DE LA RECHERCHE À L'INDUSTRIE

NUCLEAR FUEL CYCLES

6 – *PARTITIONING, HOW ?*

(an introduction to actinide separation processes)

Bernard BOULLIS

bernard.boullis@cea.fr

www.cea.fr

Joliot Curie School, St Pierre d'Oleron, 22-27 September, 2019

An PARTITIONING, HOW ?

6-1 **ABOUT SEPARATION SCIENCE**
(some basic notions, application to An elements)

6-2 **PUREX**
(successive reprocessing operations)

6-3 **MINOR ACTINIDE SEPARATION**
(some basis for molecular and process design)

6-4 **OTHER FUELS PROCESSING**
(thorium fuels, …)

6-5 **PYRO PROCESSES**
(an introduction to…)

DE LA RECHERCHE À L'INDUSTRIE

NUCLEAR FUEL CYCLES

6-1 SEPARATION : BASIC NOTIONS

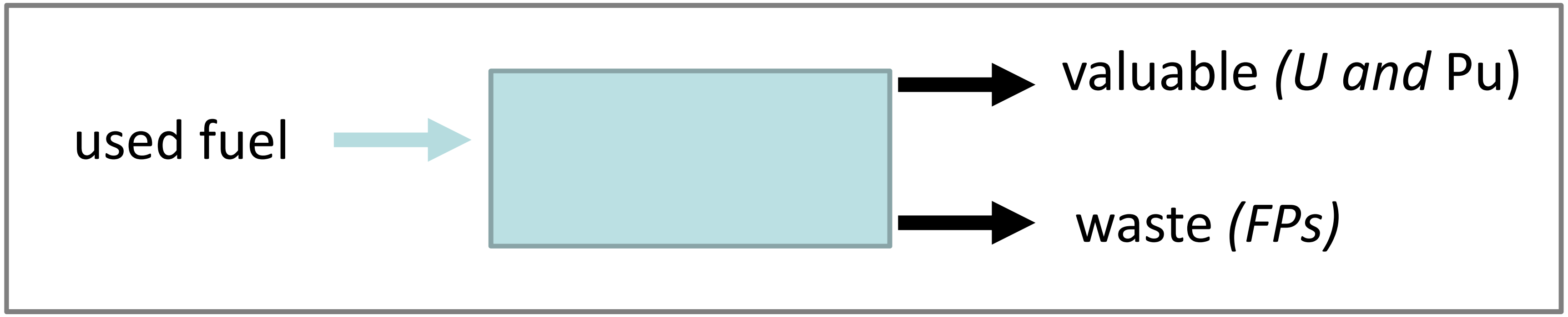
Bernard BOULLIS

bernard.boullis@cea.fr

www.cea.fr

Joliot Curie School, St Pierre d'Oleron, 22-27 September, 2019

ABOUT « NUCLEAR » SEPARATION PROCESSES…



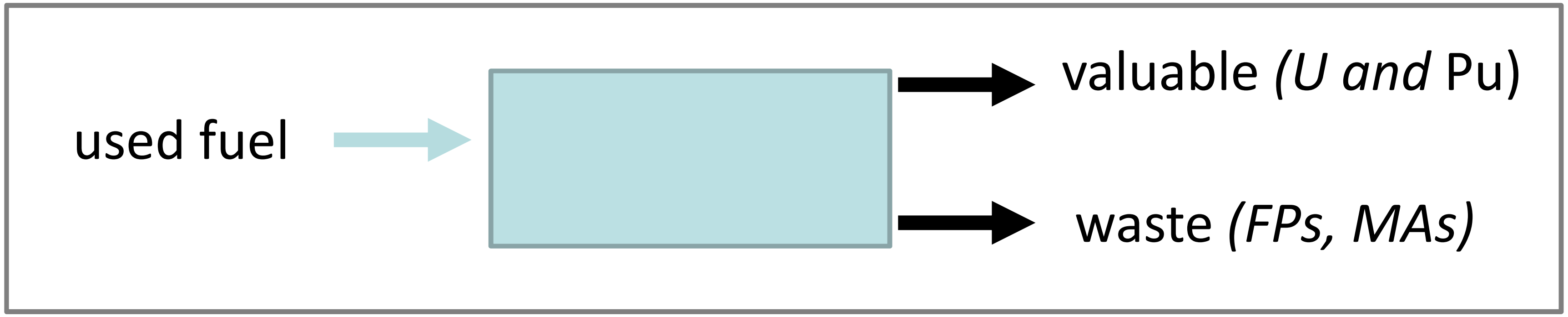
SPECIFICATIONS:

- high recovery yields for valuable elements
- very high purification factors for recovered valuable elements

CONSTRAINTS :

- *(cost)*
- low amount of secondary radwaste
- confinement (avoid dispersion)
- protection (low doses)
- criticality risk management
- radiolysis effects mitigation

ABOUT SEPARATION PROCESSES



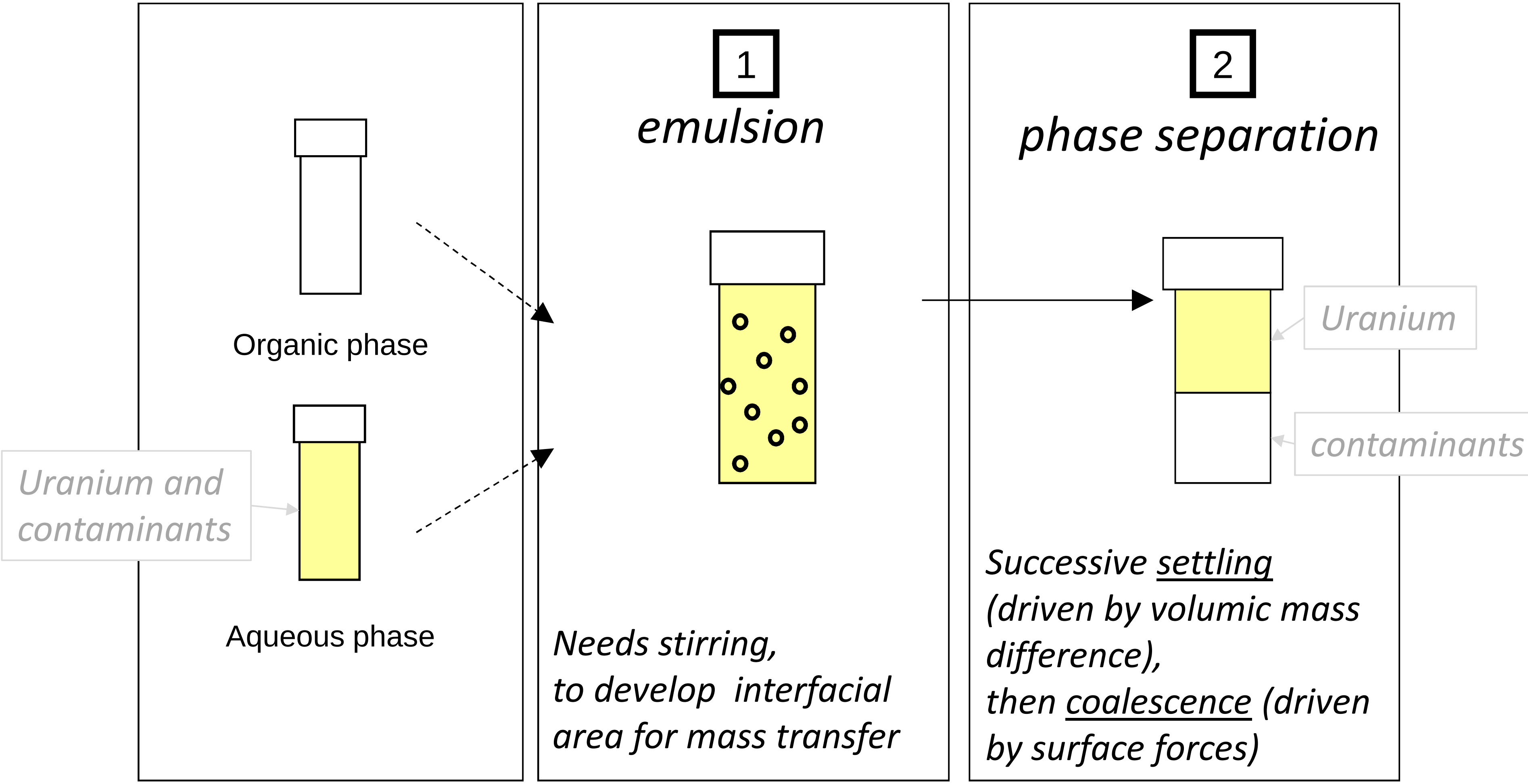
HOW TO PROCEED ?: *take advantage of differences*

- Physical properties *(mass, electric, magnetic…)*
- Chemical properties *(interactions with reagents,…)*

MAIN PROCESSES :

- "Aqueous processes" *(solvent extraction processes)* *[up to industrial scale]*
- "Dry processes" *(electrorefining pyroprocesses, selective volatility)* *[laboratory scale]*

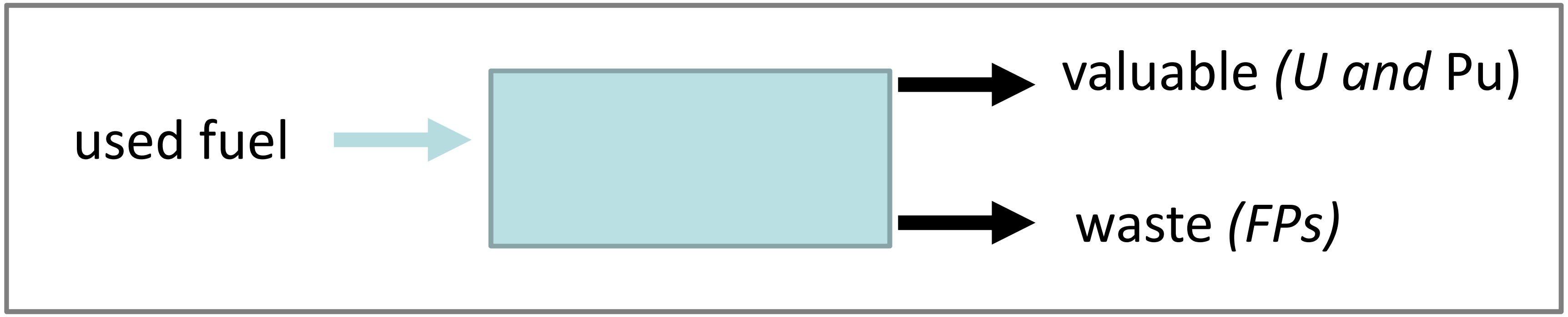
SOLVENT EXTRACTION



Needs stirring, to develop interfacial area for mass transfer

Successive settling (driven by volumic mass difference), then coalescence (driven by surface forces)

SOLVENT EXTRACTION EFFICIENCY (global approach)



$$\textbf{M recovery yield} = \frac{\text{M amount in organic phase after extraction step}}{\text{M initial amount in aqueous phase}}$$

M1 <u>purification</u> (decontamination) factor vs. M2:

$$DF = \frac{\text{[M2]/[M1] in initial aqueous solution}}{\text{[M2]/[M1] in recovered (organic) solution}}$$

SOLVENT EXTRACTION EFFICIENCY (elementary approach)

For each element M, present in initial aqueous solution:

$$D_M \left(\text{or } K_D\right) = \frac{\left[\overline{M}\right]_{org}}{\left[M\right]_{aq}}$$

D_M adimensional

$$D_M = \frac{\left[\overline{M}\right] + \left[\overline{complex\,1}\right] + \left[\overline{complex\,2}\right] + \ldots}{\left[M\right] + \left[complex\,1\right] + \left[complex\,2\right] + \ldots}$$

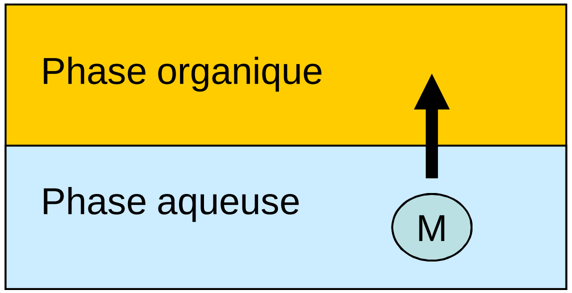
For two elements, M_1 and M_2 to be separated :

$$\mathbf{SF}_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}}$$

SOLVENT EXTRACTION : EXEMPLES (1)

- « **PASSIVE EXTRACTION** »,

  (solvation of a lipophilic compoud in the organic phase)



$$M \xrightleftharpoons{K_{ex}(M)} \overline{M}$$

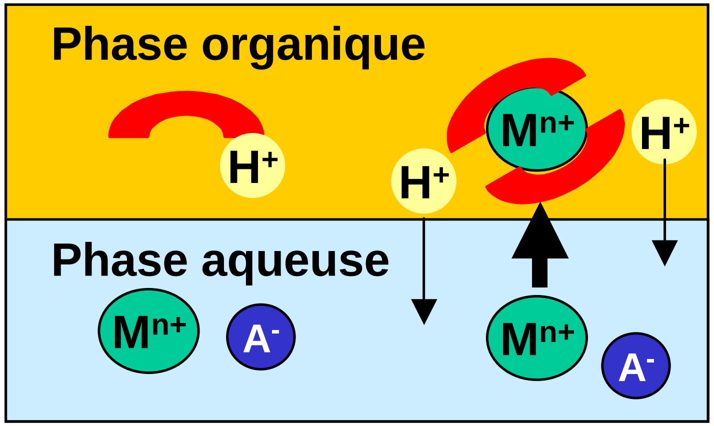
- ***Iodine in the system: water/CCl_4***

SOLVENT EXTRACTION : EXEMPLES (3)

- ***CATION EXCHANGE***

$$M^+ + \overline{HA} \longrightarrow \overline{MA} + H^+$$

$$M^{n+} + m\,\overline{HA} \underset{}{\overset{K_{ex}}{\rightleftarrows}} \overline{MA_n(HA)_{m-n}} + n\,H^+$$



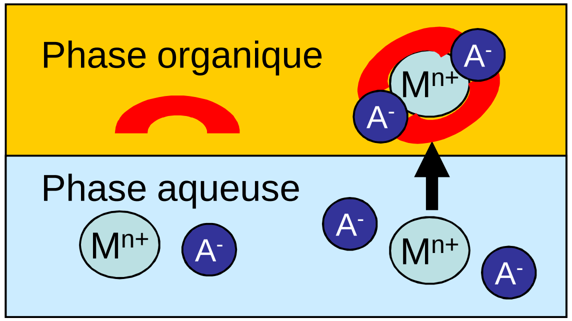
$$K_{ex} = \frac{\left[\overline{MA_n(HA)_{m-n}}\right].\left[H^+\right]^n}{\left[M^{n+}\right].\left[\overline{HA}\right]^m} = \frac{D_M.\left[H^+\right]^n}{\left[\overline{HA}\right]^m}$$

- ***Am^{3+} by HDEHP (diethylhexyl phosphoric acid)***

- ***SOLVATION OF*** **A** **NEUTRAL COMPLEX :**

  (acid or metallic salt in the initial aqueous solution)

$$M^+ + A^- + \overline{E} \longrightarrow \overline{MAE}$$

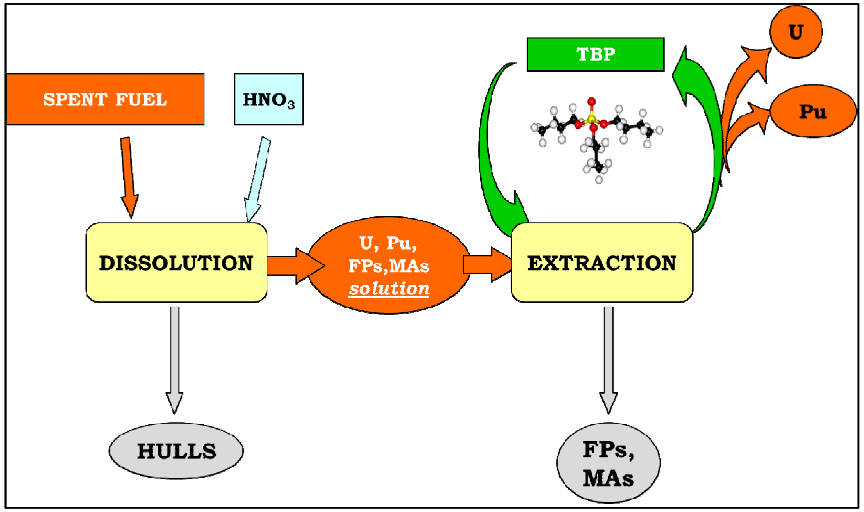


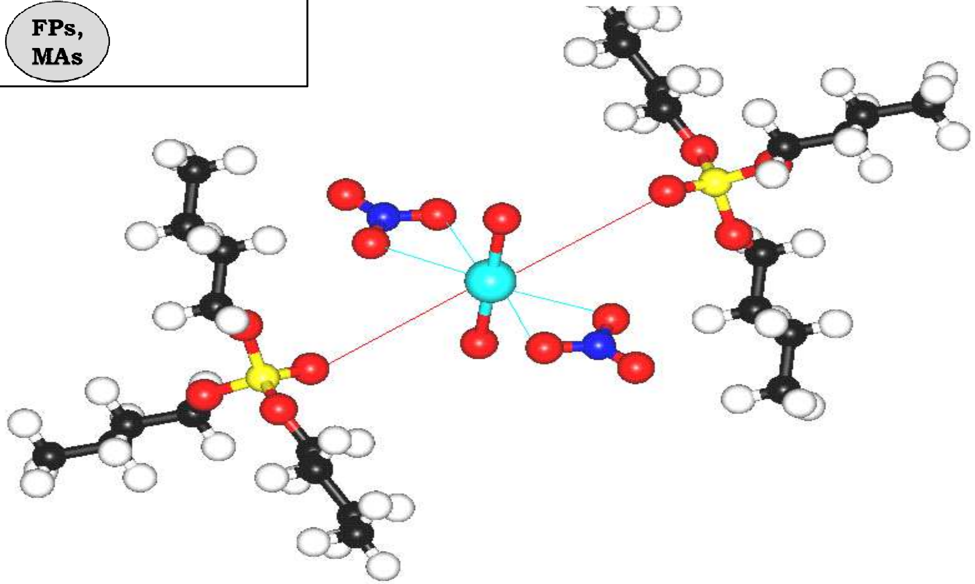
$$M^{n+} + e\,\overline{E} + n\,A^- \underset{K_{ex}(M)}{\rightleftarrows} \overline{MA_nE_e}$$

$$K_{ex}(M) = \frac{\left[\overline{MA_nE_e}\right]}{\left[M^{n+}\right] \cdot \left[\overline{E}\right]^e \cdot \left[A^-\right]^n} = \frac{D_M}{\left[\overline{E}\right]^e \cdot \left[A^-\right]^n}$$

- *Uranyl nitrate by TBP (tri-butyl phosphate)*

THE PUREX PROCESS





$$UO_2^{2+} + 2\,NO_3^{-} + 2\,\overline{TBP} \Leftrightarrow \overline{UO_2(NO_3)_2, 2\,TBP}$$

UO_2^{2+} EXTRACTION by TBP

$$UO_2^{2+} + 2\,NO_3^- + 2\,\overline{TBP} \leftrightarrows \overline{UO_2(NO_3)_2,\,2\,TBP} \quad [\Delta H < 0]$$

- *«salting out effect »* : if $[NO_3^-]$ ↗, then D ↗
- *«saturation effect»* : $[\overline{TBP}]$ defines $[\overline{U}]_{max}$

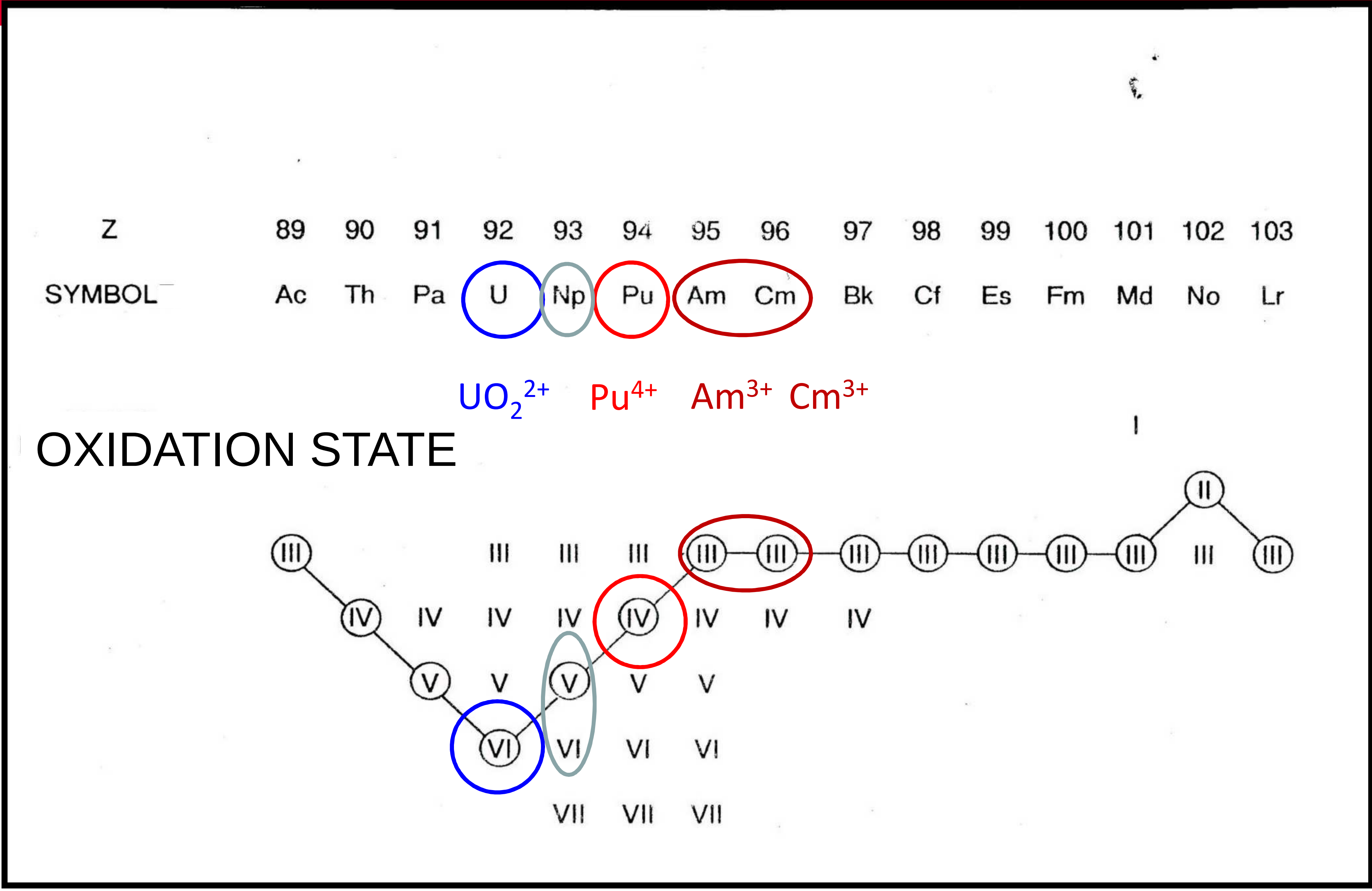
  (if $\overline{TBP}$ = 1.1 M, $[\overline{U}]max$ = 0,55 mol/l # 120 g/l)

