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E. Mendes, T. Ducasse, Q. Chambon, J. Serp, M. Bertrand

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FROM RESEARCH TO INDUSTRY

cea den

*CEA Marcoule / Nuclear Energy Division,
RadioChemistry & Processes Department
Modelling and Separation Chemistry Service
Development of Separation Processes
Laboratory*

OVERVIEW OF APPLICATIONS OF THE PYROCHEMICAL PROCESS DEVELOPED BY THE CEA FOR THE TREATMENT OF TRANSMUTATION

FUEL TARGETS

**E. Mendes, T. Ducasse, Q. Chambon, J. Serp,
M. Bertrand**



IPRC 2016

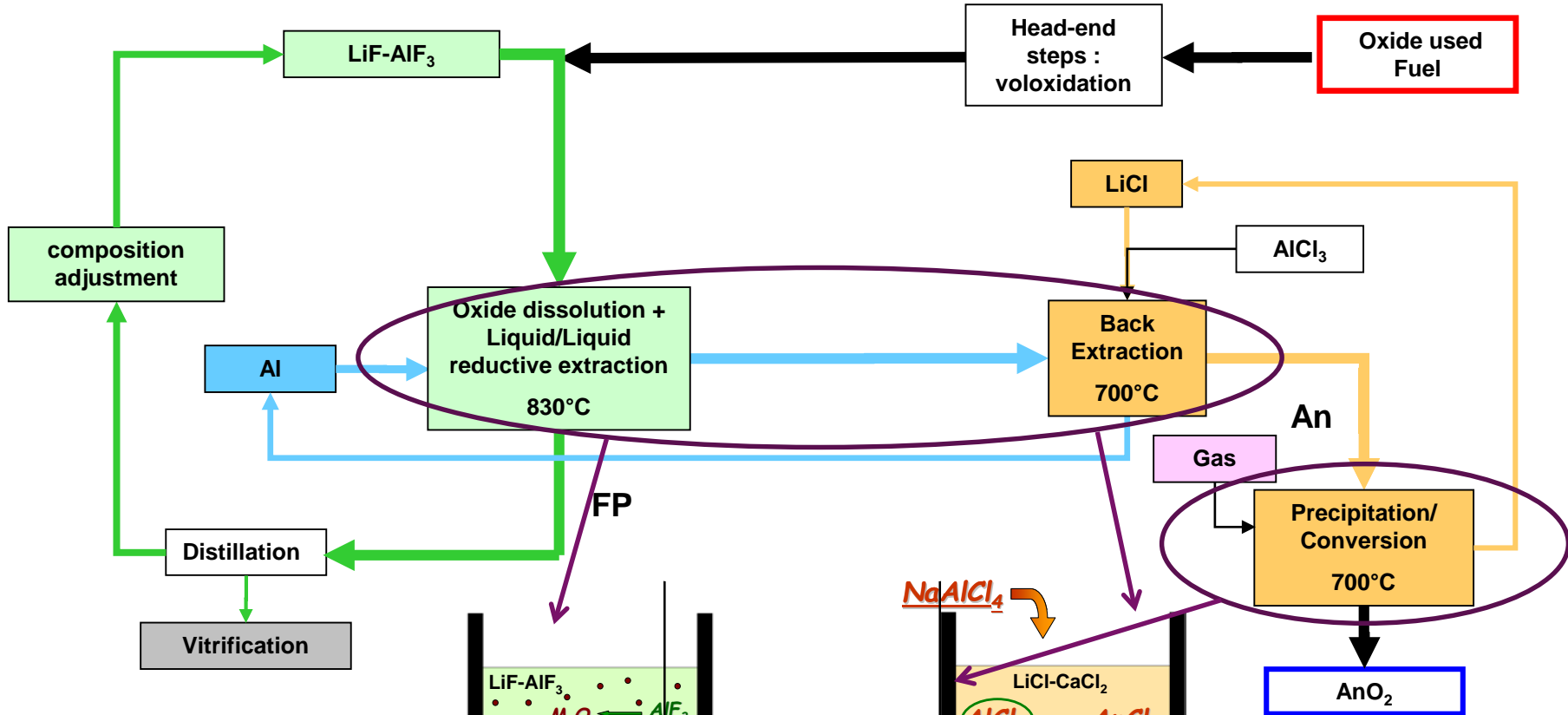
2016 International Pyroprocessing Research Conference

