

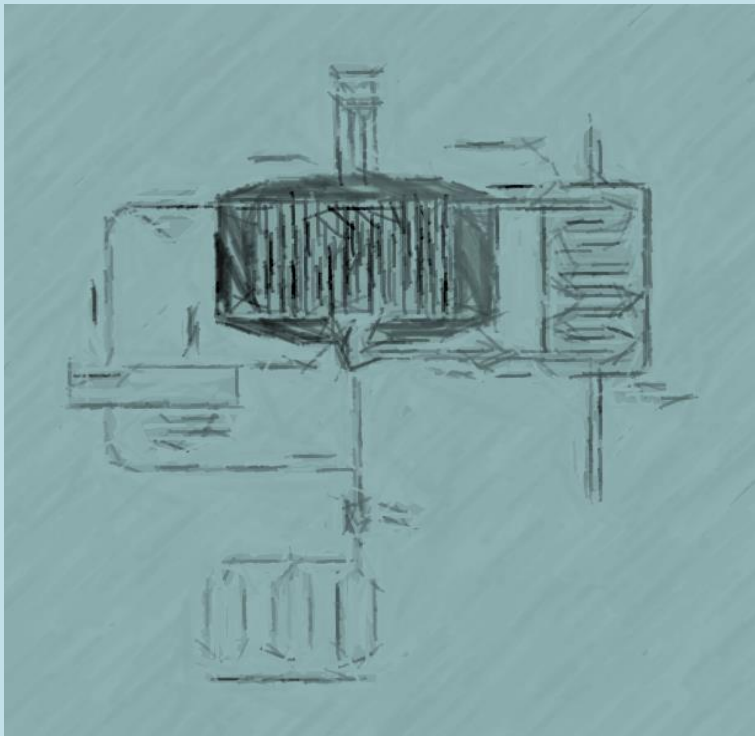
**The European Commission's
science and knowledge service**

Joint Research Centre

The chemistry behind the Molten Salt Reactor

Rudy Konings

European Commission, Joint Research Centre, Karlsruhe



European
Commission

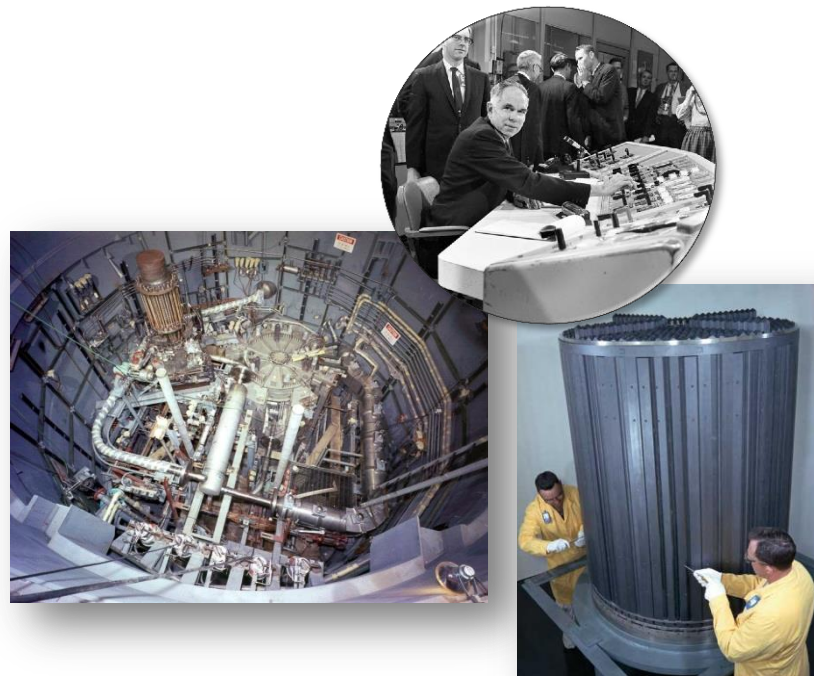
Molten Salt Reactors are nuclear fission reactors in which a liquid salt is used as coolant and as solvent for the fuel

... and they are nothing new

Aircraft Reactor Experiment



Molten Salt Reactor Experiment



Aircraft Reactor Experiment

Power	2.5 MW
Fuel Salt	53% NaF, 41% ZrF ₄ , 6% UF ₄ (93% enriched)
Fuel melting temperature	532 °C
Fuel inlet temperature	663 °C
Fuel outlet temperature	860 °C
Fuel flow rate	205 l/min
Moderator	BeO hexagonal blocks (9.1 cm across, 15.2 cm high) 3.18 cm coolant passages
Coolant	Helium to water
Containment	Inconel (Ni-Cr-Fe alloy)
Critical	3 November 1954
Shut down	12 November 1954

Molten Salt Reactor Experiment

Power	7.4 MW
Fuel Salt	71% ⁷ LiF, 29.1 % BeF ₂ , 5% ZrF ₄ , 0.9% UF ₄ (33% enriched)
Fuel melting temperature	434 °C
Fuel inlet temperature	635 °C
Fuel outlet temperature	860 °C
Fuel flow rate	1818 l/min
Moderator	Pyrolytic graphite
Coolant	66% ⁷ LiF, 34% BeF ₂
Containment	Hastaloy-N (68% Ni, 17% Mo, 7% Cr, 5% Fe)
Critical on ²³⁵ U	1 June 1965
Critical on ²³³ U	2 October 1968
Shut down	December 1969

Reactor classifications

According to

- Coolant
- Spectrum
- Temperature
- ...
- Core configuration

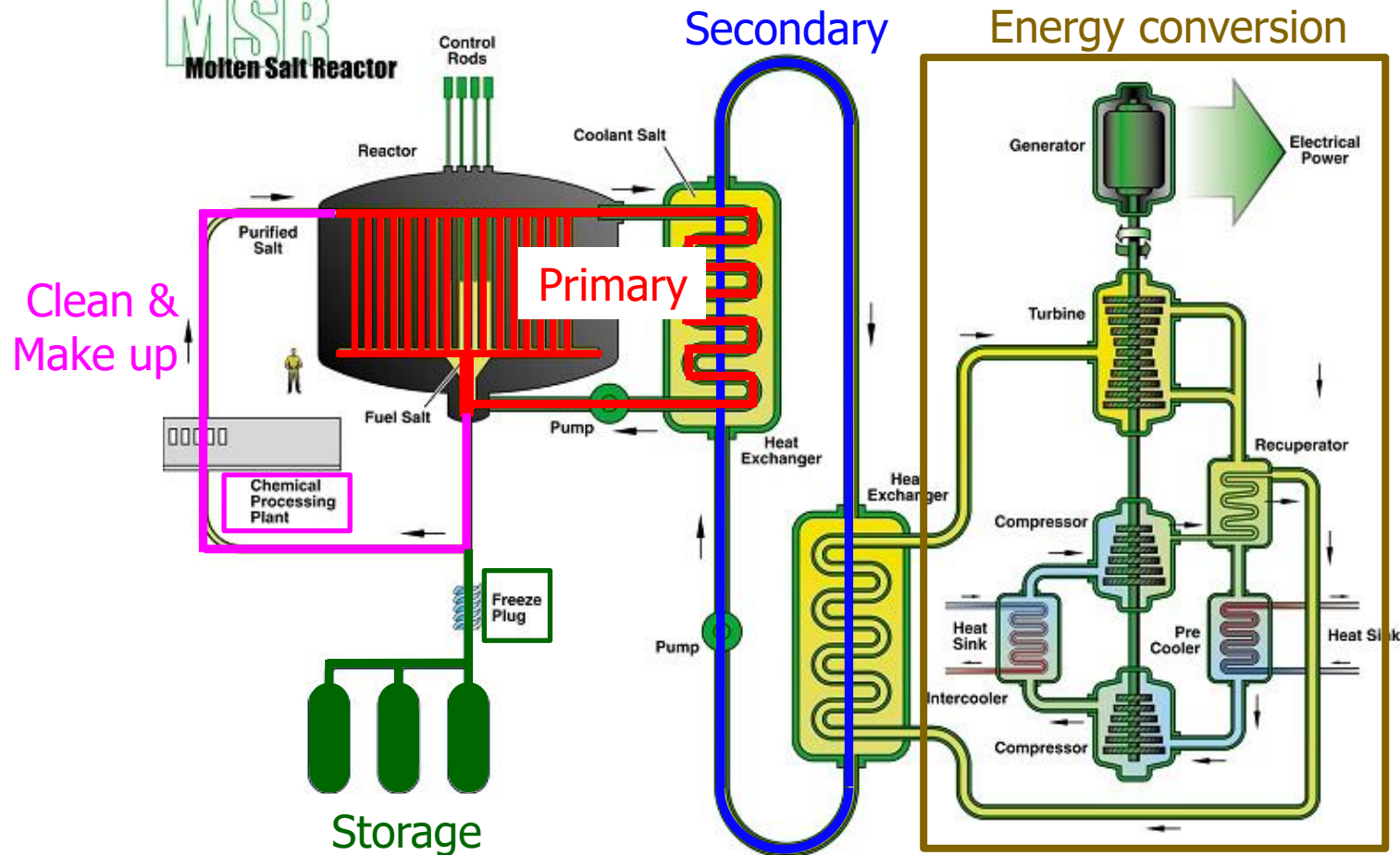
- Molten salt
- Thermal spectrum
- Moderate to high temperature

