The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

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Joint ICTP/IAEA School on Physics and Technology of Fast Reactors Systems

9 - 20 November 2009

Advanced partitioning of MOX fuels by aqueous route (1)

Dominique Warin

CEA / Nuclear Energy Division
Radiochemistry and Processes Department
Marcoule
France

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CEA/Nuclear Energy Directorate missions

A WORLD CLASS LABORATORY FOR SUSTAINABLE NUCLEAR FISSION ENERGY DEVELOPMENT

REACTORS

- R and D in support of existing LW Reactors (material ageing, fuels, power plant life time, safety,...)
- R and D for innovative future GEN IV Fast Neutron Reactors
- Basic nuclear science and technology studies, materials
- Thermal and fast neutron Test Reactors
- Simulation program

FUEL CYCLE

- R and D in support of existing reprocessing plants (Areva La Hague, Sellafield, Rokkasho Mura,..) and for future recycling plants
- R and D for nuclear waste management (1991 and 2006 French Acts)
- Hot radioactive facilities

INTERNATIONAL COLLABORATIONS : Europe (SNE-TP), USA (GNEP), Japan, China,…

CEA/ Nuclear Energy Directorate organization

CADARACHE

➲ Nuclear reactors
- Core design, neutronics
- Fuels
- Nuclear technology
- Test reactors for PWRs, (RJH 2014)

MARCOULE

➲ Nuclear fuel cycle
- Radiochemistry, reprocessing
- Fuel cycle technology
- Long term waste management
- Na fast test reactor (Phénix, ASTRID 2020)
- Decommissioning

