Thermochemistry of fuel, fission products and corrosion products in Molten Salt Reactor

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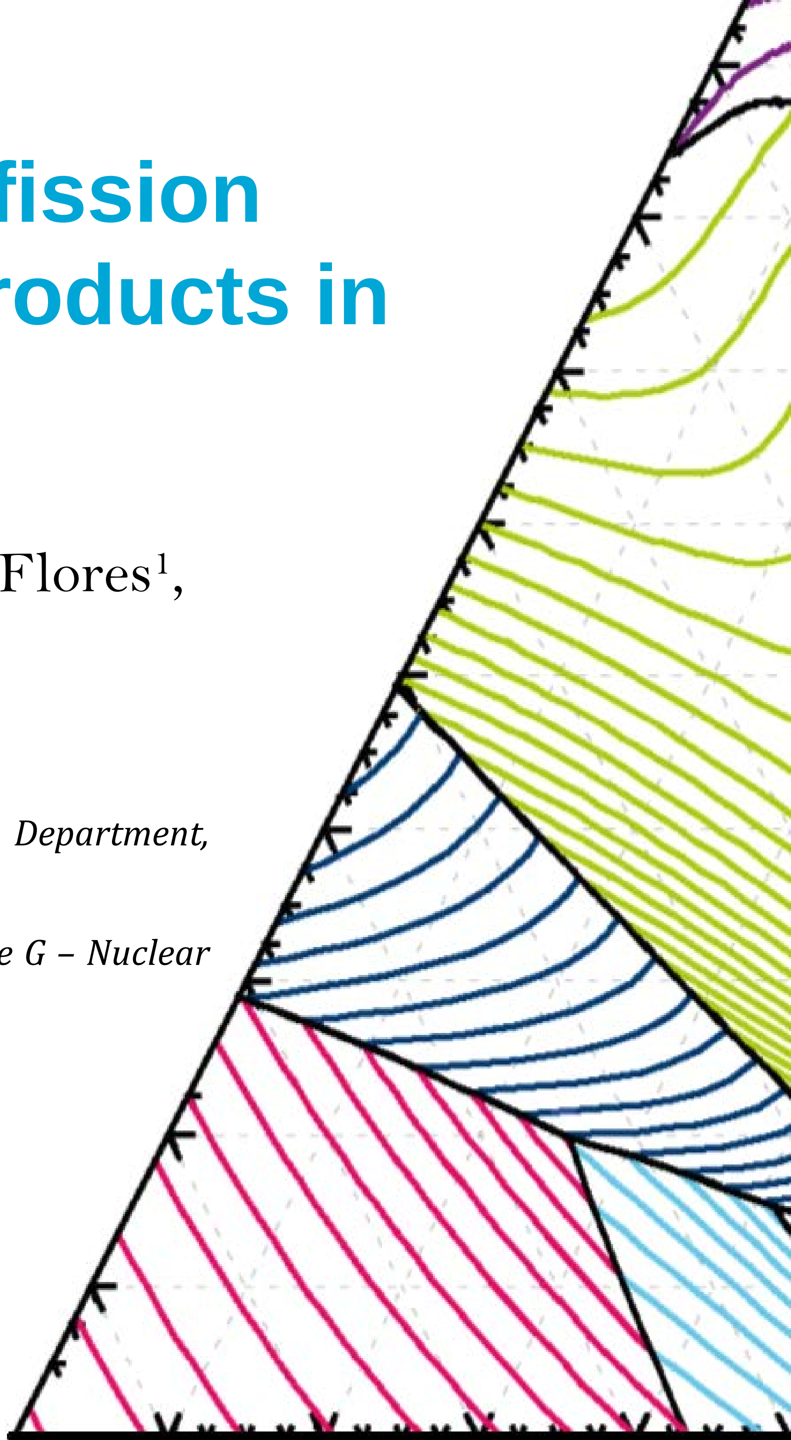

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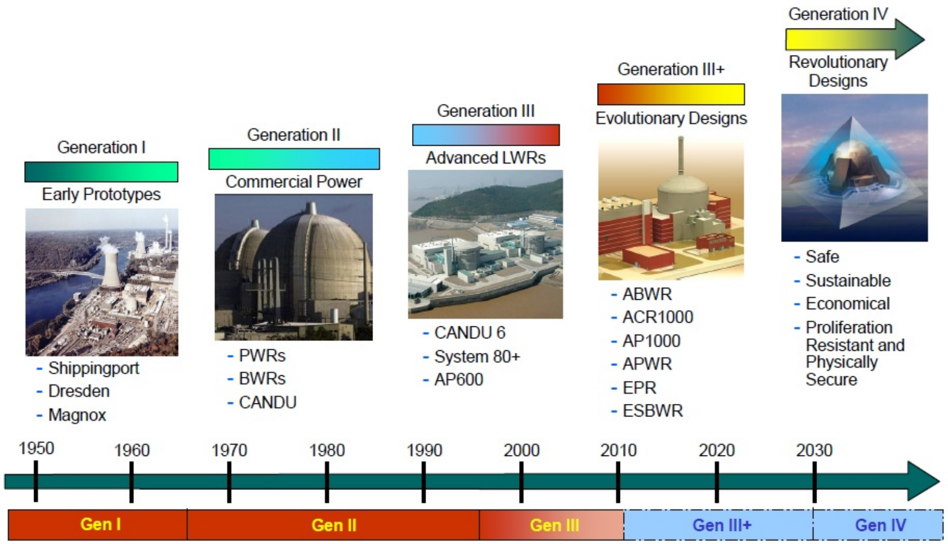
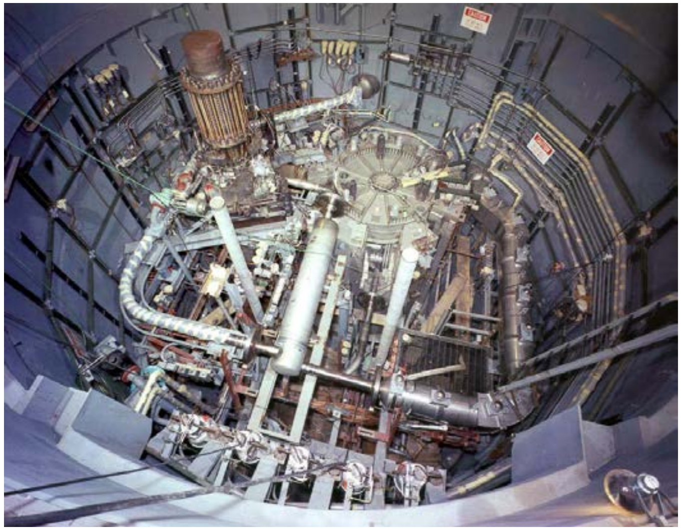
Background and context of research

