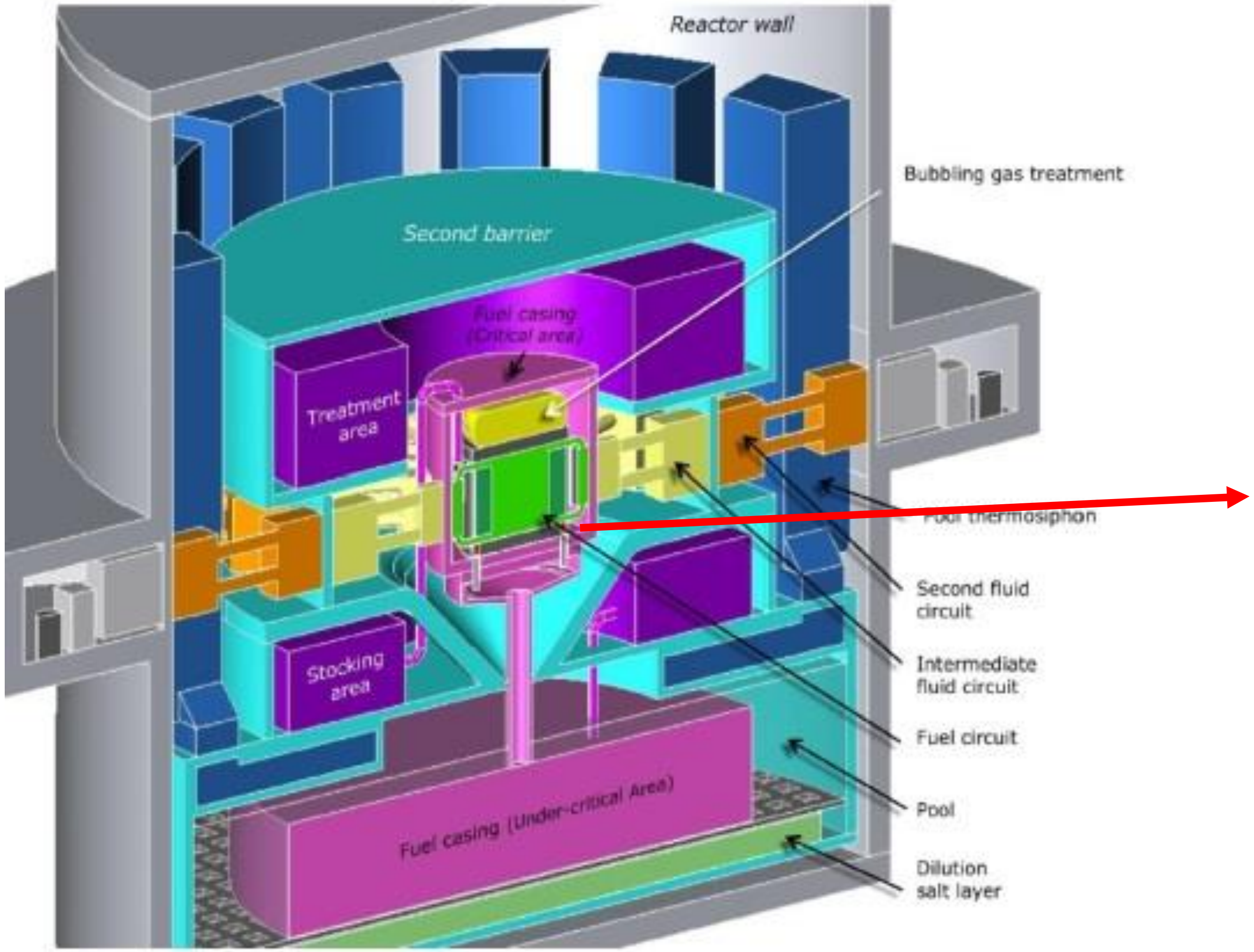
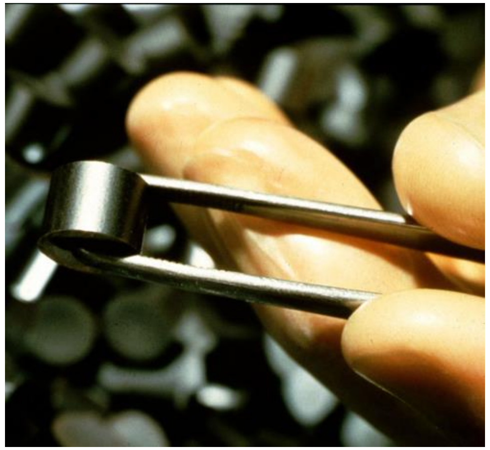
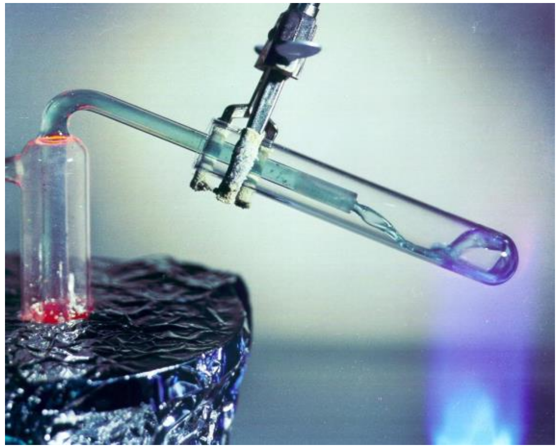
Fuel cycle in MSRs:

Fuel fabrication, fuel chemistry and in-reactor behaviour

Elisa Capelli

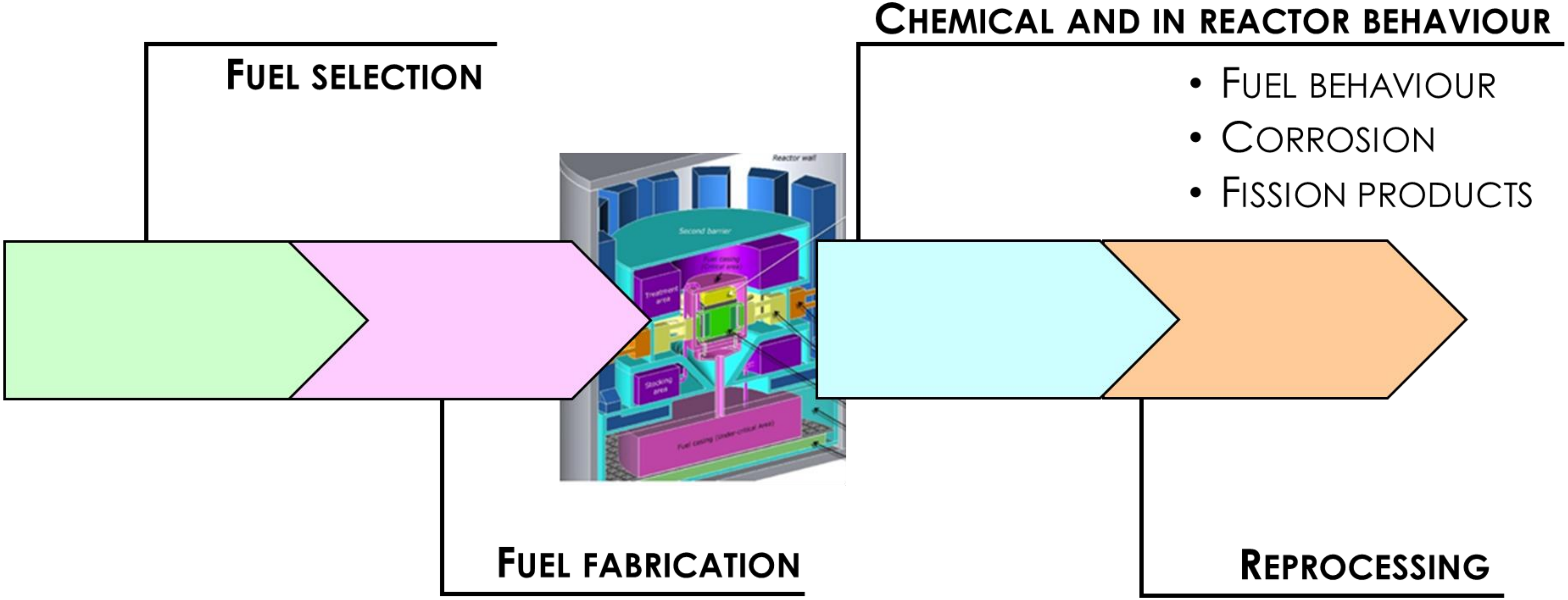
Molten Salt Reactor



Solid Fuel VS **Liquid Fuel**

Contents



FUEL SELECTION

FUEL FABRICATION

CHEMICAL AND IN REACTOR BEHAVIOUR

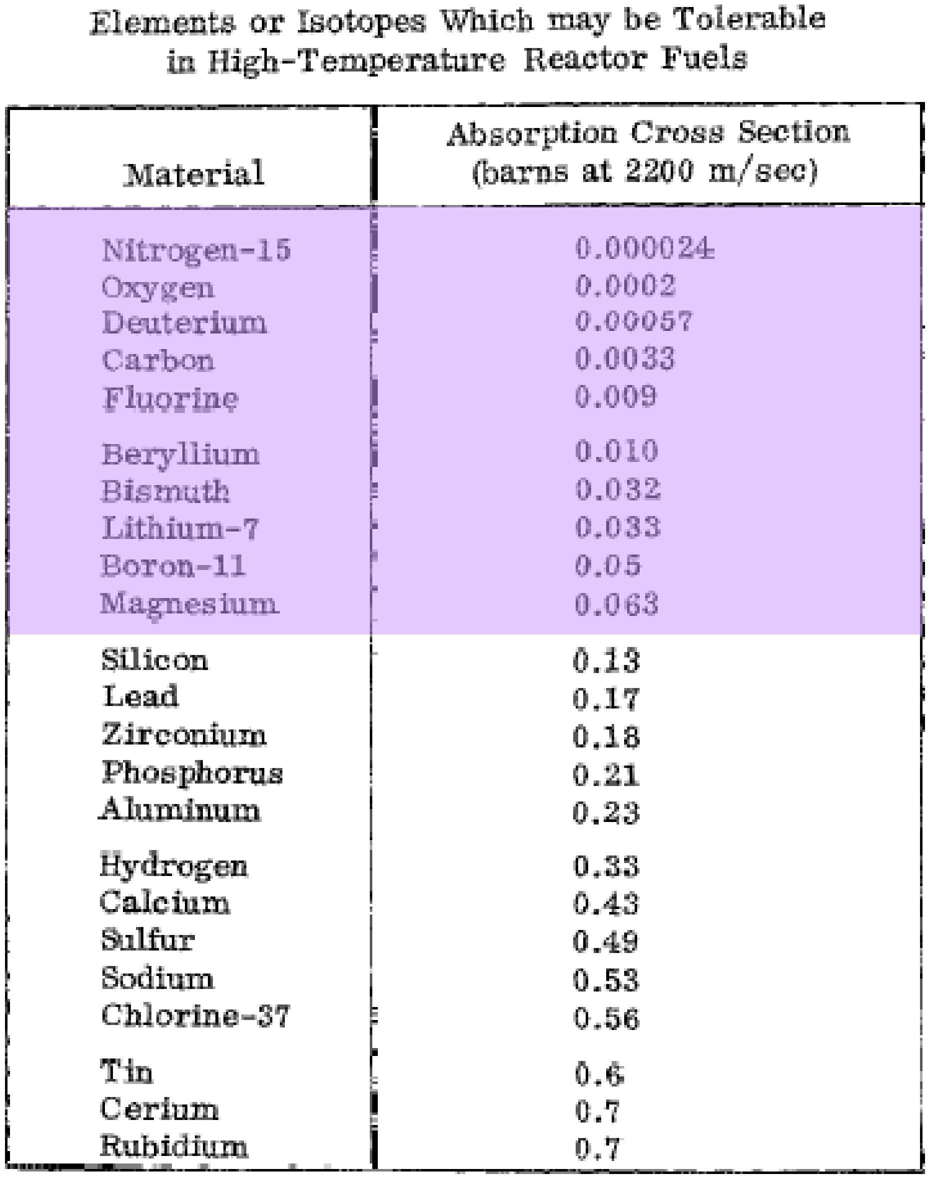
- FUEL BEHAVIOUR
- CORROSION
- FISSION PRODUCTS

REPROCESSING

Fuel selection

Screening criteria for MSR fuel

- **NEUTRONIC PROPERTIES**
  - **small capture cross section**
  - moderation capability
  - low neutronic activation
  - stable under irradiation
- **CHEMICAL PROPERTIES**
  - chemical/thermal stability
  - low melting point
  - high solubility of actinides
  - low vapour pressure and high boiling point
  - low corrosion / chemical reactivity
  - compatibility with salt clean-up strategy
- **THERMAL AND TRANSPORT PROPERTIES**
- **ECONOMIC FEATURES**