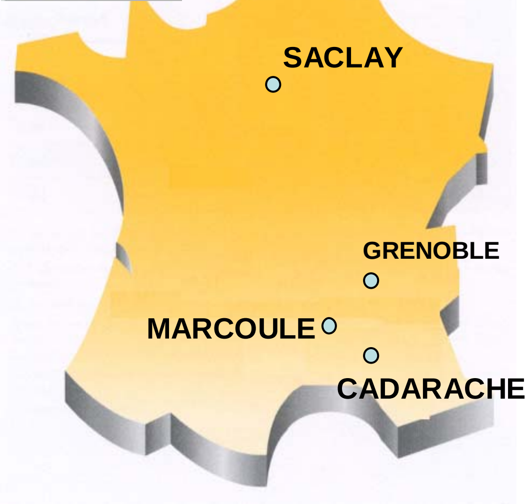
DEN

SACLAY

➲ Nuclear materials
➲ Simulation, codes
➲ Nuclear physics and chemistry

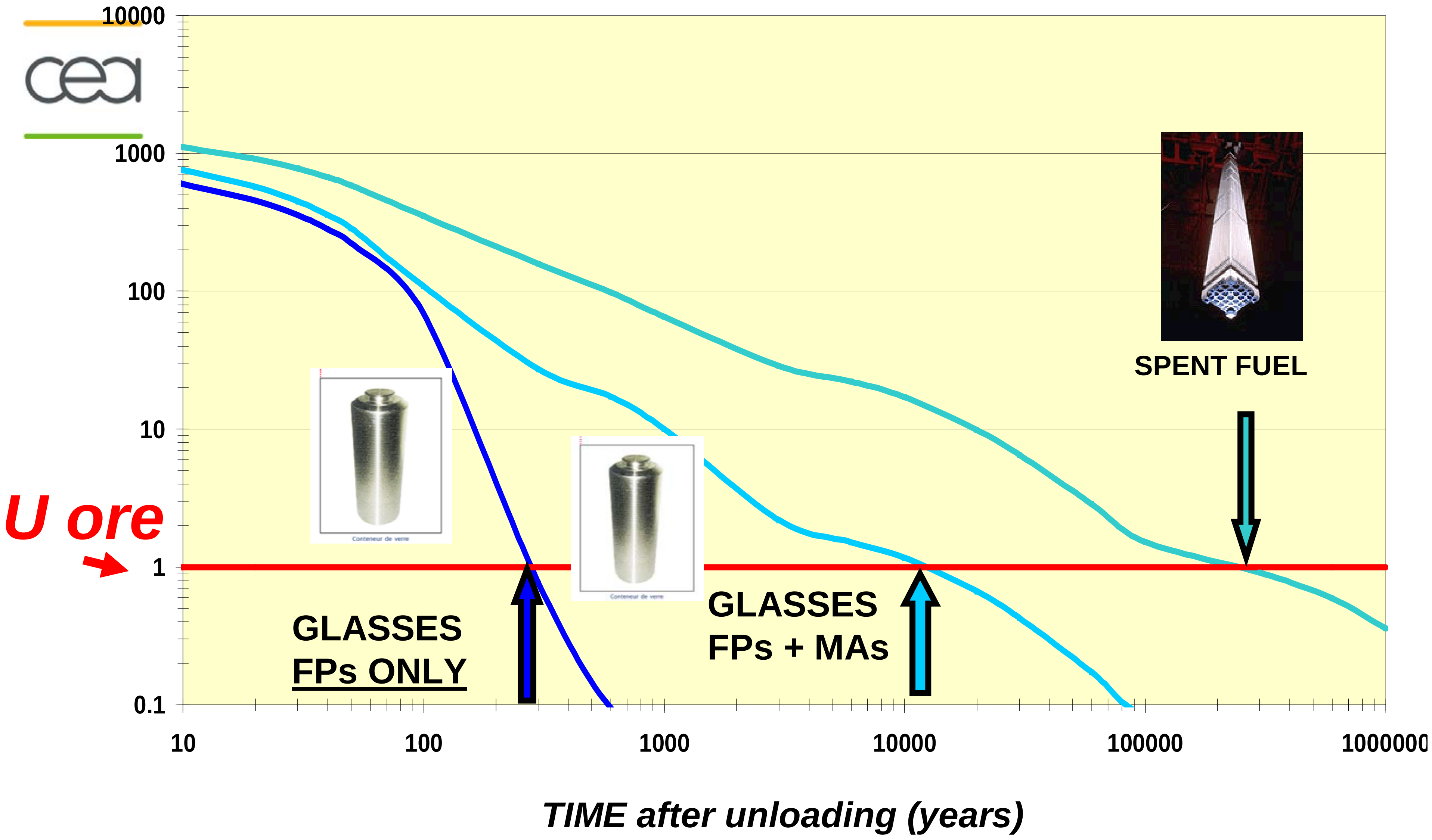
GRENOBLE

➲ Thermo hydraulics

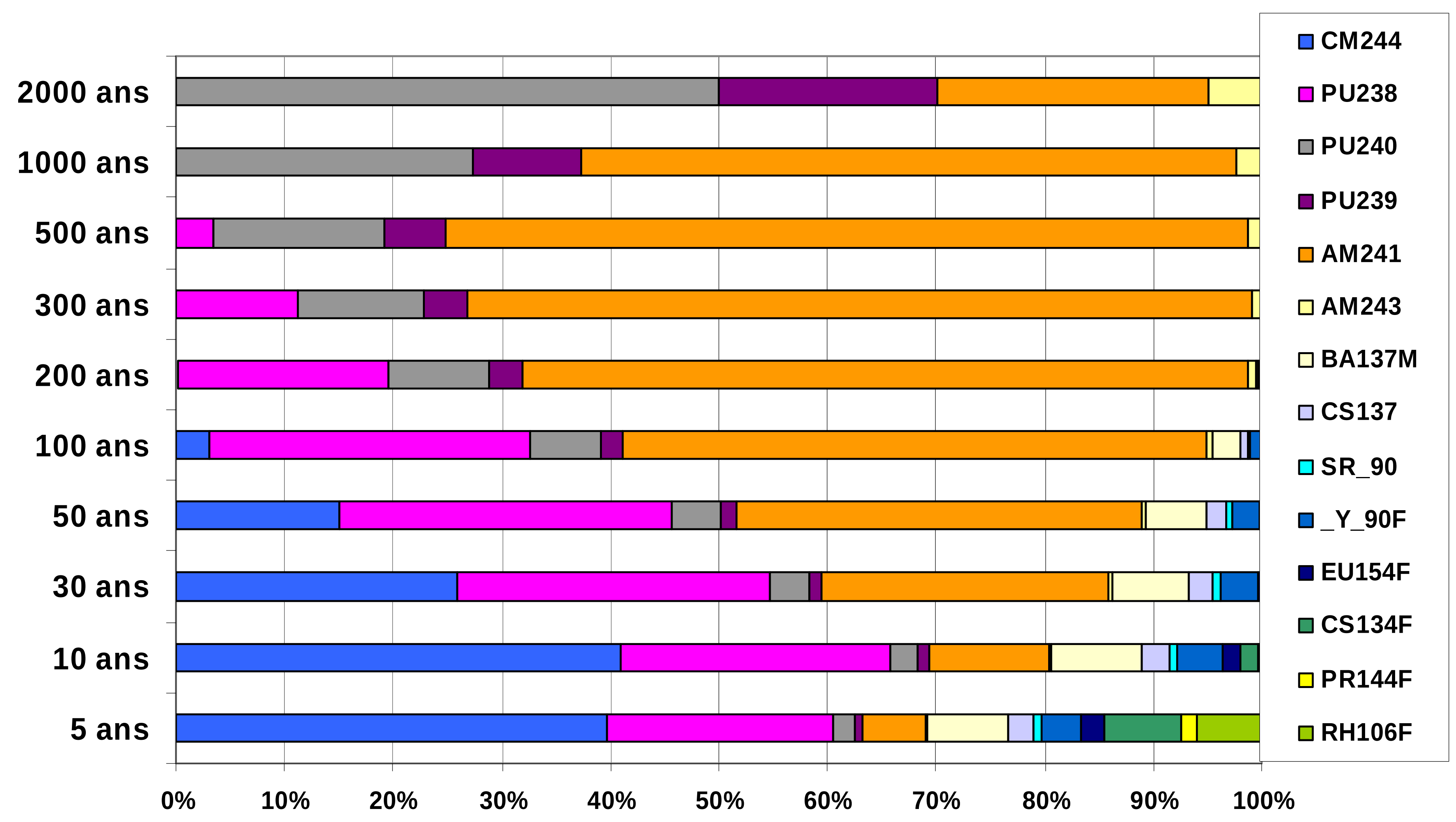


4500 staff, 900 M€/year

