Module 3: Overview of Fuel and Coolant Salt Chemistry and Thermal Hydraulics

Presentation on Molten Salt Reactor Technology by:
David Holcomb, Ph.D.
Advanced Reactor Systems and Safety Group
Reactor and Nuclear Systems Division

Presentation for:
US Nuclear Regulatory Commission Staff
Washington, DC

Date:
November 7–8, 2017
What are “Molten Salts”? 

- Salts are ionic compounds formed from a combination of electronegative and electropositive elements
  - At elevated temperatures salts liquefy and are termed “molten salts”

- Halide salts are ionic compounds formed from the combination of a halogen (electronegative) and another electropositive element – commonly, but not exclusively, alkali metals or alkaline earths
  - Examples: LiF, BeF\(_2\), MgCl\(_2\), NaCl (aka table salt), ZrF\(_4\), RbF, UF\(_4\), UC\(_3\)

(left) Solid “Frozen” and (right) Liquid “Molten” 2LiF-BeF\(_2\) salt
Molten Halide Salts Have Attractive Heat Transfer Properties

<table>
<thead>
<tr>
<th>Coolant (Reactor Concept)</th>
<th>High Working Temperature(^a)</th>
<th>High Volumetric Heat Capacity(^b)</th>
<th>Low Primary Pressure(^c)</th>
<th>Low Reactivity with Air &amp; Water(^d)</th>
<th>Coolant &amp; Materials Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (PWR)</td>
<td>😞</td>
<td>☺</td>
<td>😞</td>
<td>☺</td>
<td>☺</td>
</tr>
<tr>
<td>Sodium (SFR)</td>
<td>😞</td>
<td>😞</td>
<td>☺</td>
<td>😞</td>
<td>☞</td>
</tr>
<tr>
<td>Helium (GCR)</td>
<td>☺</td>
<td>😞</td>
<td>😞</td>
<td>☺</td>
<td>☞</td>
</tr>
<tr>
<td>Salt (FHR/MSR)</td>
<td>☺</td>
<td>☺</td>
<td>☺</td>
<td>☺</td>
<td>😞</td>
</tr>
</tbody>
</table>

\(^a\) High system working temperature desirable for high efficiency power conversion and process heat applications

\(^b\) High coolant volumetric heat capacity enables ~constant temperature heat addition / removal (\(\eta_C = 1 - T_C/T_H\) ~ Carnot cycles), compact system architectures, and reduces pumping power requirements

\(^c\) Low primary system pressure reduces cost of primary vessel and piping and reduces energetics of pipe break accidents

\(^d\) Low reactivity with air and water reduces energetics of pipe break accidents
Molten Salts Are Attractive Coolants for Very High Temperatures

Compared to 20°C water

Fluorides:
- ~ 2X density
- ~ 1/2X heat capacity
- ~ 1–5X viscosity
- ~ 2X thermal conductivity
- ~ 1X coefficient of expansion as a liquid
- Very low vapor pressure

Chlorides:
- ~ 1 1/2X density
- ~ 1/4X heat capacity
- ~ 1 1/2X viscosity
- ~ 1X thermal conductivity
- ~ 1 1/2X coefficient of expansion as a liquid
- Very low vapor pressure
Characteristics of *Fuel Salts* and *Coolant Salts* Are Available from Review Articles

- A fuel salt is a molten salt that contains fissile material

- Coolant salts are molten salts with advantageous heat transfer properties
  - D. F. Williams, *Assessment of Candidate Molten Salt Coolants for the NGNP/NHI Heat-Transfer Loop*, ORNL/TM-2006/69
Composition of Fuel Salts Are Tailored to Performance Objectives

- Fuel salts consist of a mixture of
  - Fissile material
  - Fertile material (if used)
  - Solvent (diluent)
    - Lowers melting point
    - Decreases power density
    - Decreases viscosity
  - Fissile oxidation prevention material
    - Preferentially oxidizes to avoid creation of fissile oxide particles due to contamination
      \[ \text{ZrF}_4 + \text{UO}_2 \leftrightarrow \text{ZrO}_2 + \text{UF}_4 \]
  - Fission products (upon use)

\[7\text{LiF} = 6\text{BaF}_2 - 2\text{ZrF}_4\]
Fuel Salts Must Integrate Reactor Physics, Heat Transfer, and Material Compatibility