21-23/09/2016 - Jeju (South Korea)

| Eric Mendes

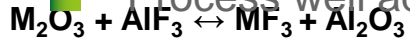
SEPTEMBER 21ST – 23RD 2016

Process developed by CEA: Reductive liquid/liquid extraction in fluoride media

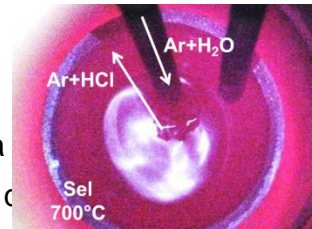
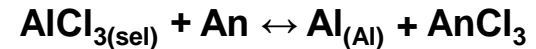
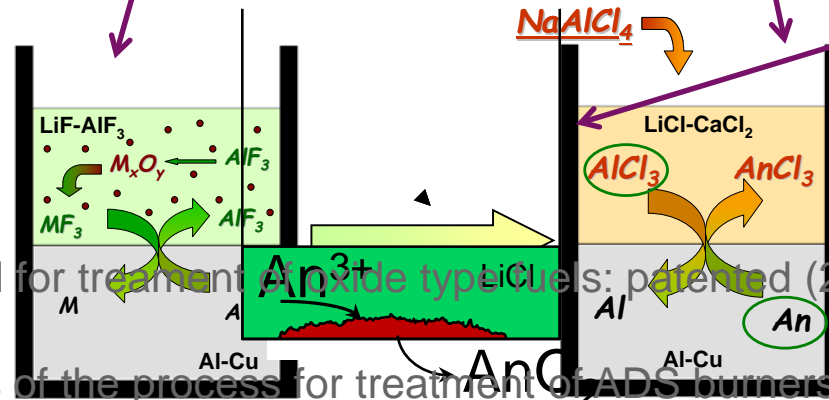
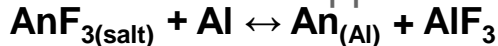


LiF-AIF₃ at 830°C

Conversion of oxides



L/L extraction Al selective reductor



Process well adapted for treatment of actinide type fuels: patented (2013)

Potential applications of the process for treatment of ADS burners fuels!

MATERIAL TO BE REPROCESSED

Two types of fuels considered : CERCER and CERMET

CERCER

- Ceramic matrices, e.g. oxide MgO, ZrO₂...
- **MgO** suitable for ADS burners.
- Reference Composition:

Ref.	Composition	Vol. frac. Mg
FUTURIX	(Pu _{0.5} Am _{0.5})O _{2-δ} -MgO	70%

- Compatibility with the DOS process.
→ Oxide form

Assessment requirements:

- Behaviour of matrix material in the process, e.g. **dissociation of oxide** into the salt and behaviour regarding the **reductive extraction** by Al.
- **Feasibility** of the reprocessing of surrogate or genuine material
- Influence of matrix material on the **extraction efficiency** of MA

CERMET

- Metallic matrix.
- **Mo** suitable for ADS burners.
- Composition:

Ref.	Composition	Vol. frac. Mo	Mo/MA Ratio
ITU-5	(Pu _{0.797} Am _{0.198} Np _{0.005})O _{2-x}	86%	29,3
ITU-6	(Zr _{0.532} Pu _{0.228} Am _{0.124} Np _{0.006})O _{2-x}	60%	6,1

- Compatibility with the DOS process:
Needs prior conversion of Mo into oxide → MoO₂ and/or MoO₃

TREATMENT OF CERCER MATRICES

Dissolution of MgO in LiF-AlF₃ at 830°C

Starting material:

MgO powder → **solubility limit**

Pellets → **dissolution kinetic**

Sintering: similar to condition as for preparation

of CERCER pellets.



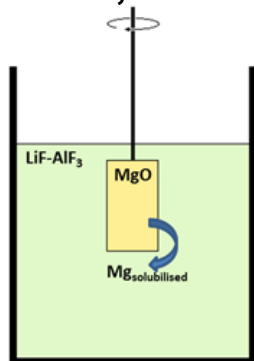
Dissociation in the salt:

Mechanism:



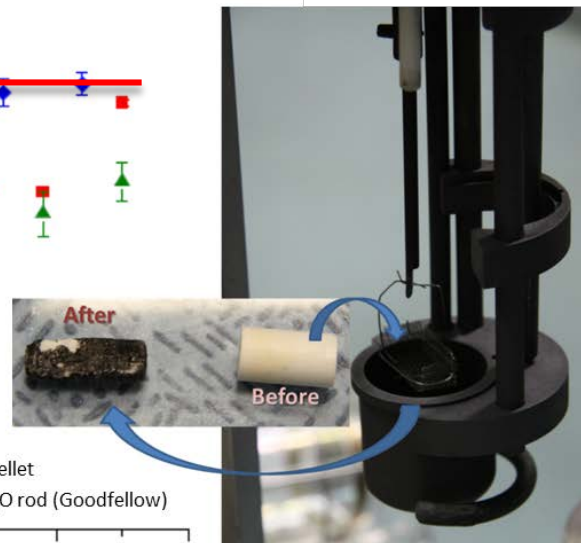
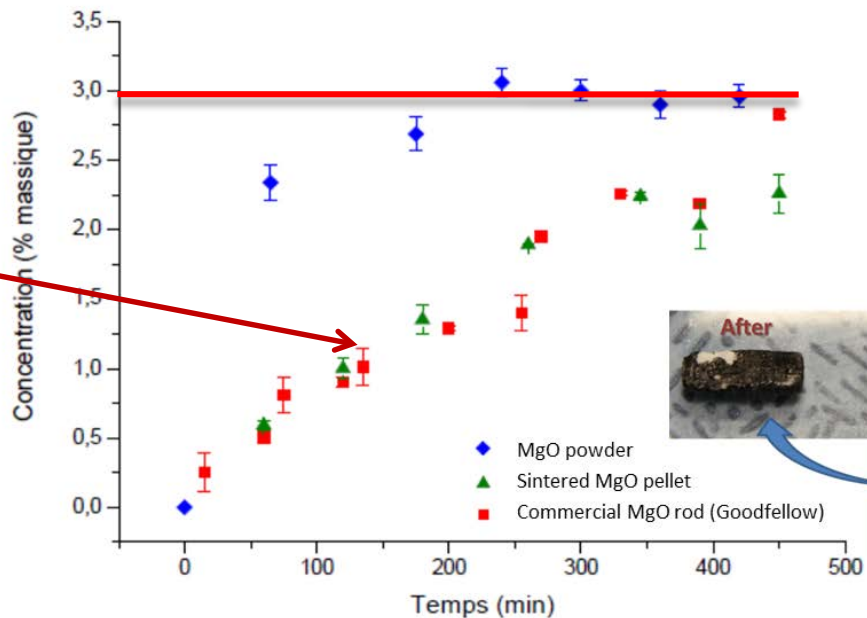
Kinetics: $V = \frac{dC}{dt} = kA(C_s - C)$

$v = 2,53 \cdot 10^{-4}$
to $3,13 \cdot 10^{-4} \text{ cm}^3 \cdot \text{s}^{-1}$



DEN/DRCP/SCI

Solubility seems to reach a limit: ~3 wt%



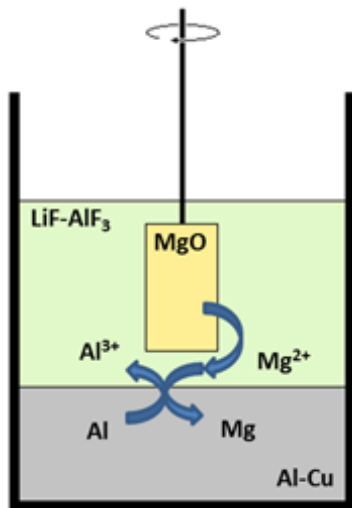
Behaviour of Mg regarding extraction

Theoretical study: Redox standard potential calculations (HSC chemistry)



From thermodynamic approach : No Mg should be reduced by the metallic phase

Experiments



Results	[Mg] (wt%) in Al
Run 1	< LD
Run 2	0,01
Run 3	0,02
Run 4	0,02

Good agreement with Thermodynamic approach: **Al not reductive enough to reduce Mg²⁺**

■ Reprocessing of a non irradiated CERCER pellet

Unirradiated pellet prepared in ATALANTE facility within the FP6 Eurotrans framework program

Experimental conditions:

Pellet containing 200mg of Pu, 200mg of Am and 325 mg MgO

Addition 125mg of Nd_2O_3 (simulating FPs)

Prefusion step needed to dissolve the pellet in the salt: due to very high activity

L/L contact 4h at 830°C, sampling after contact. Pu and Am quantified by α and γ spectrometry, Nd and Mg quantification by ICP-MS

Results:

97% of Am and 99% of Pu in the metallic phase after contact ($\text{Nd} < 5\%$, $\text{Mg} < \text{DL}$).

Successful demonstration for reprocessing of CERCER material



Impact of MgO accumulation in the salt: reuse of salt

- Uranium → simulating An behaviour
- Experiments performed :

Same amount of U_3O_8 in each experiment (~500mg U)

Progressive addition of MgO in the salt from run 1 to 4: 0 – 13.5 wt%.