- The **Molten Salt Reactor** is among the most promising future nuclear fission reactor technologies as defined by the Generation IV International Forum. It is **safe, sustainable, economical** and **proliferation resistant.**

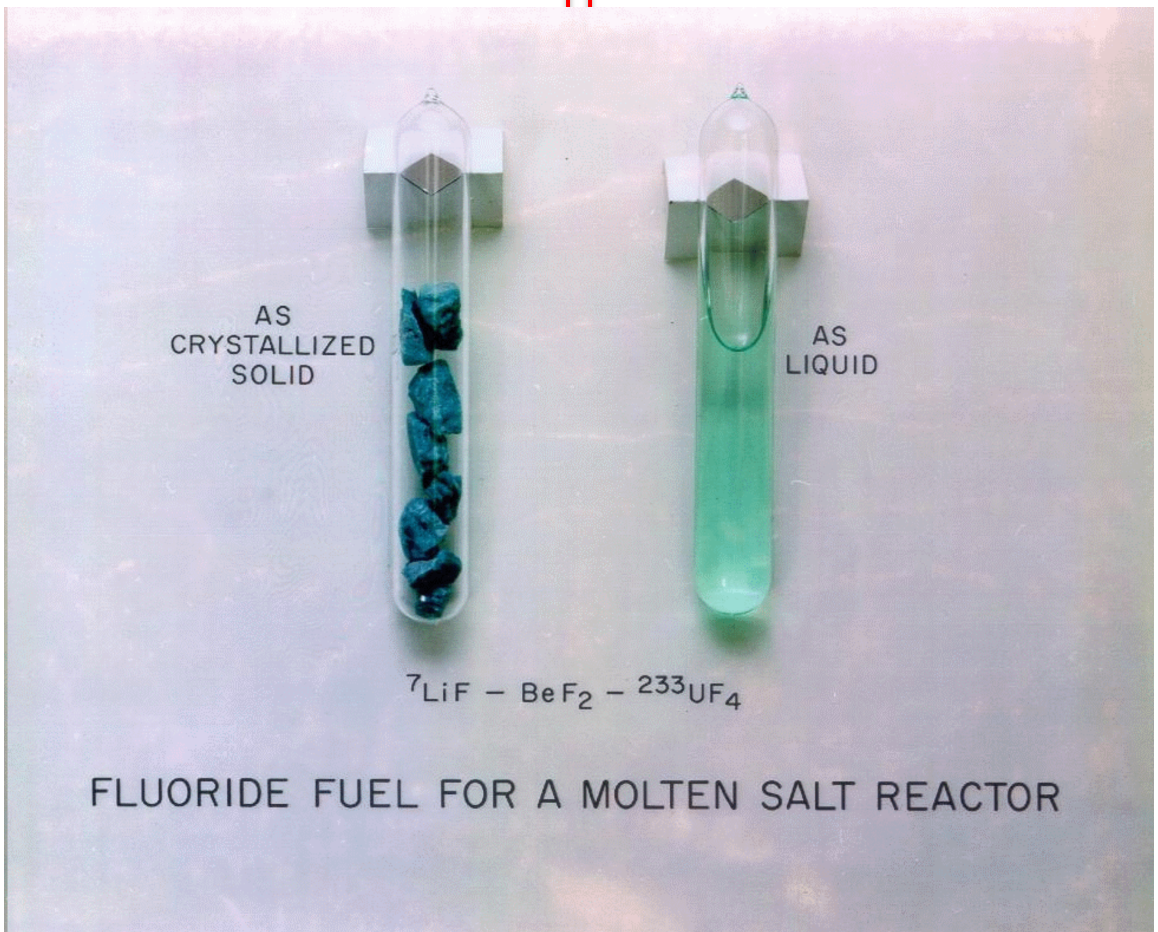




Molten Salt Reactor - components

FUEL

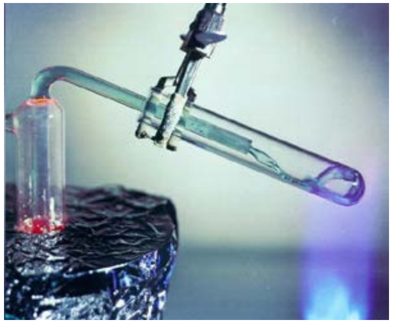
COOLANT



Molten Salt Reactor - Fuel

Which are the constrains for a liquid fuel?

- NEUTRONIC PROPERTIES
  - small capture cross section, moderation capability, low neutronic activation, stable under irradiation
- CHEMICAL PROPERTIES
  - chemical stability, low corrosion, chemical reactivity, actinide solubility, salt clean-up
- THERMAL AND TRANSPORT PROPERTIES
  - Low melting point
  - Low vapour pressure and high boiling point
  - Large heat capacity
  - High solubility of actinides
- ECONOMIC FEATURES



Molten Salt Reactor – Fuel options

Only a limited number of compounds are suitable from neutronic considerations and **fluoride salts** are one of the best candidates.

BASIC MIXTURE

- $^{7}LiF - ThF_4 - UF_4$
- $^{7}LiF - ThF_4 - PuF_3 - UF_4$
- $^{7}LiF - BeF_2 - ThF_4 - UF_4$

+ additional components to improve the fuel properties if needed (NaF, KF, CaF_2,..)

