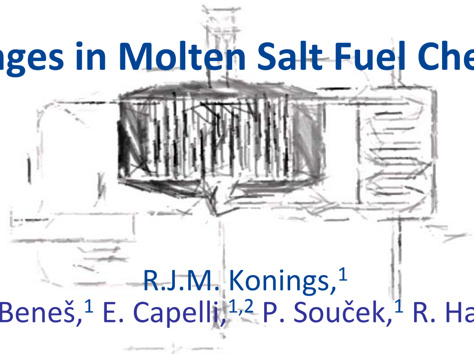
Challenges in Molten Salt Fuel Chemistry



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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 clean-up technology

Only a limited number of metals is suitable from neutronic consideration

Solvent/fuels for MSR

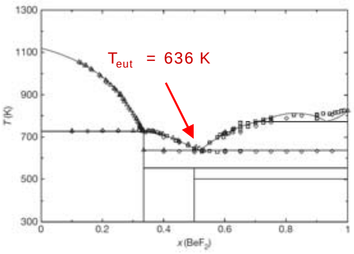
Solvent

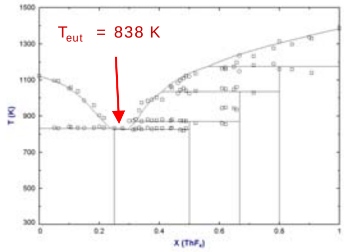
Fissile Material

Oxygen getter

ARE	NaF - ZrF_4	- UF_4	
MSRE	^7LiF - BeF_2	- ZrF_4	- UF_4
MSBR	^7LiF - BeF_2	- ThF_4	- UF_4
MSFR	^7LiF -	ThF_4 -	UF_4

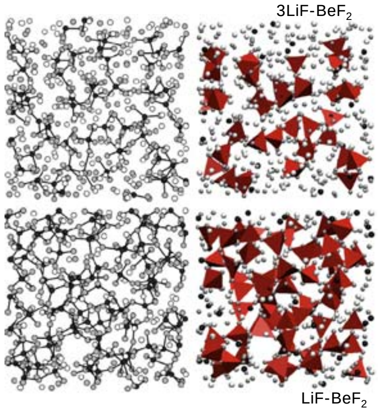
Fertile Material





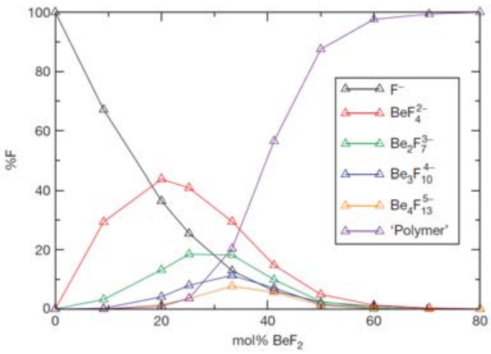
Structure of a molten fluoride salt

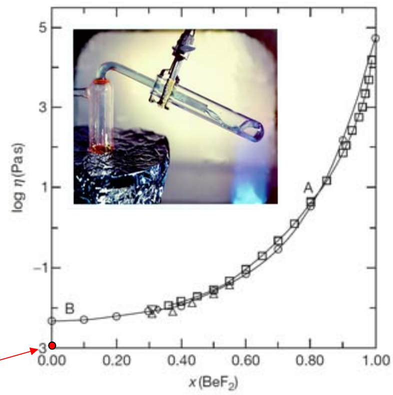
- LiF is a strongly ionic liquid: Li^+ and F^- species
- BeF_2 is a polymeric liquid: $Be_nF_{3n+1}^{-(n+1)}$ species
- ThF_4 is a molecular liquid: ThF_5^- and ThF_6^{2-} species



Picture from: M. Salanne et al., in: Molten Salts Chemistry, Chapter 1, Elsevier, 2013.

Structure & properties of the salt

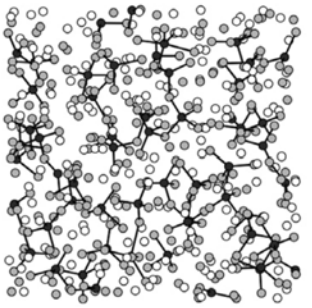


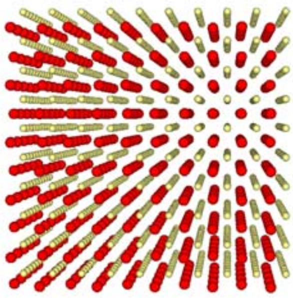


Percentage of F atoms involved in various species observed in the LiF–BeF_2 system as a function of composition (Salanne et al. J. Phys. Chem. B, 111, 4678)