- Reactor physics requirements
  - Low neutron absorption
    - Thermal neutron absorption is of lower importance for fast spectrum reactors
  - Radiolytic stability under in-core conditions
  - Dissolve fissile materials

- Both chloride and fluoride salts are industrially used as heat transfer fluids
  - High heat capacity, high boiling point, low thermal conductivity fluids
  - Melting point must be below ~525°C
  - Relatively insensitive to fission products

- Both fluoride and chloride salts, under mildly reducing conditions, are reasonably compatible with high temperature structural alloys and graphite

Fuel Salts Have Multiple Subclasses

- Thermal spectrum reprocessing optimized fluoride salts
  - FLiBe (27LiF-BeF₂) solvent provides optimal neutronic performance
    - Lithium to beryllium ratio selected to minimize melt temperature with acceptable viscosity
    - High tritium production – need isotopically separated lithium
  - NaF-ZrF₄ solvent does not require isotopic separation
    - Much lower tritium production
    - Higher vapor pressure
  - ~1% fissile loading
  - Fertile loadings vary but are typically much higher (~20%)

- Fast spectrum and thermal spectrum, once-through fuel cycle optimized fluoride salts
  - Much higher fissile loading (actinide-rich eutectics)
  - Adequate fissile material content is a significant design challenge

- Chloride salts
  - Enables harder neutron spectrum and enhanced breeding
  - Isotopically separated chlorine preferable - ³⁵Cl from ³⁷Cl
    - ³⁵Cl has a moderate capture cross-section (n,γ) E < 0.1 MeV < E (n,p)
Fluoride Fuel Salts Have Substantially More Experimental Data Than Chloride Fuel Salts

- **Fluoride salts**
  - Two operating molten salt reactors
  - Multiple in-pile loops
  - Many capsule tests
  - Fast-spectrum fluoride salts have much less experience

- **Chloride salts** – laboratory measurements of physical properties
  - No in-core testing of fuel salts
  - Use in pyroprocessing
Thermal Spectrum Fuel Salt Behaves Similarly to Solvent Salt

- MSRE nominal fuel mixture was 65 LiF, 29.1 BeF$_2$, 5 ZrF$_4$, 0.9 UF$_4$ (mol %)
- Uranium enriched to 33%
- Uranium trifluoride disproportionates in most molten fluoride solutions

$$4\text{UF}_3 \leftrightarrow 3\text{UF}_4 + \text{U}^0$$
- Large UF$_4$/UF$_3$ ratio prevents disproportionation

- Isotopically pure $^7\text{Li}$ - nominally 99.993% at MSRE
- Means to limit tritium production due to large $^6\text{Li}$ cross-section

Fluoride Fuel Salts Have Limited Solubility for Actinide Trifluorides

- Fast spectrum systems operate near solubility limits
  - Lanthanide trifluorides compete with actinide trifluorides
    - CeF$_3$ substantially displaces PuF$_3$
  - Log of actinide trifluoride solubility is roughly linear versus inverse temperature
- Monovalent solvent fluorides dissolve much higher levels of actinide trifluorides
  - Joint solubility of PuF$_3$+UF$_3$ is much less than individual components up to 600°C
  - Solubility has strong temperature dependence
    - Plate out during transients possible
  - Polyvalent fluorides (e.g., ThF$_4$, UF$_4$, or BeF$_2$) substantially reduce solubility

Fuel Salt Properties Will Be Impacted by Fission Products

- Fission products may be gaseous, solid, or dissolved
  - Alkaline and alkaline earth fission products (e.g., Cs and Sr) form stable fluorides (or chlorides)
  - Semi-noble fission products plate out on metal surfaces
    - Potential heat load issue following rapid draining
  - Noble fission products form suspended clusters that may plate out

- May elect to actively strip gaseous fission products
  - Lowers the in-core accident source term
  - Requires cooling fission product traps
  - Bubble formation and collapse results in reactivity burps

- Fluoride salts have been extensively examined
  - Reactors, in-pile loops, capsules
  - Some uncertainty remains - especially about impact of long-term build up of fission products

- Chloride fuel salts almost entirely untested in core environments
  - Potential for development of undesirable compounds and phases

“I am pleased, without benefit of rack and thumbscrew, to recant. More realistic calculations based on the single-region ‘reference design’ MSBR heat exchangers indicate that peak afterheat temperatures, while still uncomfortably high, will be much lower than originally anticipated.”