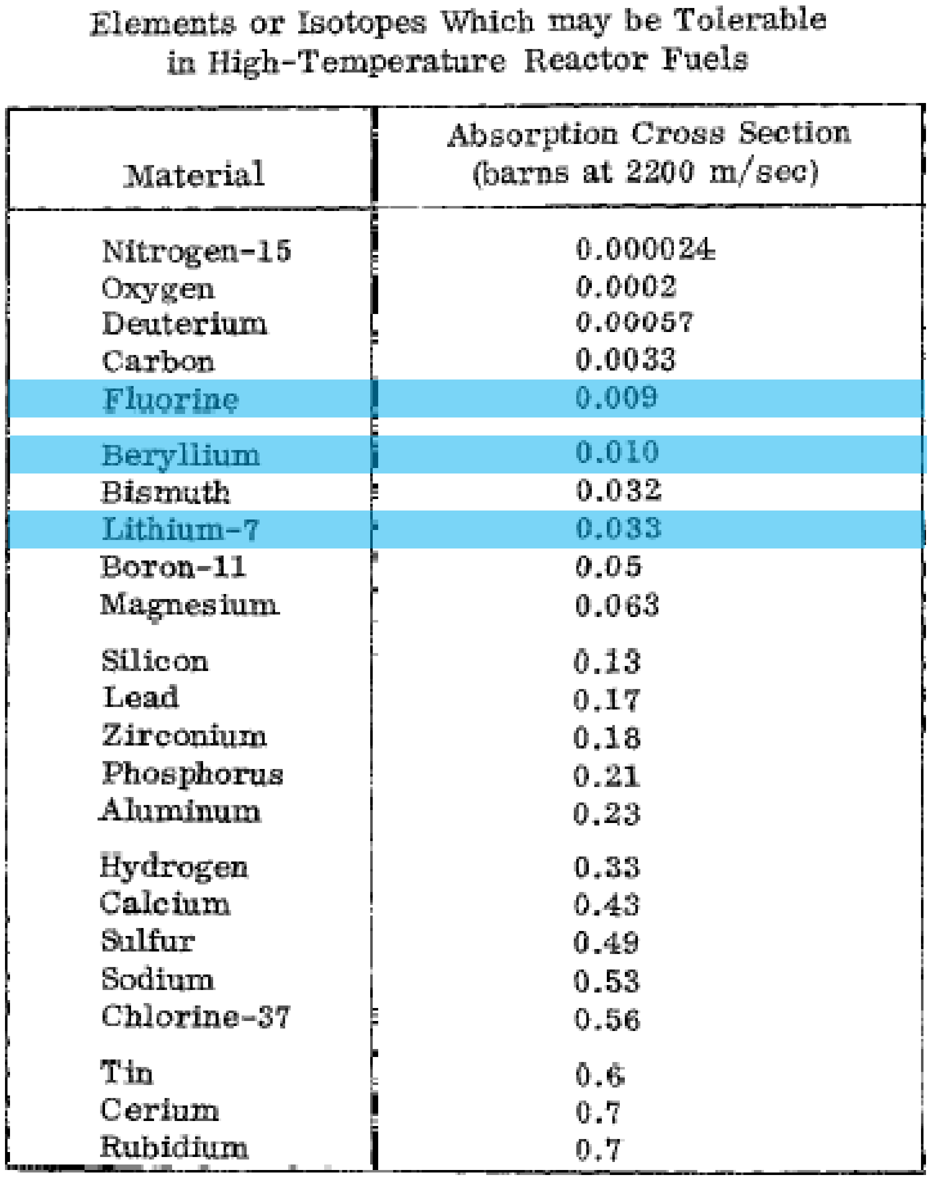


Elements or Isotopes Which may be Tolerable in High-Temperature Reactor Fuels

Material	Absorption Cross Section (barns at 2200 m/sec)
Nitrogen-15	0.000024
Oxygen	0.0002
Deuterium	0.00057
Carbon	0.0033
Fluorine	0.009
Beryllium	0.010
Bismuth	0.032
Lithium-7	0.033
Boron-11	0.05
Magnesium	0.063
Silicon	0.13
Lead	0.17
Zirconium	0.18
Phosphorus	0.21
Aluminum	0.23
Hydrogen	0.33
Calcium	0.43
Sulfur	0.49
Sodium	0.53
Chlorine-37	0.56
Tin	0.6
Cerium	0.7
Rubidium	0.7

Screening criteria for MSR fuel sovent

- **NEUTRONIC PROPERTIES**
  - **small capture cross section**
  - moderation capability
  - low neutronic activation
  - stable under irradiation
- **CHEMICAL PROPERTIES**
  - **chemical/thermal stability**
  - **low melting point**
  - **high solubility of actinides**
  - low vapour pressure and high boiling point
  - low corrosion / chemical reactivity
  - compatibility with salt clean-up strategy
- **THERMAL AND TRANSPORT PROPERTIES**
- **ECONOMIC FEATURES**



Elements or Isotopes Which may be Tolerable
in High-Temperature Reactor Fuels

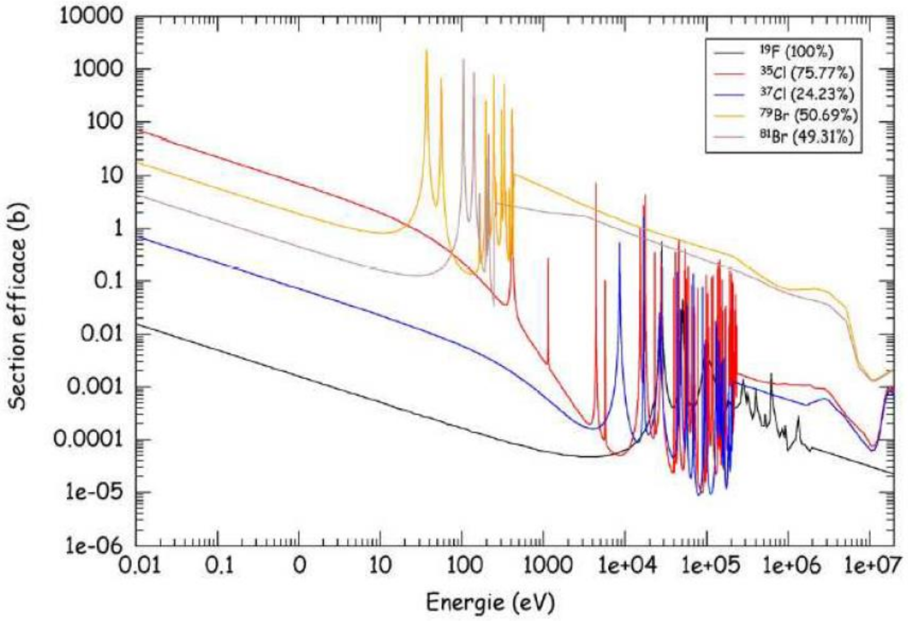
Material	Absorption Cross Section (barns at 2200 m/sec)
Nitrogen-15	0.000024
Oxygen	0.0002
Deuterium	0.00057
Carbon	0.0033
Fluorine	0.009
Beryllium	0.010
Bismuth	0.032
Lithium-7	0.033
Boron-11	0.05
Magnesium	0.063
Silicon	0.13
Lead	0.17
Zirconium	0.18
Phosphorus	0.21
Aluminum	0.23
Hydrogen	0.33
Calcium	0.43
Sulfur	0.49
Sodium	0.53
Chlorine-37	0.56
Tin	0.6
Cerium	0.7
Rubidium	0.7

Fuel options

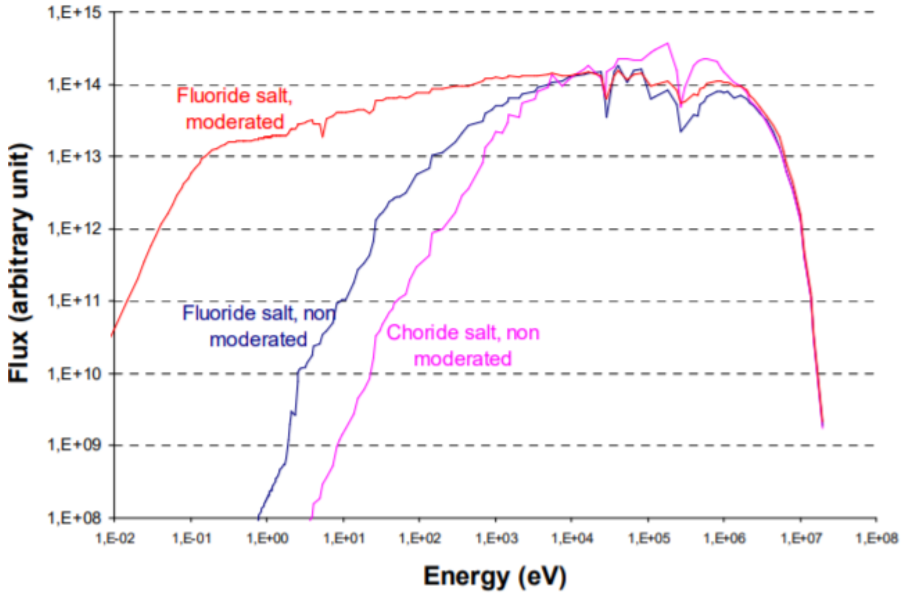
	Fuel solvent		Oxygen getter	Fertile	Fissile	
MSRE	^{7}LiF	BeF_2	ZrF_4		UF_4	
MSBR, TMSR	^{7}LiF	BeF_2		ThF_4	UF_4	
MSFR	^{7}LiF			ThF_4	UF_4	
MSFR	^{7}LiF			ThF_4	UF_4	TRU/PuF_3
MOSART	^{7}LiF	BeF_2, NaF, KF				TRU/PuF_3

Chlorides vs fluorides

- Although technology is much less developed, chloride salts are also considered as an option for non-moderated concepts.
- They have a rather fast spectrum, resulting in better breeding capabilities with U-Pu cycle.
- Chlorine must be purified to isolate the heavier stable isotope ^{37}Cl, thus reducing production of ^{36}Cl and ^{36}S .
- In terms of their physico-chemical properties, chlorides have lower melting points and higher vapour pressures.



Neutron spectra for different MSR types



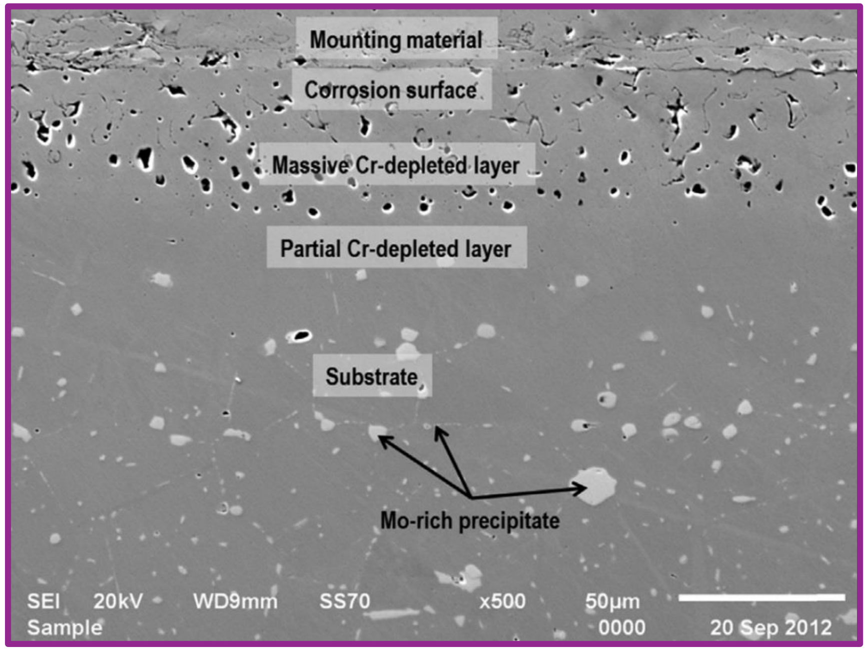
Review report on liquid salts for various applications, ALISIA deliverable D-50.

Physico-chemical properties

Melting temperature and crystallization path

- The liquid range of the salt must fit with the foreseen applications and include a sufficiently wide **margin toward solidification**.
- A fuel mixture with low melting point allows reactor operation at lower temperature with significant benefits with regards to structural material corrosion.

➢ The maximum operating temperature should not exceed 750 °C to avoid corrosion issues.

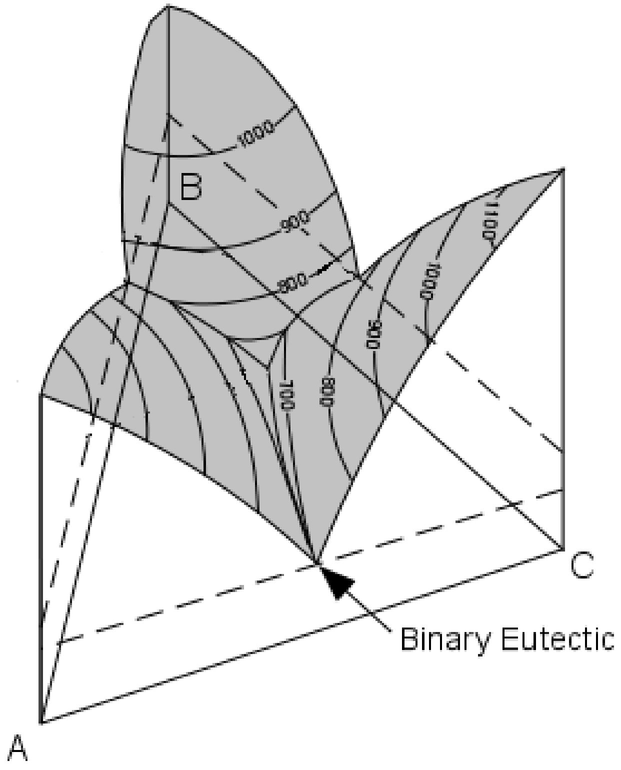


SEM image of Hastelloy N sample after corrosion tests in KF–ZrF_4 salt at 850 C for 1000 h.

P. Sabharwall, D. Clark, M. Glazoff, G. Zheng, K. Sridharan, M. Anderson, Advanced heat exchanger development for molten salts, Nucl. Eng. Des., 280 (2014) 42-56.

Melting temperature and crystallization path

- The liquid range of the salt must fit with the foreseen applications and include a sufficiently wide **margin toward solidification.**
- A fuel mixture with low melting point allows reactor operation at lower temperature with significant benefits with regards to structural material corrosion.

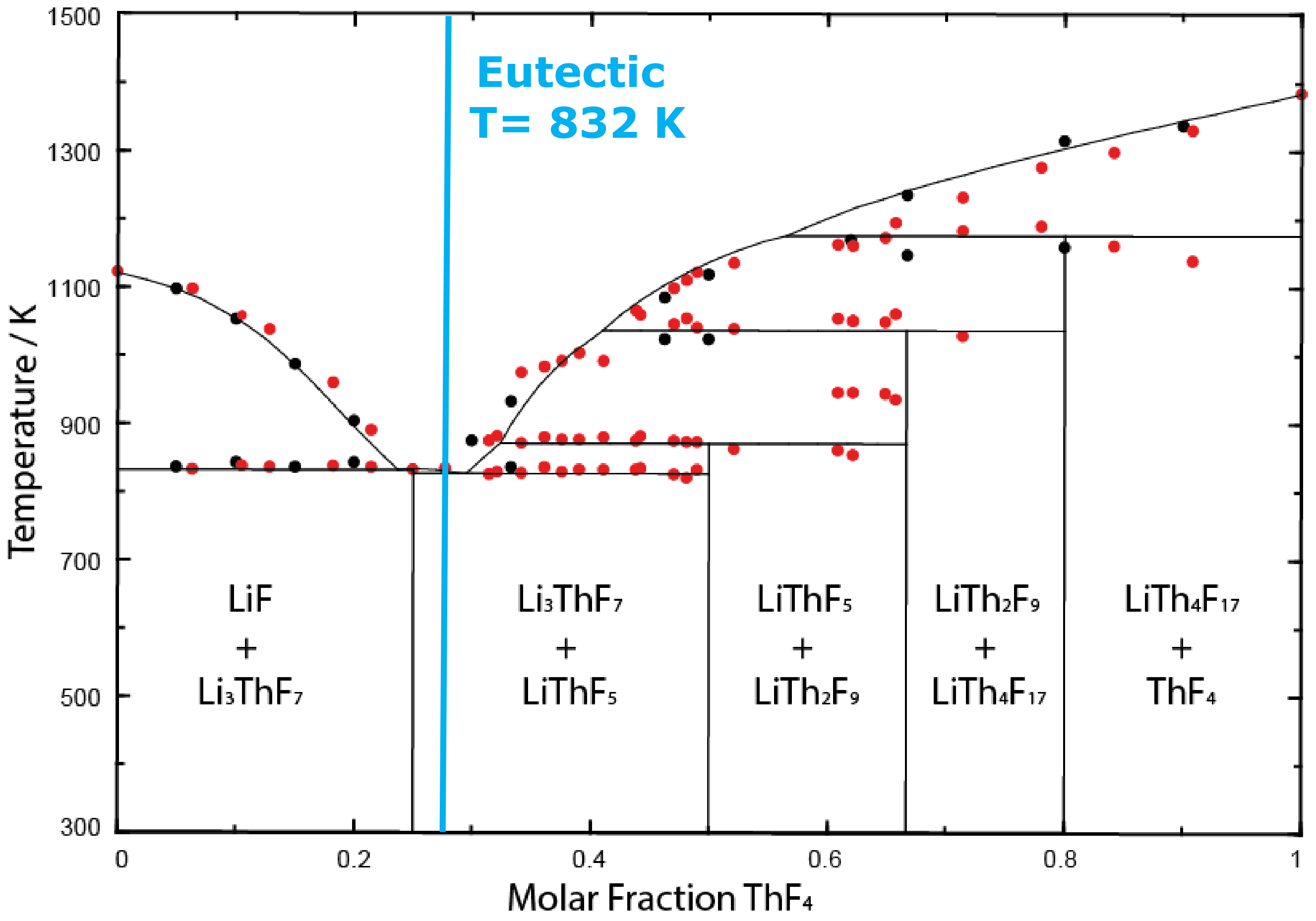


- The melting point of the fuel mixture depends on the exact **composition** and in particular on the **amount of dissolved actinide fluoride** and its form, e.g. trifluorides are less soluble than tetrafluoride.

