Actinides separation chemistry in molten salts and its applications at the CEA

E. Mendes, J. Serp, D. Bengio, L. Diaz, D. Quaranta, G. Serve, M. Bertrand

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Nuclear Energy Division

Radiochemistry & Processes Department

Modelling and Separation Chemistry Service

Development of Separation Processes Laboratory

CEA Marcoule, Direction à l'énergie atomique,
Département radiochimie et procédés
Service modélisation et chimie des procédés de séparation

Introduction

"Pyrochemistry" : High temperatures chemical reaction processes

Zeus or Poseidon, Athens National museum.

Igneous metallurgy (→ pyrometallurgy): materials upgrading well-being for everyday life (art, stained glass windows and ...).

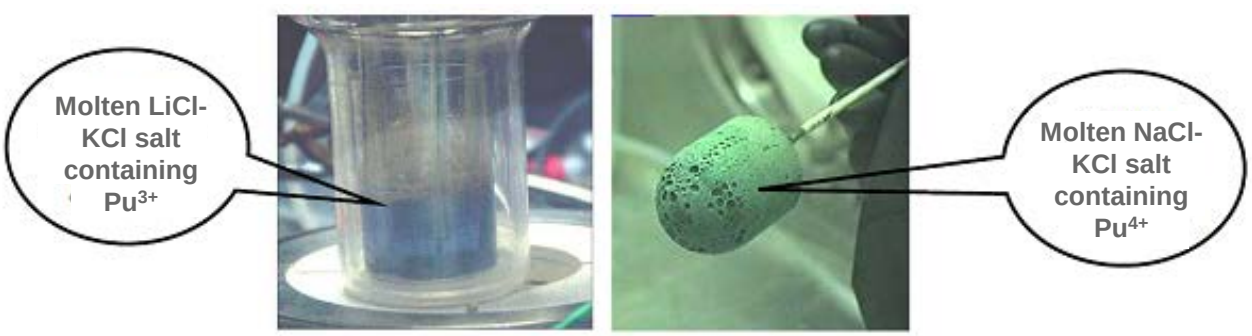
Weapons for defence… or conquest!

Pyrochemistry *- Molten salt chemistry*
- Liquid metals chemistry

Pyrochemical reprocessing

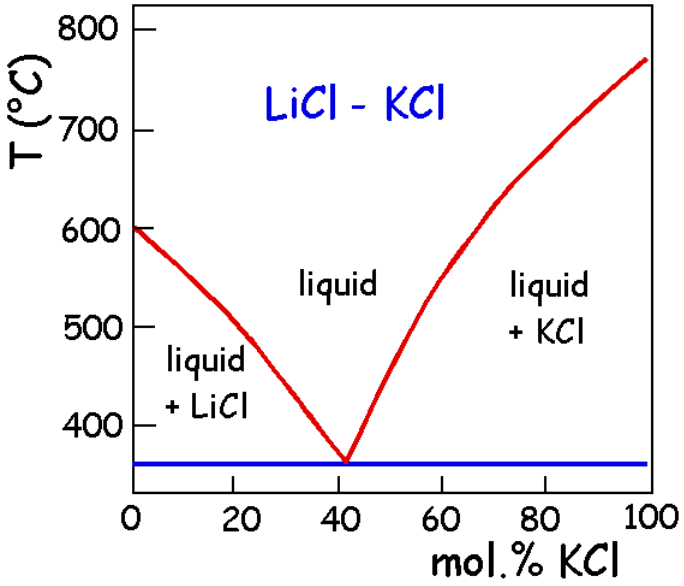
Can be defined as: set of chemical separations and/or conversion processes avoiding aqueous media.

Pyrochemical processing is, generally, associated to the molten salts media, however molten salts are a sub-set of pyrochemistry.



Advantages of molten salts for An/Ln separation

- High conductivity and large electrochemical window: well adapted for treatment of metallic fuels.
- Radiation resistance: treatment of high burn-up fuels, or shorter cooling time of spent fuel.
- Simplified management of criticality: compact installations.
- Processes essential for treatment of MSR fuels



Molten salts: ionic liquids

- Non ideal behaviour liquids: notion of **activity** must be considered.

*Activity: active concentration. Electrostatic interaction between different species decrease their reactivity potential, thus the concentration must be corrected by introducing an **activity coefficient**.*

- Largely used.
- Eutectic mixture
  352°C (41 mol% KCl)
- Working temperature range: 400- 550°C
- Anodic limitation: chlorine
- Cathodic limitation: lithium
- Electrochemical window: 3.6 V

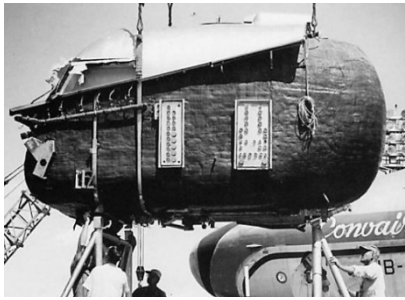
Nuclear applications of pyrochemistry

First uses of pyrochemistry in the nuclear field

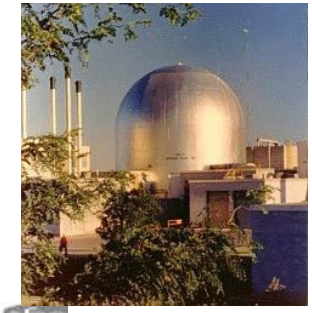
- 1930 – First experiment in molten salt to produce metallic Uranium (Manhattan project)

- 1950 – ARE project (Aircraft Reactor Experiment):

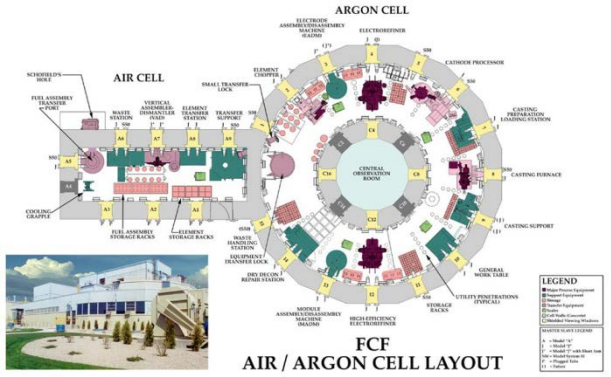
Molten salt reactor NaF-ZrF_4 -UF_4 (53-41-6 mol%) nuclear propulsion



- 1960 – MSRE (Molten Salt Reactor Experiment)- LiF-BeF_2 -ZrF_4 -UF_4 (65-30-5-0.1) (molten salt = fuel and heat exchanger) – pyrometallurgic reprocessing



- 1964 – EBR II (Na reactor, metallic fuel)
  Pyroreprocessing on site: IFR concept



Laboratories dedicated to pyrometallurgy at the CEA Marcoule

Two laboratories dedicated to molten salt chemistry in the Radiochemistry & Processes Department

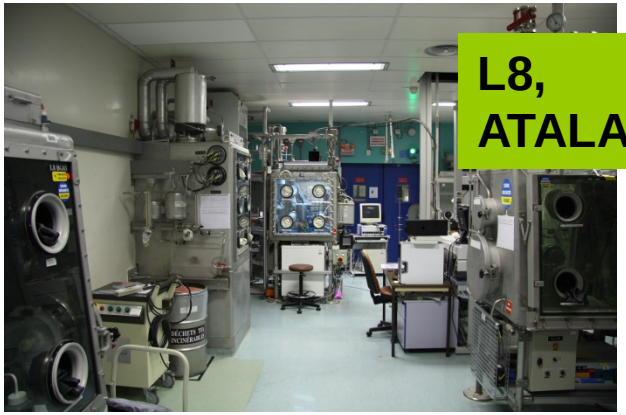
Inactive laboratory

- Two gloveboxes under argon + three fume cupboards
- Electrochemistry studies (CV, OCP…), TGA

Alpha laboratory

- Four gloveboxes (under Air or N_2 inert atmosphere)
- Analysis : fluorescence X, alpha and gamma spectrométry , electrochemical studies, in-situ monitoring: LIBS

ZIP, CHIMENE



L8, ATALANTE

R&D:

Fundamental and applied studies on pyrochemical separation processes

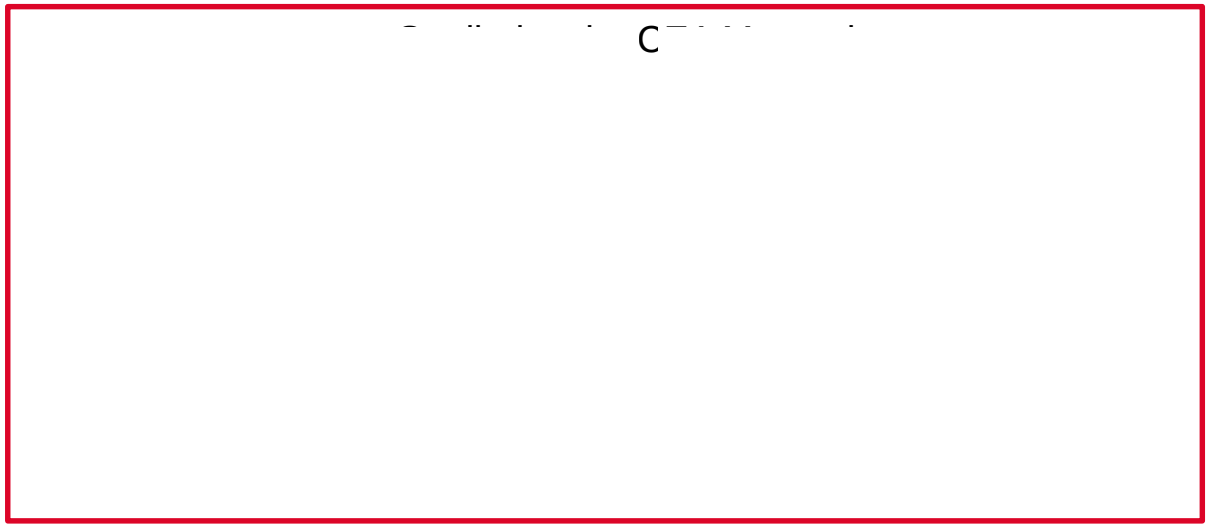
Separation processes in molten salts

Three main separation processes:

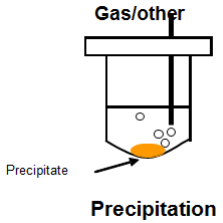
Precipitation – role of oxoacidity

Electrochemical processes – electrorefining, electrolywining

Reductive **liquid-liquid extraction**



➢ AIDA-Mox process



Conversion of military Pu into non military PuO_2

- Starting alloy: Pu, Ga (<5 wt%) and ^{241}Am (<1 wt%) (coming from ^{241}Pu activity)
- NaCl-KCl salt at 700°C