It is a chemical reactor

Homogeneous

Coolant and fuel are one phase
that is homogeneously
distributed in the core

MSR Molten Salt Reactor

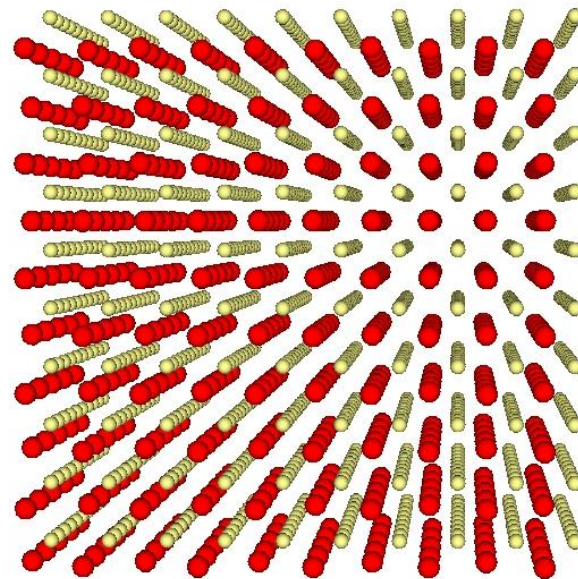
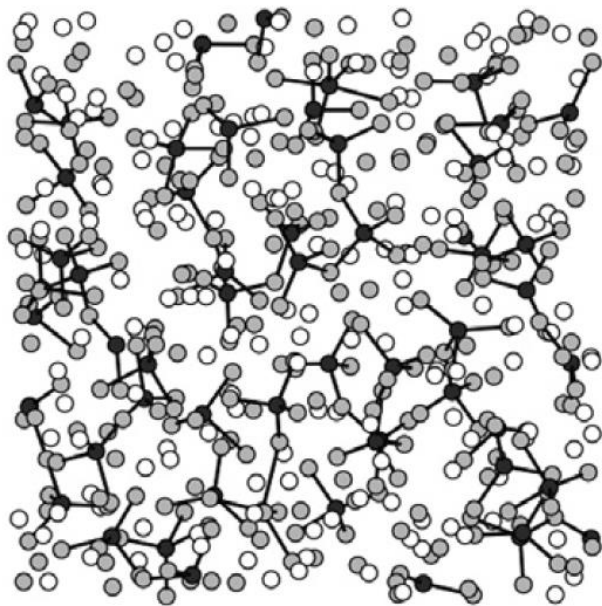


02-GA50807-02

Claimed advantages of molten salt fuel

- Ambient pressure
 - Salt expands with temperature
 - No radiation damage constraints
 - Can be extracted from core
 - Fission gases can be removed
 - Fission products are retained
- No driving force for dispersion
 - Negative temperature & void coefficients
 - No fuel replacement
 - No melt-down scenario
 - Better neutron economy (^{135}Xe extraction)
 - No Cs and I release

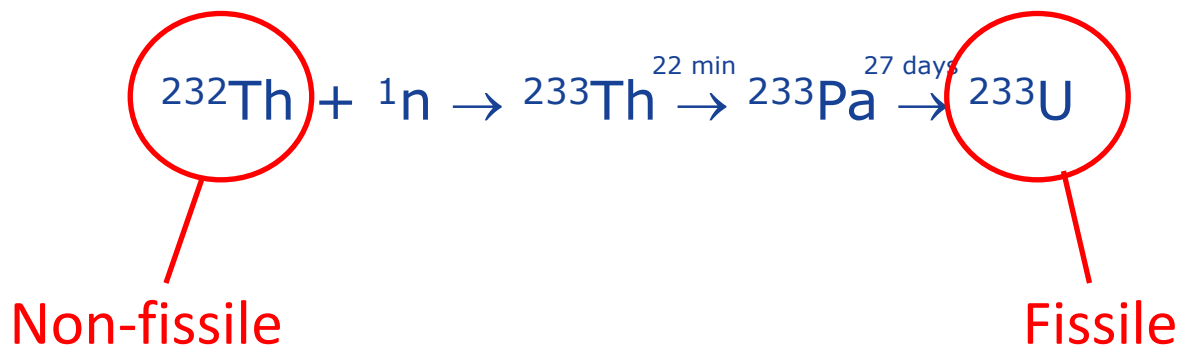
Molten fluoride salt vs. solid oxide fuel



Claimed advantages of molten salt fuel

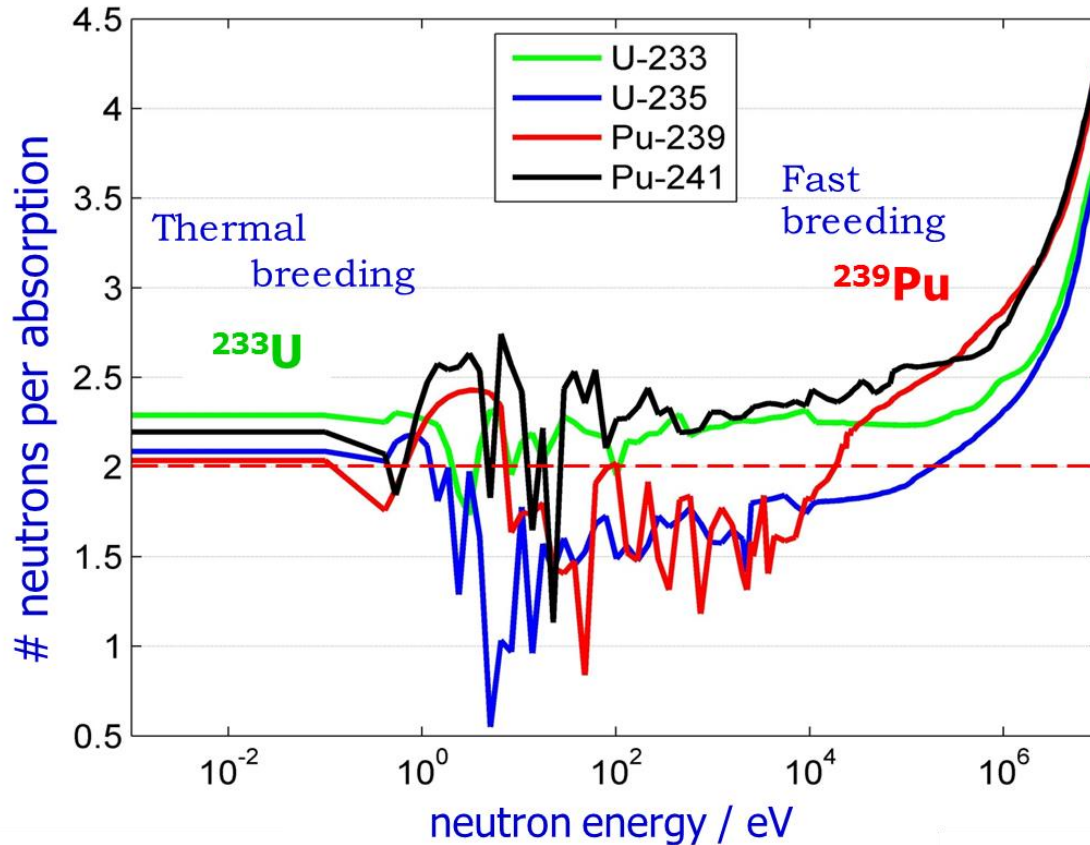
- Ambient pressure
 - Salt expands with temperature
 - No radiation damage constraints
 - Can be extracted from core
 - Fission gases can be removed
 - Fission products are retained
 - Allows on-line clean up and refueling
- No driving force for dispersion
 - Negative temperature & void coefficients
 - No fuel replacement
 - No melt-down scenario
 - Better neutron economy (^{135}Xe extraction)
 - No Cs and I release
 - Low(er) initial fissile inventory
 - Reduced fission product content
 - Low(er) decay heat

Claimed advantages: Thorium-based breeding

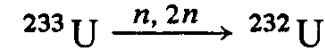
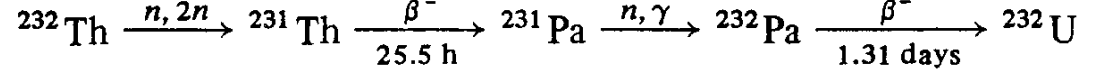
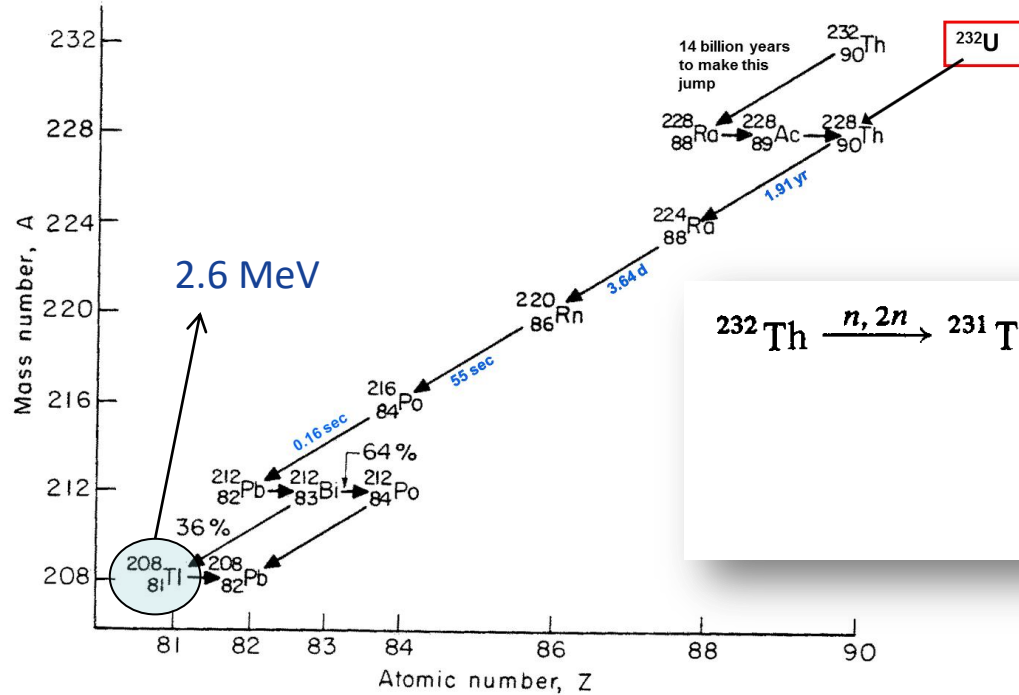


