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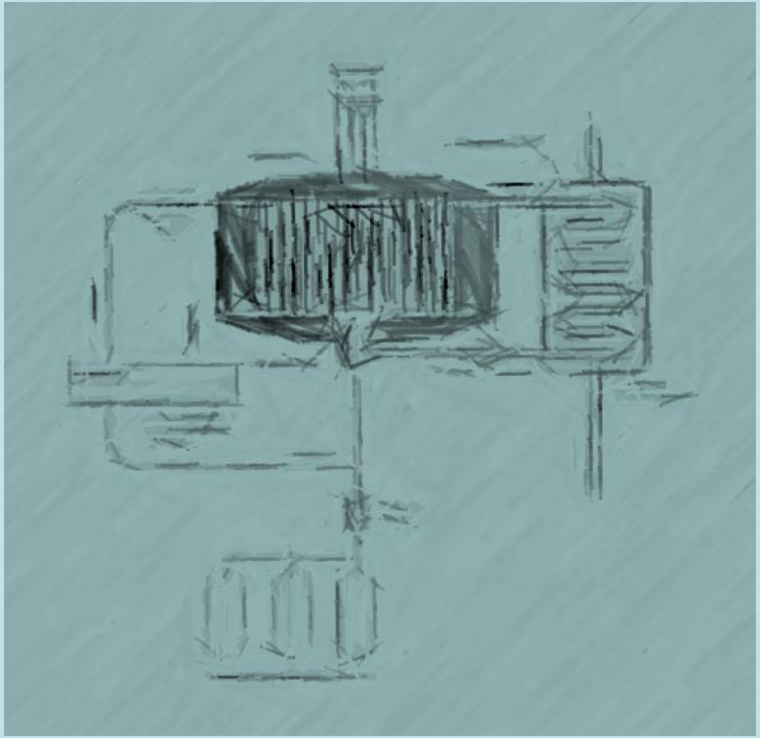


The chemistry behind the Molten Salt Reactor

Rudy Konings

European Commission, Joint Research Centre, Karlsruhe

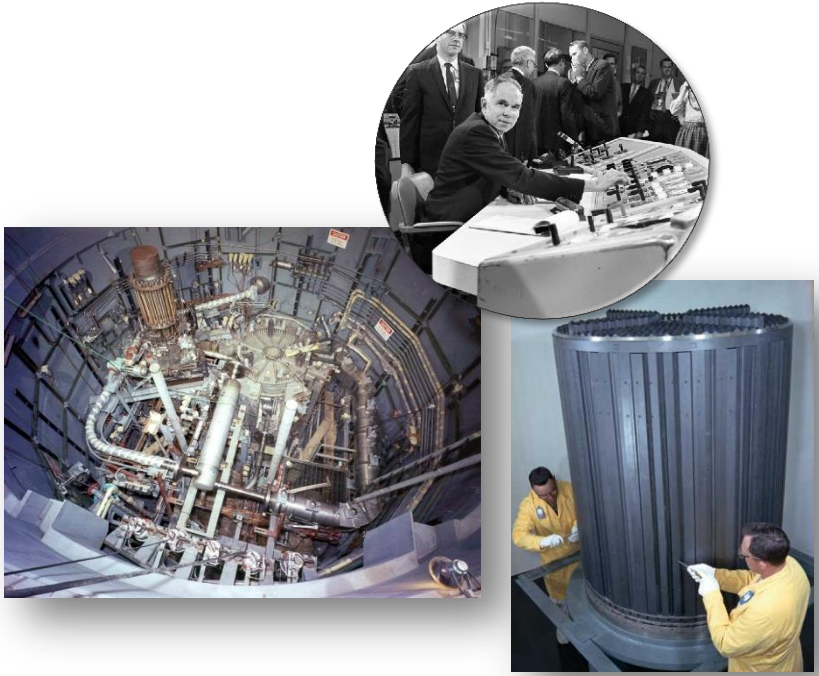
European Commission

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 o
- Mo igh
- Homogeneous

It is a chemical reactor

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

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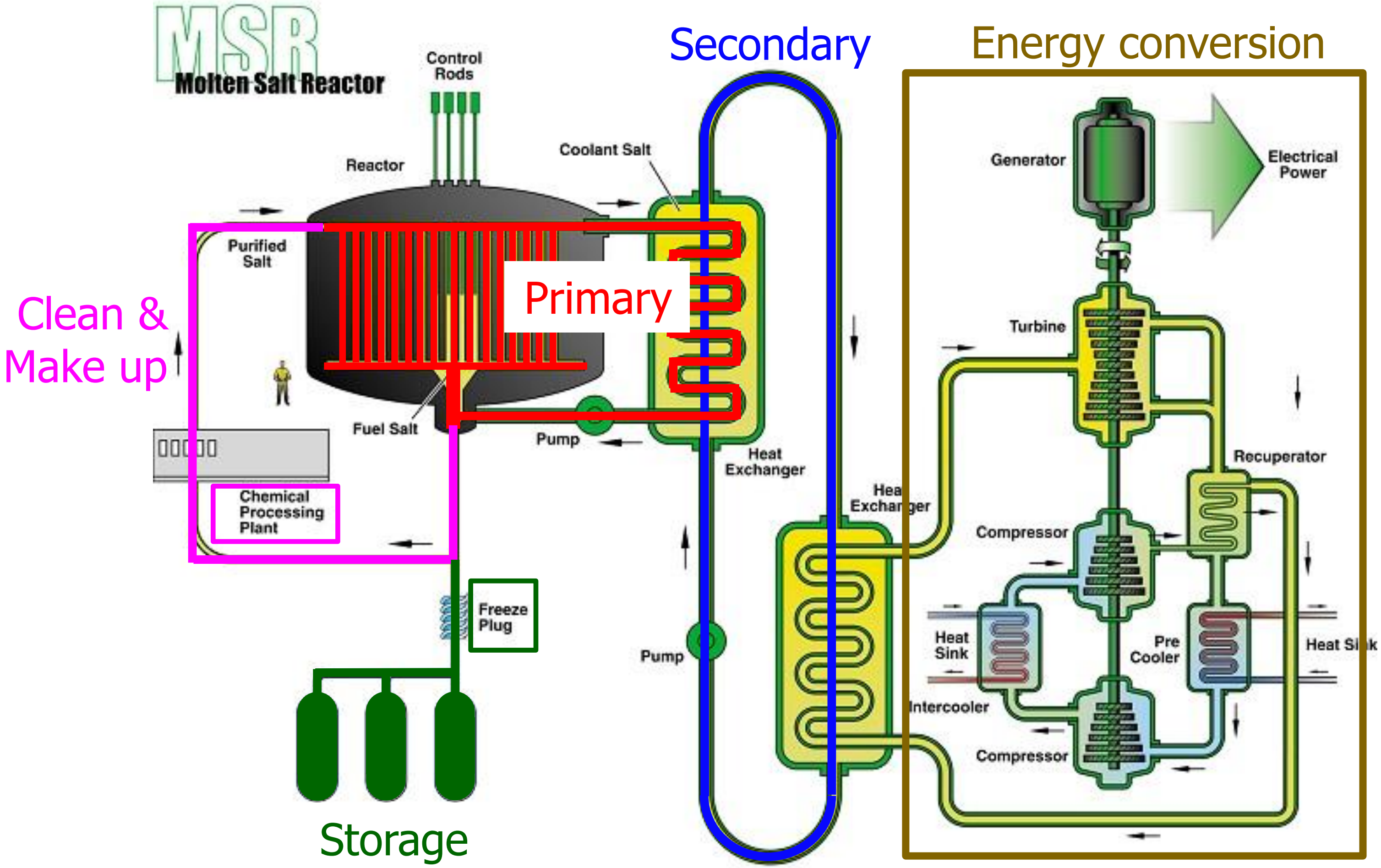