OPTIMIZATION OF THE COMPOSITION DONE BY THERMODYNAMIC MODELING

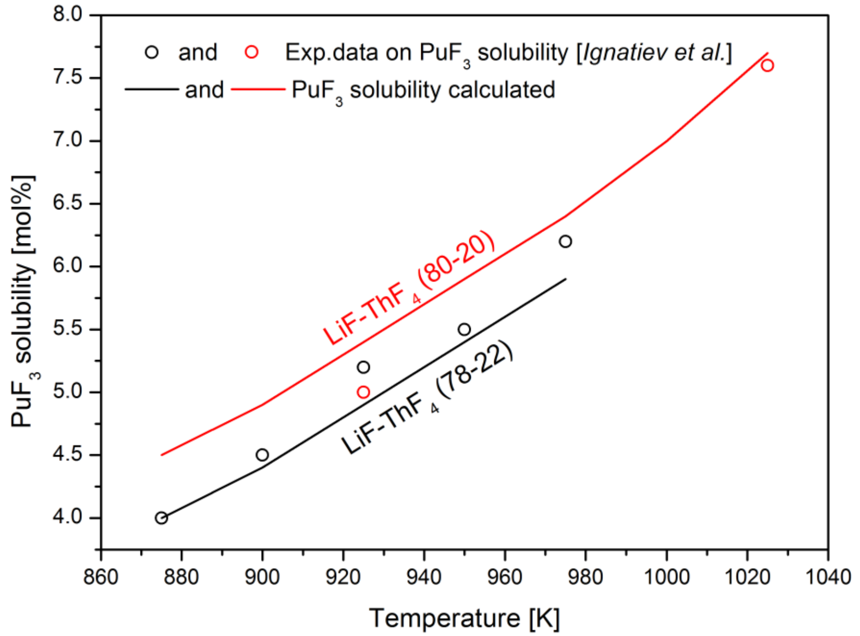
Fuel composition optimization – MSFR case

One of the proposed MSFR designs considers as fuel the LiF-ThF_4-UF_4-PuF_3 mixture.



Fuel constraints:

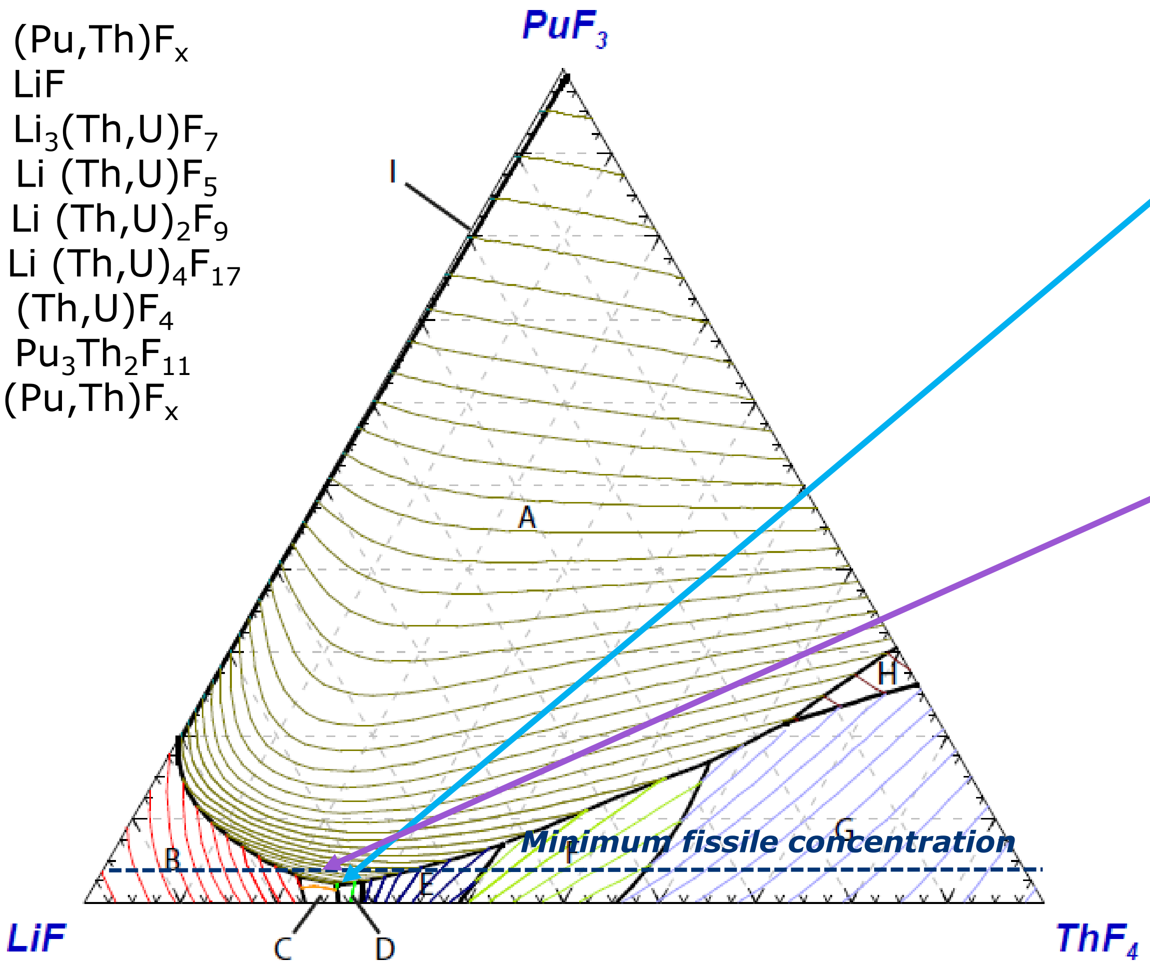
- Minimum concentration of fissile material: 5%
- Minimum concentration of UF_4: 1%
- Maximum enrichment UF_4: 20%



Fuel composition optimization – MSFR case

Fixed concentration of UF_4 of 1 mol% (redox control):

A: $(Pu,Th)F_x$
B: LiF
C: $Li_3(Th,U)F_7$
D: $Li\ (Th,U)F_5$
E: $Li\ (Th,U)_2F_9$
F: $Li\ (Th,U)_4F_{17}$
G: $(Th,U)F_4$
H: $Pu_3Th_2F_{11}$
I: $(Pu,Th)F_x$



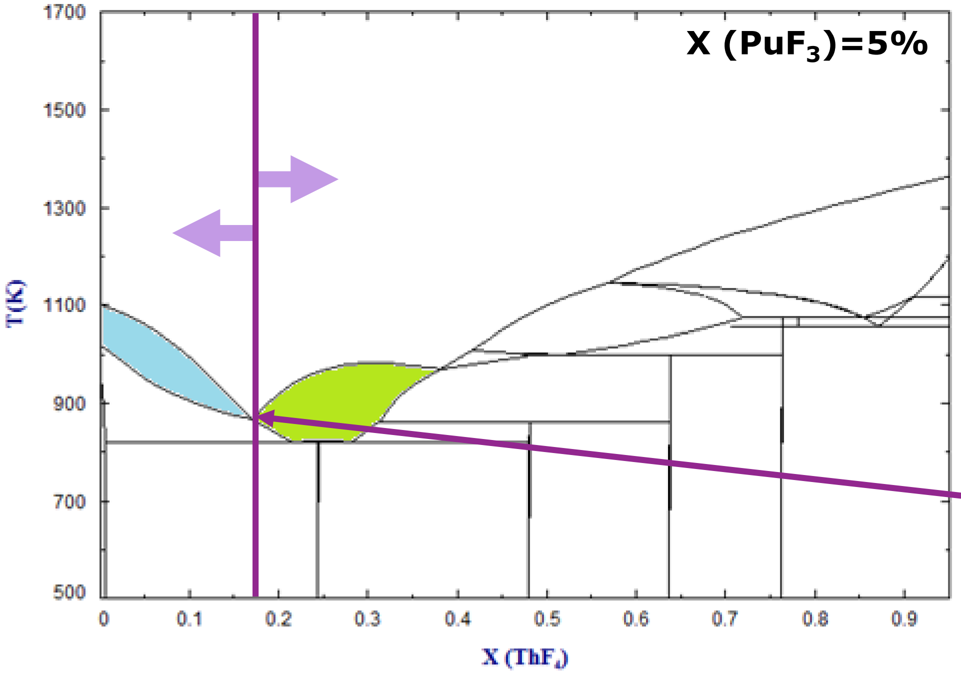
Lowest liquidus point **(T=819 K)**
$LiF-ThF_4-UF_4-PuF_3$ (75.3-20.6-1.0-3.1)

Optimized composition having fixed conc. of UF_4 and PuF_3
$LiF-ThF_4-UF_4-PuF_3$ (78-16-1.0-5)

Liquidus temperature = 867 K
Primary crystallization phase= $(Pu,Th)F_x$
Boiling temperature = 2035 K
P @ 917K = 5.33 E-3 Pa

Vapour pressure and boiling point

- The boiling point of the fuel mixture represents the ultimate temperature limit. Fluorides salts have fairly **high boiling points**, in the range 1700- 2000 C.
- In addition, the **vapour pressure** of the fuel salt must be **low** (< 1 mm Hg) in the complete relevant temperature range to assure salt stability and low pressure during operation.



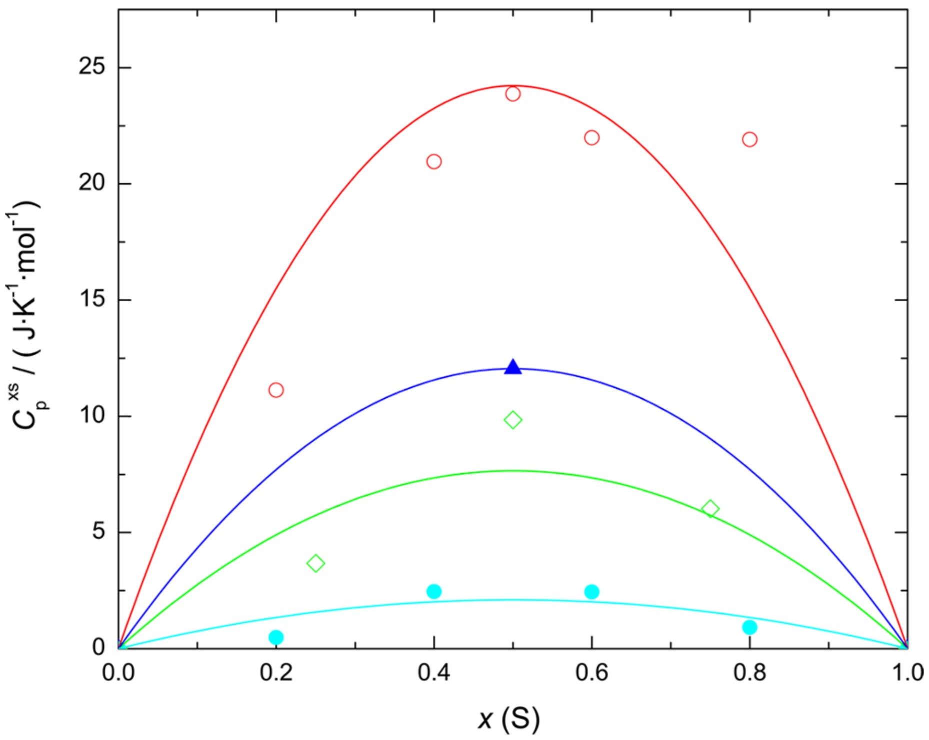
A low vapour pressure reduces the risk of shift in the composition and precipitation.

Optimized composition
LiF-ThF_4-UF_4-PuF_3 (78-16-1.0-5)

Thermo-hydraulic behaviour

- As one of the prime goal of the salt in MSR is the transport of heat, its thermohydraulic behaviour must be well characterized.
- Experimental data are lacking for some mixtures: ideal behaviour is usually assumed.

