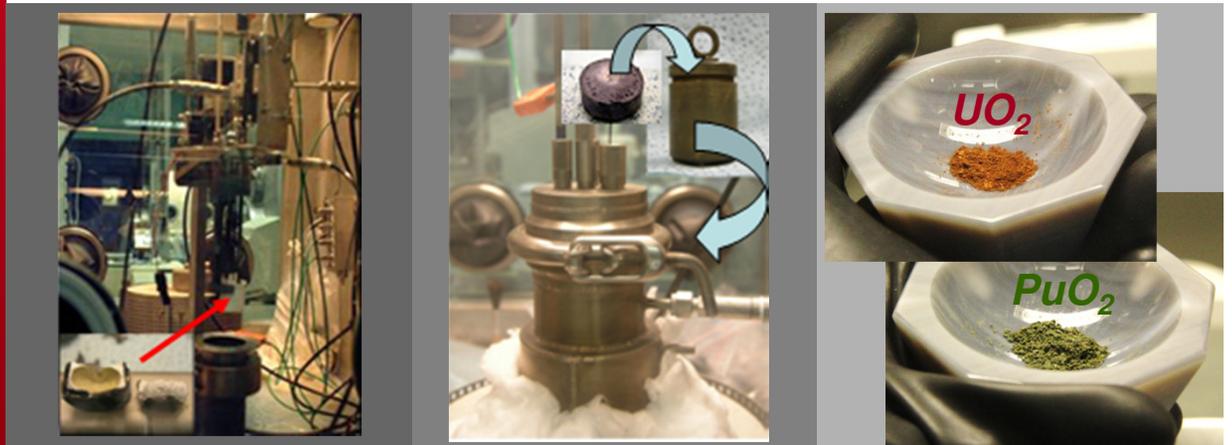


DE LA RECHERCHE À L'INDUSTRIE

cea

Development status on the pyrochemistry R&D program at CEA

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IPRC 2012 | Eric Mendes,

26-30/08/2012 Fontana (USA)

IPRC | AUGUST 26 – 30th 2012

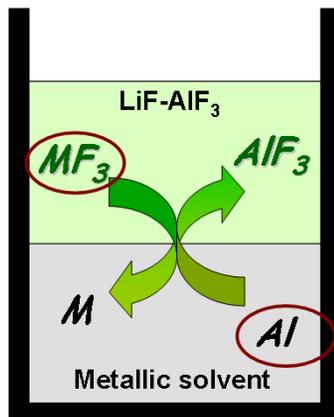
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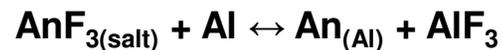
Outlines

- Several spent fuel pyrochemical processes studied worldwide:
 - Electrorefining/Electrolysis in molten chloride melts → most studied technique
 - Precipitation/Electrolysis assessed
 - Reductive extraction in molten chlorides also investigated
mainly as a step of the electrorefining complete process

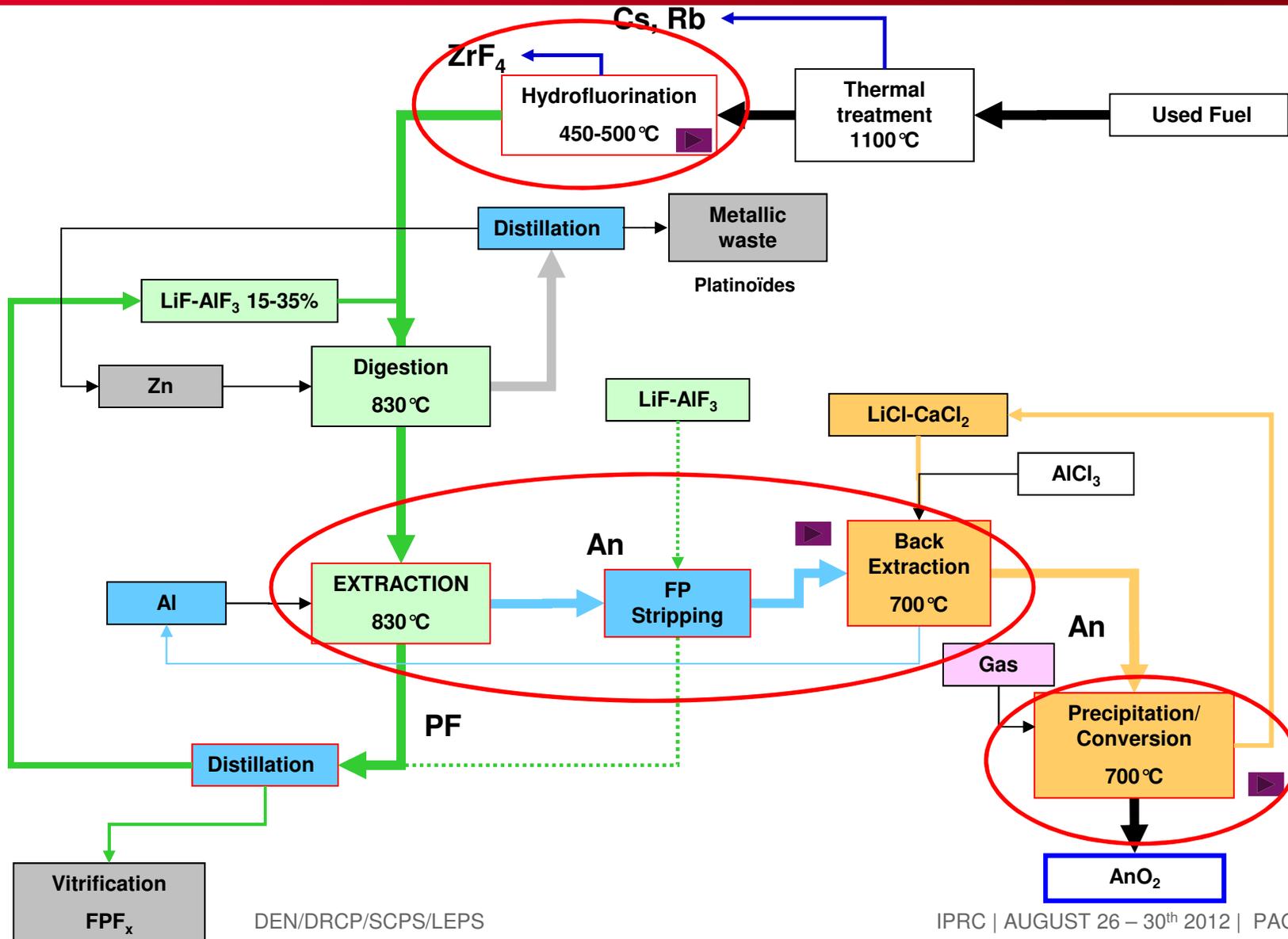
- Reference route developed by CEA: Reductive liquid/liquid extraction in fluoride media
 - France: only country currently considering this alternative route for fuel reprocessing



