



HAL
open science

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

► To cite this version:

E. Mendes, T. Ducasse, Q. Chambon, J. Serp, M. Bertrand. Overview of applications of the pyrochemical process developed by the CEA for the treatment of transmutation fuel targets. 2016 International Pyroprocessing Research Conference, Sep 2016, Jeju, South Korea. cea-02438359

HAL Id: cea-02438359

<https://cea.hal.science/cea-02438359>

Submitted on 14 Jan 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

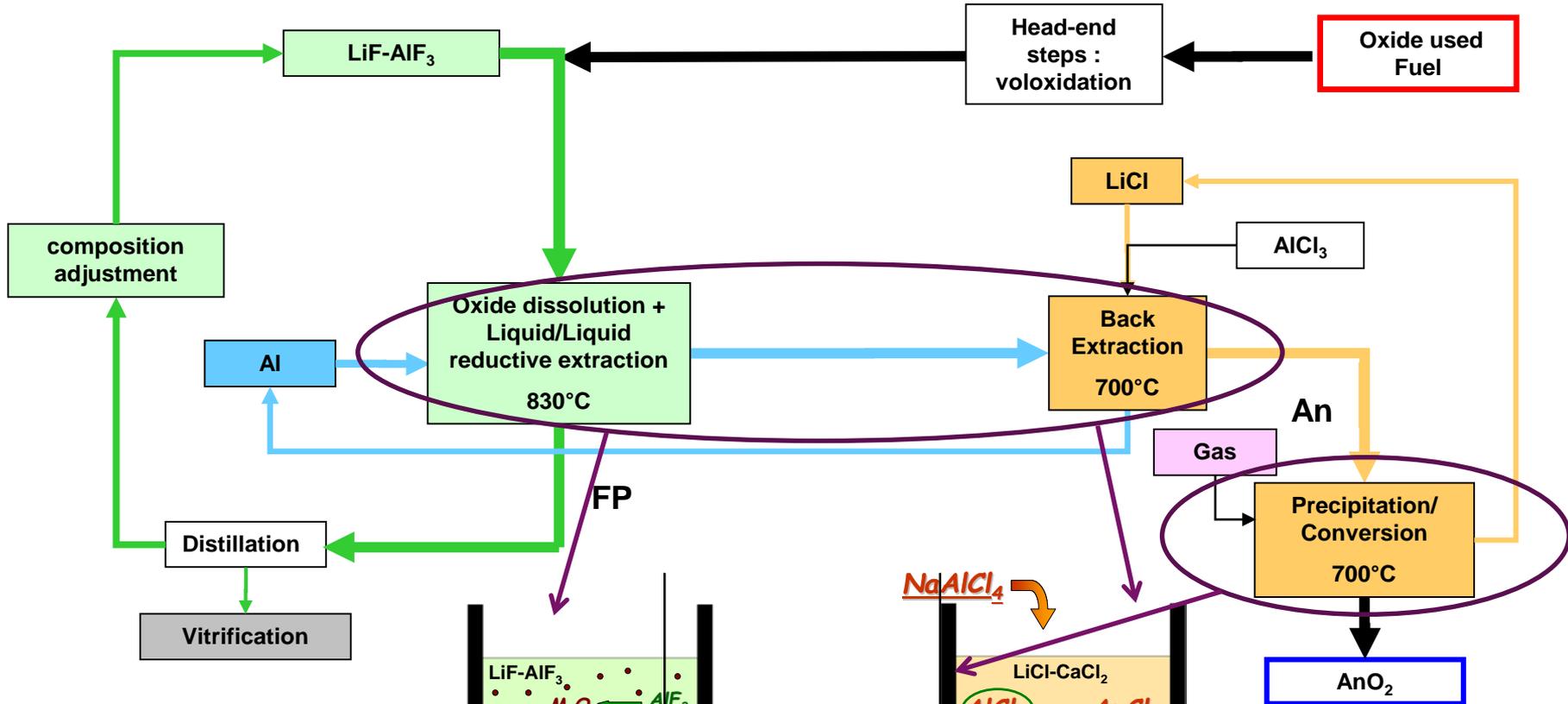
2016 International Pyroprocessing Research Conference