- *«compétition effect»* : U, Pu, H^+ « *candidates* » for extraction
- *«température effect »* : if T ↗ , then D ↘

⇨ **potentially quantitative extraction**

⇨ **possible reversibility**

ACTINIDE ELEMENTS CHEMICAL PROPERTIES



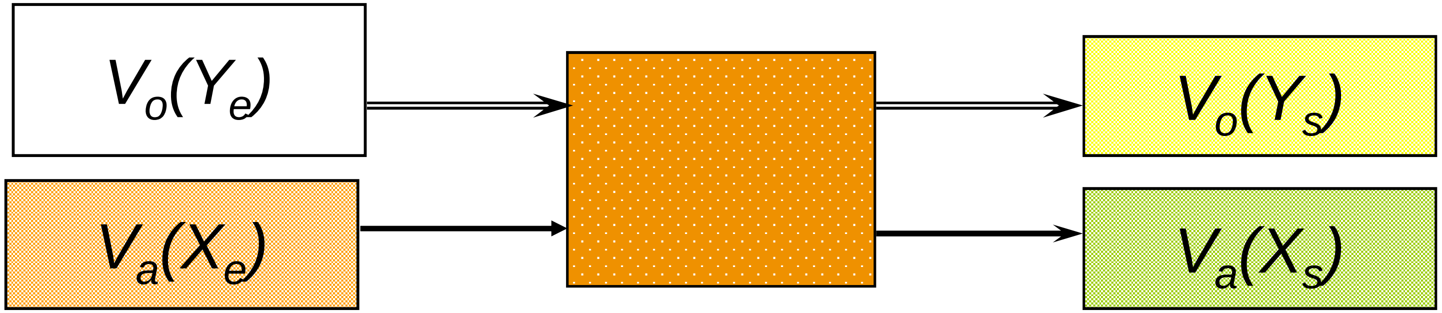
PUREX PROCESS: BASIS

Element	SPECIE	$D_{M^{n+}}$
U	UO_2^{2+}	**25**
Pu	Pu^{4+}	**11**
Np	NpO_2^{2+} (NpO_2^{+})	**10 (2.10^{-2})**
Am	Am^{3+}	**< 10^{-2}**
Ln	Ln^{3+}	**< 10^{-2}**

$$D_{M^{n+}} = \frac{[M^{n+}]_{org}}{[M^{n+}]_{aq}}$$

25°C, [TBP] = 1,1 M in dodecane, [HNO_3] = 3 M

THEORETICAL STAGE : BASIC NOTIONS



DEFINITION :

- Outlet phases at thermodynamical equilibrium
- Outlet phases perfectly separated

BASIC RELATIONS :

- équilibrium : $Ys = D.Xs$
- mass balance : $Va(Xe-Xs) = Vo(Ys-Ye)$

THEORETICAL STAGE : BASIC NOTIONS

(Hypothesis : organic phase without solute before contact)

- ***équilibrium***: Ys = D.Xs
- ***Mass balance***: Xe = (Va. Xs + Vo.D.Xs) /Va (batch)

  Xe = (A. Xs + O.D.Xs) /A (continuous)

$$X_s = \frac{X_e}{1+E} \quad avec \quad E = \frac{V_o}{V_a} \cdot D = \frac{O}{A} \cdot D$$

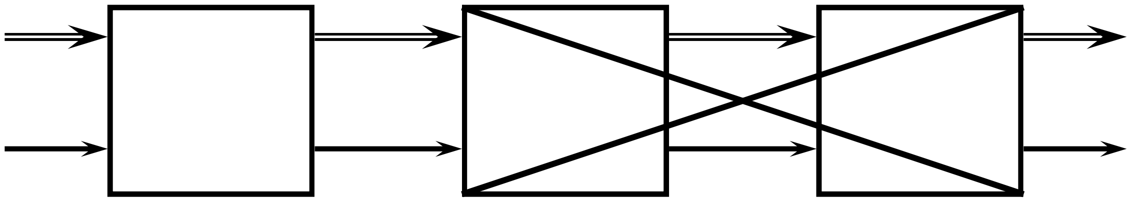
(E “extraction factor")

to get high E value → $\frac{V_o}{V_a}$ *ou* $\frac{O}{A}$ high

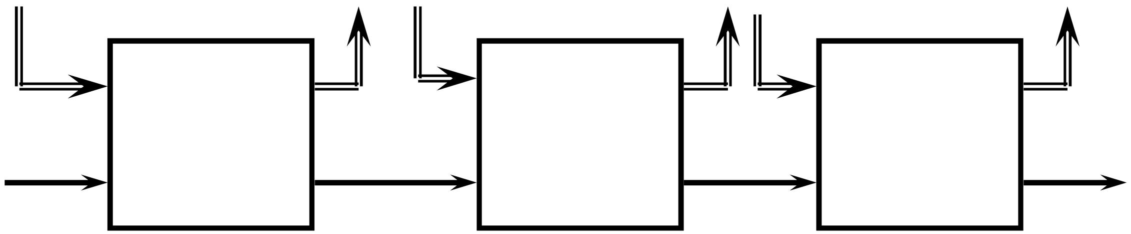
→ D high

LIQUID / LIQUID EXTRACTION : *CONTINUOUS & REPEATED PROCESSES*

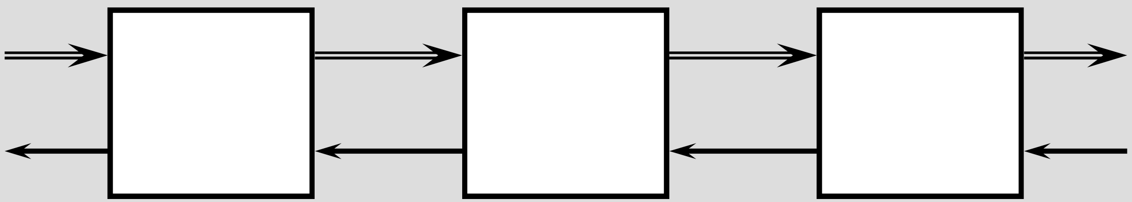
Co-flow ?



Possible flow-sheet :



Cross-flow: the way for high separation yields



EFFECT OF CUMULATIVE CROSS-FLOW STAGES : *KREMSER RELATION*

$$\frac{x_{inlet}}{\varepsilon_{residue}} = \frac{E^{n+1} - 1}{E - 1}$$

with

$$\mathbf{E} = \frac{\mathbf{O}}{\mathbf{A}}.\mathbf{D}$$

A aqueous flowrate
O extractant flowrate
D distribution coeff.

Ex: D=10 , O=A , n= 1 , residue fraction = 1/10
2 — 1/100
3 — 1/1000
... — ....

DE LA RECHERCHE À L'INDUSTRIE

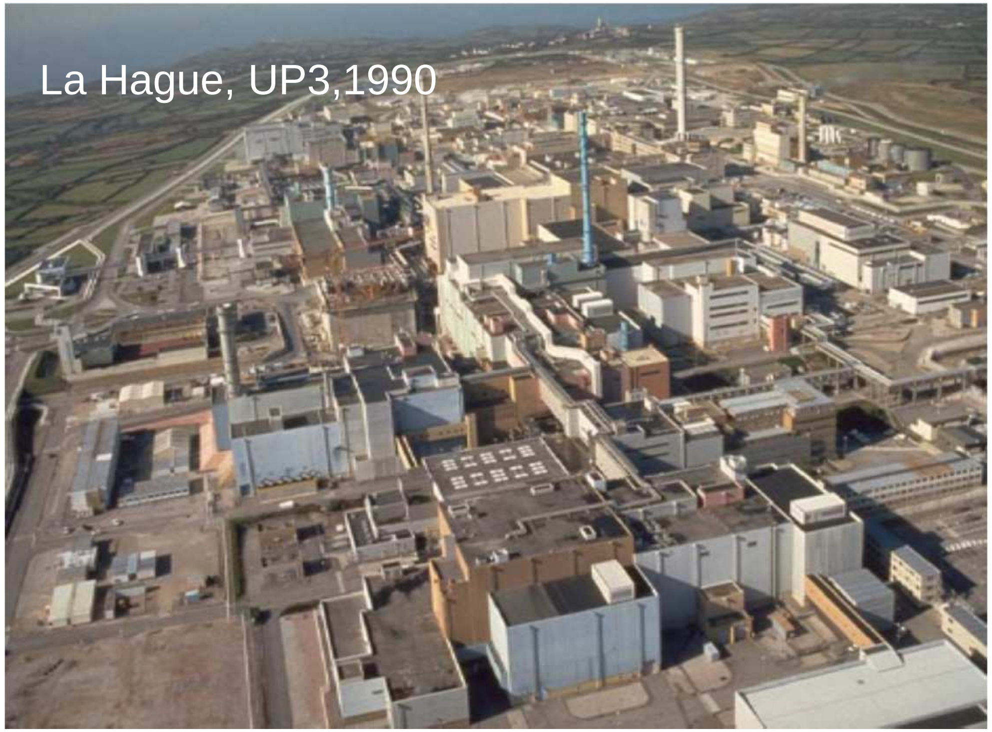
NUCLEAR FUEL CYCLES

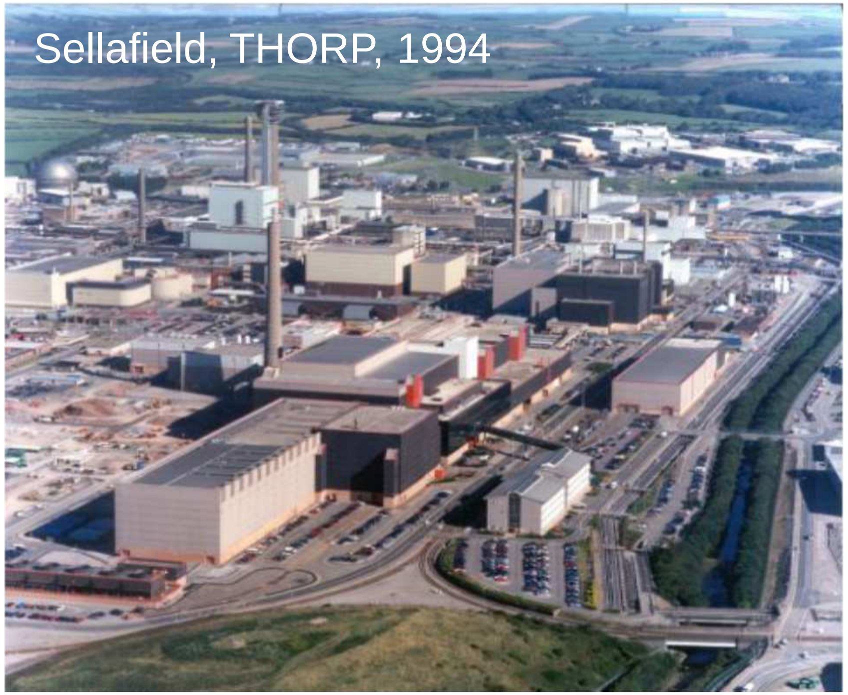
6 –2 THE PUREX PROCESS

Bernard BOULLIS
bernard.boullis@cea.fr

www.cea.fr

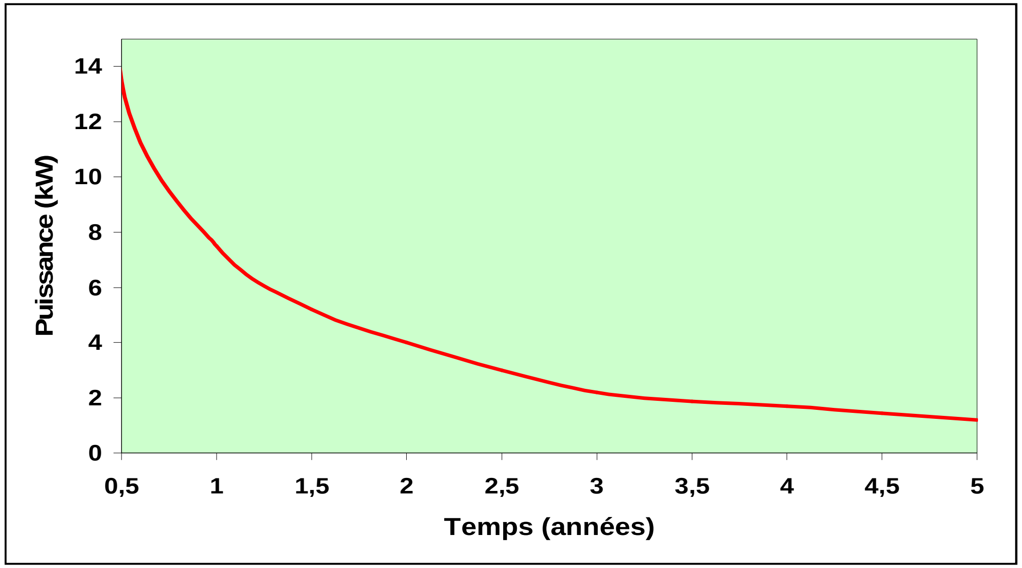
Joliot Curie School, St Pierre d'Oleron, 22-27 September, 2019


La Hague, UP3,1990

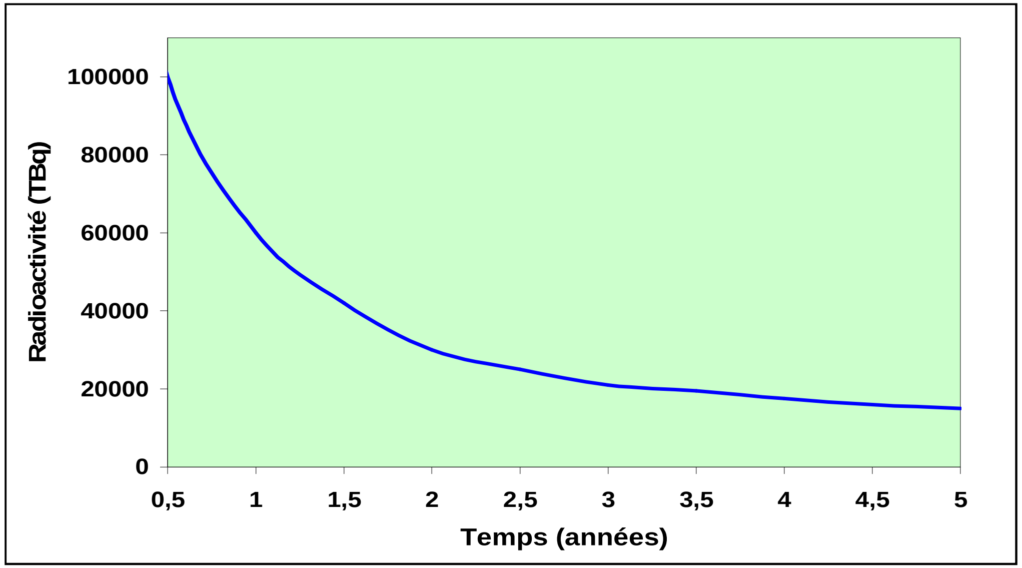

Sellafield, THORP, 1994

Rokkashomura

PUREX PROCESS: CURRENT INDUSTRIAL OPERATION (1)

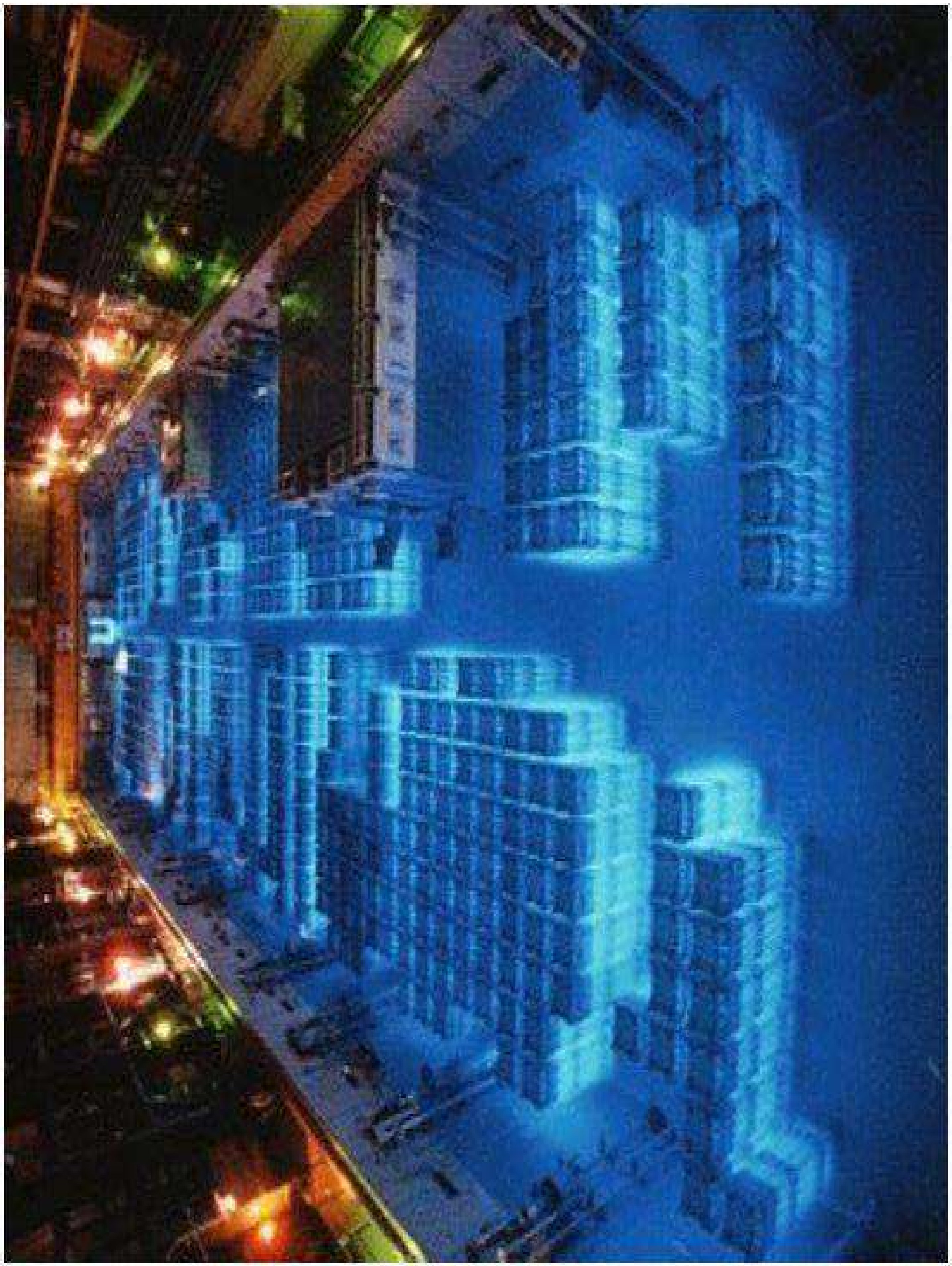


- Residual heat (assembly)



- Radioactivity (assembly)

USED FUELS TRANSPORTATION



PUREX PROCESS: CURRENT INDUSTRIAL OPERATION (2)

✓ **UO_2 DISSOLUTION** : ΔH = - 420 J/kg

< 2M : $UO_2 + 8/3\ HNO_3 \rightarrow UO_2(NO_3)_2 + 2/3\ NO + 4/3\ H_2O$

> 8M : $UO_2 + 4\ HNO_3 \rightarrow UO_2(NO_3)_2 + 2\ NO_2 + 2\ H_2O$

$UO_2 + 3\ HNO_3 \rightarrow UO_2(NO_3)_2 + ½\ NO + ½\ NO_2 + 3/2\ H_2O$

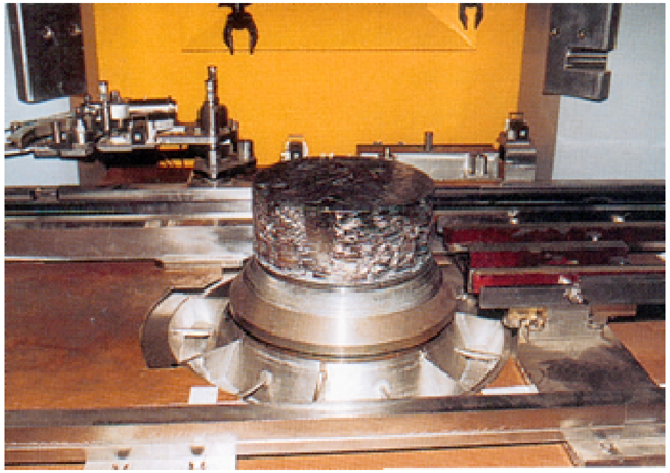
✓ **PuO_2 DISSOLUTION** :

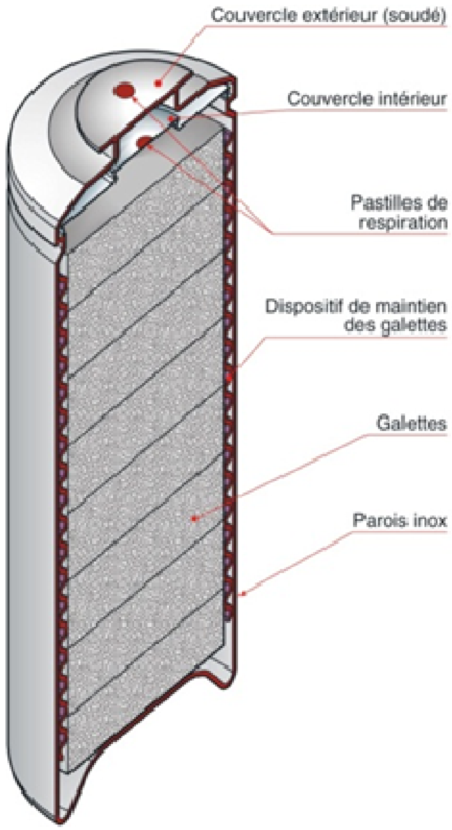
$PuO_2 + 4\ HNO_3 \rightarrow Pu(NO_3)_4 + 2\ H_2O$ (très lent)

