Development of In-Pile Electrochemical Corrosion Measurements and Waste Management of Molten Fluoride Salts

Konstantin Kottrup, 08-06-22

Young MSR Conference, Lecco Italy

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Outline

- Introduction
- Molten Salt Electrochemistry
- SALIENT-03
- LUMOS Waste project
- Closing remarks

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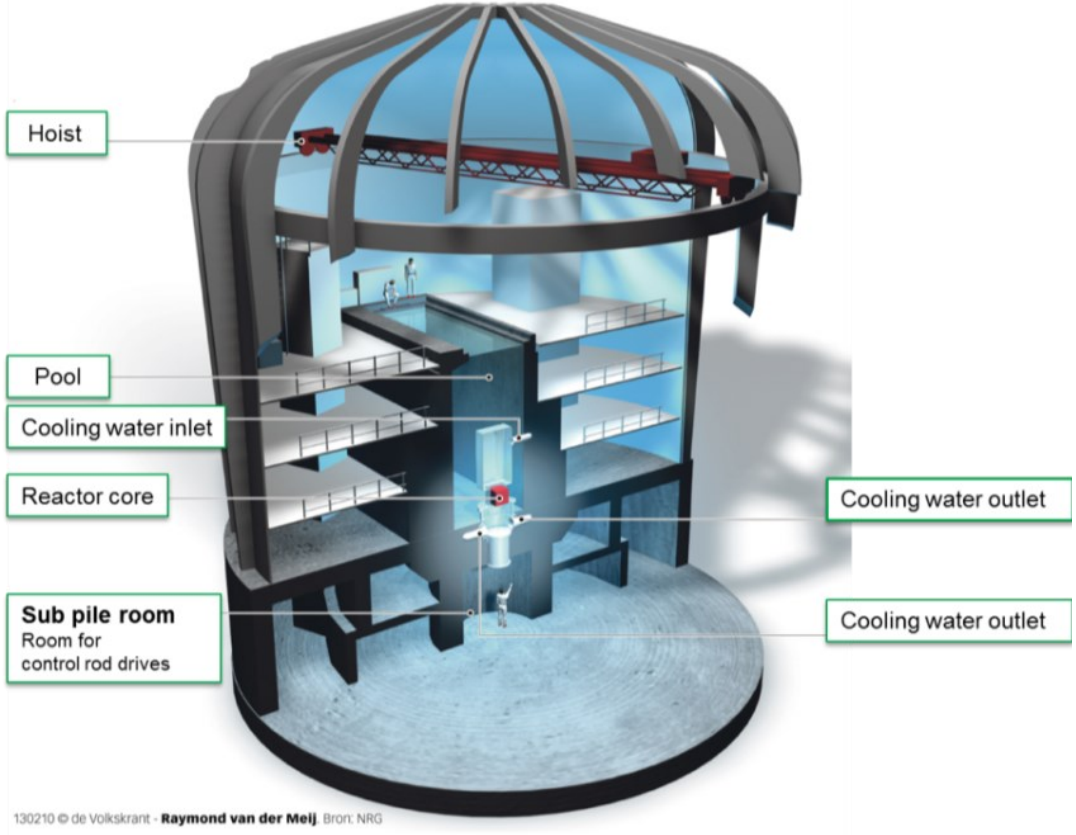
Who Are We?

- NRG is a **N**uclear **R**esearch and consultancy **G**roup

- We operate a research reactor called **HFR** (high flux reactor)

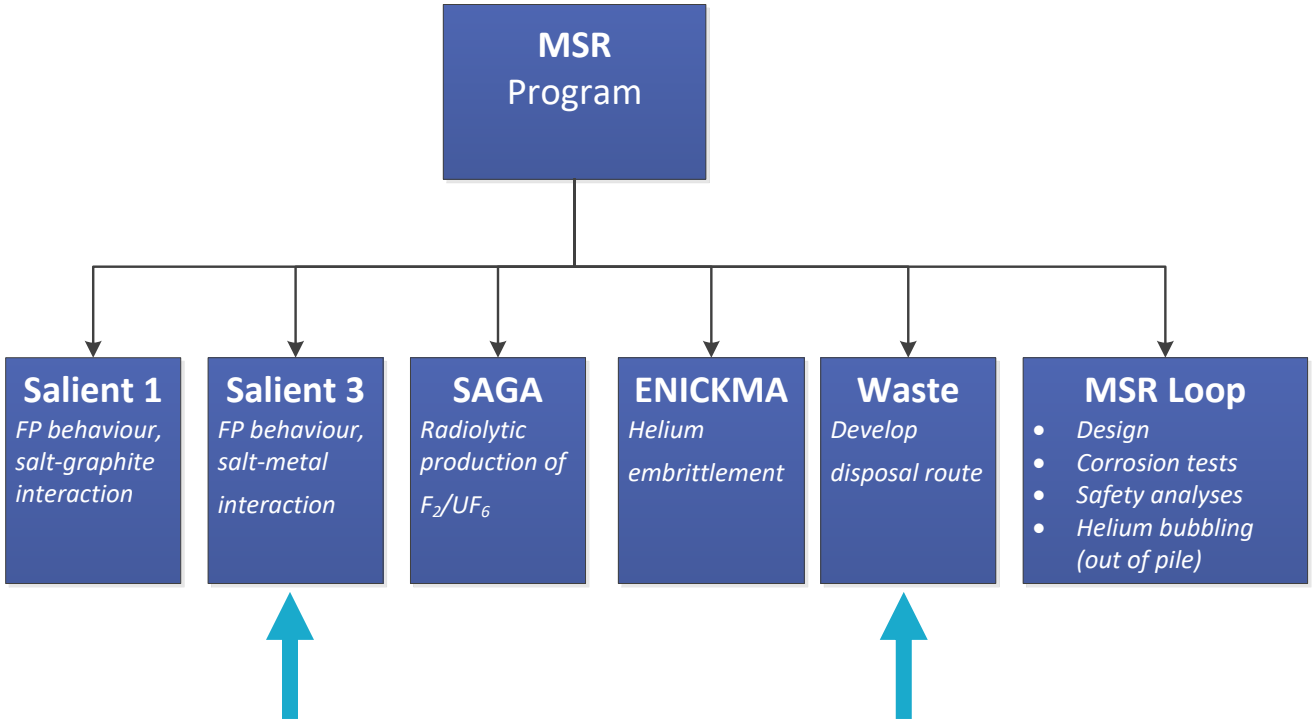
- Our main efforts are
  - Manufacturing of **medical isotopes**
  - Materials and fuels **qualification**
  - R&D in the field of **nuclear energy** (including Molten Salt Reactors)