J. R. Tallackson, ORNL-TM-3145
**Fission Product Solubility Changes Along Decay Chain**

A few elements are very sensitive to redox changes:

- **Nb** behavior changed during MSRE operation after addition of Be°

Transitional *(soluble → gas → soluble)* decay example:

\[
\begin{align*}
137^I & \rightarrow 137^\text{Xe} & \rightarrow 137^\text{Cs}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Element</th>
<th>Solubility Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>soluble</td>
<td><strong>insoluble</strong></td>
</tr>
<tr>
<td>sometime soluble</td>
<td></td>
</tr>
</tbody>
</table>

- **24 sec. half-life**
- **4-min. half-life**
- **6 % cumulative \(^{235}\text{U}\) fission yield**

---

13 Module 3 Overview of Fuel and Coolant Salt Chemistry and Thermal Hydraulics
Cover Gas Handling System Is a Key Element of Any MSR

• Distribution of fission products is a central safety issue
  – Reduction of fission products in the core limits potential fuel accident source term
  – Fission products away from core change decay cooling requirements and radionuclide containment requirements

• Cover gas will inevitably contain some fission products
  – Aggressive sparging may result in up to 40% of fission products in cover gas (nearly all of the fission products with gaseous precursors)
  – Results in substantial heat load in short term fission product trap
  – Longer term fission product traps contain much lower levels of activity

• Transition from fission product barrier function to waste handling system along carbon beds is conceptually significant
  – $^{85}$Kr emerging from final stage could be vented

• Some fuel salt fissile components have significant vapor pressures
  – UCl$_4$ boils at 791°C

• Some solvents vaporize incongruently
  – ZrF$_4$ sublimes resulting in snow-like deposits in exhaust piping
NRG (Petten) Recently Began Irradiation Tests of Fuel Salt Capsules

- SALIENT program is trilateral collaboration between NRG, JRC, and TUD
- Fluoride salts initially
  - Chlorides later stage
- Goals
  - Handling experience
  - Salt–graphite interaction
  - Fission product stability / redistribution
  - Metal particle size distribution
- Longer term
  - Waste route for spent molten salt fuel
  - In-pile molten salt loop for the HFR Petten

Cartoon of potential Petten MSR loop

Image provided by NRG; used with permission.
Isotope Separation Is a Significant Issue for Both Fluoride and Chloride MSRs

• Lithium enables optimal reactor physics
  – Lithium-6 is a large cross-section thermal neutron absorber that yields tritium
  – Lithium isotope separation is also necessary for fusion and PWR chemistry control
  – Mercury amalgam-based lithium isotope separation was performed at industrial scale in the 1950s for defense purposes

• Chlorine
  – Absorption reactions in $^{35}$Cl both produces $^{36}$Cl (long-lived radionuclide) and results in a reactivity penalty
  – Lack of chlorine isotope separation technology was a key element in US decision in 1956 to pursue thermal breeder MSR
Removing Oxygen Is a Key Technology Requirement for Both Fluorides and Chlorides

- Salts containing excess oxygen are much more corrosive
- Hydrofluorination for fluoride salts
  - HF is highly corrosive - performed offline
  - Also removes other electronegative impurities - sulfur and chlorine
  - Ammonium hydrofluoride - NH₄HF₂ alternative
- Carbochlorination for chloride salts – phosgene (COCl₂) or carbon tetrachloride used as reactant
  - MO₂ + CCl₄ → MCl₄ + CO₂
- Oxygen can also be removed from some chloride melts by precipitation as aluminum oxide
  - AlCl₃ + UO₂ → AlO₂ + UCl₃

Source: Taube EIR-332; p.156
Tritium is Significant Issue For Lithium-Bearing Salts

- Tritium is produced by neutron reactions with lithium, beryllium, and fluorine as well as being a ternary fission product
  - Tritium production levels are similar to HWRs
- Tritium chemical state in salt is determined by redox conditions
  - TF (oxidizing) or T⁺ (reducing)
- Above 300°C tritium readily diffuses through structural alloys
  - Heat exchangers represent largest surface area for diffusion
- Escape through power cycle is potential route for radionuclide release into environment

---

Table 1. Sources and rates of production of tritium in a 1000-MW(e) MSBR

<table>
<thead>
<tr>
<th>Ternary fission</th>
<th>Production rate (Ci/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁶Li(n,α)³H</td>
<td>31</td>
</tr>
<tr>
<td>⁷Li(n,α)³H</td>
<td>1210</td>
</tr>
<tr>
<td>⁹Be(n,α)³He → ⁶Li</td>
<td>1170</td>
</tr>
<tr>
<td>¹⁹F(n,¹⁷O)³H</td>
<td>9</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>2420</strong></td>
</tr>
</tbody>
</table>