✓ **PF/TU (III) DISSOLUTION** :

$M_2O_3 + 6\ HNO_3 \rightarrow 2\ M(NO_3)_3 + 3\ H_2O$

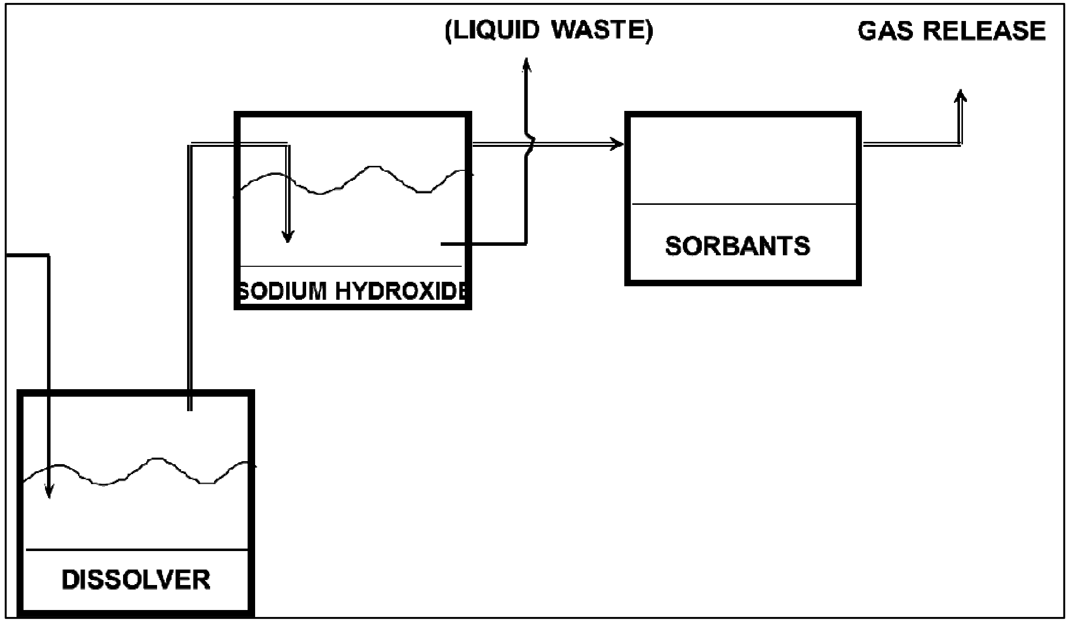
CLADDING MATERIAL





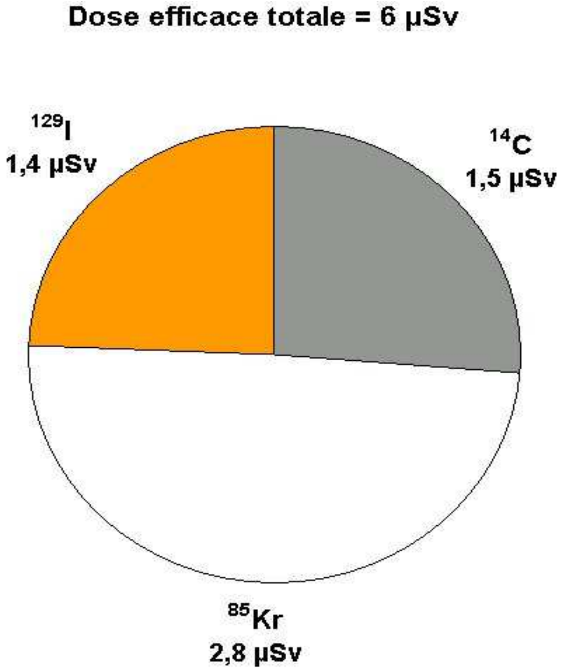
PUREX PROCESS: CURRENT INDUSTRIAL OPERATION (3)

➔ IODINE	(I_2)	[^{129}I]
➔ CARBONE	(CO_2)	[^{14}C]
➔ TRITIUM	(HTO)	[^{3}H]
➔ KRYPTON	(Kr)	[^{85}Kr]

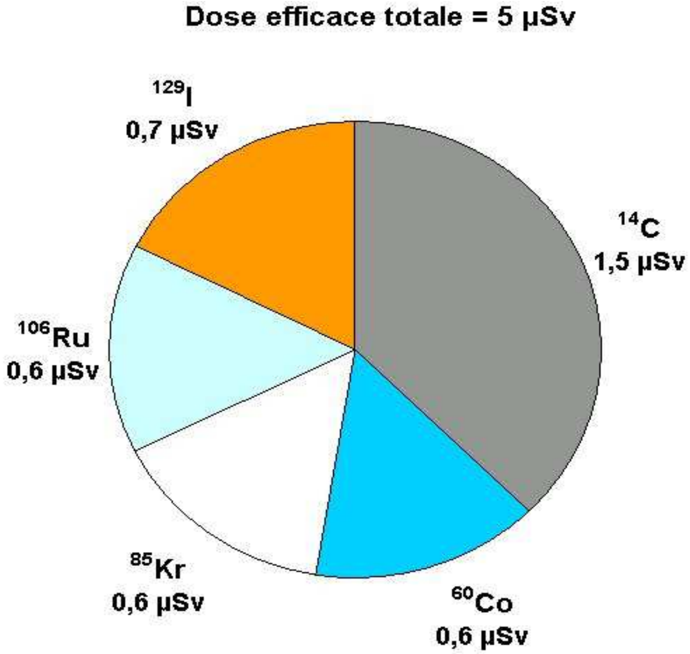


IMPACT REJETS LA HAGUE

(groupe radioecologie Nord Cotentin, 1996)

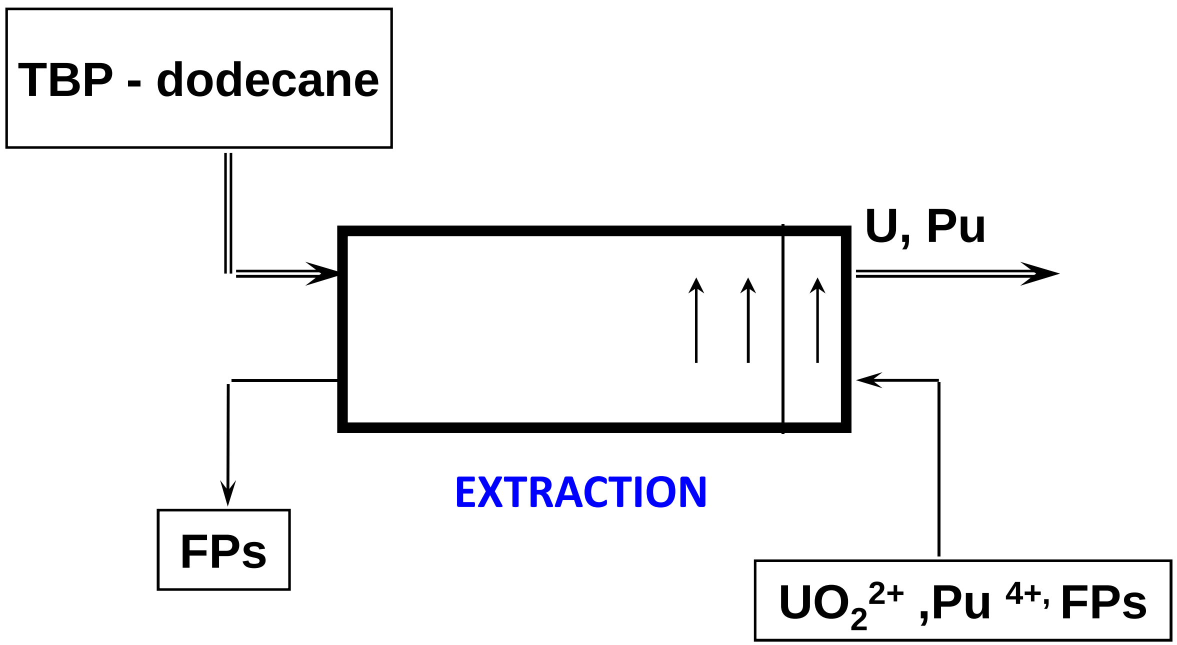


"Adultes de Digulleville" (groupe de référence associé aux rejets atmosphériques), 1996



"Pêcheurs de Goury" (groupe de référence associé aux rejets liquides en mer), 1996

PUREX PROCESS: CURRENT INDUSTRIAL OPERATION (4)



OPERATING CONDITIONS : $[HNO_3]$ rather high

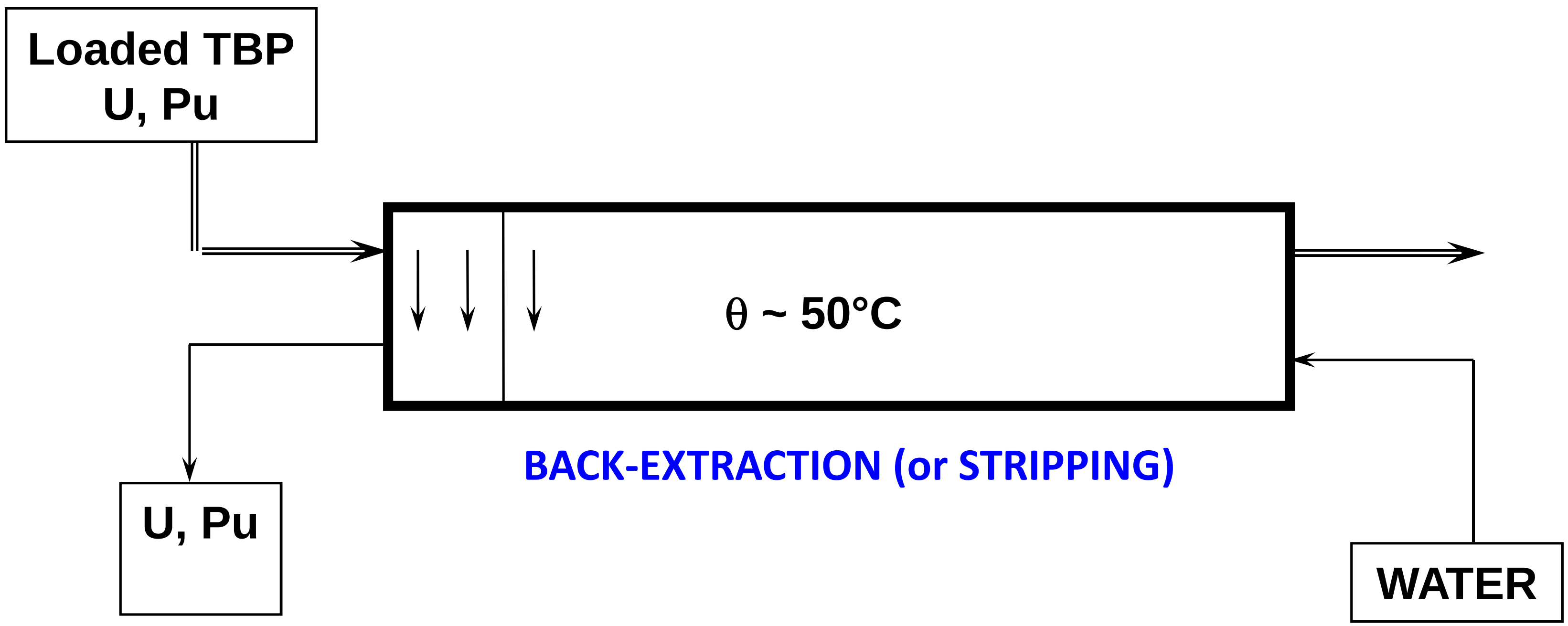
$[U]_{org}$ rather high

$$UO_2^{2+} + 2\,NO_3^- + 2\,\overline{TBP} \leftrightarrows \overline{UO_2(NO_3)_2, 2\,TBP} \quad [\Delta H < 0]$$

$$Pu^{4+} + 4\,NO_3^- + 2\,\overline{TBP} \leftrightarrows \overline{Pu(NO_3)_4, 2\,TBP}$$

PURPOSE PROCESS:

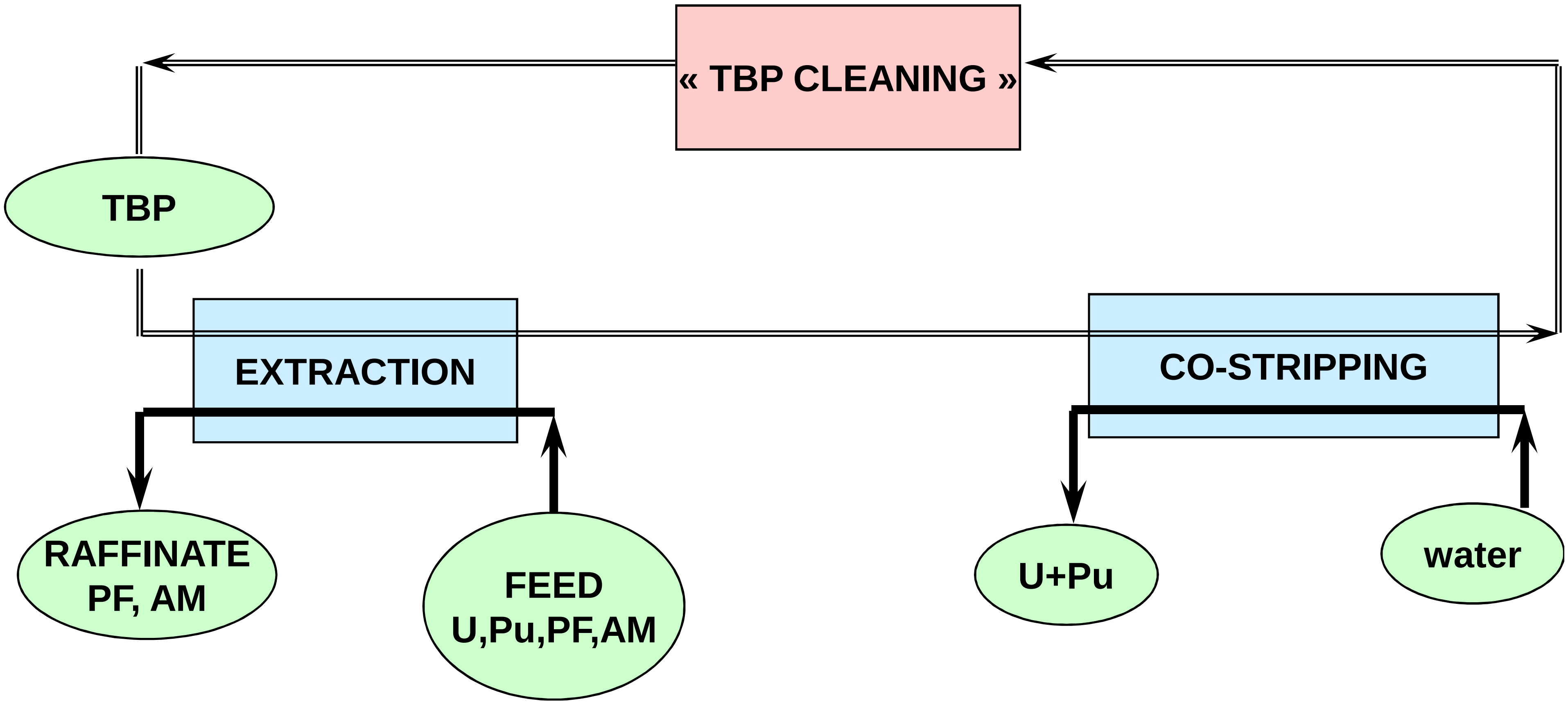
CURRENT INDUSTRIAL OPERATION (5)



BACK-EXTRACTION (or STRIPPING)

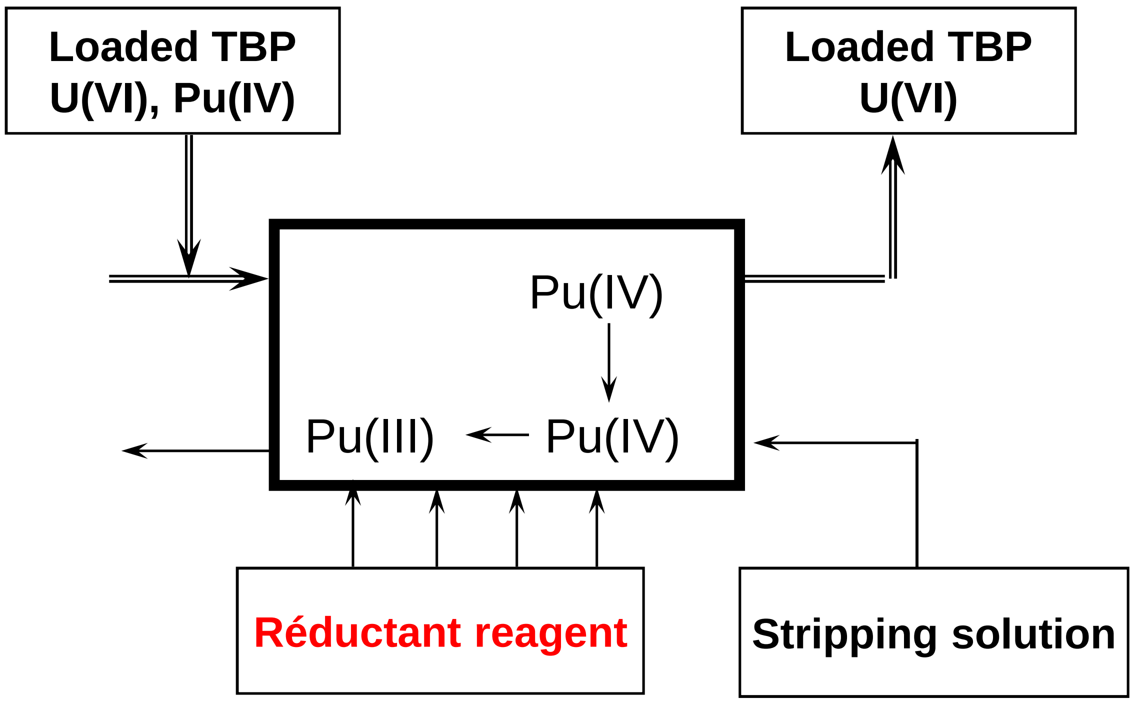
$$UO_2^{2+} + 2\,NO_3^- + 2\,\overline{TBP} \leftrightarrows \overline{UO_2(NO_3)_2,\,2\,TBP} \quad [\Delta H < 0]$$

PUREX PROCESS:
CURRENT INDUSTRIAL OPERATION (6)



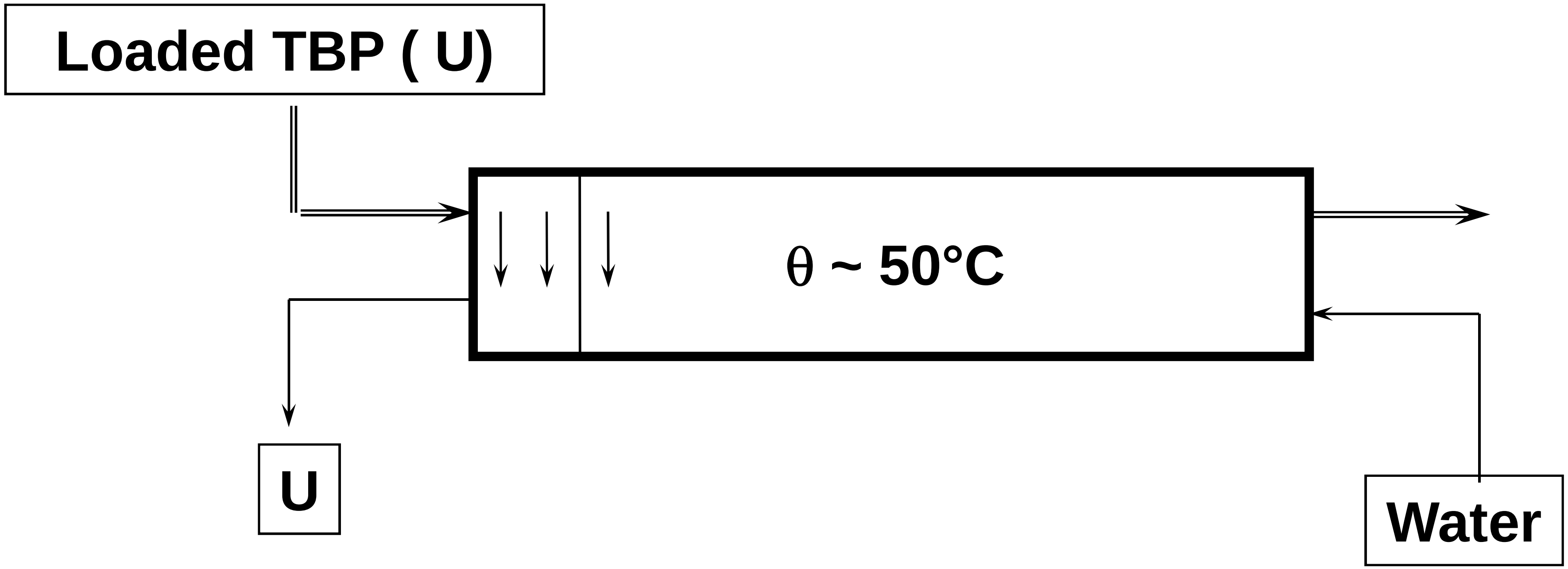
PUREX PROCESS: CURRENT INDUSTRIAL OPERATION (7)