MgO: 3wt%. Based on used CERCER pellets, corresponds of reprocessing of 150 pellets/Kg of salt

After L/L contact samples of the two phases. U quantified by fluorescence X spectroscopy

Run	MgO wt%	Uranium		
		Metal phase (%)	Salt phase (%)	Undissolved (%)
1	0	93,6 (± 4,5)	3,3 (±1,8)	3,1 (±6,3)
2	3	85,9 (±6,5)	1,2 (±0,5)	12,9 (±7)
3	6	66 (±5,9)	5,8 (±3,7)	28,2 (±9,6)
4	13,5	45,7 (±1,3)	–	–

U in metal decreases when MgO increase: mainly due to U_3O_8 dissolution decrease.

→ Solubilisation affected by excess of oxides in the salt.

Accumulation of MgO: possible change of physical properties of the salt

High contents of non dissolved MgO: **strong decrease of extraction efficiency.**

→ Accumulation of oxides at the salt/met. Interface + changes of physical properties of the salt (viscosity).

Summary on the application of DOS for treatment of CERCER

Feasibility of the process: demonstrated on genuine CERCER pellet

Behaviour of MgO in the process could be assessed

- Regarding solubilisation of the oxide
- Regarding reductive extraction

Impact of its accumulation in the salt:

- Significant influence of MgO accumulation:
- Decrease of An oxide solubility
 - Decrease of extraction efficiency



**Dimensioning of
the process**

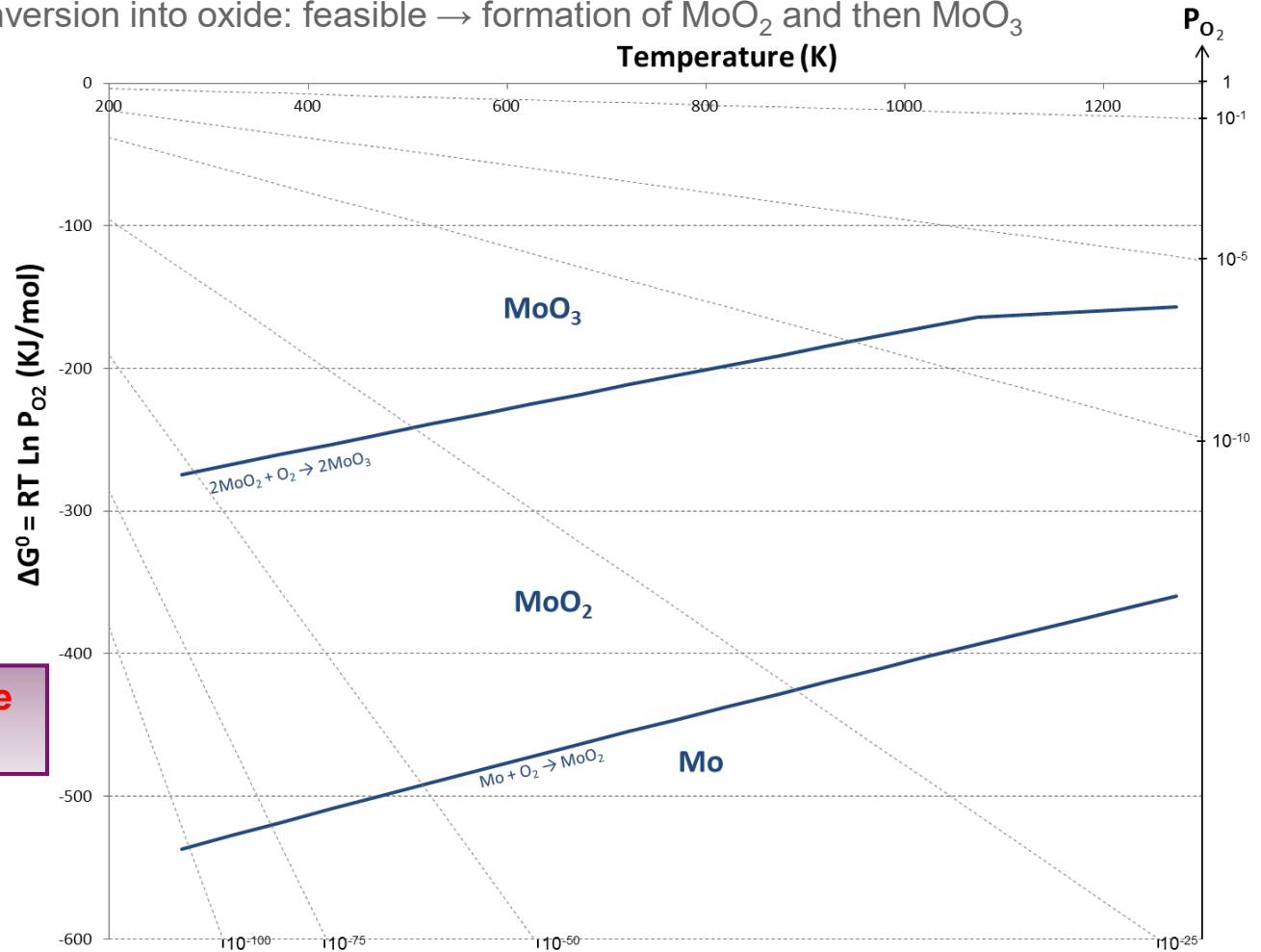
e.g. **150 pellets/kg of salt**
→ Optimisation needed

