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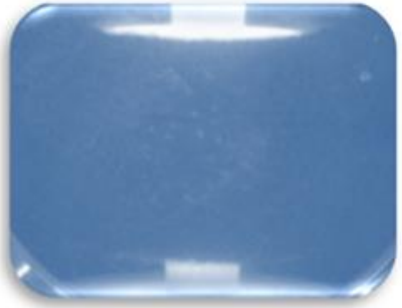

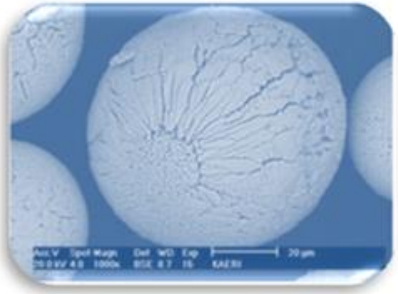

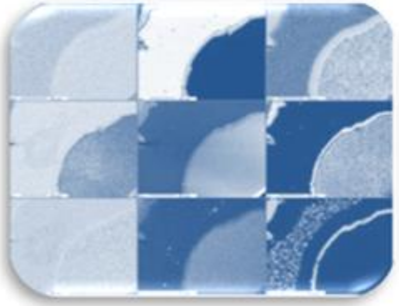

CALPHAD Studies on KCl as a Candidate Base Salt for U/Pu Fast Breeding Molten Salt Reactor Cycles

Woei Jer Ng[a], Ho Jin Ryu[a,b*]

[a] *Department of Nuclear and Quantum Engineering, KAIST, Daejeon*
[b] *Department of Materials Science and Engineering, KAIST, Daejeon*
**For Correspondence: hojinryu@kaist.ac.kr*

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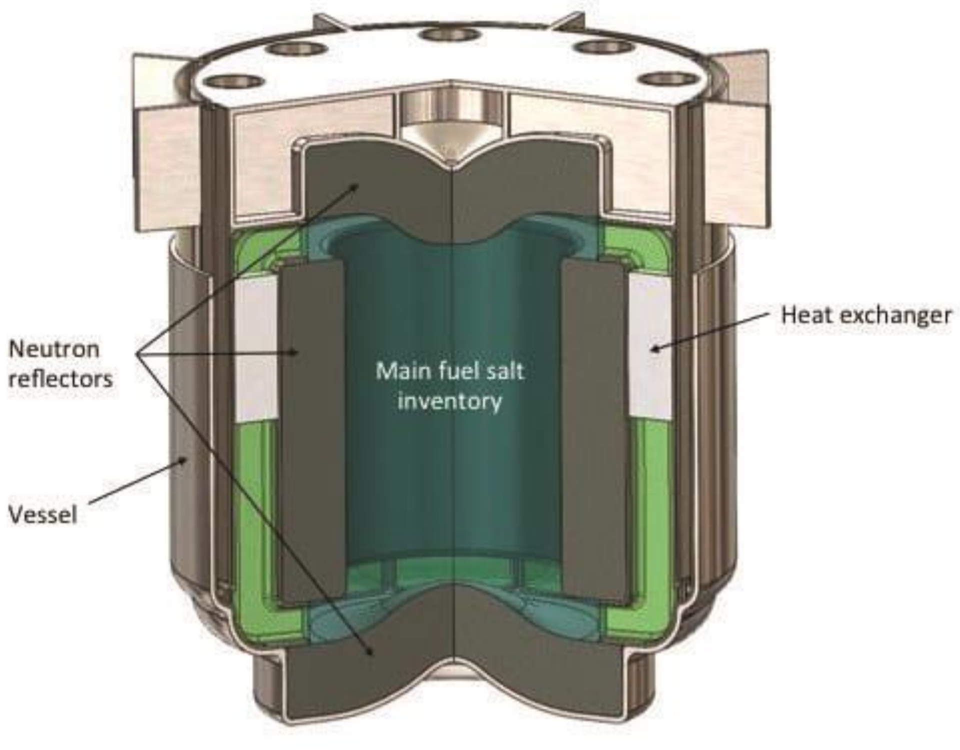
Introduction: Molten Salt Reactors (MSR)



(TerraPower MCFR)

- **Inherently safe Gen IV reactor concept**
  - Strong negative temperature coefficient
  - Operation at atmospheric pressure (eliminates radioactive release due to *high pressure gradient*)
- **Projected Economic Value**
  - High operating temperature
  - High thermal efficiency
- **Zero/Low Radioactive Waste Production**
  - Low initial inventory of fissile material
  - Recycling of minor actinides as fuel

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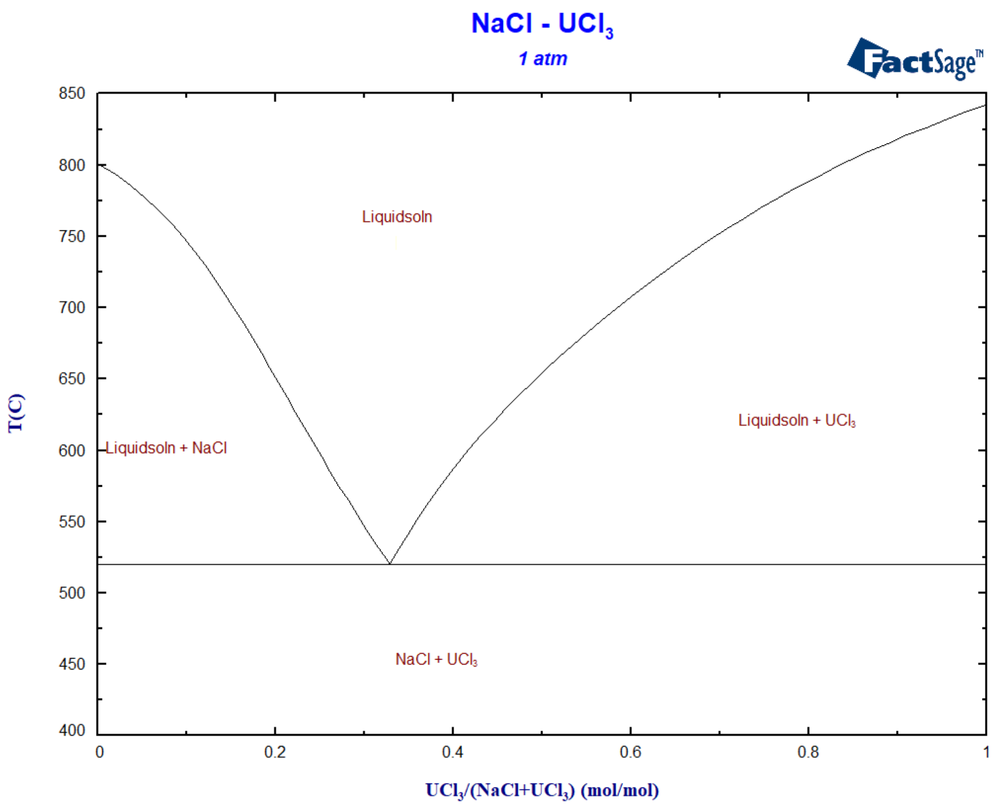
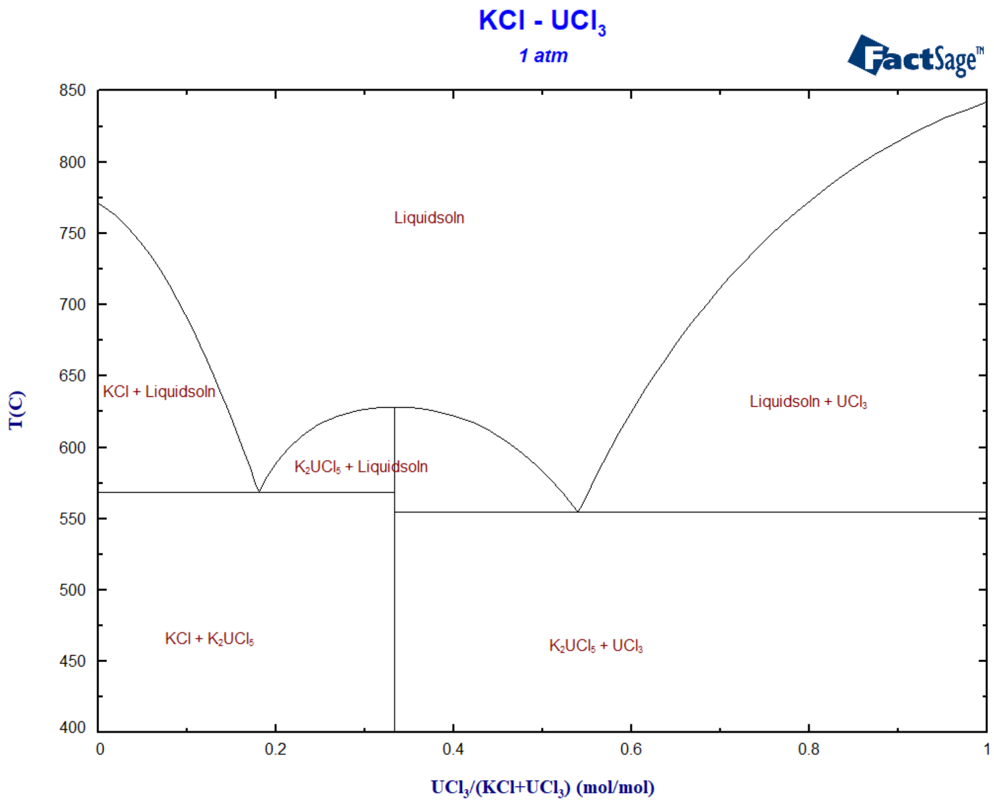
Introduction: Choice of Base Salt