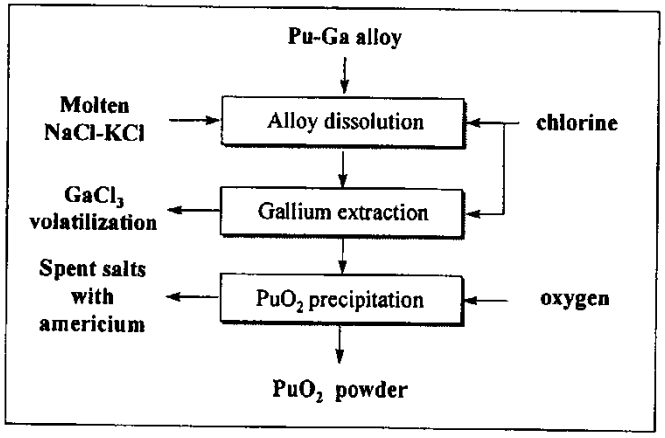
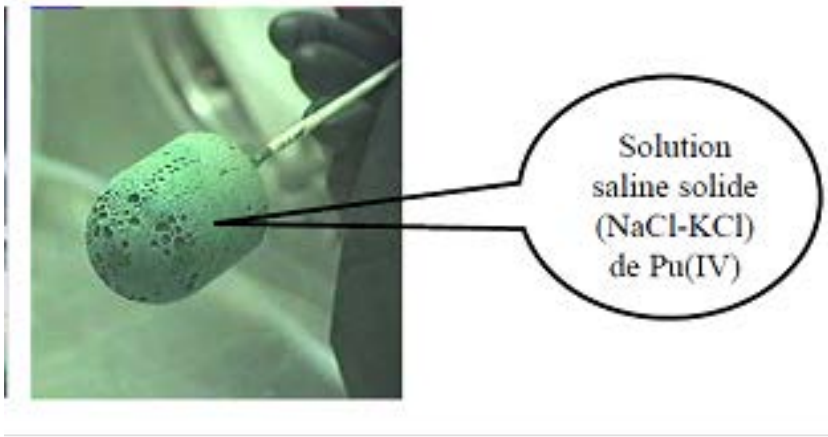


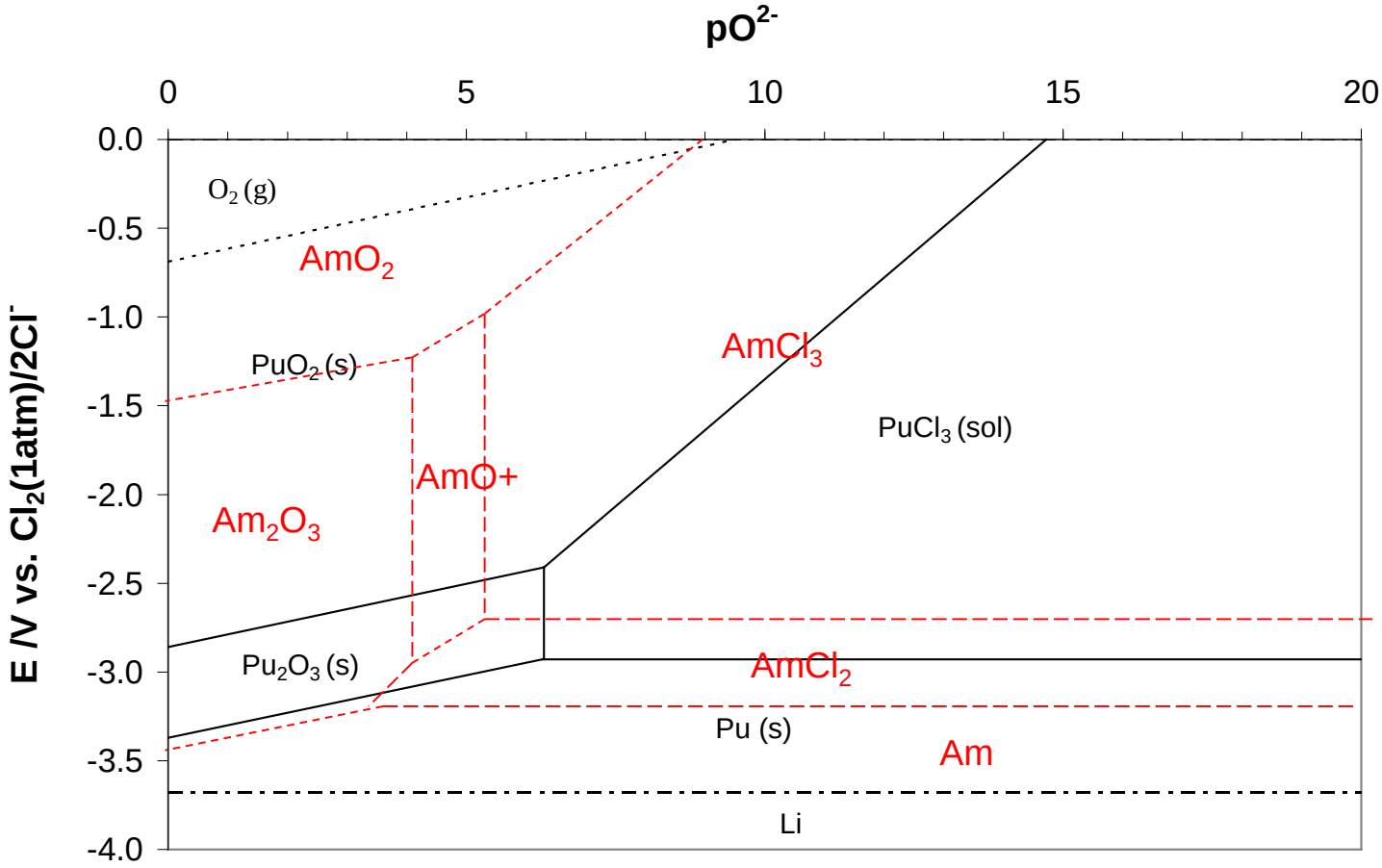
Figure 1 : Pyrochemical conversion of Pu-Ga alloy into PuO_2



A.G. Osipenko et al, Molten Salt Forum, vol.5-6, 553 (1997)

- Alloy chlorination: Pu(IV), Am(III), $GaCl_3$ volatile
- Selective precipitation of PuO_2 by bubbling $O_{2(g)}$, Am(III) remains soluble

Separation processes in molten salts: Precipitation



E-pO^{2-} Diagram of Pu in LiCl-KCl at 450°C, [Pu(III)]=0.01mol/kg, et à 0.001mol/kg pour l'Am

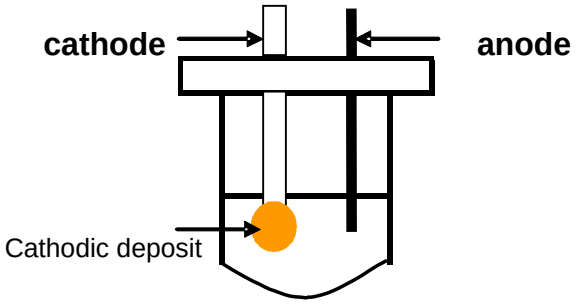
Pu: C. Caravaca et al., J. Nucl. Mat., 377, 340 (2008), Am: D. Lambertin et al., Plasma and ions., 3, 65-72 (2000)

Three main separation processes:

Precipitation – role of oxoacidity

Electrochemical processes – electrorefining, electrolywining

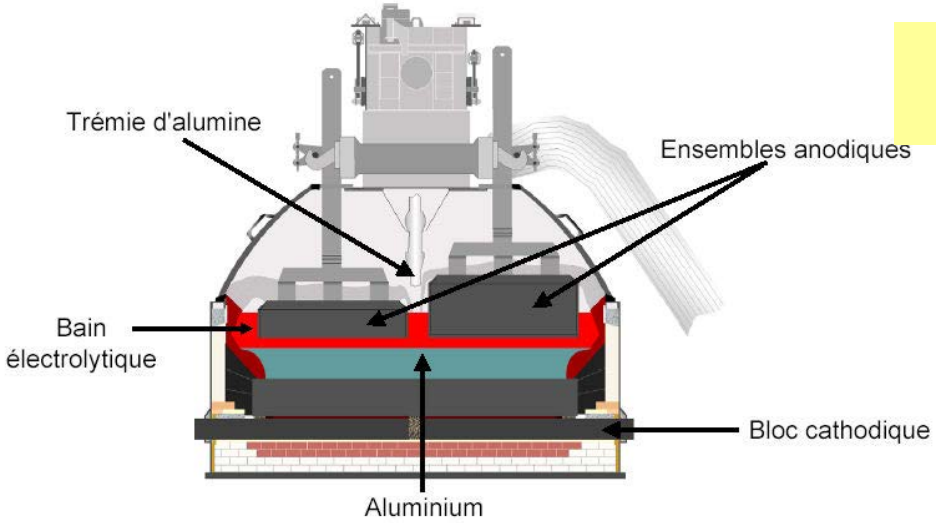
Reductive **liquid-liquid extraction**



Electrodeposition

Industrial uses of molten salts

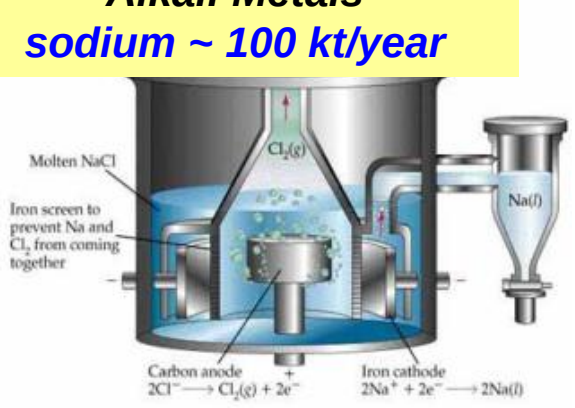
Aluminium production
~24 Mt/year



Alumina Electrolysis in molten cryolite (Na_3AlF_6) at 950°C

Pool AP30 (Alcan) : 14m length, ~300kA, Far. Yeald = 96%, 2,3t/d

Alkali Metals
sodium ~ 100 kt/year



Electrolysis of alcali chlorides.
Ex: production of sodium at 600°C
$(2NaCl = 2Na + Cl_2)$

Pool Down : charge 8t, 45 kA, Far. yeld = 90%, 0,8t/j (Na), 1,3t/j (Cl_2)