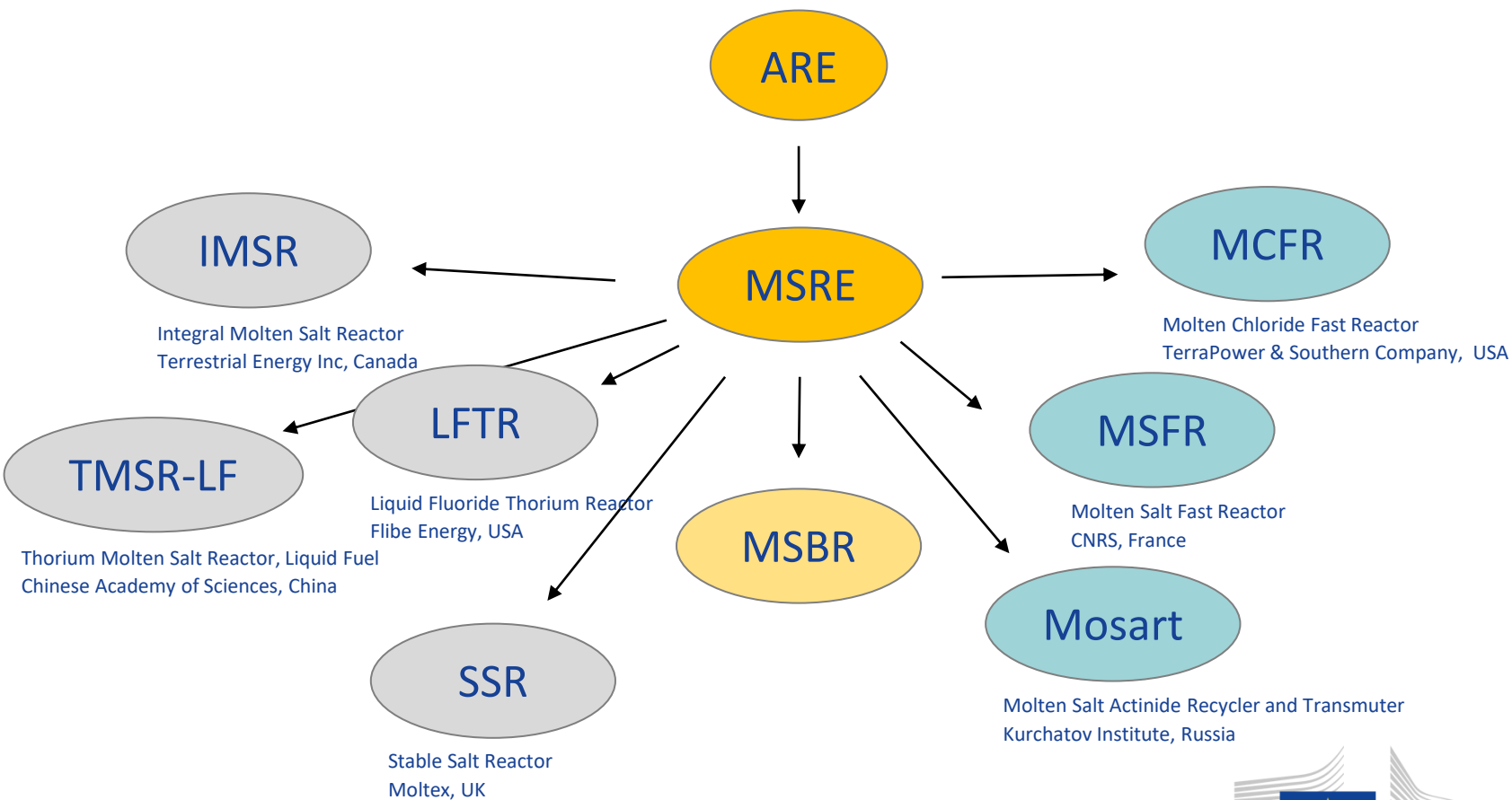
- ^{233}U is an excellent fissile material
- Strongly reduced transuranium element production (Pu, Np, Am)
- The Th/U cycle needs start-up (U, Pu)

Claimed advantages: Thorium-based breeding



Claimed advantages: Thorium-based breeding





Thermal versus Fast

Thermal

- Fluoride salt needed, low atomic number metals
- Low breeding ratio (Th/U)
- High clean-up frequency
- Low fissile inventory
- Moderator (graphite) – life time issues

Fast

- Chloride salt gives harder spectrum
- Actinide burning capability
- Smaller through-put
- High fissile inventory
- -

Fuel salt requirements 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

Fluoride versus Chloride

Fluoride

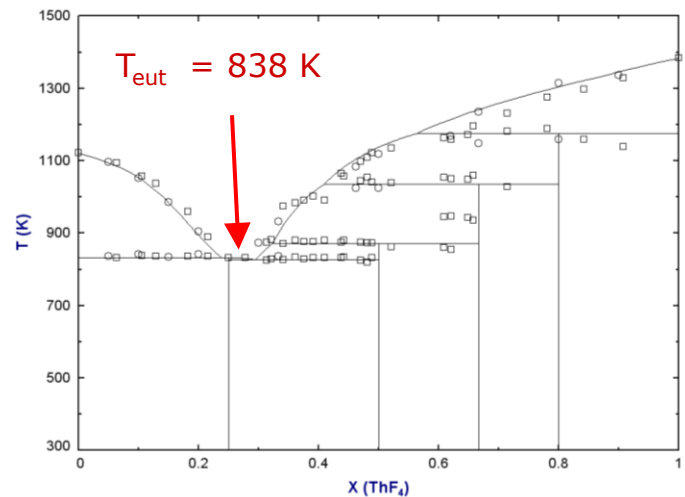
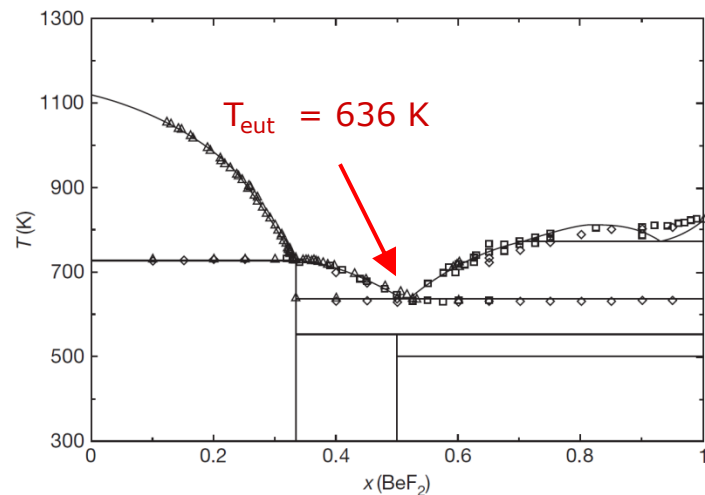
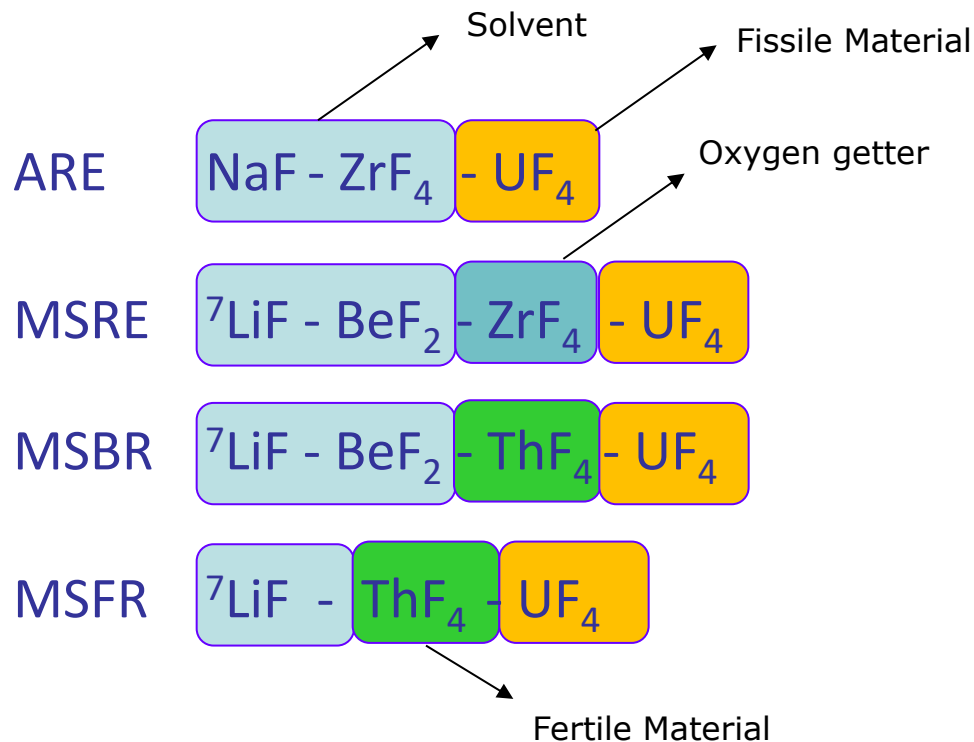
- Radiation resistance
- -
- ¹
- Strong moderator
- Stable hexafluorides
- Low solubility of Pu

Chloride

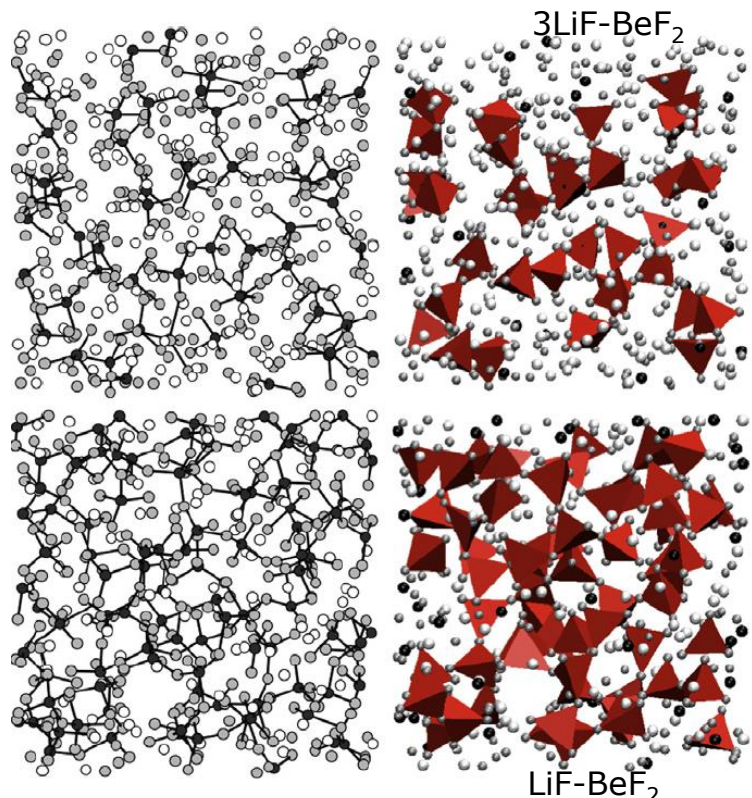
- -
- Lower melting points
- ³⁶Cl formation ($3.01 \cdot 10^5$ y)
- Harder spectrum
- -
- High solubility
transuranium elements