- LiF-AIF₃ solvent at 830 °C
- Al both solvent and reductor



Liquid/Liquid extraction process flowsheet



Liquid/liquid extraction core of process demonstration

Experimental conditions

- LiF-AlF₃ (20g) / Al-Cu (20g) system at 830 °C
- Chosen salt compositions :
E1 (85-15% mol. LiF-AlF₃), C (75-25) and E2 (65-35)
- U: 200mg, Pu: 25mg, Am: 100mg and Nd: 50mg
- Liquid/liquid extraction reaction:

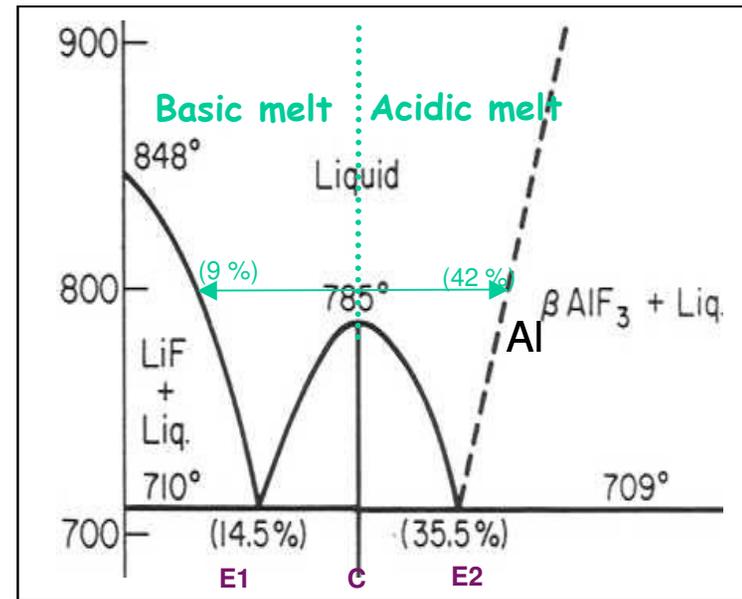


- Distribution coefficient: $D = X_{\text{An}_{(\text{Al})}} / X_{\text{AnF}_{3(\text{salt})}}$

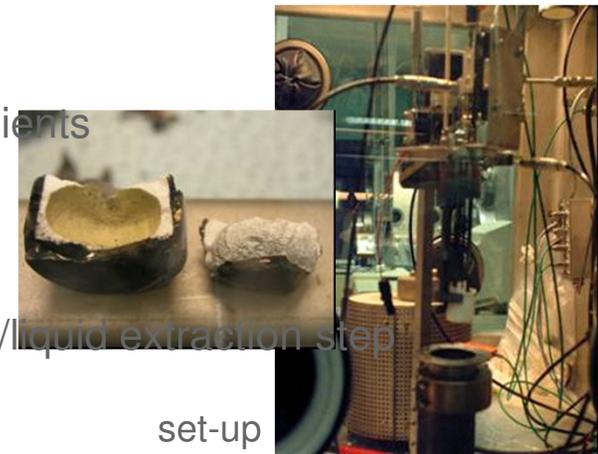
- Salt composition (LiF-AlF₃) modifies the distribution coefficients

$$D_{\text{An}} = K \cdot \frac{\gamma_{\text{AnF}_3}}{\gamma_{\text{An}_{(\text{Al})}}} \cdot \frac{1}{a_{\text{AlF}_3}}$$

- Excellent An/Ln separation factors: >100 for a single liquid/liquid extraction step
- Good agreement with previous studies



LiF-AlF₃ system, J.L Holm and B.J Holm, *Thermochim. Acta*, 6 [4] 375 (1973)



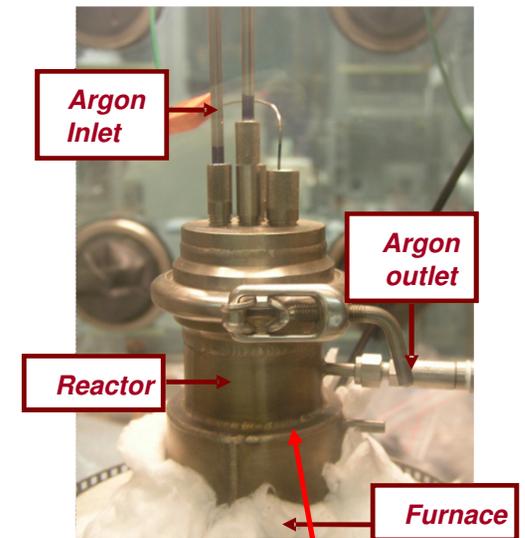
After experiment in E1 → stripping step using pure LiF-AlF₃ (C)

- An oxidative liquid/liquid back-extraction step:
In chloride media, using oxidizing reagent $\rightarrow \text{AlCl}_3$

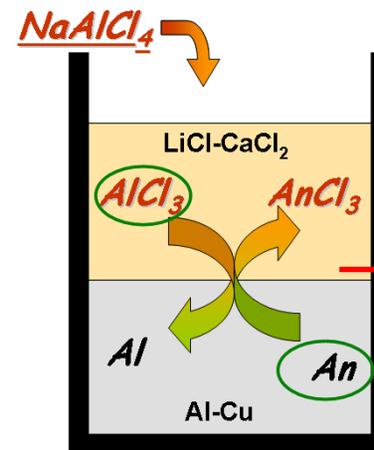


- From previous studies, optimal operating conditions:
 - LiCl-CaCl₂ (30-70 mol.%) at 700 °C (4h experiment)
 - Reagent NaAlCl₄, overstoichiometry: 7 (stabilisation of AlCl₃)
 - Crucible filled inside tightened container (prevent AlCl₃ volatilisation during experiment)
 - Al-Cu ingots coming from reductive extraction step (ingot from run E1 coming from stripping step)
- Back-extraction efficiency:
 - Pu, Am: >99%
 - U: 87 to 95% \rightarrow as expected, most difficult actinide to be back-extracted
(redox potential U^{III}/U⁰ close to Al^{III}/Al⁰)
 - Nd: 86 to 92%
- No An/Ln selectivity during back-extraction step (as expected)

