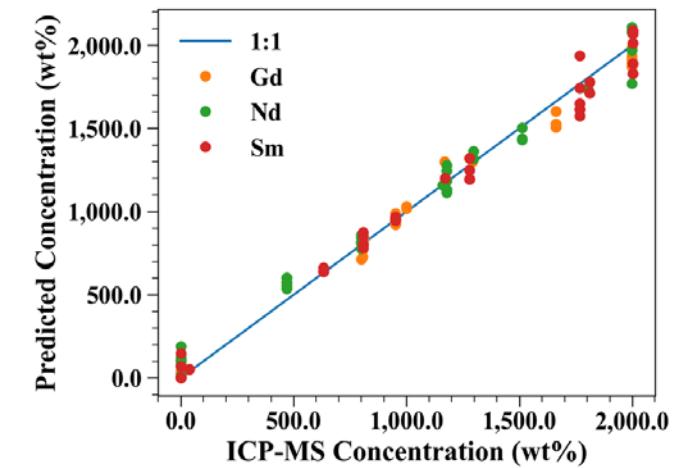
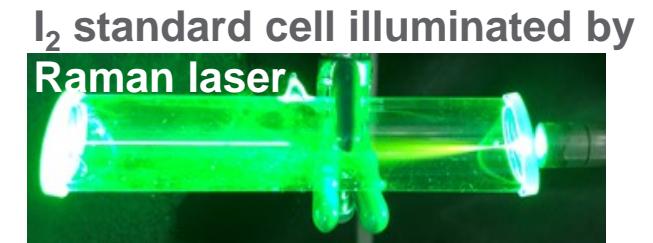


These pictures have been approved for public release, ORNL 73908, 92129 respectively

Review of Hazards Associated with Molten Salt Reactor Fuel Processing Operations

# Fuel cycle hazards can be mitigated by processing monitoring and control.

- On-line off-gas monitoring provides allows for efficient and informed operation of off-gas treatment systems
  - Gamma spectrometry (radionuclides), molecular (Raman/IR/UV Visible) and elemental spectroscopies (LIBS) for gas composition
  - Temperature, pressure drop, flow rates
- On-line salt monitoring allows for real-time process control and performance verification
  - Reactor power, temperature, salt physical characteristics
  - Electrochemistry (redox state) – signals need for online salt processing (e.g., Pa removal)
  - Entrained particulates, corrosion products
- Advanced data analysis: Chemometrics, Data Fusion, Genetic Algorithms



# Other design strategies for safe operation

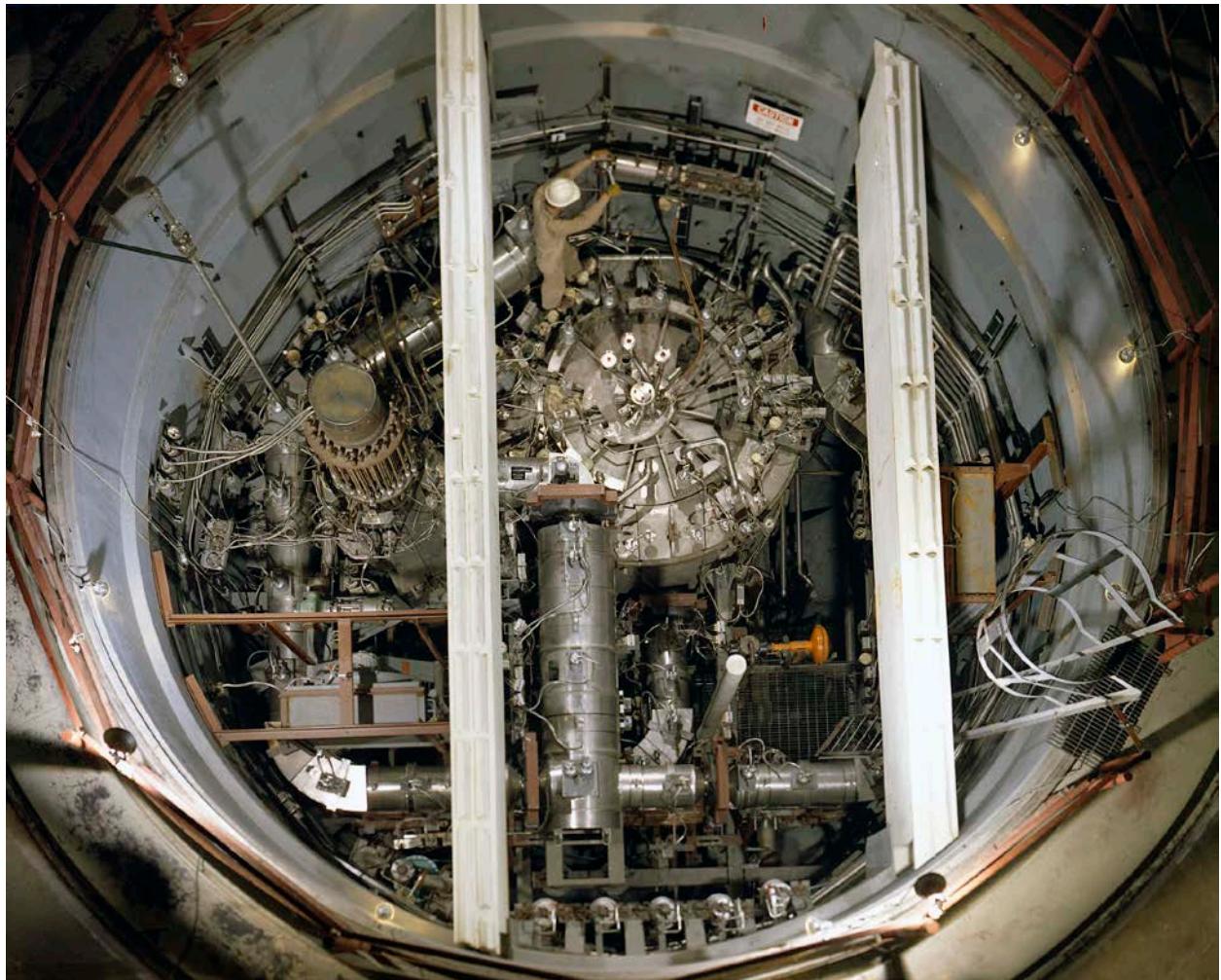
- Accounting for fuel and burnup during operation (radionuclide tracking)
- Cover gas
  - Secondary containment
  - Purify cover gas to remove  $\text{H}_2\text{O}$ ,  $\text{O}_2$
- Drain tank if the salt needs to be removed salt from core (heated with circulating cover gas, passive heat removal)
- Physical barriers:
  - Encase core in stainless steel vessel (inert atmosphere) that also has heat removal
  - Envelope fuel salt pins in coolant salt
- Plan for waste handling and disposal up front

# Summary—Wide range of hazards

- Hazards depend on fuel salt type, processing operation, fissile material concentration, radiation level, and other toxic or hazardous materials
- Differences from solid-fueled reactors:
  - Refueling and adjustment of fuel salt chemistry online
  - Fuel processing closely coupled with reactor operations
  - Off-gas important for fission product confinement during normal operations
  - Spent salt needs to be processed before disposal unless using direct disposal into stable salt formation

# Limitations of assessment

- MSR designs for the reactors and support systems are not fully mature, so only an overview of hazards can be provided based on the likely salt processing steps
- Limited experience with MSRs, especially chloride-based systems; however, can extrapolate from larger non-nuclear halide salt use
- Radiolytic effects need more study



MSRE in containment cell. Photo 67501.  
Authorized for public release

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