The High Flux Reactor (HFR)



- Intense neutron source
- 45 MW thermal power
- Key applications
  - Medical isotope production
  - Irradiation services for nuclear industry
  - R&D
- 31 days of operation per cycle, 9 cycles per year

Molten Salt Reactor Research Program



- Focus on irradiation technology
- Obtain hands-on experience
- Demonstrate safety
- Waste disposal

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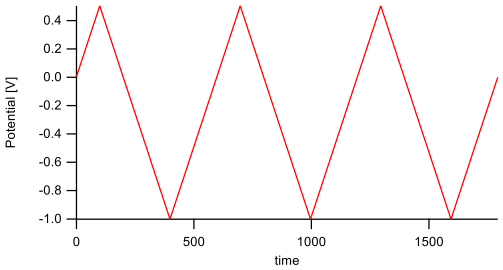
Corrosion

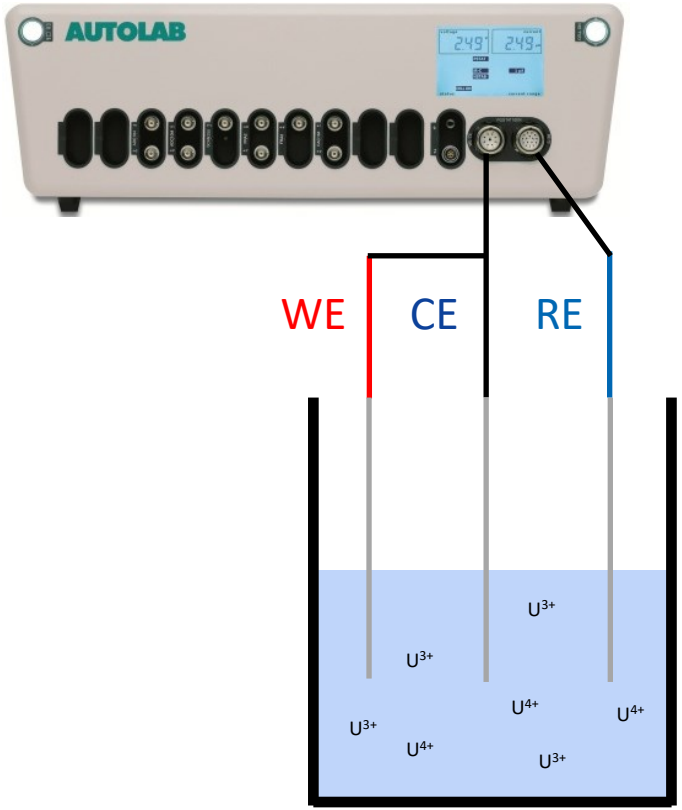
- Issue: Molten Salt becomes more **corrosive** over time
  - $UF_4 \rightarrow M + LnF_3 + ½\ F_2$
- Solutions: High-Ni alloys & **corrosion monitoring** & control
- **Electrochemistry** could play a role in corrosion monitoring
- Use of U(IV)/U(III) couple as **redox indicator**

$$E = E° + \frac{RT}{F} ln \frac{[U(IV)]}{[U(III)]}$$

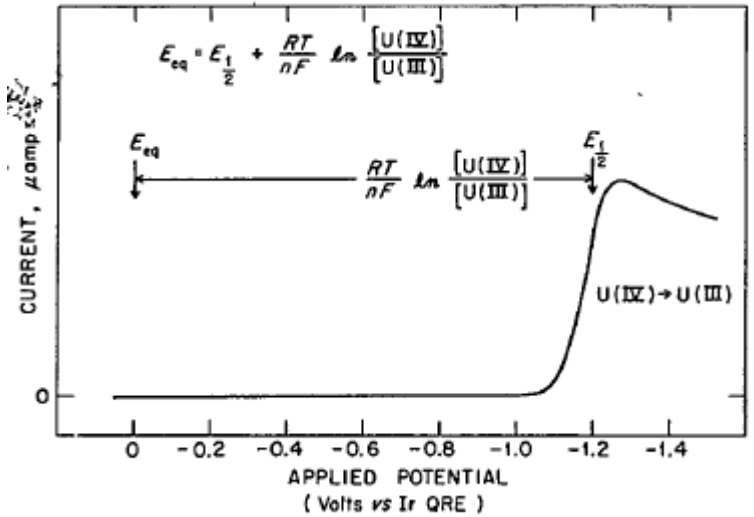
Molten Salt Electrochemistry

(Cyclic) Voltammetry





Method of $E_{1/2}$ determination



- Doesn't require calibration
- Has been shown to work in presence of convection
- Relies on clear voltammogram for reliable determination of peak position