\Rightarrow Importance of the selectivity during reductive extraction step



Experimental set-up



Run		Efficiency (%)			Global efficiency	
		Extraction	Scrubbing	Back-extraction		
E1	U	82	2.3	87	73	3
	Pu	99	3.3	99	96	0.4
	Am	99	2.8	99.9	96	0.4
	Nd	27	78	92	2	-
C	U	85		95	82	2
	Pu	98		99	98	0.3
	Am	98.5		99.8	98.5	0.2
	Nd	11		92	11	-
E2	U	64		94	59	4
	Pu	84		99	83	2
	Am	84		99.98	84	2
	Nd	4.4		86	3.8	-

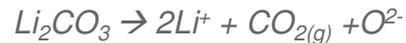
Results for a one-stage experiment promising

- E1 and C: more than 96% global recovery of Pu and Am. U: 73% with 2% of Nd (after stripping)
- E2: worse results than expected (mainly due to metal drops transferred into the salt during experiment → distortion of the results)
- U behaviour: no quantitative recovery could be achieved in a one-stage experiment. Could be due to a possible precipitation of U during reductive extraction step
- Advantages of implementing run E1 with stripping step: Nd back-extraction 92%
 - If no stripping implemented: 25% of initial Nd together with An.
 - Stripping: only 1.8% of the initial Nd in the chloride salt.

Conversion to oxide step

- After Back-extraction step:
An(III) in molten chlorides must be converted into oxide form.
- For nuclear fuel re-fabrication:
 - Quantitative
 - Oxide form AnO_2
 - Solid solution $(U,Pu,MA)O_2$

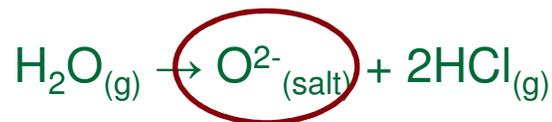
- Reference routes: *precipitation with carbonates*



Leads to increase of salt volume

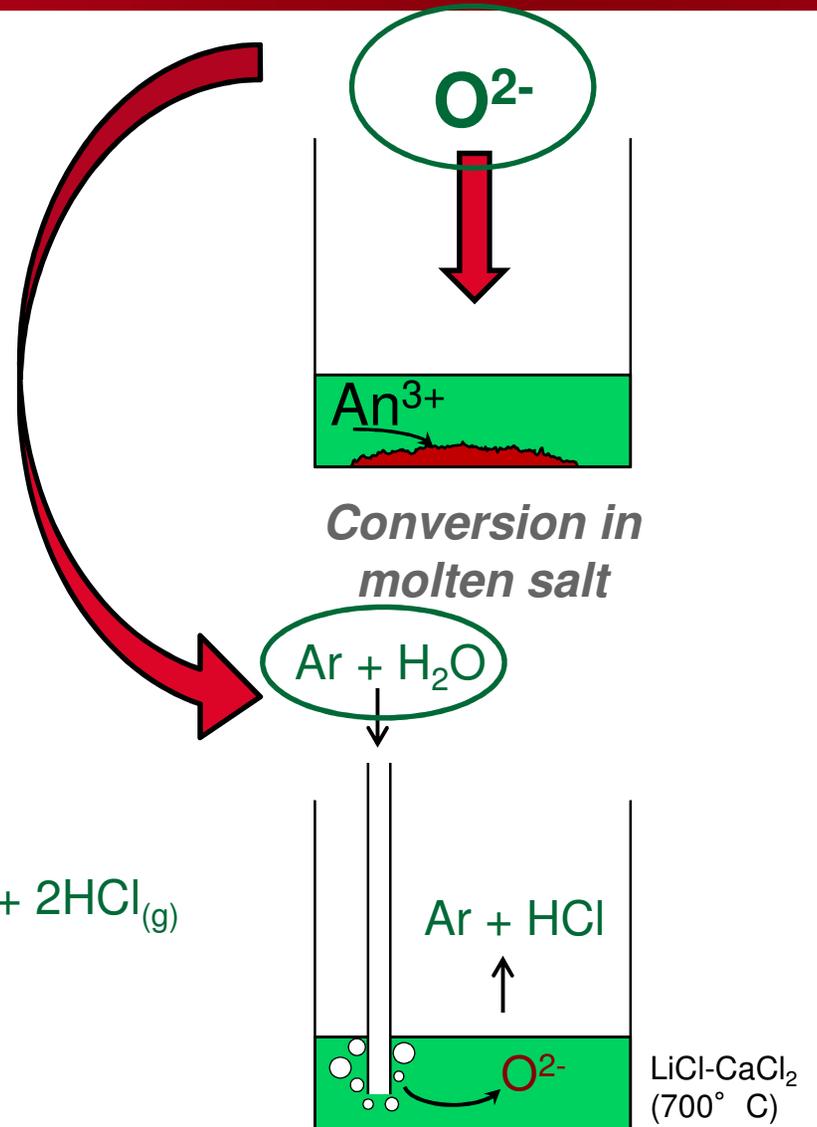
- **Chosen route:** precipitation using a process gas