*From Ref. 1.*
Tritium Mitigation Methods Include Stripping, Blocking, and Trapping

• Largest technical challenge for stripping is the small diffusion of tritium in salt
  – Necessitates intimate mixing of salt and stripping material
    • Gas sparging or spraying in gas space using fine droplets
    • Turbulent flow (to promote mixing) across large surface area window (e.g., double-walled heat exchanger)
    • Flow through packed bed of absorbers
  – Palladium alloys have highest tritium diffusion coefficient
    • Nickel may be acceptable and is much less expensive
  – Carbon traps tritium at operating temperatures - desorbs at high temperatures (peak storage at ~800°C)
    • Nickel coating carbon improves trapping kinetics
    • Irradiation damage significantly increases number of traps
  – Several lanthanides form stable tritides (e.g., Y or Sm)

• Tritium trapping in coolant salt was demonstrated in NaF-NaBF$_4$ (8–92 mol%) at engineering scale for MSBR
Molten Salts Have Attractive Heat Transfer Properties

- Large heat capacity and low viscosity are key properties

Source: Nuclear Engineering Handbook 9-90, D. F. Williams et al., ORNL/TM-2006/12

\[ \text{Laminar} = \frac{\rho^2 c_p^2}{\mu} \]

\[ \text{Turbulent} = \frac{\rho^2 c_p^{2.8}}{\mu^{0.2}} \]

\( \rho \) = density
\( c_p \) = heat capacity
\( \mu \) = dynamic viscosity
\( \beta \) = volumetric expansion coefficient
Molten Salt Passive Cooling Characteristics are Favorable

- Volumetric expansion with temperature provides buoyancy driving force

\[ \text{Laminar} = \left( \frac{\beta \rho^2 c_p}{\mu} \right)^{0.5} \]

\[ \text{Turbulent} = \left( \frac{\beta \rho^2 c_p^{1.8}}{\mu^{0.2}} \right)^{0.36} \]

\[ \rho = \text{density} \]
\[ c_p = \text{heat capacity} \]
\[ \mu = \text{dynamic viscosity} \]
\[ \beta = \text{volumetric expansion coefficient} \]

Source:
Nuclear Engineering Handbook 9-90,
D. F. Williams et al., ORNL/TM-2006/12
Salts Have Sharp Boundary Layer (High Prandtl Number)

- Turbulence is required for effective heat transfer (or tritium stripping)

Source: Nuclear Engineering Handbook 9-90,
D. F. Williams et al., ORNL/TM-2006/12

\[ \text{Laminar} = \frac{\rho^2 c_p^2 k^4}{\mu} \]

\[ \text{Turbulent} = \frac{\rho^2 c_p^{1.167} k^{2.333}}{\mu^{1.835}} \]

\[ \text{if metals} = \frac{\rho^2 c_p^{2.8} k^{0.7}}{0.747 \mu^{0.2}} \]

\( \rho \) = density
\( c_p \) = heat capacity
\( \mu \) = dynamic viscosity
\( \beta \) = volumetric expansion coefficient
Salt Viscosity Decreases with Temperature

- Flow increases to hotter regions
- Improves temperature uniformity

Source:
D. F. Williams et al., ORNL/TM-2006/12
D. F. Williams, ORNL/TM-2006/69
Significant Uncertainty Remains in Fluoride Salt Turbulent Heat Transfer

- Little experimental data with few material combinations and geometries
- Y-axis is a common heat transfer correlation for fully developed turbulent flow in tubes

Source:
Yoder, ICAPP 14332, 2014

Nu = Nusselt number
Pr = Prandtl number
Re = Reynolds number
Laminar Flow Heat Transfer Also Has Significant Remaining Uncertainty

- Axes selected to enable comparison with prior laminar flow correlations (Seider and Tate)

- Peclet number is a dimensionless ratio of the thermal energy convected to the fluid to the thermal energy conducted within the fluid

Source: Yoder, ICAPP 14332, 2014
Significant Remaining Uncertainty in Prediction of Conductive / Convective Heat Transfer Ratio

- Plot compares experimental and predicted conductive/convective heat transfer ratios
  - Prediction based upon reference Gnielinski correlation - commonly used for heat transfer comparisons