¹ However, tritium formation from Li and Be

Solvent/fuels for MSR



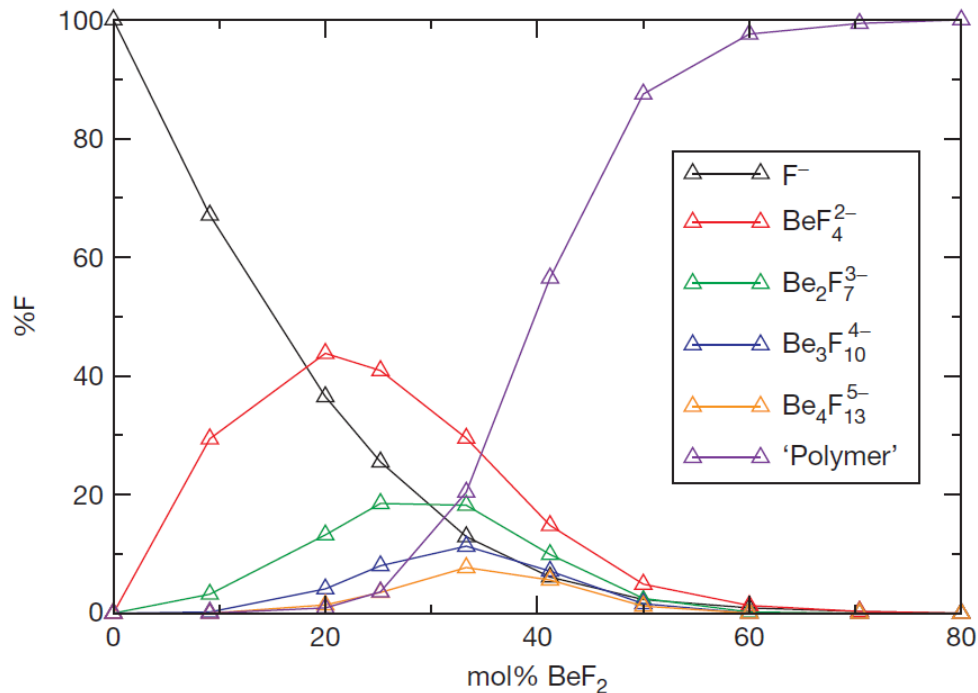
Structure of a molten fluoride salt



- LiF is a strongly ionic liquid: Li⁺ and F⁻ species
- BeF₂ is a polymeric liquid: Be_nF_{3n+1}⁻⁽ⁿ⁺¹⁾ species
- ThF₄ is a molecular liquid: ThF₅⁻ and ThF₆²⁻ species

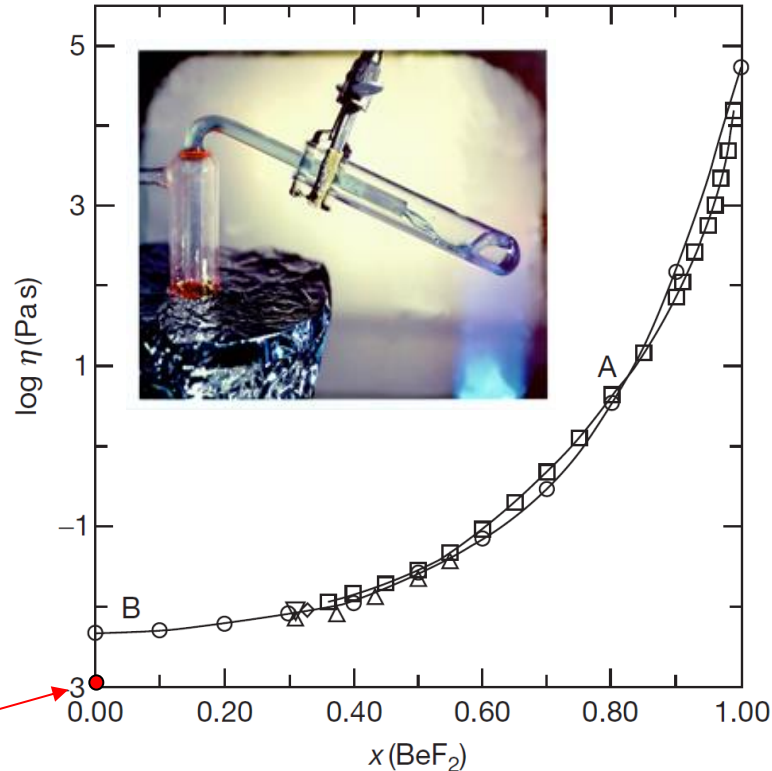
Picture from: M. Salanne et al., in: Molten Salts Chemistry, Chapter 1, Elsevier, 2013.

Structure & properties of the salt



Percentage of F atoms involved in various species observed in the LiF-BeF₂ system as a function of composition (Salanne et al. J. Phys. Chem. B, 111, 4678)

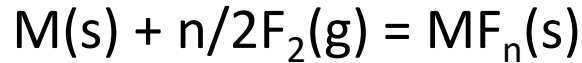
water



Viscosity of LiF-BeF₂ as a function of the BeF₂ concentration at 873 K. (Beneš & Konings, J. Fluor. Chem., 130, 22)

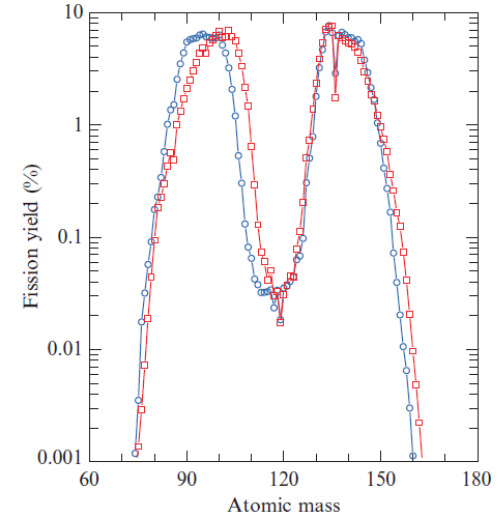
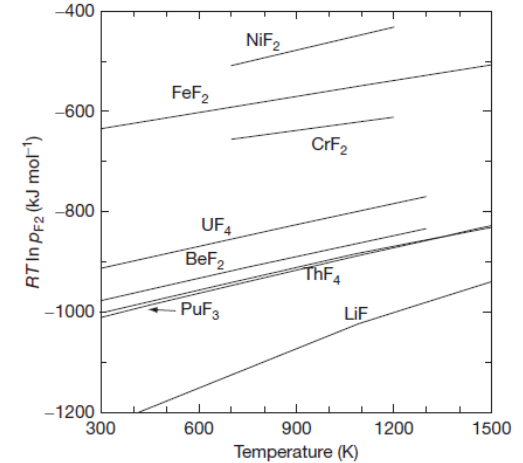
Chemical potential of fluorine

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

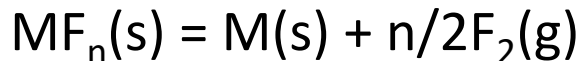


$$K_p = \frac{1}{p(F_2)^{\frac{n}{2}}}$$

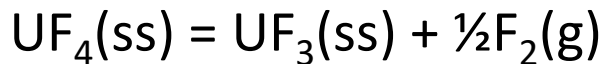
- ✓ Fission increases the fluorine potential
 - The average valence of the fission products is lower than 4+ of uranium



Fluorine potential and electropotential

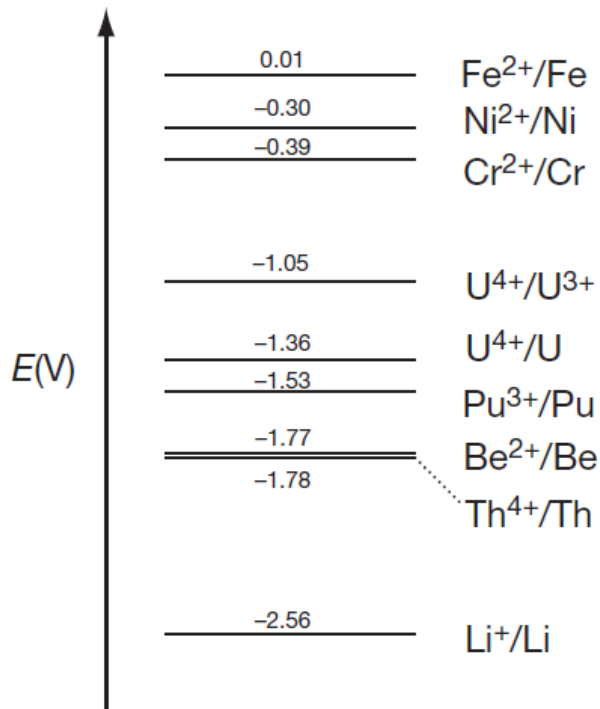


$$\Delta G_r = \mathbf{RT} \ln(p(\text{F}_2)) = n\mathbf{F}E$$

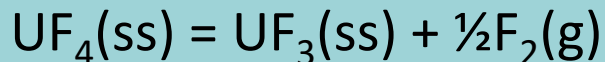


$$E = E^0 + \frac{\mathbf{RT}}{n\mathbf{F}} \ln \frac{a(\text{UF}_3)}{a(\text{UF}_4)}$$

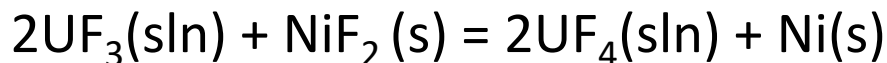
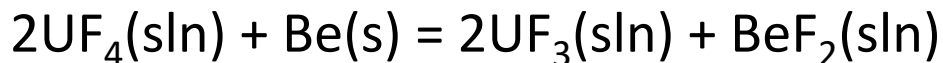
Standard potential in LiF-BeF₂ (66–34)
relative to the HF(g)/H₂ couple 1000 K.