Coolant	**Water 293K**	**Na 700 K**	**Pb 700 K**	**LiF-ThF$_4$ 973K**
Density (kg m^{-3})	998.2	852	10480	4125
Viscosity (cP, 10^3 Pa s)	1.0016	0.264	2.095	10.1
Heat Capacity (J kg^{-1} K^{-1})	4157	1277	150	1594
Thermal conductivity (W m^{-1} K^{-1})	0.598	68	16	1.0097

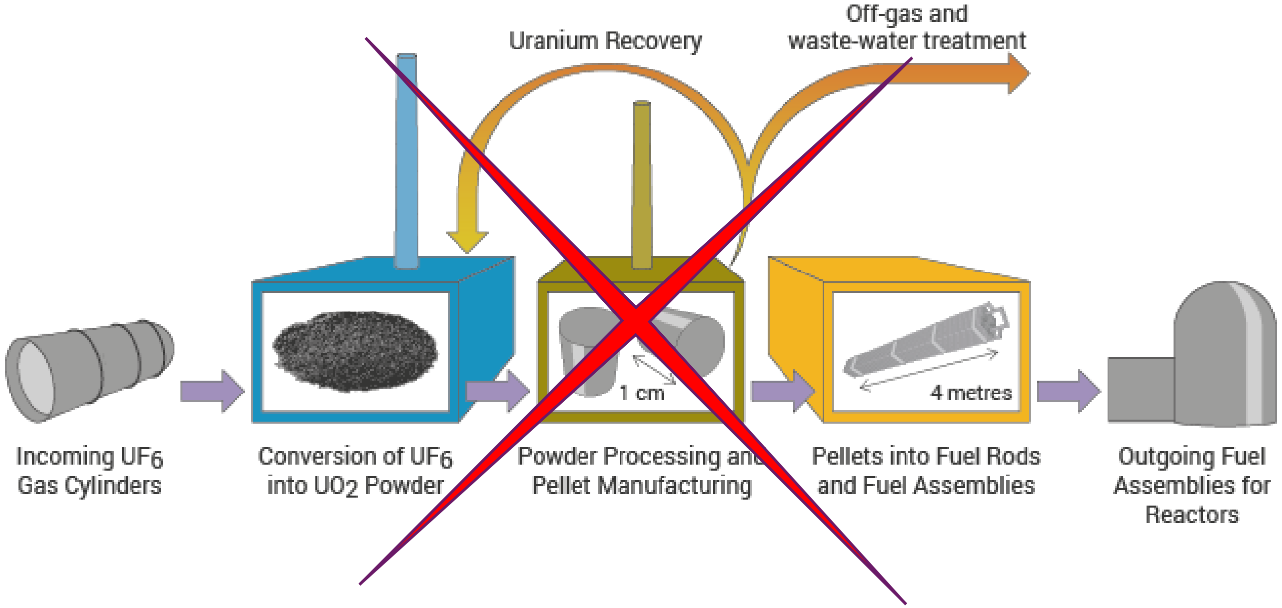


➢ **NEED FOR MORE DATA/BETTER MODELS.**

Fuel fabrication

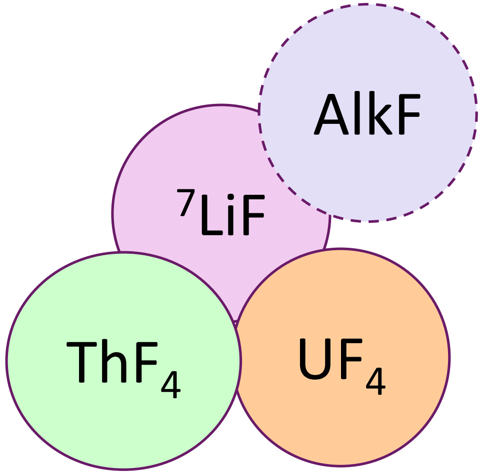
Fuel fabrication

- MSRs compared with solid-fuel reactors have a very simplified fuel fabrication process. This also represents an advantage in the case of closed fuel cycle as there is no need of transport and fabrication of new fuel elements.

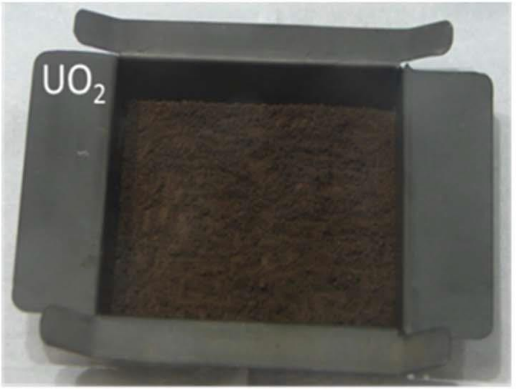


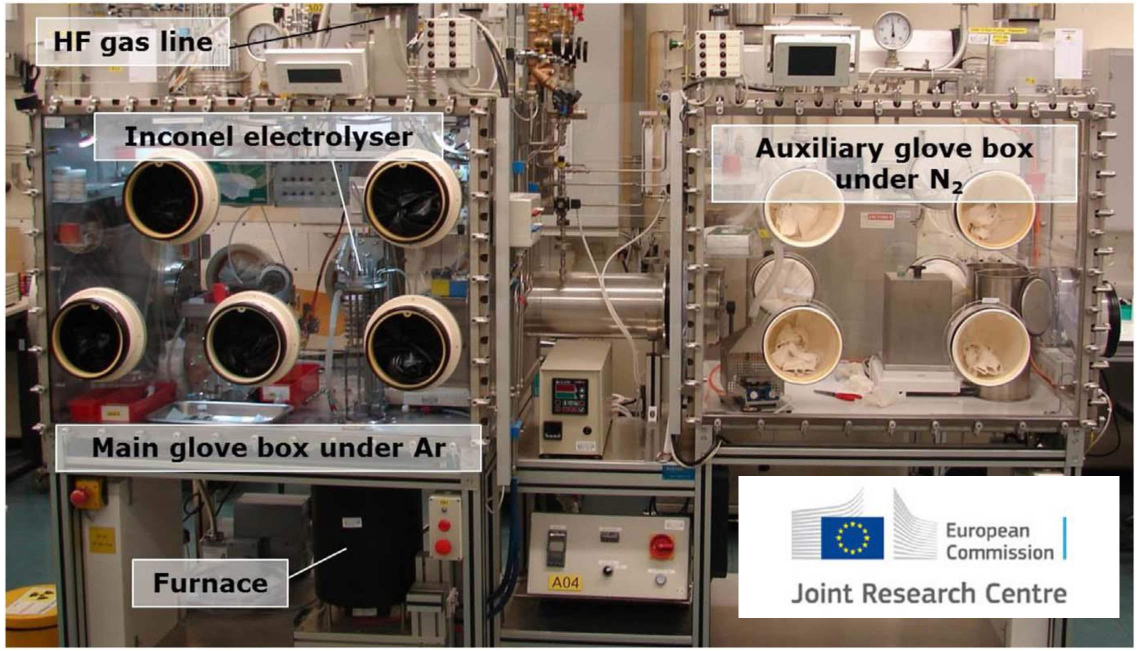

SYNTHESIS HIGHLY PURE FLUORIDE SALTS

Synthesis of the starting materials



- **Lithium fluoride** must be isotopically pure ^{7}Li. It is converted to fluoride starting from LiOH.
- Synthesis of pure **actinide fluorides** is achieved starting from the oxides using a fluorinating agent:
  - ammonium bifluoride NH_4HF_2,
  - **hydrogen fluoride HF,**
  - fluorine F_2.

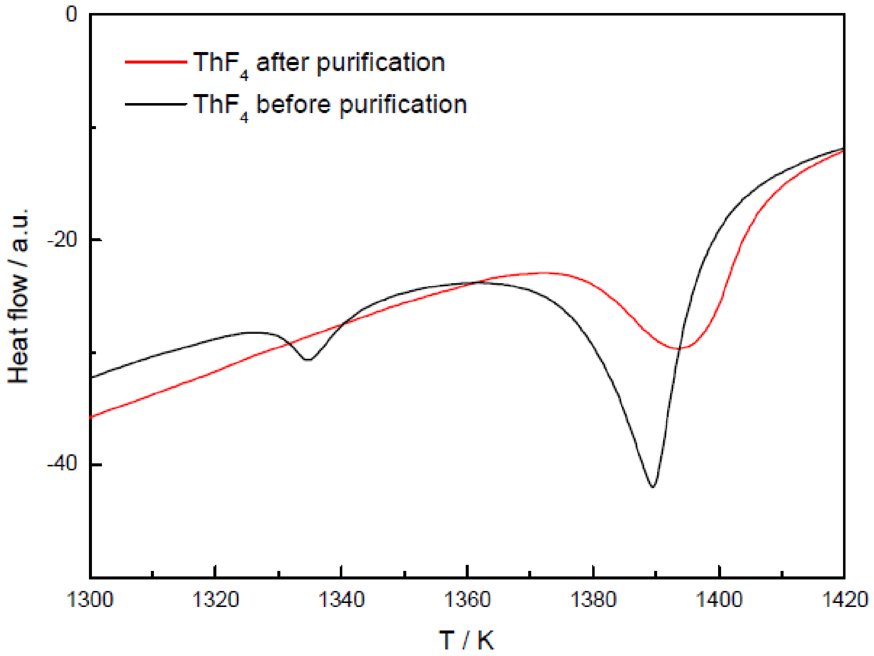




P. *Souček, O. Beneš, B. Claux, E. Capelli, M. Ougier, V. Tyrpekl, J.-F. Vigier, R. J.M. Konings J. Fluor. Chem. 200 (2017) 33–40.*

Fuel handling

- An approach is needed for removing oxygen and water, and potentially other contaminants from the fuel and coolant salts:
  - ➢ Moisture absorbed during transport/handling
  - ➢ Oxides and oxyflurides from reaction of the actinides fluorides with oxygen and water.



EFFECT ON THE PHYSICO-CHEMICAL PROPERTIES

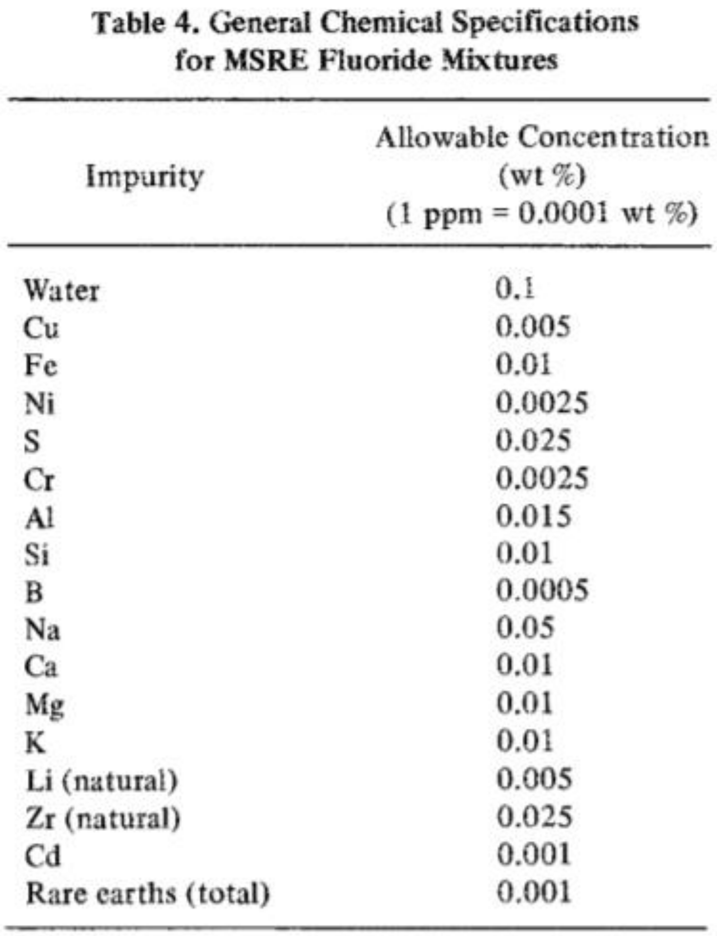


Table 4. General Chemical Specifications for MSRE Fluoride Mixtures

Impurity	Allowable Concentration (wt %) (1 ppm = 0.0001 wt %)
Water	0.1
Cu	0.005
Fe	0.01
Ni	0.0025
S	0.025
Cr	0.0025
Al	0.015
Si	0.01
B	0.0005
Na	0.05
Ca	0.01
Mg	0.01
K	0.01
Li (natural)	0.005
Zr (natural)	0.025
Cd	0.001
Rare earths (total)	0.001

J. H. Koger, Tech.Rep. ORNL-4616 (1971).

Why is it so important to have pure starting materials?

Cylinder Leak

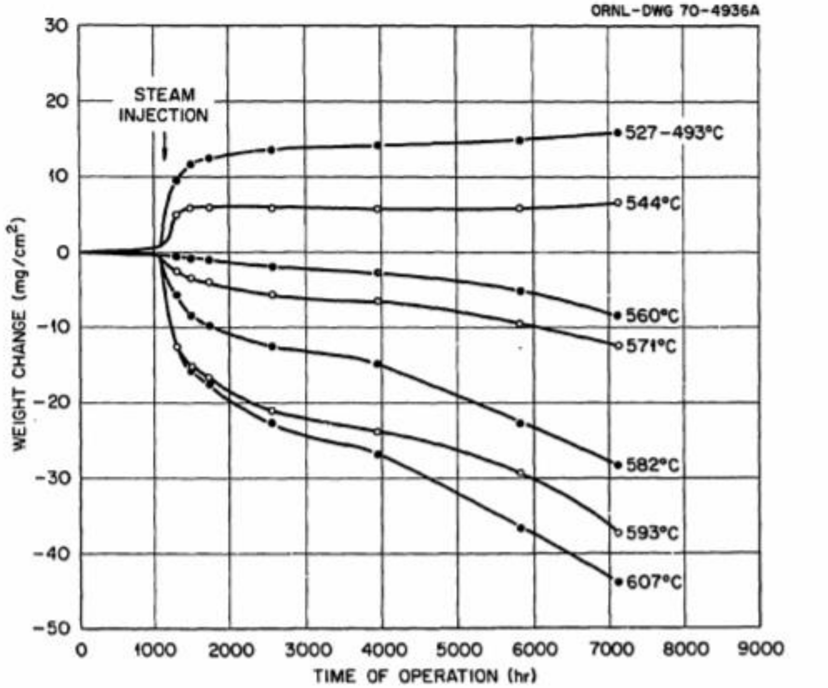
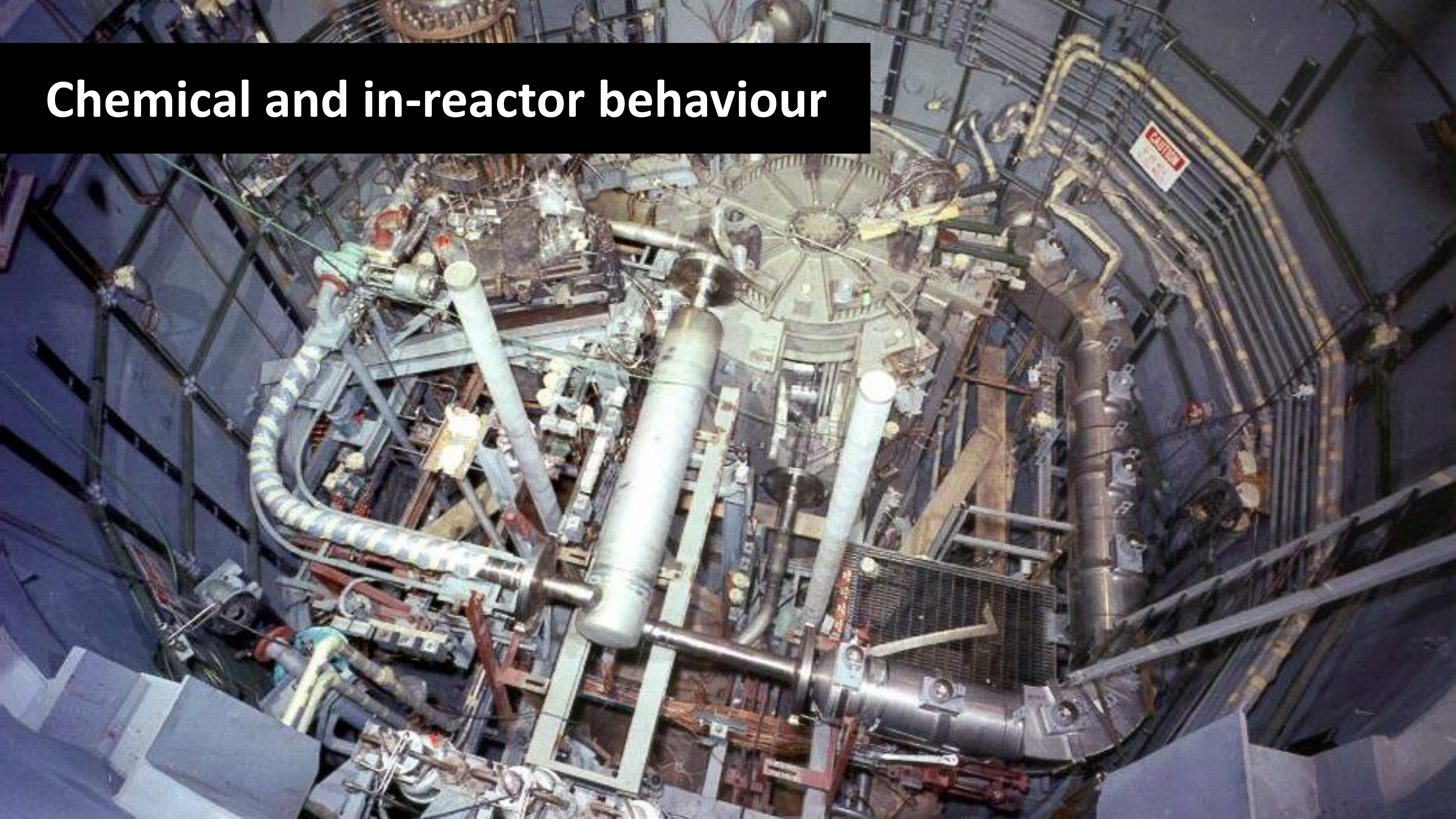


Fig. 10. Weight Change Versus Time for Hastelloy N Specimens in NCL-17 Exposed to $NaBF_4$–8 mole % NaF at Various Temperatures.