We selected this approach or our experiment

Manning D.L., Mamantov G. *Recent Electroanalytical Studies in Molten Fluorides. In: Mamantov G. (eds) Characterization of Solutes in Nonaqueous Solvents*. **1978** Springer, Boston, MA

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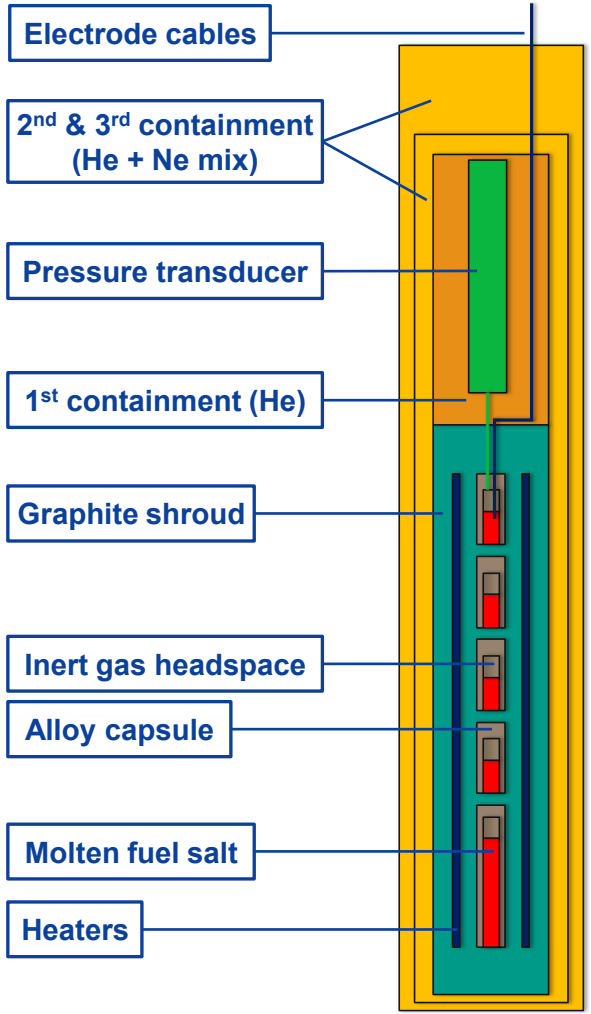
SALIENT-03 Design

Irradiation of $LiF-ThF_4-UF_x$

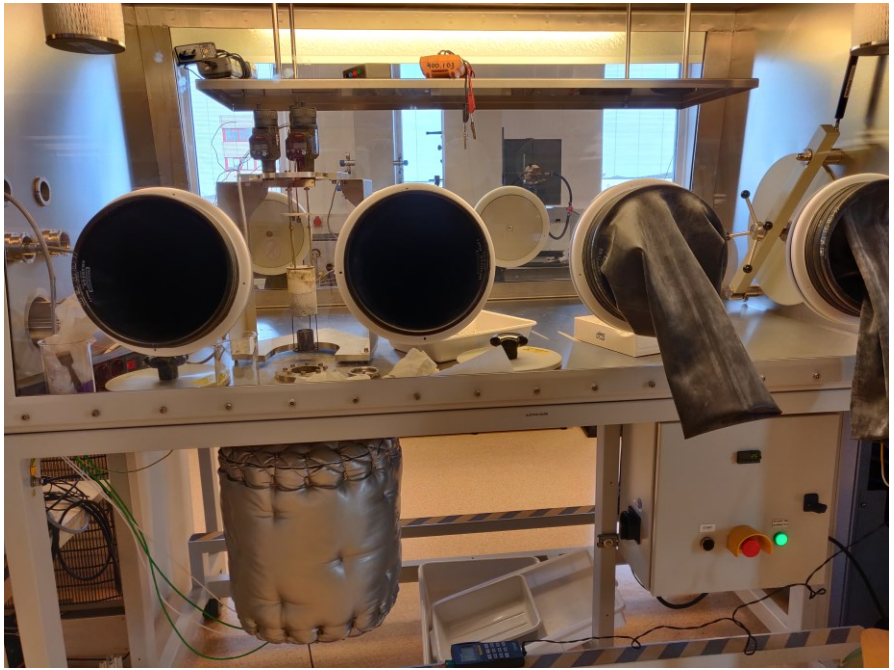
Changes with respect to SALIENT-01

- **Closed** Alloy N capsules
  - Pressure measurement
- Focus on **corrosion**
- Addition of **electrodes** for electrochemistry
- Addition of UF_x for **redox buffering**



Lab-scale experiments

- Built lab-scale setup for electrochemical experiments with molten salts
- Goal is to gain operational experience
- Go through series of experiments:
  - FLiNaK
  - FLiNaK + EuF_x
  - LiF-ThF_4
  - LiF-ThF_4 + EuF_x
  - LiF-ThF_4 + UF_x (provided by JRC Karlsruhe)
  - Adjusting UF_4/UF_3 with “extra” UF_3