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

| Eric Mendes

SEPTEMBER 21ST – 23RD 2016

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

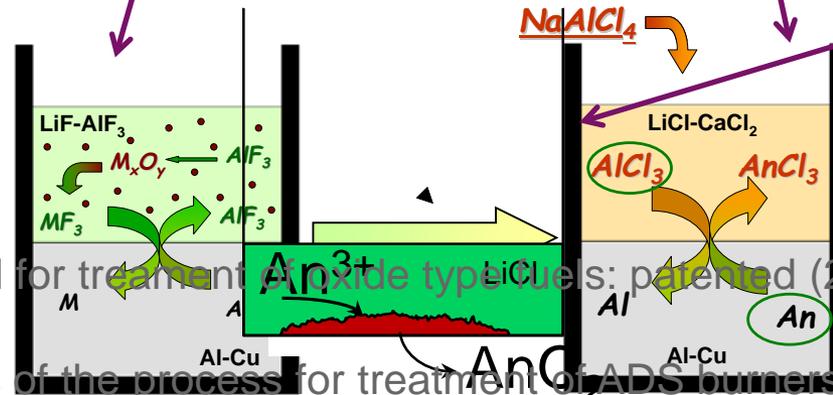
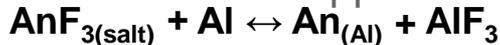


LiF-AIF₃ at 830°C

Conversion of oxides

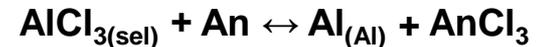
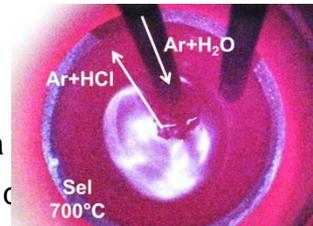


L/L extraction Al selective reductor



LiCl à

Addition of



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

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

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.



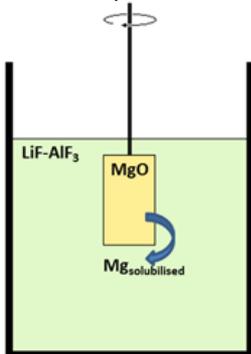
Dissociation in the salt:

Mechanism:



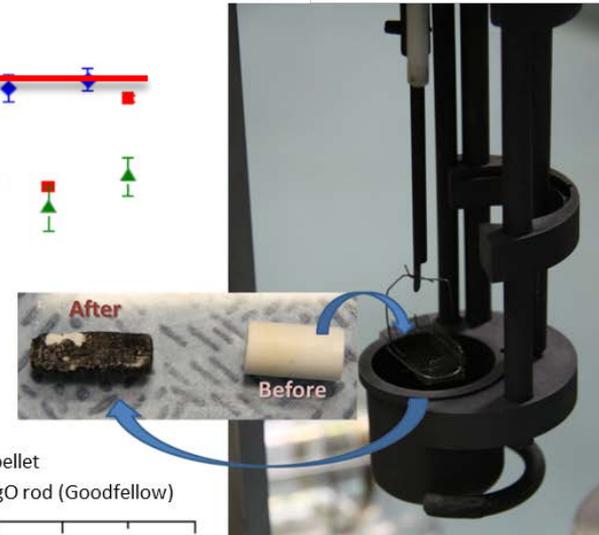
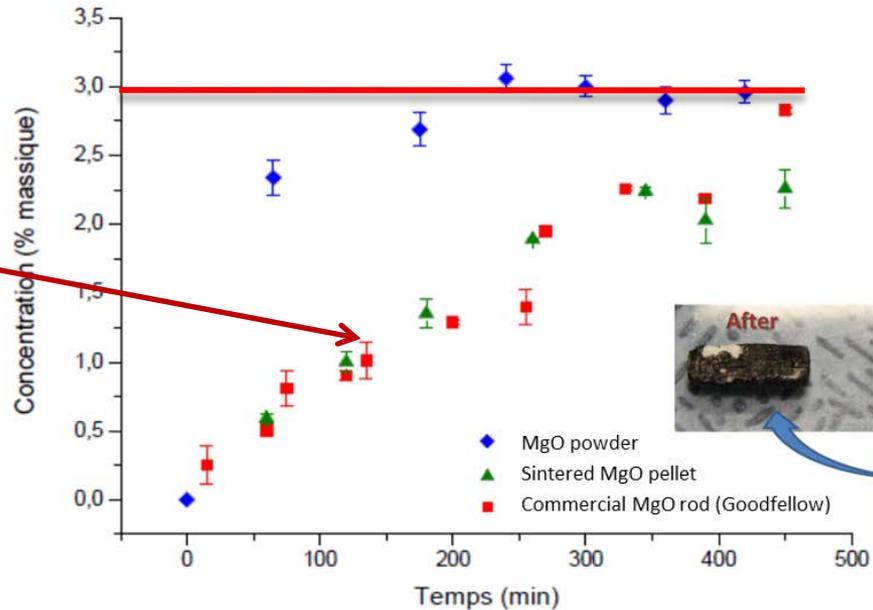
Kinetics: $V = \frac{dC}{dt} = kA(C_s - C)$