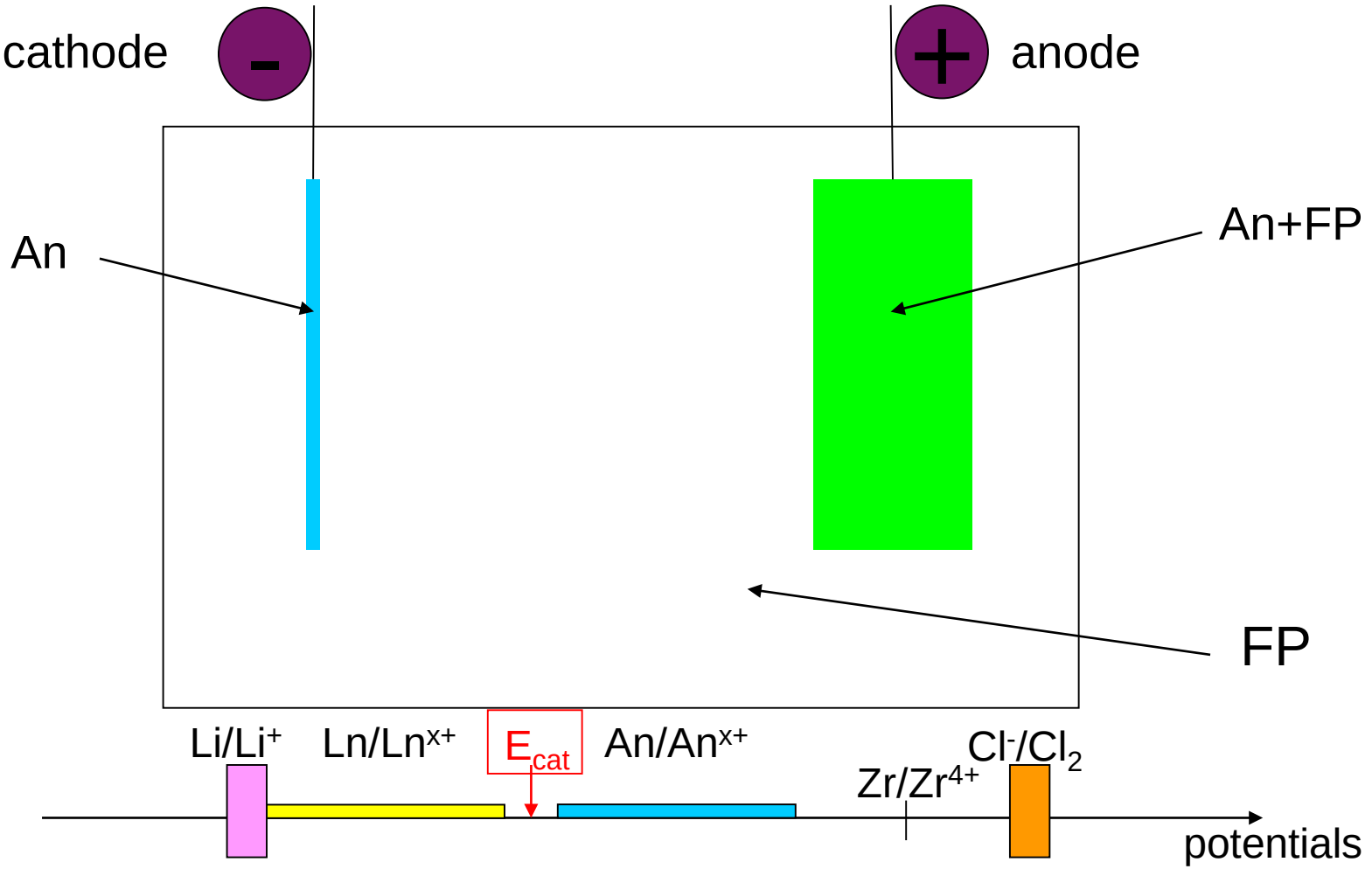
F_2 production
~ 1,5 kt/year

Electrolysis of 2HF,KF at ~85-105°C
$(2HF_{liq} = H_2 + F_2)$

Monel pool: porous carbone anode, steel cathode, 6 kA, Far. yeld = 90-95%, 4kg/h (F_2)

Other metals *(Mg, Ca, Li, Zr…)*

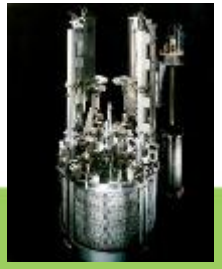
Nuclear applications : Electrorefining process



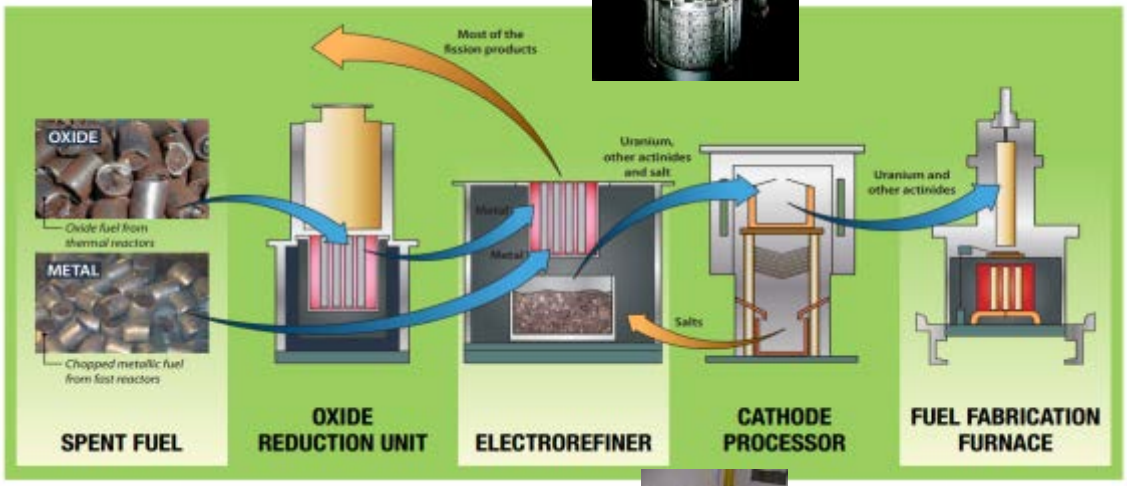
- Purification process: anodic dissolution of impure metal and cathodic deposition of purified metal

Nuclear applications: Reprocessing of metallic fuels

EBR-II



U deposit



Purified metal

Source: ANL website
http://www.ne.anl.gov

- **Most adapted process for metallic fuel recycling (US, Japan, South Korea, Russia, India)**
- **Analogue process for nitride fuels (Japan, Russia)**

Table I. Inventory of Spent Fuel Designated for Pyroprocessing at INL.

Fuel Type	EBR-II Driver (MTHM)	FFTF Driver (MTHM)	EBR-II Blanket (MTHM)	Total (MTHM)
Initial Fuel in June 1996	3.1	0.25	22.4	25.75
Fuel Treated as of January 2012	0.8	0.22	3.6	4.62
Remaining Untreated Fuel	2.3	0.03	18.8	21.13

Electrochemical processes

- **Nernst equation, equilibrium**

$$Ox + ne^- \rightarrow Red$$

$$E_{eq}(An^{n+}/An) = E°(An^{n+}/An) + \frac{2.3RT}{nF}\log\left(\frac{a(An^{n+})}{a(An)}\right)$$

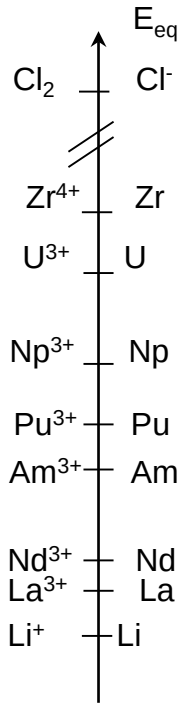
$$E_{eq}(An^{n+}/An) = E°(An^{n+}/An) + \frac{2.3RT}{nF}\log\left(\frac{\gamma_{An^{n+}}}{\gamma_{An}}\right) + \frac{2.3RT}{nF}\log\left(\frac{x_{An^{n+}}}{x_{An}}\right)$$

– Use of inert solid electrode *(deposition of pure An, a(An)=1)*

$$E_{eq}(An^{n+}/An) = E°(An^{n+}/An) + \frac{2.3RT}{nF}\log(\gamma_{An^{n+}}) + \frac{2.3RT}{nF}\log(x_{An^{n+}})$$

$$= E'°(An^{n+}/An) + \frac{2.3RT}{nF}\log(x_{An^{n+}})$$

⇒ E'° apparent standard potential
Determined by electrochemical measurments



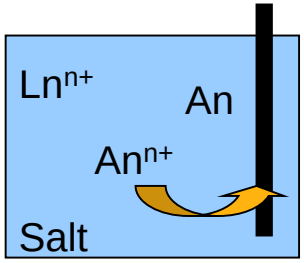
An/Ln separation depends on ΔE

↳ **Electrodeposition of metal: more cathodic potential compared to E_{eq} (= more negative than E_{eq})**

Influence of thermodynamic on electroseparation

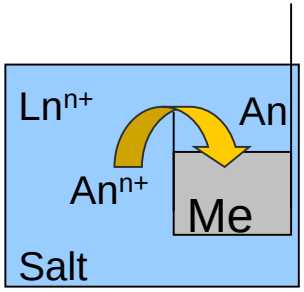
An/Ln Electroseparation: $\Delta E_{An/Ln} = E_{An^{n+}/An} - E_{In^{n+}/Ln}$

On inert electrode



↳ Pure An deposit

On non-inert electrode



↳Deposition of solubilised in metal or intermetallic formation

$$\Delta E_{An/Ln} = \Delta E^{\circ}_{An/Ln} + \frac{2{,}3RT}{nF}\log\left(\frac{x_{An^{n+}}}{x_{Ln^{n+}}}\cdot\frac{x_{Ln(Me)}}{x_{An(Me)}}\right) + \frac{2{,}3RT}{nF}\log\left(\frac{\gamma_{An^{n+}}}{\gamma_{Ln^{n+}}}\right) + \frac{2{,}3RT}{nF}\log\left(\frac{\gamma_{Ln(Me)}}{\gamma_{An(Me)}}\right)$$

Thermo data (pure comp.)