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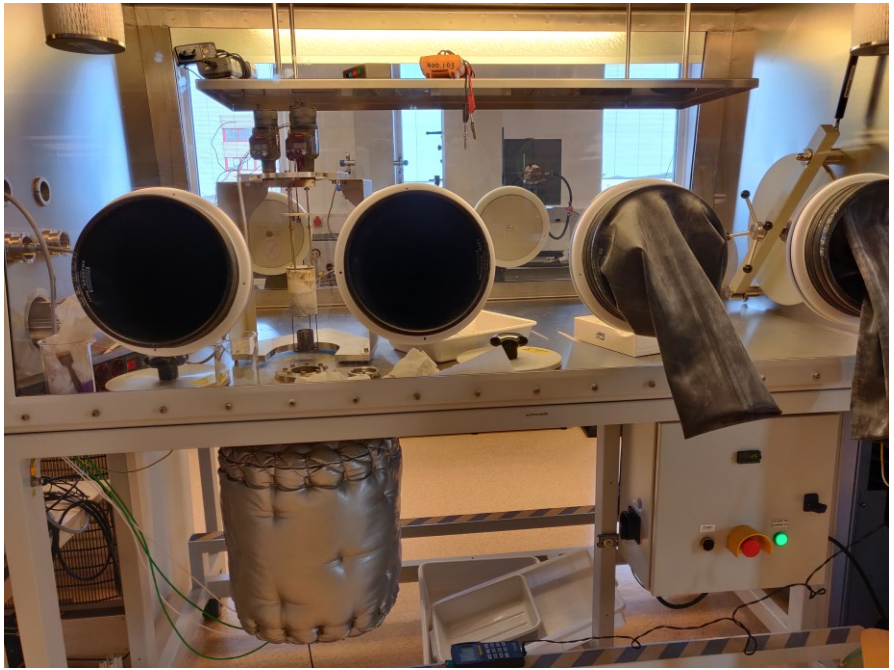
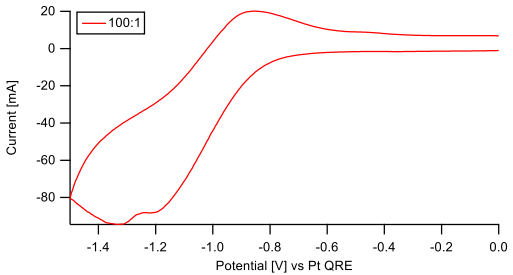


Lab-scale experiments

UF_4/UF_3 in LiF-ThF_4 comparison



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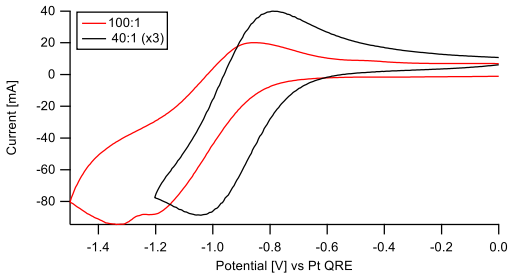

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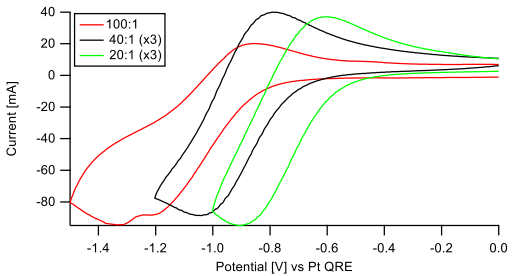

- Clear trend towards more anodic potential
- None of the peak positions match the expected value
- e.g. nominal 40:1 vs calcd. 10^5:1

$$E = E° + \frac{RT}{F} ln \frac{[U(IV)]}{[U(III)]} \quad \Rightarrow \quad E - E° = \frac{8.314 \cdot 923}{96485} \ln(40) = -0.293\ V$$

Reasons?

- Error in the calculations/assumptions?
- Reference is not stable over time?
- Oxidation of UF_3 in sample due to oxygen impurities?
- No independent method for determining UF_4/UF_3
- Hopefully in-pile measurements will clarify…

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Background

- Halide-containing waste is **not accepted** by authorities
  - Currently no guidelines for acceptance criteria of fluoride waste streams
- Conversion to **stable** waste form required (e.g. oxide)
- **Complex** salt samples due to FP
- Focus for now on converting our **irradiated** samples
  - Scaling up to litres of salt desirable