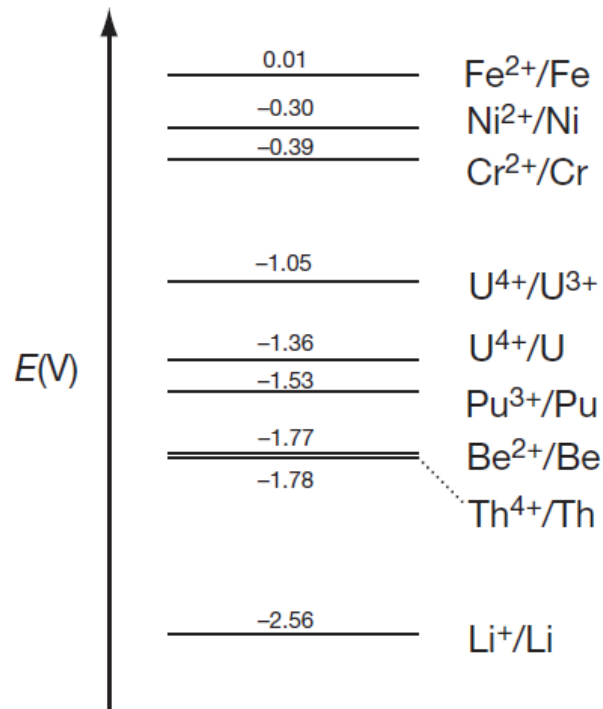
Redox control of the salt



Options tested in MSRE:

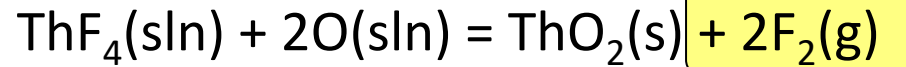


Standard potential in LiF-BeF₂ (66–34)
relative to the HF(g)/H₂ couple 1000 K.



Oxygen chemistry of the salt

- ✓ Oxygen plays an important role in the fuel chemistry



dissolved

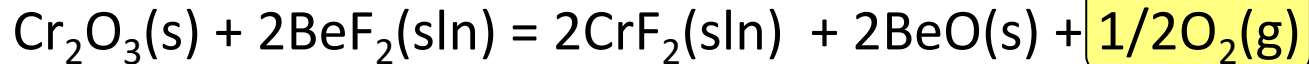


precipitate

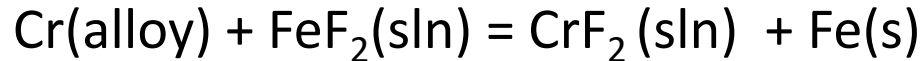
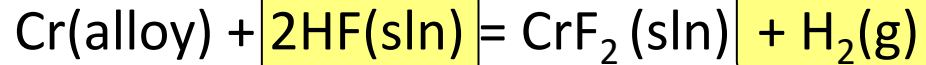
- Oxygen concentration in fuel salt must be low ($x_{\text{O}} < 8 \cdot 10^{-4}$)
- Requires fluorination of starting material (with $\text{HF}(\text{g})$)
- Control of the oxidation potential of the fuel

Corrosion

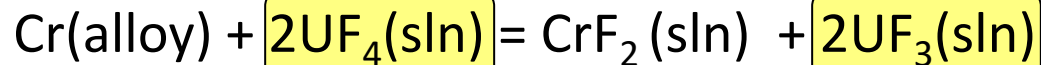
1. Reaction with the oxide film on the metal



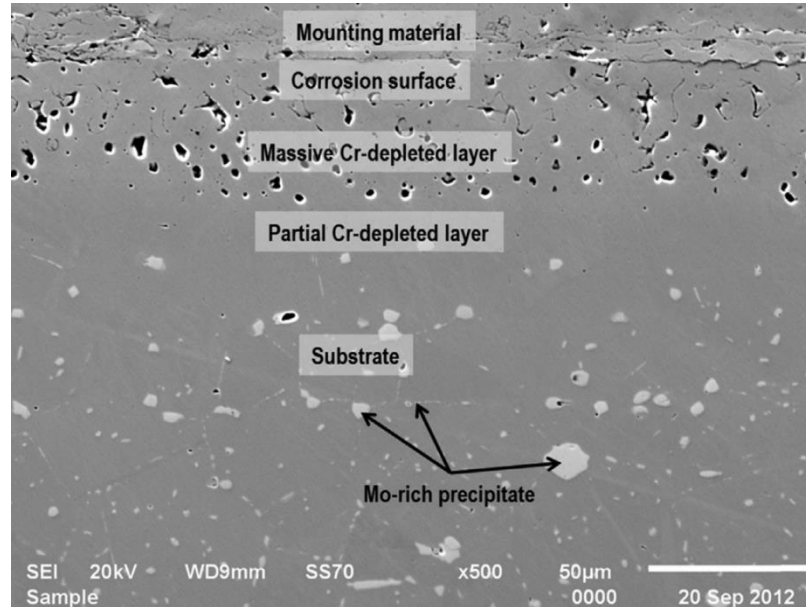
2. Reaction with impurities from fabrication process



3. Reaction with fuel constituents



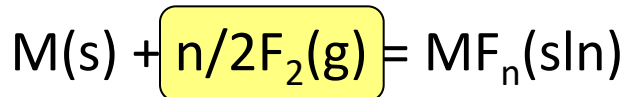
Corrosion



Hastelloy N for 1000 h at 850°C in
 KF-ZrF_4 salt (Sabharwall, 2014)

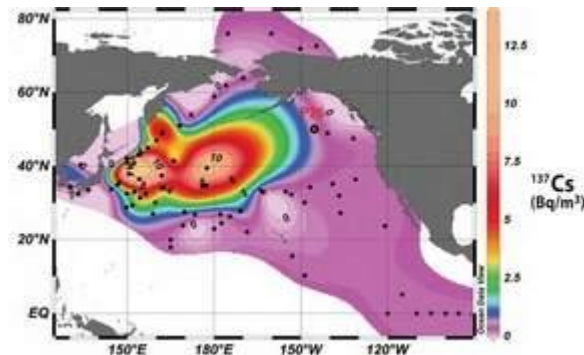
Fission product chemistry of the salt

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



Chemical state of the FPs:

- Dissolved in the liquid salt
- Metallic precipitates
- Gas



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

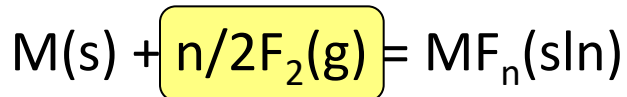
Cs, Ba, Sr, Zr, La, I, ...

Mo, Pd, Rh, Tc, Te

Kr, Xe

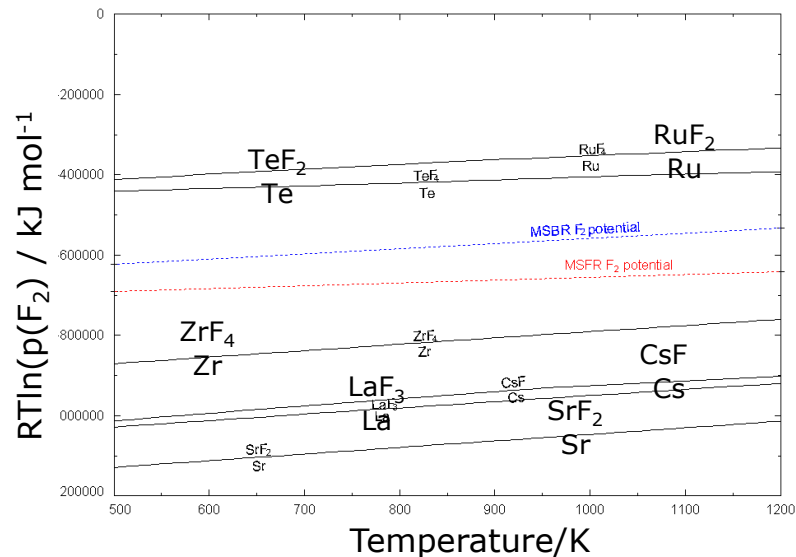
Fission product chemistry of the salt

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Cs, Ba, Sr, Zr, La, I, ...