Evolution of concentrations

Activity coef. in salt

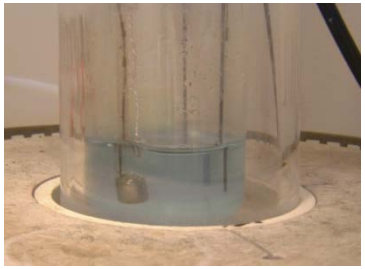
Ratio ~1

Activity Coef. In Metallic solvent

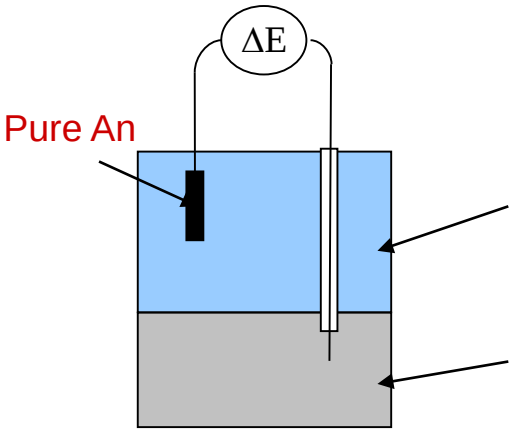
- γ ratio in metal may be very important

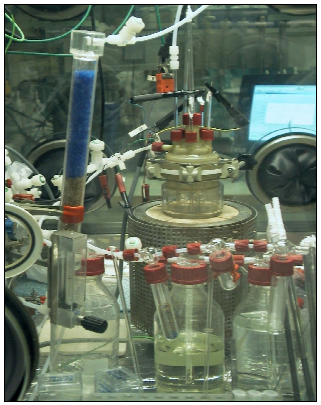
Activity coefficient in metal

- **Determination of activity coefficient in metal**
  - Galvanic Cell: An | molten salt, $AnCl_3$ | $An_{(Me)}$



LiCl-KCl-$PuCl_3$, Bi electrode at 500°C





Electromotive force (e.m.f.) :

$$f.e.m = E_{An} - E_{An(Me)} = \frac{2.303RT}{nF}\log(\gamma_{An(Me)}) + \frac{2.303RT}{nF}\log(x_{An(Me)})$$

↳ **e.m.f. =f(log$x_{An(Me)}$)**

→ log$\gamma_{An(Me)}$

→ Number of exchanged electrons

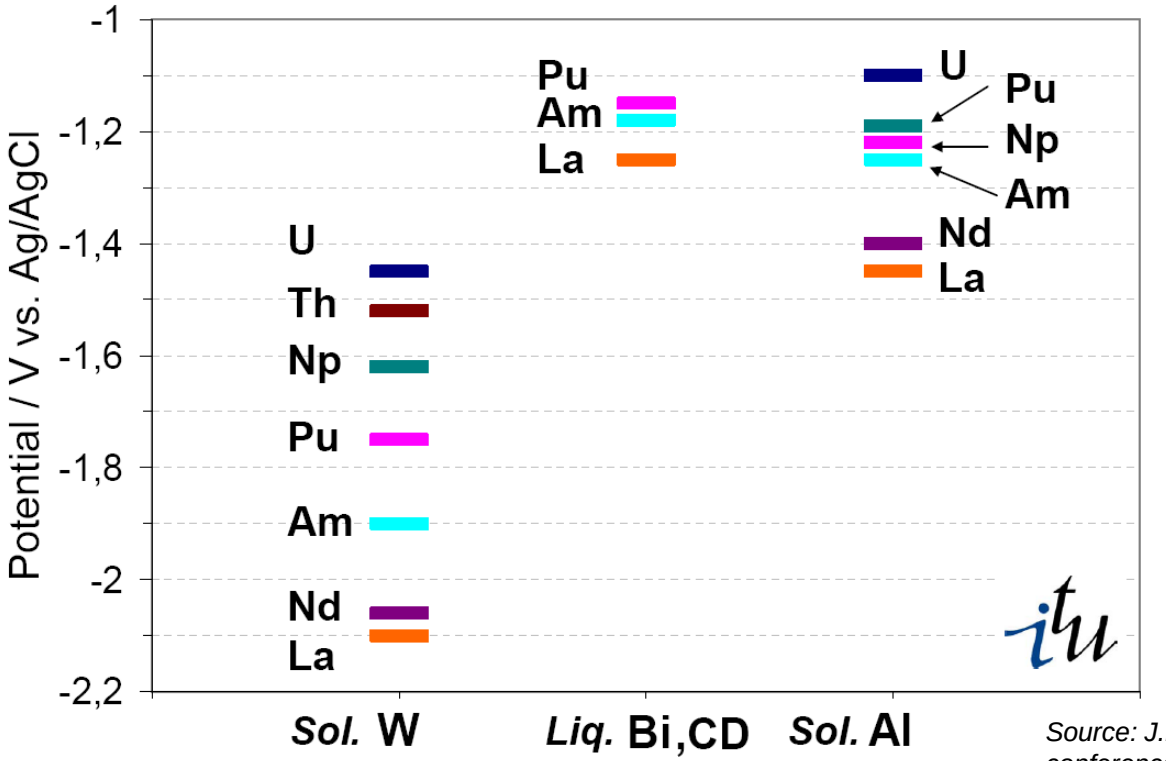
↳ **Measurement does not depend on electrolyte**

Activity coefficient in metal

Inert cathode / reactive cathode

- Inert
- Liquid cathode: solubilisation of An in metal
- Solid reactive cathode: intermetallic formation

$\gamma_{An}=1$
$\gamma_{An} \neq 1$ (Cd, Bi)
$a_{An} \neq 1$



Source: J.P. Glatz, Atalante conference 2008

Example : $\log\gamma(Pu_{(Bi)})=-8,7$ at 550°C

Inert cathode: high An/Ln separation, but deposit may be difficult to stabilise on cathode

Liquid cathode: lower separation but stabilisation of species in liquid metal.

Applications at the CEA: Salt cleaning

Exhaustive electrolysis or electrowinning (FP7 - SACSESS)

Key step of the process: salt coming from E. ref step still contain An

→ ***Necessity to recover these An***

- **First electrolysis realised on simulated electrorefining salt baths**

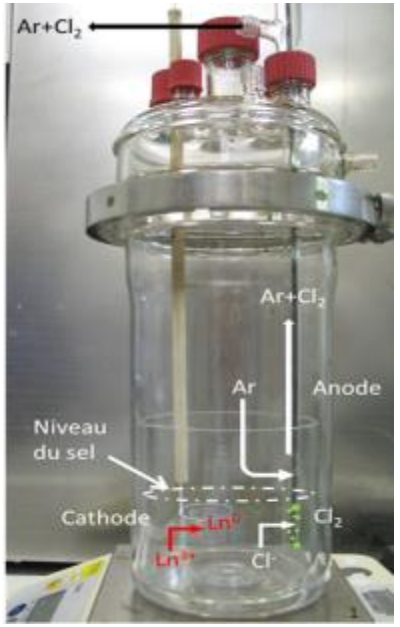
  Anode → production of $Cl_{2(g)}$

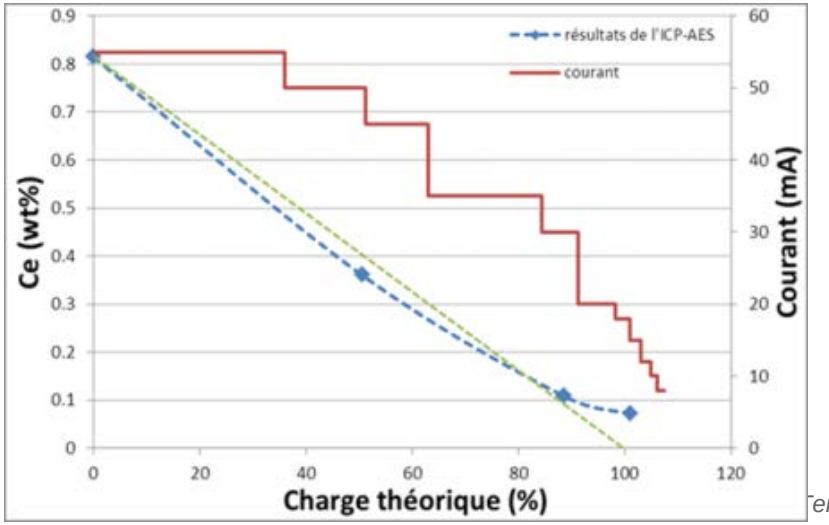
  (first tests on lanthanides at the inactive laboratory)

- **Understanding of the electrolysis behaviour:**
  - determination of faradic yelds, characterisation of the obtained deposit at the cathode,
  - optimisation of Cl_2 producing anode,
  - influence of the cathode material (Al, Mo)

- **Active tests on salts containing actinides (Pu) and lanthanides (Ce)**

  → ***An/Ln Separation***



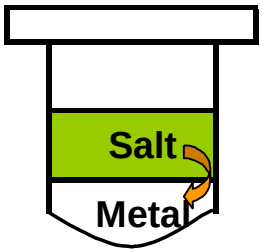


Three main separation processes:

Precipitation – role of oxoacidity

Electrochemical processes – electrorefining, electrolywining

Reductive **liquid-liquid extraction**



Liquid-liquid extraction

Influence of thermodynamic on L/L extraction

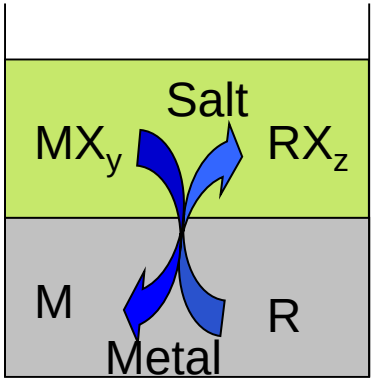
Principe

$$MX_{y\,(salt)} + y/z\ R_{\,(metal)} = M_{\,(metal)} + y/z\ RX_{z\,(salt)}$$

R: reductive metal dissolved in a Metallic solvent

$$K = \frac{a_M a_{RX_z}^{y/z}}{a_{MX_y} a_R^{y/z}}$$

$$\begin{cases} a_{Salt} = X_{Salt} * \gamma_{Salt} \\ a_{MS} = X_{MS} * \gamma_{MS} \end{cases}$$



- Important parameters:
  - Distribution coefficient $D_M = x_{M(metal)} / x_{MXy(salt)}$
  - Separation Factor $SF_{M/M'} = D_M/D_{M'}$

In general, **molar fractions (thermo)** or wt**% (exp.)**

- Example : $PuF_3 + 3Li_{(Bi)} = Pu_{(Bi)} + 3LiF$

  $D_{Pu} = x_{Pu(Bi)} / x_{PuF3}$

  $S_{Pu/Nd} = D_{Pu}/D_{Nd}$

Influence of thermodynamic on L/L extraction

Example

- Pu/Nd separation by Al, in LiF-AlF_3

$PuF_3 + Al = Pu_{(Al)} + AlF_3$

$$K_{Pu} = \frac{a_{Pu(Al)} a_{AlF_3}}{a_{PuF_3} a_{Al}} = \frac{\gamma_{Pu(Al)} . x_{Pu(Al)} . \gamma_{AlF_3} . x_{AlF_3}}{\gamma_{PuF_3} . x_{PuF_3}} \qquad D_{Pu} = \frac{x_{Pu(Al)}}{x_{PuF_3}}$$