TerraPower MSR
$(\mathrm{NaCl} - \mathrm{UCl_3})$

KAIST MSR
$(\mathrm{KCl} - \mathrm{UCl_3})$

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Introduction: NaCl vs KCl as Base Salt

TerraPower MSR ($NaCl - UCl_3$)		KAIST MSR ($KCl - UCl_3$)
520°C	Min. Eutectic Temperature	554°C
33mol%	UCl_3 fraction at eutectic composition	54mol%
15.7 wt%	U-235 Enrichment	14.1wt%
Sharp resonance peak in 1~10 keV region	Base Salt Resonance Cross Section	Resonance peaks not as sharp
0.575	Calculated Conversion Ratio	0.610

Hong et al., *Transactions of the Korean Nuclear Society Virtual Spring Meeting 2021.*

Introduction: NaCl vs KCl as Base Salt

From a neutronics' perspective….

Hong et el. concluded that $\mathrm{KCl} - \mathrm{UCl_3}$ was the better fuel candidate as the fuel allows for smaller core sizes and better breeding capabilities.

However, from a materials' perspective….

$\mathrm{NaCl} - \mathrm{UCl_3}$ may be more advantageous for the following reasons:

- Lower viscosity, thereby improving pumpability and heat transfer efficiency.
- Lower eutectic temperature, which enables lower operating temperature, hence mitigating risk of structural material corrosion.
- Does not form intermediate compounds with actinide chlorides.

Important property when considering transient compositional shifts due to Pu breeding and FP evolution!

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Q: How does KCl compare to NaCl in the transient performance of MSR fuels?

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Methodology: Modeling Compositional Shifts in MSR Fuels

Differential equations of composition change due to fission and neutron capture transmutation:

$$\frac{dU}{dt} = -\alpha\omega_{f_U}U - \beta\left(1-\omega_{f_U}\right)U$$

$$\frac{dP}{dt} = \beta\left(1-\omega_{f_U}\right)U - \alpha\omega_{f_P}P$$

$$\frac{dF}{dt} = n\left(\alpha\omega_{f_U}U + \alpha\omega_{f_P}P\right)$$

ω_{f_U}: *weight fraction of U − 235*
ω_{f_P}: *weight fraction of fissile plutonium*
α : *annual consumption of fissile isotopes by fission*
β : *annual consumption of fertile isotopes by neutron capture*
n : *average number of FP per fission*

Solution to linear system of differential equations:

$$U(t) = U_0 \cdot \exp(-\lambda_1 t)$$

$$P(t) = \frac{\beta\left(1-\omega_{f_U}\right)U_0}{\lambda_2-\lambda_1}\cdot\exp(-\lambda_1 t) + \left[P_0 - \frac{\beta\left(1-\omega_{f_U}\right)U_0}{\lambda_2-\lambda_1}\right]\cdot\exp(-\lambda_2 t)$$

$$F(t) = \frac{n\alpha}{\lambda_1}\left[\omega_{f_U}U_0 + \frac{\beta\omega_{f_P}\left(1-\omega_{f_U}\right)U_0}{\lambda_2-\lambda_1}\right]\cdot\{1-\exp(-\lambda_1 t)\} + \frac{n\alpha\omega_{f_P}}{\lambda_2}\left[P_0 - \frac{\beta\left(1-\omega_{f_U}\right)U_0}{\lambda_2-\lambda_1}\right]\cdot\{1-\exp(-\lambda_2 t)\}$$

$$\lambda_1 = \alpha\omega_{f_U} + \beta\left(1-\omega_{f_U}\right)\ ;\ \lambda_2 = \alpha\omega_{f_P}$$