CORROSION PRODUCTS

Element	Hastelloy-N (INOR-8)
Ni	Base
Cr	7.52
Mo	16.28
Ti	0.26
Fe	3.97
Mn	0.52
Nb	–
Si	0.5
Al	0.26
W	0.06
Cu	0.02
Co	0.07
Ce	–
Zr	–
B	<0.01
S	0.004
P	0.007
C	0,05

FISSION PRODUCTS

Fission product	Yield
Kr+Xe	0.606
Lanthanides + Y	0.538
Zr	0.318
Sr+Ba	0.072
Br+I	0.015
Rb+Cs	0.004
Mo	0.201
Ru	0.126
Tc	0.059
Nb	0.014

IRRADIATION

Thermodynamic modelling

DEVELOPMENT OF A THERMODYNAMIC DATABASE ON RELEVANT FLUORIDE SALTS

FUEL COMPOSITION OPTIMIZATION

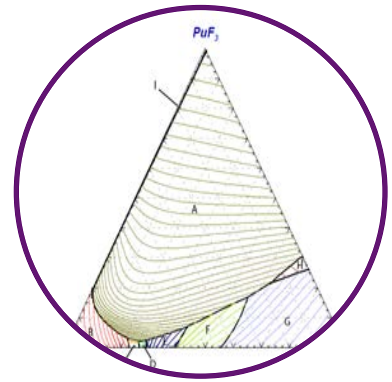
ADDITION OF FISSION PRODUCTS AND CORROSION PRODUCTS TO THE DATABASE

COMPLETE UNDERSTANDING OF FUEL BEHAVIOUR IN OPERATIONAL AND ACCIDENTAL CONDITIONS

Database development

EXPERIMENTAL MEASUREMENTS

- Thermodynamic properties of pure compounds (heat capacity, enthalpy of fusion,..)
- Phase determination/stability
- Equilibrium data for phase diagram studies
- Vapor pressure/composition



THERMODYNAMIC MODELING

- Assessment of binary and ternary phase diagrams
- DFT calculations
- Gas phase properties estimates

Thermodynamic model

Binary and ternary system are assessed according to the CALPHAD approach. Three databases were developed:

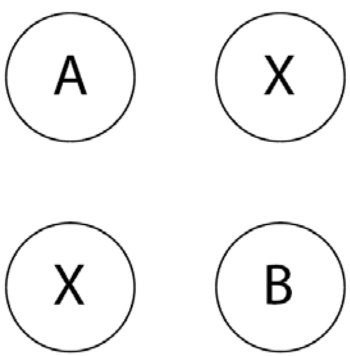
❖ **<u>Pure end-members and intermediate compounds</u>**

❖ **<u>Solid solution</u>**

❖ **<u>Liquid solution</u>**

Modified Quasi-chemical Model - Two sublattice Quadruplet approximation

- Two sublattices: (A,B,…) cations and (X,Y,…) anions
- Variable composition of short range ordering
- Simultaneous treatment of FNN and SNN interactions



FLUORIDE SYSTEMS (common-anions systems)

$$(A-X-A)+(B-X-B)=2(A-F-B) \qquad \Delta g_{AB/X}$$

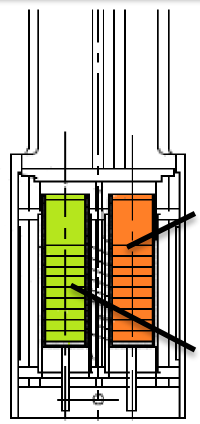
Experimental data

Requirements for fluorides samples:

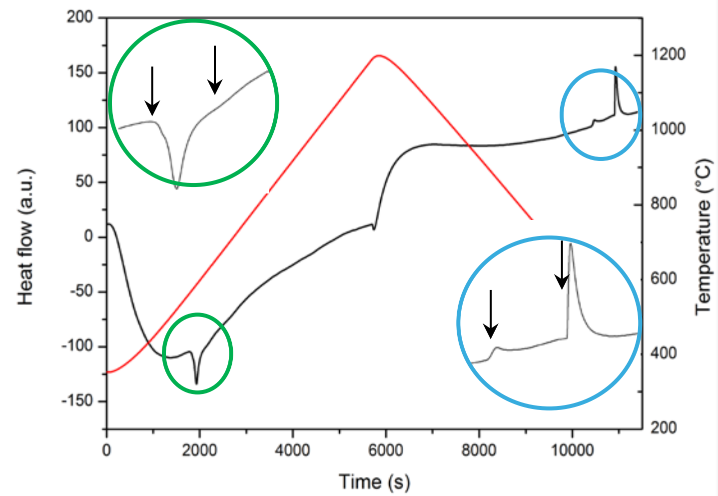
- Purification step
- Inert atmosphere
- Encapsulation technique

Experimental techniques:

- Differential Scanning Calorimetry
- X-ray Diffraction
- Knudsen Effusion Mass Spectrometry



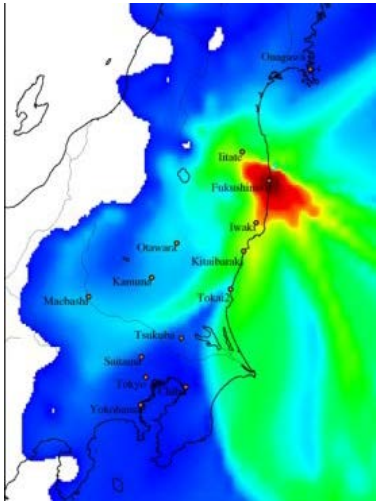
Differential Scanning Calorimetry



Example of assessed systems

Fuel salt with fission products

- $LiF-ThF_4-CsF-CsI$ system



Fission products with relatively high production yield which deserve strong attention due to their volatility and radiological effects in accidental scenarios.

Fuel salt with corrosion products

- $LiF-NiF_2$, $NaF-NiF_2$, $KF-NiF_2$ phase diagrams

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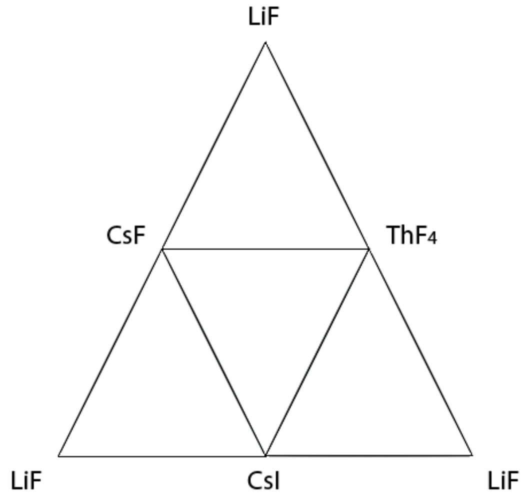
Fuel salt with fission products

Assessment of the LiF-ThF_4-CsF-CsI system:

:

- **CsI** is the most stable iodide in the considered mixture
- **CsF** is also formed by the cesium in excess
- Little / negligible presence of I and I_2
- Little / negligible presence of Cs
- Little / negligible presence of IF_x compounds