TREATMENT OF CERMET MATRICES

Mo conversion into oxide form

Thermodynamic approach:

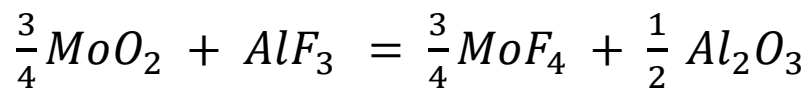
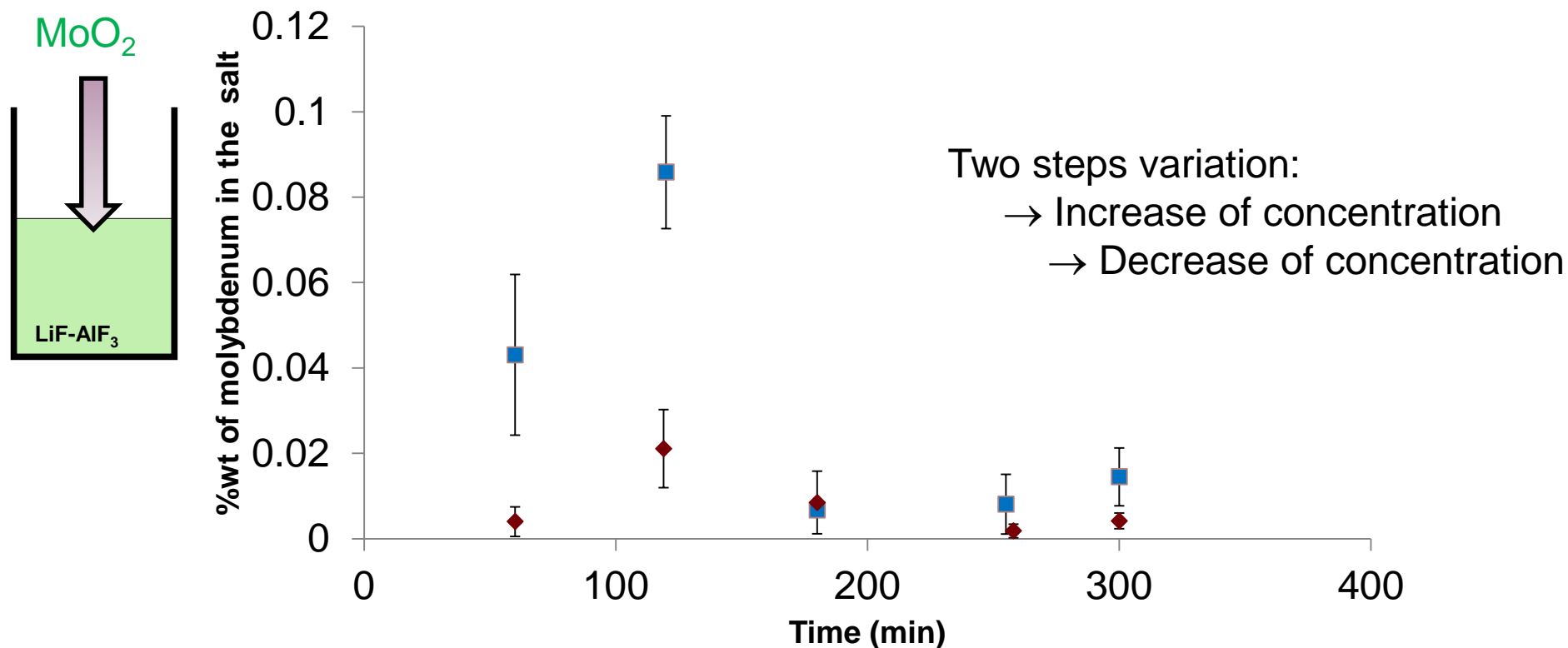
- Mo conversion into oxide: feasible → formation of MoO₂ and then MoO₃