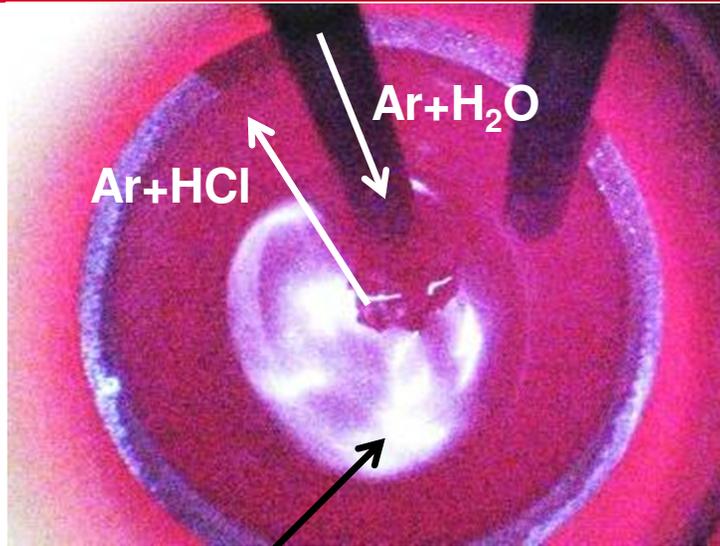
\Rightarrow *Wet Argon sparging*



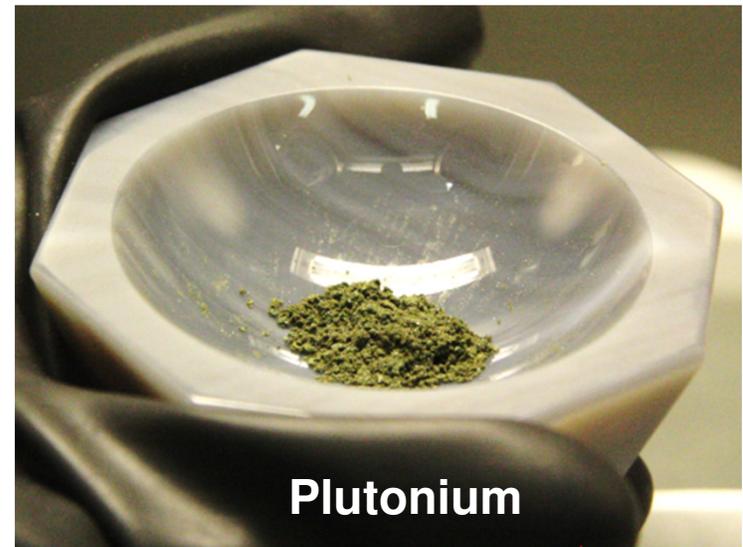
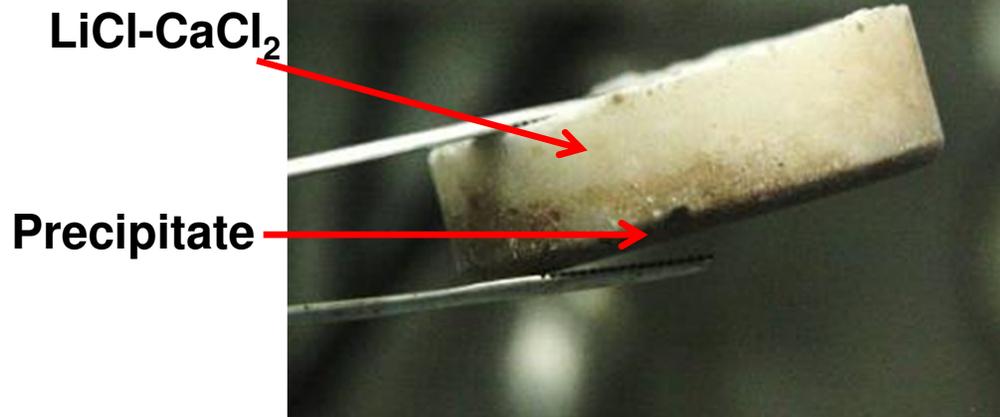
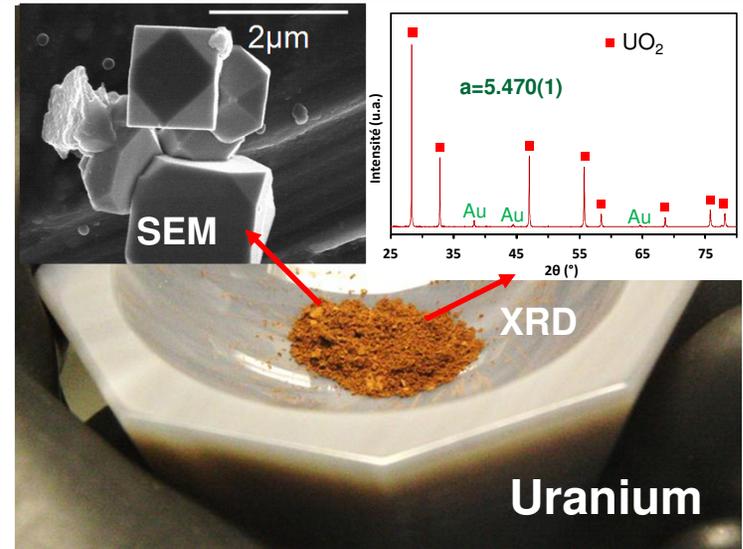
Studied systems:

Nd – Ce (inactive study) and U – Pu



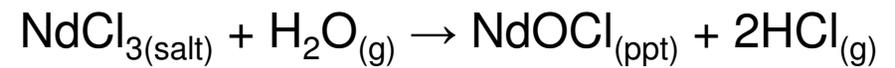
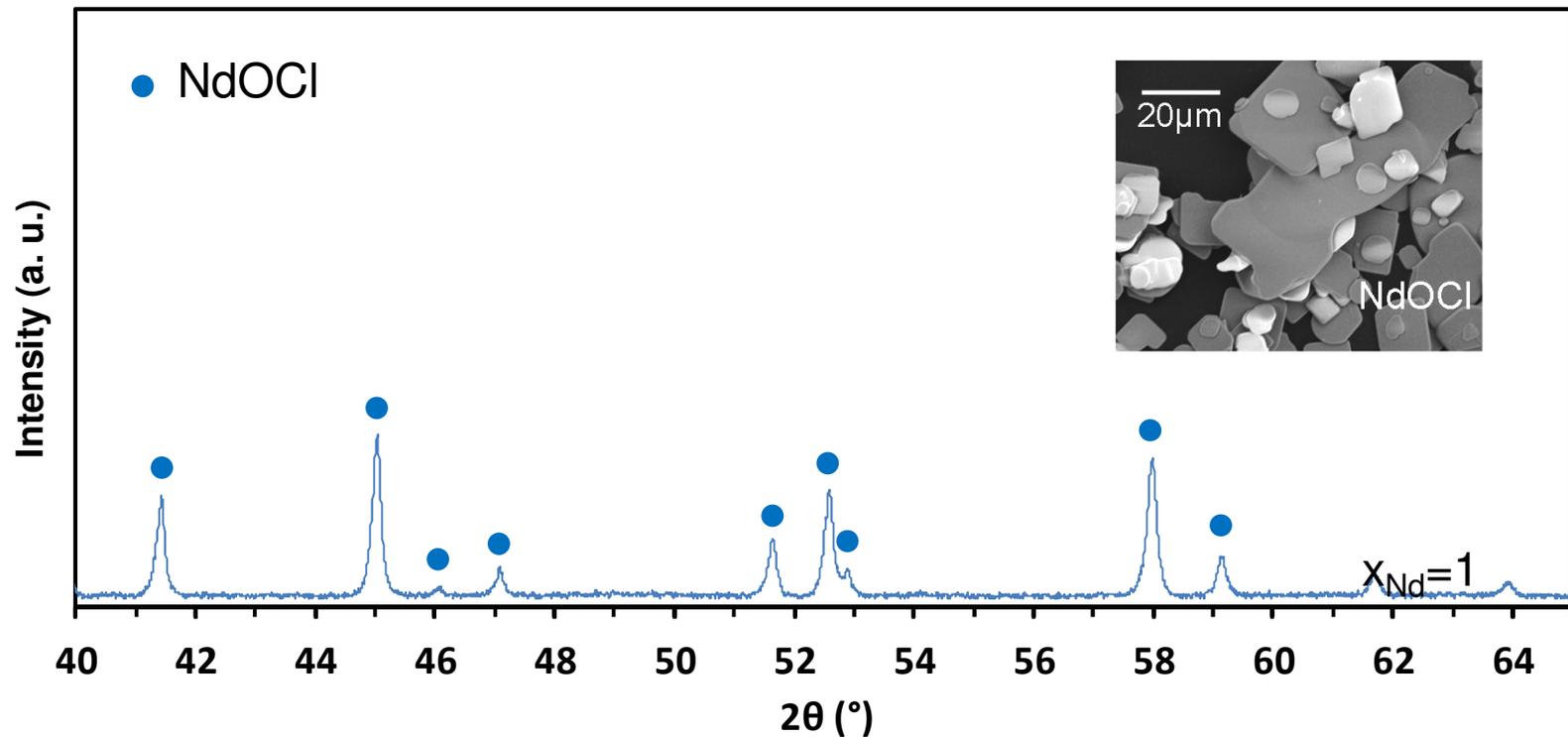