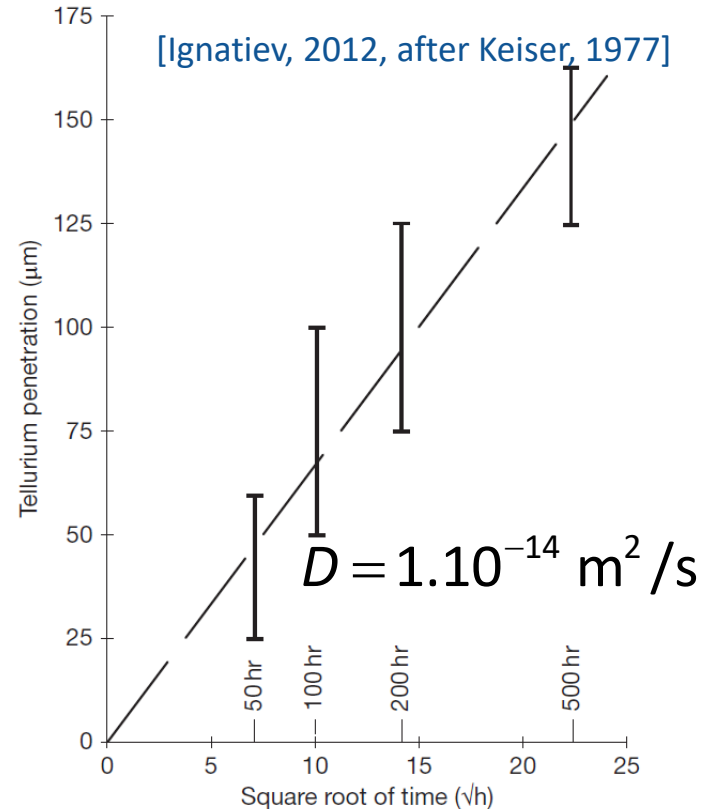
Mo, Pd, Rh, Tc, Te

Kr, Xe

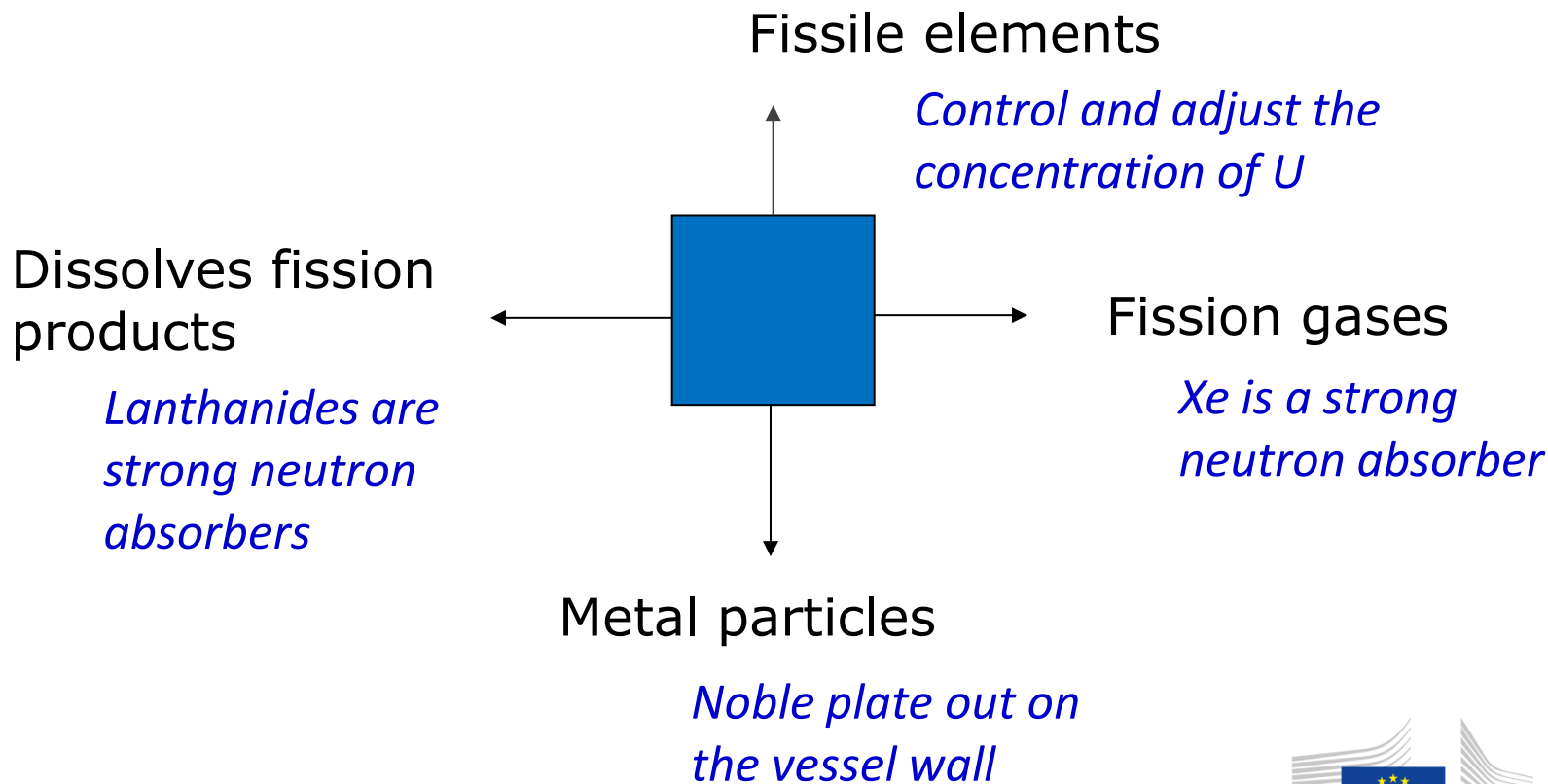
Fission product chemistry of the salt

- ✓ Tellurium attacks the Hastalloy
 - Selective diffusion along grain boundaries
 - Intergranular cracking in strained samples
 - Laboratory experiments show similar cracking as MSRE

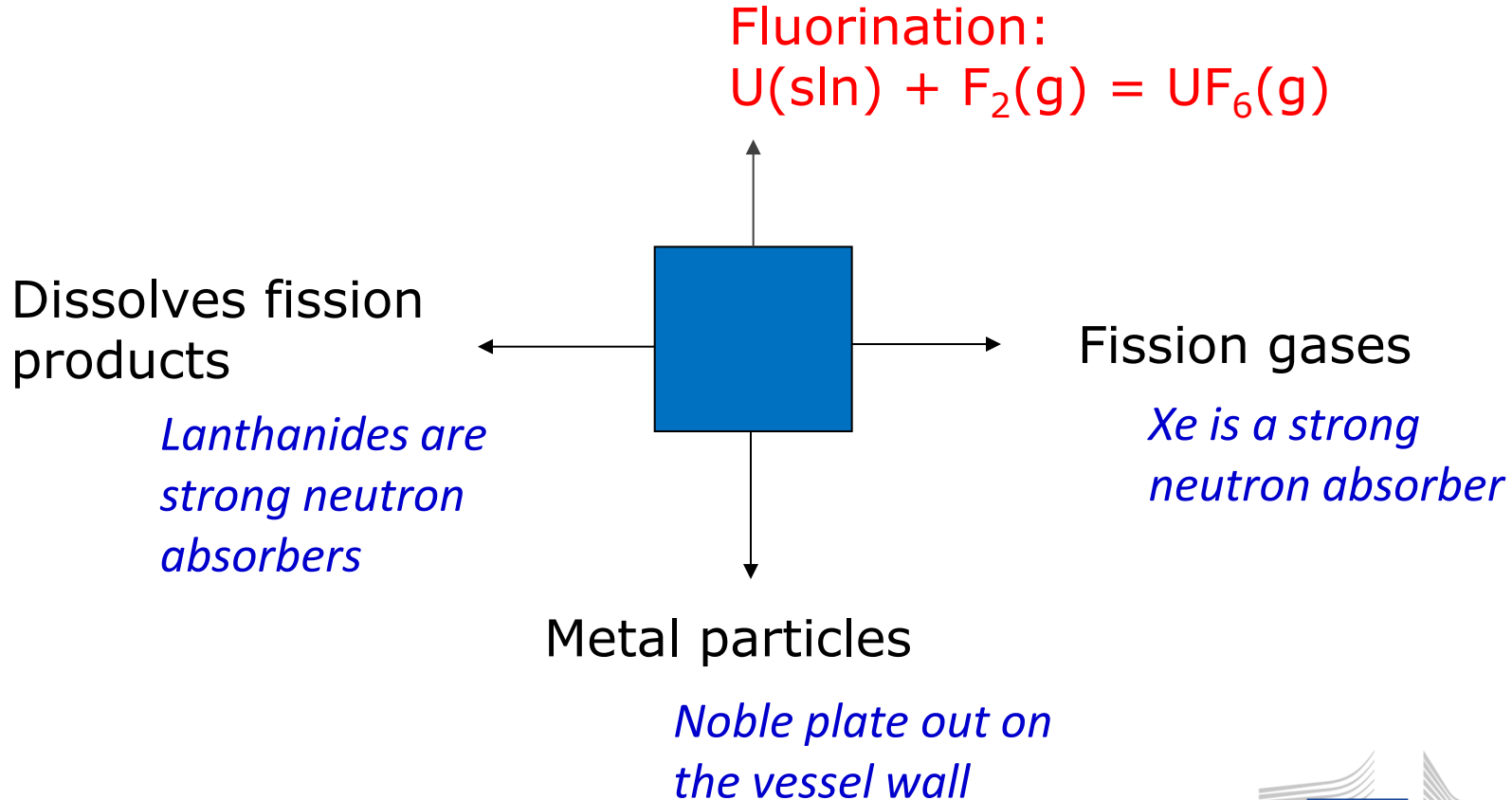
Minimised in reducing environment



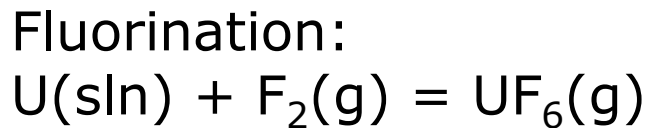
Fuel salt clean-up



Fuel salt clean-up

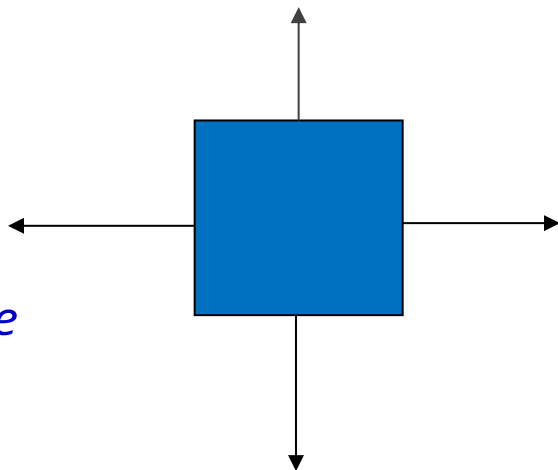


Fuel salt clean-up



Dissolves fission
products

*Lanthanides are
strong neutron
absorbers*



Helium bubbling

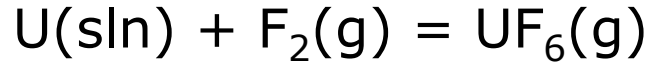
Metal particles

*Noble plate out on
the vessel wall*



Fuel salt clean-up

Fluorination:

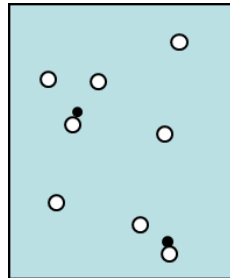


Dissolves fission products

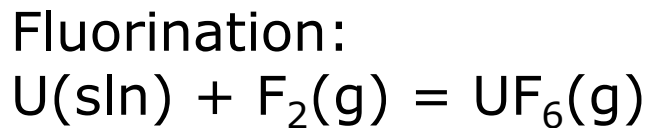
Lanthanides are strong neutron absorbers

Helium bubbling

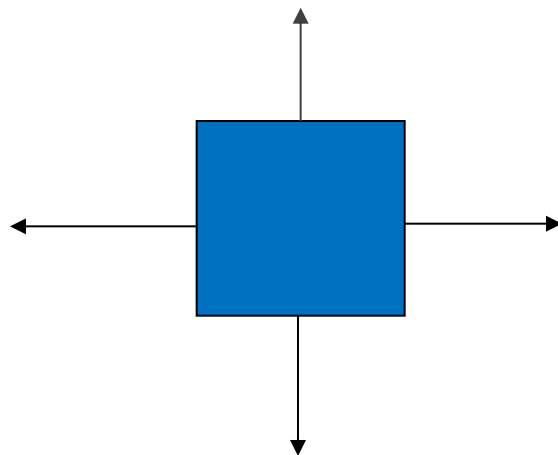
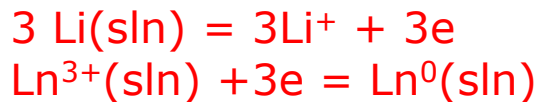
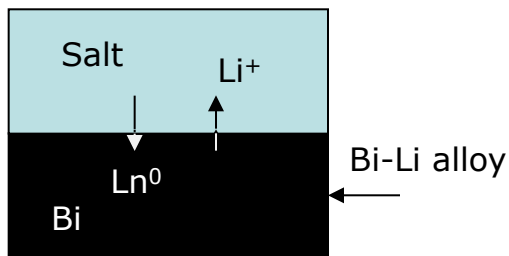
Helium bubbling



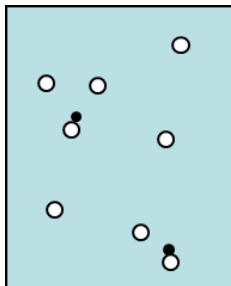
Fuel salt clean-up



Liquid/liquid
extraction



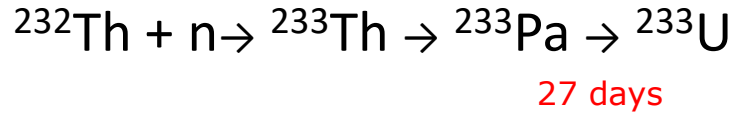
Helium bubbling



Helium bubbling



Fuel salt clean-up: Protactinium



^{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

Conclusion from MSRE: still relevant

- ✓ The management of the tritium production in 7LiF-BeF_2 to avoid release to secondary system and environment.
- ✓ Corrosion of Hastelloy-N by tellurium.
- ✓ Fuel chemistry surveillance and control.
- ✓ Control of gas entrainment in the circulating fuel to levels $< 0.1 \text{ vol\%}$ to avoid reactor instabilities.
- ✓ Continuous removal of ^{233}Pa from the fuel to achieve high conversion/breeding ratios.
- ✓ Thermal heat transfer performance of salt/salt and salt/air heat exchangers.