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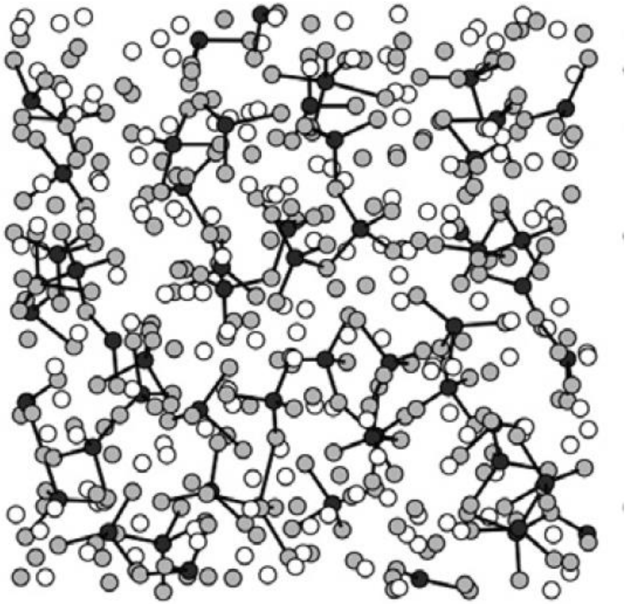
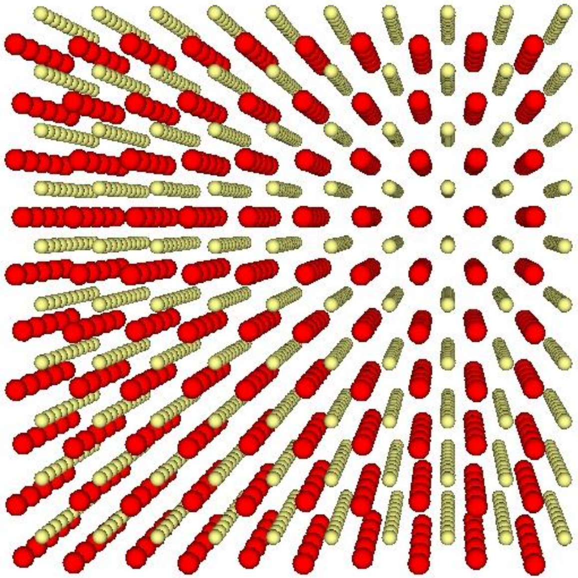
Claimed advantages of molten salt fuel

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

Molten fluoride salt vs. solid oxide fuel





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• No radiation damage constraints	- No fuel replacement
• Can be extracted from core	- No melt-down scenario
• Fission gases can be removed	- Better neutron economy (^{135}Xe extraction)
• Fission products are retained	- No Cs and I release
• Allows on-line clean up and refueling	- Low(er) initial fissile inventory - Reduced fission product content - Low(er) decay heat

Claimed advantages: Thorium-based breeding

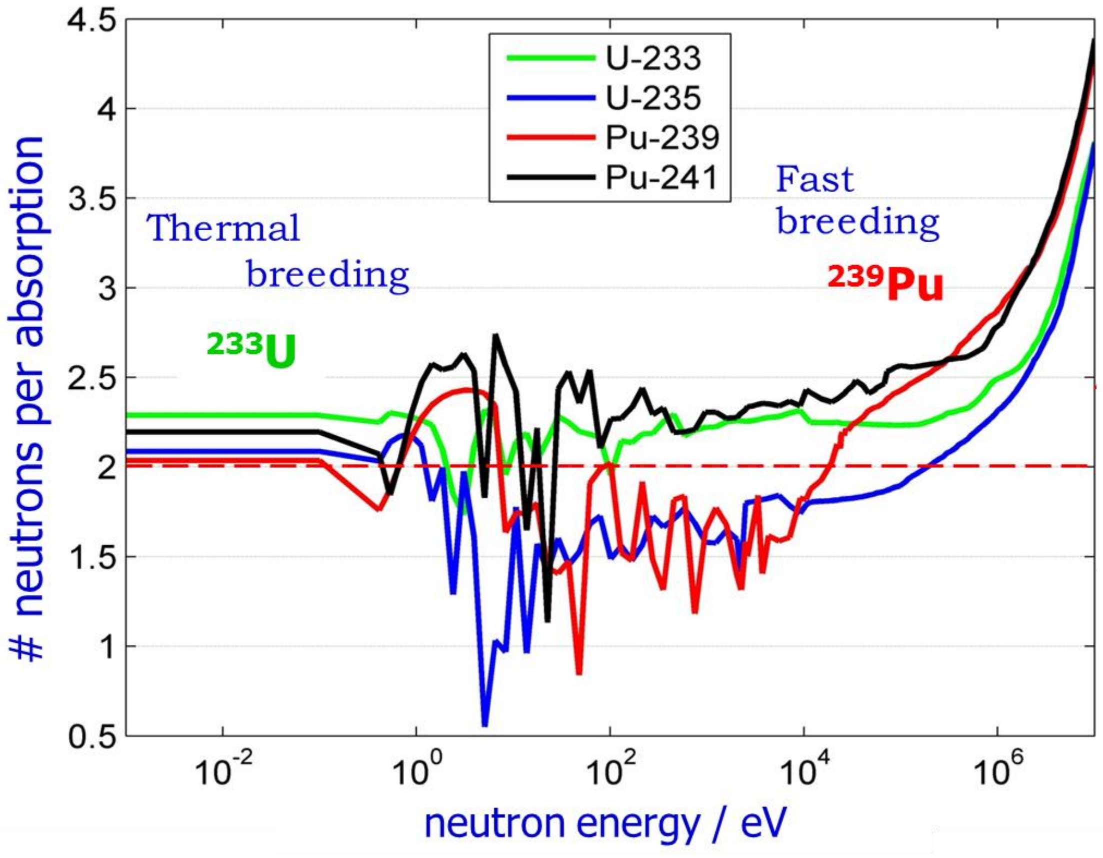
$$^{232}\text{Th} + {}^{1}\text{n} \rightarrow {}^{233}\text{Th} \xrightarrow{22\ \text{min}} {}^{233}\text{Pa} \xrightarrow{27\ \text{days}} {}^{233}\text{U}$$

Non-fissile

Fissile

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

Claimed advantages: Thorium-based breeding



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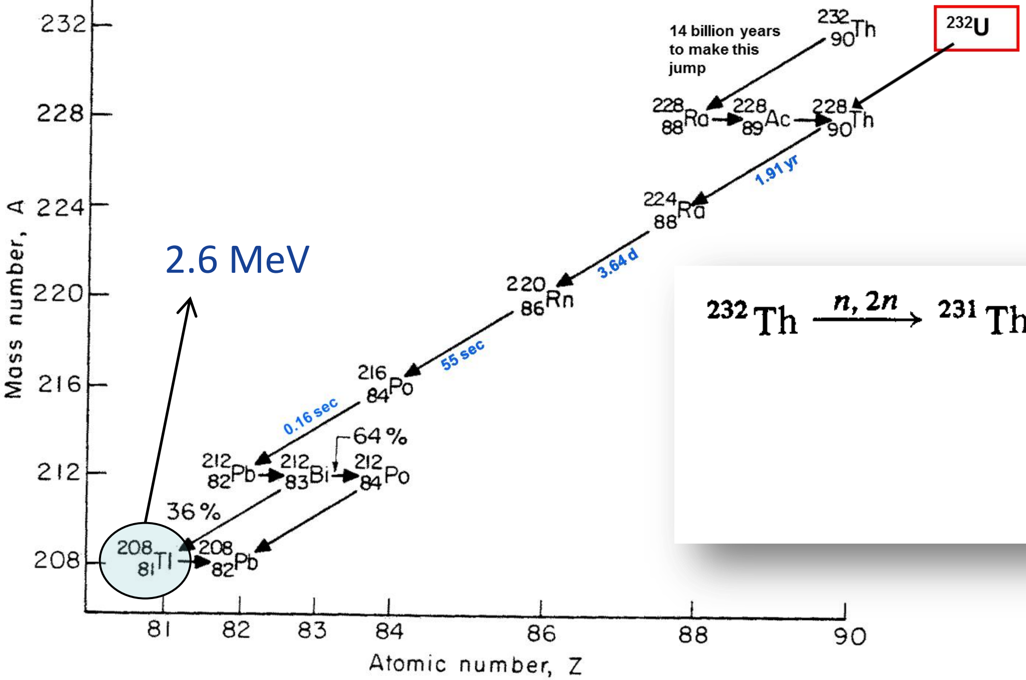
Claimed advantages: Thorium-based breeding