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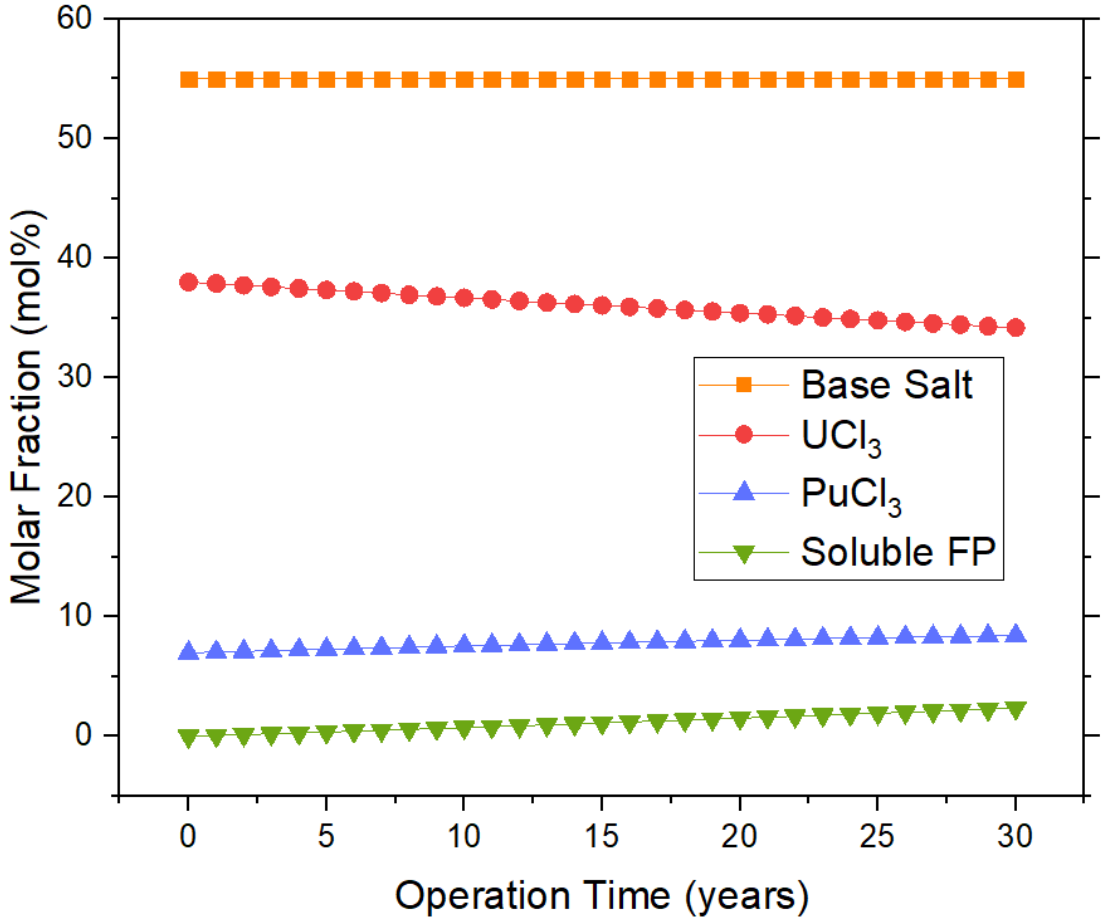
Methodology: Modeling Compositional Shifts in MSR Fuels

Applying the compositional shift model to the proposed REBUS-3700 fuel composition
(55mol% Base Salt–38mol% UCl_3–7mol% $PuCl_3$):



$$\omega_{f_U} = 0.002;\ \omega_{f_P} = 0.644$$
$$\alpha = 0.0155/year\ ;\ \beta = 0.0035/year$$

No composition change for base salt is assumed.

UCl_3 is consumed with increasing operation time.

Molar fraction of $PuCl_3$ increases due to breeding

One soluble fission product ($n = 1$) per fission reaction assumed. Fission gases and noble metals do not interact with fuel and are ignored.

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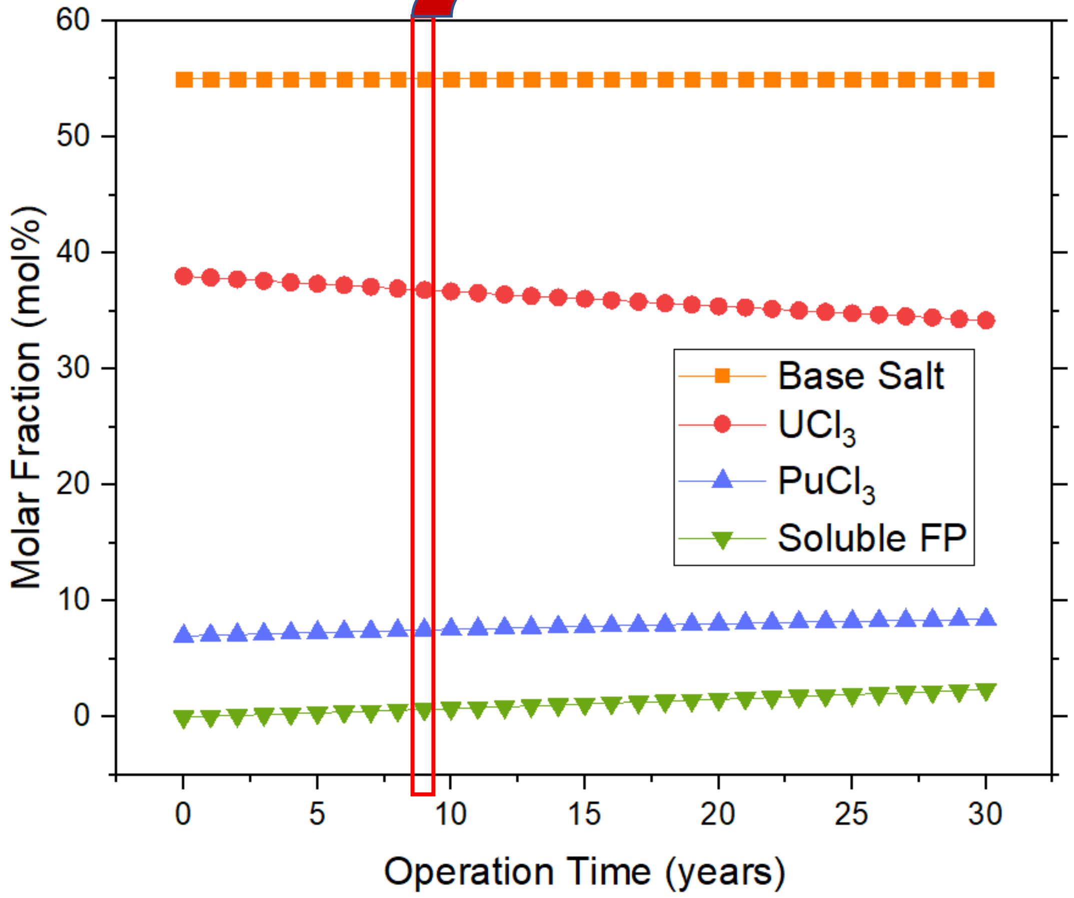
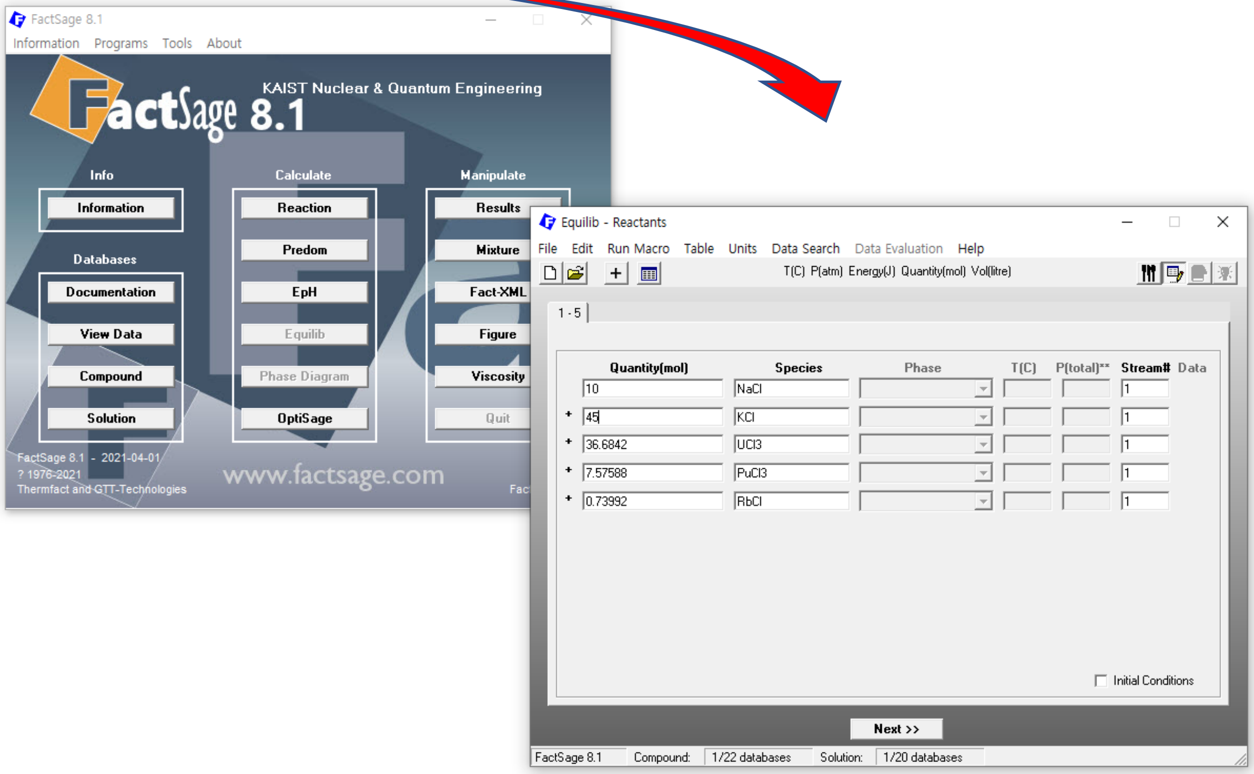
Methodology: Modeling Liquidus Temperature Changes due to Compositional Shifts