- Moisture reacts with molten salts to produce HF (highly corrosive) and metal oxides of much higher melting point and correspondingly lower solubility.

$$2H_2O+UF_4 \leftrightarrow 4HF+UO_2$$

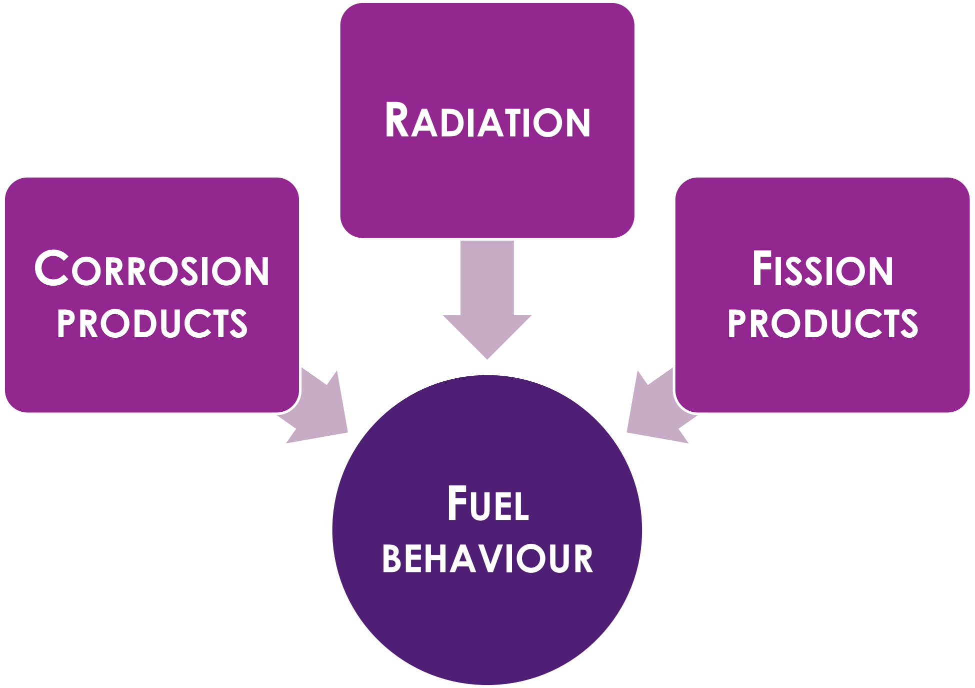
J. W. Koger ORNL-TM-3866 (1972).



Chemical and in-reactor behaviour

Chemical aspects of the fuel

- For the feasibility of the concept, it is essential that under **all likely conditions** throughout reactor lifetime the fuel:
  - do not undergo phase transitions (solidification, vaporization, precipitation of phases..)
  - is compatible with the container.



Behaviour under radiation

- One of the effect of radiation is the cleavage of chemical bonds (**radiolysis**) and the formation in fluoride salts of F_2 gas.

$$\boxed{LiF + h\nu \rightarrow Li\cdot + F\cdot \rightarrow F_2}$$

High temperature	RECOMB. > PROD.
T = 70-150 °C	RECOMB. < PROD.

- No pressure build-up during reactor operation.

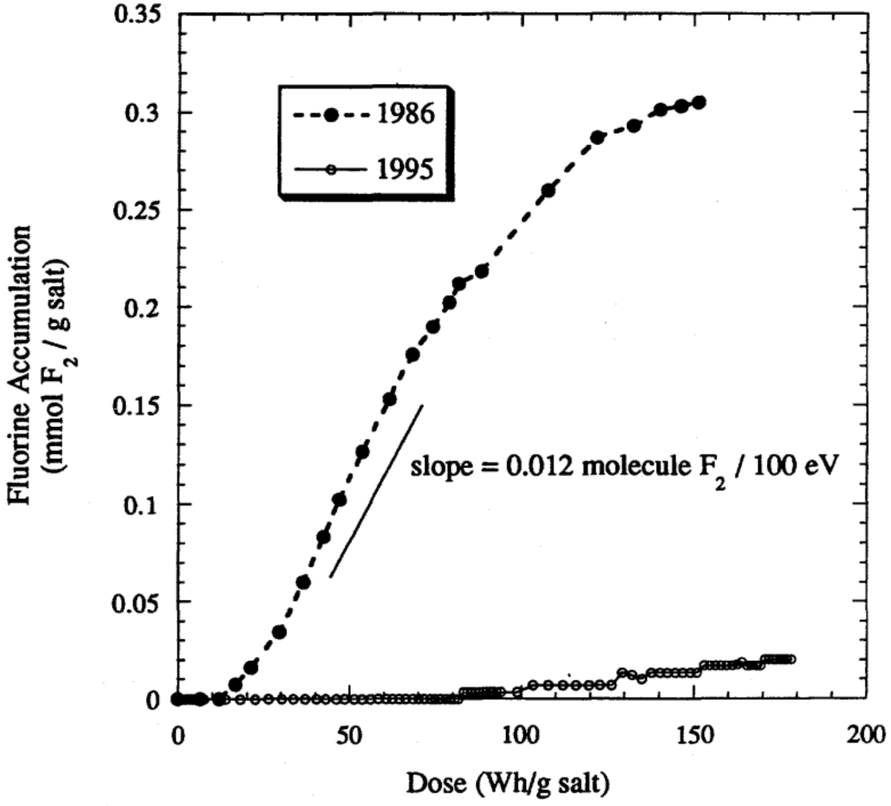
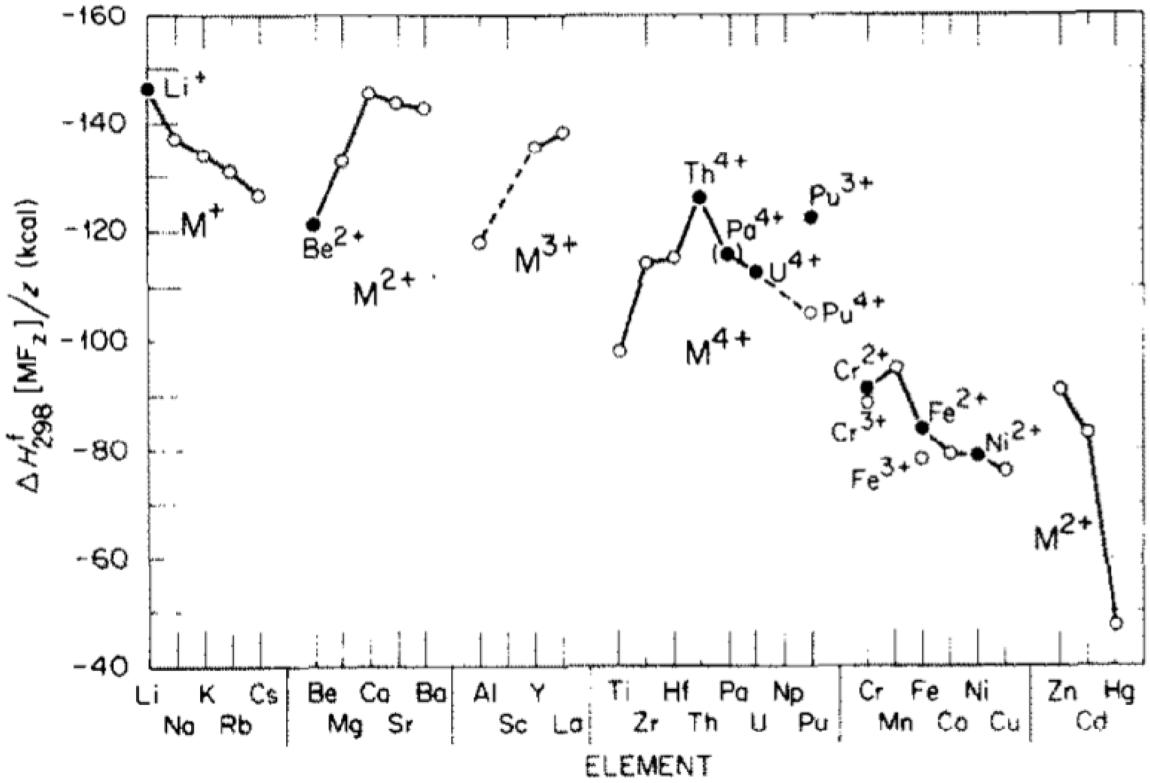


Fig. 3. Fluorine generation curves for 1986 and 1995 irradiation experiments.

Fuel stability and corrosion

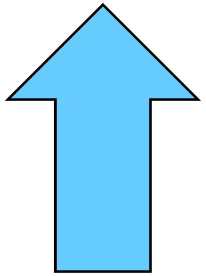
Fuel interaction with structural materials

- Compatibility with structural materials is achieved by:
    - ensuring good purity of the initial materials in the salt mixture
    - selecting materials for the containment which form relatively unstable fluorides
- Passivation of the structural material in precluded as the oxide are quite soluble.



Fuel interaction with structural materials

Element	Most Stable Fluoride
Chromium	CrF_2
Iron	FeF_2
Nickel	NiF_2
Molybdenum	MoF_2



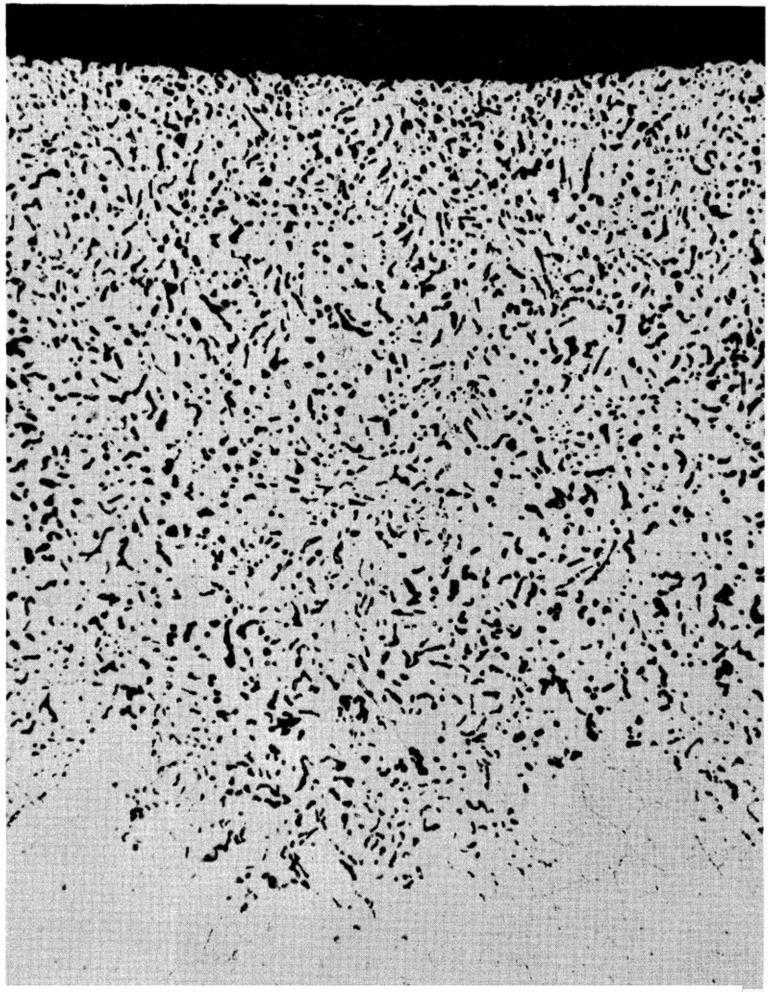


Figure 1. Photomicrograph of a sample of INCONEL 600 (20%Ni–15%Cr–5%Fe) after exposure to fluoride salt in a pumped loop for 15,000 hours at 1300°F. Voids near the surface are formed as chromium is removed selectively by the salt.

- In fluoride environment, chromium is much more readily attacked than Fe, Ni, or Mo.
- Therefore, Ni-based alloy having less Cr than traditional stainless steel (Hastelloy N, MoNiCr, HNM80..) are used for fluoride melts as they are more resistant to corrosion.