$$^{232}\mathrm{Th} \xrightarrow{n,\,2n} {}^{231}\mathrm{Th} \xrightarrow[25.5\ \mathrm{h}]{\beta^-} {}^{231}\mathrm{Pa} \xrightarrow{n,\,\gamma} {}^{232}\mathrm{Pa} \xrightarrow[1.31\ \mathrm{days}]{\beta^-} {}^{232}\mathrm{U}$$

$$^{233}\mathrm{U} \xrightarrow{n,\,2n} {}^{232}\mathrm{U}$$

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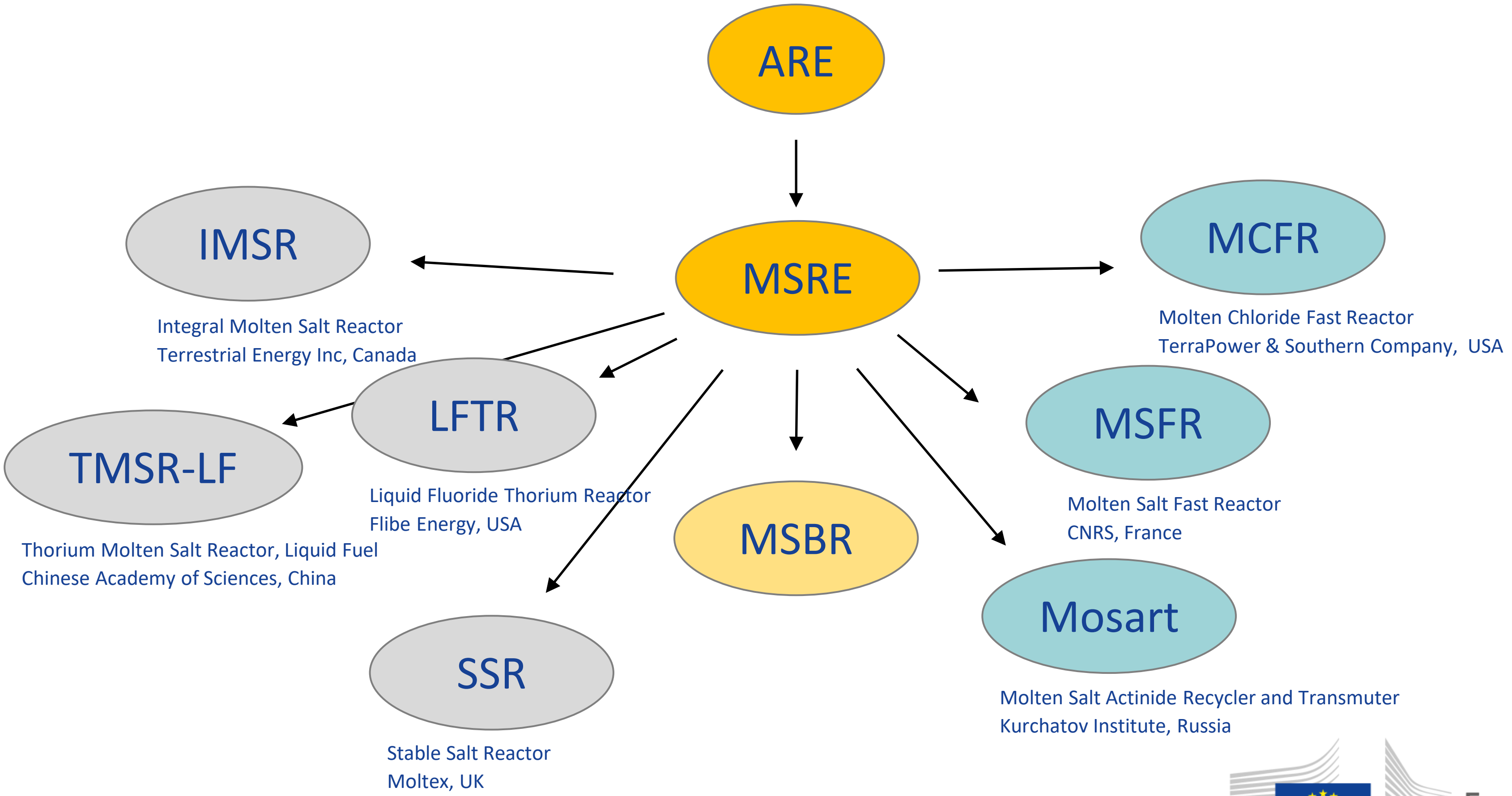

ARE
MSRE
IMSR
Integral Molten Salt Reactor
Terrestrial Energy Inc, Canada
MCFR
Molten Chloride Fast Reactor
TerraPower & Southern Company, USA
LFTR
Liquid Fluoride Thorium Reactor
Flibe Energy, USA
TMSR-LF
Thorium Molten Salt Reactor, Liquid Fuel
Chinese Academy of Sciences, China
MSBR
MSFR
Molten Salt Fast Reactor
CNRS, France
Mosart
Molten Salt Actinide Recycler and Transmuter
Kurchatov Institute, Russia
SSR
Stable Salt Reactor
Moltex, UK

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
- ^{36}Cl formation (3.01 10^5 y)
- Harder spectrum
- -
- High solubility transuranium elements

[1] However, tritium formation from Li and Be

Solvent/fuels for MSR

Solvent

Fissile Material

Oxygen getter

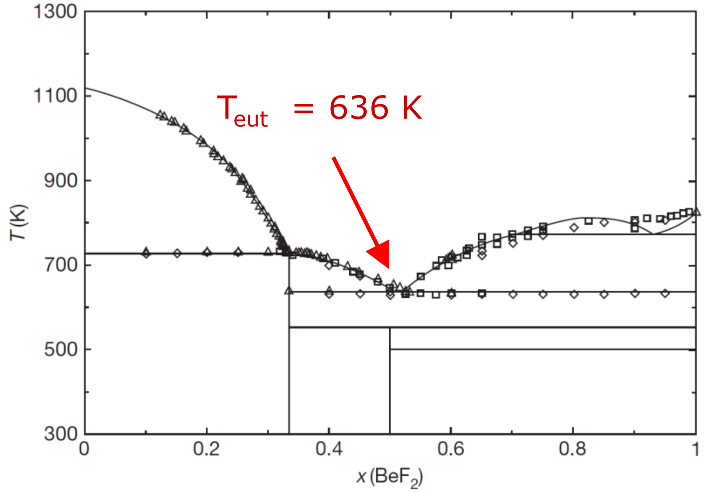
ARE — $NaF - ZrF_4$ $- UF_4$

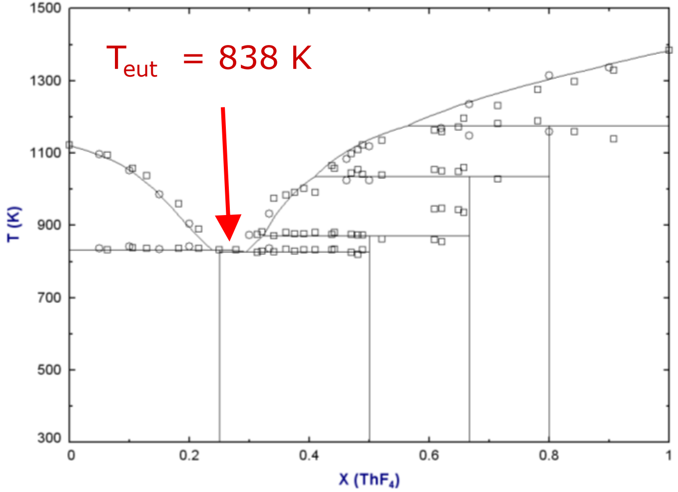
MSRE — $^7LiF - BeF_2$ $- ZrF_4$ $- UF_4$