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



DEN/DRCP/SCI

Solubility seems to reach a limit: ~3 wt%



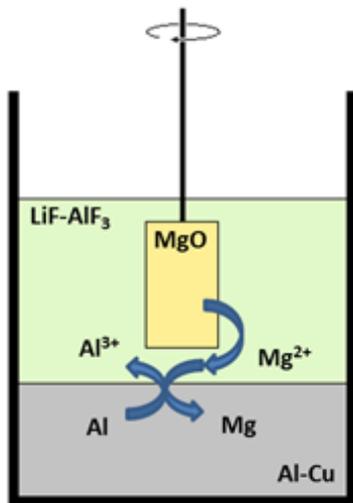
Behaviour of Mg regarding extraction

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

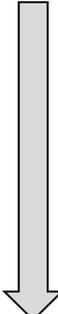
Feasibility of the process: demonstrated on genuine CERCER pellet

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**

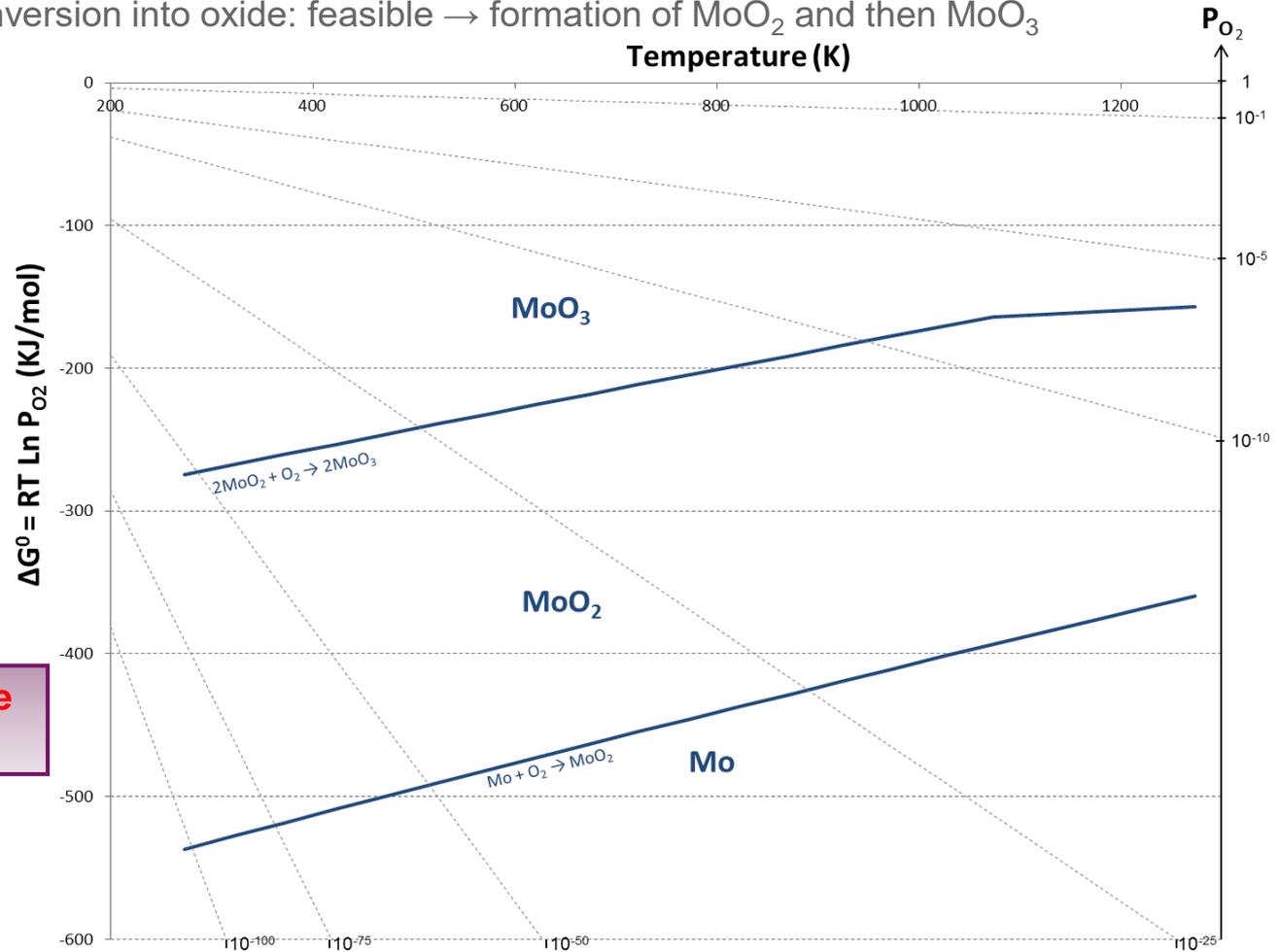
e.g. **150 pellets/kg of salt**
→ Optimisation needed