Redox chemistry

- The "redox state" of the fuel salt is a key parameter for corrosion issues and, in general for the fuel behaviour. It can be defined by the **fluorine potential:**

$$\boxed{\Delta G_{F_2} \equiv RT \ln p_{F_2}}$$

- There are three ways of controlling the fluorine potential in a fluoride mixture:
  - by the gas mixture H_2/HF;
  - by one of the major metals of the salt;
  - by a dissolved salt.

$$\frac{1}{2}\mathrm{H_2(g)} + \frac{1}{2}\mathrm{F_2(g)} \leftrightarrow \mathrm{HF(g)}$$

$$\Delta G_{F_2} \equiv RT \ln p_{F_2} = 2\mathrm{RT}\ln\left(\frac{p_{HF}}{\sqrt{p_{H_2}}}\right) + 2\Delta G^0_{HF}$$

$$\mathrm{UF_3(sln)} + \frac{1}{2}\mathrm{F_2} \leftrightarrow \mathrm{UF_4(sln)}$$

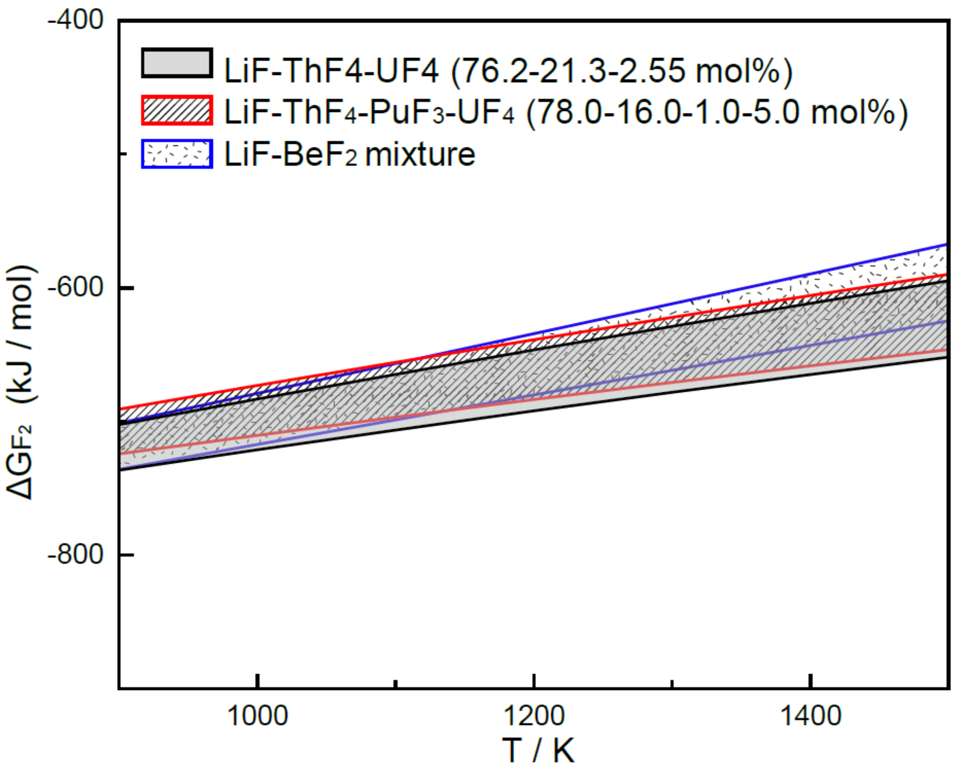
$$\Delta G_{F_2} \equiv RT \ln p_{F_2} = 2\mathrm{RT}\ln\left(\frac{a_{UF_4}}{a_{UF_3}}\right) + 2\Delta G^0_{UF_3/UF_4}$$

$$\mathrm{Be(s)} + \mathrm{F_2} \leftrightarrow \mathrm{BeF_2(sln)}$$

$$\Delta G_{F_2} \equiv RT \ln p_{F_2} = \mathrm{RT}\ln\left(a_{BeF_2}\right) + \Delta G^0_{BeF_2}$$

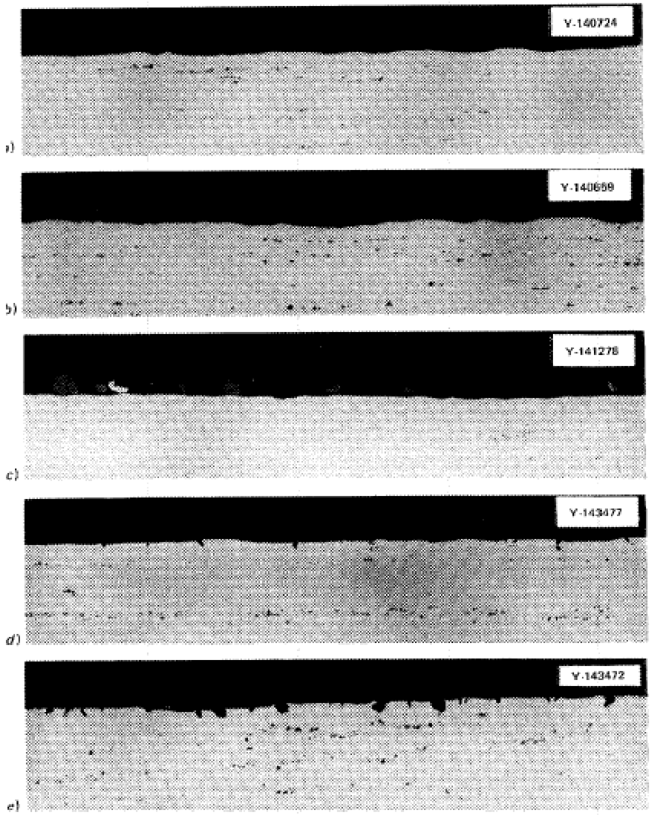
Redox chemistry

- For the redox control of MSRs, the redox buffer **UF_4/UF_3** is used to control the fluorine potential.
- Operation of the MSRE have confirmed that the required reducing conditions in the reactor can be achieved maintaining the UF_4/UF_3 ratio in the range 10-100.



ENHANCED CORROSION

REDUCTION OF URANIUM



$U^{4+}/U^{3+} = 10$

$U^{4+}/U^{3+} = 30$

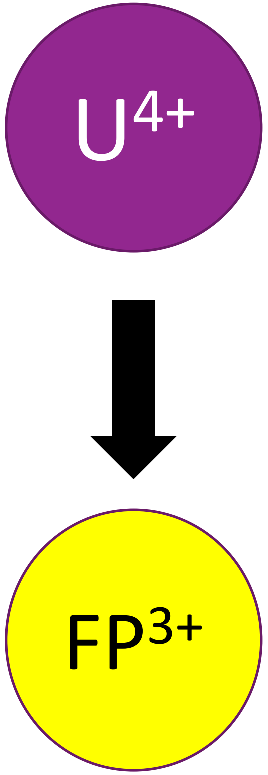
$U^{4+}/U^{3+} = 60$

$U^{4+}/U^{3+} = 85$

$U^{4+}/U^{3+} = 300$

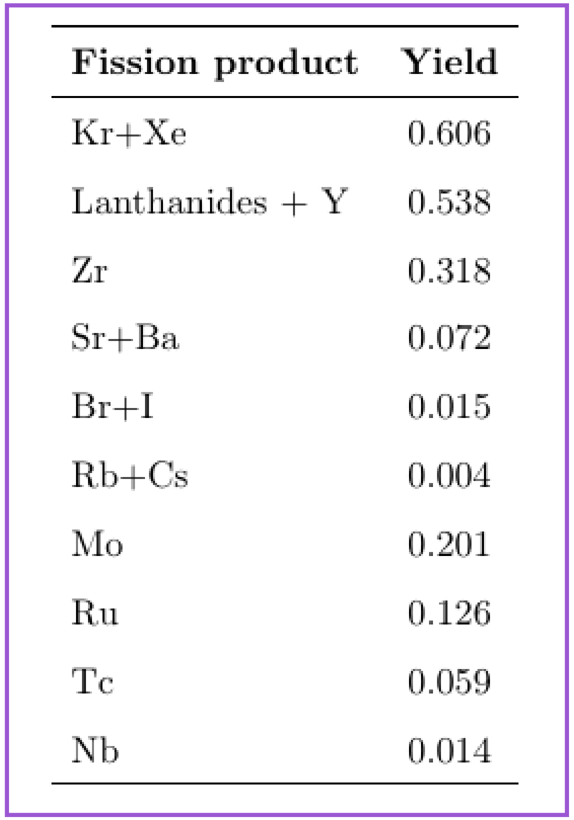
Redox chemistry

- As the burnup of the fuel proceeds, the redox conditions will change due to the difference in the total charge of fission products generated and the fissioned fluoride.
- The excess fluorine produced reacts with the strongest reducing agent present, UF_3, forming UF_4.



U^{4+}

FP^{3+}

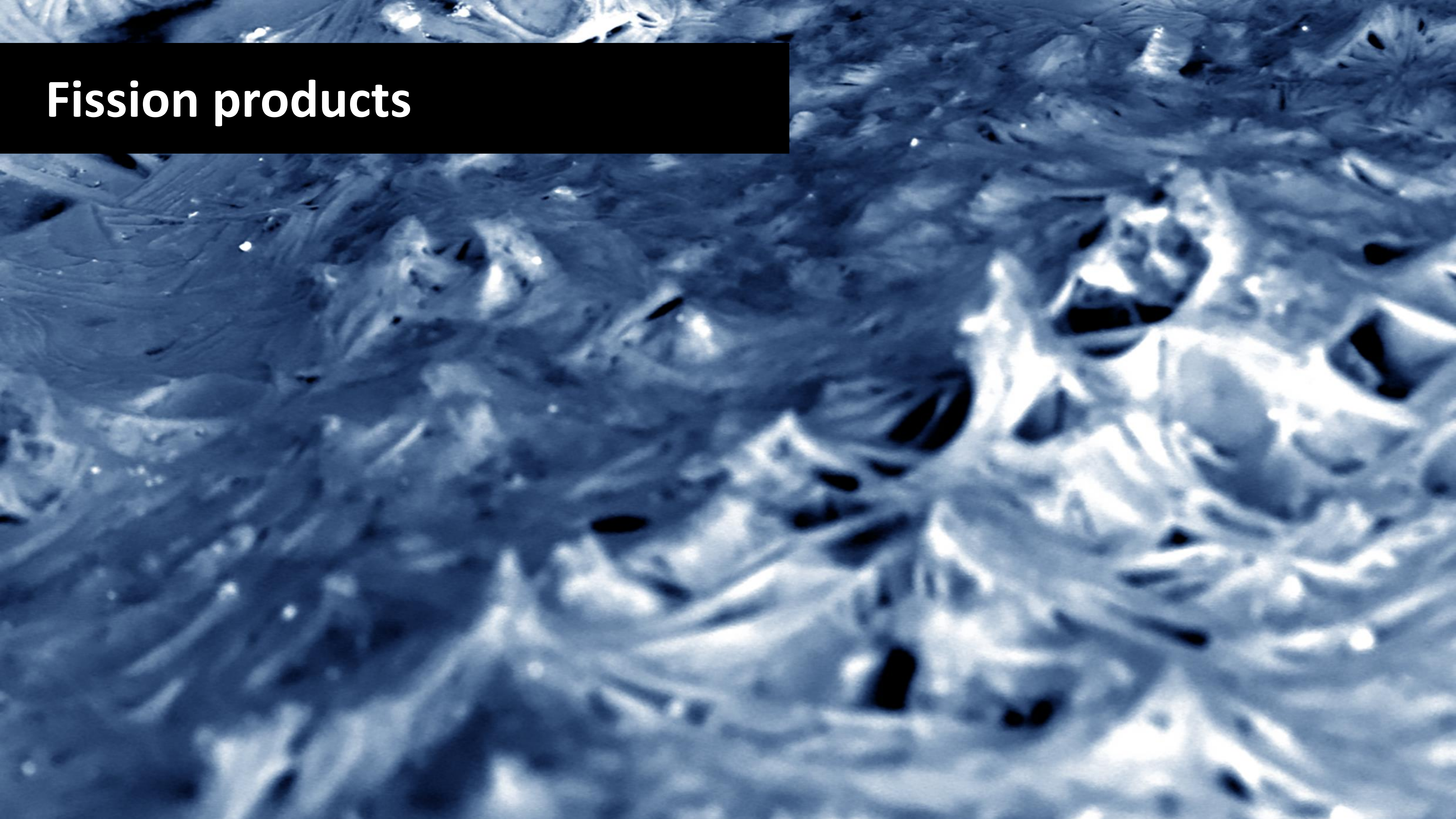


Fission product	**Yield**
Kr+Xe	0.606
Lanthanides + Y	0.538
Zr	0.318
Sr+Ba	0.072
Br+I	0.015
Rb+Cs	0.004
Mo	0.201
Ru	0.126
Tc	0.059
Nb	0.014

- The concentration of UF_3 is maintained at acceptably low levels by reacting the fuel salt with, for example, metallic Be.

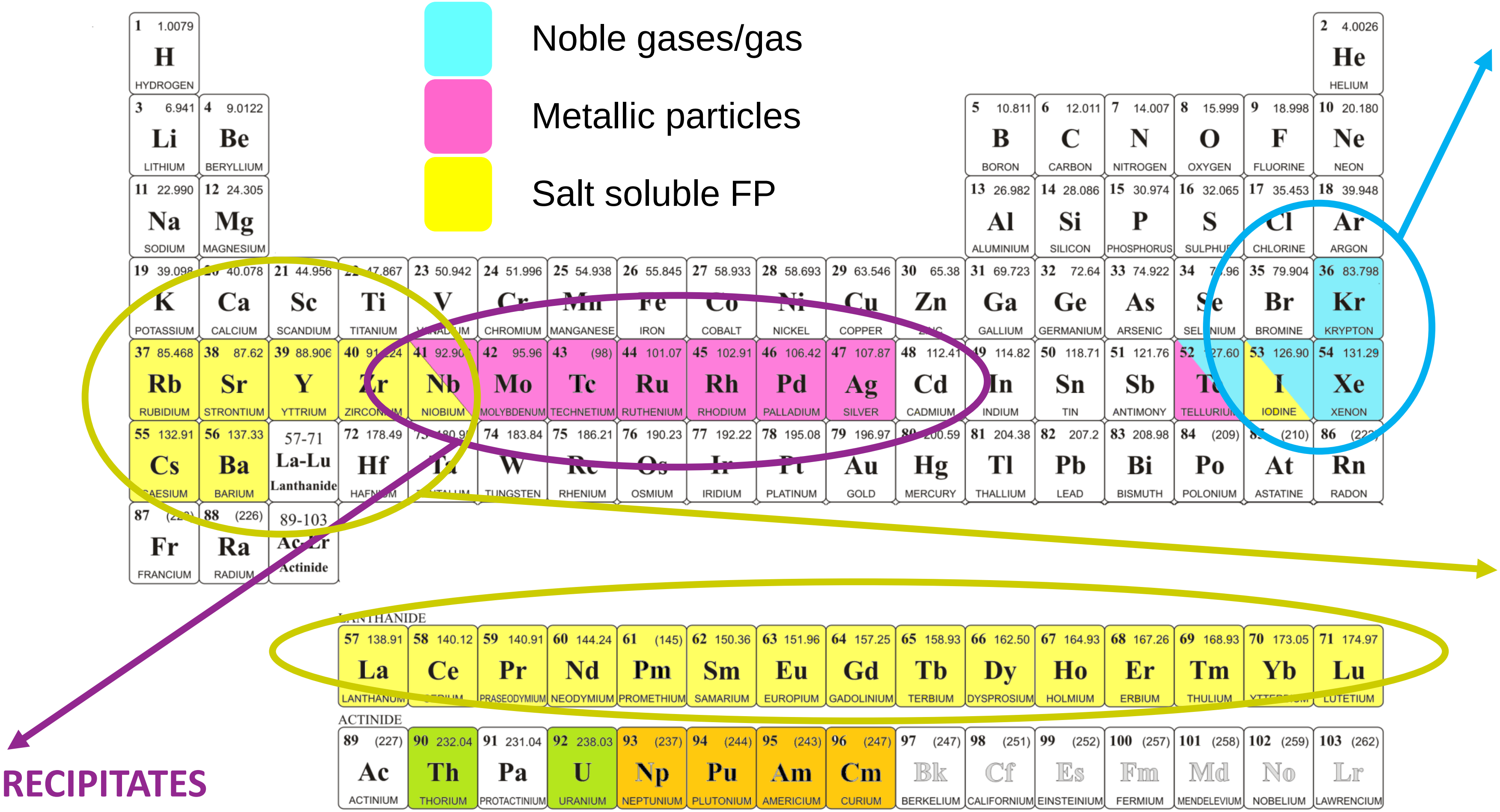
- A robust **method for monitoring** real time the redox potential of the fuel salt is needed.