Source: Yoder, ICAPP 14332, 2014
Natural Circulation Heat Transfer Has Significant Remaining Uncertainty

Product of Grashof and Prandtl number (X-axis) is the Rayleigh number associated with buoyancy-driven flow

- Above critical Rayleigh number heat transfer is primarily convection below primarily conduction
- Y-axis is ratio of convective to conductive heat transfer

Source: Yoder, ICAPP 14332, 2014
Heat Transfer Uncertainties Affect Operating Margin Calculations

- Material combinations and geometries of interest to MSRs have not been thoroughly characterized in past experiments.

- Sources of experimental uncertainty include:
  - Salt purity and purification during the experiment
  - Film layers/deposits on heated surfaces
  - Temperature

- More targeted, controlled experimental data is required to improve the confidence in thermophysical property correlations.
Molten Fluorides Are Highly Thermodynamically and Radiolytically Stable

- Salts are combinations of strongly electronegative elements with strongly electropositive metals
  - Very high bond energies
  - Negative change in Gibbs free energy ($\Delta G_f$) > 100 kcal/mol-F
  - Structural metal fluorides have Gibbs free energies at least 20 kcal/mol-F less negative
    - MSRE graphite and Hastelloy N exposed to coolant salt was untouched after ~3 years of operation
  - Salt radiolysis is overwhelmed by recombination at operating temperatures

Source: ORNL/TM-4174
Thermochemical Stability Drives Both Corrosion and Fissile Solubility

- Increased free chlorine results in larger amounts of dissolved structural alloy chlorides.
- Increasing ratios of UCl$_4$/UCl$_3$ restrict acceptable choice of structural alloys.
- Use of nickel-based structural alloys restricted to UCl$_4$/UCl$_3$ ratios of roughly 0.003 to 5%.
  - Smaller amounts of UCl$_4$ results in disproportionation of UCl$_3$.
    
    \[ 4\text{UCl}_3 \rightleftharpoons \text{UCl}_4 + \text{U}^0 \]

- Refractory coatings would enable higher UCl$_4$/UCl$_3$ ratios.
- PuCl$_3$ disproportionation is less favorable than that of UCl$_3$.

Phase Diagrams of Chloride Fuel Salts Show Fuel System Design Options

- A ~500°C melt point can be achieved with a range of UCl$_3$ to UCl$_4$ ratios
  - Systems with higher UCl$_3$ fractions have lower uranium loading
  - Systems with higher UCl$_4$ fractions are more oxidizing (corrosive)

Maintaining Mildly Reducing Redox Conditions
Key to Enabling Use of Engineering Alloys

- Use of a circulating redox buffer provides means to maintain redox condition
  - Fission changes oxidation state of salts
- Ratio of $\text{U}^{4+}/\text{U}^{3+}$ serves as a measure of the redox potential of the salt
  - Applicable to both fluoride and chloride salts
  - Adding beryllium to FLiBe
- Fluoride salts will likely have an ideal ratio of $\sim$10–100

Source: Baes, Keiser, ORNL/TM-6002

Fig. 12. Cracking Behavior of Hastelloy N Exposed 260 hr at 700°C to MSBR Fuel Salt Containing CrTe1.266.
Fission Process Continuously Alters the Fuel Salt Redox Conditions

• When a U or Pu ion fissions, the available electrons will rearrange on each fission product to satisfy its valence requirements and produce either net oxidizing or reducing conditions in the melt
  – For $^{235}\text{U}$ (as UF$_4$) four F ions are released. The fission products require less than four and thus there will be an excess of F ions with net oxidizing conditions
  – For $^{239}\text{Pu}$ (as PuF$_3$) three F ions are released. The fission products require more than three and thus there will be a F ion deficit with net reducing conditions
• MSRE periodically added metallic beryllium (strong reducing agent) to maintain UF$_4$/UF$_3$ ratio