MSBR — $^7LiF - BeF_2$ $- ThF_4$ $- UF_4$

MSFR — ^7LiF $- ThF_4$ $- UF_4$

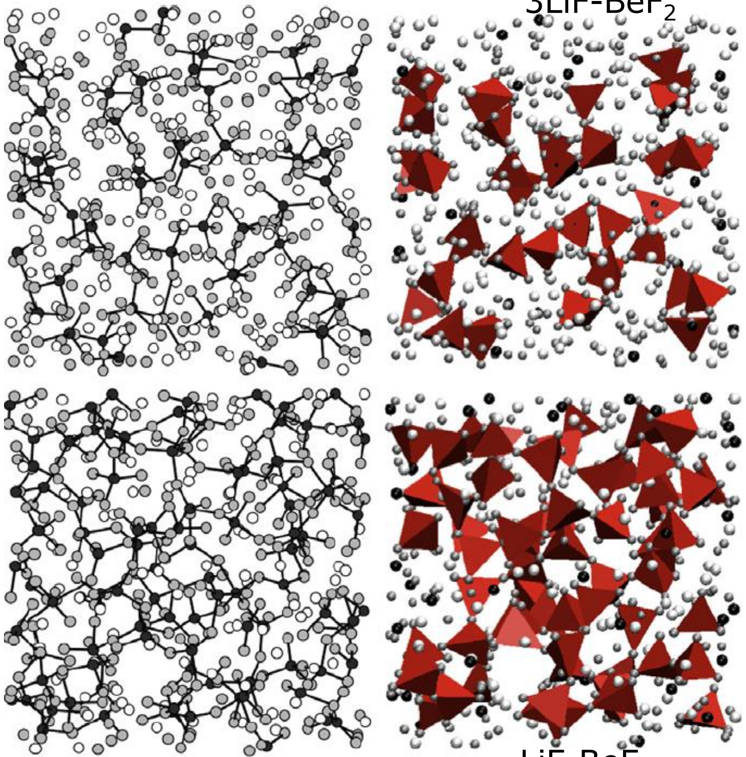
Fertile Material





Structure of a molten fluoride salt

3LiF-BeF$_2$

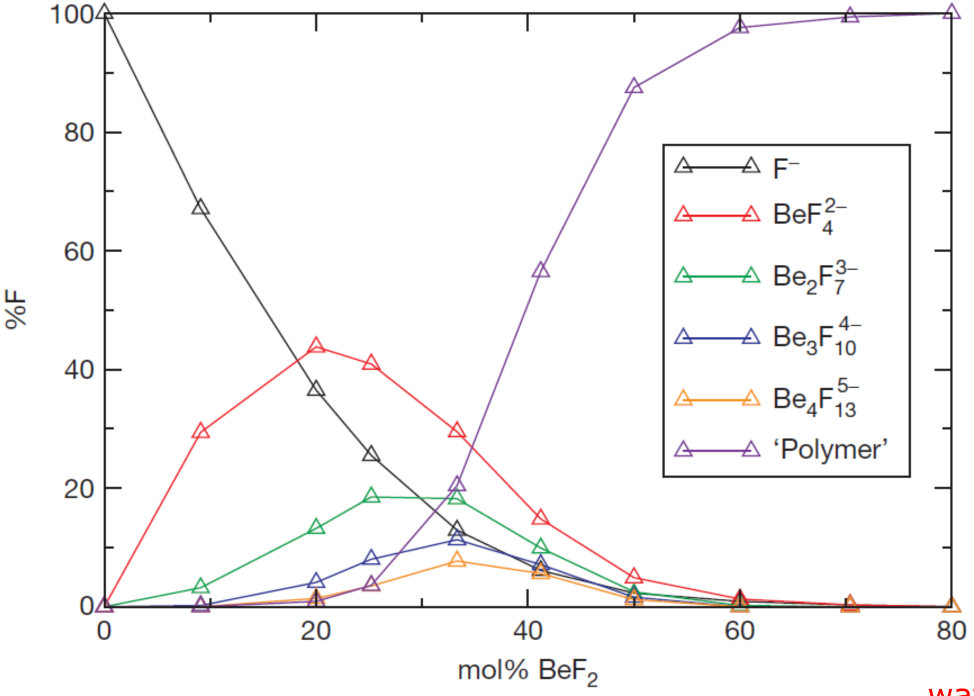


LiF-BeF$_2$

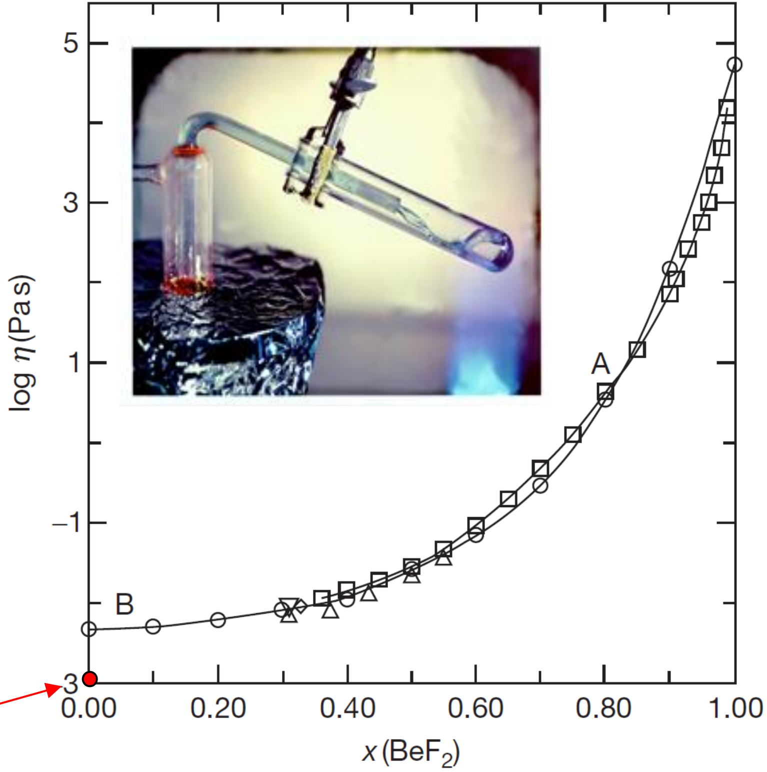
Picture from: M. Salanne et al., in: Molten Salts Chemistry, Chapter 1, Elsevier, 2013.

- 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

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

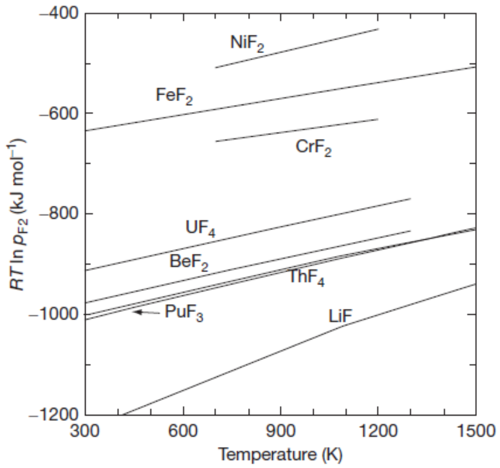
Chemical potential of fluorine

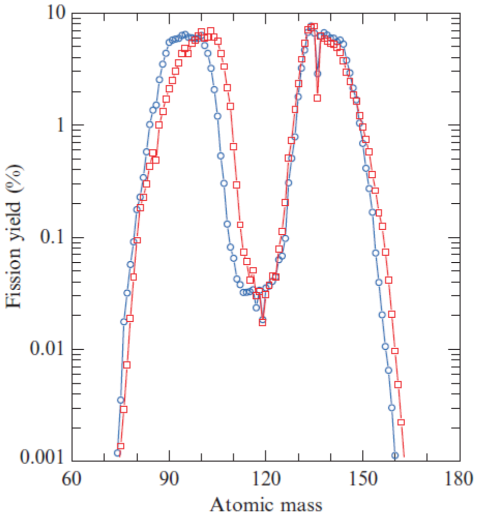
- ✓ is the equilibrium fluorine pressure of a reduction/oxidation reaction:

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

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

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





Fluorine potential and electropotential

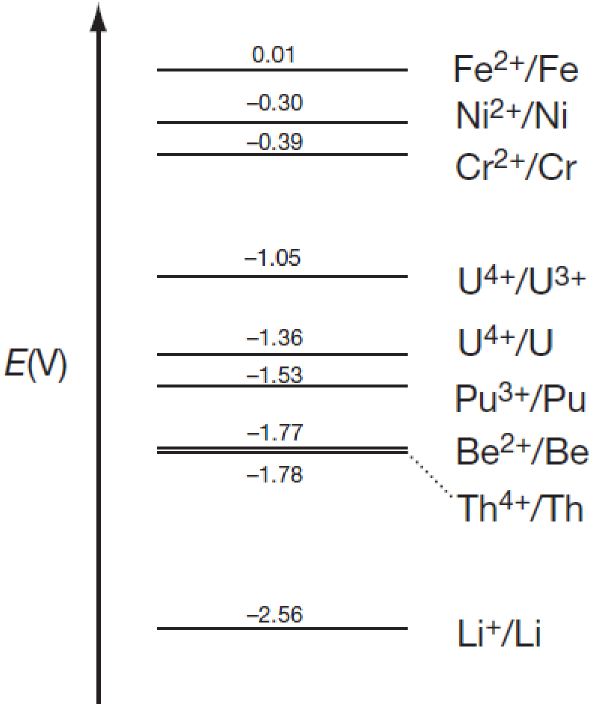
$$MF_n(s) = M(s) + n/2F_2(g)$$

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

$$UF_4(ss) = UF_3(ss) + ½F_2(g)$$

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

Standard potential in LiF–BeF$_2$ (66–34) relative to the HF(g)/H$_2$ couple 1000 K.



Redox control of the salt

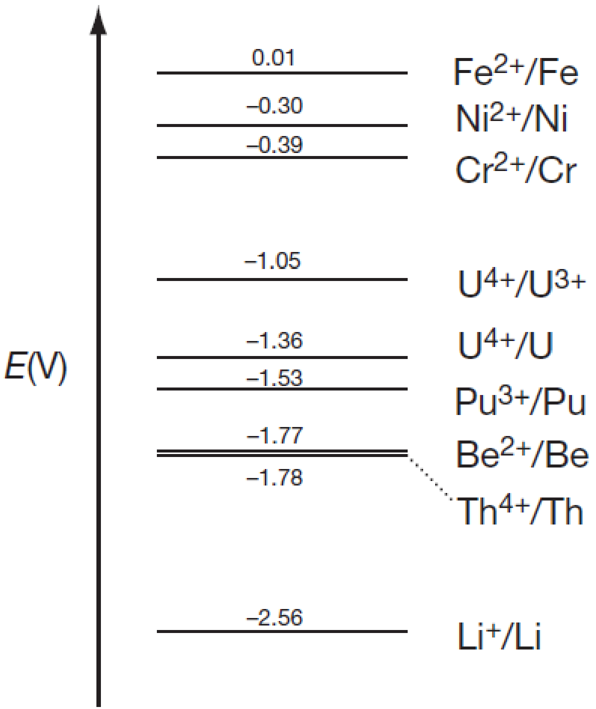
$$UF_4(ss) = UF_3(ss) + \tfrac{1}{2}F_2(g)$$

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

$$ThF_4(sln) + 2O(sln) = ThO_2(s)\ \boxed{+ 2F_2(g)}$$

$\downarrow$ dissolved $\qquad\qquad$ $\downarrow$ 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

$$Cr_2O_3(s) + 2BeF_2(sln) = 2CrF_2(sln) + 2BeO(s) + \boxed{1/2O_2(g)}$$

2. Reaction with impurities from fabrication process

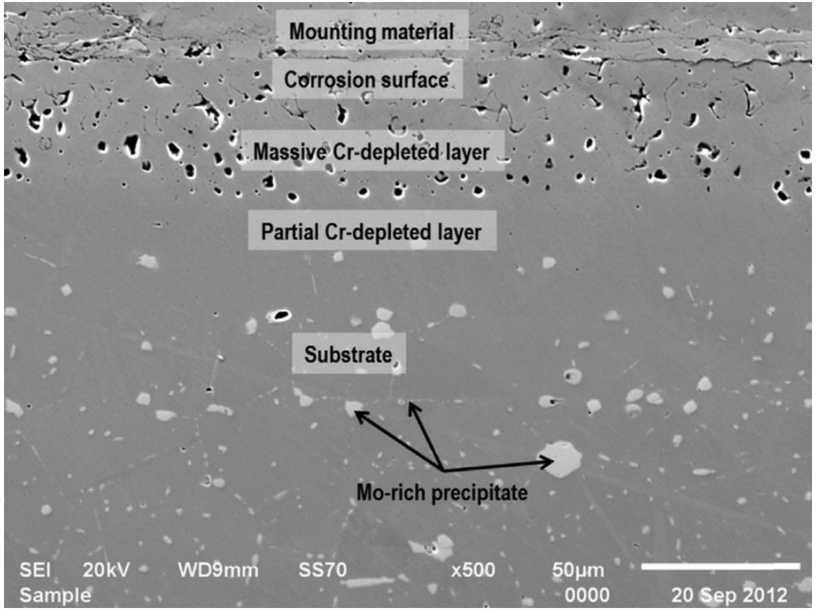
$$Cr(alloy) + \boxed{2HF(sln)} = CrF_2\,(sln) \boxed{+ H_2(g)}$$

$$Cr(alloy) + FeF_2(sln) = CrF_2\,(sln) + Fe(s)$$

3. Reaction with fuel constituents

$$Cr(alloy) + \boxed{2UF_4(sln)} = CrF_2\,(sln) + \boxed{2UF_3(sln)}$$

Corrosion

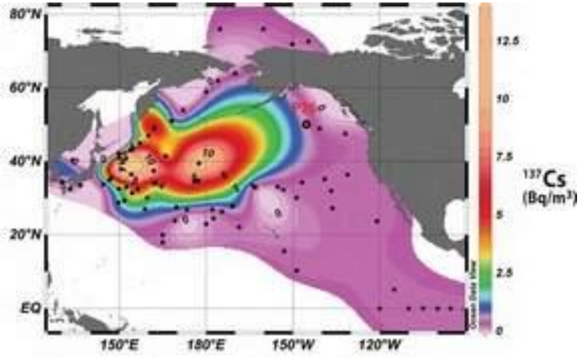


Hastelloy N for 1000 h at 850°C in $KF\text{-}ZrF_4$ salt (Sabharwall, 2014)

Fission product chemistry of the salt

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

$$M(s) + \boxed{n/2F_2(g)} = MF_n(sln)$$



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

Fission product chemistry of the salt

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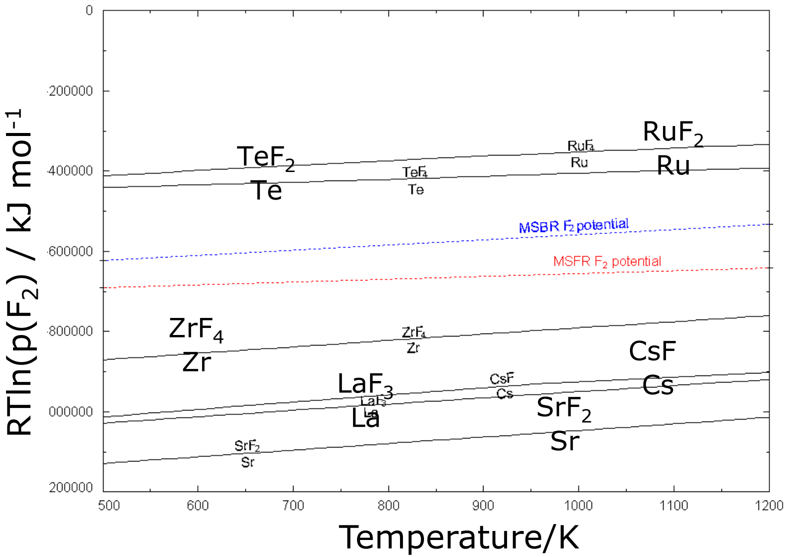