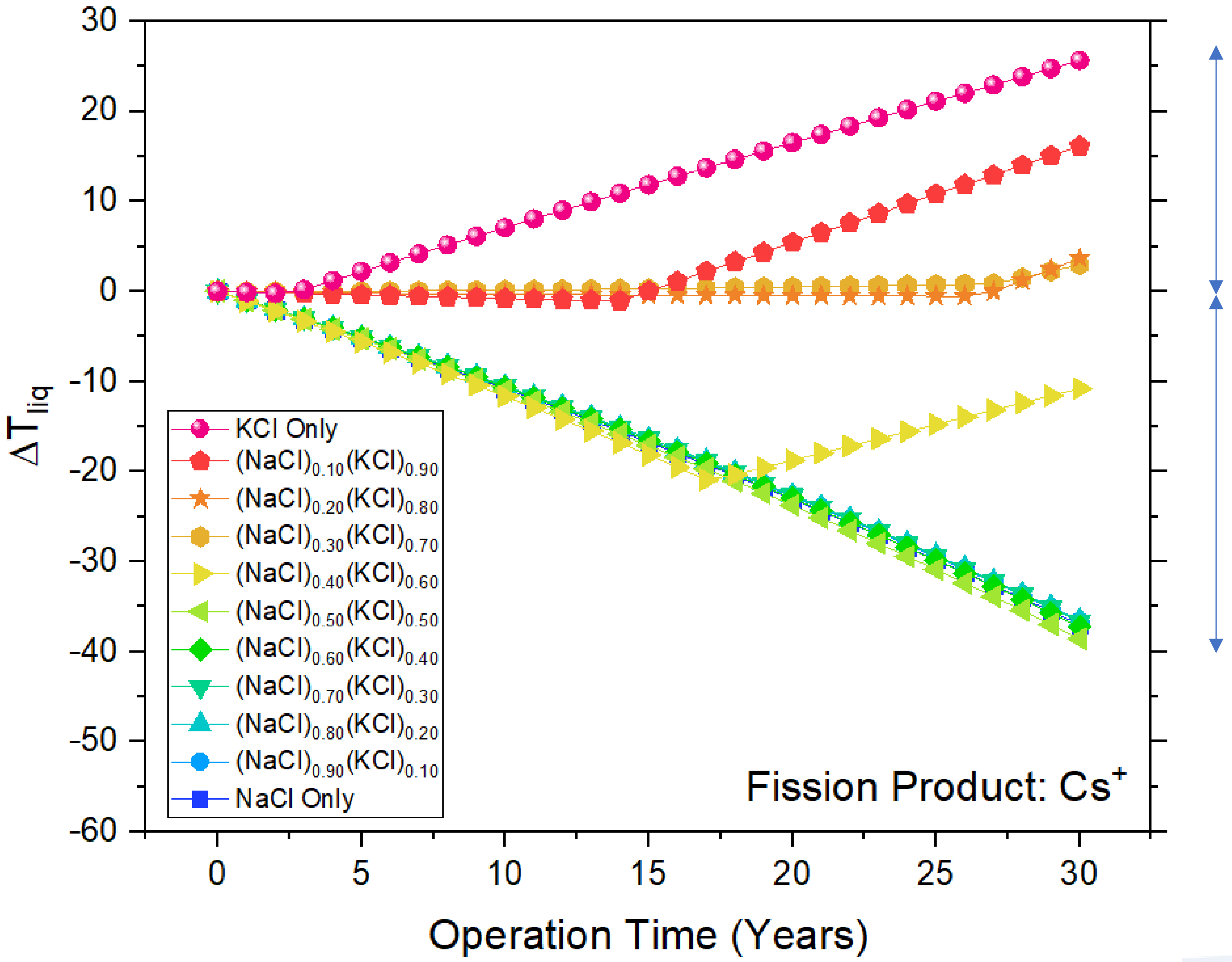


(Output: Equilibrium Liquidus Temperature)

Repeat calculations for Base Salt: $(NaCl)_x(KCl)_{1-x}$

Results: Liquidus Temperature Change of MSR Fuel

Assuming only all soluble fission products are Cs^+ (for simplicity):



MSR fuels with KCl as the dominant base salt experience increasing T_{liq} with operation time