- ✓ LiF-ThF_4
- ✓ CsF-ThF_4
- ✓ LiF-CsF
- ✓ CsI-CsF
- ✓ LiF-CsI
- ✓ CsI-ThF_4

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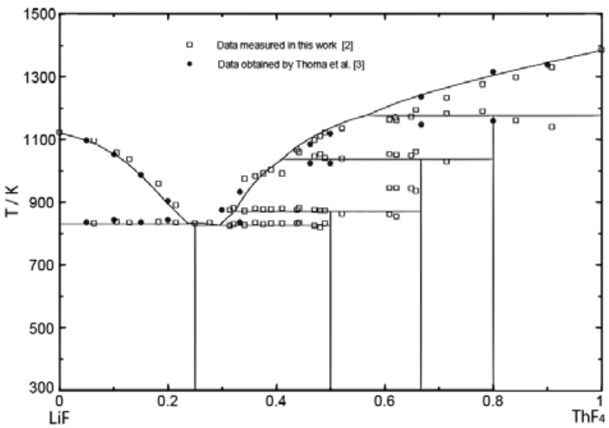
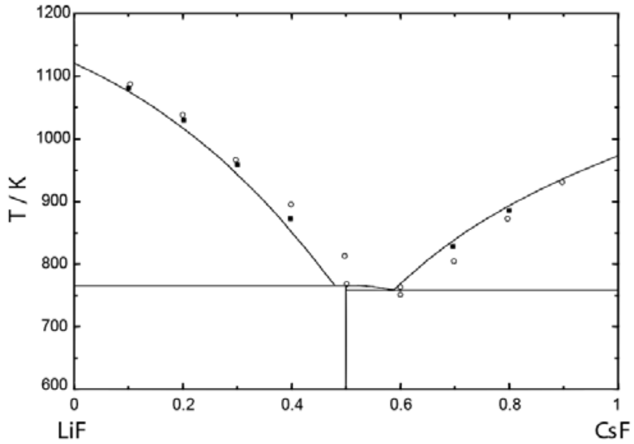
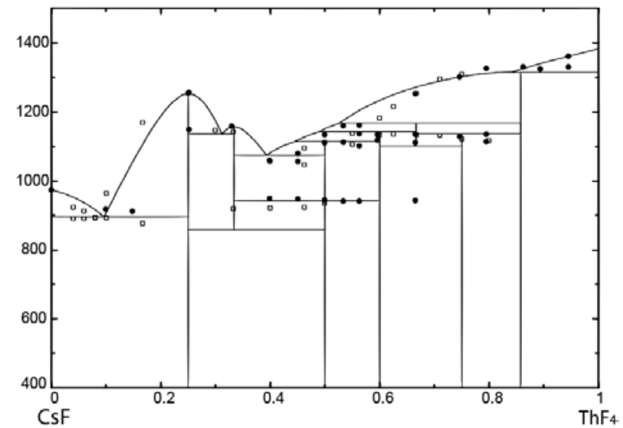
Binary phase diagrams – (I)







LiF-ThF$_4$ system

- Phase equilibrium points
- Enthalpy of mixing
- LiF and ThF$_4$ activities
- Li$_3$ThF$_7$ enthalpy of fusion

LiF-CsF system

- Reviewed properties for CsF
  (Beneš et al. 2013)
- Phase equilibrium points
  (*Bukhalova 1965; Thoma et al. 1975*)
- Enthalpy of mixing
  (*Holm and Kleppa 1968*)

CsF-ThF$_4$ system

- Phase equilibrium points
- Vapour pressure data
- Activity data for CsF and ThF$_4$ in the liquid solution
- Phase stability

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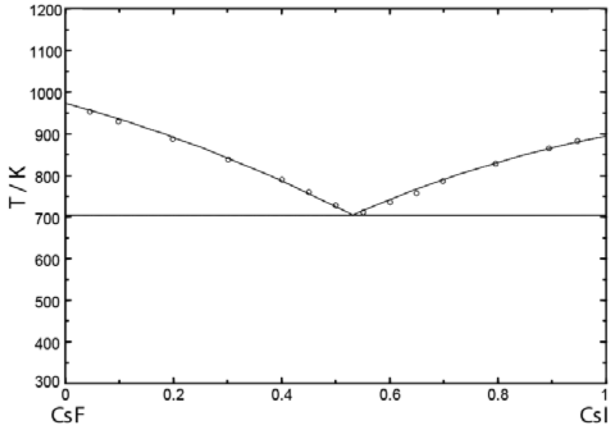
Binary phase diagrams – (II)



CsF-CsI system

- Phase equilibrium points *(Bukhalova et al. 1973)*

LiF-CsI system

ThF_4-CsI system

$$(A_2X_2)_{quad} + (B_2X_2)_{quad} = 2(ABX_2)_{quad} \quad \Delta g_{AB/X_2}$$

$$(A_2X_2)_{quad} + (A_2Y_2)_{quad} = 2(A_2XY)_{quad} \quad \Delta g_{A_2/XY}$$

$$\frac{1}{2}(ABX_2 + ABY_2 + A_2XY + B_2XY) = 2(ABXY)_{quad} \quad \Delta g_{AB/XY}$$

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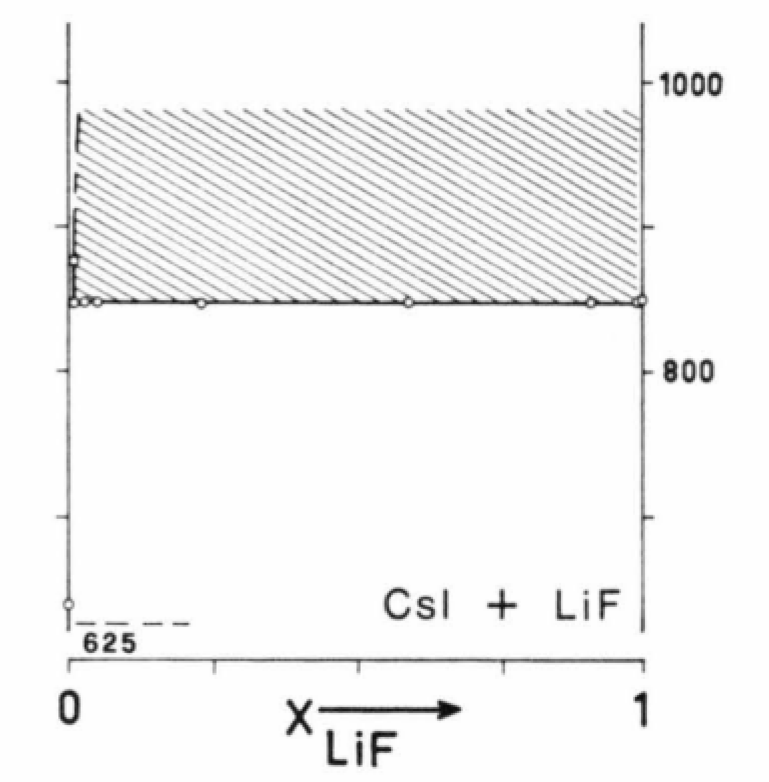
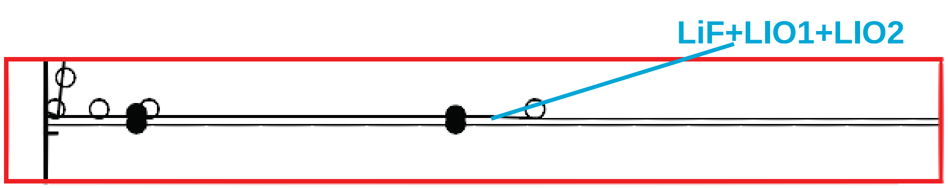
Binary phase diagrams – LiF-CsI