SELECTIVE Pu STRIPPING: PRINCIPLE

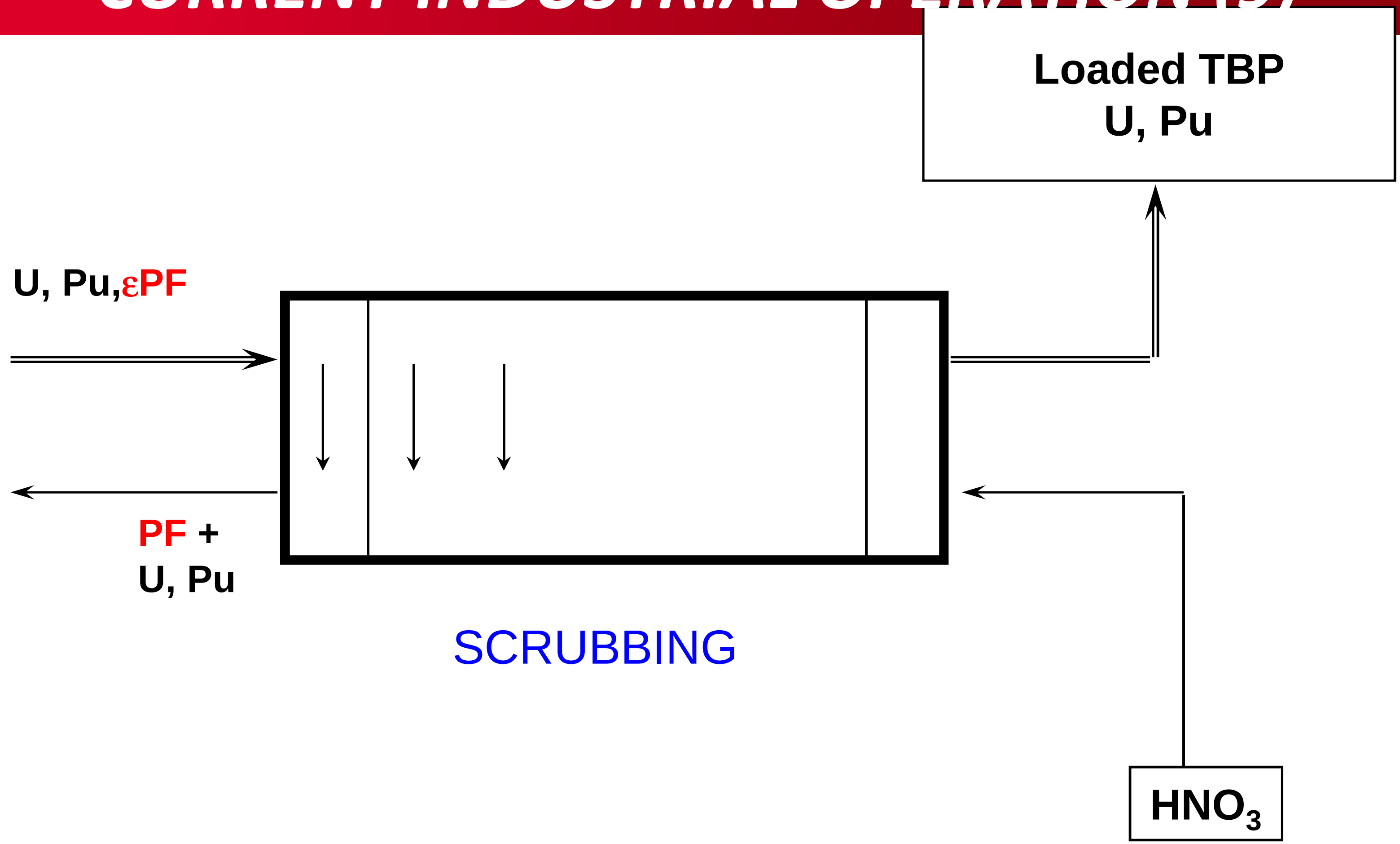


PURREX PROCESS:
CURRENT INDUSTRIAL OPERATION (8)

URANIUM STRIPPING



PUREX PROCESS: CURRENT INDUSTRIAL OPERATION (9)

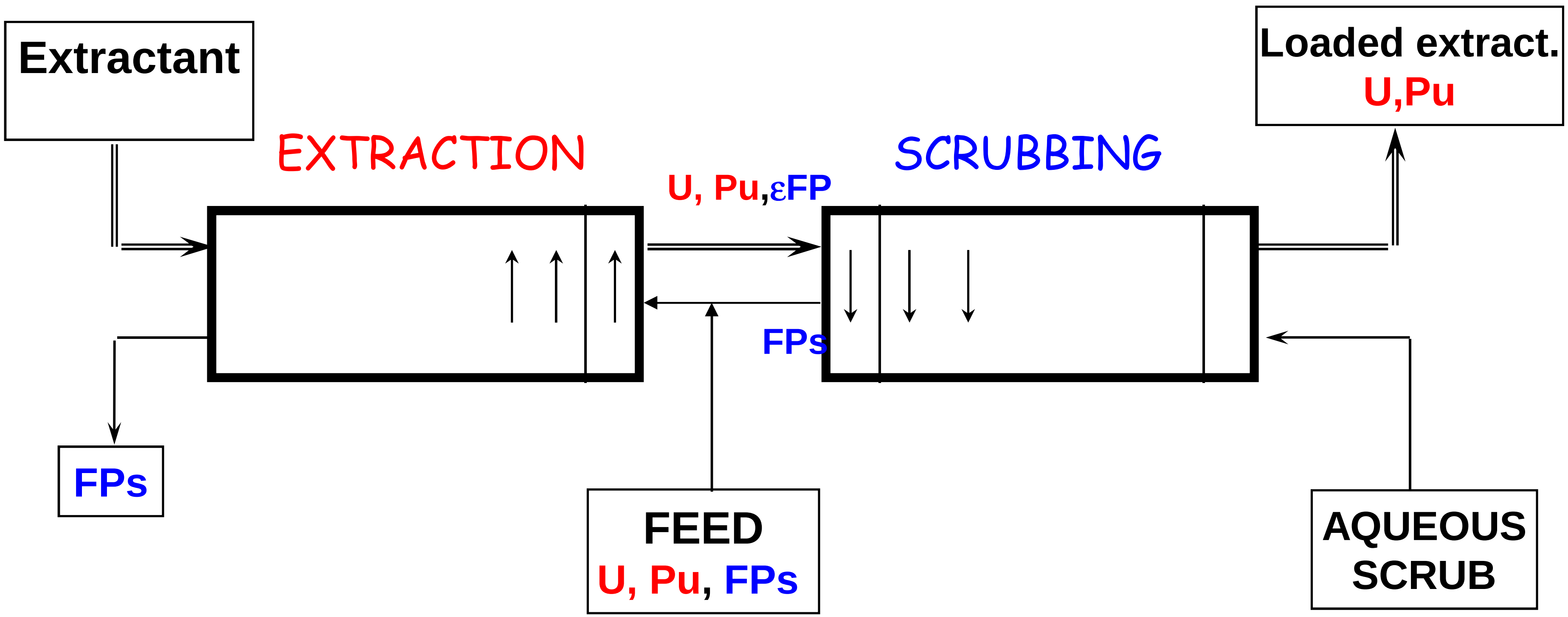


SCRUBBING OPERATIONS : PRINCIPLE

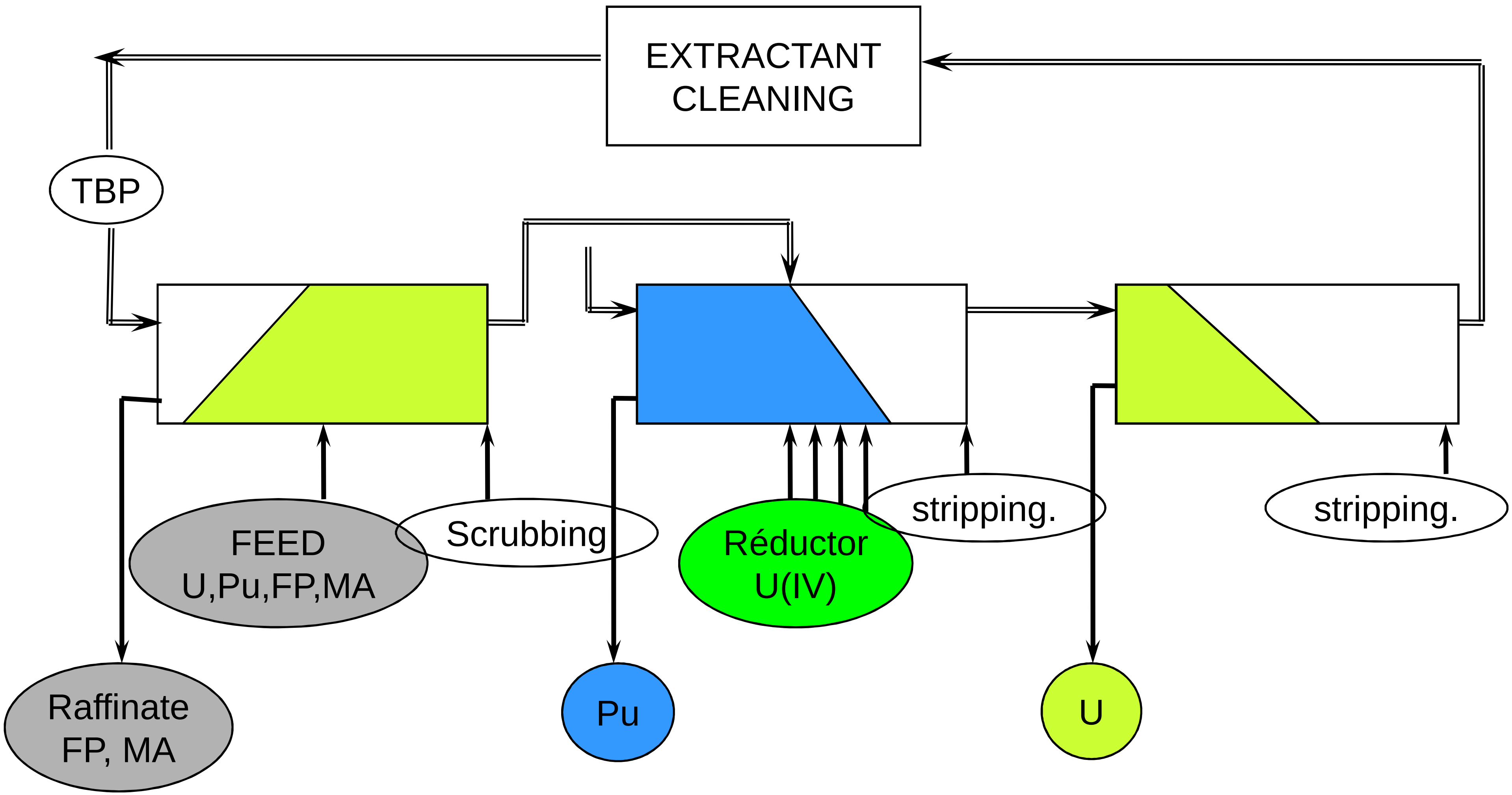
$$UO_2^{2+} + 2\ NO_3^- + 2\ TBP \leftrightarrows UO_2(NO_3)_2, 2\ TBP \quad [\Delta H < 0]$$

PUREX PROCESS:
CURRENT INDUSTRIAL OPERATION (10)

SOLVENT EXTRACTION : High recovery yields, High purification yields !



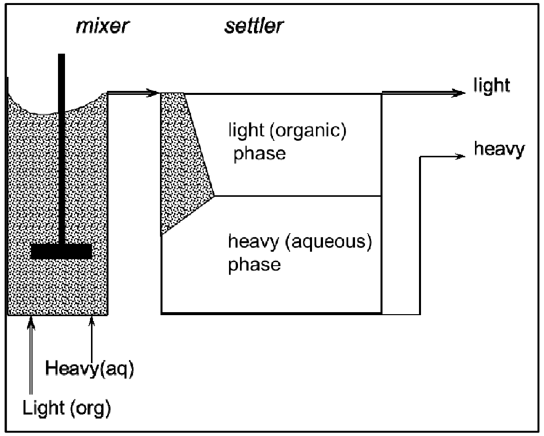
PUREX PROCESS: CURRENT INDUSTRIAL OPERATION (11)



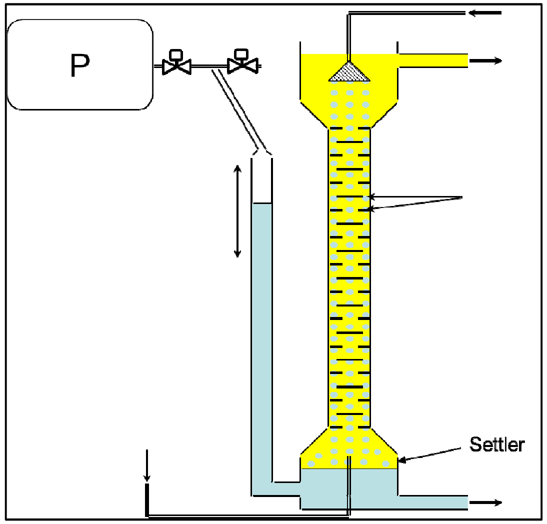
1st CYCLE U-Pu WITH U/Pu PARTITIONING

PURFEX PROCESS:
CURRENT INDUSTRIAL OPERATION (12)

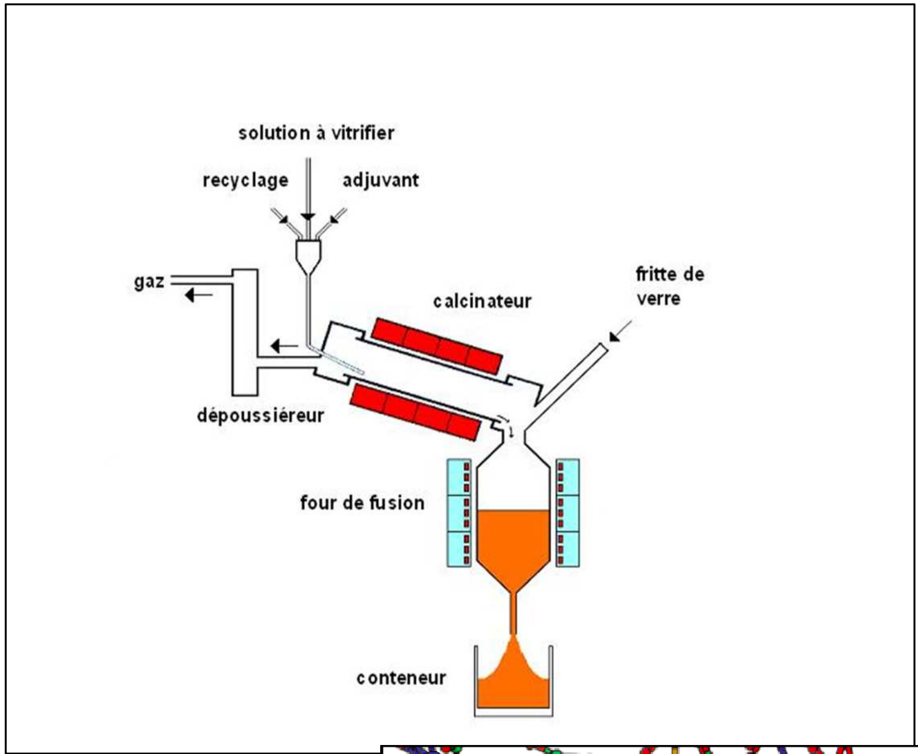
- **COMPARTIMENTED EXTRACTORS :**
  - *MIXERS-SETTLERS*
  - *CENTRIFUGAL CONTACTORS (MONO OU MULTI-ÉTAGES)*



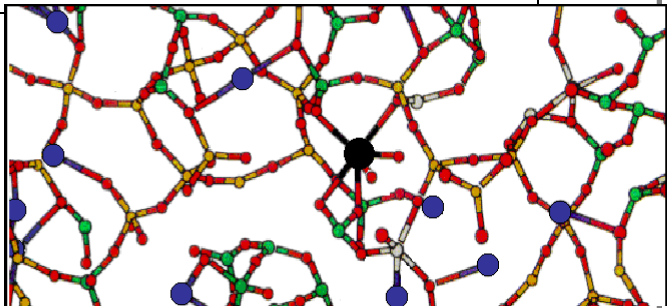
- **CONTINUOUS CONTACTORS :**
  - *PULSED COLUMNS*



HLW CONDITIONING

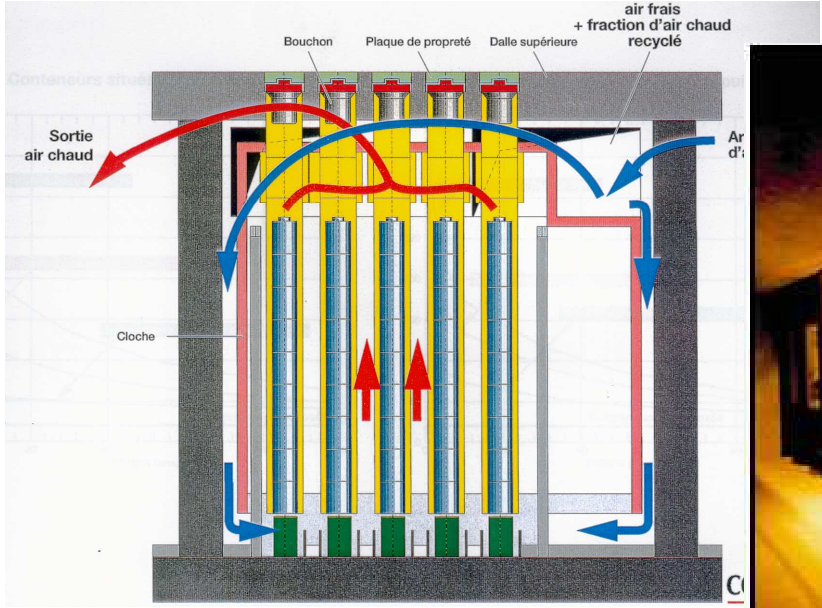


GLASSES

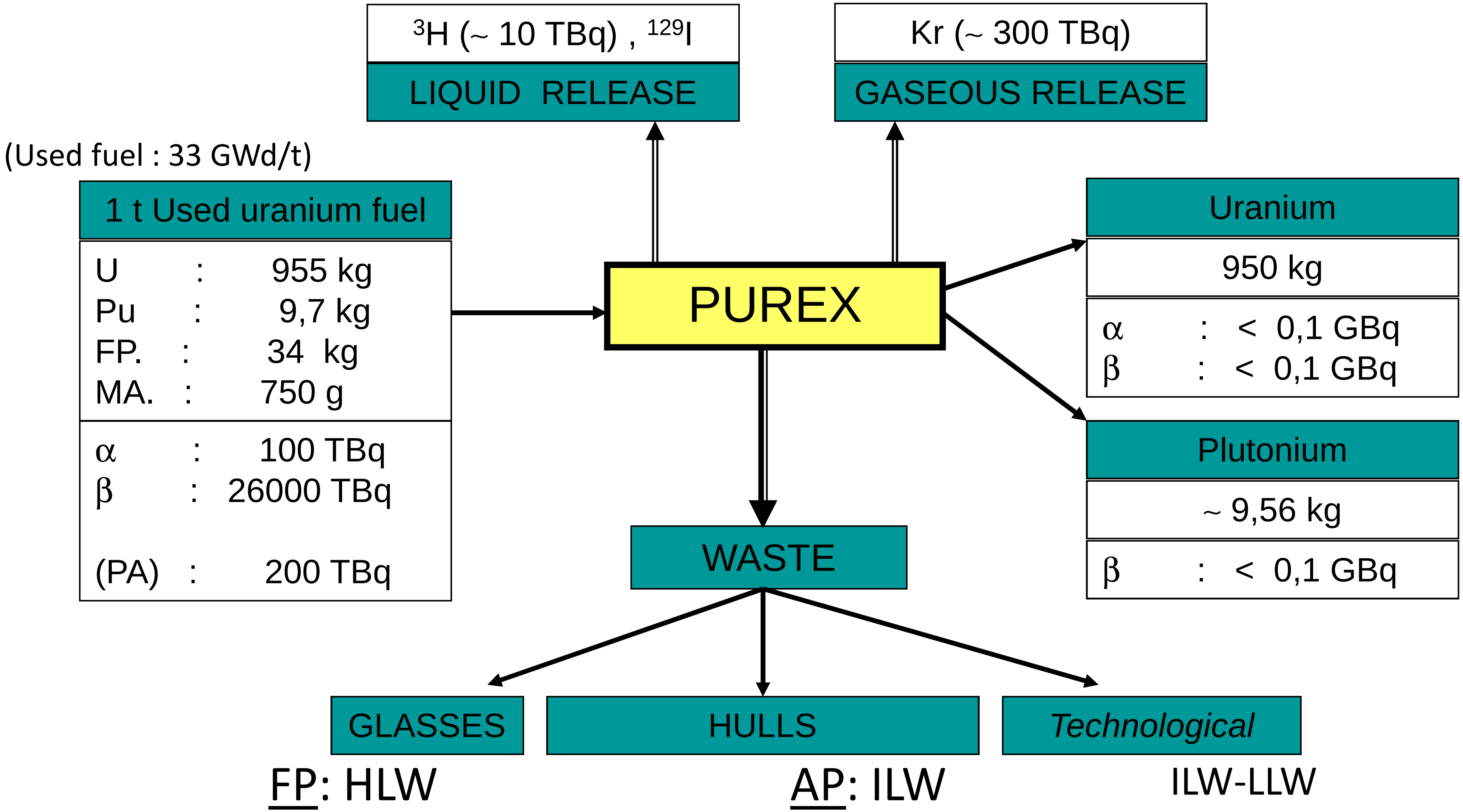


180 liters,
PF #15%, #2KW,
>15 000 TBq

GLASS CANISTERS INTERIM STORAGE
(La HAGUE)



PUREX PROCESS AT LA HAGUE PLANT : RESULTS



DE LA RECHERCHE À L'INDUSTRIE

cea

NUCLEAR FUEL CYCLES

6 –3 MINOR ACTINIDE SEPARATION

Bernard BOULLIS

bernard.boullis@cea.fr

www.cea.fr

Joliot Curie School, St Pierre d'Oleron, 22-27 September, 2019

ADDITIONAL PROCESSES… ?

PUREX

U & Pu

Minor actinides

Fission Products

MINOR ACTINIDES SELECTIVE EXTRACTION after PUREX ?