- Nd: $NdF_3 + Al = Nd_{(Al)} + AlF_3$

$$K_{Pu} = \frac{a_{Nd(Al)} a_{AlF_3}}{a_{NdF_3} a_{Al}} = \frac{\gamma_{Nd(Al)} . x_{Nd(Al)} . \gamma_{AlF_3} . x_{AlF_3}}{\gamma_{NdF_3} . x_{NdF_3}} \qquad D_{Nd} = \frac{x_{Nd(Al)}}{x_{NdF_3}}$$

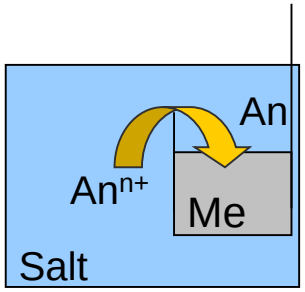
- Separation factor can be expressed from previous equations:

$$SF_{Pu/Nd} = \frac{D_{Pu}}{D_{Nd}}$$

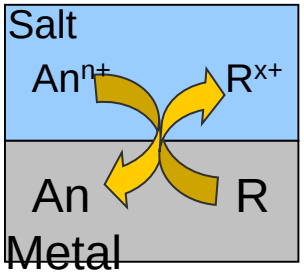
$$\log SF_{Pu/Nd} = \log\left(\frac{K_{Pu}}{K_{Nd}}\right) + \log\left(\frac{\gamma_{Pu^{3+}}}{\gamma_{Nd^{3+}}}\right) + \log\left(\frac{\gamma_{Nd(Al)}}{\gamma_{Pu(Al)}}\right)$$

Influence of thermodynamic on L/L extraction

Electrolysis



Liquid / liquid extraction



Electrolysis

$$\Delta E_{An/Ln} = \Delta E^{\circ}_{An/Ln} + \frac{2{,}3RT}{nF}\log\left(\frac{x_{An^{n+}}}{x_{Ln^{n+}}}\cdot\frac{x_{Ln(Me)}}{x_{An(Me)}}\right) + \frac{2{,}3RT}{nF}\log\left(\frac{\gamma_{An^{n+}}}{\gamma_{Ln^{n+}}}\right) + \frac{2{,}3RT}{nF}\log\left(\frac{\gamma_{Ln(Me)}}{\gamma_{An(Me)}}\right)$$

Extraction

$$\log SF_{An/Ln} = \log\left(\frac{K_{An}}{K_{Ln}}\right) + \log\left(\frac{\gamma_{An^{n+}}}{\gamma_{Ln^{n+}}}\right) + \log\left(\frac{\gamma_{Ln(Me)}}{\gamma_{An(Me)}}\right)$$

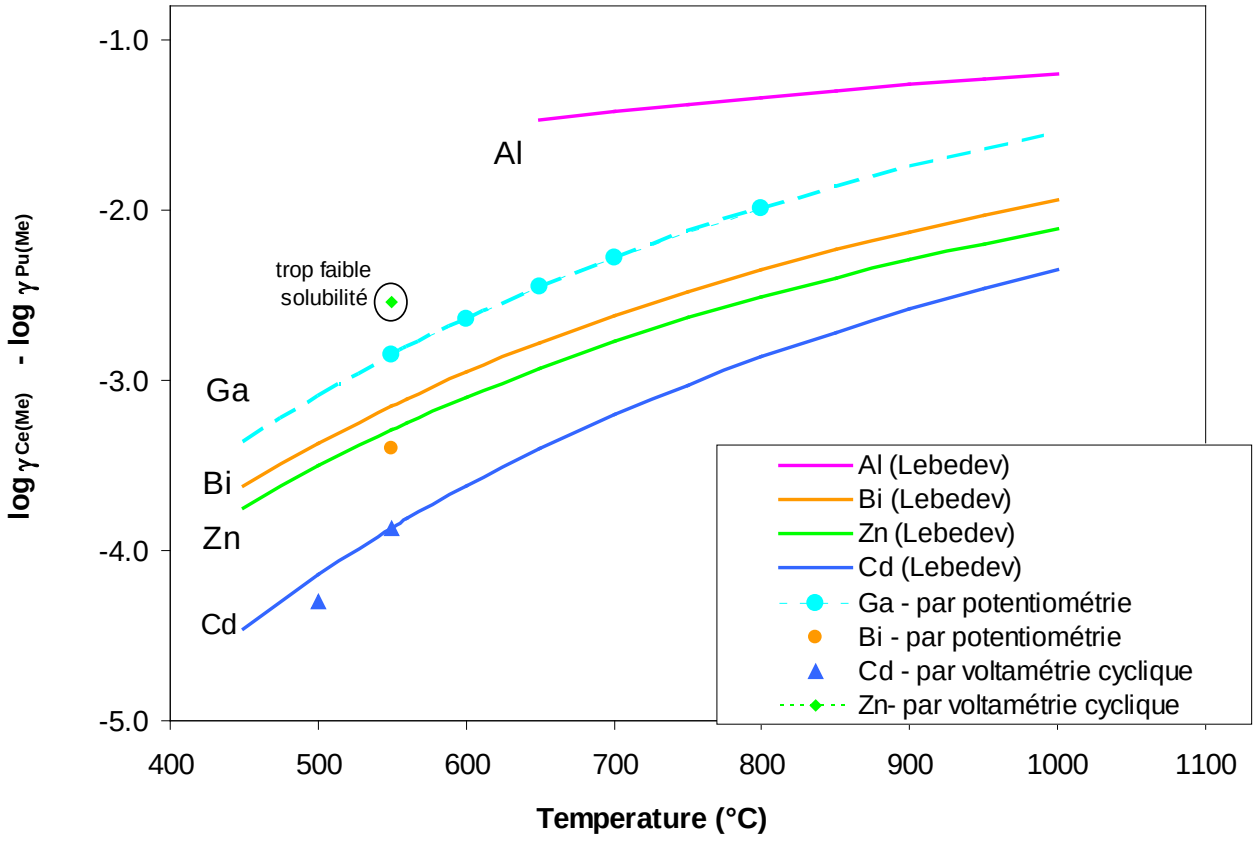
Thermo. data (pure comp.)

Activity coefficients Salt

Activity coefficients Metal

Influence of thermodynamic on L/L extraction

- **Pu/Ce Separation– activity coefficient dependency**



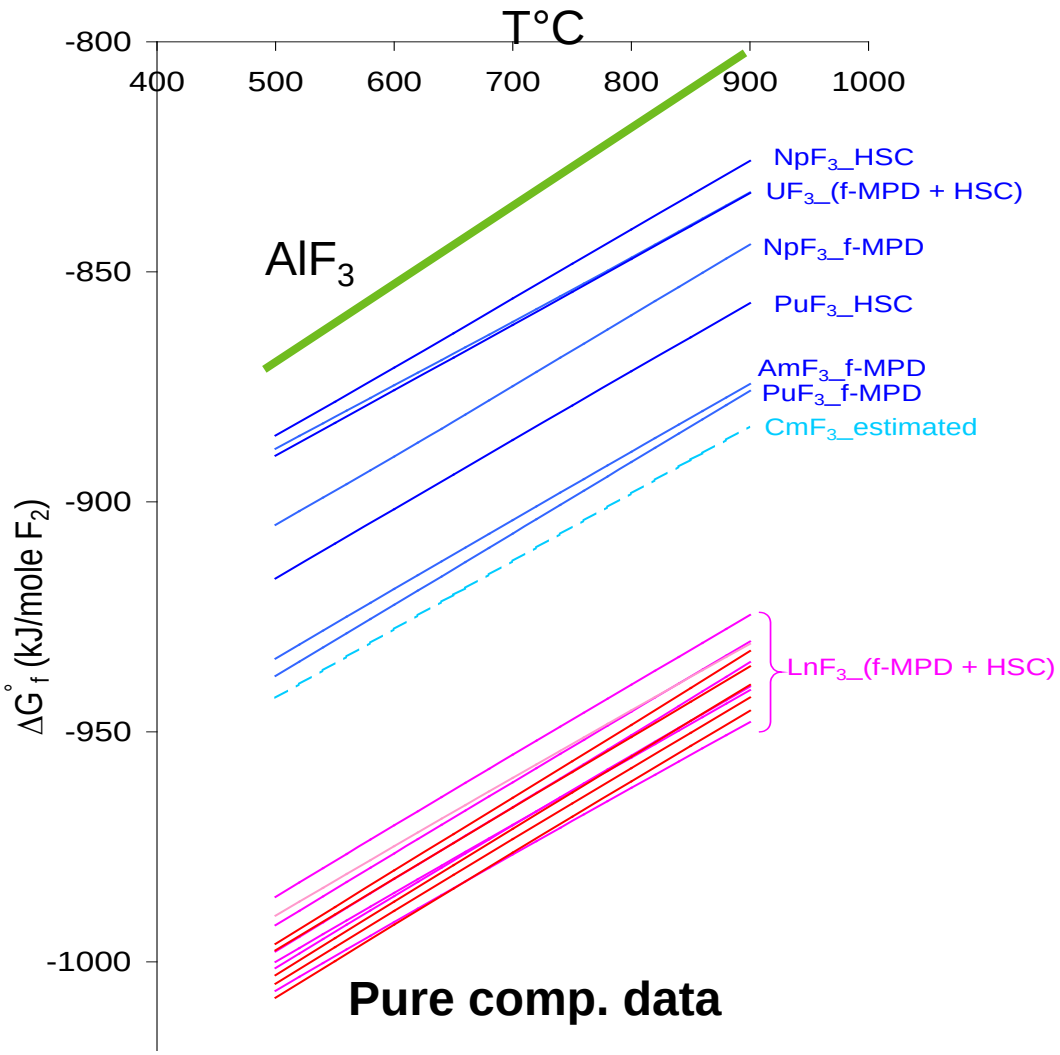
Comparison of activity coefficients in different metallic solvents

↳ Al best solvent

(A. Laplace et al., Proceeding 9th IEMPT, Nimes, September 2006)

Influence of thermodynamic on L/L extraction

Importance of activity coefficients!