Challenges for the fuel chemistry

- ✓ Optimise composition with respect to safety margins and properties
 - Oxygen measurement and control
 - 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 demonstrate the clean-up technology
 - Helium bubbling for metallic particles
 - Fission product removal using extraction techniques

Research in the European Union

- MOST (FP5 2001-2004) [Review of molten salt reactor technology](#)
- ALISIA (FP6) [Assessment of Liquid Salts for Innovative Applications](#)
- EVOL (FP7 2011-2013) [Evaluation and Viability Of Liquid fuel fast reactor](#)
- SAMOFAR (H2020 2015-2019) [Safety Assessment of the Molten Salt Fast Reactor](#)

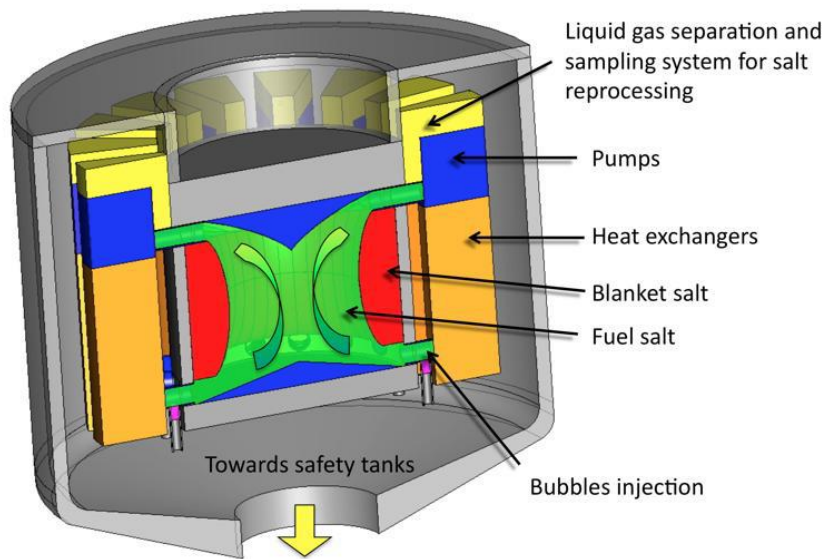
Grand Challenge SAMOFAR

The grand objective of this proposal is to prove the innovative safety concepts of the MSFR by advanced experimental and numerical techniques, to deliver a breakthrough in nuclear safety and optimal waste management, and to create a consortium of stakeholders to demonstrate the MSFR beyond SAMOFAR.

List of Participants

Number	Organisation	Country
1 (Coordinator)	Technische Universiteit Delft (TU Delft)	The Netherlands
2	Centre National de la Recherche Scientifique (CNRS)	France
3	JRC - Joint Research Centre- European Commission (JRC)	Germany
4	Consorzio Interuniversitario Nazionale per la Ricerca Tecnologica Nucleare (CIRTEN)	Italy
5	Institut de Radioprotection et de Sûreté Nucléaire (IRSN)	France
6	Centro de Investigacion y de Estudios Avanzados del Instituto Politecnico Nacional (CINVESTAV)	Mexico
7	AREVA NP SAS (AREVA)	France
8	Commissariat a l'Energie Atomique et aux Energies Alternatives (CEA)	France
9	Electricité de France S.A. (EDF)	France
10	Paul Scherrer Institute (PSI)	Switzerland
11	Karlsruher Institut für Technologie (KIT)	Germany

The Molten Salt Fast Reactor



Working parameters

- High temperature (750 °C)
- Low pressure (1 bar)
- Circulation time (4 sec)
- $\text{LiF-ThF}_4\text{-UF}_4\text{-(TRU)F}_3$
(77.5-6.6-12.3-3.6 mol%).
- Online processing / fueling
- Fuel & blanket salt

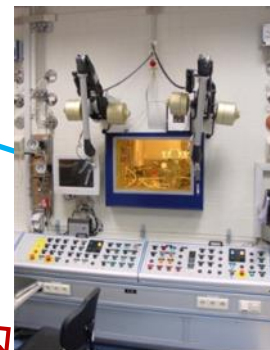
Synthesis and purification
of **An and Ln fluorides**
and chlorides



Electrochemical studies of
actinides and Ln in molten
fluoride and chloride media



Demonstration of
pyrochemical
separation
methods for
irradiated
materials



**JRC-Karlsruhe
Molten Salt Research**

High temperature properties
and **phase diagrams** of An
halides and mixtures



RAMAN spectroscopy
of molten salts



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

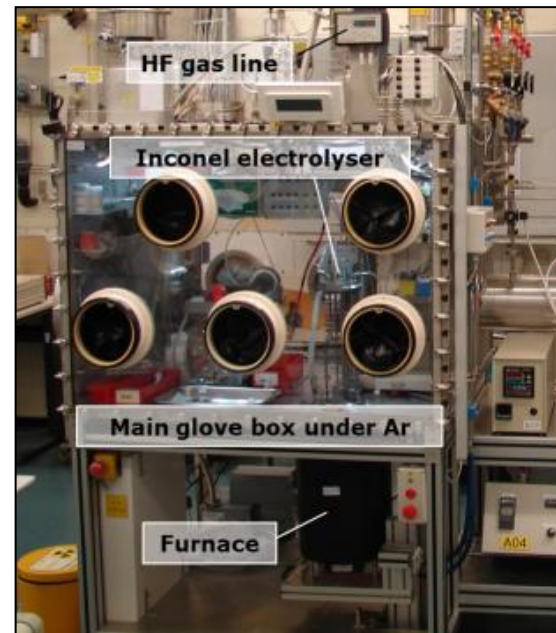
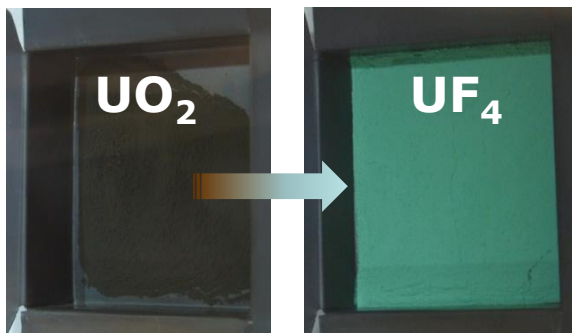


NMR high temperature
probe for **molten salts**



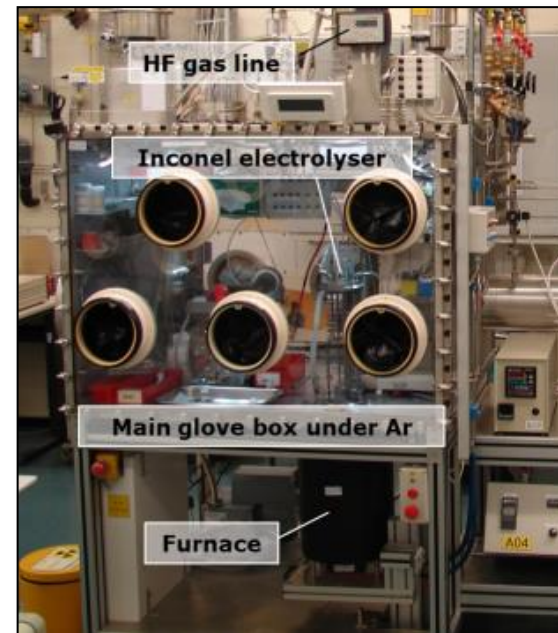
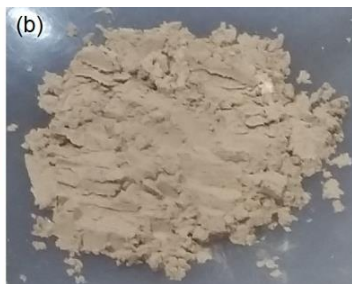
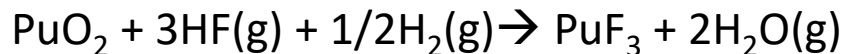
Fluorination line for synthesis & purification

- HF gas line + Inconel fluorination reactor (up to 1200° C)
- ThF₄, UF₄ and PuF₃ synthesised from nano-sized ThO₂, UO₂ and PuO₂ with very high purity