- *AMOUNTS (UOX "standard" fuel, 45 GWd/t) :*
  - **NpO_2^+ / NpO_2^{2+} 610 g/t**
  - **Am^{3+} 600 g/t**
  - **Cm^{3+} 90 g/t**

  ~ 1% used fuel content

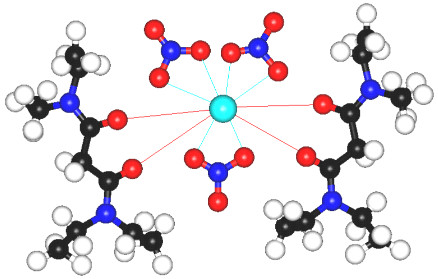
- *after PUREX :*
  - **Highly acidic *([HNO_3] ~ 3 $mol.L^{-1}$)***
  - **Highly radioactive *(FPs ~ 5.10^{12} $Bq.L^{-1}$)***
  - **Very diverse , and *[Ln] ~ 50 × ([Am] +[Cm])***

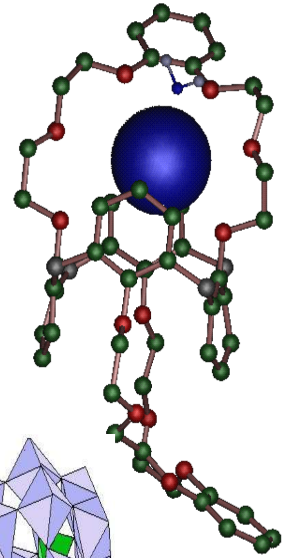
- *CHEMICAL BEHAVIOR :*
  - **Light actinides (Th to Pu) : *specific redox (PUREX basis*)**

    ⇨ Np recovery achievable by PUREX
  - **Heavier actinides (from Am) : *behave like lanthanides***

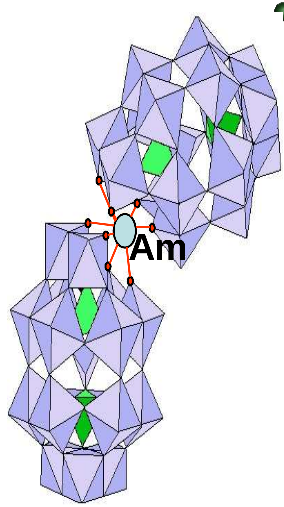
DESIGN OF NEW EXTRACTANTS : MAIN CRITERIA

- Ability to separate
  - ***Affinity***
  - ***Selectivity***
  - ***Reversibility***





- Medium effects
  - ***Solubility***
  - ***Stability / hydrolysis, radiolysis***
- Industrialization
  - ***Kinetics***
  - ***Physical properties***
  - ***Cost***



- *Secondary waste minimization*
  - **Incinerability (C, H, O, N)**

DESIGN GUIDELINES FOR EXTRACTANTS…

HARD AND SOFT ACID BASE THEORY

A : Lewis acid, electron acceptor **B : Lewis base, electron donor**

$$A + :B \rightleftharpoons A:B$$

PEARSON CLASSIFICATION : HARD / SOFT ACID/BASE (HSAB) THEORY

Hard acid or base	**Soft acid or base**
small size	*large*
high charge density	*low charge density*
hardly polarizable	*polarizable*

«HARD ACIDS INTERACT RATHER WITH HARD BASES » (ionic bounds)

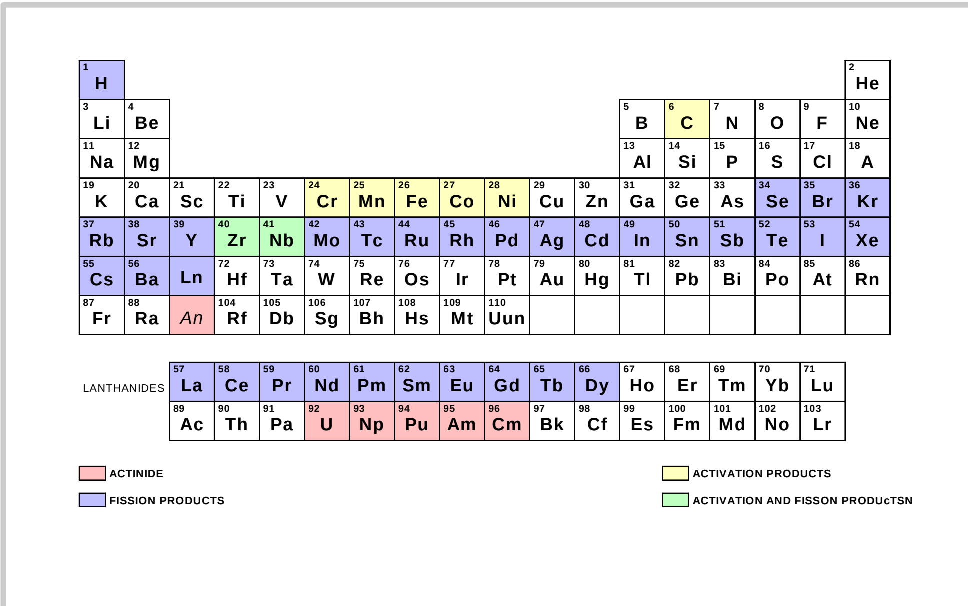
« SOFT ACIDS INTERACT RATHER WITH SOFT BASES » (covalent bounds)

Am^{3+} and Cm^{3+} SELECTIVE EXTRACTION : A KEY-ISSUE

- An^{3+} "hard cations" ⇨ "<u>hard donor" ligands</u> (O:)

  (ionic bounds)

  <u>but poor selectivity vs Ln^{3+} !</u>



Am^{3+} and Cm^{3+} SELECTIVE EXTRACTION : A KEY-ISSUE

- An^{3+} "hard cations" ⇨ "hard donor" ligands (O:)

  (ionic bounds)

  but poor selectivity vs Ln^{3+} ***!***

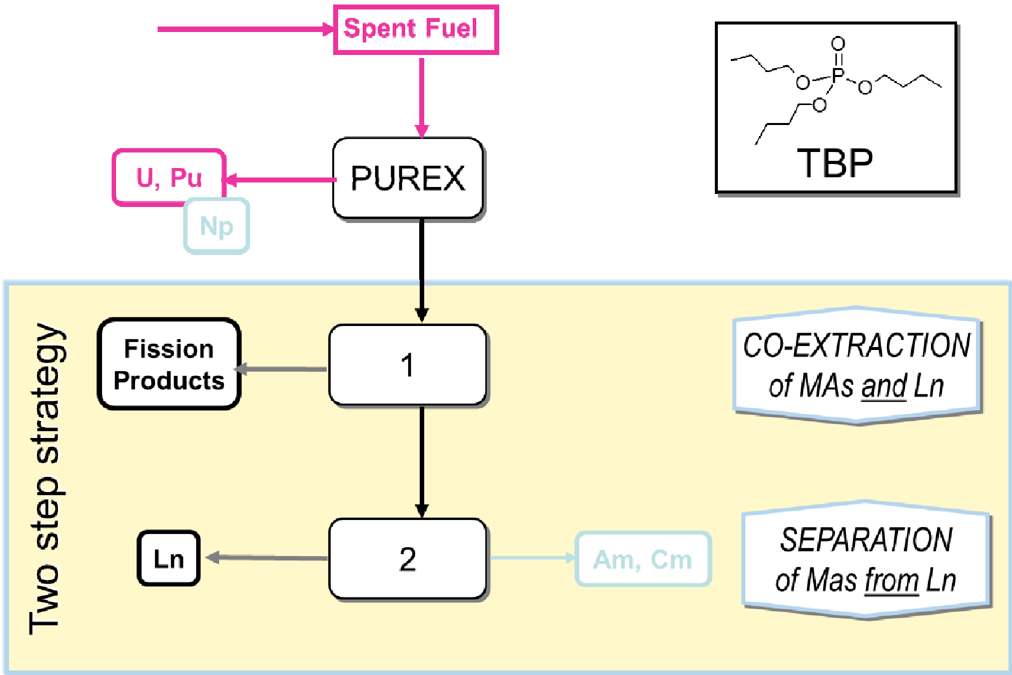
- An^{3+} "softer" than Ln^{3+} ⇨ "soft donor" ligands (N, S)

  (partly covalent bounds)

  but poor selectivity vs other FPs !

  vs H^+***!***

Am^{3+} and Cm^{3+} SELECTIVE EXTRACTION : A TWO-STEP STRATEGY?



1 - (An + Ln) co-extraction *using hard-donor ligands*

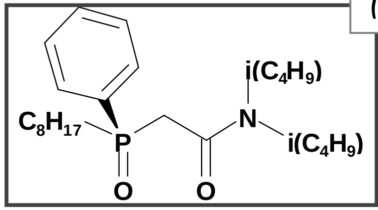
(e..g.CMPO, TRUEX process) (DIAMEX)

2 - An / Ln separation *using soft-donor ligands*

(e.g. DTPA, TALSPEAK process) (SANEX concept)

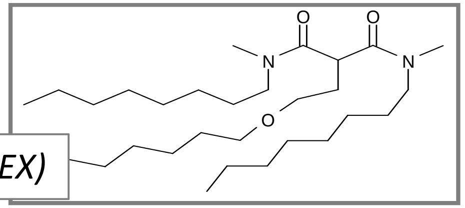
An(III) and Ln(III) CO-EXTRACTION

CMPO



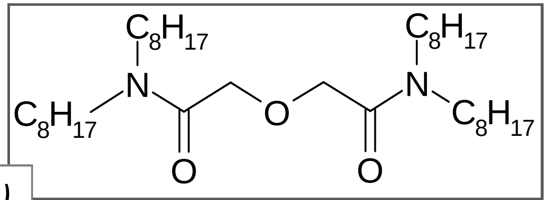
(USA – TRUEX)

- <u>BI</u>DENDATE *O –donnor* LIGANDS



(FRANCE – DIAMEX)

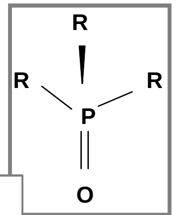
DMDOHEMA



(JAPAN- EU)

TODGA

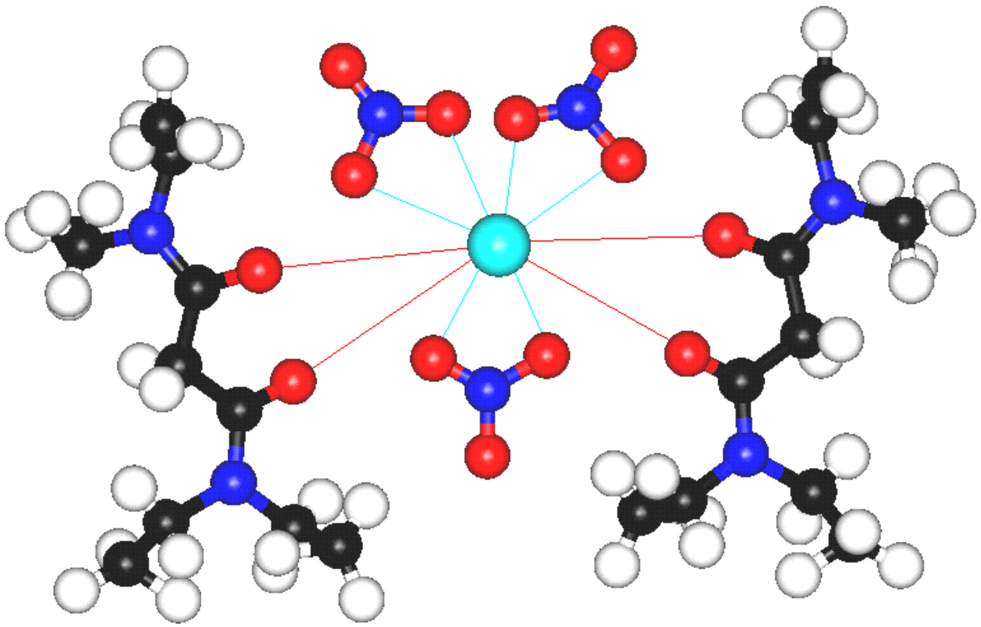
- *rather than* <u>MONO</u>DENDATE ?



(CHINA)

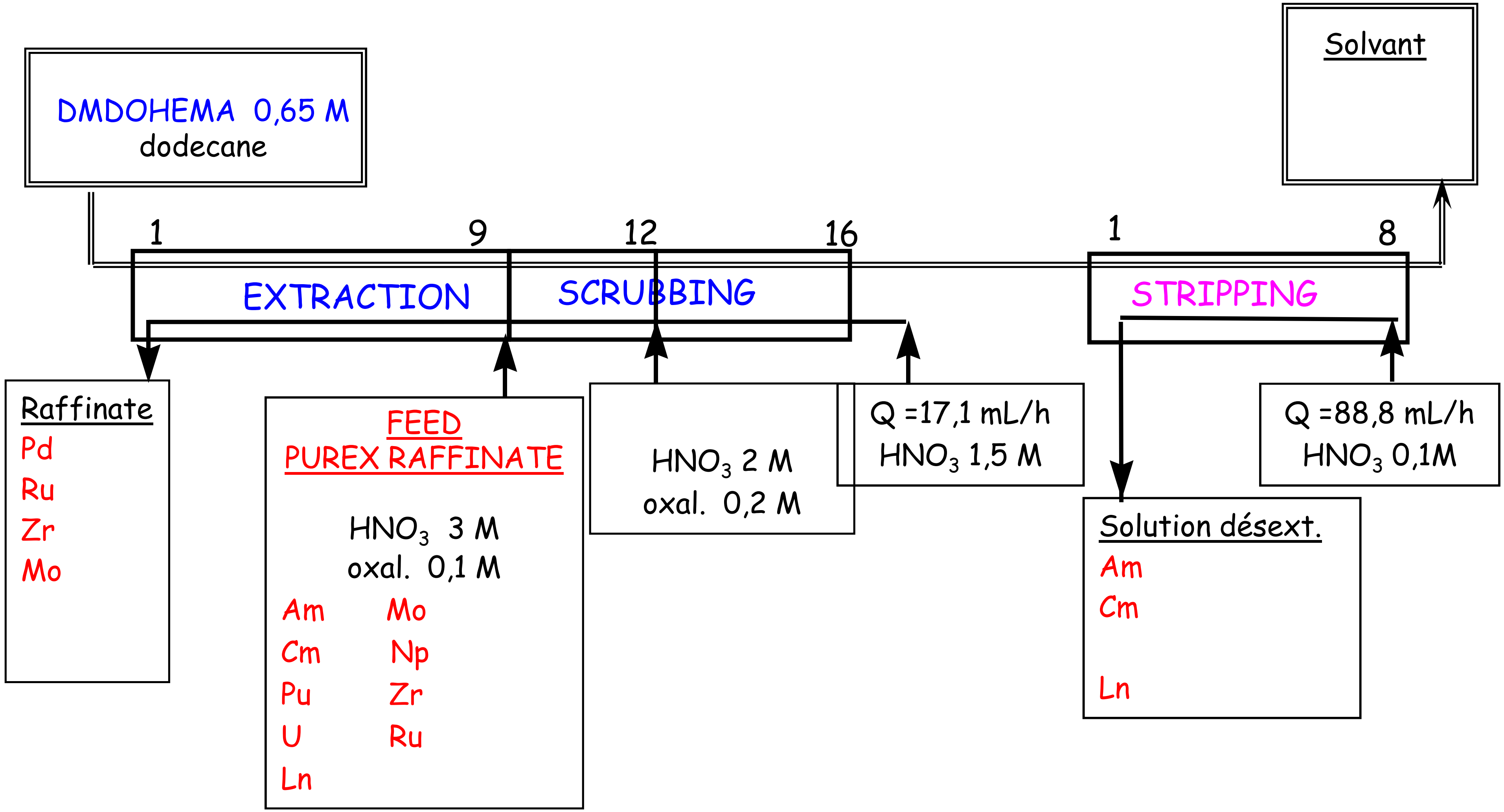
TRPO

ACTINIDE EXTRACTION BY DIAMIDE

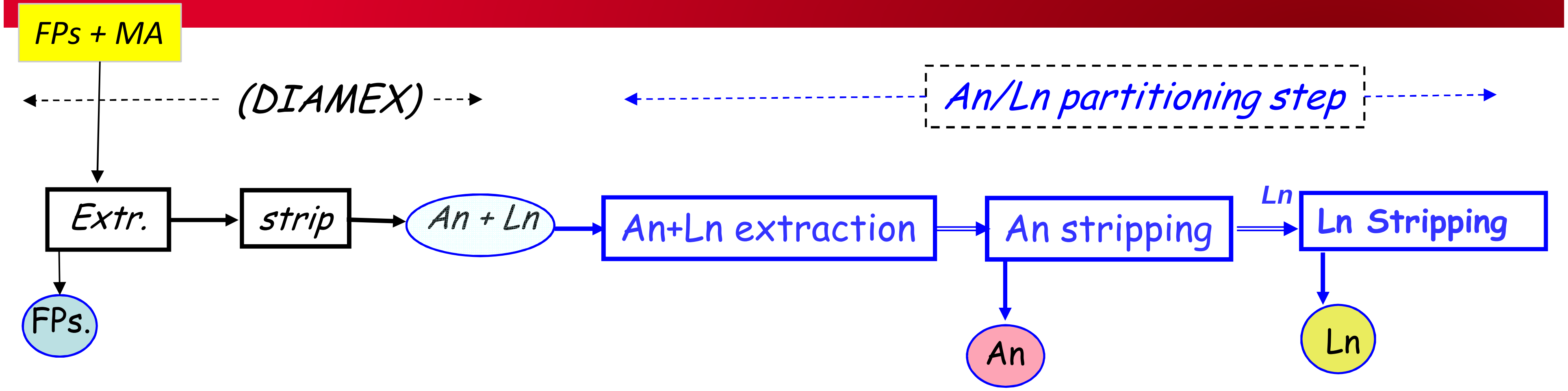


$$An^{3+} + 3NO_3^- + 2\overline{diamide} \Leftrightarrow \overline{An(NO_3)_3, 2diamide}$$

EXTRACTION USING DIAMIDE



An / Ln SEPARATION



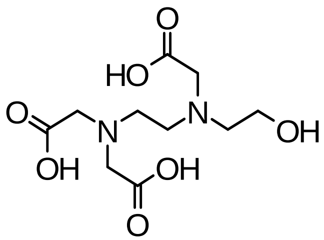
To be designed : An-selective complexant (« soft ligands)

A difficulty: efficient only if low acid content solutions…

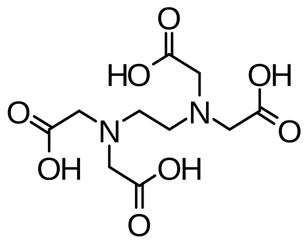
Options: adjust the nitric acid concentration in the stripping section
(but Ln must remain extracted!)

POLYAMINOPOLYCARBOXYLATES IN An / Ln SEPARATION

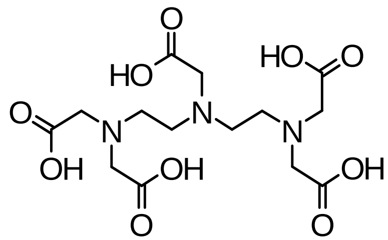
aqueous ligands, great selectivities for An vs Ln