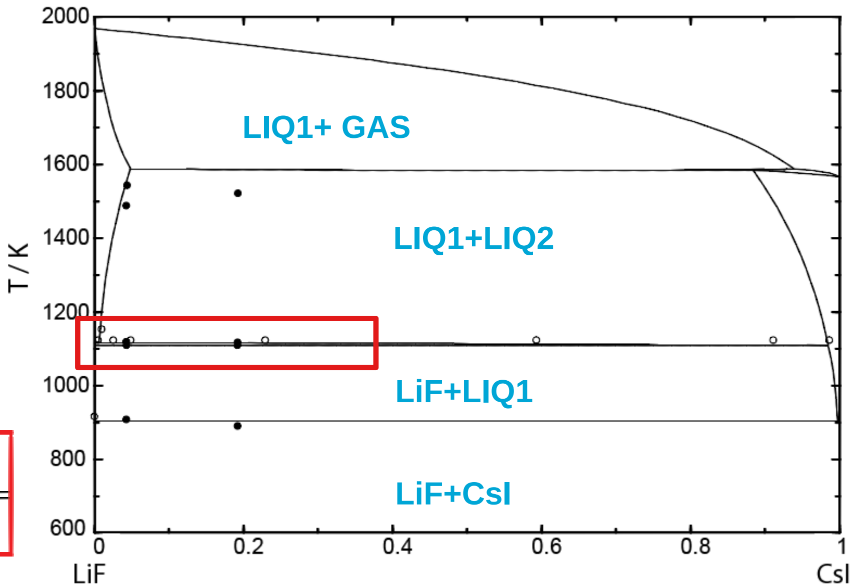
- Phase equilibrium points from literature *(Margheritis,1973)*
- Liquid-liquid immiscibility gap



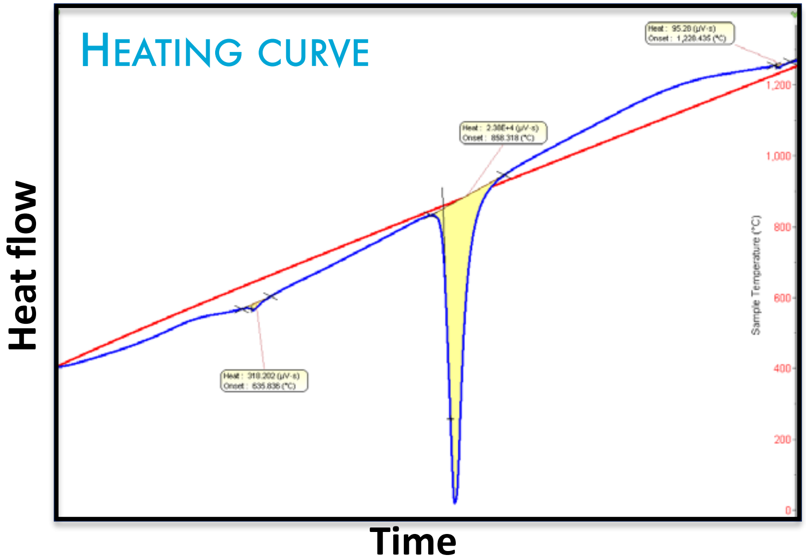
Binary phase diagrams – LiF-CsI

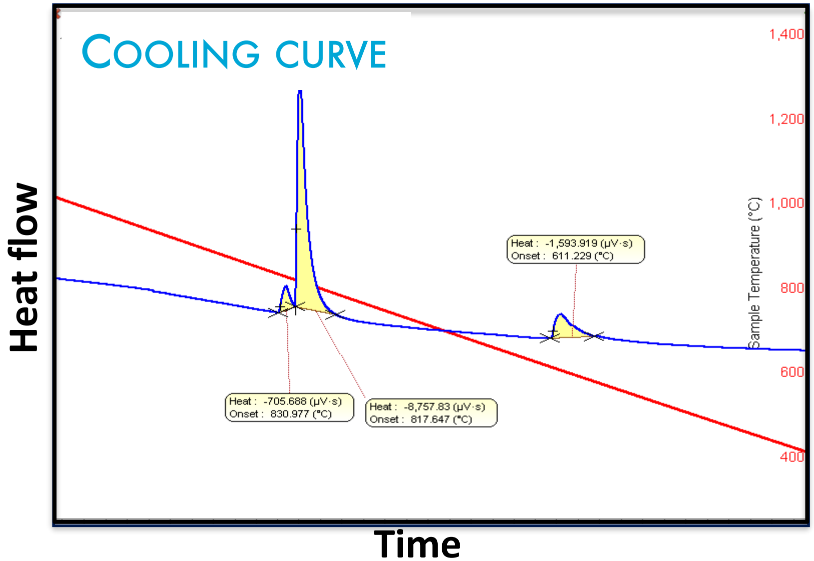
- Phase equilibrium points from literature *(Margheritis,1973)*
- Liquid-liquid immiscibility gap
- New equilibrium point