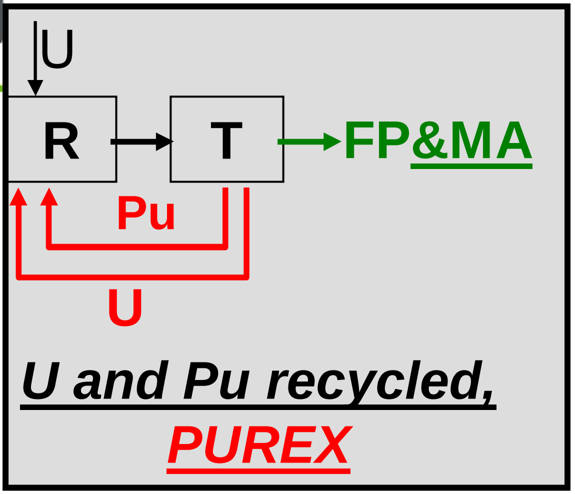
Final waste radiotoxicity



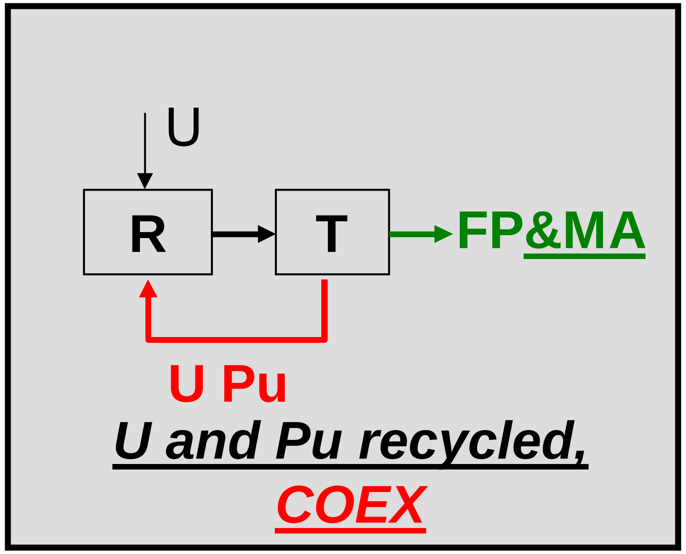
Contributions to residual heat (UOX spent fuel)