The effect is opposite for MSR Fuels with NaCl as the dominant base salt

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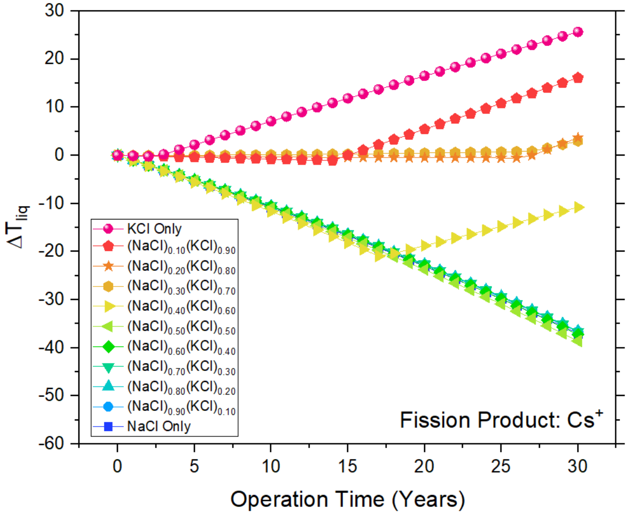
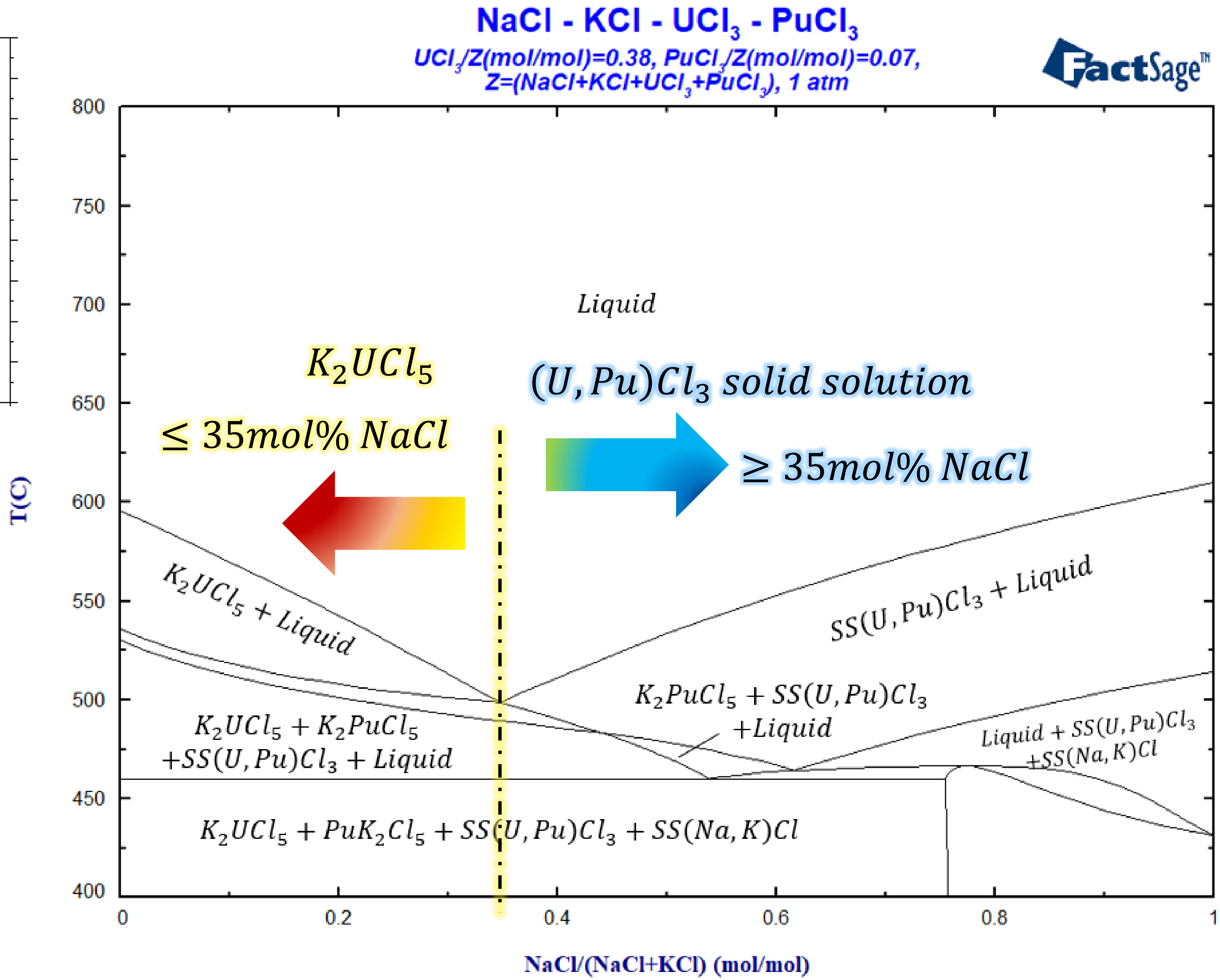
Discussion: Interaction between Fuel Constituents





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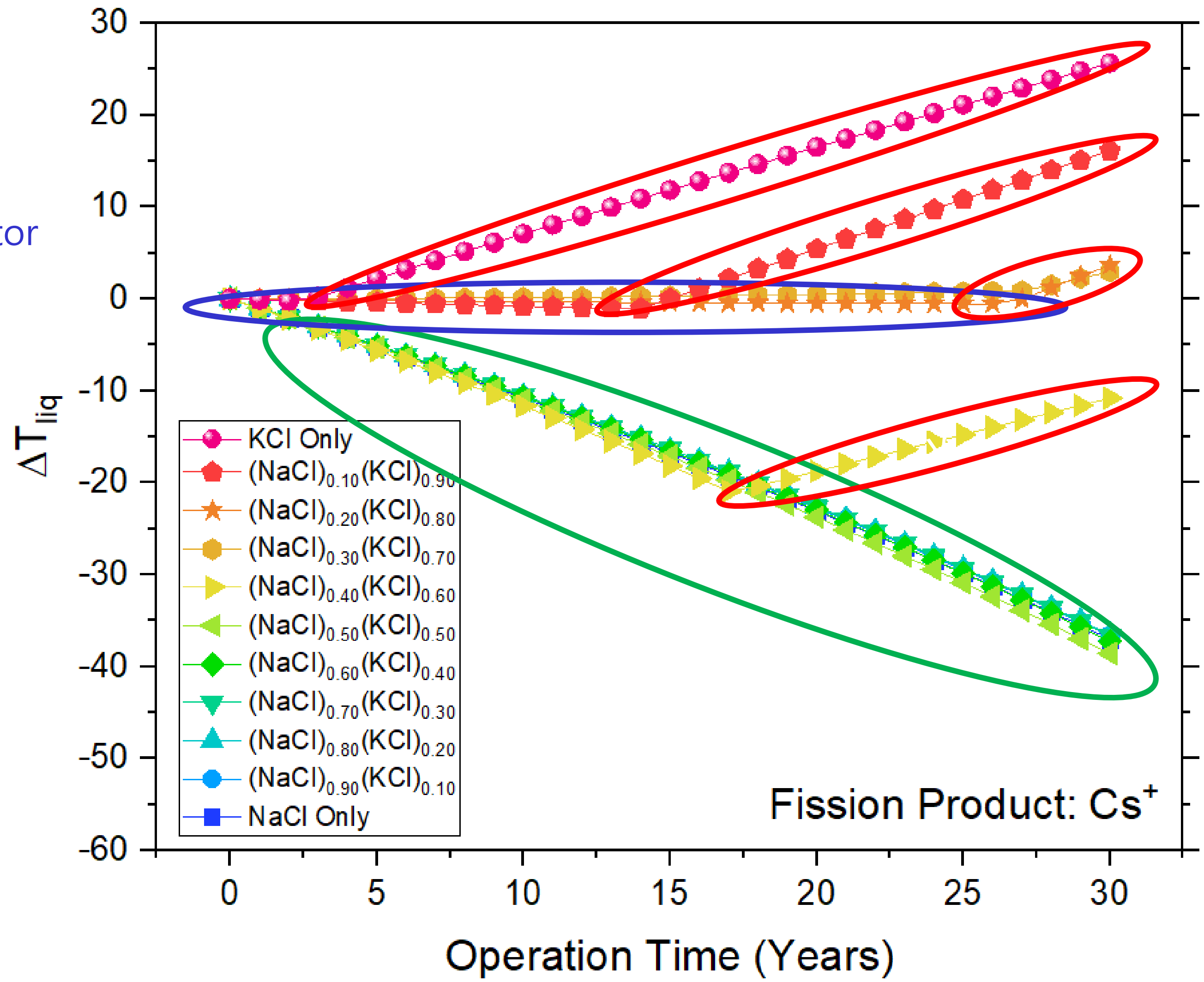
Discussion: Interaction between Fuel Constituents

Near-zero slope: K_2UCl_5

- UCl_3 conc. does not decrease drastically throughout the reactor lifetime.
- K_2UCl_5 melting point does not change significantly.