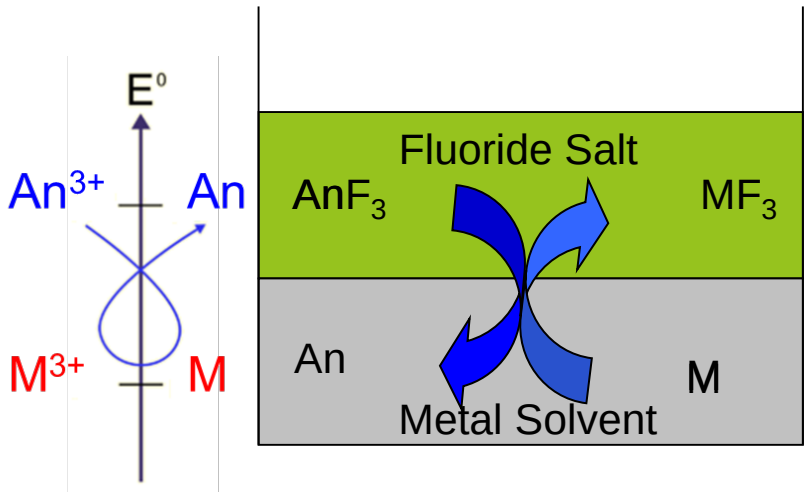


If we don't take into account activity coefficients, Al should not reduce An^{n+}

Liquid/liquid extraction process developped at the CEA

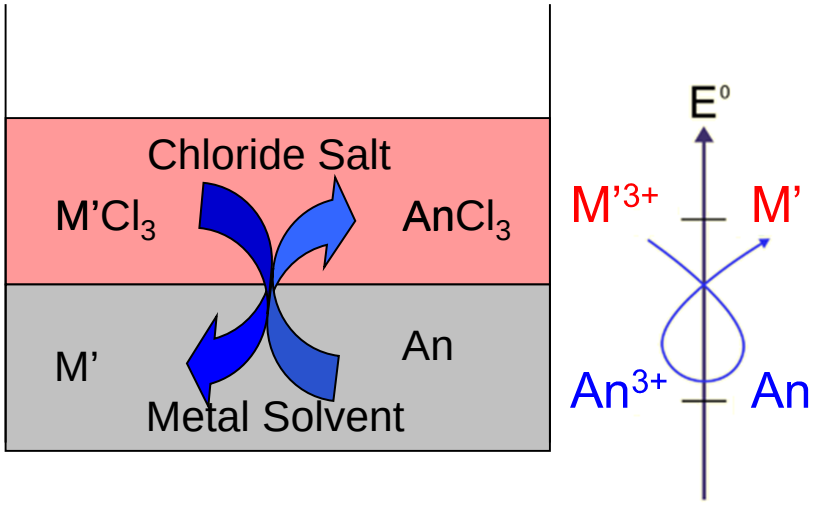
Reductive Extraction

$An^{3+}_{(salt)} + M_{(metal)} \Leftrightarrow An_{(metal)} + M^{3+}_{(salt)}$



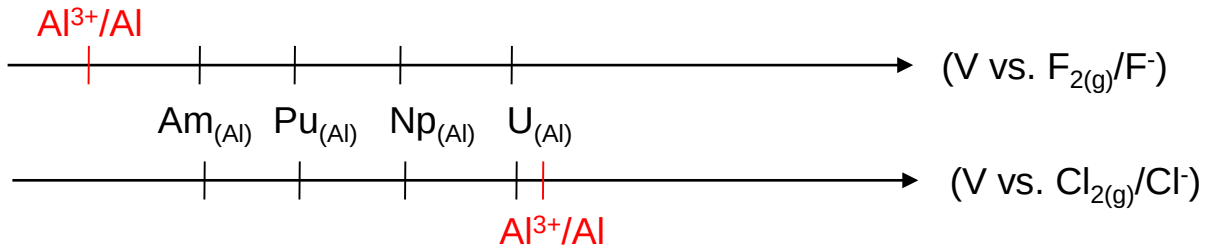
Oxidative Back-extraction

$An_{(metal)} + M'^{3+}_{(salt)} \Leftrightarrow An^{3+}_{(salt)} + M'_{(metal)}$



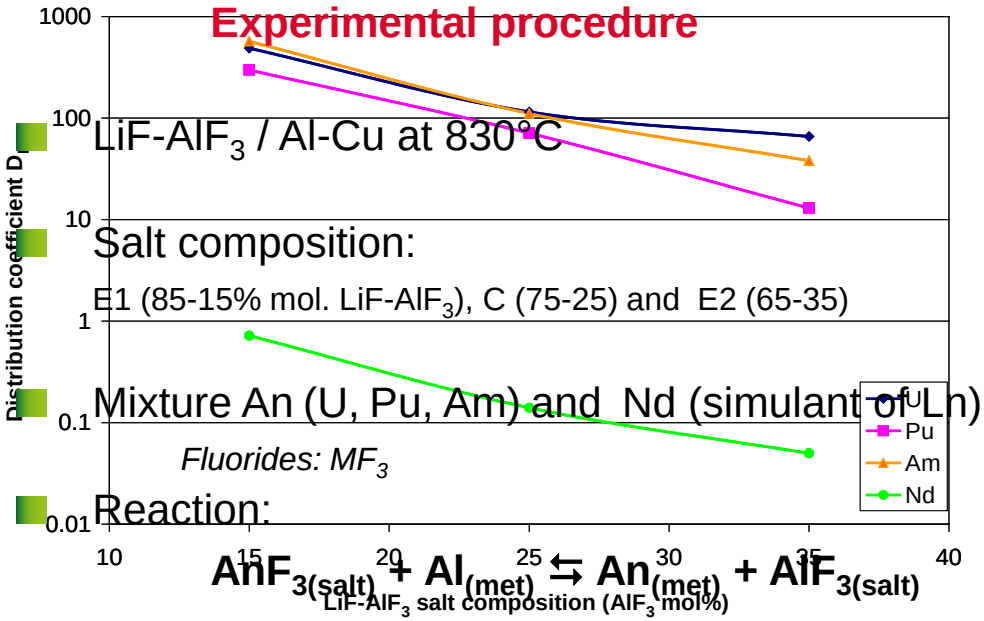
In fluorides

In chlorides



Experiemental approach of the reductive extraction

Experimental procedure

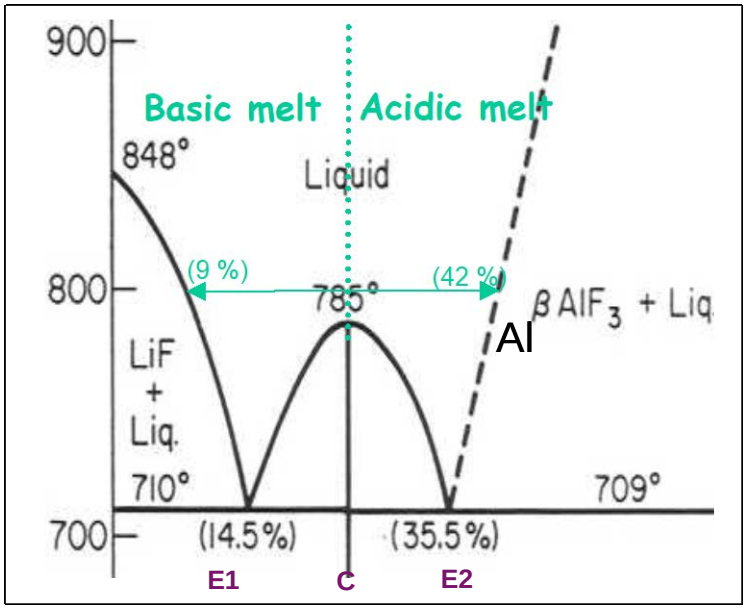


- $LiF\text{-}AlF_3$ / Al-Cu at 830°C
- Salt composition:

  E1 (85-15% mol. $LiF\text{-}AlF_3$), C (75-25) and E2 (65-35)
- Mixture An (U, Pu, Am) and Nd (simulant of Ln)

  Fluorides: MF_3
- Reaction:

$$AnF_{3(salt)} + Al_{(met)} \leftrightarrows An_{(met)} + AlF_{3(salt)}$$

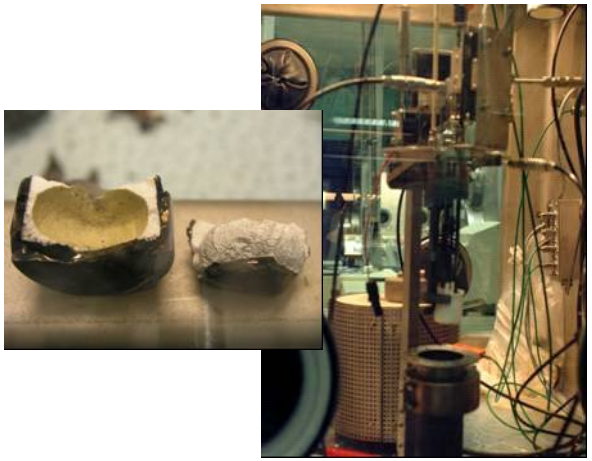


$LiF\text{-}AlF_3$ system, J.L Holm and B.J Holm, *Thermochim. Acta*, 6 [4] 375 (1973)

- **Distribution coefficient:** $D = x_{An_{(Al)}} / x_{AnF_{3(sel)}}$
- D variation as function of salt composition

$$D_{An} = K \cdot \frac{\gamma_{AnF3}}{\gamma_{An(Al)}} \cdot \frac{1}{a_{AlF3}}$$