Chemical state of the FPs:

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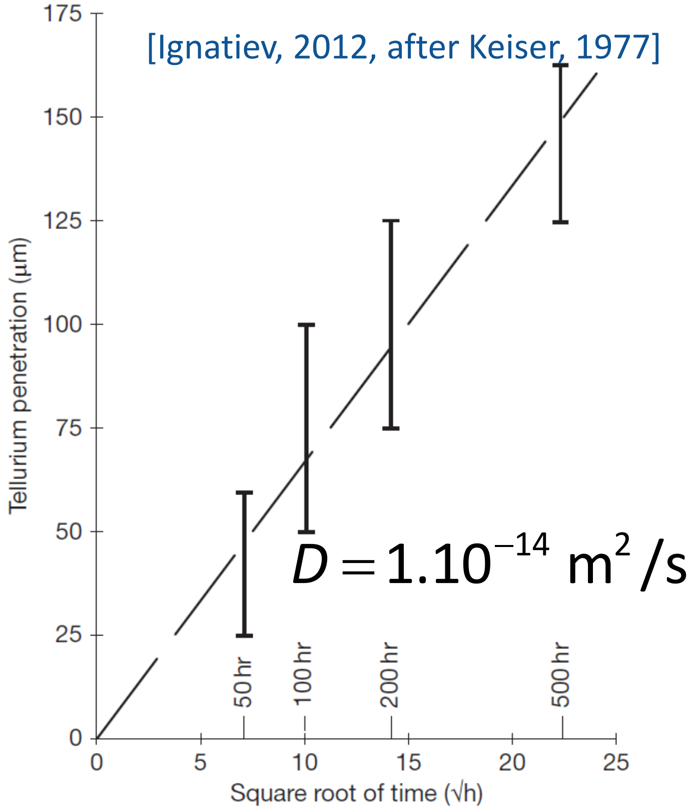
Fission product chemistry of the salt

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

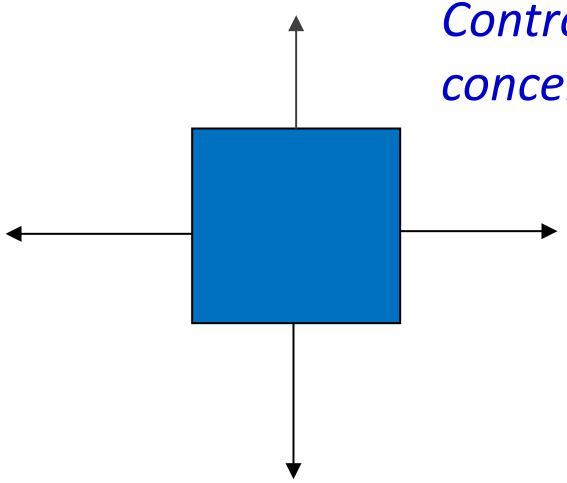


Minimised in reducing environment

Fuel salt clean-up

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

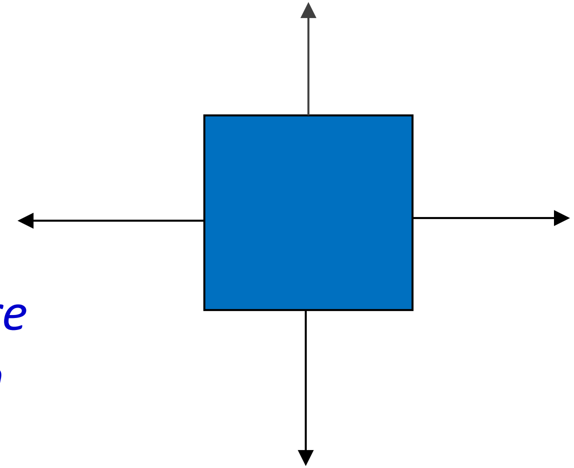
Metal particles

Noble plate out on the vessel wall

Fuel salt clean-up

Fluorination:

$U(sln) + F_2(g) = UF_6(g)$



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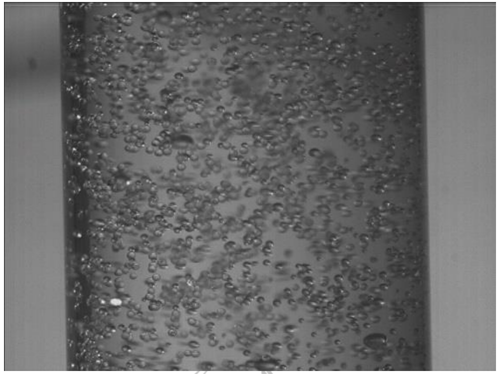
$U(sln) + F_2(g) = UF_6(g)$

Dissolves fission products

Lanthanides are strong neutron absorbers

Helium bubbling



Metal particles

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Fuel salt clean-up

Fluorination:
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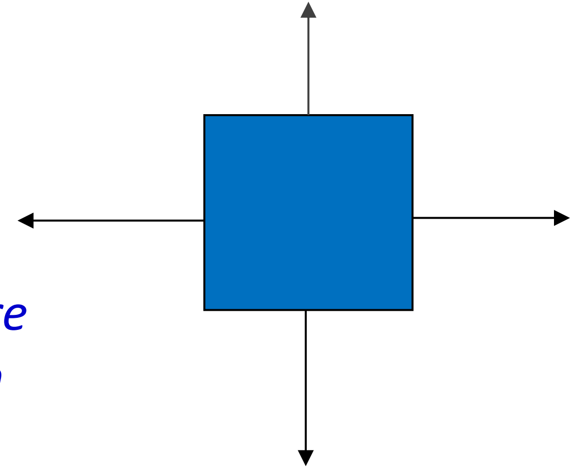

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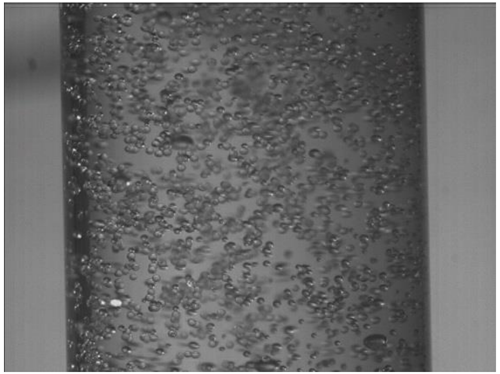
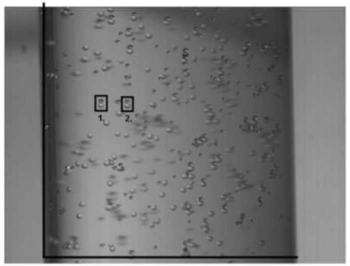
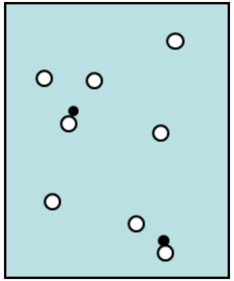


Helium bubbling

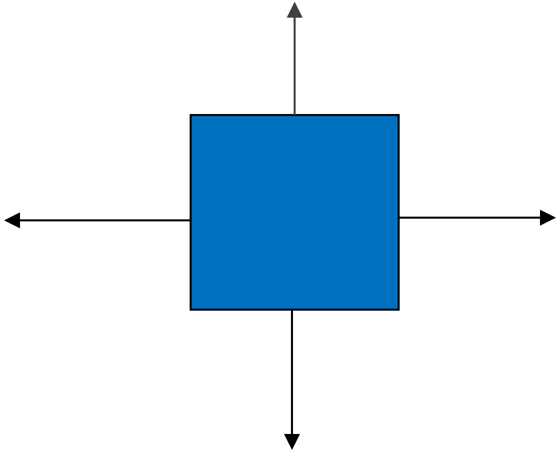




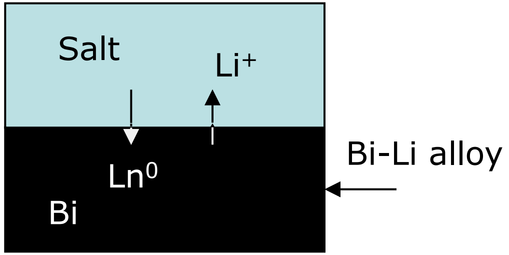
Fuel salt clean-up

Fluorination:

$U(sln) + F_2(g) = UF_6(g)$



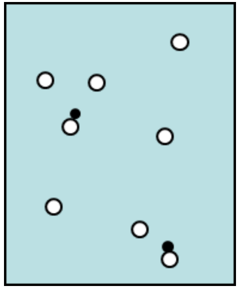
Liquid/liquid extraction



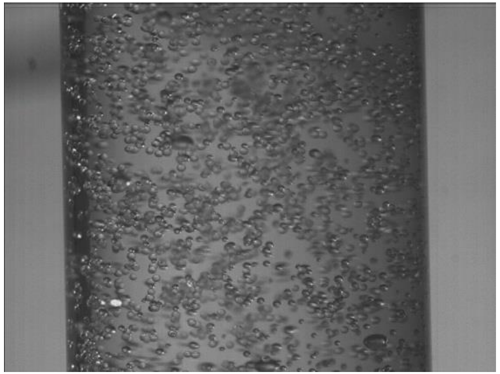
$3\ Li(sln) = 3Li^+ + 3e$

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

Helium bubbling



Helium bubbling



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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

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Conclusion from MSRE: still relevant

- ✓ The management of the tritium production in 7LiF-BeF2 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 vol% to avoid reactor instabilities.
- ✓ Continuous removal of 233Pa 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
  - 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

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

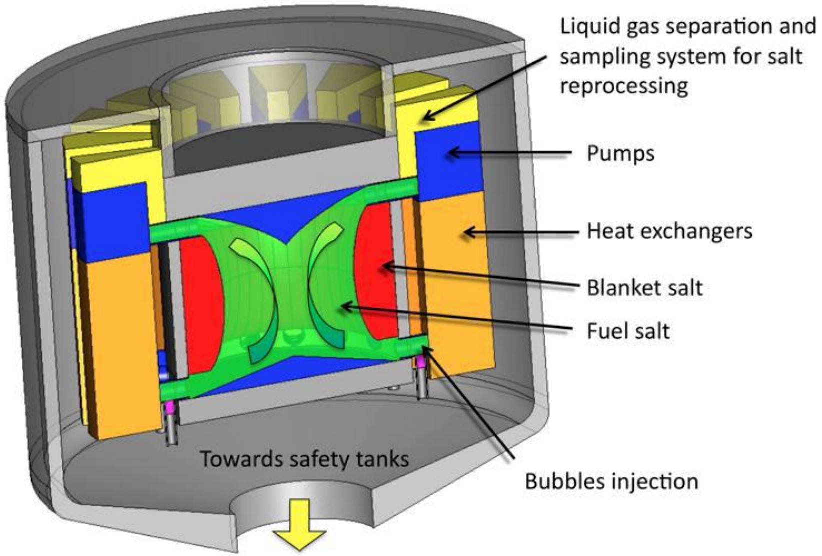
Grand Challenge SAMOFAR

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 Investigaciony 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

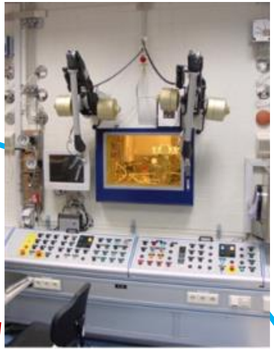


Working parameters

- High temperature (750 ^{0}C)
- Low pressure (1 bar)
- Circulation time (4 sec)
- $LiF\text{-}ThF_4\text{-}UF_4\text{-}(TRU)F_3$ (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 diagramsof **An halides** and mixtures

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

RAMAN spectroscopy of molten salts

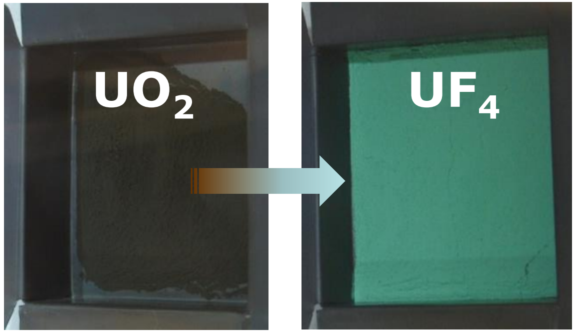
NMR high temperature probe for **molten salts**

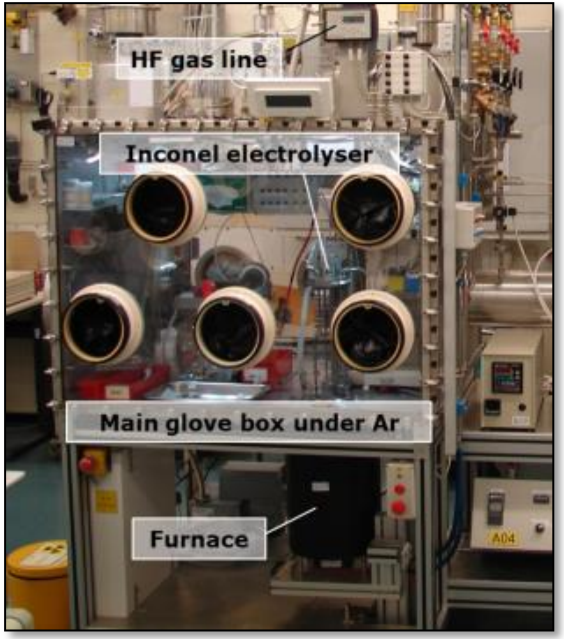
Fluorination line for synthesis & purification

- HF gas line + Inconel fluorination reactor (up to 1200° C)

- ThF_4, UF_4 and PuF_3 synthesised from nano-sized ThO_2, UO_2 and PuO_2 with very high purity

$$UO_2 + 4HF(g) \rightarrow UF_4 + 2H_2O(g)$$



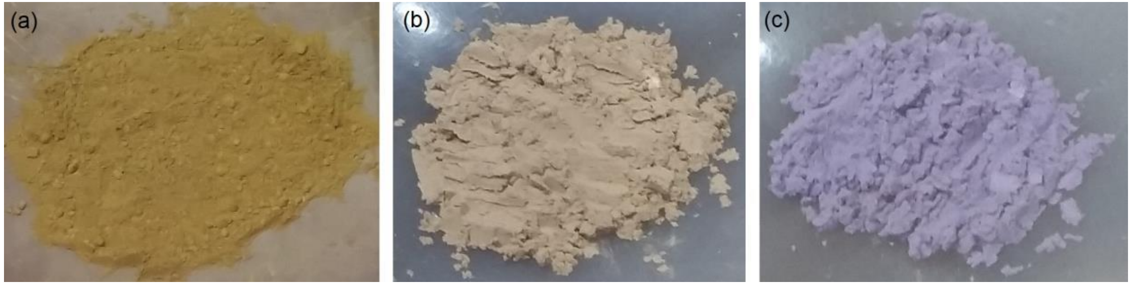


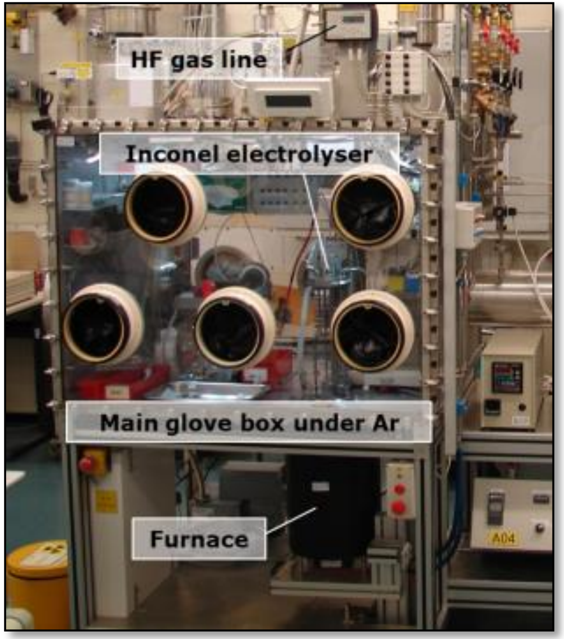
Fluorination line for synthesis & purification