Positive slopes: K_3PuCl_6 ,K_2PuCl_5

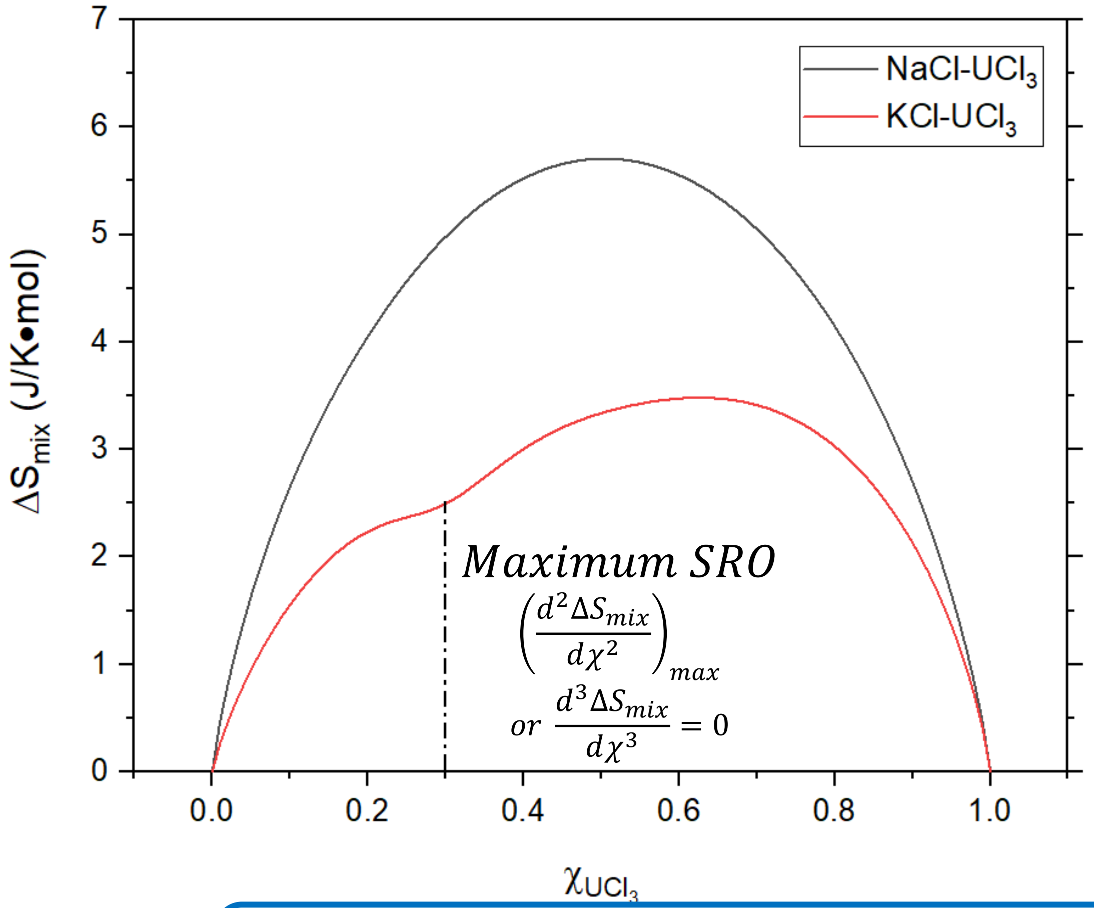
- Preferential short-range ordering between KCl and $PuCl_3$.
- High melting point of K_3PuCl_6 and K_2PuCl_5 raises fuel liquidus temperature.

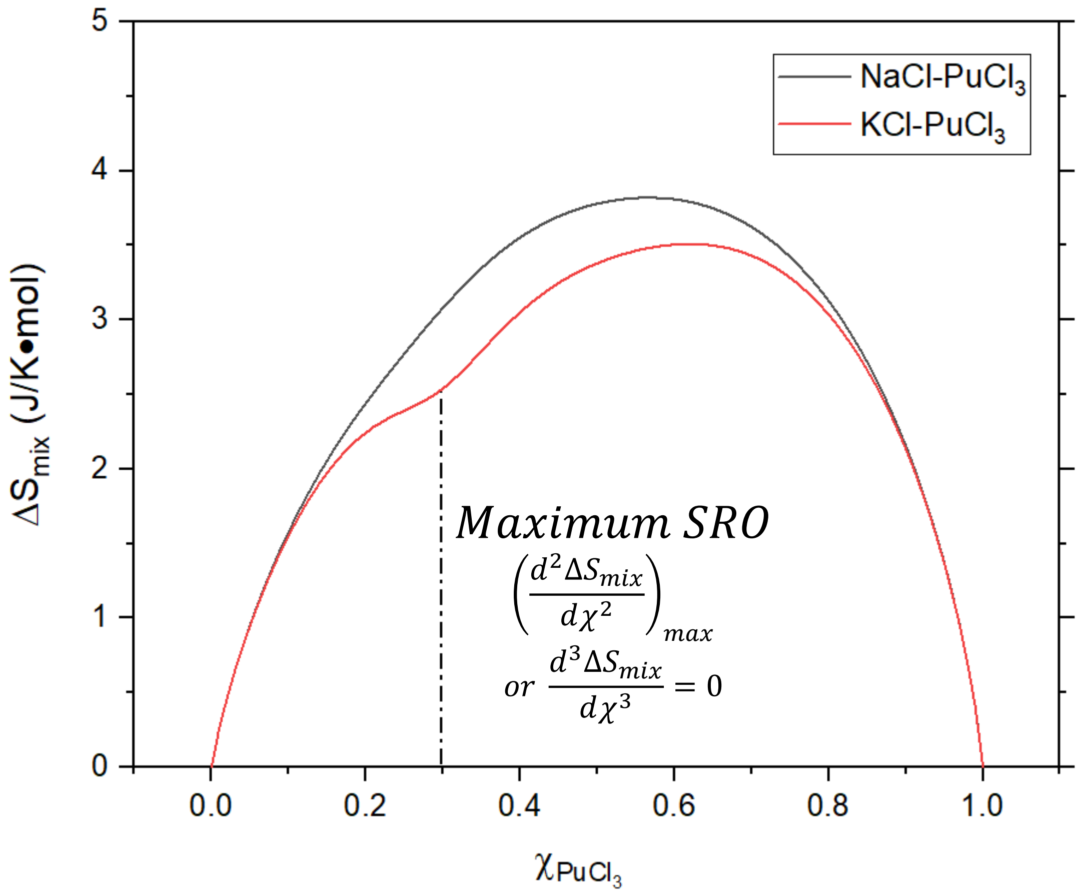
Negative slopes: $(U,Pu)Cl_3$

- Consumption of UCl_3 is faster than breeding of $PuCl_3$.
- Brings UCl_3:$PuCl_3$ ratio closer to their eutectic composition.

Discussion: Interaction between Fuel Constituents

Plotting entropy of mixing (ΔS_{mix}) curves at $1000°C$:





Maximum SRO occurs at $\chi_{PuCl_3} = 0.30$, meaning K^+ and Pu^{3+} ions prefer to order near the stoichiometries of K_2PuCl_5 and K_3PuCl_6 in liquid fuels.