HEDTA
N-(2-hydroxyethyl) ethylenediaminetriacetic acid



EDTA
ethylenediaminetetracetic acid

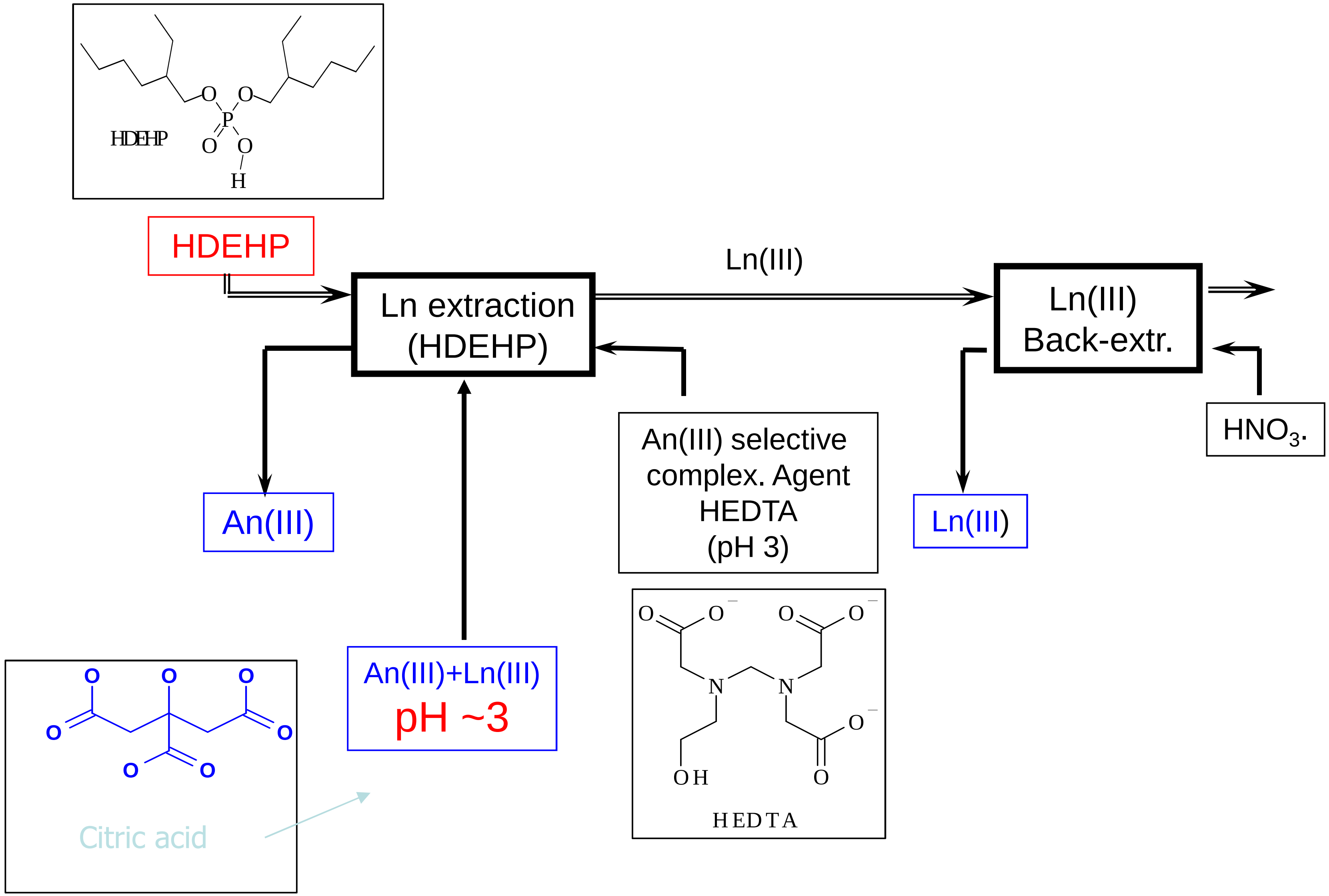


DTPA
diethylenetriaminepentacetic acid

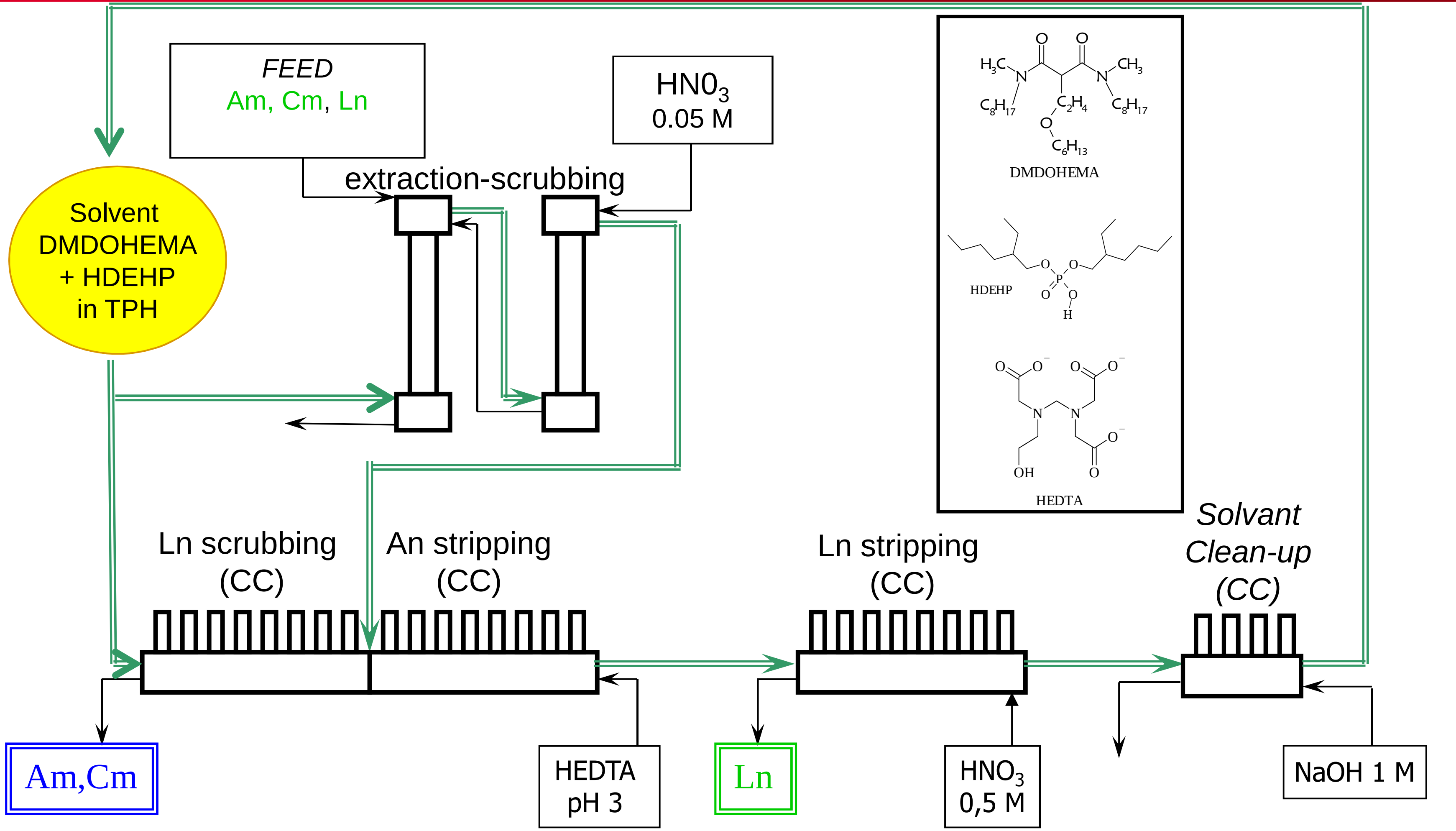
- **Selective *extraction of Ln***
  - **TALSPEAK (US – 60s, DTPA)**
- **Selective *back extraction of An***
  - **Reverse TALSPEAK (variant of TALSPEAK)**
  - **SETFICS (Japon – 98, DTPA)**
  - **DIAMEX-SANEX (France – 99, HEDTA)**

TALSPEAK PROCESS

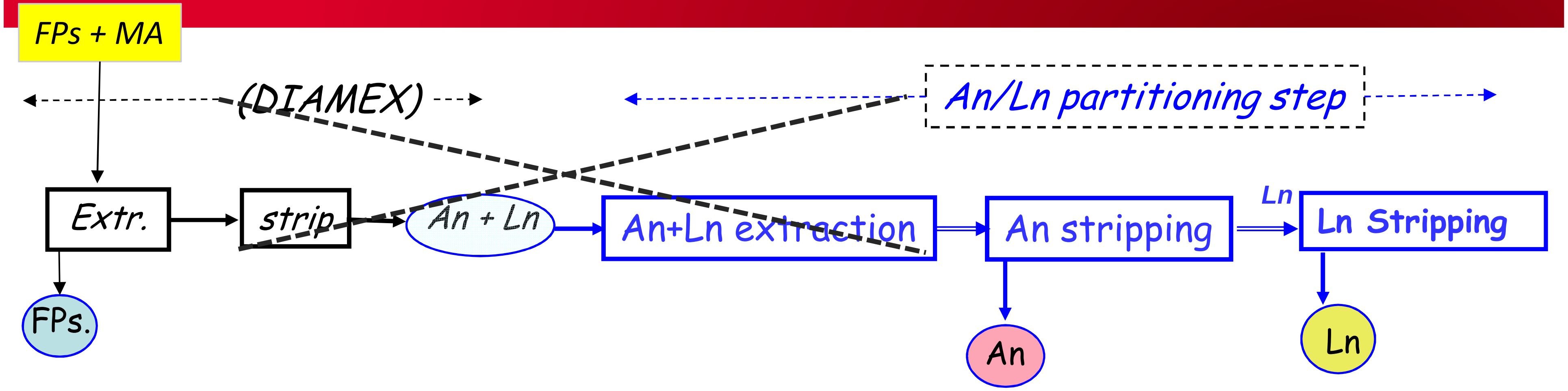
(An/Ln separation step, after TRUEX)



An/Ln PARTITIONING :*EXTRACTANTS MIXTURE ?*

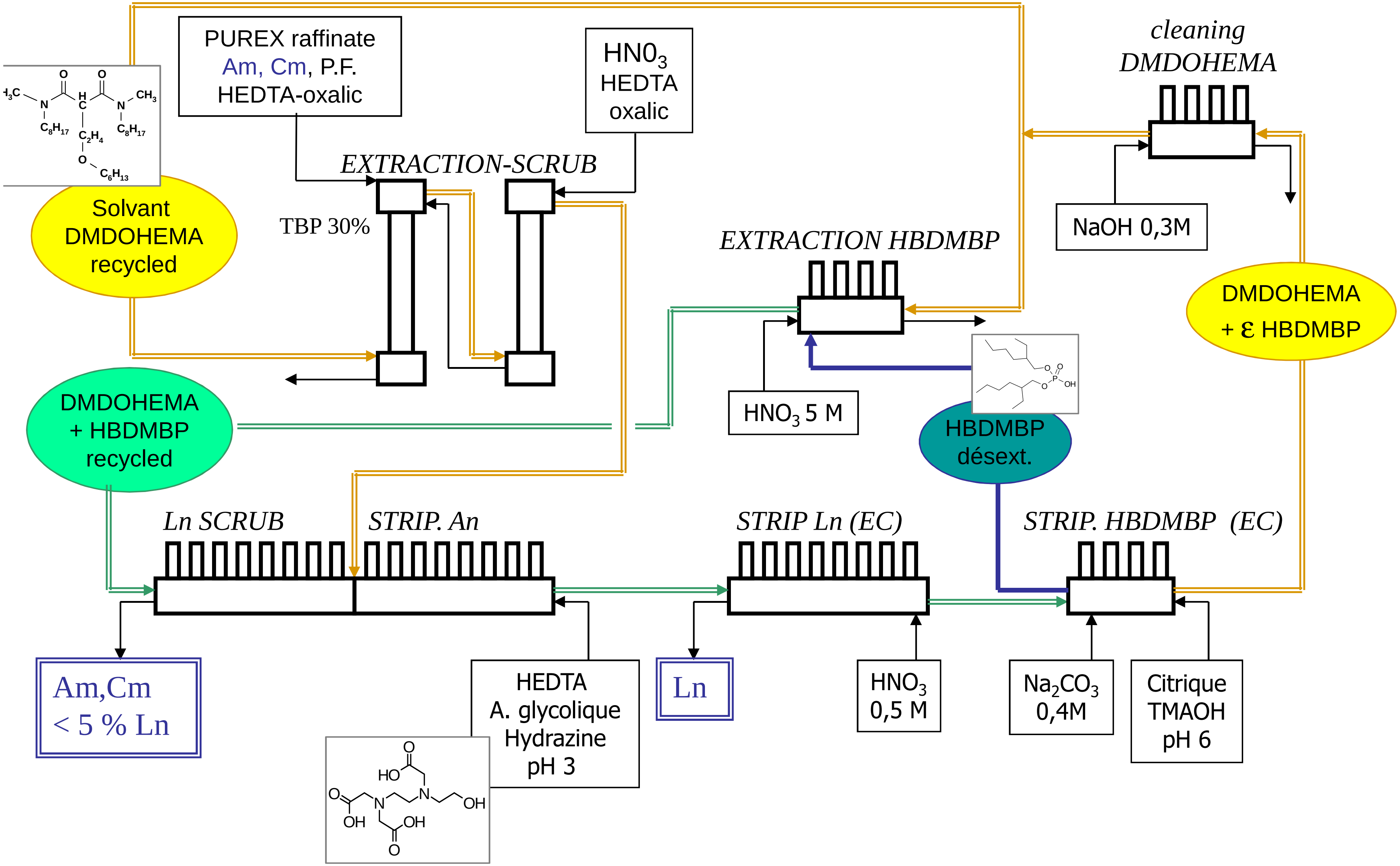


An / Ln SEPARATION

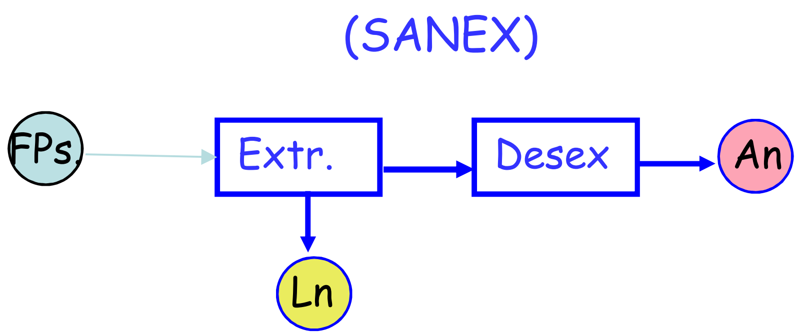


A single cycle after PUREX ?

A DIAMEX- SANEX *single cycle* FLOWSHEET ?



An / Ln SEPARATION



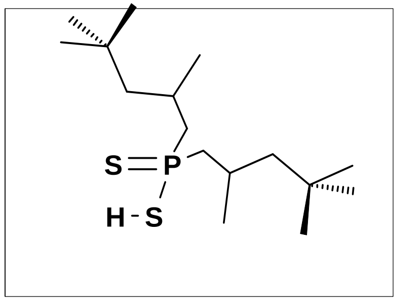
To be designed : An-selective extractant (« soft ligands » based)

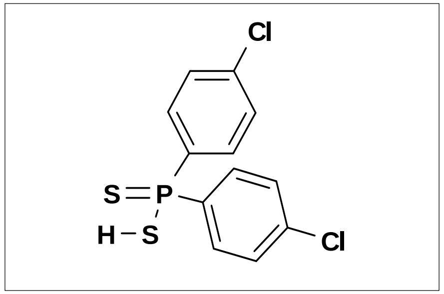
A difficulty: efficient only if low acid content solutions…

Options: adjust the nitric acid concentration in the feed ?
extractant design?

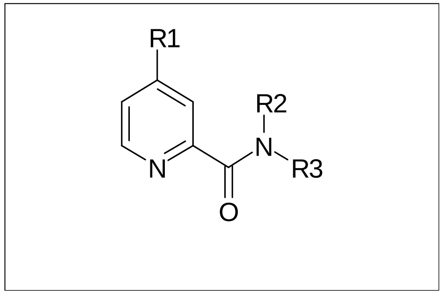
An / Ln SEPARATION : MANY MOLECULES TESTED

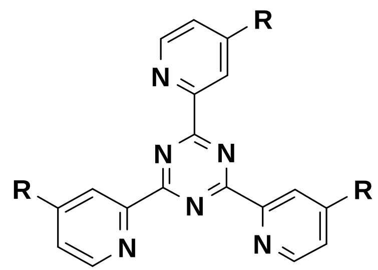
- Cation exchangers



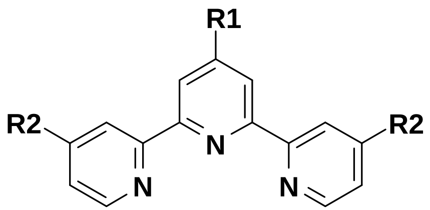


- Neutral extractants



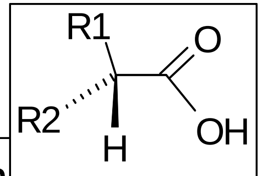


R-Tripyridyltriazines (*R*-TPTZ)



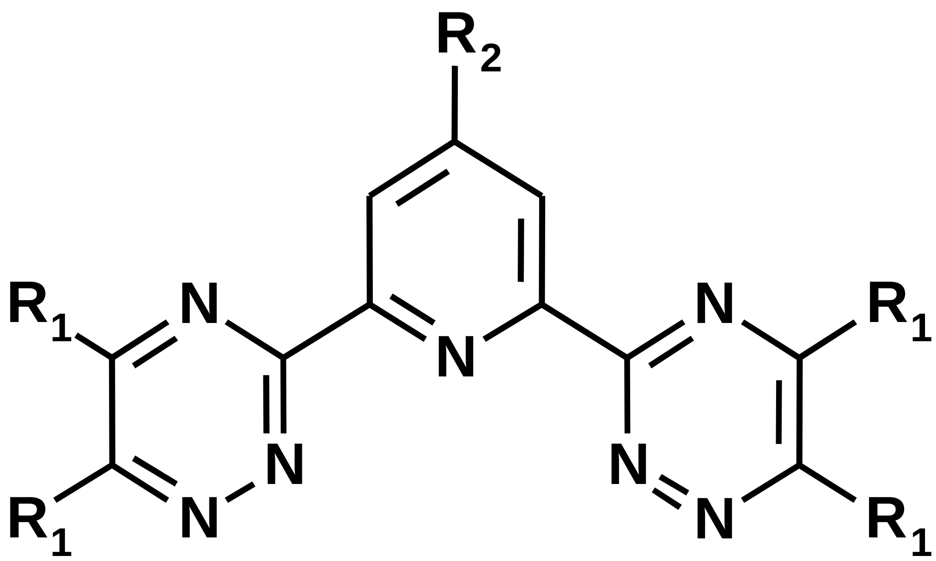
R-Terpyridines (*R*-Tpy)

with synergistic (lipophilic) counter ions?



Bis-Triazinyl-Pyridines (BTP*s*)

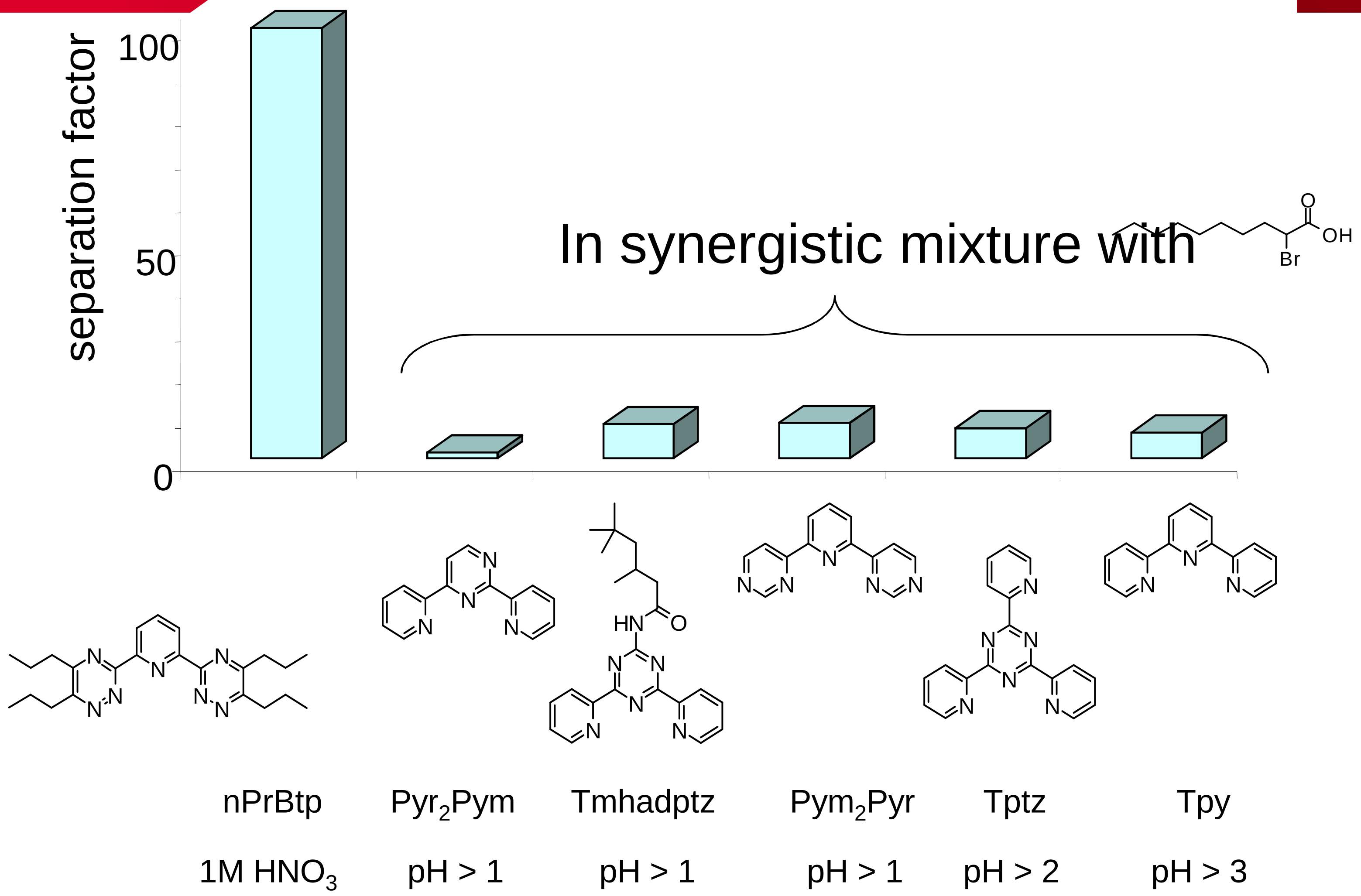
discovered by Dr. Z. KOLARIK in 1998 (NEWPART project)



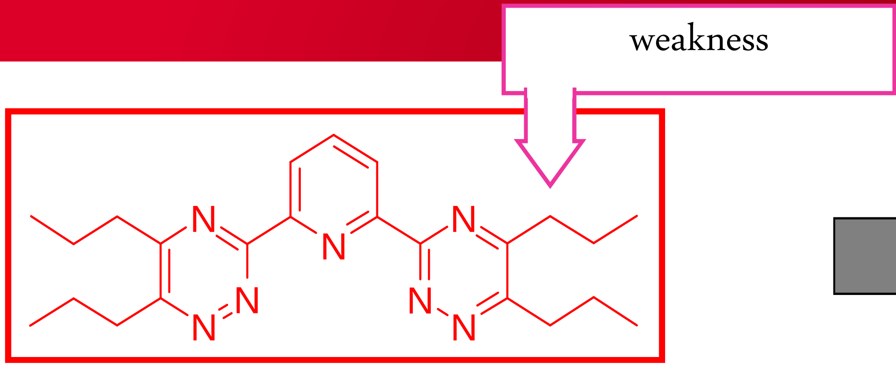
R_1 = H, Me, *n*-Propyl, *i*-Pr, *n*-Butyl, *i*-Bu, (1-Me)Pr, *neo*-Pe, *i*-Pe, ϕ, ϕ-OMe, Phen, Pyr

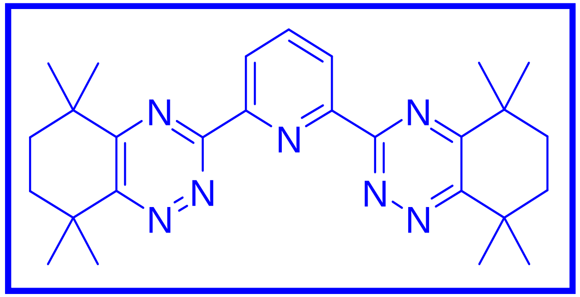
R_2 = H, *i*-Nonyl

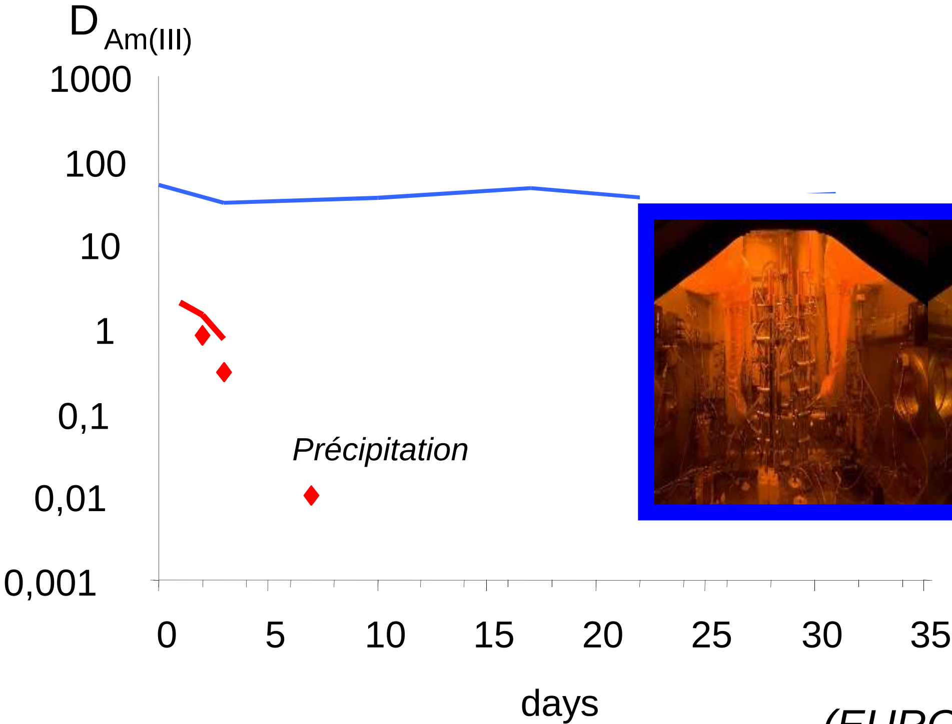
An(III) / Ln(III) SEPARATION BY POLYAZINES