Compatibility with the process: OK

- Good agreement with literature. Volatility of MoO₃ observed (starting ~500°C)

Experiments performed on **MoO₂ powder** (1 – 4g) in LiF-AlF₃ (65 – 35 mol%) at 830°C
first tests on MoO₃ solubility → not possible due to high volatility of Mo(VI)

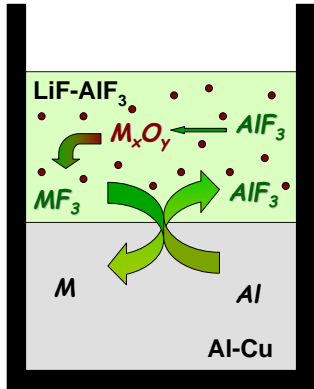


$$\Delta G_{830^\circ C} = -261,541 \text{ kJ/mol}$$

Possible oxidation of Mo^{IV} into Mo^{VI} → Volatilisation

Metallic phase added: L/L contact 4h at 830°C

→ Sampling of each phase: quantification of Mo



% Mo in metal	% Mo in the salt	%Mo remaining
38,9 ± 2,8	1,6 ± 0,4	59,5 ± 3,2

~40% of Mo in the metallic phase => possible reduction of Mo by Al

Mo extraction by aluminium: possible mechanism		
Mechanism	Reaction	ΔG (kJ/mol) at 830°C
Direct	$\frac{3}{4} MoO_2 + Al = \frac{3}{4} Mo + \frac{1}{2} Al_2O_3$	-372,338
Indirect	$\frac{3}{4} MoF_4 + Al = \frac{3}{4} Mo + AlF_3$	-604,275
	$\frac{1}{2} MoF_6 (g) + Al = \frac{1}{2} Mo + AlF_3$	-599,056

Coextraction of molybdenum together with actinides suspected

60% Mo not measured : Volatility + possible **solid Al-Mo intermetallic** compounds formed



MO INFLUENCE ON U EXTRACTION EFFICIENCY

Experiments:



Significant influence of Mo on U extraction efficiency

Inhomogeneity of metal sample

Possibly due to U-Al-Mo solid intermetallics

	Initial Mo (g)	Initial U (g)	%U in metal	%U in salt
Extraction 1	0	0,500	97,8 ± 4,0	4,1 ± 0,1
Extraction 2	0,500	0,500	83,1 ± 11,2	21,6 ± 3,6
Extraction 3	1,000	0,500	23,3 ± 6,4 (Hot sample) 120,7 ± 13,7 (cold sample)	30,5 ± 1,3
Extraction 4	2,000	0,500	44,1 ± 8,7	–

Max. Mo/U = 4

Ref.	Composition	Vol. frac. Mo	Mo/MA Ratio
ITU-5	(Pu _{0.797} Am _{0.198} Np _{0.005}) O _{2-x}	86%	29,3
ITU-6	(Zr _{0.532} Pu _{0.228} Am _{0.124} Np _{0.006}) O _{2-x}	60%	6,1

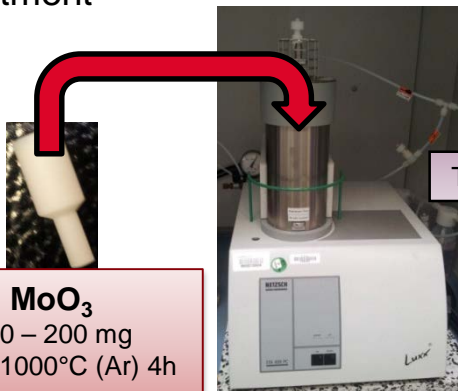


Process can't be applied as it is

Molybdenum must be removed prior the DOS process step

MO OXIDE VOLATILISATION

From thermodynamic approach, metallic **Mo** easily converted into **MoO₂** and **MoO₃** at high temperature
 MoO₃: high volatility → **Possibility to remove Mo prior the DOS process** with appropriate thermal treatment



MoO₃
 100 – 200 mg
 830 – 1000°C (Ar) 4h

At 830°C
 MoO₃ volatilisation:
79.6 ± 0.8%

At 1000°C
 MoO₃ volatilisation:
99.2%

Reference pellet	Mo/AM initial ratio	theoretical Mo/MA ratio after treatment at 830°C	theoretical Mo/MA ratio after treatment at 1000°C
ITU 5	29.3	6,0	0,3
ITU 6	6.1	1,3	0,06