Fission products



Fission product classification

- The redox potential of the fuel mixture is also the key parameter that define the actual chemical state for each of the fission product species.



Noble gases/gas

Metallic particles

Salt soluble FP

GAS BUBBLES

DISSOLVED IN THE FUEL SALT

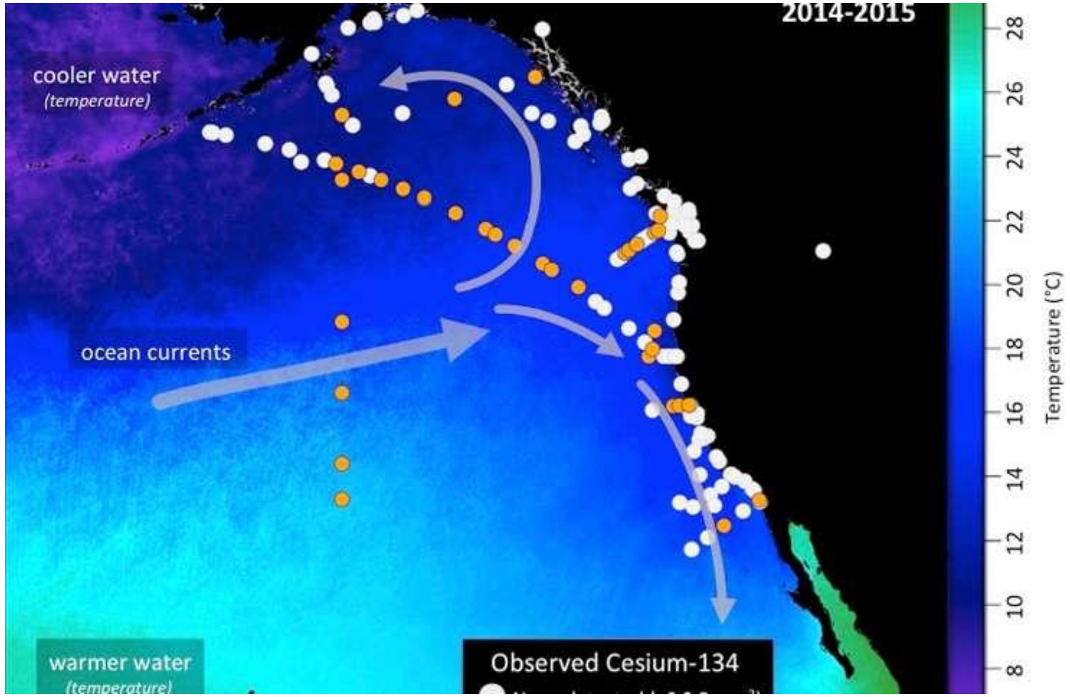
METALLIC PRECIPITATES

Fission product retention

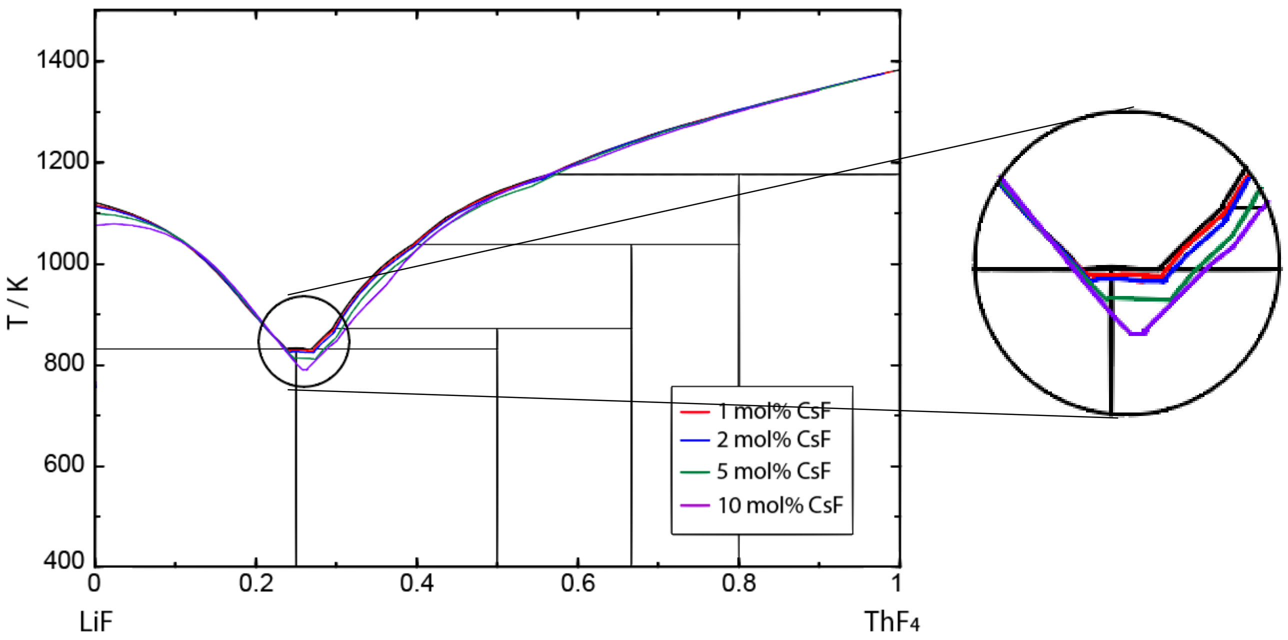
- The fluoride matrix has the potential to retain some relevant fission products, such as Cesium and Iodine which deserve strong attention due to their volatility and radiological effects in accidental scenarios.

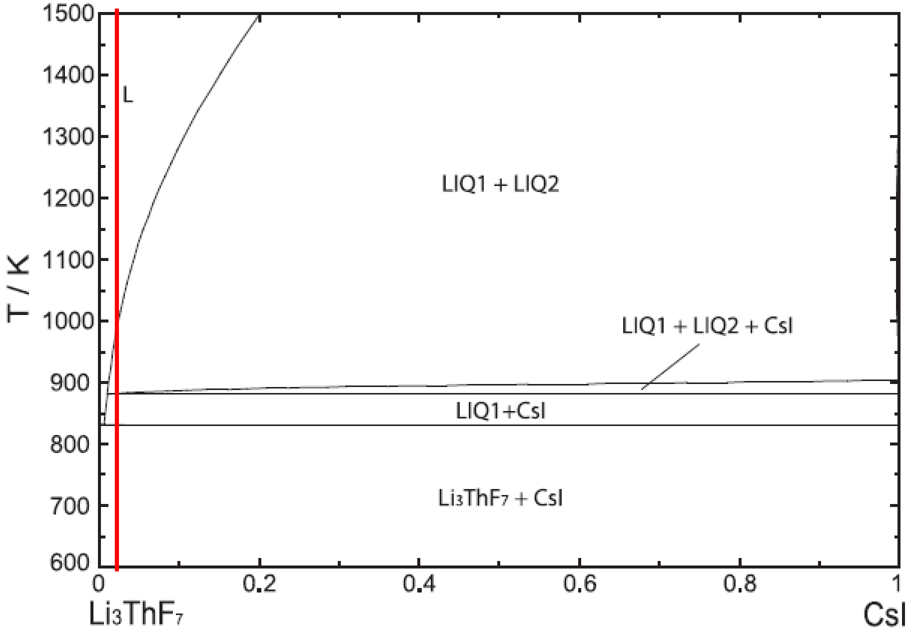
- The speciation of these elements is very important with this respect.

- For example, in the form of CsF cesium is not released from the fuel even at high temperature while in the form of CsI its solubility is lower.



Cesium and Iodine forms

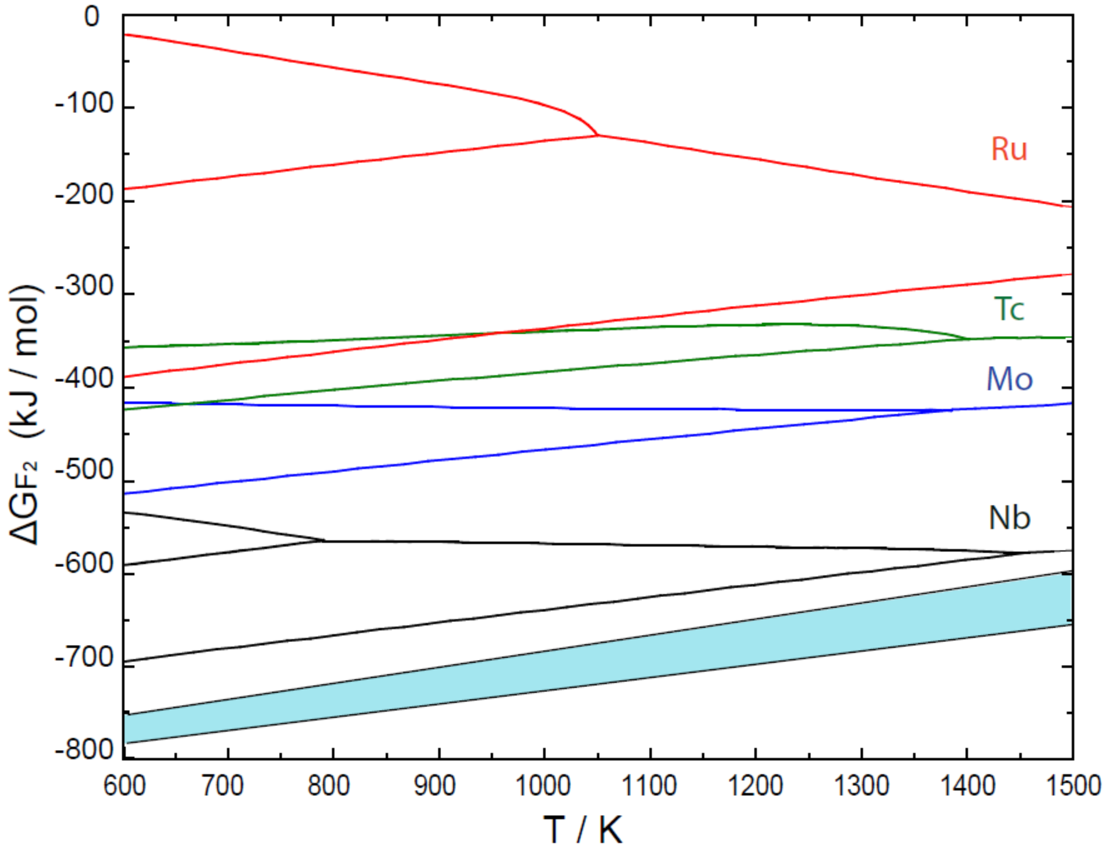


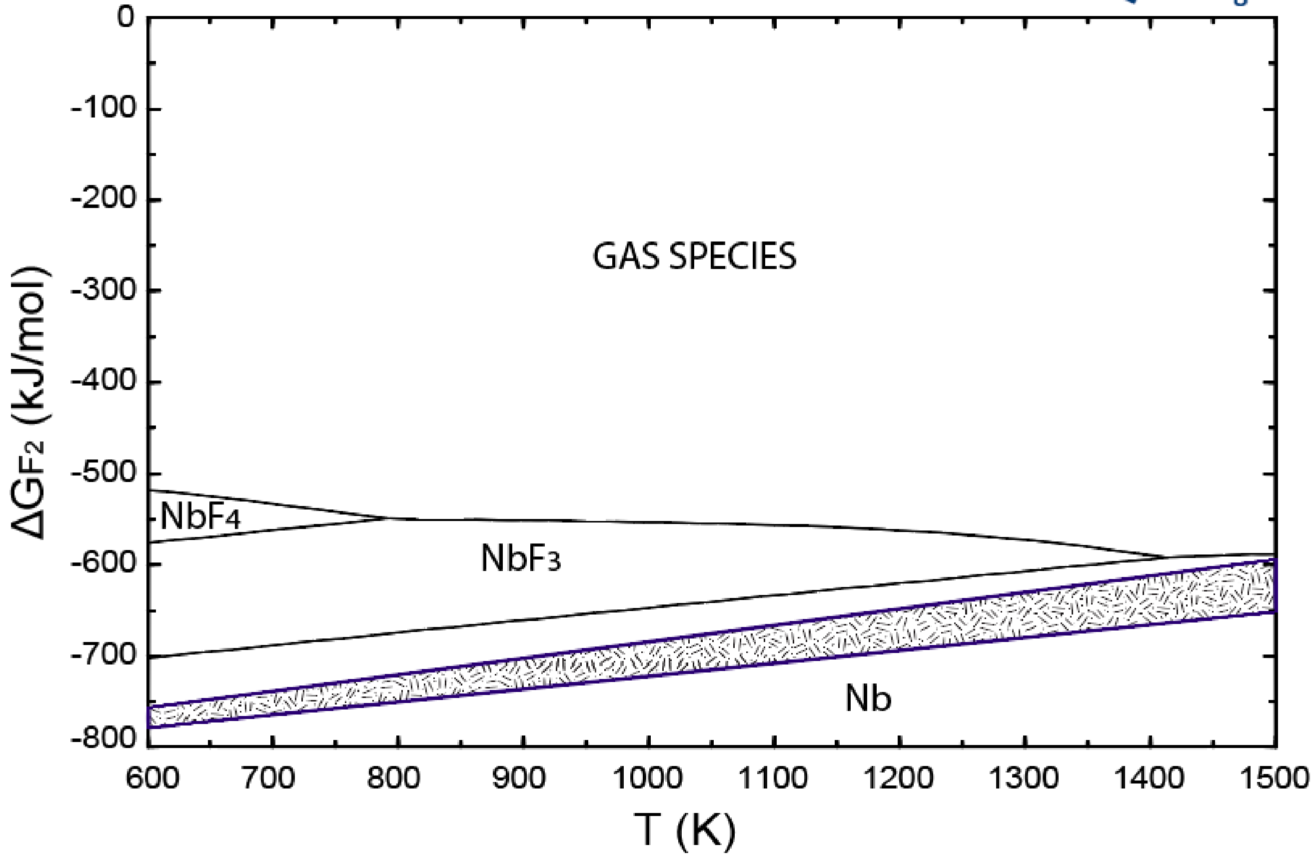


Composition (mol%) ***fixed LiF/ThF$_4$ ratio***	**CsF accumulation**		**CsI accumulation**	
	T liquidus	**P @ 900 K / Pa**	**T liquidus**	**P @ 900 K / Pa**
LiF-ThF$_4$ (76.2-23.8)	832 K	$2{,}44 \cdot 10^{-3}$	832 K	$2{,}44 \cdot 10^{-3}$
LiF-ThF$_4$-CsI/CsF (75.438-23.562-**1.00**)	834 K	$2{,}74 \cdot 10^{-3}$	877 K	$2{,}28 \cdot 10^{1}$
LiF-ThF$_4$-CsI/CsF (76.676-23.324-**2.00**)	837 K	$3{,}06 \cdot 10^{-3}$	880 K	$2{,}31 \cdot 10^{1}$
LiF-ThF$_4$-CsI/CsF (72.39-22.61-**5.00**)	848 K	$4{,}25 \cdot 10^{-3}$	886 K	$2{,}38 \cdot 10^{1}$

Fission products speciation in MSR: noble metals

- Under normal reactor conditions are reduced to the metallic state.
- If the redox control of the reactor fails, the first element to appear in solution is niobium (Nb^{3+}).