LiCl-CaCl₂
700°C

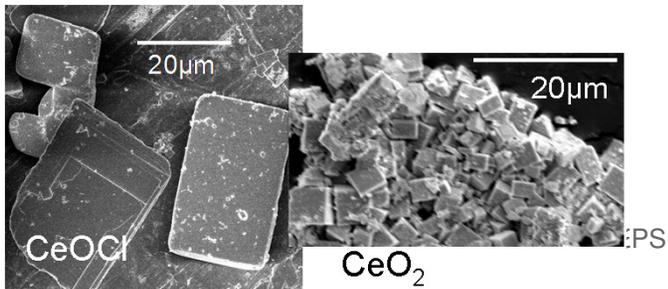
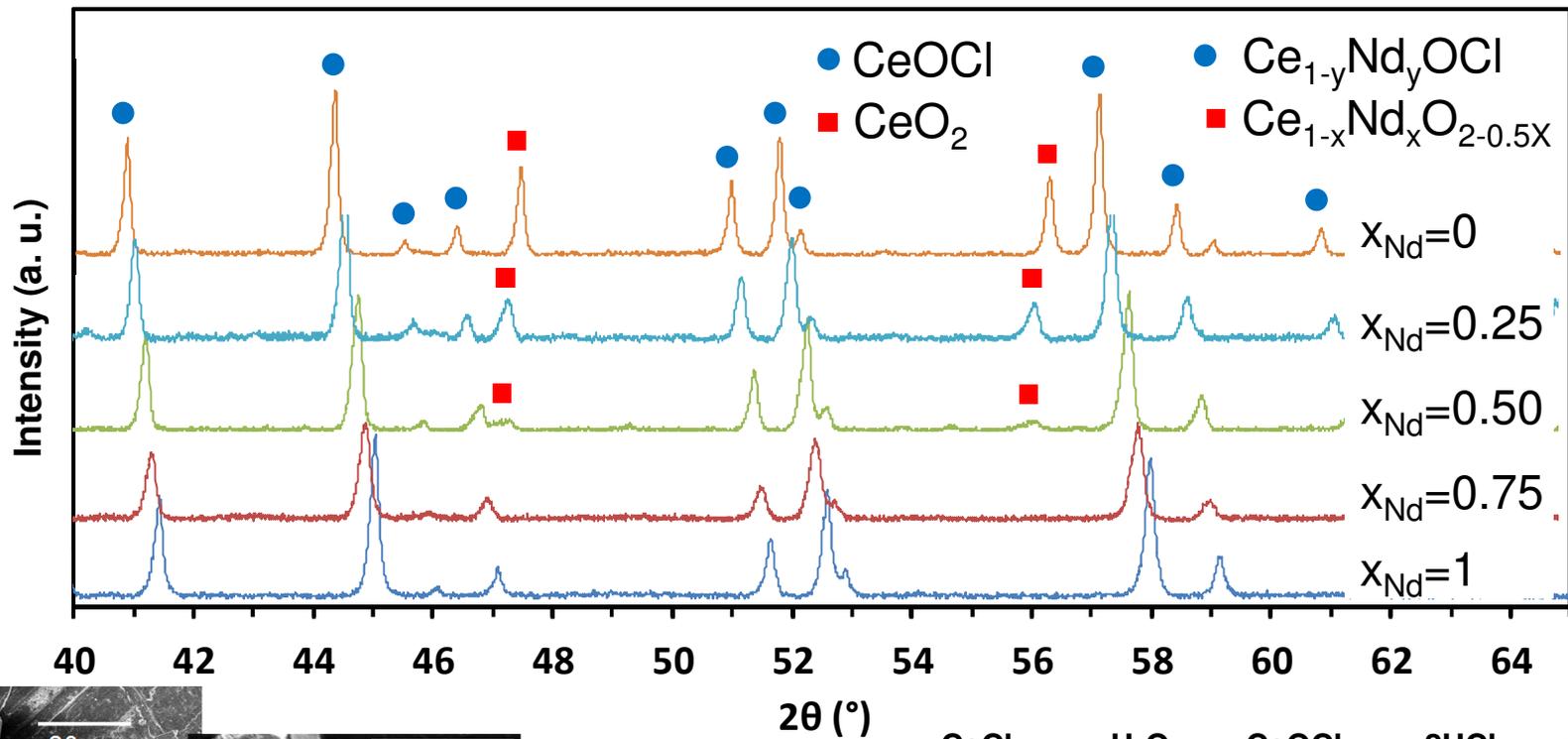


■ Conversion of Nd(III) – Ce(III)