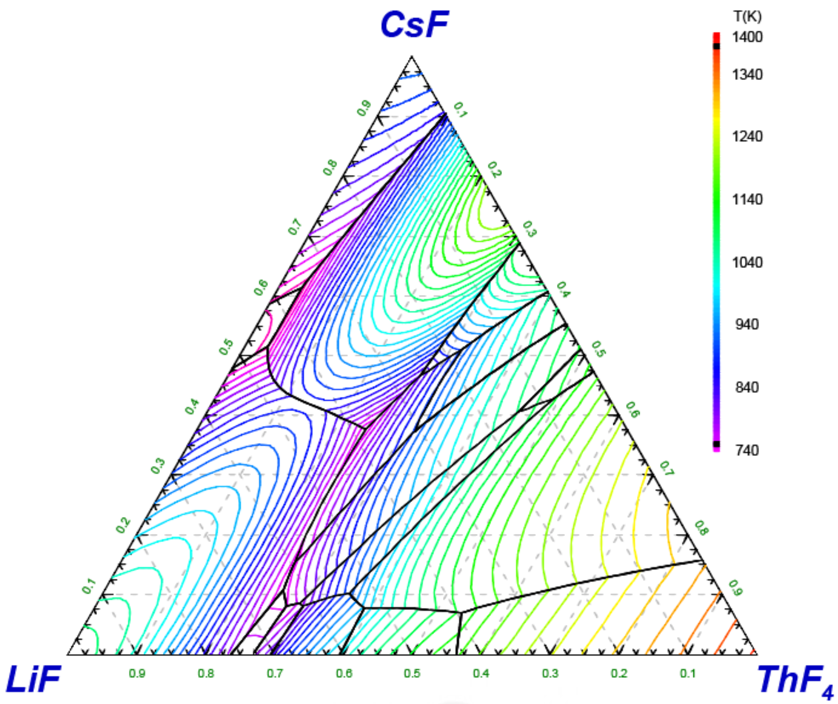
DSC measurement – Sample LiF-CsI (xCsI = 4 mol%)

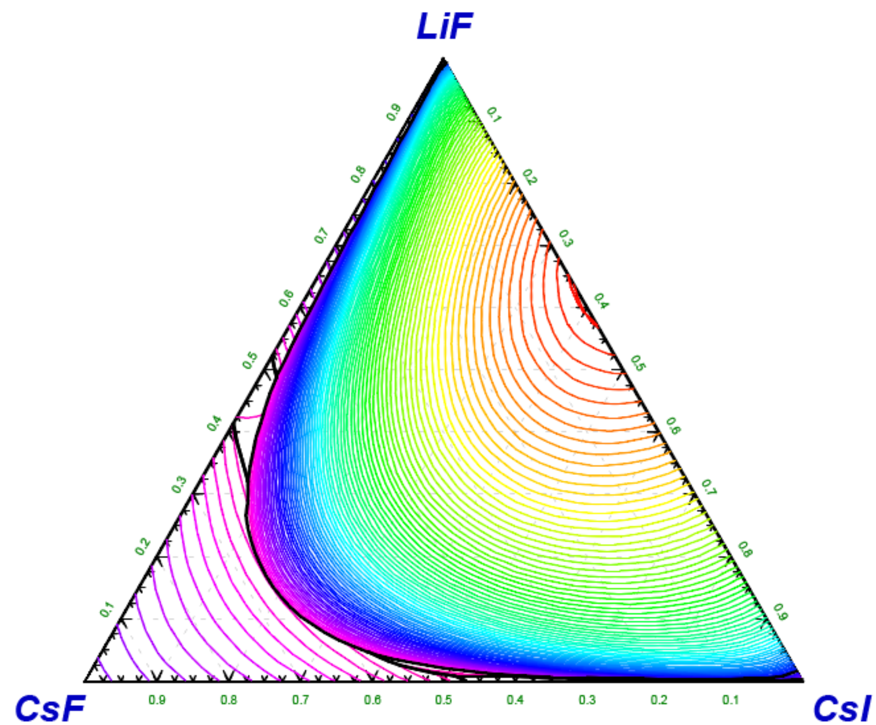




Ternary systems

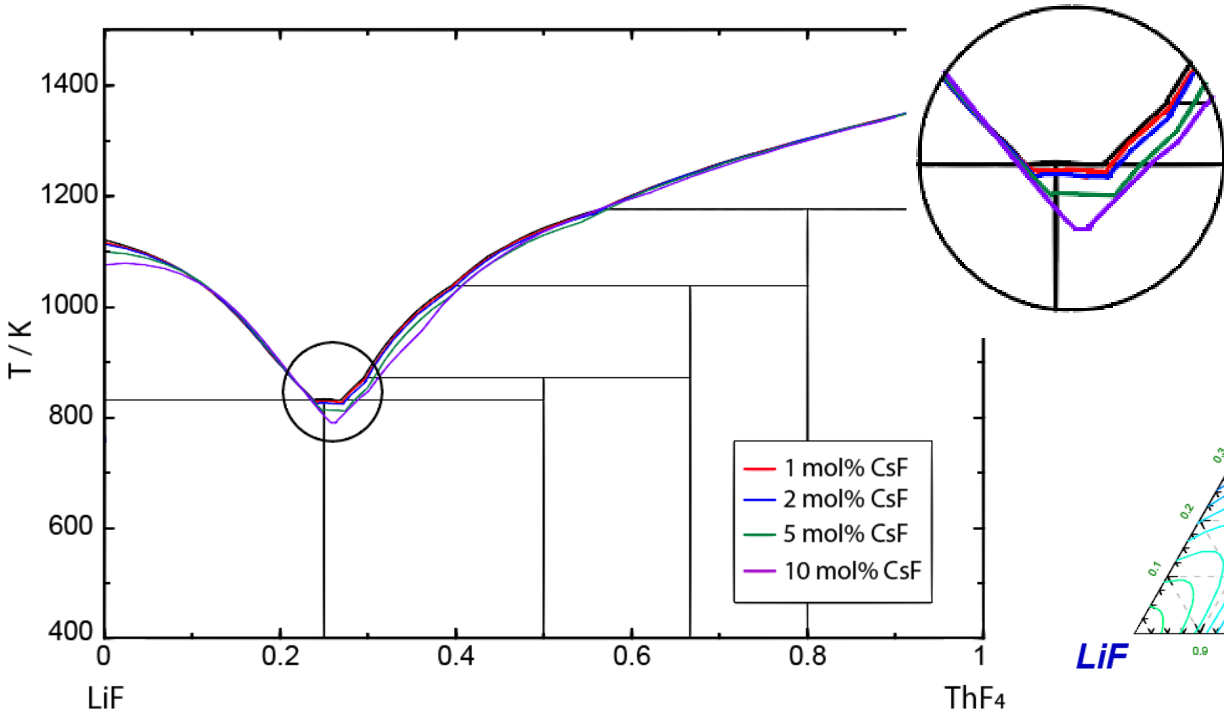
- Extrapolation using Kohler or Kohler/Topp interpolation methods.
- Small ternary parameters were introduced.