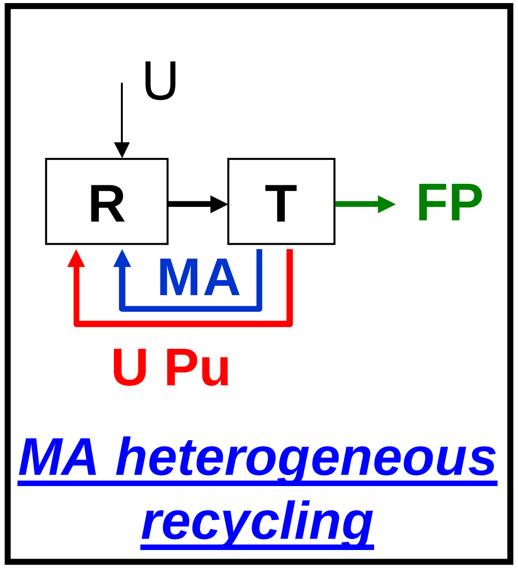
Actinide recycling : what fuel cycle option ?



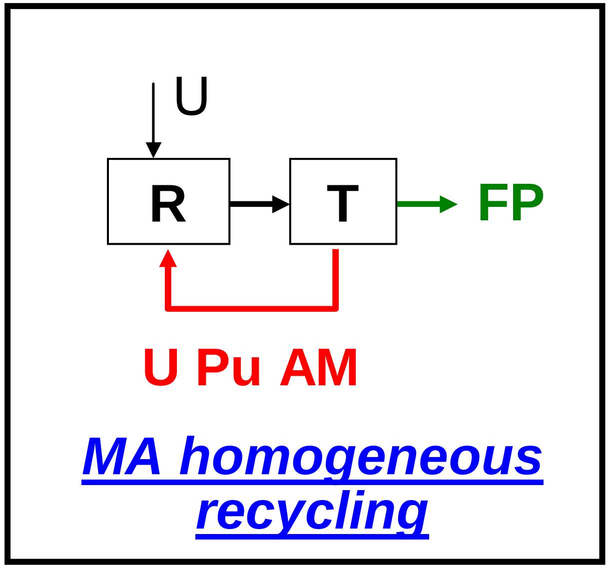
U and Pu recycled,
PUREX



U and Pu recycled,
COEX

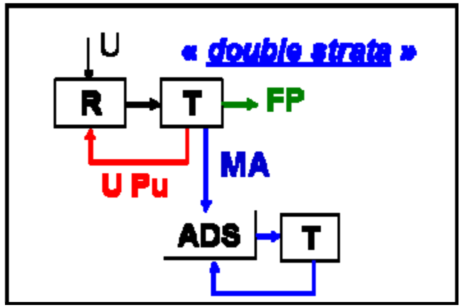


MA heterogeneous recycling



MA homogeneous recycling

MA : Np, Am, Cm

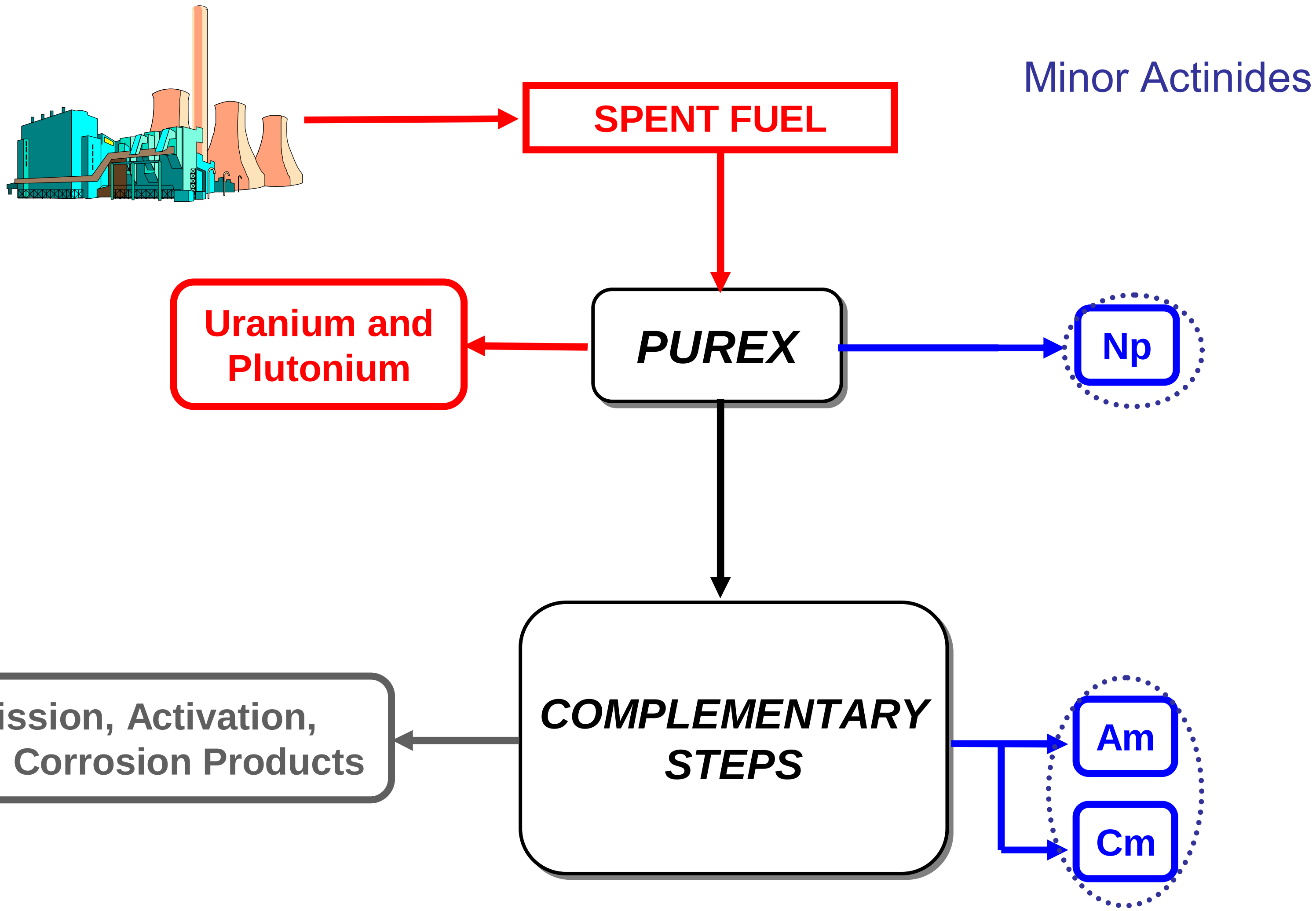


How to partition Np, Am and Cm ?