- HF gas line + Inconel fluorination reactor (up to 1200° C)

- ThF_4, UF_4 and PuF_3 synthesised from nano-sized ThO_2, UO_2 and PuO_2 with very high purity

$$PuO_2 + 3HF(g) + 1/2H_2(g) \rightarrow PuF_3 + 2H_2O(g)$$





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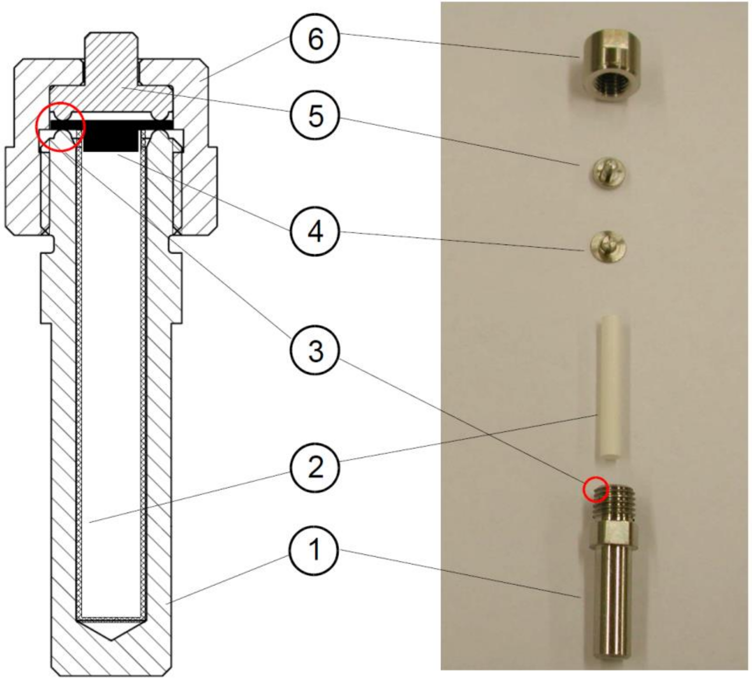
Experimental approach for phase diagram studies



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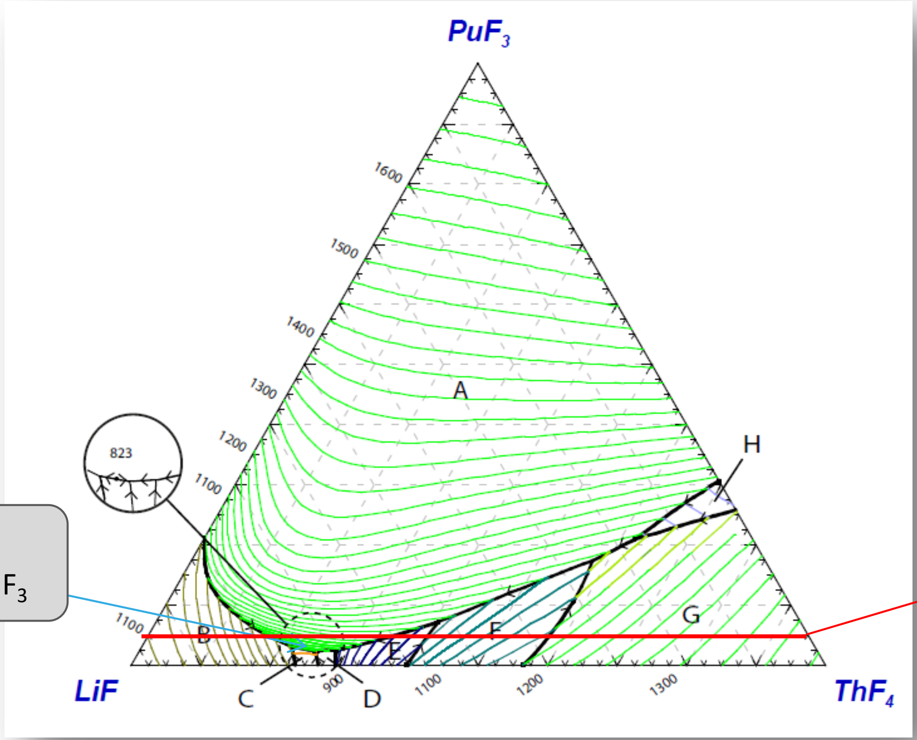
Phase diagram determination: fuel optimisation



820 K
1.7 mol % PuF_3

Target for MSFR

5 mol% PuF_3

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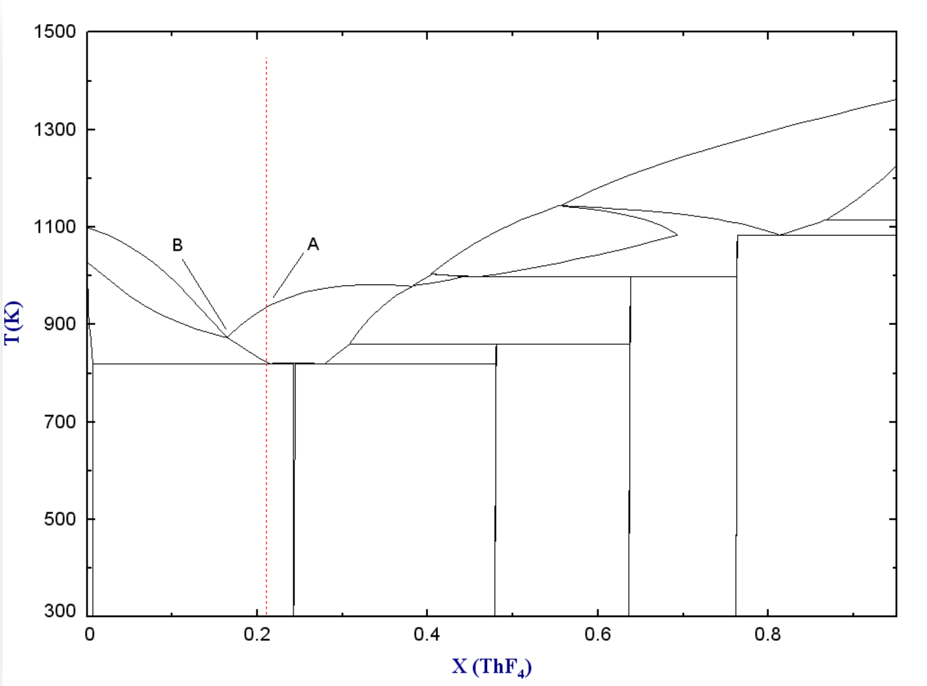
Phase diagram determination: fuel optimisation



Pseudobinary LiF-ThF_4 for 5 mol% PuF_3

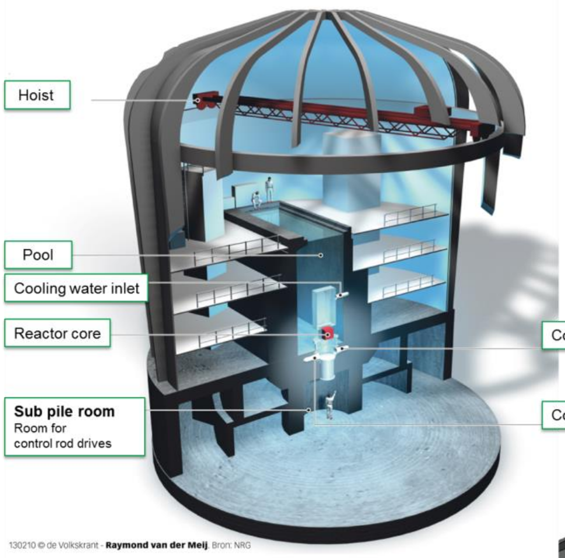
Point A: LiF-ThF_4-PuF_3 (74-21-5 mol%)

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

Point B: LiF-ThF_4-PuF_3 (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



130210 © de Volkskrant - **Raymond van der Meij**, Bron: NRG

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_{melt} + 50 K

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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 !

Stay in touch

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