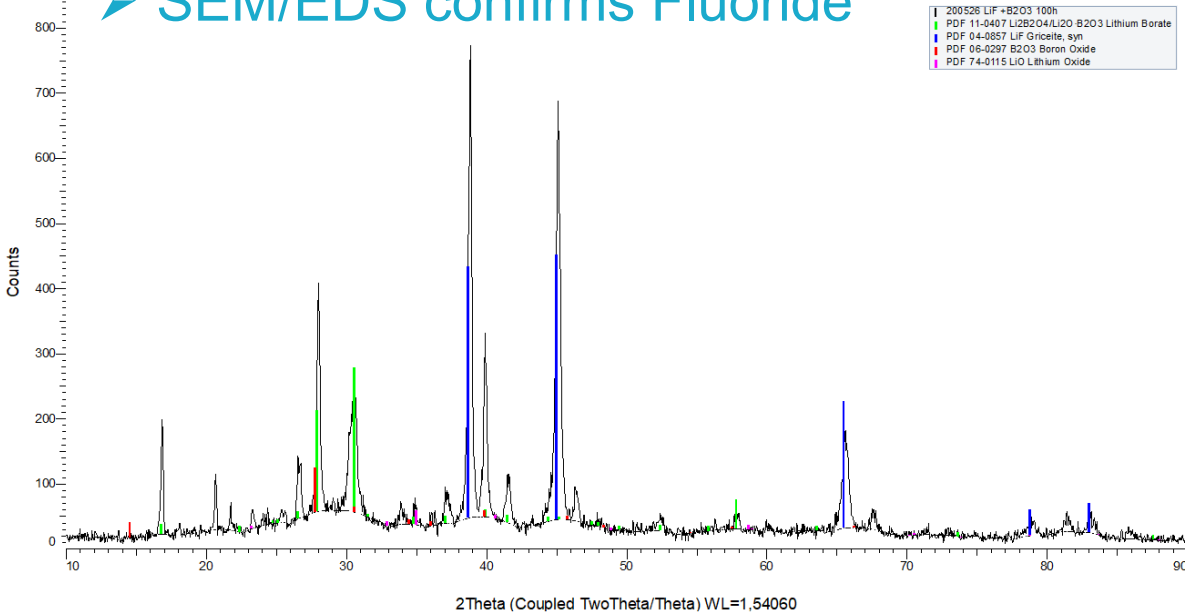
Approach

- Using test batches, mainly of LiF and/or ThF_4
  - Occasionally also more complicated mixes including LaF_3, ZrF_3, BaF_2, CsF etc.
- Analysis by XRD and SEM/EDS
- Aqueous processing
  - Dissolution/precipitation
  - Constrained by solubility of e.g. ThF_4
- Direct defluorination using B_2O_3 or SiO_2
  - Formation of volatile fluoride species (BF_3/SiF_4)
  - Has been shown to work with uranium fluoride[1]
- Vitrification
  - Boro-silicate glasses do not tolerate Fluoride

[1] J.B. Bulko, D.S. Schlier, Recovery of high value fluorine products from uranium hexafluoride conversion, WM'99 conference, February 28-March 1, 1999

Reaction with B_2O_3/SiO_2

- ThF_4 is readily converted but conversion of LiF is challenging
- XRD shows remaining LiF
- SEM/EDS confirms Fluoride



Vitrification

- **Iron phosphate** glass may tolerate some halide ions[1]

- Reaction with $Fe(C_2O_4)$ and $(NH_4)H_2PO_4$ at elevated temperatures shows **high degree** of defluorination[2]
  - XRD shows hardly any remaining LiF
  - SEM/EDS does not show any Fluoride

- To achieve vitrification even **higher temperatures** are needed
  - Current setup is not suited for these temperatures

[1] B. Riley et al. *J. Nucl. Mater.* **2020**, *529*, 151949
[2] D. Wang et al. *J. Solid State Chem.* **2004**, *177*, 4582-4587.

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Outlook

- Hopefully SALIENT-03 irradiation will start later this year
- Even if EChem doesn't work out, SALIENT-03 will provide plenty of interesting data during PIE
- Look into possible vitrification of spent salt
- Currently testing prototype of high-temp furnace for inside hot-cell

Acknowledgements

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Ensuring Nuclear Performance

JRC
EUROPEAN COMMISSION

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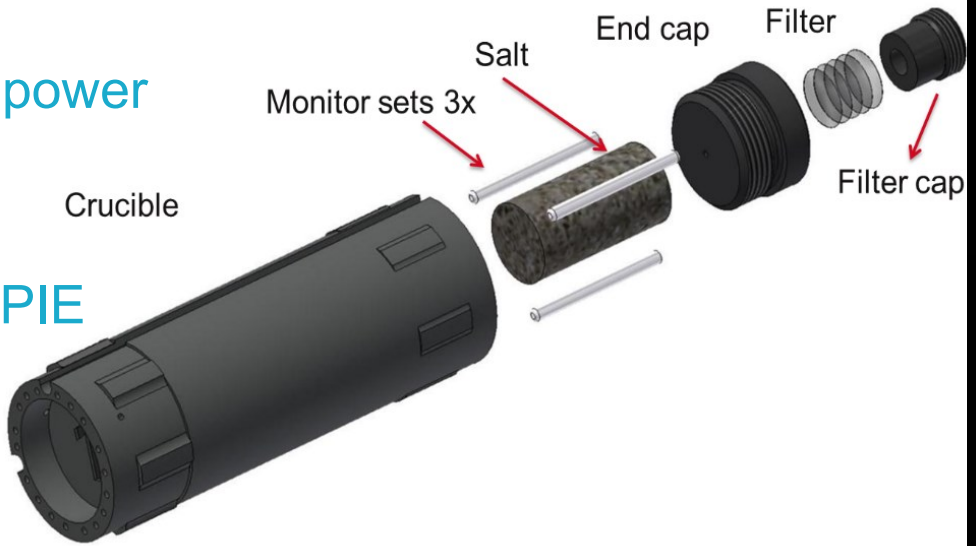
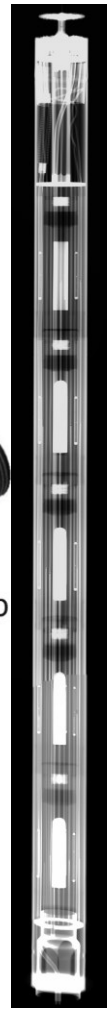
Context

- Salient-01:
  Irradiation of 78LiF-22ThF_4
- Open capsules of graphite
- Irradiation for 508 full power days (2 years)
- Currently undergoing PIE





Method 1: diffusion current

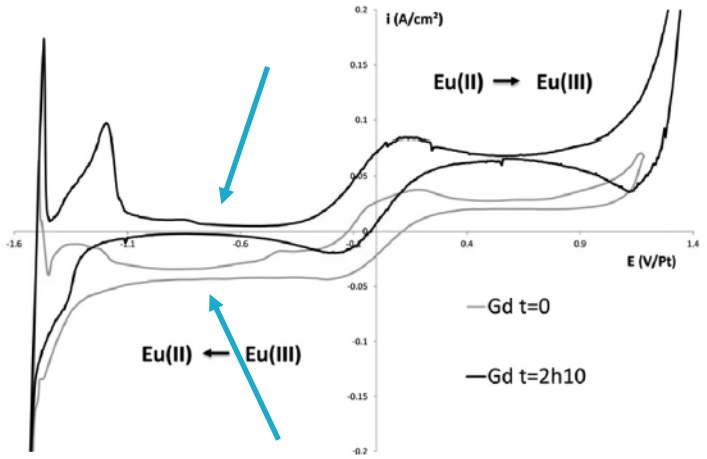


Fig. 4. Cyclic voltammetry on Ag in LiF-CaF_2 + EuF_3 (2.5 wt%) + Gd at 850 °C at 50 mV.s^{-1}; Scan direction: from the initial potential (E = 0 V/Pt) to the electrode oxidation.