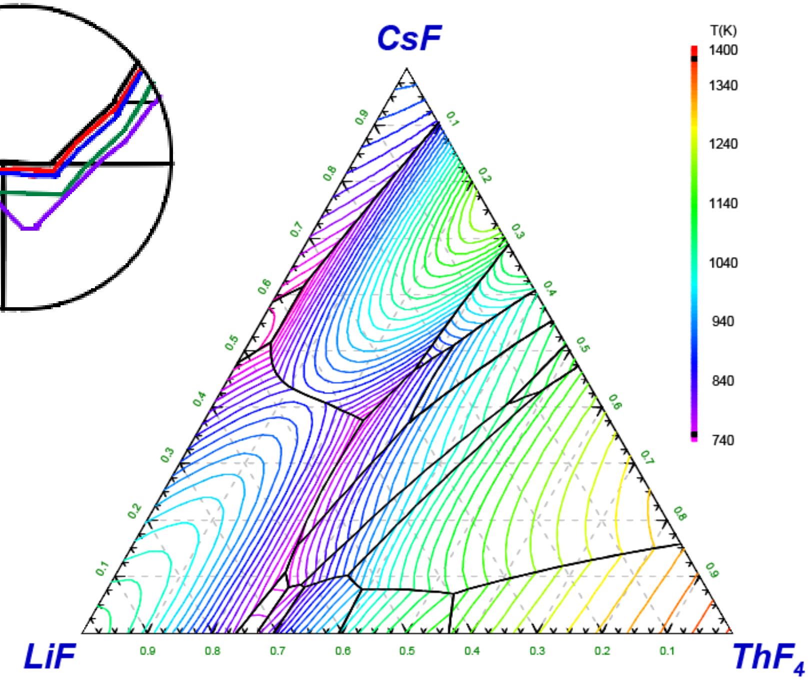




The developed database is a useful tool to predict the fuel mixture properties during operation.

The LiF-CsF-ThF$_4$ system





Fixed LiF/ThF$_4$ ratio

Composition	T liquidus /K	P @ 900 K / Pa
LiF-ThF$_4$ (76.2-23.8)	832 K	$2{,}44 \cdot 10^{-3}$
LiF-ThF$_4$-CsF (75.438-23.562-**1.00**)	834 K	$2{,}74 \cdot 10^{-3}$
LiF-ThF$_4$-CsF (7.676-23.324-**2.00**)	837 K	$3{,}06 \cdot 10^{-3}$
LiF-ThF$_4$-CsF (72.39-22.61-**5.00**)	848 K	$4{,}25 \cdot 10^{-3}$
LiF-ThF$_4$-CsF (68.58-21.42-**10.00**)	871 K	$7{,}38 \cdot 10^{-3}$

Example of assessed systems

- **Fuel salt with fission products**
  - LiF-ThF_4-CsF-CsI system

- **Fuel salt with corrosion products**
  - LiF-NiF_2, NaF-NiF_2, KF-NiF_2 phase diagrams

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Corrosion products in MSRs

- **Ni-based alloys** are found to withstand harsh operational conditions in MSRs (high temperatures, contact with corrosive salts)

- **The redox potential** of the salt is a key parameter for corrosion issues and it is controlled by the **UF_4/UF_3 ratio.**

- However during **irradiation**, this ratio increases and corrosion products can be dissolved in the mixture:

$$\mathrm{Cr\ (alloy) + 2UF_4\ (salt) \rightarrow CrF_2\ (salt) + 2UF_3\ (salt)}$$

$$\mathrm{Ni\ (alloy) + 2UF_4\ (salt) \rightarrow NiF_2\ (salt) + 2UF_3\ (salt)}$$

Study of the phase equilibria of fuel salt with corrosion products as a function of temperature and salt composition

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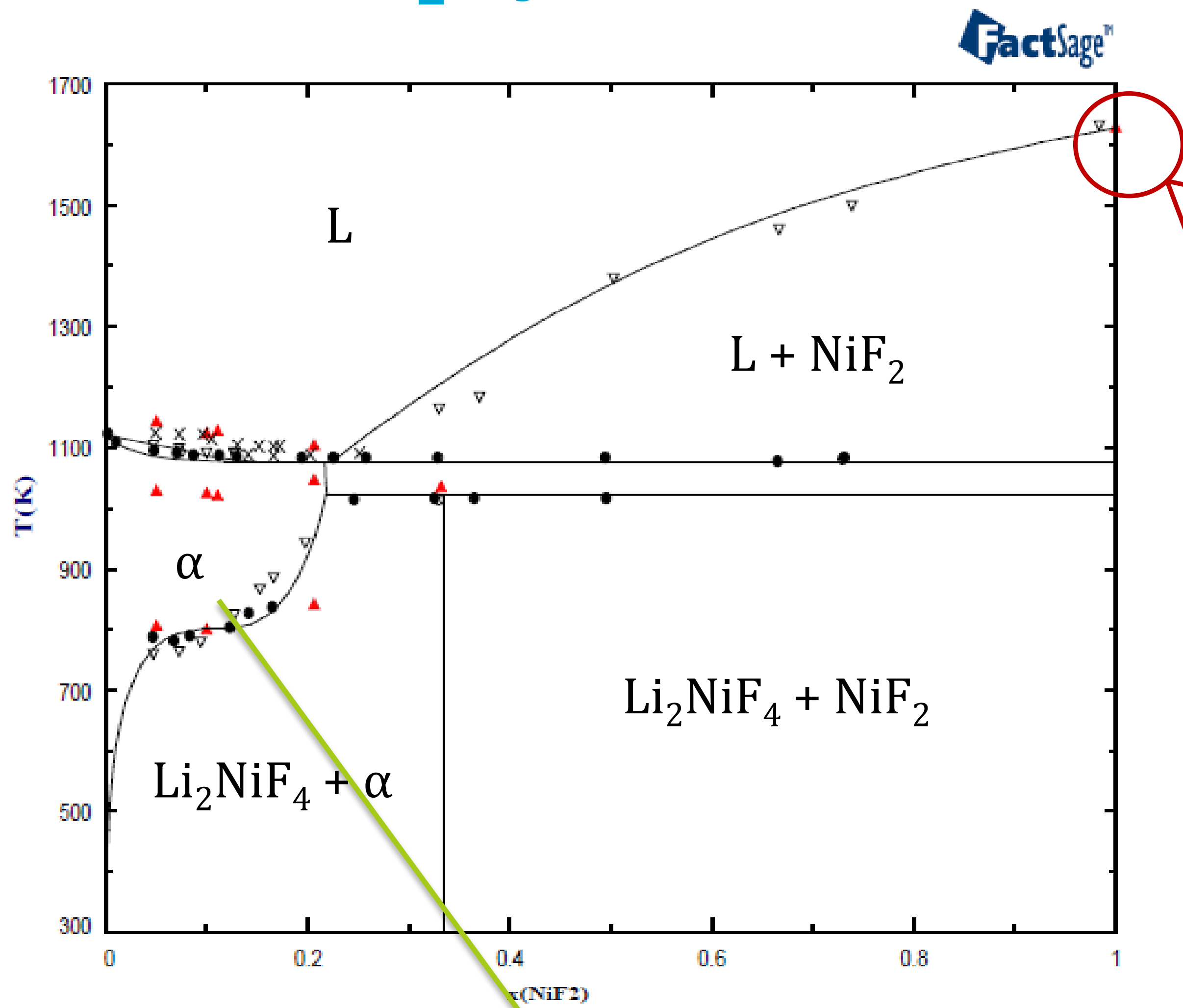
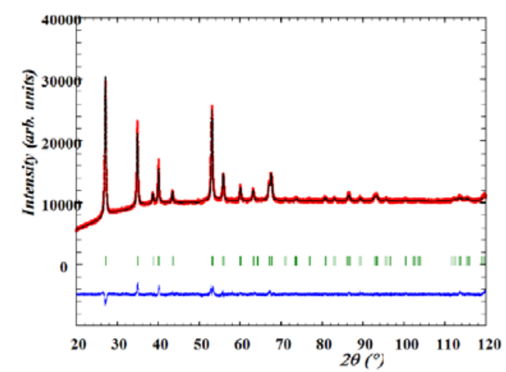
The LiF-NiF_2 system