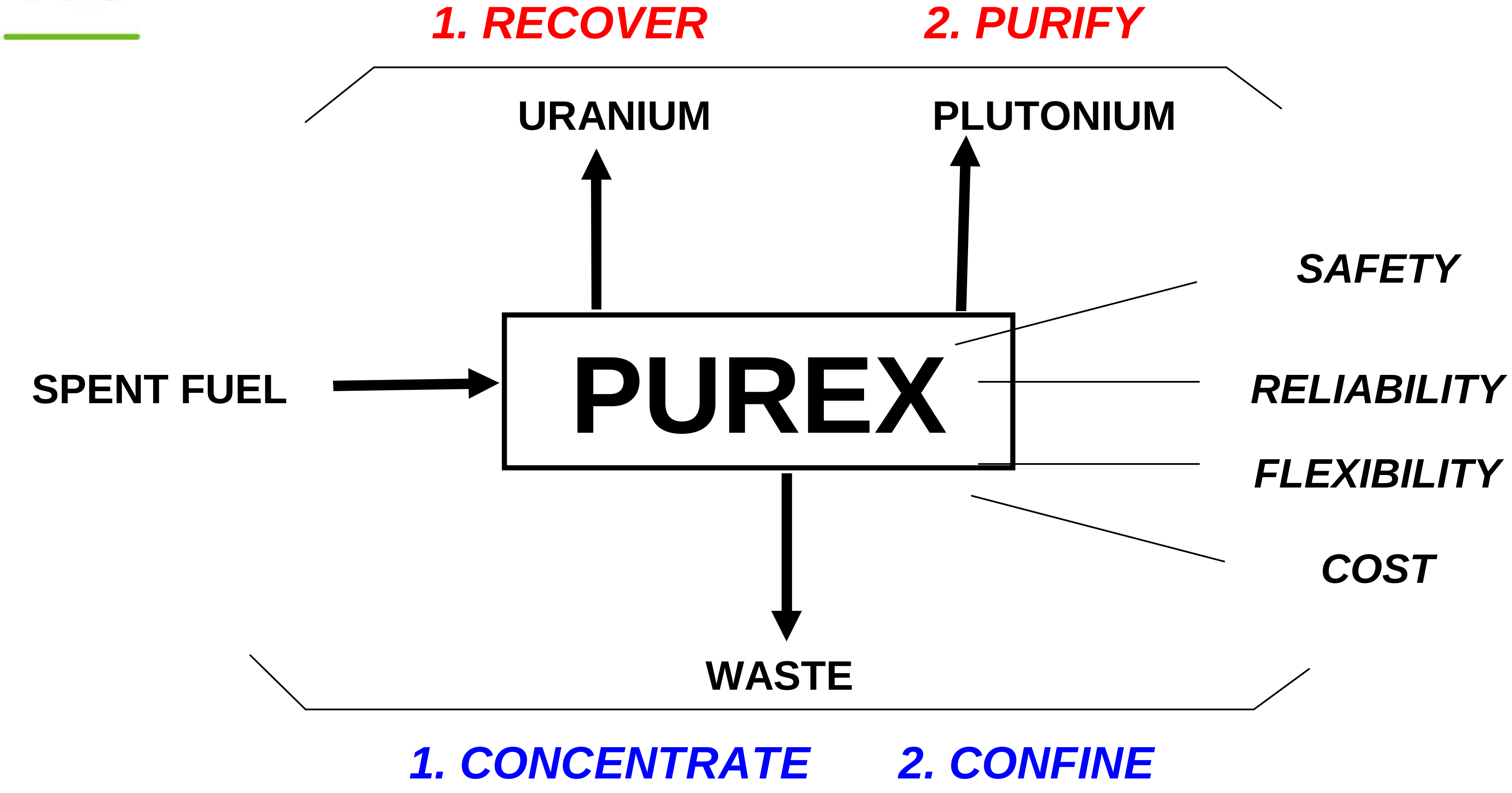
- **How to reprocess spent nuclear fuels?**
- **Which industrial technology?**
  - **Criteria**
    - ***Safety, performance, cost, secondary waste…***
  - **Reference route**
    - **Solvent extraction, PUREX Process**
    - ***Already mastered at the industrial scale***
    - ***La Hague plant (AREVA NC)***

      UP3 plant: *800 tons reprocessed / year*
      - » **High separation yields achieved**
      - » **Few technological waste generated**