TREATMENT OF CERMET MATRICES

Mo conversion into oxide form

Thermodynamic approach:

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

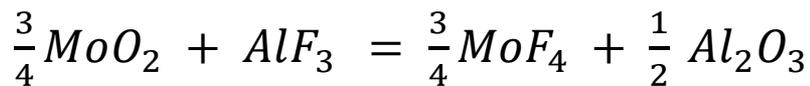
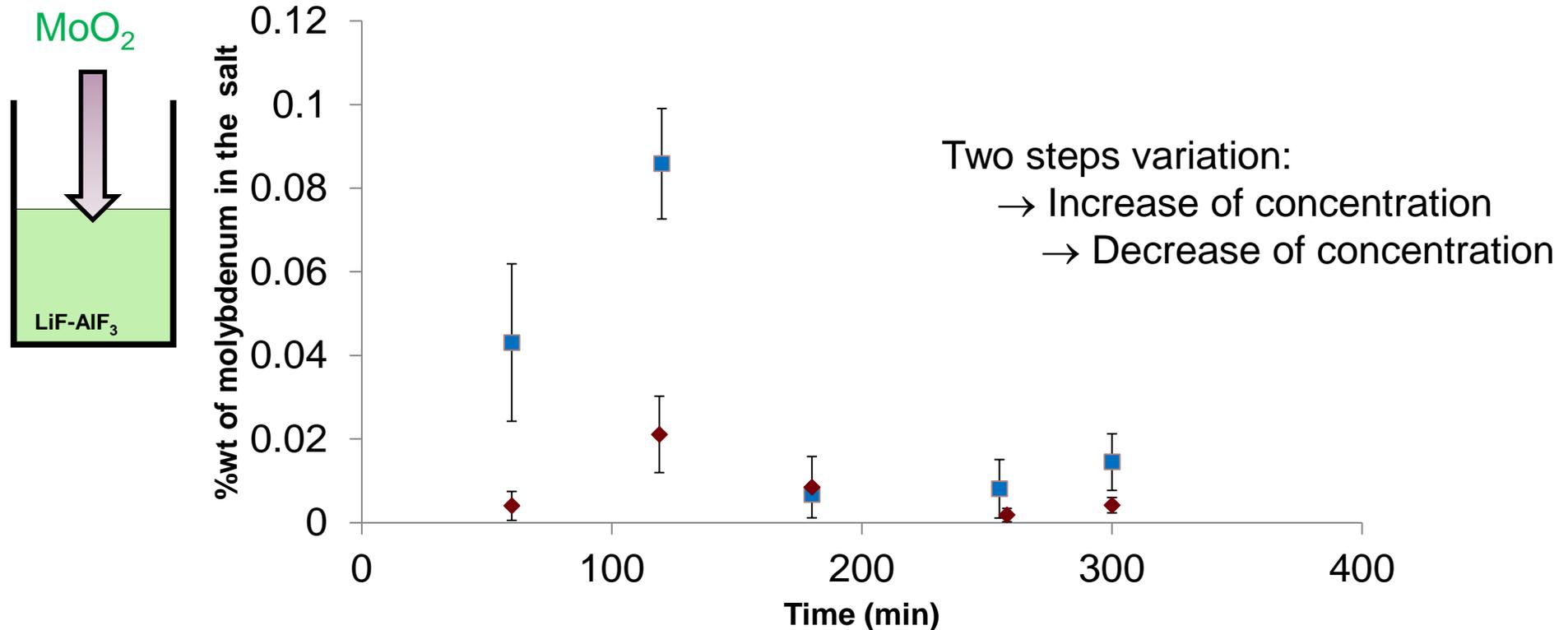