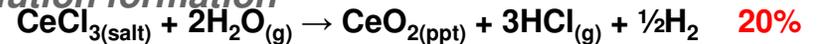
$$X_{\text{Nd}} = \text{Nd}/_{\text{Ce+Nd}} \rightarrow 0; 0.25; 0.5; 0.75 \text{ and } 1$$

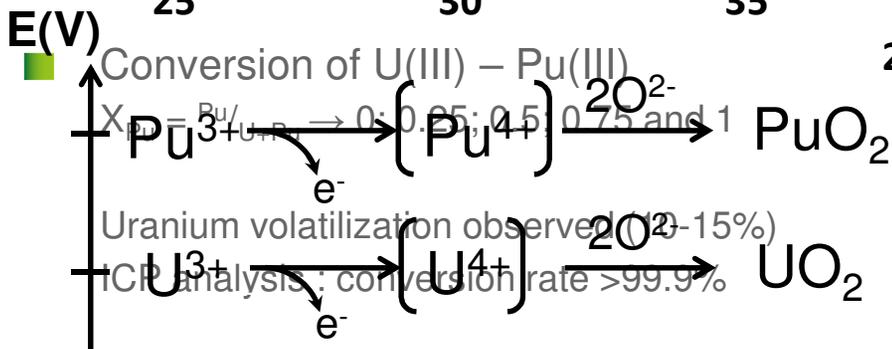
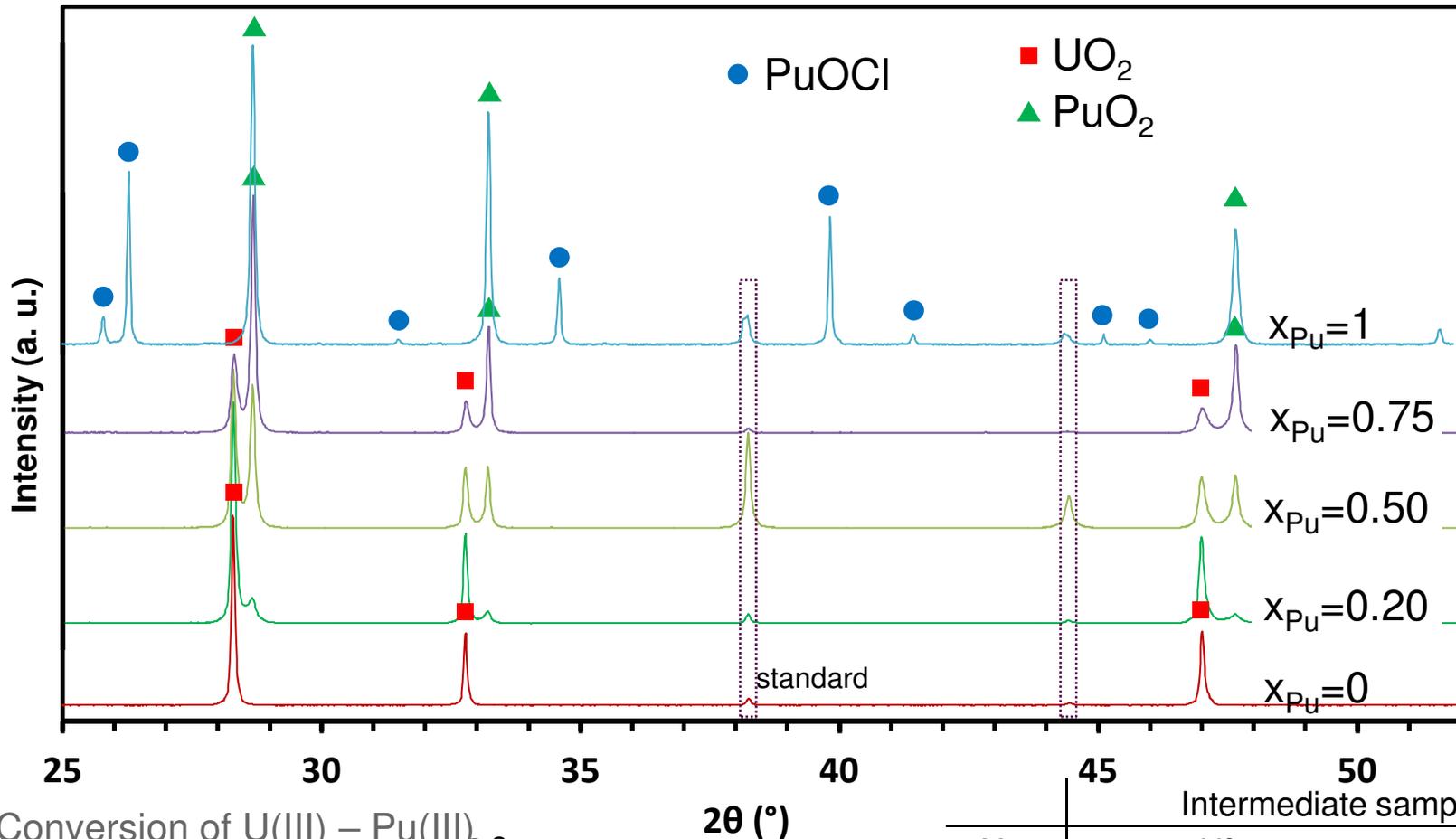


- Conversion of Nd(III) – Ce(III) $\xrightarrow{\text{conversion rate}}$ ICP analysis : 99.9%
 $X_{Nd} = \frac{Nd}{Ce+Nd} \rightarrow 0; 0.25; 0.5; 0.75 \text{ and } 1$



Nd-Ce Solid solution formation





X_{Pu}	Intermediate sample	
	U^{3+}	Pu^{3+}
0.75	< 1%	70%
0.5	< 1%	76%
0.2	< 1%	61%

Nd(III)-Ce(III) precipitation :