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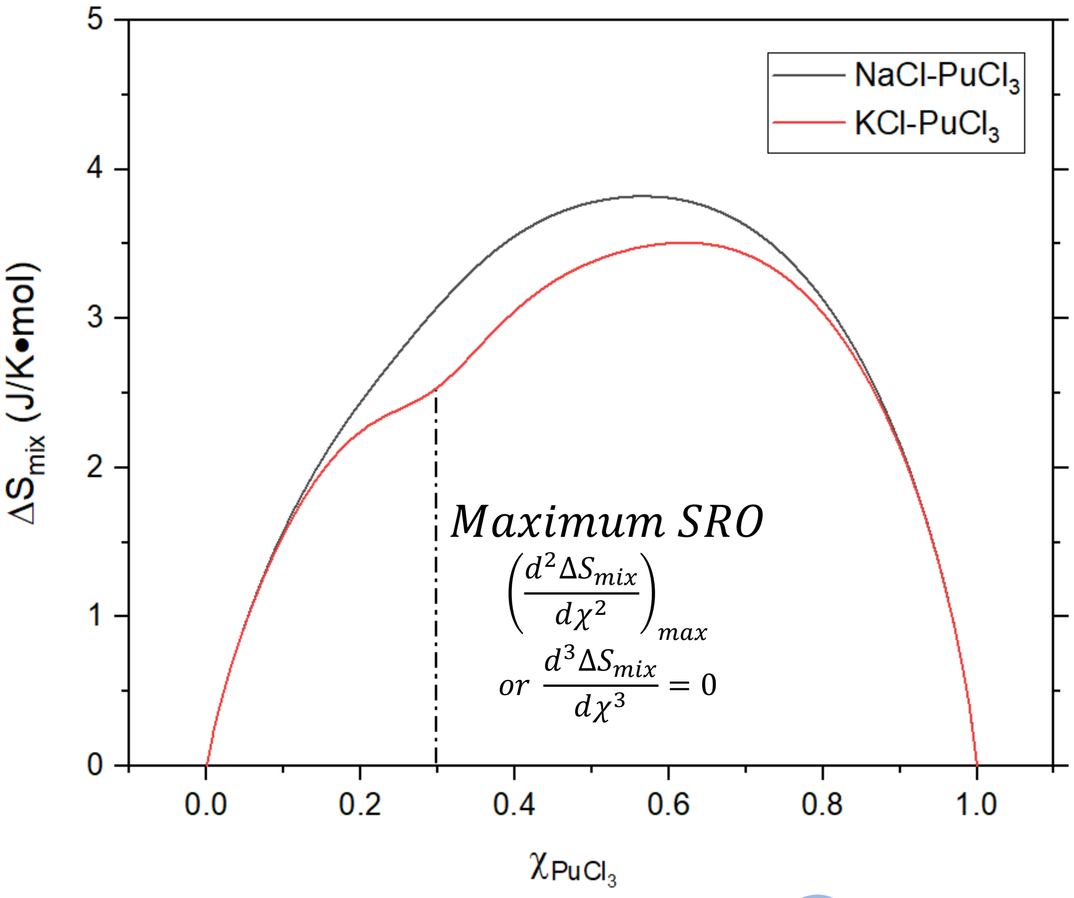
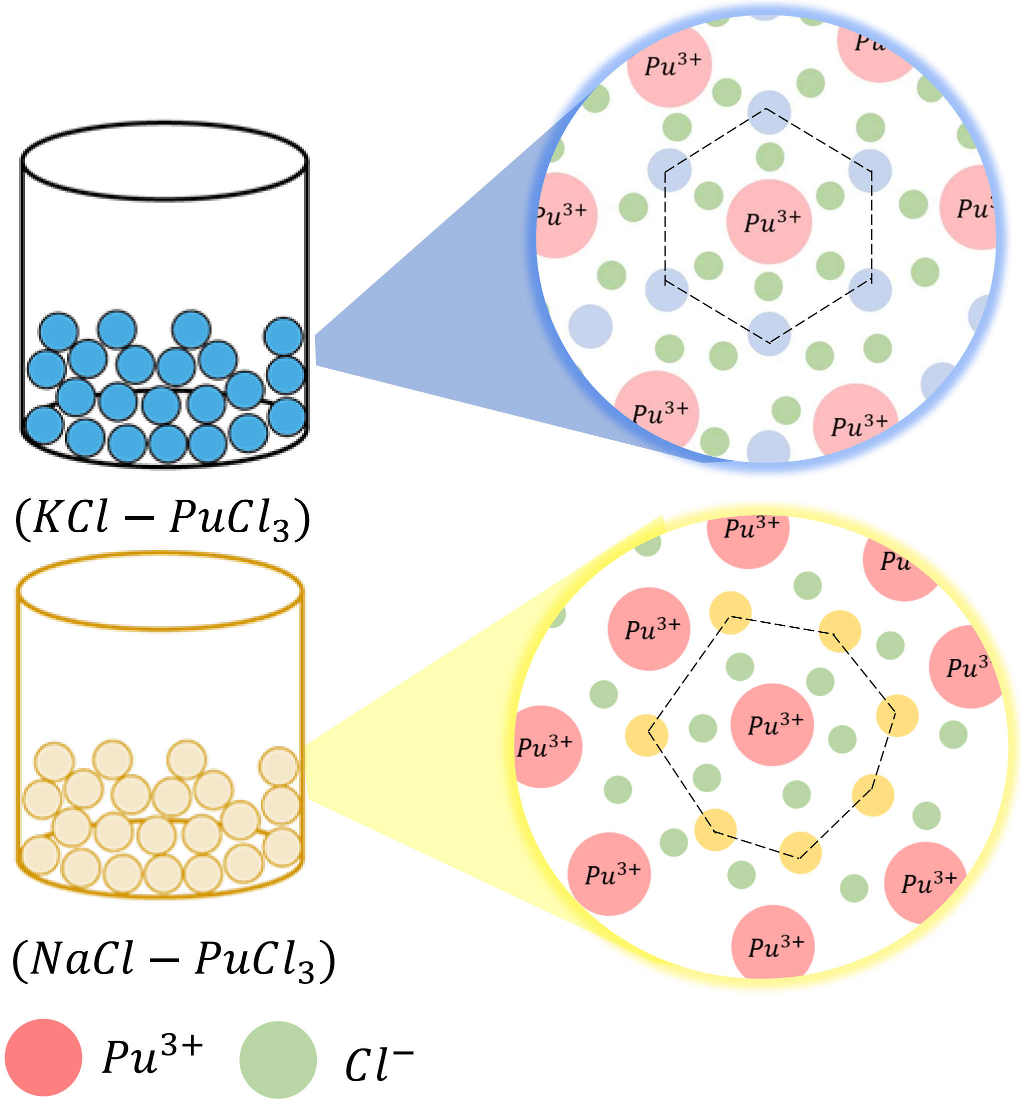
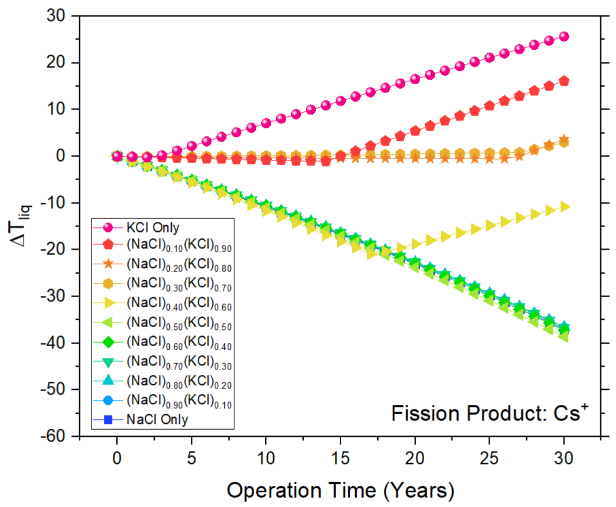
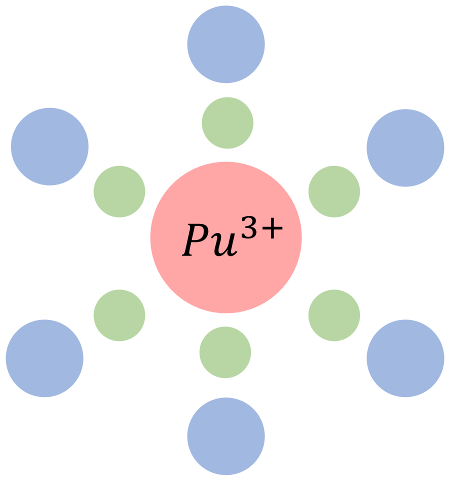
Discussion: Interaction between Fuel Constituents