FactSage™

Tellurium: Intergranular cracking

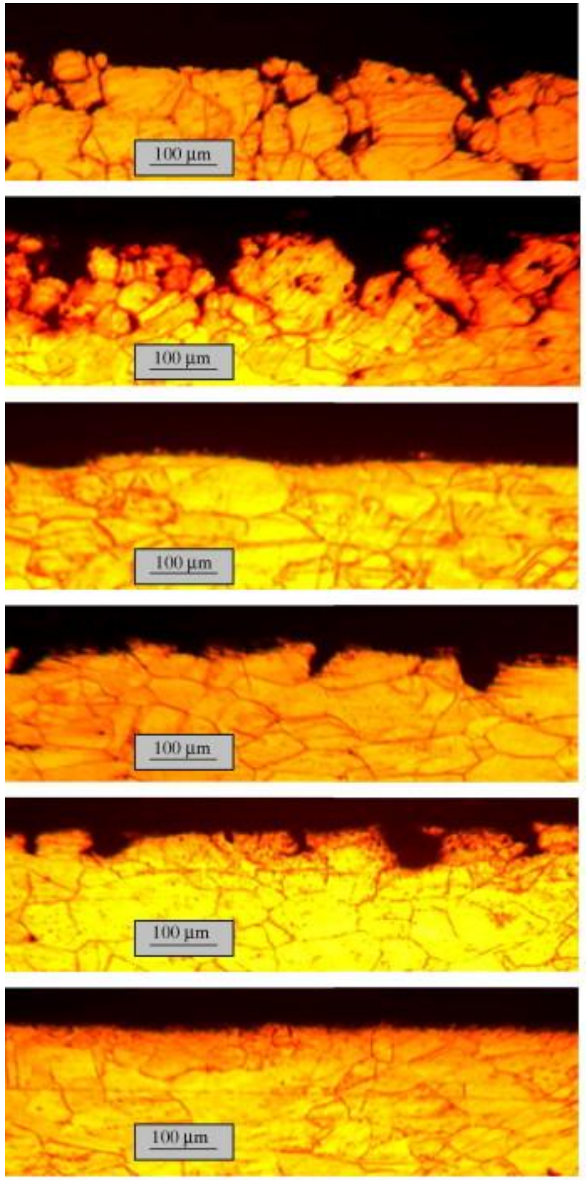
- As the redox potential of the mixture increases, metallic tellurium can react to form telluride compounds:

$$xTe + yNi \rightarrow Ni_yTe_x$$

$$xCr + yTe \rightarrow Cr_xTe_y$$

- This could cause specific intergranular cracking at the grain boundaries of the construction material.

- Significant effect of tellurium cracking on the alloys strength characteristics was established after corrosion testing with $U^{4+}/U^{3+} = 500$.



(a) K = 3360 pc×µm/cm

(b) K = 8300 pc×µm/cm

(c) no IGC

(d) K = 1660 pc×µm/cm

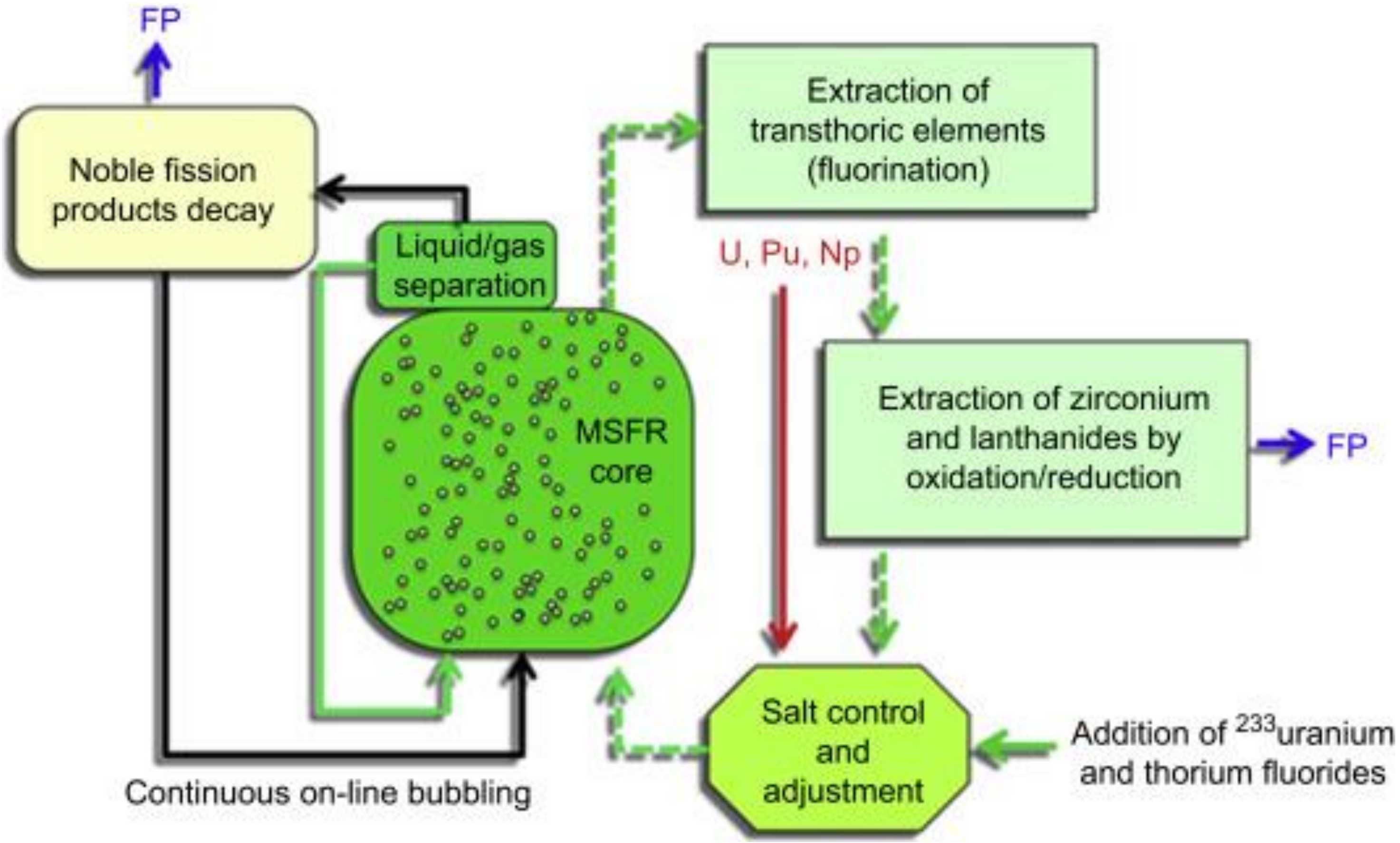
(e) K = 1850 pc×µm/cm

(f) no IGC

V. Ignatiev, A. Surenkov, I. Gnidoy, A. Kulakov, V. Uglov, A. Vasiliev, M. Presniakov, Intergranular tellurium cracking of nickel-based alloys in molten Li, Be, Th, U/F salt mixture, J. Nucl. Mat., 440 (2013) 243-249.

Reprocessing scheme

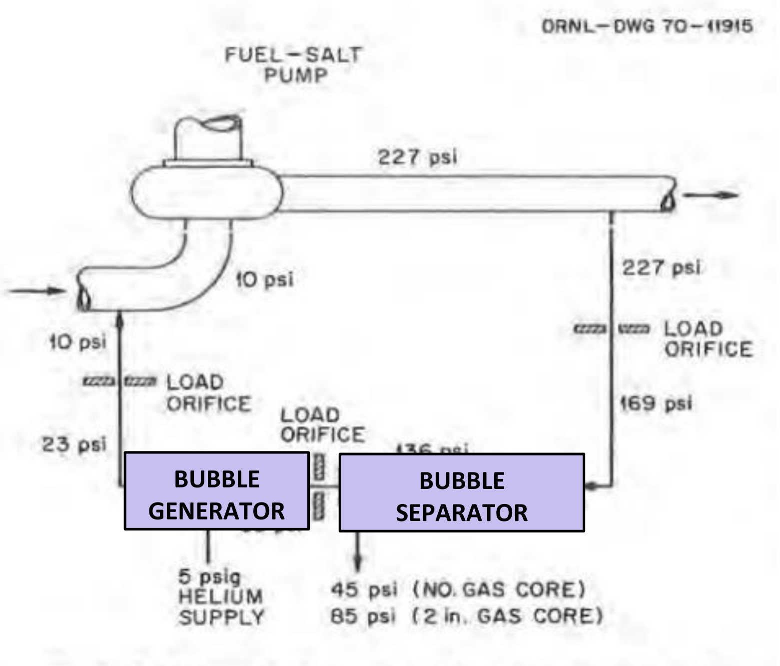
- Processes are envisaged to mantain the concentration of fission products at some acceptable equilibrium levels.

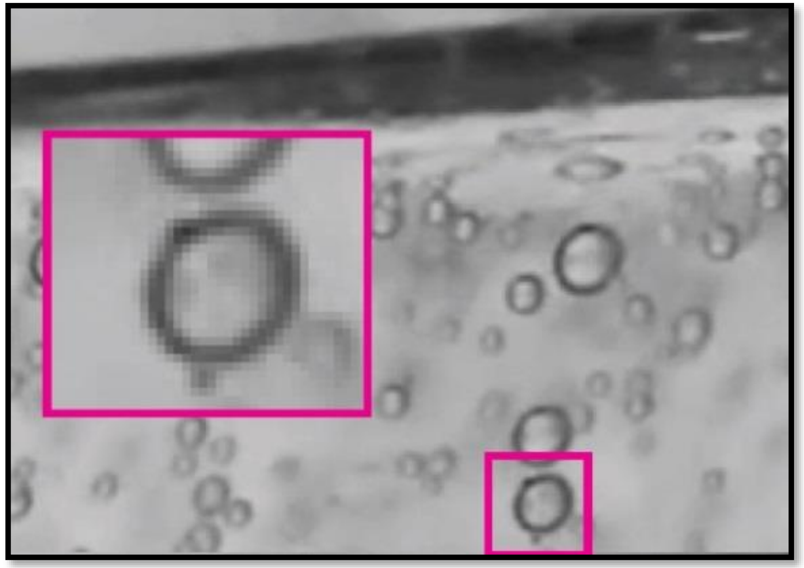


I. L. Pioro Handbook of Generation IV Nuclear Reactors, Elsevier (2016).

Noble gases & noble metals

- Removal of ^{135}Xe is very important for neutron economy as it is a strong neutron absorber.
- Noble metals are less problematic than the noble gases but if not extracted they plate out on the reactor wall. In particular they deposits on heat exchanger.
- The physical separation is performed **online** in the reactor core. Both gaseous species and particle in suspension are expected to be extracted by helium bubbling.

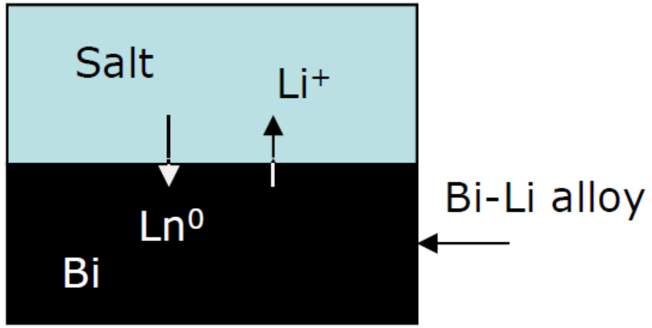




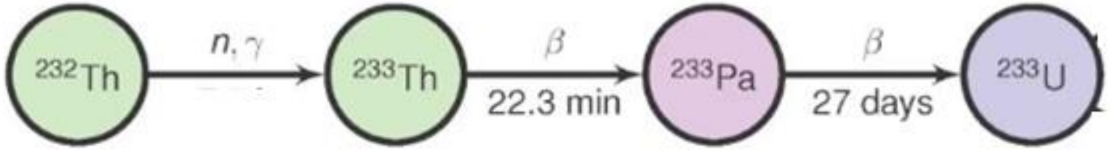
Dissolved fission products

- The influence of the salt soluble fission products on the fuel salt properties must be careful evaluated to ensure good physico-chemical properties of the salt and neutronic performance during reactor operation.

- Lanthanides, which are neutron absorber, can be extracted (in a salt batch reprocessing step) via liquid-liquid extraction.



- Protactinium is co-extracted with lanthanides. It must be separated and stored to fully decay to ^{233}U. Finally, the ^{233U} is fed back into the cycle.



Summary

- Molten salts used as fuel in MSRs show interesting physico-chemical properties with respect to reactor safety.
- Chemical aspects of MSR fuel (from fuel fabrication to reprocessing) are of paramount importance for the feasability of this concept.
- Control of the **redox potential** and of the **accumulation of impurities** are required to limit corrosion and mantaining good physico-chemical properties of the fuel.

> *...he called the Molten Salt Reactor Experiment "a chemist's reactor" because the "make-or-break problems" of the reactor required chemical solutions.*
>
> **Review of the Weinberg years at ORNL**

Molten Salt Reactors:

Fuel fabrication, fuel chemistry and in-reactor behaviour

Elisa Capelli