Results obtained with uranium

Mo/AM	%U in metal	%U in salt
0	97,8 ± 4,0	4,1 ± 0,1
1	83,1 ± 11,2	21,6 ± 3,6

Thermal treatment not sufficient

⇒ Thermal treatment sufficient

⇒ DOS process can be applied to CERMET reprocessing

CONCLUSIONS

■ CERCER reprocessing

- **Process successfully demonstrated on genuine unirradiated pellet**
 - Mg remains in the salt → **No influence on Pu and Am extraction efficiency**
 - Accumulation of Mg in the process:
 - Significant influence on extraction efficiency of An
 - *MgO : 0 – 3 wt%: no major influence*
 - *MgO : > 3wt% strong influence*
 - Further accumulation of MgO: **Salt treatment needed**
 - Process needs to be optimised (*use of Na_3AlF_6 → higher solubility expected*)
- } Dimensioning of the process:
Possible **treatment of 150 CERCER pellets/Kg of salt**

■ CERMET reprocessing

- Significant influence of Mo on An extraction efficiency
 - Coextraction of Mo
 - Solid intermetallic U-Al-Mo possibly formed
 - Mo oxides volatility:
 - *Thermal treatment at 1000°C volatilises 99.2% of Mo*
- } **Prior removal of Mo needed**

DOS process can be applied with and additional thermal treatment prior extraction step

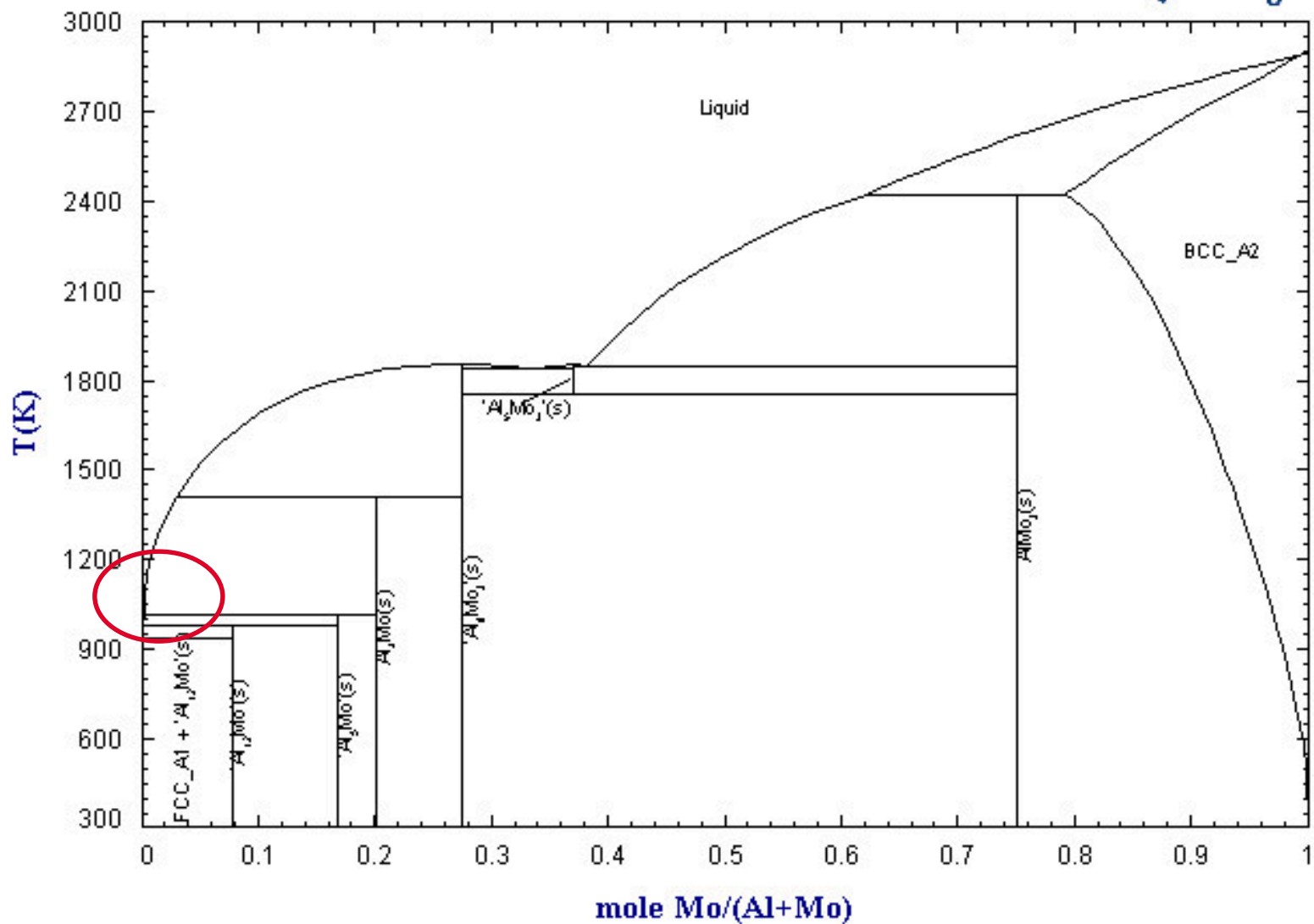
Mo/volatile FP separation? → Refabrication of fresh matrix