Partially oxidative method

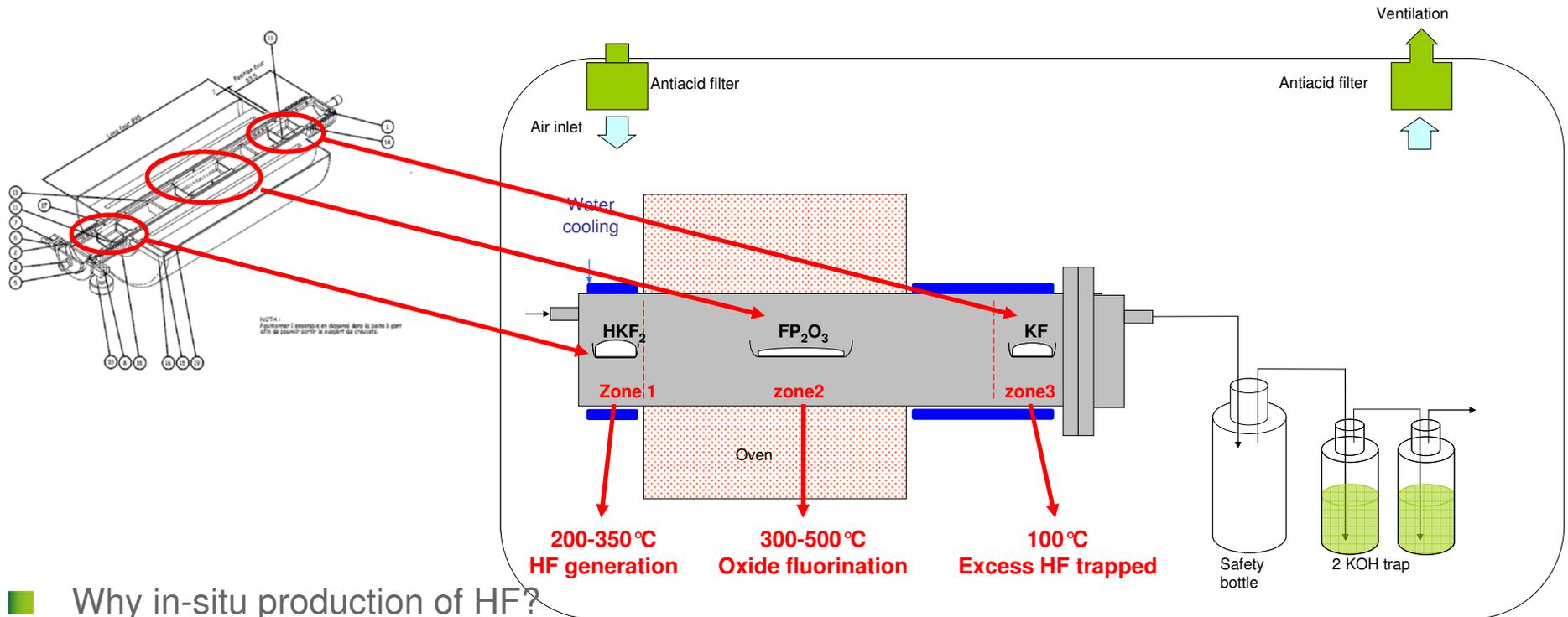
- 1 - Quantitative → OK
- 2 - Oxide Form LnO_2 → ~~OK~~ calcination
- 3 - Solid solution → OK

U(III)-Pu(III) precipitation

- 1 - Quantitative → OK
- 2 - Oxide Form AnO_2 → OK
- 3 - Solid solution → ~~OK~~



**Hydrofluorination : in situ HF
production**

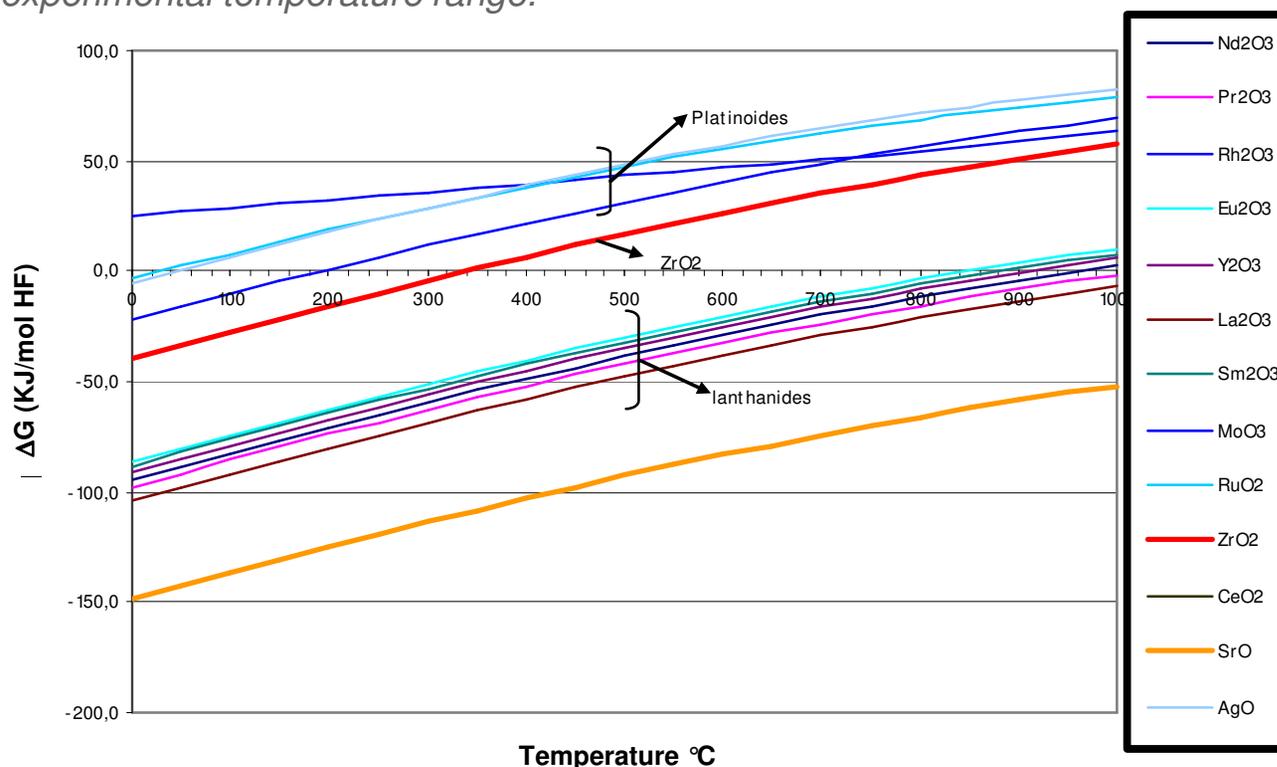


Why in-situ production of HF?