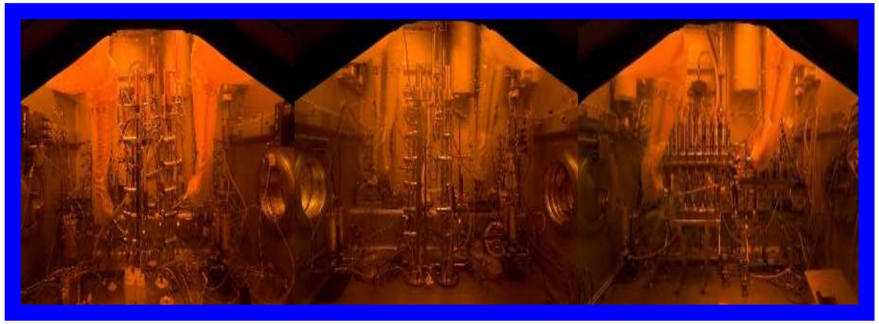


EXTRACTANT's STABILITY



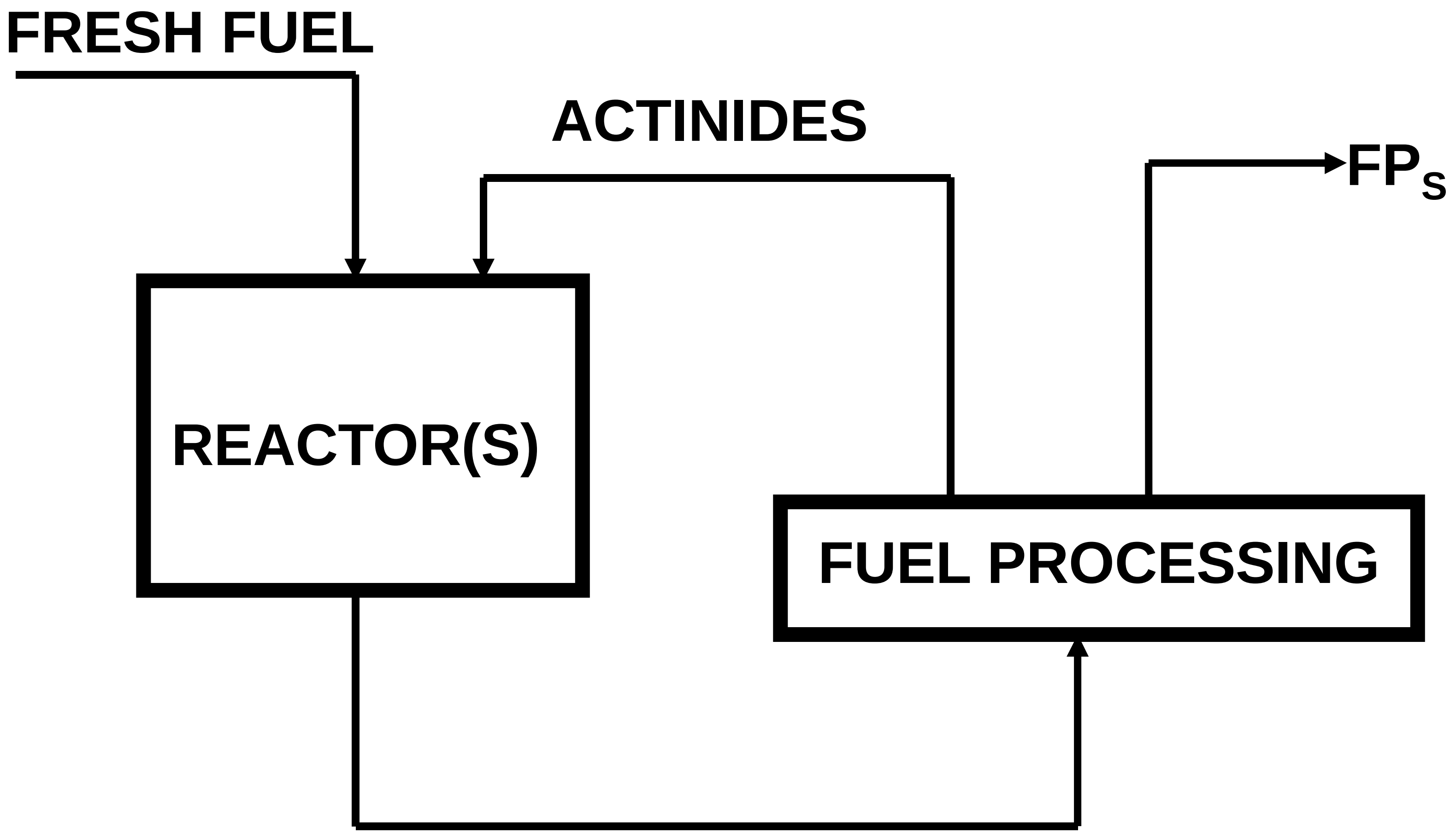




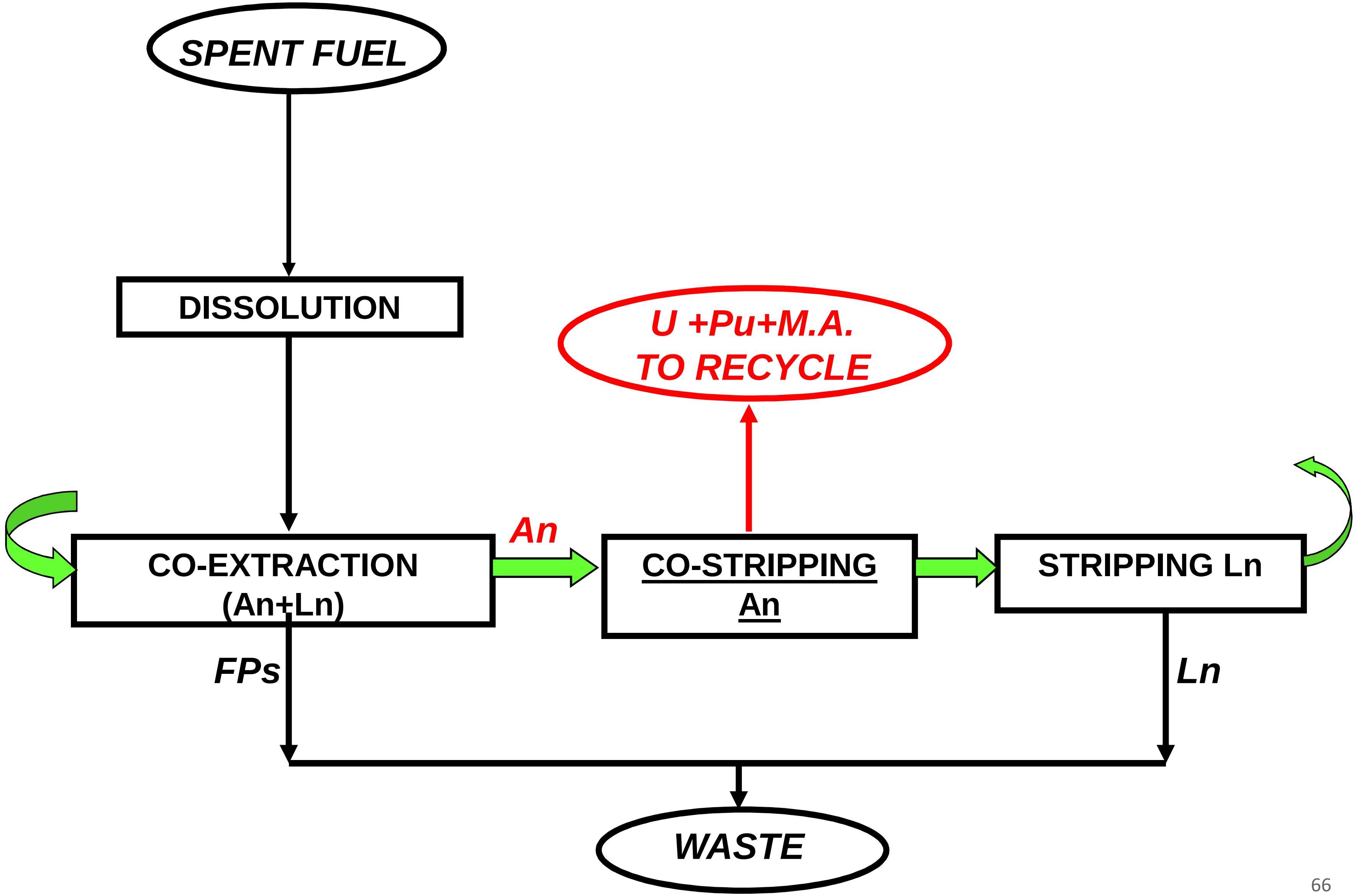


(EUROPART project, PCRD 5th)

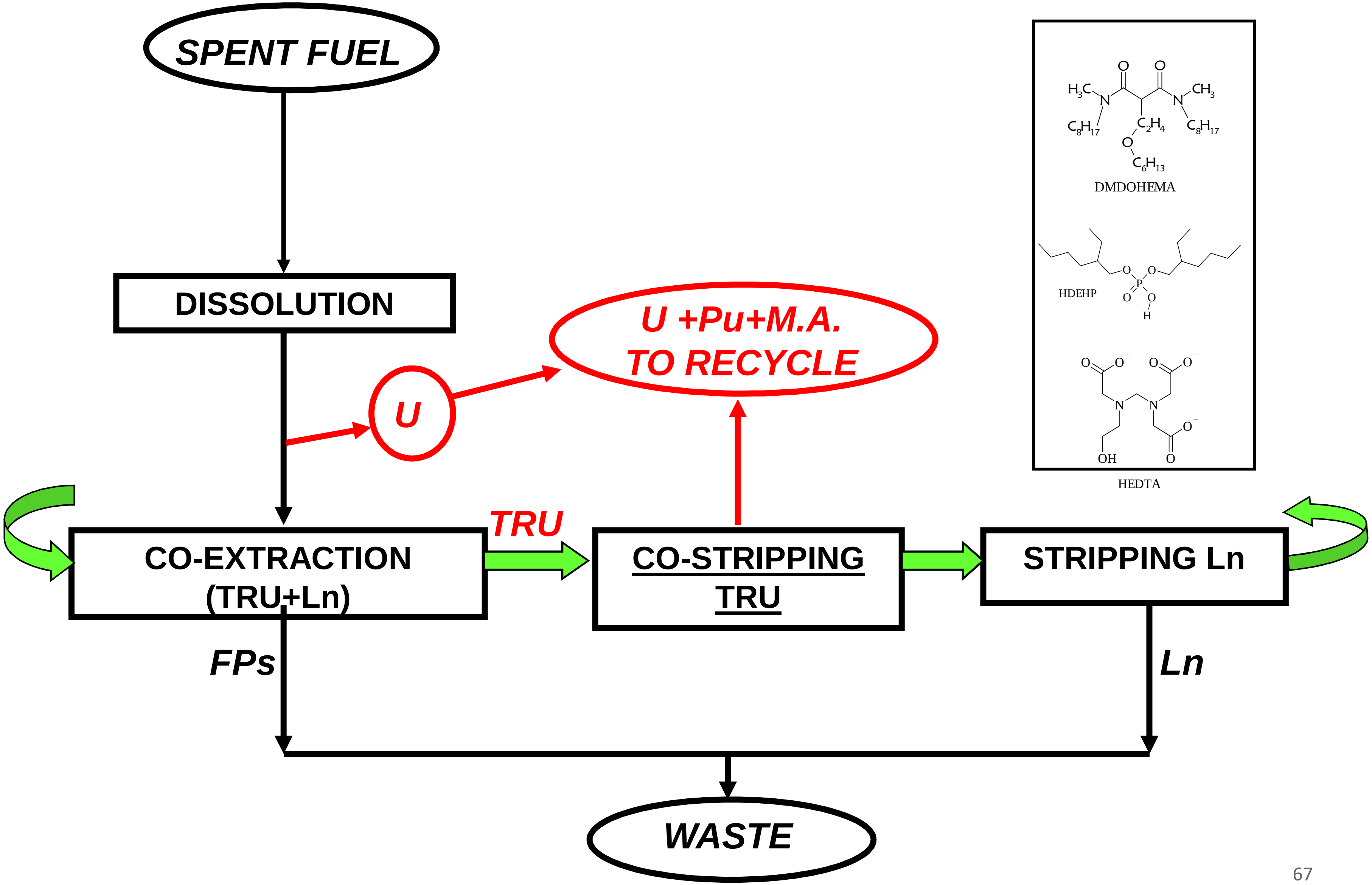
ALL-ACTINIDE RECYCLE ?



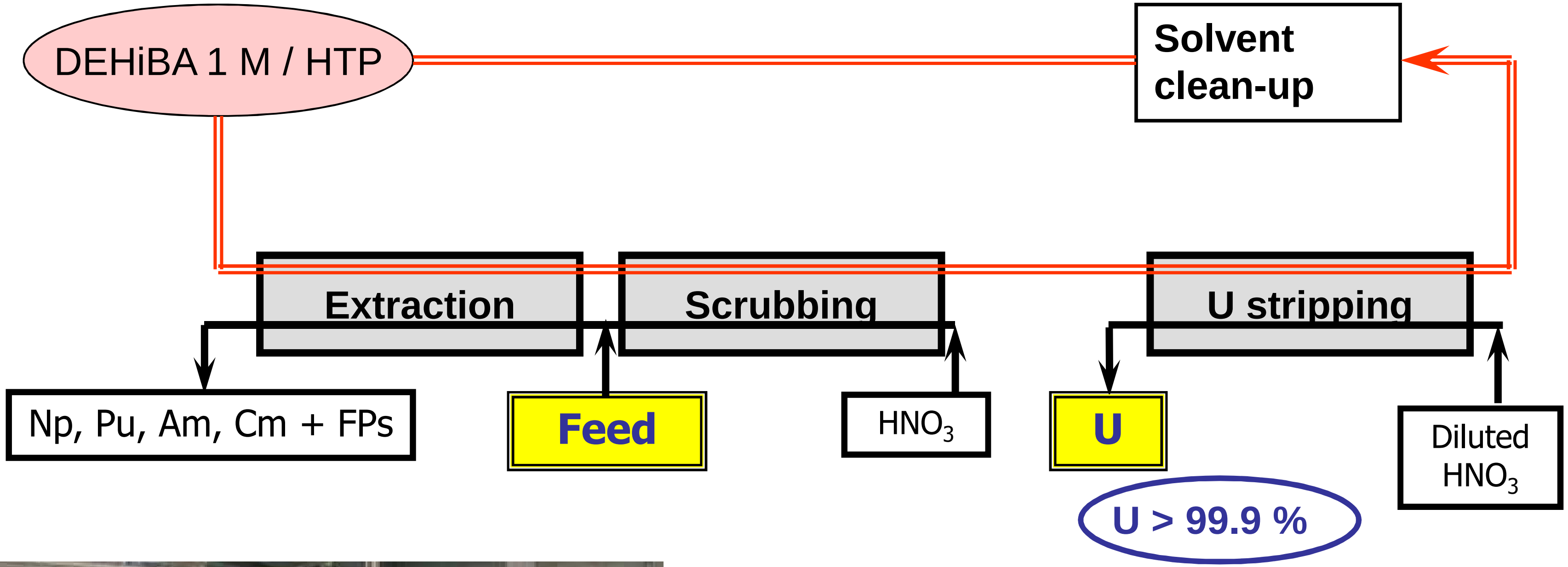
GROUPED ACTINIDE EXTRACTION *(« GANEX »)*

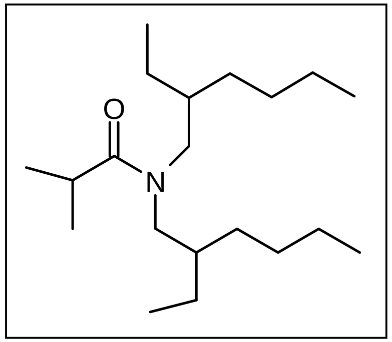


GROUPED ACTINIDE EXTRACTION (« *GANEX* »)

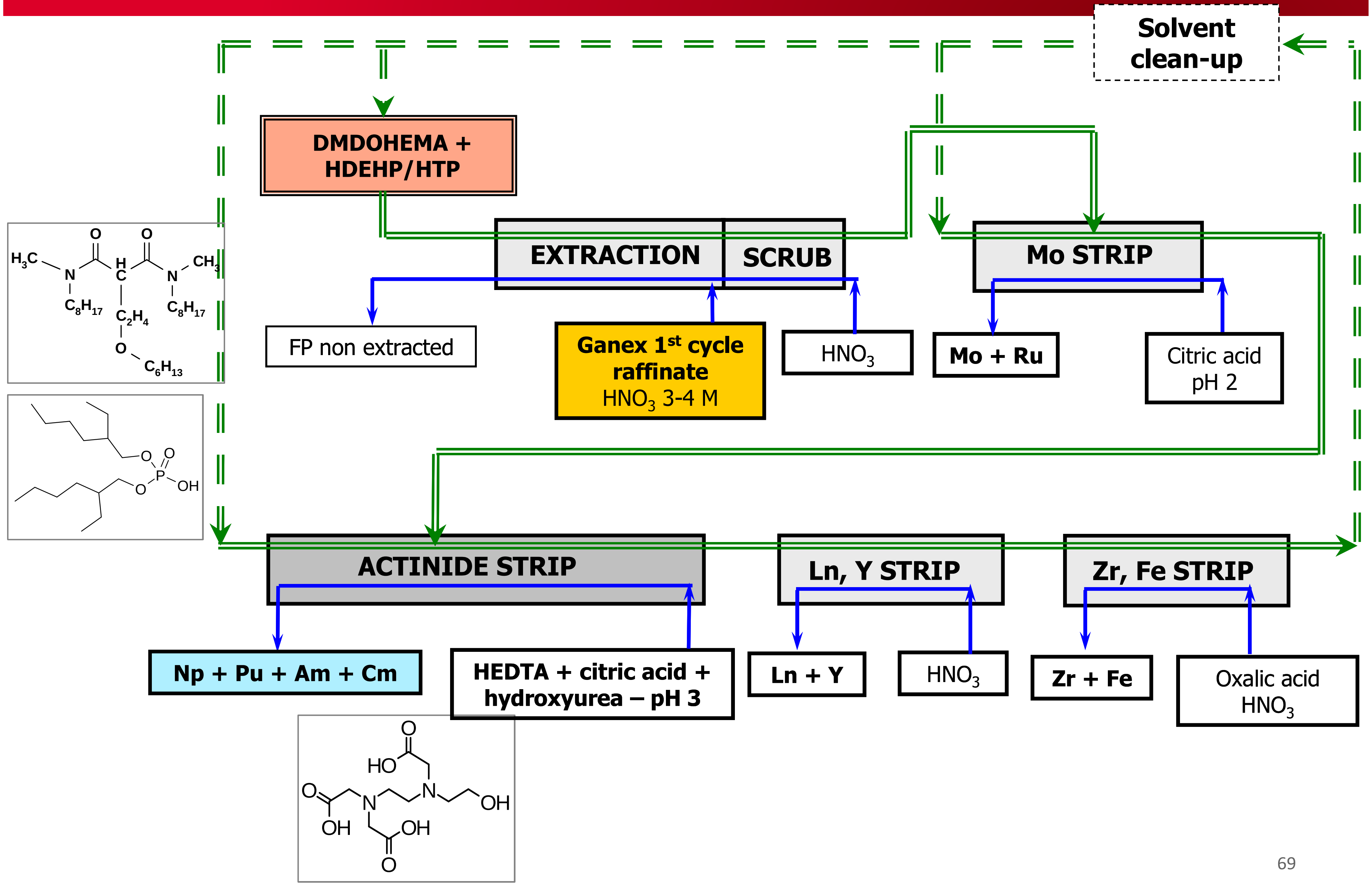


GANEX 1st step *(U extraction)* (Monoamide)



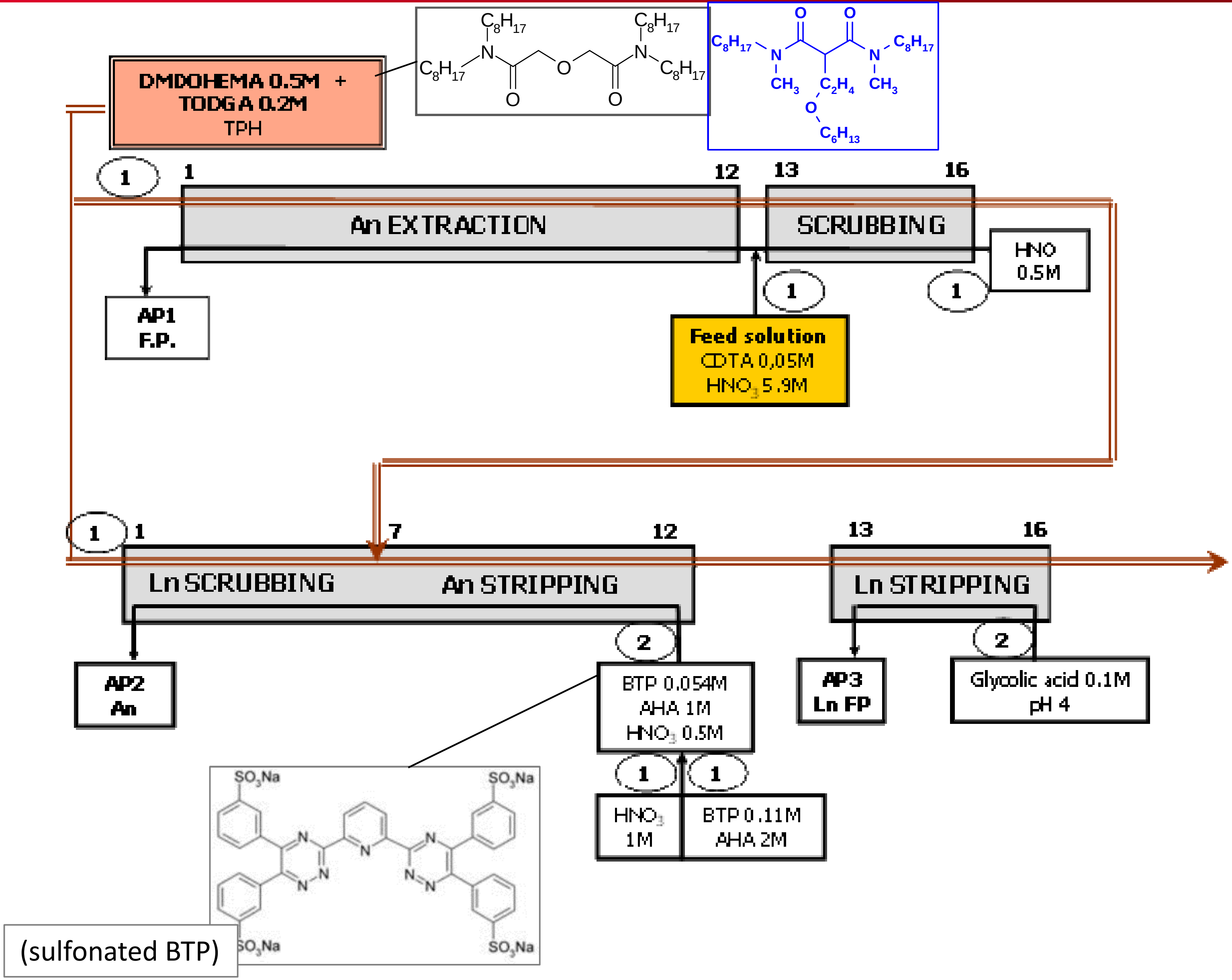


GANEX 2nd step (TRU extraction) (=DIAMEX-SANEX Process)



« EUROGANEX »

(SACCESS &GENIORS EU projects)



DE LA RECHERCHE À L'INDUSTRIE

cea

NUCLEAR FUEL CYCLES

6-4 AND FOR OTHER FUELS….