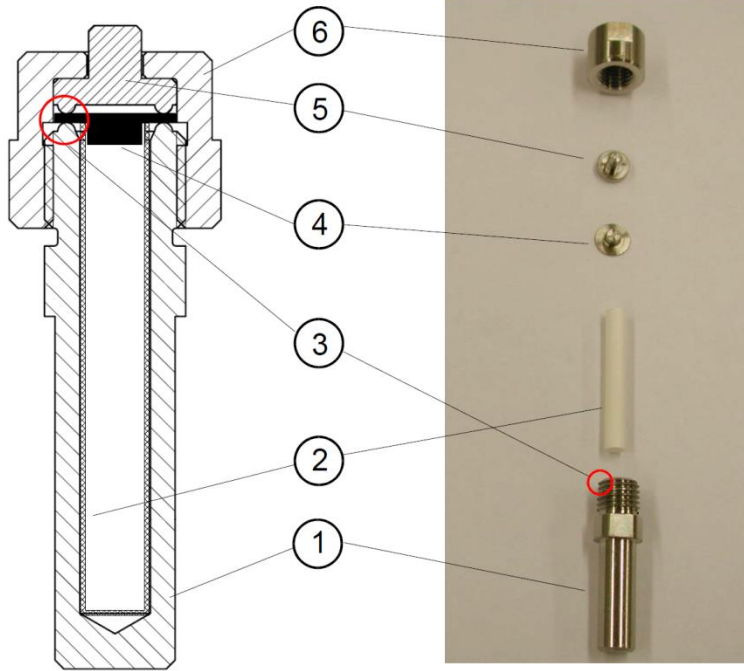


Fluorination line for synthesis & purification

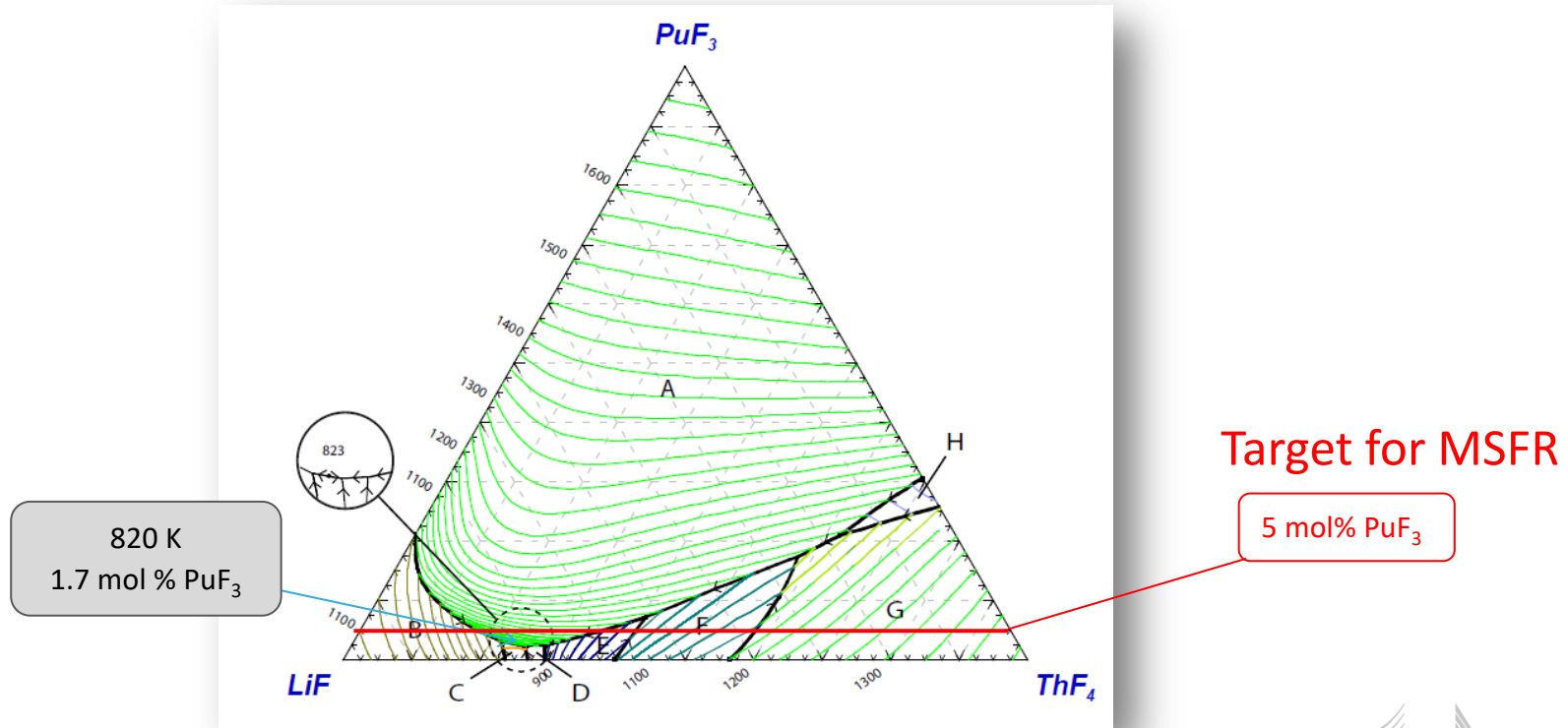
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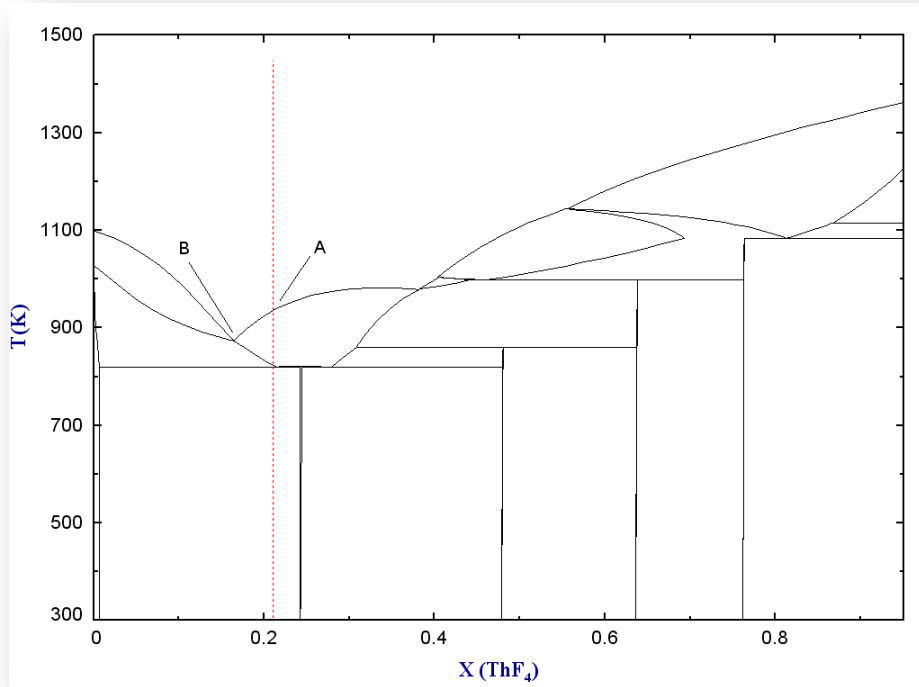
Experimental approach for phase diagram studies



Phase diagram determination: fuel optimisation



Phase diagram determination: fuel optimisation



Pseudobinary LiF-ThF₄ for 5 mol% PuF₃

Point A: LiF-ThF₄-PuF₃ (74-21-5 mol%)

- liquidus point **935 K** (662° C)
- inlet temperature **985 K** (712° C) when 50 K margin

Point B: LiF-ThF₄-PuF₃ (78.6-16.4-5 mol%)

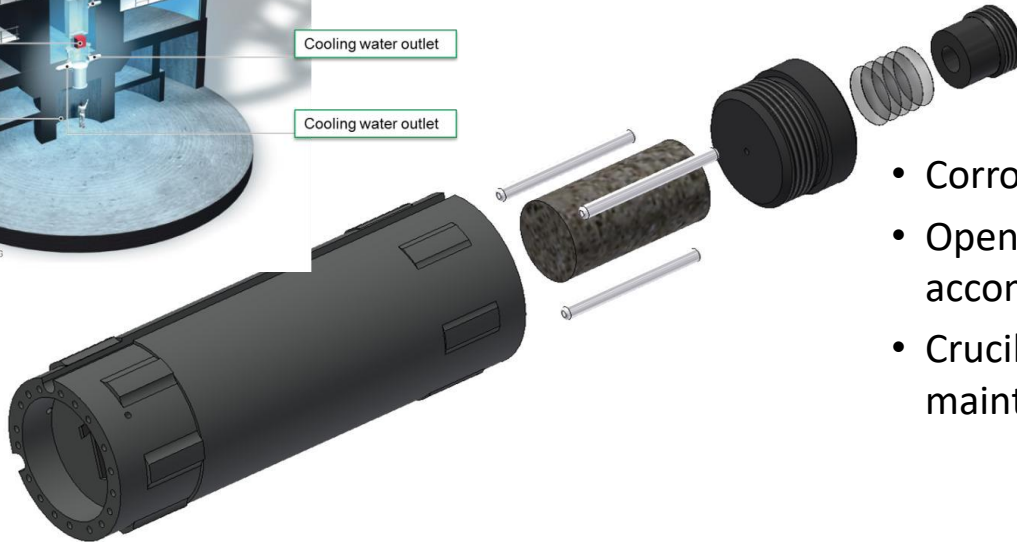
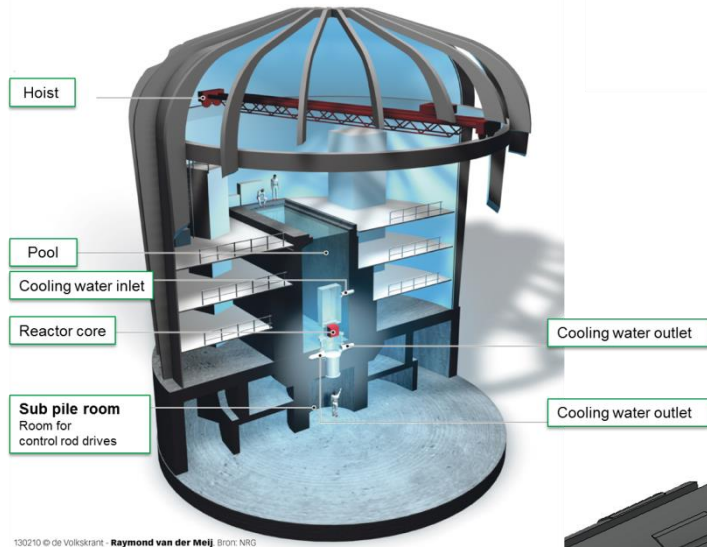
- liquidus point is **873 K** (600° C)
- inlet temperature is **923 K** (650° C) when 50 K margin

Salient irradiation experiment in HFR-Petten

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

– ThF_4 -LiF eutectic mixture

Collaboration NRG and JRC



- Corrosion-resistant graphite crucible
- Open container (metallic filter) to accommodate FG release
- Crucible wall temperature maintained at $T_{\text{melt}} + 50 \text{ K}$

Ultimate challenge

An reactor loop to test

- Materials in dynamic conditions and under irradiation
- Test the helium bubbling on real fuels
- Test the fuel chemistry & redox control in real conditions
- Validate thermohydraulic and heat transfer models
- ...



Thank you for listening !

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