Compatibility with the process: OK

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

SOLUBILITY OF MO OXIDE IN THE SALT

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)

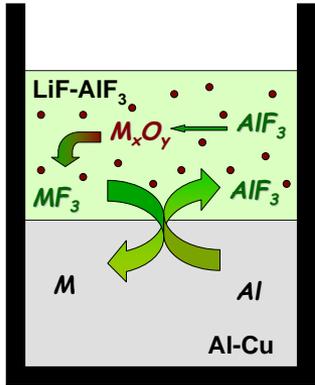


$$\Delta G_{830^\circ C} = -261,541 \text{ kJ/mol}$$

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



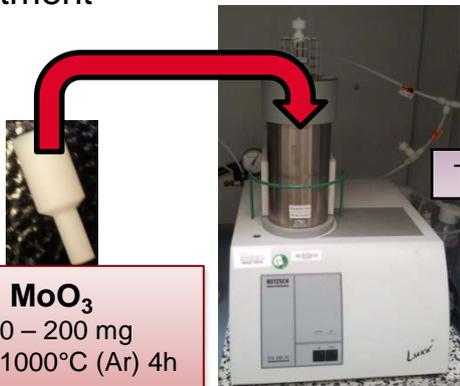
Ref.	Composition	Vol. frac. Mo	Mo/MA Ratio
ITU-5	(Pu _{0.797} Am _{0.198} Np _{0.005}) O _{2-x}	86%	29,3
ITU-6	(Zr _{0.532} Pu _{0.228} Am _{0.124} Np _{0.006}) O _{2-x}	60%	6,1

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

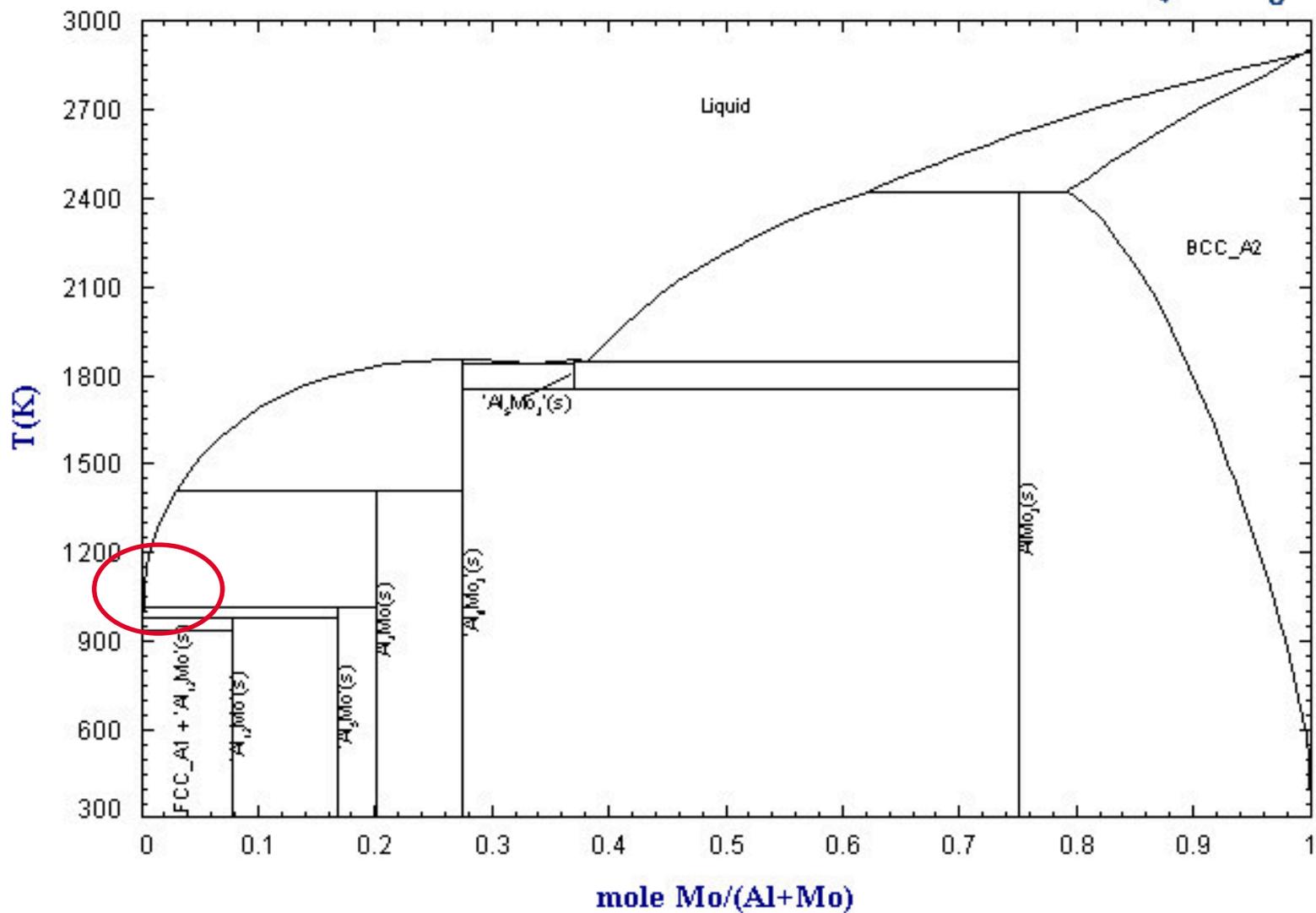
DOS process can be applied with and additional thermal treatment prior extraction step
Mo/volatile FP separation? → Refabrication of fresh matrix