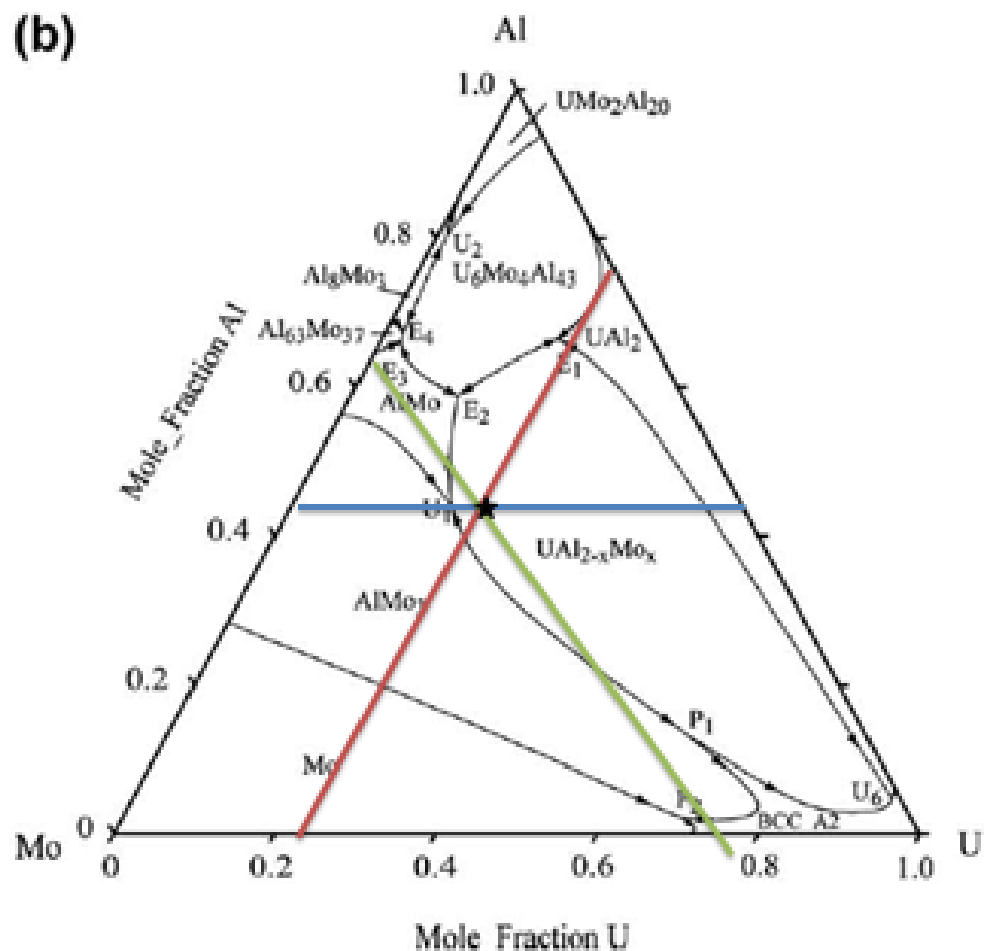
Thank you for your attention

Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Marcoule | 30207 Bagnols sur Cèze
T. +33 (0)4 66 79 63 11 | F. +33 (0)4 66 79 65 67

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X. Zhang, Y.F. Cui, G.L. Xu, W.J. Zhu, H.S. Liu, B.Y. Yin, Z.P. Jin, Thermodynamic assessment of the U-Mo-Al system, *Journal of Nuclear Materials* 402 p 15-24, 2010

TGA experiments on MoO₃ volatility

