Molten Salt Reactor Fuel: experiments and assessments on metal fluoride fluoride phase diagrams

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Materials requirements for solvents for the MSR

✓ Wide range of solubility for actinides
✓ Thermodynamically stable up to high temperatures
✓ Stable to radiation (no radiolytic decomposition)
✓ Low vapour pressure at the operating temperature of the reactor
✓ Compatible with nickel-based structural materials
✓ Compatible with the reprocessing technology

ARE          NaF - ZrF$_4$ - UF$_4$
MSRE         $^7$LiF - BeF$_2$ - ZrF$_4$ - ThF$_4$ - UF$_4$
MSBR         $^7$LiF - BeF$_2$ - ThF$_4$ - UF$_4$
MSFR         $^7$LiF - ThF$_4$ - UF$_4$
Some of the questions to be addressed

- Do we have a sufficient understanding of the $^7\text{LiF}-\text{ThF}_4-\text{UF}_4$ salt?
- Are there alternative solvent components that could be considered?
- Can $\text{UF}_4$ be replaced by $\text{PuF}_3$ as fissile source?
- How do the physical properties vary in the multicomponent systems?

Thermochemical approach:
- CALPHAD modelling
- Experimental studies
Relevant physical properties to be considered

- Melting point
- Actinide solubility
- Vapour pressure
- Heat capacity
- Density
- Viscosity
- Thermal conductivity

Phase diagram optimisation

Quasichemical model with quadruplet approximation (Chartand & Pelton)

\[(A \cdots X) + (B \cdots Y) = (A \cdots Y) + (B \cdots X)\]

\[\Delta g_{AB/XY}^{exchange}\]
Fig. 218. The system LiF–BeF₂–ThF₄.
Purification of ThF$_4$

Ni-liner and Ni-gasket

stainless steel crucible

Ni-crucible

(\text{NH}_4)_2\text{HF}_2$ - bed
The experimental approach for the LiF-ThF$_4$ phase diagram
Enthalpy of mixing of the LiF–KF system. (●) this study at \( T = 1121 \text{ K} \). (▲▼) Hong and Kleppa at \( T = 1176 \text{ K} \) and \( T = 1360 \text{ K} \).

Enthalpy of mixing of the LiF–ThF4 system. (○, ●) Data obtained in this study at \( T = 1121 \text{ K} \) and \( T = 1383 \text{ K} \). Solid line: Calculated enthalpy of mixing from the assessment performed in this work. Dashed line: Calculated enthalpy of mixing from the previous assessment.
\[ \Delta_{\text{mix}} S / (\text{J K}^{-1} \cdot \text{mol}^{-1}) \]

Graph showing the relationship between \( X (\text{ThF}_4) \) and \( \Delta_{\text{mix}} S \). The graph indicates two distinct regions:

- **Free F\(^-\) ions** at 1343 K
- **F\(^-\) bridging** at 1121 K

The graph peaks at approximately 2500 J K\(^{-1}\) mol\(^{-1}\) and decreases as \( X (\text{ThF}_4) \) increases.
DSC analysis of Li$_3$ThF$_7$

**DSC output**

- $T_m = 831.3$ K

**Fusion enthalpy values**

- our experiment
  $\Delta_{fus}H = 13.7 \pm 2$ kJ/mol

- Gilbert 1962
  $\Delta_{fus}H = 14.6$ kJ/mol

- our LiF-ThF$_4$ assessment
  $\Delta_{fus}H = 14.6$ kJ/mol

- congruent melting of Li$_3$ThF$_7$

- melting of Ag standard
Thermodynamic assessment of LiF-ThF₄-UF₄-PuF₃ system

- CeF₃ is considered as proxy compound to PuF₃.

**Binary sub-systems:**
- LiF-ThF₄
- LiF-PuF₃
- ThF₄-PuF₃
- UF₄-PuF₃
- LiF-UF₄
- ThF₄-UF₄

**Ternary sub-systems:**
- LiF-ThF₄-UF₄
- LiF-ThF₄-PuF₃
- LiF-UF₄-PuF₃
- ThF₄-UF₄-PuF₃

*Optimized based on the ThF₄-CeF₃ system*

*Optimized based on the exp. data*
Experimental measurements

- Five compositions have been measured using the DSC technique.
- Fixed LiF/ThF₄ ratio and different CeF₃ concentrations:
  - LiF-ThF₄-CeF₃ (77.5-18.9-3.6)
  - LiF-ThF₄-CeF₃ (77.6-18.9-3.5)
  - LiF-ThF₄-CeF₃ (77.7-18.9-3.4)
  - LiF-ThF₄-CeF₃ (77.7-19.0-3.3)
  - LiF-ThF₄-CeF₃ (77.8-19.0-3.2)