- Requires (extensive) calibration data
- Has only been demonstrated for stagnant solutions
- May not work when convection is present

M. Gibilaro, L. Massot, P. Chamelot, *Eletrochim. Acta* **2015**, *160*, 209-213

Aqueous processing

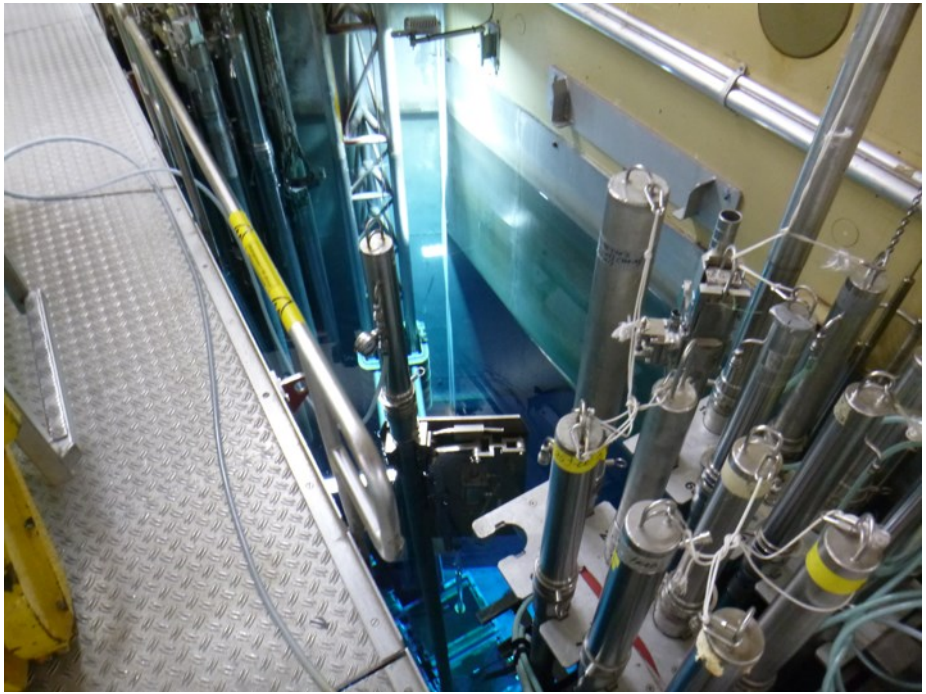
- Initially **preferred** solution

- Challenges arise from poor **solubilities**
  - Several salt components such as ThF_4 or LaF_3 require strongly acidic media

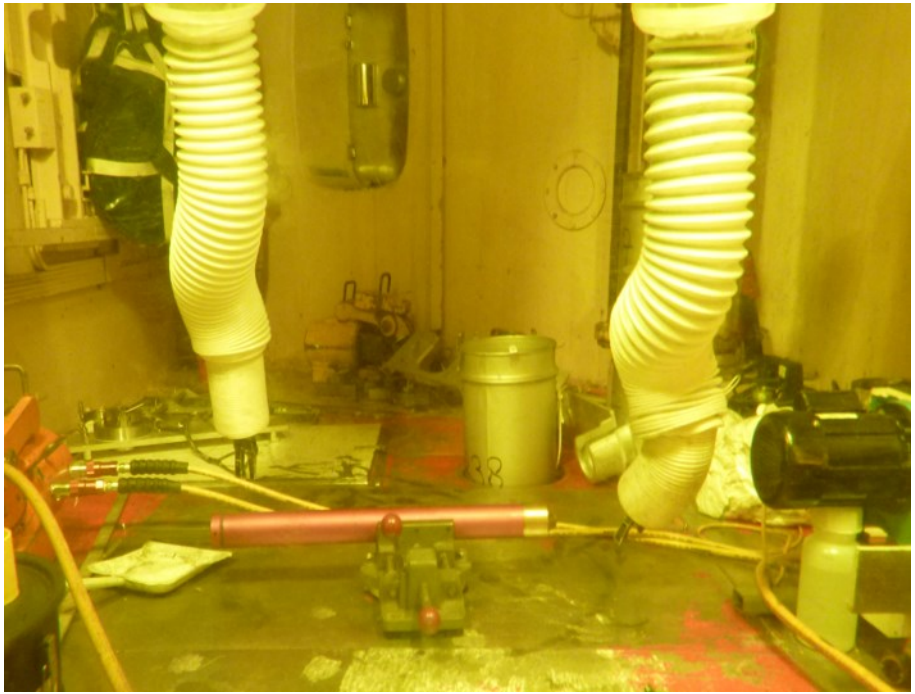
- Direct **metathesis** with strong alkaline solution
  - Works only well for fine powders

Transfer to Hot Cell Laboratories

Transfer to HFR Hot cell



Cutting and packaging for transport to labs



SALIENT-03 Electrochemistry

- The U^{3+}/U^{4+} couple can be used as a redox buffer/indicator:

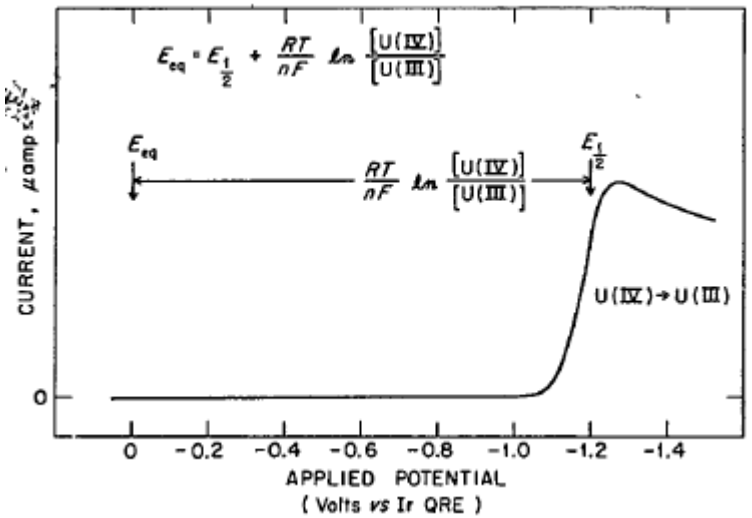
$$E = E° + \frac{2.3\ RT}{F} \lg \frac{[U(IV)]}{[U(III)]}$$

- Experimentally limited to pseudo-reference electrode
  - Space constraints and lack of established, reliable reference

- No consensus experimental procedure
  - Lab-scale experiments ongoing

SALIENT-03 Electrochemistry

Scan from OCP to $E_{1/2}$



Pro:

- Works without thermodynamic reference
- Doesn't require calibration
- Has been demonstrated to work with convection

Contra:

- Not continuous
- Relies on accurate determination of $E_{1/2}$

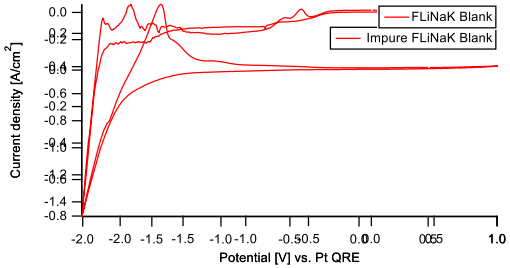
Manning D.L., Mamantov G. Recent Electroanalytical Studies in Molten Fluorides. In: Mamantov G. (eds) Characterization of Solutes in Nonaqueous Solvents. 1978 Springer, Boston, MA

SALIENT-03 Lab Experiments

- Lab-scale experiments to obtain experience prior to irradiation
- Molten salt test-system
  - Matrix: Initially FLiNaK, later LiF-ThF_4
  - Redox active component: EuF_2/EuF_3 as surrogate before moving on to for UF_3/UF_4
- Using Pt wires as WE/CE/RE

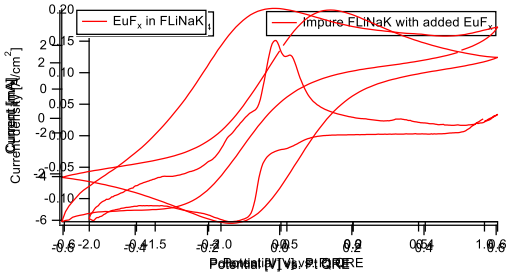
SALIENT-03 Lab Results

Blank measurement



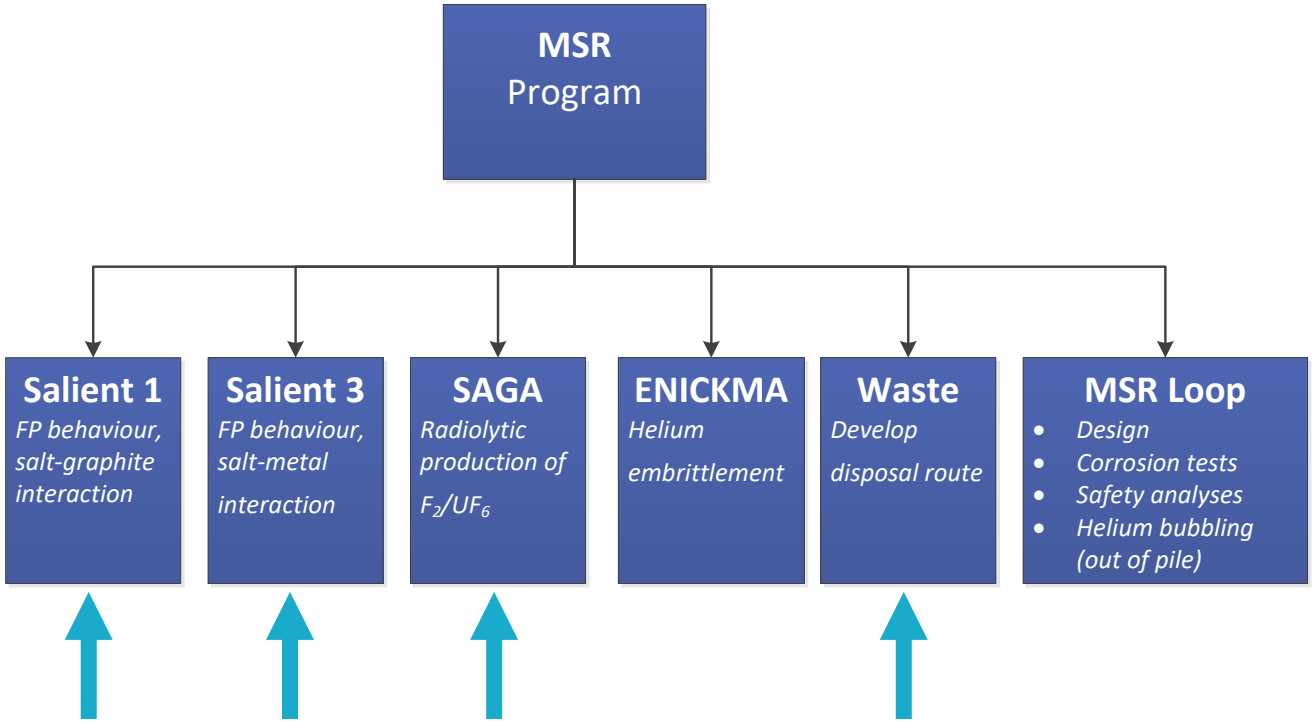
SALIENT-03 Lab Results

Added EuF_2/EuF_3



➢ Next step: Move on to UF_3/UF_4

Molten Salt Reactor Research Program



Why Molten Salts?