<table>
<thead>
<tr>
<th>Salt Type</th>
<th>Fission Product</th>
<th>Oxidation State (Z)</th>
<th>Yield (Y) [atoms]</th>
<th>Cl atoms reacted (Y*Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Salt (UCl$_3$)</td>
<td>Kr, Xe</td>
<td>0</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Rb, Cs</td>
<td>1</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Sr, Ba</td>
<td>2</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Rare Earths</td>
<td>3</td>
<td>46</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>3</td>
<td>22</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>Nb, Mo</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Te, I</td>
<td>0</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Pd, Re, Rh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ag, Cd</td>
<td>0</td>
<td>61</td>
<td>0</td>
</tr>
<tr>
<td>Total Cl atoms reacted out of 300 available</td>
<td></td>
<td></td>
<td></td>
<td>243</td>
</tr>
<tr>
<td>Fluoride Salt (UF$_4$)</td>
<td>Br, I</td>
<td>-1</td>
<td>1.5</td>
<td>-1.5</td>
</tr>
<tr>
<td></td>
<td>Kr, Xe</td>
<td>0</td>
<td>60.6</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Rb, Cs</td>
<td>1</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Sr, Ba</td>
<td>2</td>
<td>7.2</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>Lanthanides, Y</td>
<td>3</td>
<td>53.8</td>
<td>161.4</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>4</td>
<td>31.8</td>
<td>127.2</td>
</tr>
<tr>
<td></td>
<td>Nb</td>
<td>0</td>
<td>1.4</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Mo</td>
<td>0</td>
<td>20.1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Tc</td>
<td>0</td>
<td>5.9</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>0</td>
<td>12.6</td>
<td>0</td>
</tr>
<tr>
<td>Total F atoms reacted out of 400 available</td>
<td></td>
<td></td>
<td></td>
<td>301.9</td>
</tr>
</tbody>
</table>

Sources: Baes (fluoride salts), Harder (chloride salts)
Because Chemical Activity in Molten Salts Is Controlled by Melt Composition...

- Monovalent salts are “basic” in that they supply fluoride ions (F⁻)
- Polyvalent salts are “acidic” in that they form complexes with F⁻
- Lewis acid/base coordination equilibria are established
  - \( \text{ZrF}_4 + 3\text{F}^- \leftrightarrow \text{ZrF}_7^{3-} \)
  - \( \text{BeF}_2 + 2\text{F}^- \leftrightarrow \text{BeF}_4^{2-} \)
- The chemical reactivities of these and other metal ions are higher when they are not sufficiently coordinated with fluoride ions
- In the absence of the extra fluoride ions supplied by LiF component, for example, \( \text{ZrF}_4 \) and \( \text{BeF}_2 \) would be volatile and distill from the system
Fission Products and Contaminants Would Alter Fuel Salt and Cover Gas Properties

- Oil leak along MSRE pump shaft resulted in foaming in pump bowl
  - Foam overflowed into gaseous waste handling system

- Noble fission products do not dissolve into salt and consequently lack a surface tension inhibition for entering cover gas (i.e., they readily enter the cover gas)

- Contamination particles, solid oxide precipitate, etc., may form a scum layer on the salt surface

Source:
Yoder et al., ORNL/TM-2014/499
Fluoride Salts Are Vulnerable to Radiolytic Decomposition at Low Temperatures

• Intense radiation creates more free fluorine than is recombined below ~200°C

• Experience with chloride salts is almost nonexistent
  – Likely has similar vulnerability as fluoride salts
  – Pyroprocessing salts and conditions are different from fuel salts

• Free fluorine can react with structural materials resulting in dramatically increased corrosion or converting solid UF$_4$ to gaseous UF$_6$
  – Origin of the issue with the stored MSRE fuel salt in the 1990s

Source: Haubenreich, ORNL-TM-3144, 1970
Long Term Waste Forms from MSRs Remain Unproven

- Primary US work remains “Applied Technology”
- Offgas sorbent could serve as ultimate fission gas disposal medium
  - Charcoal beds were employed for MSRE
- May be possible to make fluorides more stable by conversion to a fluorophosphate
- Chlorides are currently converted to a *salt-cake* waste form as part of the ongoing EBR-II processing campaign
- Synthetic rock process developed by ANSTO appears applicable
- Dutch SALIENT project has primary objective to develop final waste form for their test salts
Characteristics of MSRs Derive from the Chemistry and Physics of Halide Salts

- Low pressure, high temperature operation
- Dissolve useful amounts of fissile material
- Chemically compatible with engineering alloys in mildly reducing environments
- Strong passive safety features
  - Negative reactivity feedback
  - Natural circulation-based decay heat removal
  - Reduced potential for radionuclide release
- Fluoride salts have substantially more experimental data than chloride salts for reactor operations
- Tritium production from lithium-bearing salts can be mitigated by stripping, blocking, and trapping