Pure NiF_2 synthesis
T_{fus} = (1628 ±5) K



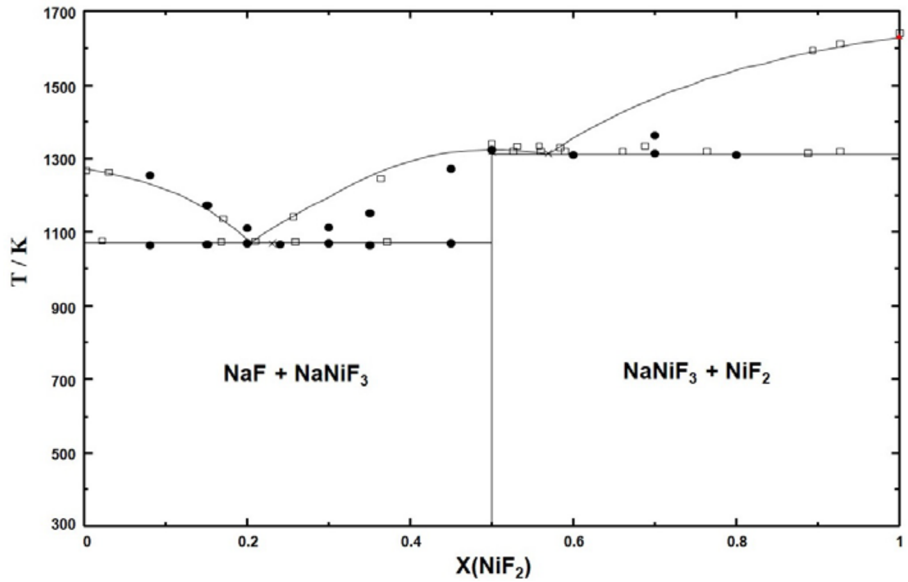
(b) XRD

☞ **Solid solution α = ($Li_{1-2x}Ni_xF$)**

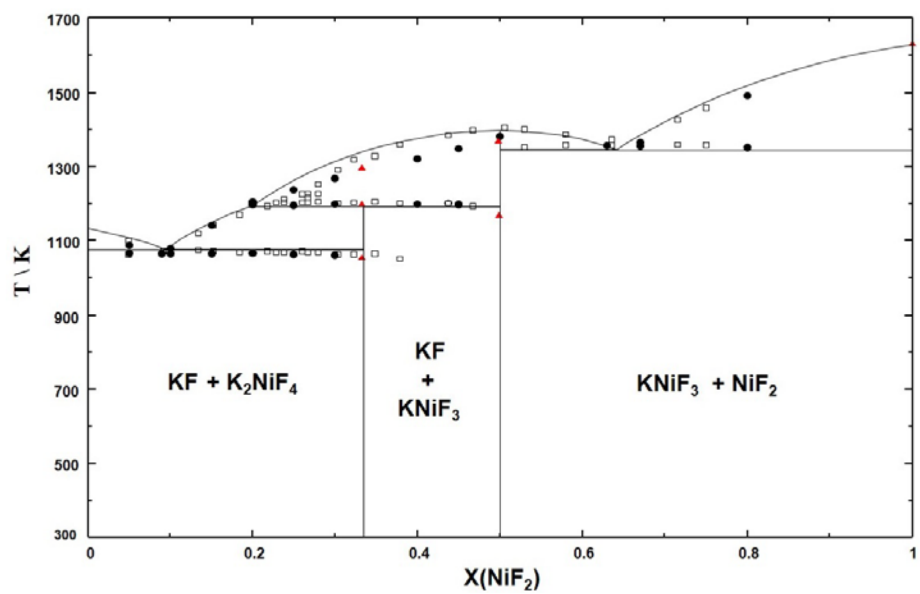
Petrov et al., 1961.

The NaF-NiF$_2$ and KF-NiF$_2$ systems

- ▲ This work
- ● Kalinnikov et al 1999.
- □ Petrov et al, 1952.
- × Thoma et al., reproduced from Mamantov and Smith, 1975.



- ▲ This work
- ● Kalinnikov et al, 1999.
- □ Wagner and Balz, 1952.



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Conclusion

- The generation of a reliable and consistent thermodynamic model is very important for multi-components system, such as the molten salt fuel mixture.

- A database containing the most relevant fluoride salts, including fission products and corrosion products is being developed in collaboration between the Joint Research Centre - Karlsruhe and Delft University of Technology.

- It is a powerful tool which allows the optimization of the fuel composition for MSR fuels and the prediction of their thermodynamic properties and behaviour during irradiation.

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Thank you