- Improved nuclear safety
- Reduction of resource consumption/waste
- Contribution to CO_2-free energy market

Objectives

- Obtain operational experience
- Demonstrate safety
- Materials qualification
- Waste management

Why Molten Salt?

- MSR technologies are very relevant today
  - Improved nuclear safety
  - Reduction of resource consumption/waste
  - Contribution to CO2-free energy market

- Collaboration between NRG, JRC, TU Delft and CV Rez
  - Complementary competences

- Objective is to contribute to MSR technology development
  - Obtain operational experience
  - Safety
  - Material qualification
  - Waste
  - Integral demonstration

JRC EUROPEAN COMMISSION

TU Delft Technische Universiteit Delft

Centrum výzkumu Řež s.r.o. Research Centre Řež

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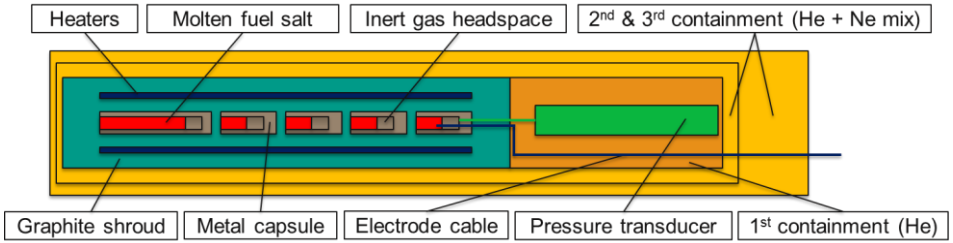
SALIENT-03

➢ Changes with respect to SALIENT-01:

- Closed Alloy N capsules
  - Corrosion
  - Pressure measurement
- Addition of Pu for fission power at start of irradiation
- Addition of U for ‘salt buffering’ (UF_3/UF_4)
- Addition of electrodes of electrochemistry
- Heaters to avoid radiolysis during HFR downtime
- Large measureable temperature gradients
  - Transport phenomena



SALIENT Experiment Series

- SALIENT stands for **SAL**t **I**rradiation **E**xperime**NT**

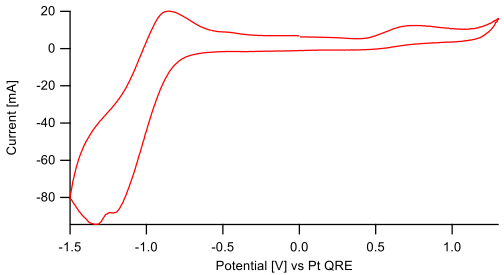
- In this series of experiments we investigate
  - The **interaction** of molten salt with various materials such as graphite or alloys
  - **Fission product** behaviour and distribution

- Ongoing experimental activities
  - SALIENT-01 – FP behaviour, salt/**graphite** interaction Status: PIE
  - SALIENT-03 – FP behaviour, salt/**metal** interaction Status: Manufacturing

- Currently in planning
  - In-pile FP removal by **helium bubbling**

Lab-scale experiments

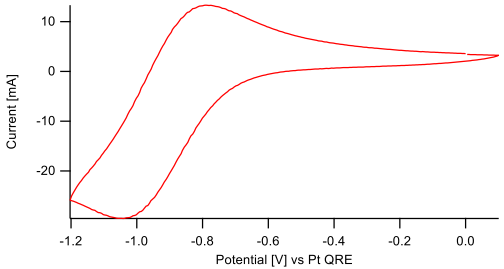
UF_4/UF_3 (100:1) in $LiF\text{-}ThF_4$



- Position of redox couple does not line up with expected value
- Nominal UF_4/UF_3 ratio: 100:1
- Implied ratio: $1 \cdot 10^6$:1

Lab-scale experiments

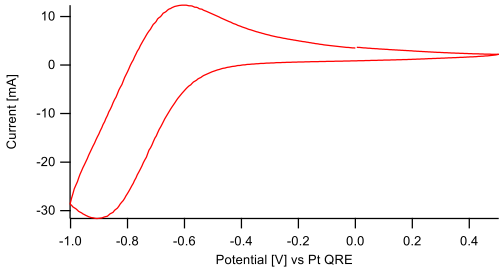
UF_4/UF_3 (40:1) in $LiF\text{-}ThF_4$



- Position of redox couple does not line up with expected value
- Nominal UF_4/UF_3 ratio: 40:1
- Implied ratio: ~$1 \cdot 10^5$:1

Lab-scale experiments

UF_4/UF_3 (20:1) in $LiF\text{-}ThF_4$



- Position of redox couple does not line up with expected value
- Nominal UF_4/UF_3 ratio: 20:1
- Implied ratio: ~$2 \cdot 10^4$:1

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Context

- Salient-01 was put into irradiation in 2018
- Post irradiation examination since 2021 (2 years/18 cycles)
- First Thorium Molten Salt irradiation in over 50 years
- Salt contained in (open) graphite capsules
- Aim is to study Salt/Graphite interaction as well as FP distribution