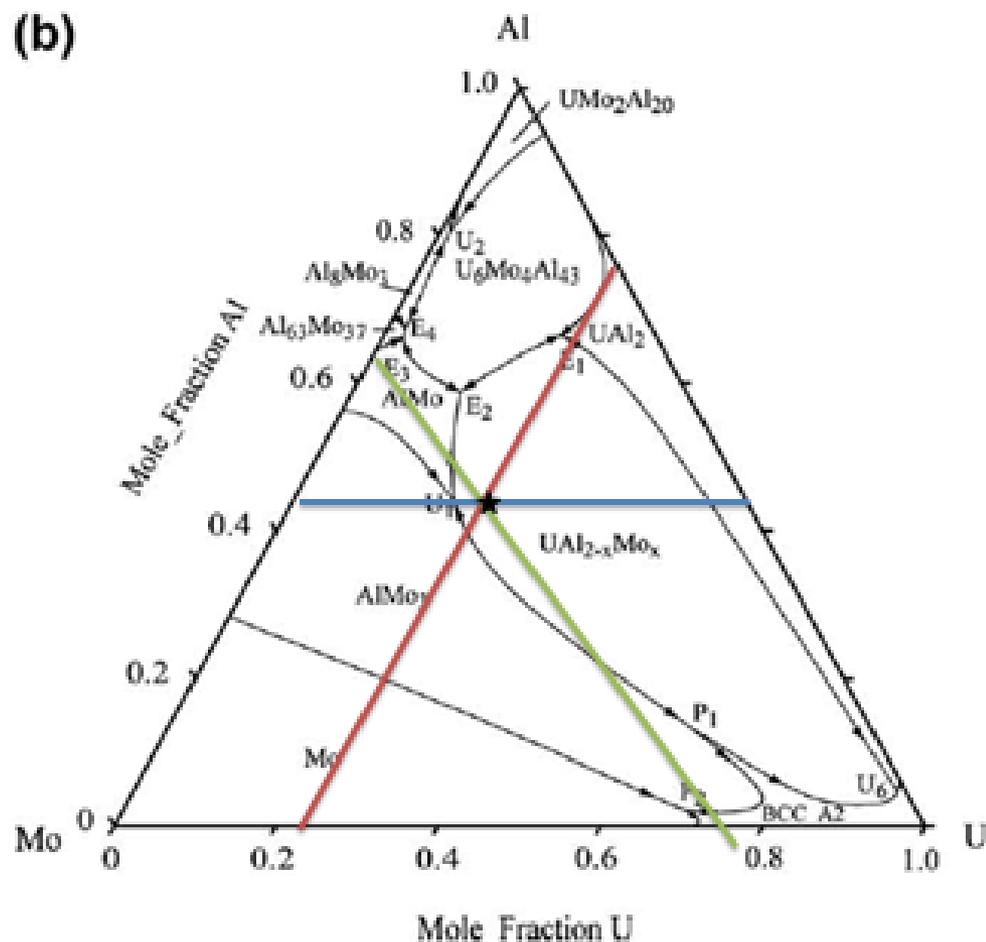
Thank you for your attention

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

Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019

DEN
DRCP
SCMS
LDPS





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