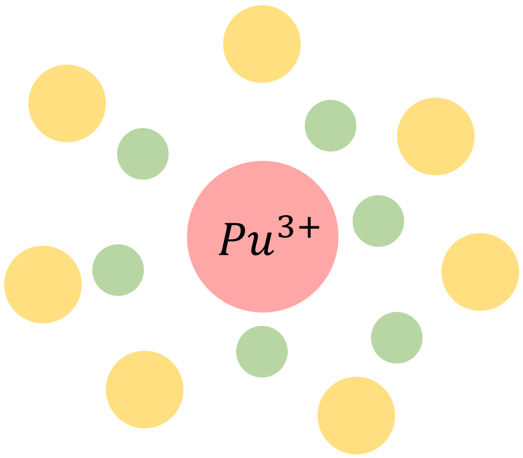


Recap & Implications





$(KCl - PuCl_3)$



$(NaCl - PuCl_3)$

- CALPHAD simulations showed that the transient behavior of MSR fuels depends primarily on the interactions between the base salt and actinide content.
- Due to short-range ordering between KCl and actinide chlorides, there is a large tendency for intermediate compound formation, which may cause inadvertent freezing during reactor operation.
- KCl should be used in tandem with NaCl as base salt to lower the fuel liquidus temperature, increase actinide solubility*, and mitigate intermediate compound formation.

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*KCl increases $AnCl_3$ solubility in $NaCl$, not vice versa.

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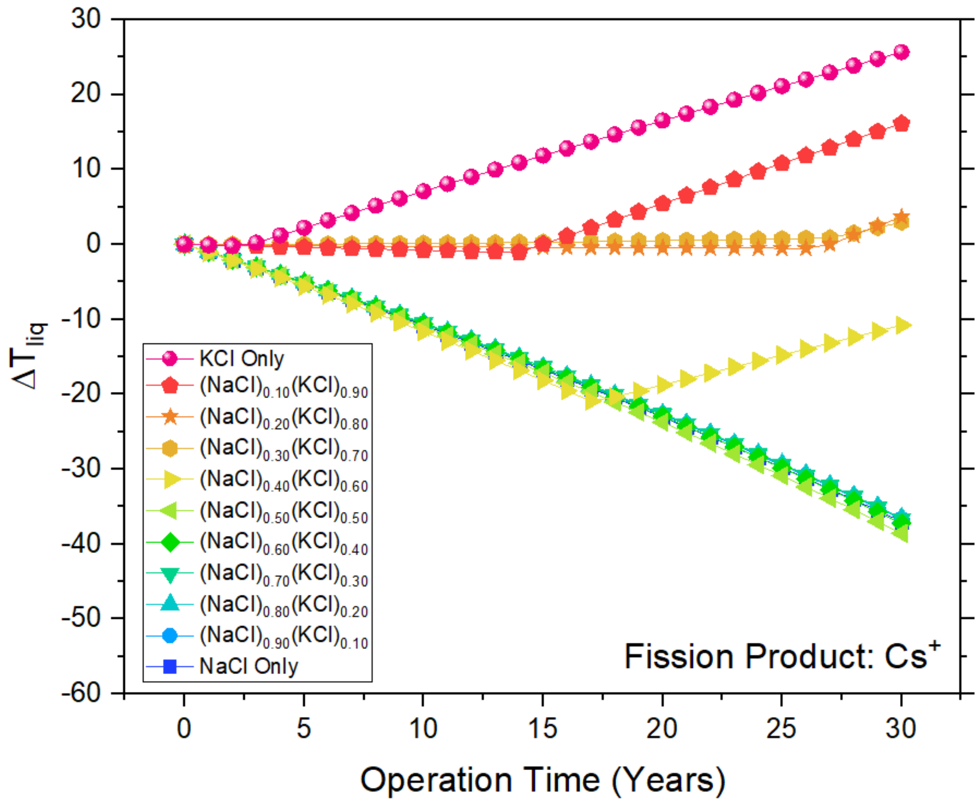
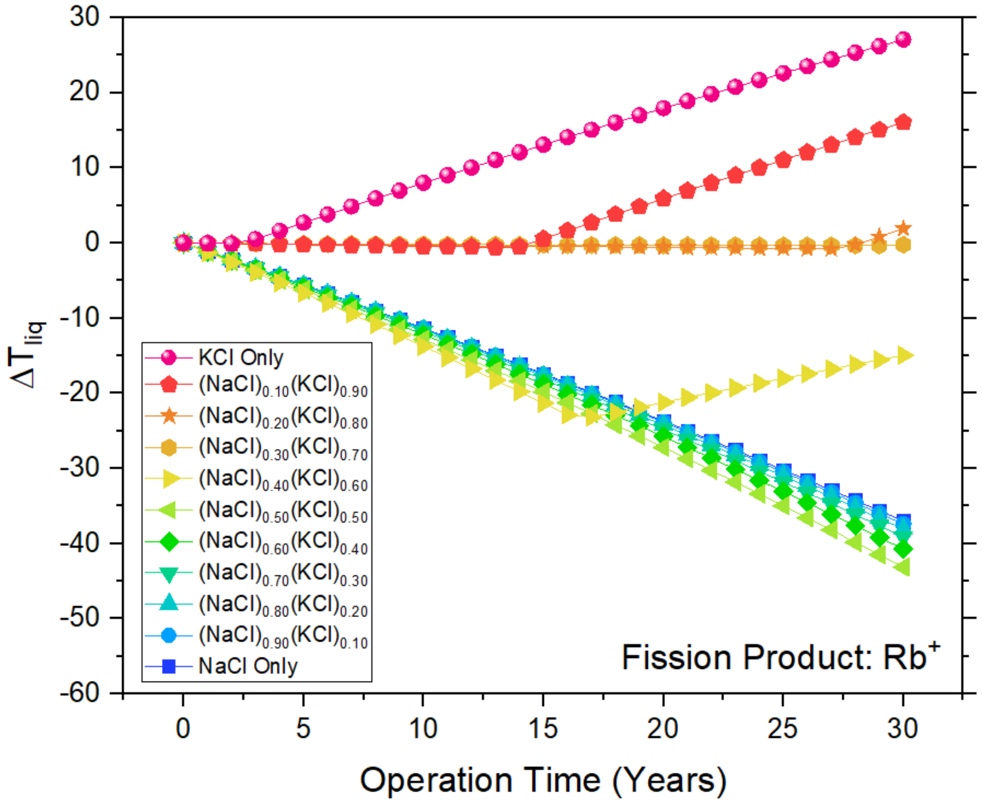
Q & A

Results: Liquidus Temperature Change of MSR Fuel

- The observed trends are similar for both Rb^+ and Cs^+.





Inference: The response of the fuel liquidus to FP evolution is largely independent of the FP species, but dependent on the interactions between the base salt and actinide content.

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