Viscosity of LiF-BeF_2 as a function of the BeF_2 concentration at 873 K. (Beneš & Konings, J. Fluor. Chem., 130, 22)

Molten fluoride salt vs. solid oxide fuel





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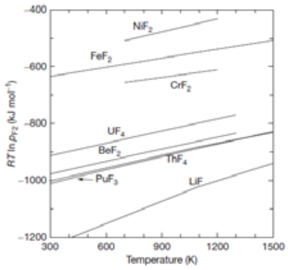
Chemical potential of fluorine

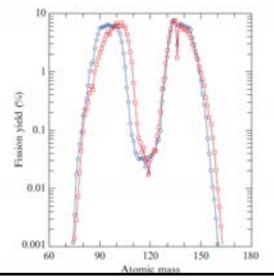
- ✓ is the equilibrium fluorine pressure of a reduction/oxidation reaction:

M(s) + n/2F_2(g) = MF_n(s)

$$K_p = \frac{1}{p(F_2)^{\frac{n}{2}}}$$

- ✓ Fission increases the fluorine potential
  - o The average valence of the fission products is lower than 4+ of uranium





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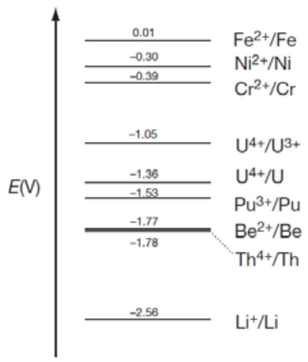
Fluorine potential and electropotential

MF_n(s) = M(s) + n/2F_2(g)

$$\Delta G_r = \mathbf{R}T\ln(p(F_2)) = n\mathbf{F}E$$

UF_4(ss) = UF_3(ss) + ½F_2(g)

$$E = E^0 + \frac{\mathbf{R}T}{n\mathbf{F}}\ln\frac{a(UF_3)}{a(UF_4)}$$



Standard potential in LiF–BeF_2 (66–34) relative to the HF(g)/H_2 couple 1000 K.

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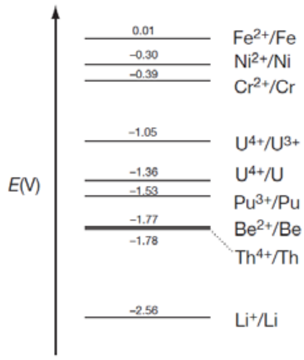
Redox control of the salt

$$UF_4(ss) = UF_3(ss) + ½F_2(g)$$

Options tested in MSRE:

$$2UF_4(sln) + Be(s) = 2UF_3(sln) + BeF_2(sln)$$

$$2UF_3(sln) + NiF_2\,(s) = 2UF_4(sln) + Ni(s)$$



Standard potential in LiF–BeF_2 (66–34) relative to the HF(g)/H_2 couple 1000 K.

Oxygen chemistry of the salt

✓ Oxygen plays an important role in the fuel chemistry

$$ThF_4(sln) + 2O(sln) = ThO_2(s) + 2F_2(g)$$

↓ dissolved ↓ precipitate

- Oxygen concentration in fuel salt must be low ($x_O < 8\ 10^{-4}$)
- Requires fluorination of starting material (with HF(g))
- Control of the oxidation potential of the fuel

Corrosion

1. Reaction with the oxide film on the metal

$$Cr_2O_3(s) + BeF_2(sln) = CrF_2(sln) + BeO(s) + 1/2F_2(g)$$

2. Reaction with impurities from fabrication process

$$Cr(alloy) + 2HF(sln) = CrF_2(sln) + H_2(g)$$
$$Cr(alloy) + FeF_2(sln) = CrF_2(sln) + Fe(s)$$

3. Reaction with fuel constituents

$$Cr(alloy) + 2UF_4(sln) = CrF_2(sln) + 2UF_3(sln)$$

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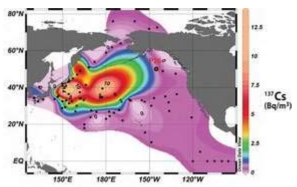
Fission product chemistry of the salt

✓ How well are the fission products retained in the fuel?

$$M(s) + n/2F_2(g) = MF_n(sln)$$



Surface water distribution of cesium-137 from Fukushima in 2012 (Department of Fisheries and Oceans, 2014)

Chemical state of the FPs:

• Dissolved in the liquid salt	Cs, Ba, Sr, Zr, La, I, …
• Metallic precipitates	Mo, Pd, Rh, Tc, Te
• Gas	Kr, Xe

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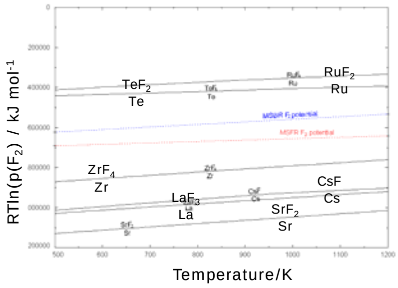