- Excellents separation factors An/Ln >100

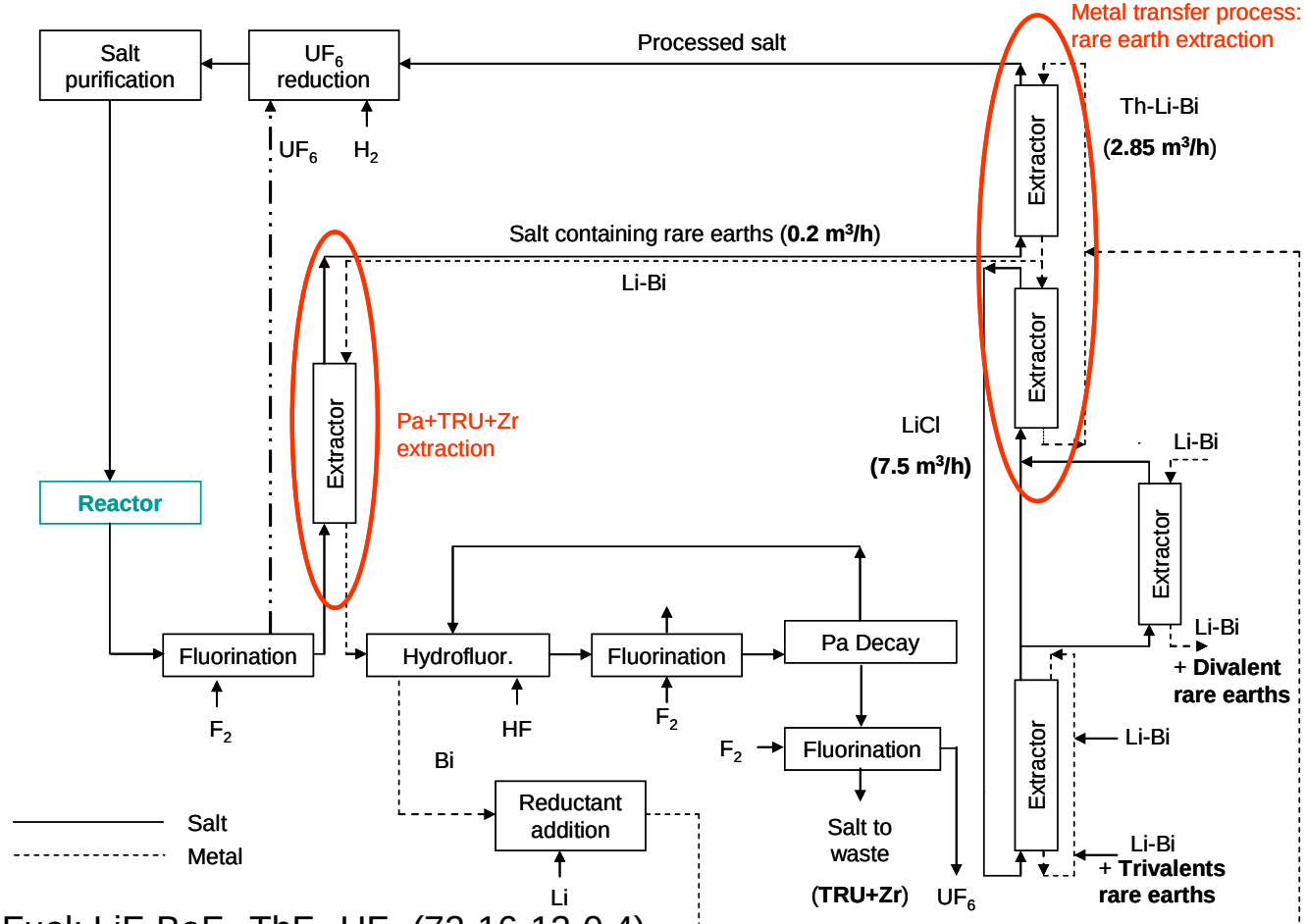


Core of process validation

Application of pyrochemical processes:

MSBR salt treatment process

Theoretical studies → online L/L extraction to reprocess part of the fuel



Fuel: LiF-BeF_2-ThF_4-UF_4 (72-16-12-0.4)

More complicated process:

needs first steps to remove An from salt + counter current L/L extraction to remove FP

Avoiding presence of Bi in the reactor

Reprocessing of 4m^3/day

MSFR: fast reactor LiF-ThF_4 fuel

Reprocessing of 40L/day

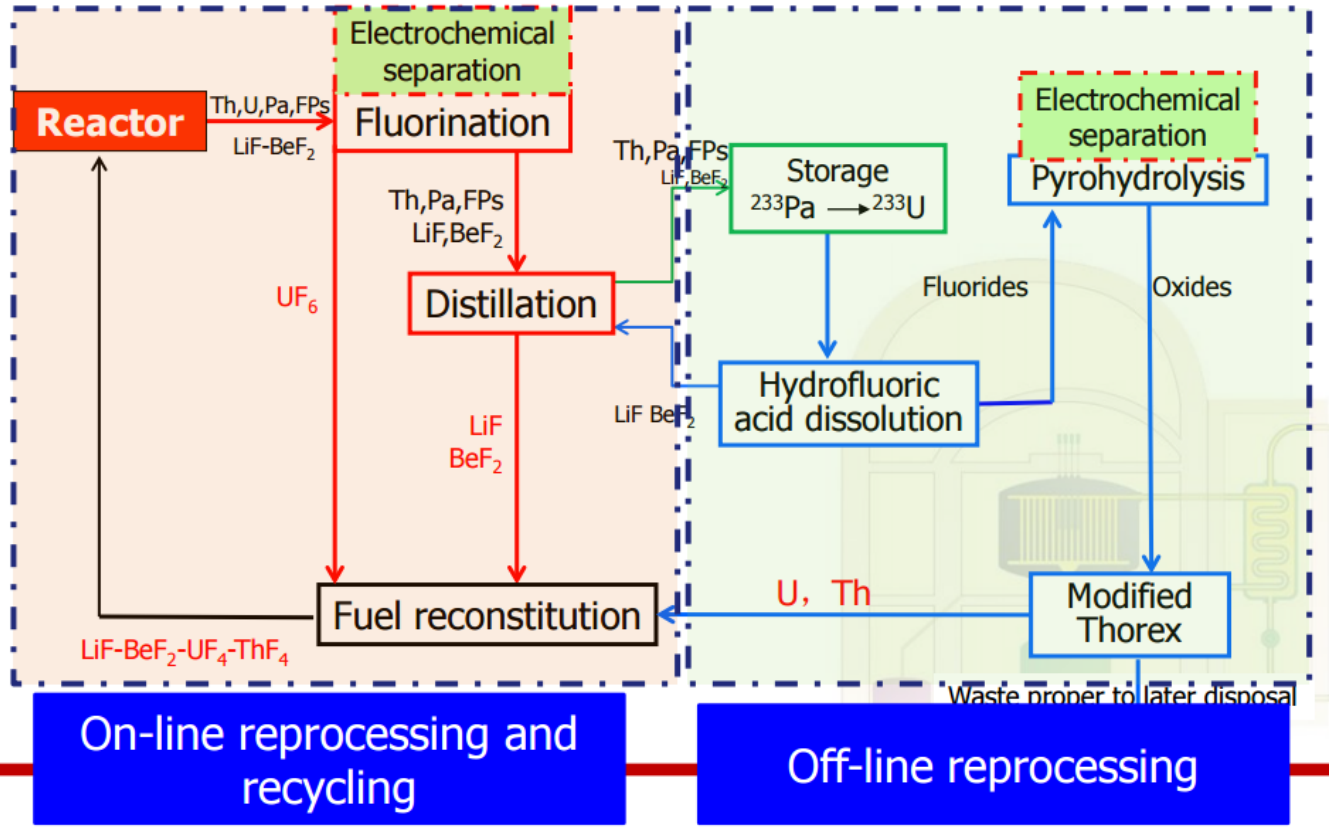
Application of pyrochemical processes:

Other option: TMSR salt treatment process

Chinese project: combination Pyro/Hydro processing

SINAP | TMSR 钍基熔盐核能系统

Flow sheet of TMSR Fuel Processing



Source: Q. Li & al, IPRC 2014

Conclusion

Pyrometallurgic processes are complementary with hydrométallurgic processes regarding several aspects → *Treatment of particular fuels combustibles (metallic, MSR)*

→ *Possible developments of hybrids hydro/pyro processes (ex : Russia)*

At the CEA Marcoule: Two processes studied

Liquid/liquid reductive extraction process:

- **Development of the core of process**
- **System studies**
- **Applications to treatment of inert matrices being investigated**

Electrochemical separation process:

- **Studies focussed on key steps of the electrorefining process**
- **Applications on recovery of strategic metals**

Thank you for your attention

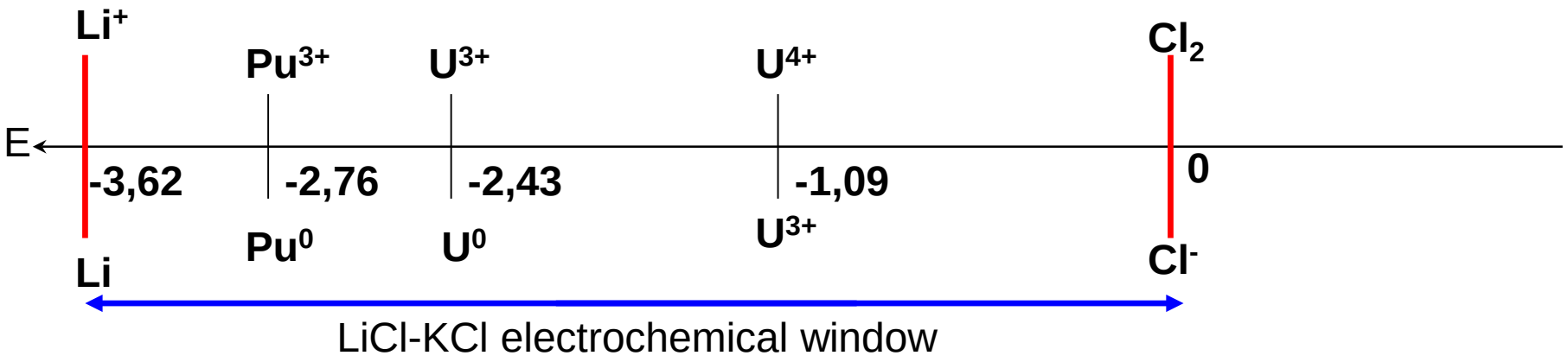
Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Marcoule | BP17171 | 30207 Bagnols-sur-Cèze Cedex
France | T. +33 (0)4 66 79 62 75 | F. +33 (0)4 66 79 63 39

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

Direction de l'énergie nucléaire
Département de radiochimie des procédés
Service de modélisation et chimie des procédés de séparation