<table>
<thead>
<tr>
<th>X (LiF)</th>
<th>X (ThF₄)</th>
<th>X (CeF₃)</th>
<th>T_{trans} [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.775</td>
<td>0.189</td>
<td>0.036</td>
<td>883.87</td>
</tr>
<tr>
<td>0.776</td>
<td>0.189</td>
<td>0.035</td>
<td>869.93</td>
</tr>
<tr>
<td>0.777</td>
<td>0.189</td>
<td>0.034</td>
<td>871.65</td>
</tr>
<tr>
<td><strong>0.777</strong></td>
<td><strong>0.19</strong></td>
<td><strong>0.033</strong></td>
<td><strong>867.28</strong></td>
</tr>
<tr>
<td>0.778</td>
<td>0.19</td>
<td>0.032</td>
<td>889.31</td>
</tr>
</tbody>
</table>
Application of the database: Fuel Optimization

Criteria:

• The fuel composition is optimized based on the melting point of the salt mixture.
• A low melting point decreases the risk of freezing and reduces corrosion problem.
• In order to keep sufficient safety margin, the inlet temperature of the reactor must be at least 50 K higher than the melting point.

Fuel constrains:

• The minimum concentration of fissile material is fixed at 5 mol%.
• In order to control the redox potential of the salt (via UF$_4$/UF$_3$ ratio), a minimum concentration of UF$_4$ of 1 mol% is needed.
• Due to non-proliferation issues, the enrichment of UF$_4$ must not exceed 20%
Fuel Optimization

- **Initial MSFR fuel composition**: Eutectic composition LiF-ThF$_4$ (78-22) with addition of 5% PuF$_3$ and 1% UF$_4$ ($T=941.5$ K)

- **Optimized composition having fixed concentration of UF$_4$ and PuF$_3$** ($T=865.8$ K)

**Fuel constrain:**
- Minimum concentration of fissile material: 5%
- Minimum concentration of UF$_4$: 1%
- Maximum enrichment UF$_4$: 20%
Fuel Optimization

- **Initial MSFR fuel composition:** Eutectic composition LiF-ThF₄ (78-22) with addition of 5% PuF₃ and 1% UF₄ \( (T=941.5 \text{ K}) \)

- **Optimized composition having fixed concentration of UF₄ and PuF₃** \( (T=865.8 \text{ K}) \)

- **Lowest liquidus point** \( (T=819.7 \text{ K}) \) LiF-ThF₄-UF₄-PuF₃ \( (75.3-20.6-1.0-3.1) \)

- **Proposed fuel composition considering neutronic calculation and exp. results** LiF-ThF₄-UF₄-PuF₃ \( (77.7-18-1.0-3.3) \) \( (T=867 \text{ K}) \)

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**Fuel constrain:**
- Minimum concentration of fissile material: 5%
- Minimum concentration of UF₄: 1%
- Maximum enrichment UF₄: 20%
Thermodynamic calculations

- Thermodynamic properties of the identified compositions:

<table>
<thead>
<tr>
<th>Composition</th>
<th>T melting (K)</th>
<th>T boiling (K)</th>
<th>P at T_{oper} (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF-ThF₄-UF₄-PuF₃</td>
<td>943.9 K</td>
<td>2035 K</td>
<td>4.62 \cdot 10^{-2}</td>
</tr>
<tr>
<td>(73.3-20.7-1.0-5.0)</td>
<td></td>
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<tr>
<td>LiF-ThF₄-UF₄-PuF₃</td>
<td>866.8 K</td>
<td>2035 K</td>
<td>5.33 \cdot 10^{-3}</td>
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<tr>
<td>(78.0-16.0-1.0-5.0)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>LiF-ThF₄-UF₄-PuF₃</td>
<td>819.3 K</td>
<td>2032 K</td>
<td>7.26 \cdot 10^{-4}</td>
</tr>
<tr>
<td>(75.3-20.6-1.0-3.1)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>LiF-ThF₄-UF₄-PuF₃</td>
<td>856.4 K</td>
<td>2033 K</td>
<td>3.58 \cdot 10^{-3}</td>
</tr>
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<td>(77.7-18.0-1.0-3.3)</td>
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- Influence of partial substitution of ThF₄ with UF₄

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</tr>
<tr>
<td>LiF-UF₄-PuF₃</td>
<td>855 K</td>
<td>2007 K</td>
<td>3.7 \cdot 10^{-3}</td>
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<td>(77.7-19.0-3.3)</td>
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Conclusions

- The combination of assessments and experiments is of key importance to develop the database for molten salt reactor fuel
- We master now the complex handling of these materials for experiments
- Thermochemical modelling has shown to be a useful in teh fuel optimisation
- Work with PuF$_3$ is the logic next step to improve/verify the database
Thank you for listening!

PuF$_3$

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