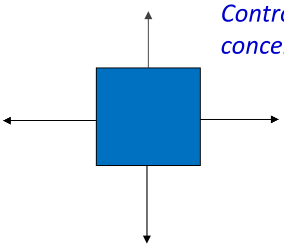
Chemical state of the FPs:

- Dissolved in the liquid salt — Cs, Ba, Sr, Zr, La, I, …
- Metallic precipitates — Mo, Pd, Rh, Tc, Te
- Gas — Kr, Xe

Fuel salt clean-up

Fissile elements

Control and adjust the concentration of U



Dissolves fission products

Lanthanides are strong neutron absorbers

Fission gases

Xe is a strong neutron absorber

Metal particles

Noble plate out on the vessel wall

Fuel salt clean-up

Fluorination:
U(sln) + F_2(g) = UF_6(g)

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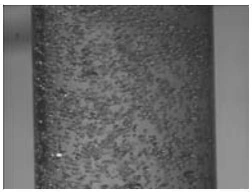
Helium bubbling



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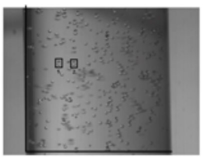
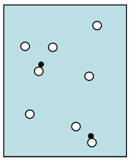
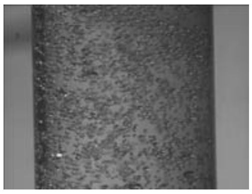


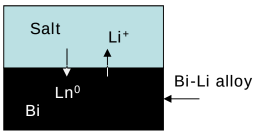




Fuel salt clean-up

Fluorination:
U(sln) + F_2(g) = UF_6(g)

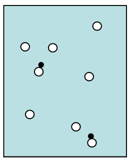
Liquid/liquid extraction

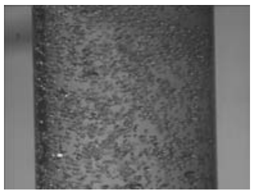


3 Li(sln) = 3Li^+ + 3e
Ln^{3+}(sln) +3e = Ln^0(sln)

Helium bubbling

Helium bubbling





Fuel salt clean-up: Protactinium

$^{232}Th + n \rightarrow {}^{233}Th \rightarrow {}^{233}Pa \rightarrow {}^{233}U$

27 days

^{233}U	^{234}U	^{235}U
	^{233}Pa	^{234}Pa
	^{232}Th	^{233}Th

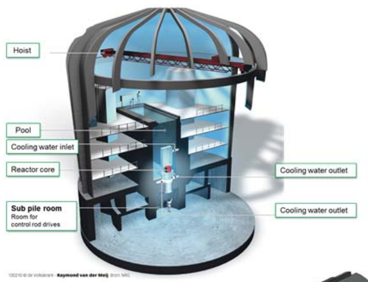
- Pa is co-extracted with the lanthanides
- Must be separated by extraction or electrochemically
- Must be stored to fully decay to ^{233}U
- The ^{233}U will be fed back into the cycle

Challenges in the fuel chemistry

- ✓ Optimise composition with respect to safety margins and properties
  - o Oxygen measurement and control
  - o Redox measurement and control (corrosion)
- ✓ Demonstration of fuel fabrication & purification techniques
- ✓ Understanding of the fission product chemistry and in particular demonstrate the behaviour of Cs, I and Te
- ✓ Optimise and demonstate the clean-up technology
  - o Helium bubbling for metallic particles
  - o Fission product removal using extraction techniques

Collaboration NRG and JRC-ITU

Salient irradiation experiment in HFR-Petten



Goal: Fission product behaviour in salt, graphite and metallic specimens

- ThF_4-LiF eutectic mixture
- AnF_4-BeF_2-LiF eutectic mixture (FLIBE)

- Corrosion-resistant graphite crucible
- Open container (metallic filter) to accommodate FG release
- Crucible wall temperature maintained at T_{melt} + 50 K
- Neutron fluence monitored through activation sets

ITU molten salt Centre of Excellence

Basic electrochemical studies of actinides and Ln in molten **fluoride and chloride** media

Synthesis and purification of **An and Ln fluorides and chlorides**

Demonstration of **pyrochemical separation** methods for **irradiated materials**

High temperature properties of **An halides** and mixtures
- phase diagrams
- melting points
- vapour pressure
- heat capacity

Combined **electrochemistry – spectrometry** (uv-vis, RAMAN, TRLF) of **An chlorides** (and fluorides)

RAMAN spectroscopy of molten salts

NMR high temperature probe for **molten salts**

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