- Conversion of spent fuel into fluoride is needed.
- Few hot cells facilities are equipped with HF gas line
- HF produced by dissociation of solid HF-KF at 200-350°C
 - Experimental set-up including three eating areas
- Study of oxide fluorination: La, Ce, Pr, Nd, Mo, Ru, Rh, Sm, Eu, Pr, Zr, Sr, Ag, Y
 - Determination of the best reaction conditions
 - Assessing behaviour of oxides under HF gas flow (*fluorination rate, final product*)

Thermodynamic cacluations (HSC Chemistry® V.4.1)

- Gibbs free energy of fluoride formation from oxide form, with HF → *Determination of optimum experimental temperature range.*



- Temperature acts in opposite direction
However, Gas/Solid reaction → higher specific surface of the solid and higher temperature should favour kinetic
- Ln oxides: temperatures ranging from 400 to 500 °C are favourable.
- ZrO₂: favourable temperature rather from 300 to 320 °C.

Experimental results

- Fluorination experiments: 6h, 330 °C to 420 °C (depending on oxide to convert), HF excess ~3.5

- Oxides behaviour: *(determined by XRD)*

Nd₂O₃, CeO₂, SrO, Eu₂O₃, La₂O₃, Y₂O₃, Sm₂O₃, Pr₂O₃ successfully converted into fluorides

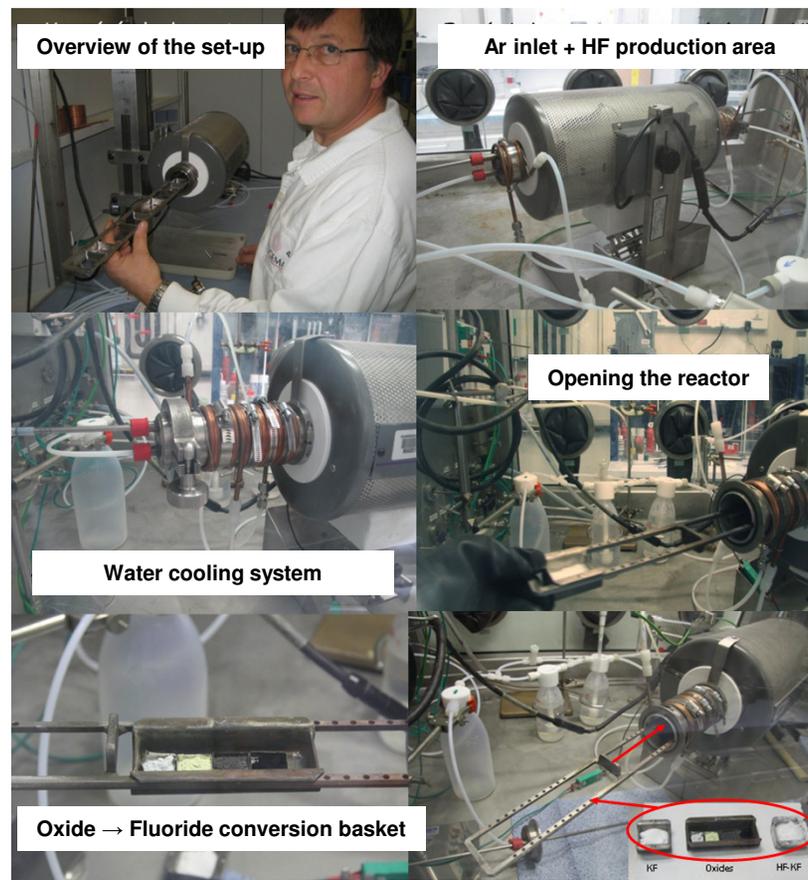
→ Pr, La, Eu presence of oxyfluorides could be evidenced

MoO₃, Rh₂O₃, RuO₂, AgO remained in oxide form
good agreement with thermodynamic calculations.

Case of ZrO₂: Several experiments on commercial and nanopowder ZrO₂.

Commercial ZrO₂ → No fluorination

Nanopowder (350 °C) → 25% of Zr fluorinated



Hydrofluorination reactor



Potential routes	Principle	Media	Average working Temp.	Predilection fuels	Remarks
Electrorefining/ Electrolysis 	Electrorefining Selective electrodeposition	LiCl, LiCl-KCl	450 °C	Metal, (oxide)	The most studied and the most advanced pyro process At pilot scale
Electrolysis 	Selective electrodeposition	NaCl- 2CsCl (with $\text{Cl}_{2(g)}/\text{O}_{2(g)}$)	550-800 °C	Oxide	At semi-pilot scale, coupled with vibrocompact fuel fabrication
Reductive extraction 	Selective extraction in a metal phase (Cd) with reductor (Li)	LiCl-KCl/Cd	450 °C	Oxide, Metal	Laboratory scale
Reductive extraction 	Selective extraction in a metal phase (Al)	LiF-AIF ₃ /Al	830 °C	Oxide Carbide	Laboratory scale, high temp. and corrosive solvents and gases → material issues Very good recovery yields and separation factors

- The core of process is now well assessed at lab scale with encouraging results on a One stage Extraction-Back-extraction experiment
- Conversion step:
Use of wet Argon → promising method. U(III) and Pu(III) coconversion lead to UO_2 and PuO_2 mixture
Still some further investigations are needed
- Hydrofluorination highlighted Zr behaviour (should be studied and simulated in the whole process)
- Analytical techniques are under development.

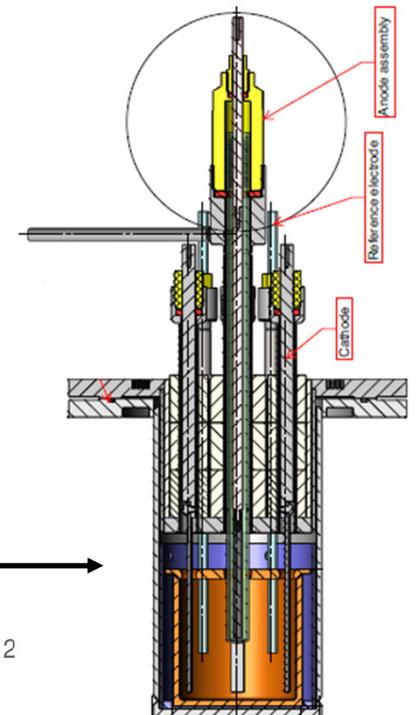
Perspectives

Reference Route in molten fluorides

- A few steps need to be tested with genuine fuel (thermal treatment, digestion)
- An alternative head of process is under investigation in order to prevent use of HF to convert oxides fuels into fluorides.

Electrorefining process in molten chloride

- CEA is collaborating with JRC-ITU and LGC (Toulouse university, France) to study the salt cleaning step by exhaustive electrolysis.
Development of a dedicated reactor within the framework of the ACSEPT program.



Thank you for your attention

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