Bernard BOULLIS
bernard.boullis@cea.fr

www.cea.fr

Joliot Curie School, St Pierre d'Oleron, 22-27 September, 2019

CARBIDE FUELS PROCESSING

WHY CARBIDE ? (HN density,thermal conductivity,…)

CARBIDE FUEL : U (Pu) C , but alsoUC2, U2C3,…

CARBIDE FUEL DISSOLUTION:

- UC + 6 HNO3 ⇨ UO2(NO3)2 + CO2 + 3 H2O + 3 NO + NO2
- PuC + 8 HNO3 ⇨ Pu(NO3)4 + CO2 + 4 H2O + 2 NO + 2 NO2

(rather high kinetics)

SOME ISSUES FOR « PUREX-CARBIDE »:

-**Organic coumpounds (carboxylic acids,…) at the dissolution step [and behavior in downstream process steps]**

-**Pyrophoricity risk ?**

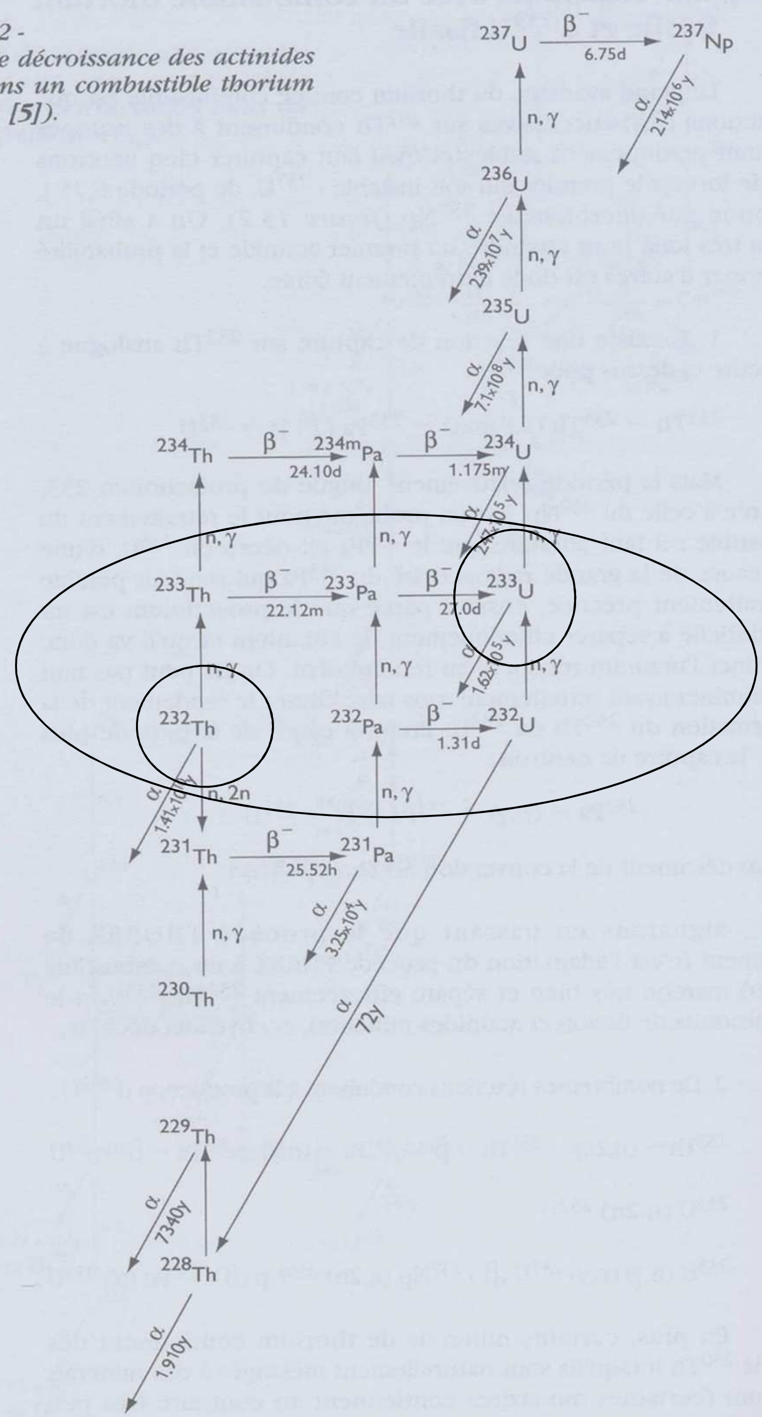
^{232}Th / ^{233}U REACTORS : THE THORIUM FUEL CYCLE

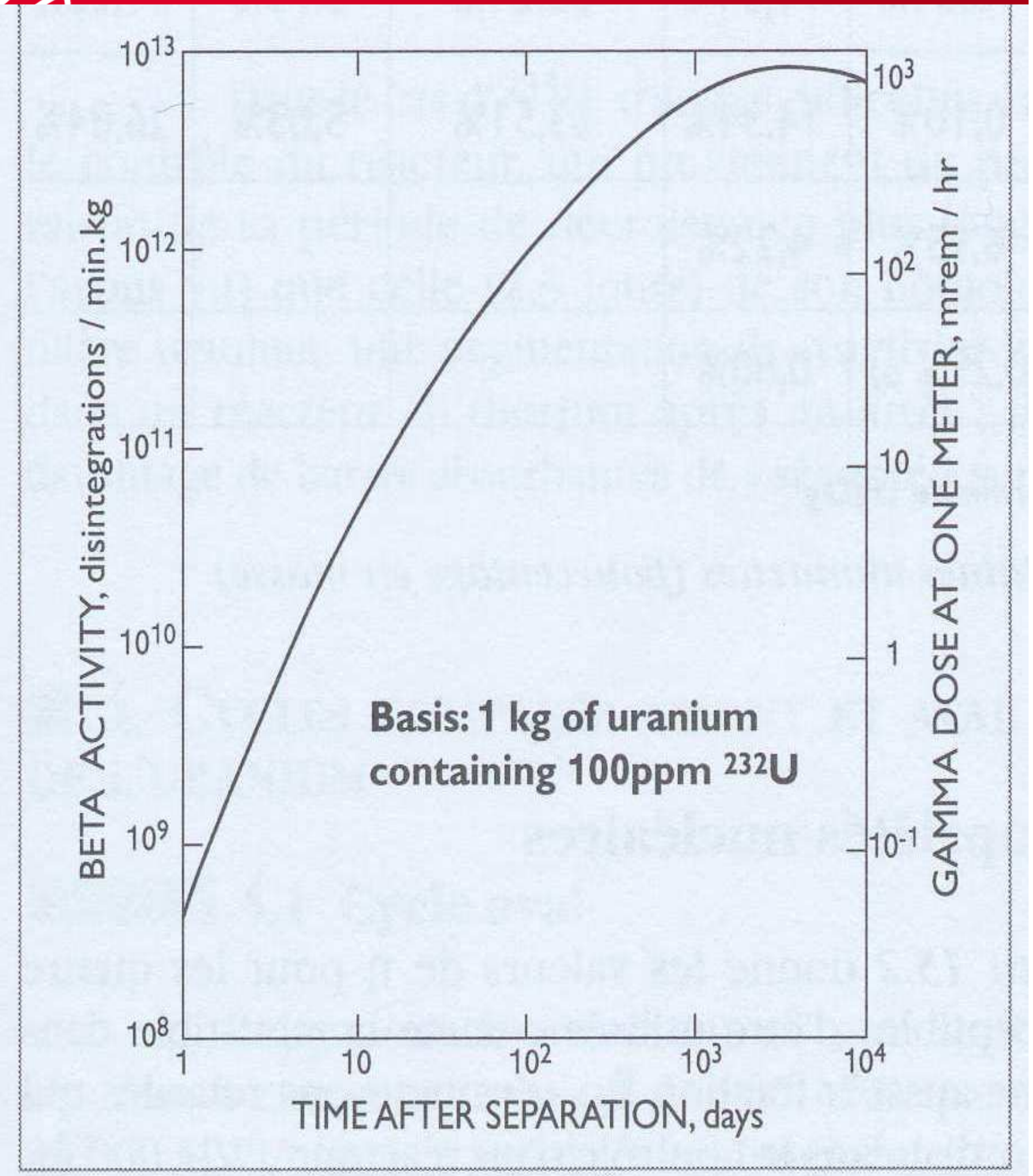
- **^{233}U fissile, but not natural**
- ***^{232}Th reserves:* 3 times uranium ones**
- ***^{232}Th « fertile »* : <u>^{233}Pa</u> , decay: <u>^{233}U</u>;**
- ***^{233}U : high multiplication factor***
- **Necessity *of prior cycle with another fissile* nuclei to fertilize ^{232}Th**

Nuclide	σa (barns)	σ*f* (barns)
^{1}H	0.332	0
^{2}H	0.00051	0
^{10}B	3844	0
^{11}B	0.0055	0
^{232}Th	**7.40**	**0**
^{231}Pa	227	0.01
^{233}Pa	41.5	0
^{232}U	149.7	77.1
^{233}U	571.1	**525.2**
^{234}U	103.5	0.46
^{235}U	**681.5**	**582.6**
^{236}U	5.21	0.047
^{238}U	**2.719**	**0.000012**
^{237}Np	181.0	0.018
^{238}Pu	563.4	17.3
^{239}Pu	**1017.7**	**747.3**
^{240}Pu	288.8	0.068
^{241}Pu	**1375.3**	**1012.3**
^{242}Pu	18.5	0.014
^{244}Pu	1.83	0
^{241}Am	618	3.2
^{242m}Am	8696	6885
^{243}Am	76	0.050
^{242}Cm	21.5	5.0
^{243}Cm	545	432
^{244}Cm	15.5	1.0
^{245}Cm	**2480**	**2131**

Nuclide	Fast neutrons	Thermal neutrons
Uranium 233	**2.3**	**2.3**
Uranium 235	**1.9**	**2.1**
Plutonium 239	**2.3**	**2.1**

Figure 15.2 - Chaînes de décroissance des actinides formés dans un combustible thorium (référence [5]).




10^13
10^12
10^11
10^10
10^9
10^8
BETA ACTIVITY, disintegrations / min.kg
10^3
10^2
10
1
10^-1
GAMMA DOSE AT ONE METER, mrem / hr
Basis: 1 kg of uranium
containing 100ppm 232U
1
10
10^2
10^3
10^4
TIME AFTER SEPARATION, days

THOREX process specific issues:
-*dissolution*
-*no redox for separation*

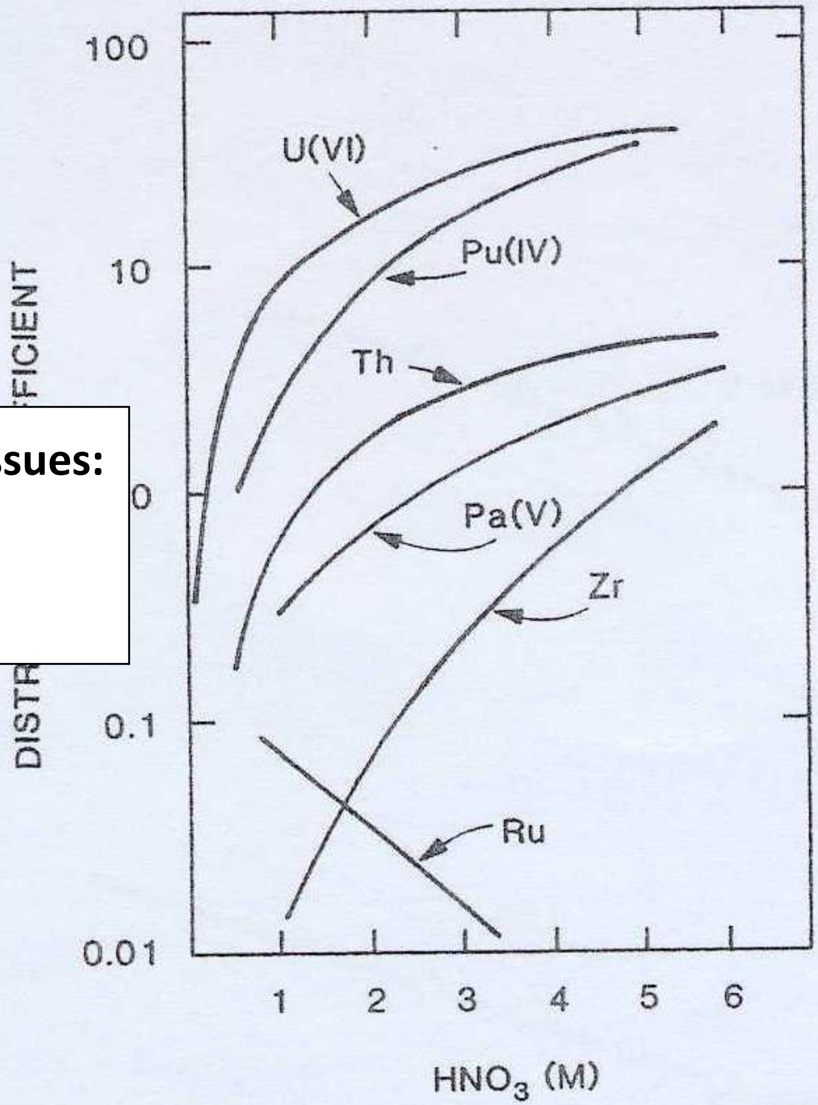


FIGURE 5. Distribution of thorium and key actinides and fission products between 30% TBP solutions and aqueous HNO_3. (Drawn from data presented in Refe ences 6 and 17 to 19.)

DE LA RECHERCHE À L'INDUSTRIE

NUCLEAR FUEL CYCLES

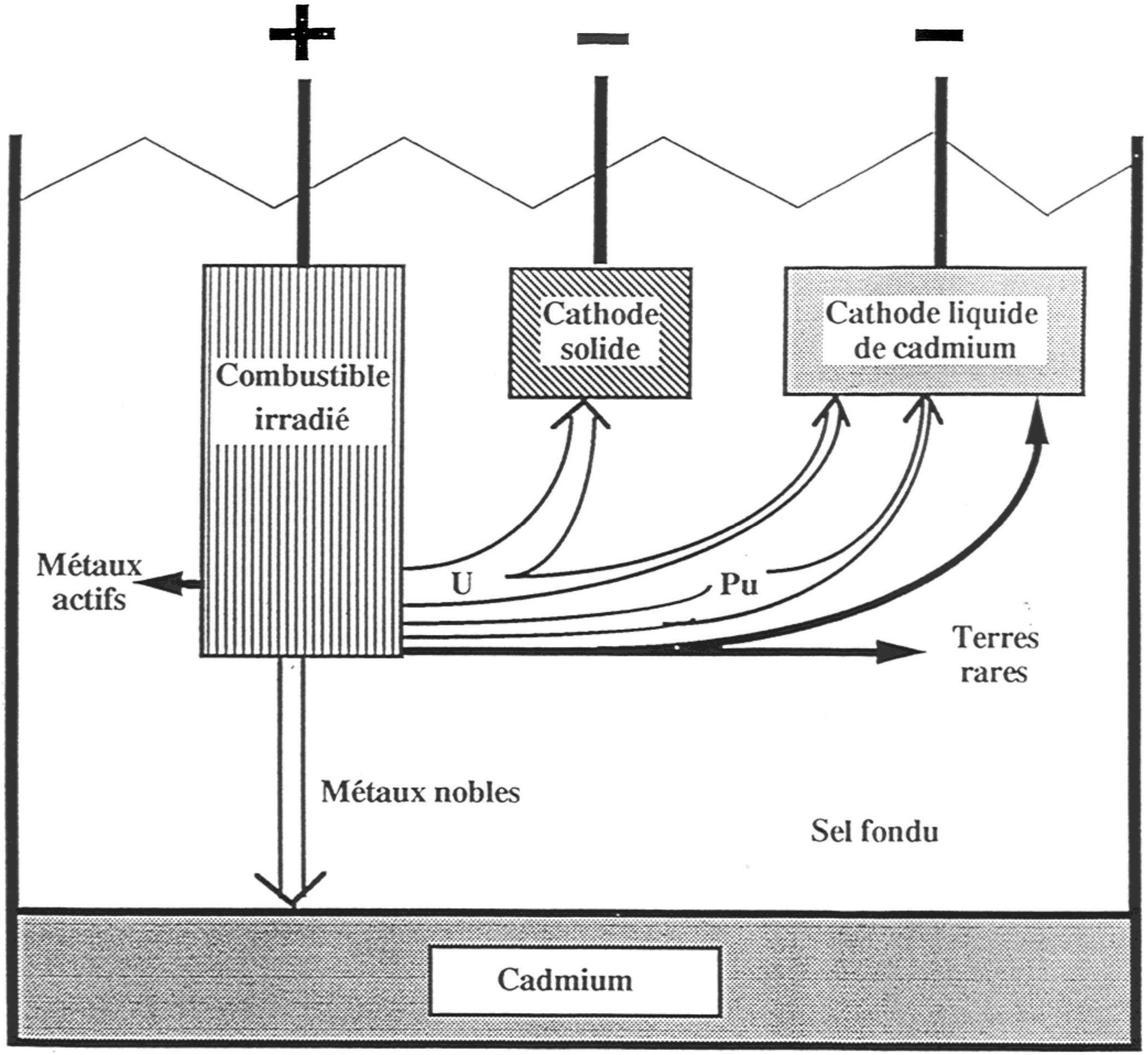
6 –5 PYRO-PROCESSES

Bernard BOULLIS
bernard.boullis@cea.fr

www.cea.fr

Joliot Curie School, St Pierre d'Oleron, 22-27 September, 2019

PYRO-PROCESSES :
ARGONNE PILOT-SCALE EXPERIENCE



PYRO-PROCESSES

- **The challenge** : to distribute selectively the actinides (An) and the fission products (FPs) :
  - ***between a salt, and a metal (solid or liquid)***
  - ***electrochemical or extraction processes***

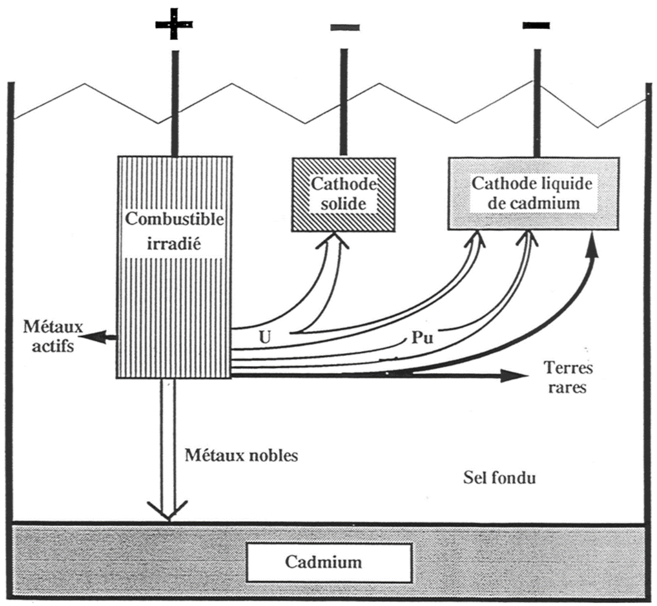
- **Scientific challenge comes down** :
  - ***to select salt phase*** *for which the gap between free energies of formation of An and FP compounds is the largest one*
  - ***to select metallic phase*** *having the highest affinity for An compounds*

- **from lab-scale to demonstrative experiments on genuine spent fuel samples**

PYROPROCESSES : *WHY ?*

<u>PRESUMED ADVANTAGES</u> :

(1) ***Low radiolytical effects***
(2) Solvating properties
(3) Compactness (in the principle)
(4) Extended range of electro-activity
(5) No neutron moderator (criticality risk)
(6) Moten salts reactors (obviously…)
(7) …



<u>UNCERTAINTIES, POTENTIAL DRAWBACKS</u> :

(1) Recovery & purification yields ?
(2) Minor actinide recovery ?
(3) Operating the technology (corrosion, technological waste,…)
(4) Oxide fuels?