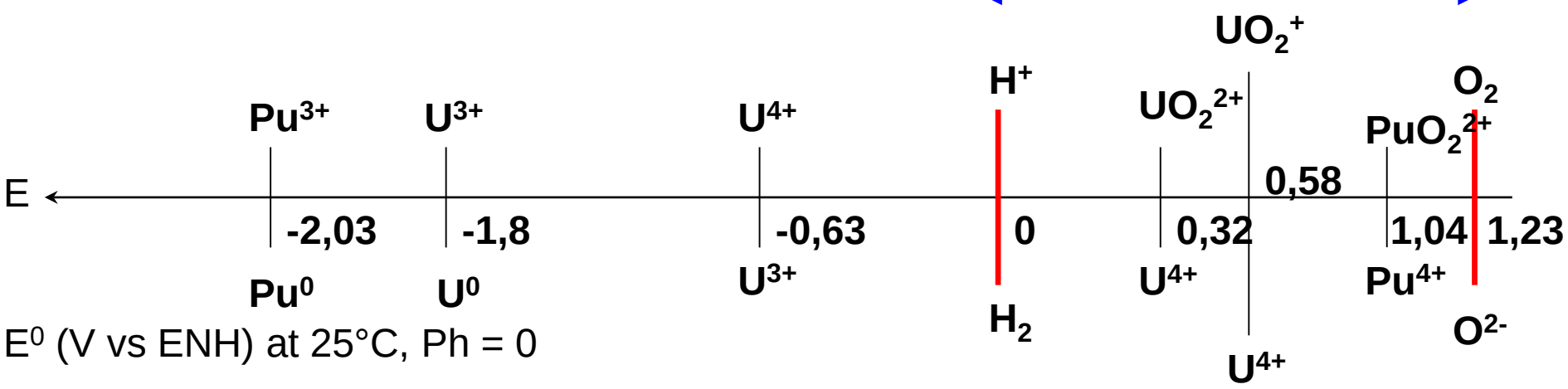
Electrochemical window : Hydro vs. Pyro

E^0 (V vs Cl_2/Cl^-) at 450°C



LiCl-KCl electrochemical window

H_2O electrochemical window

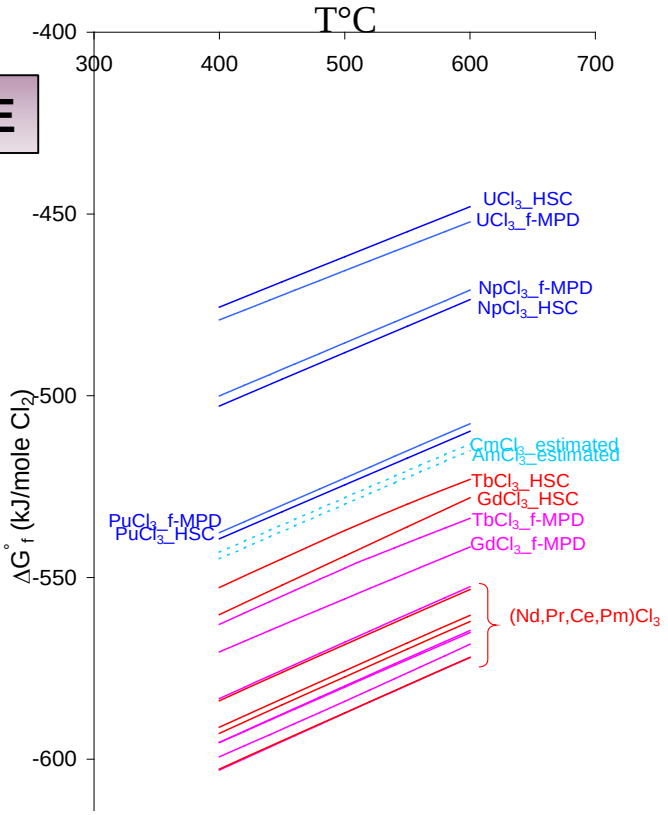


E^0 (V vs ENH) at 25°C, Ph = 0

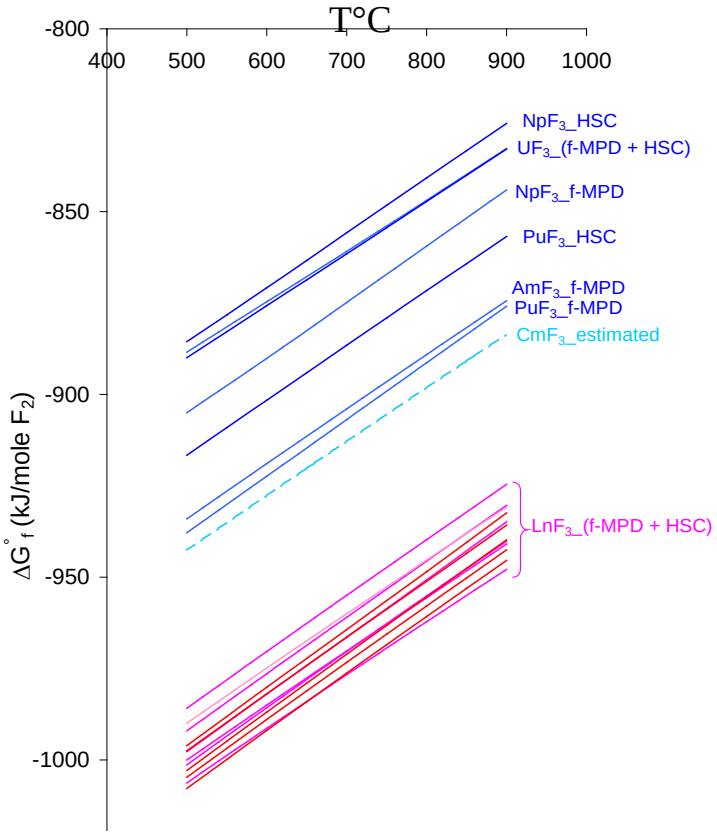
Thermodynamic properties of pure compounds

- **Gibbs free Energy of formation of pure compounds**
  - **Separation**

$$\Delta G = - n F \Delta E$$



An and Ln chlorides

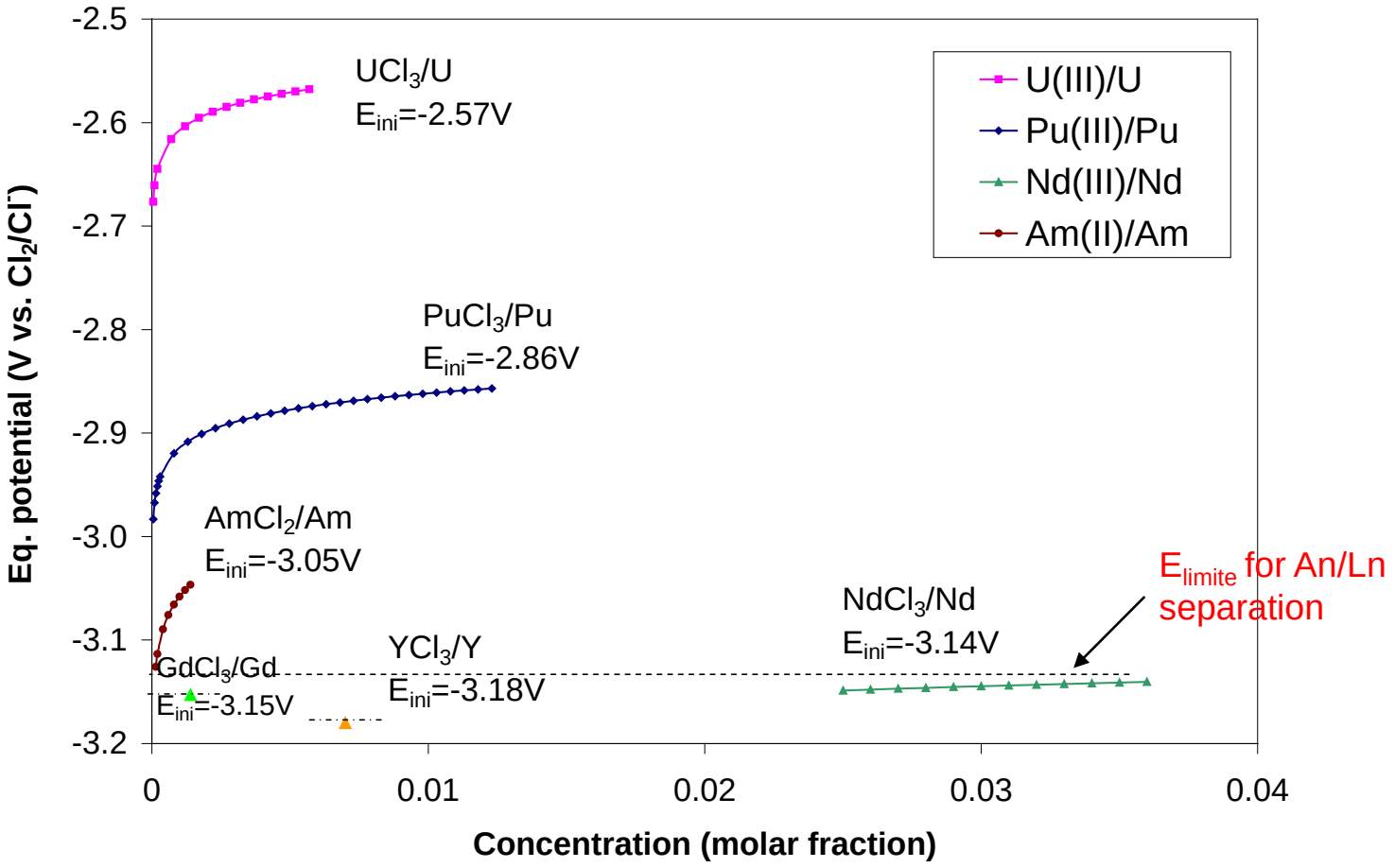


An and Ln fluorides

-"HSC chemistry for windows" (data mainly coming from Barin and Knacke tables)
-f-MPD: Windows online database: f-elements.net

Evolution of concentration in salt

- **Evolution of M^{n+}/M equilibrium potential (on solid inert electrode)**



LiCl-KCl – 527°C

Activity coefficients in salt

LiCl-KCl, 773K

MX_n	Logγ	source
$LaCl_3$	-2,27	Castrillejo Y. (PYROREP)
$CeCl_3$	-2,30	Castrillejo Y. (PYROREP)
$PrCl_3$	-2,26	Castrillejo Y. (PYROREP)
$GdCl_3$	-2,34	Caravaca C (J. Nucl. Mater. 2007)
$ThCl_4$	-3.17	Cassayre L. (Electrochim. Acta)
UCl_3	-2,34	Caravaca C. (PYROREP)
$NpCl_3$	-2,30	De Cordoba (Note CEA)
$PuCl_3$	-2,39	Roy JJ (J. Electrochem. Soc. 1996)

•Activity coefficients of An and Ln chlorides are negative : High complexation with solvent

$$x(K^+,Cl^-) + CeCl_3 \leftrightarrow (xK^+, CeCl_{3+x}^{-x}) \qquad \Delta G^{xs}=2,3RTLog\gamma$$

"Chloral basis"
Cl^- Donor

"Chloral acid"
Cl^- acceptor

"Ce(III) in solution "

•Logγ_{MClx} depend on :

- •Oxidation state of M (IV<III<II<I)
- •Ionic radius of M^{x+} (+small → +acid)

An^{3+} and Ln^{3+}: r^{3+} very close (~100pm) so γ values are also very close

Their interaction with salt can't contribute to An/Ln separation

Influence of the salt: notion of solvent-acidity