A possible route…



Reprocessing process : requirements

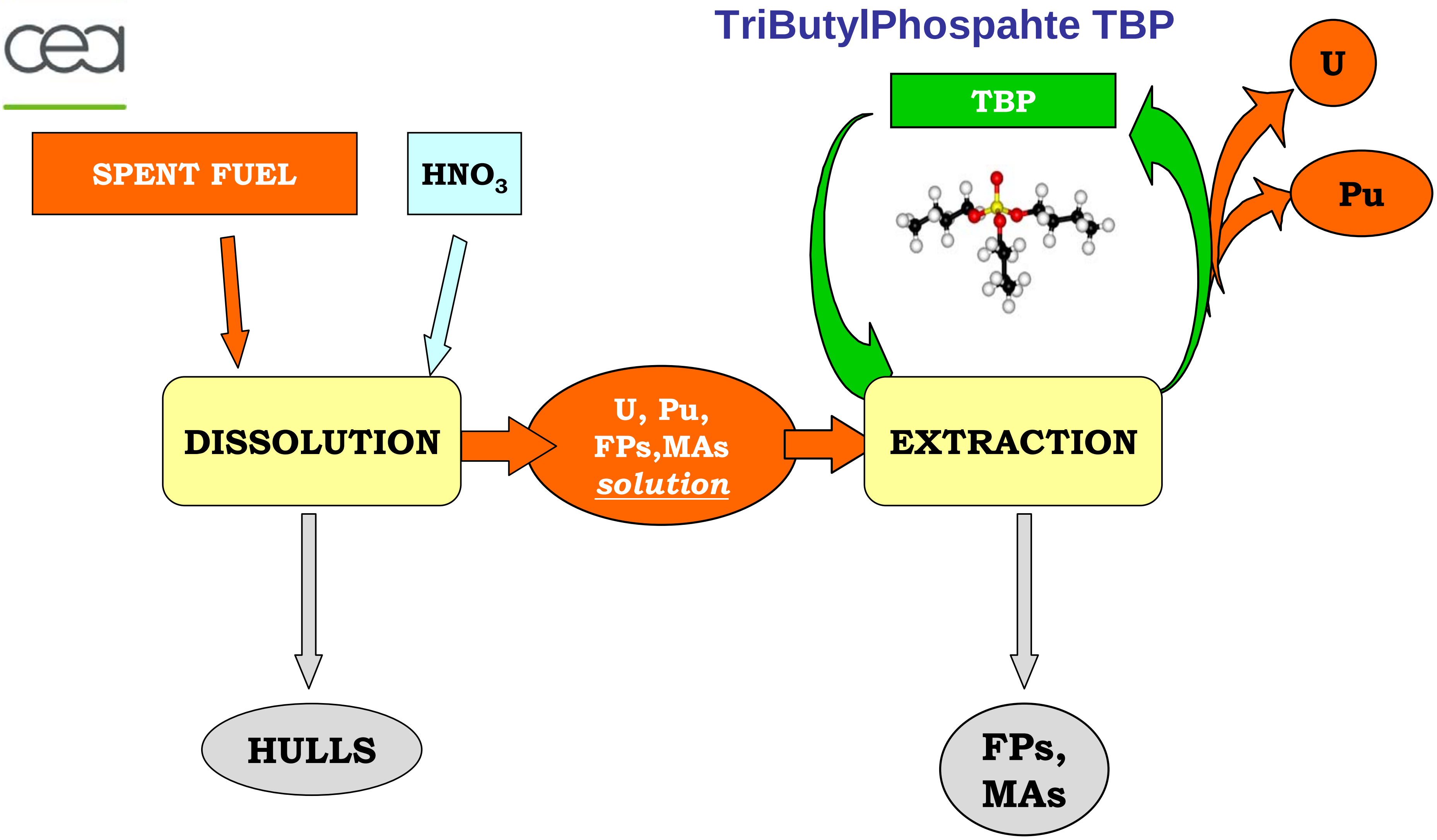


Reprocessing requirements and constraints

- **High recovery yields *(99.9 %)***
- **High purification yields (10^6)**
- **Low amount of secondary waste…**

- **Confinment**
- **Shielding**
- **Criticality risk**
- **Nuclear material accounting**
- **Radiolysis…**

The PUREX Process



TriButylPhospahte TBP

SPENT FUEL

HNO_3

TBP

U

Pu

DISSOLUTION

U, Pu, FPs,MAs *solution*

EXTRACTION

HULLS

FPs, MAs

PUREX, the reference since 1950's…

WHY ?

- **TBP, a selective and strong molecule**

- **High recovery /purification yields**

(99.9 % U &Pu recovered, DFs ~ 10^7)

- **Low secondary waste amount**
- **No extreme conditions, no severe materials issues**
- **A heavy work for development**

PUREX : some important steps

U.S.A.	**1950s**	**(Savannah, Hanford)**
UK	**1953**	**(Windscale)**
France	**1958**	**(Marcoule, UP1)**
	1967	**(La Hague, UP2)**
	1976	**(La Hague, UP2-HAO) (UOX)**
	1989	**(La Hague, UP3)**
	1994	**(La Hague, UP2-800)**
UK	**1994**	**(Sellafield, THORP)**
Japan	***2007***	***(Rokkashomura)***

PUREX main steps

1. **DISSOLVE**

2. **EXTRACT**

3. **CONDITION**

PUREX Process : 1. « HEAD-END »

GOAL : **SOLUBILIZE ALL THE SPENT FUEL COMPONENTS**

STEPS : **SHEARING- DISSOLUTION-CLARIFICATION**

DOWNSTREAMS :

1 – DISSOLUTION LIQUOR (U, Pu, P.F., A.M.) **] *to next steps***

2 - "HULLS " (and end-pieces) (AP)

3 – DISSOLUTION RESIDUES (noble metals, ...)

} ***to be conditionned*** (2, 3)

4 – GASEOUS EFFLUENTS (gaseous FPs) **] *to be purified before release***

PUREX Dissolution mechanisms

- ✓ **UO_2 Dissolution :** $\Delta H = - 420$ 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 :**

  $PuO_2 + 4\ HNO_3 \rightarrow Pu\ (NO_3)_4 + 2\ H_2O$ (very slow)

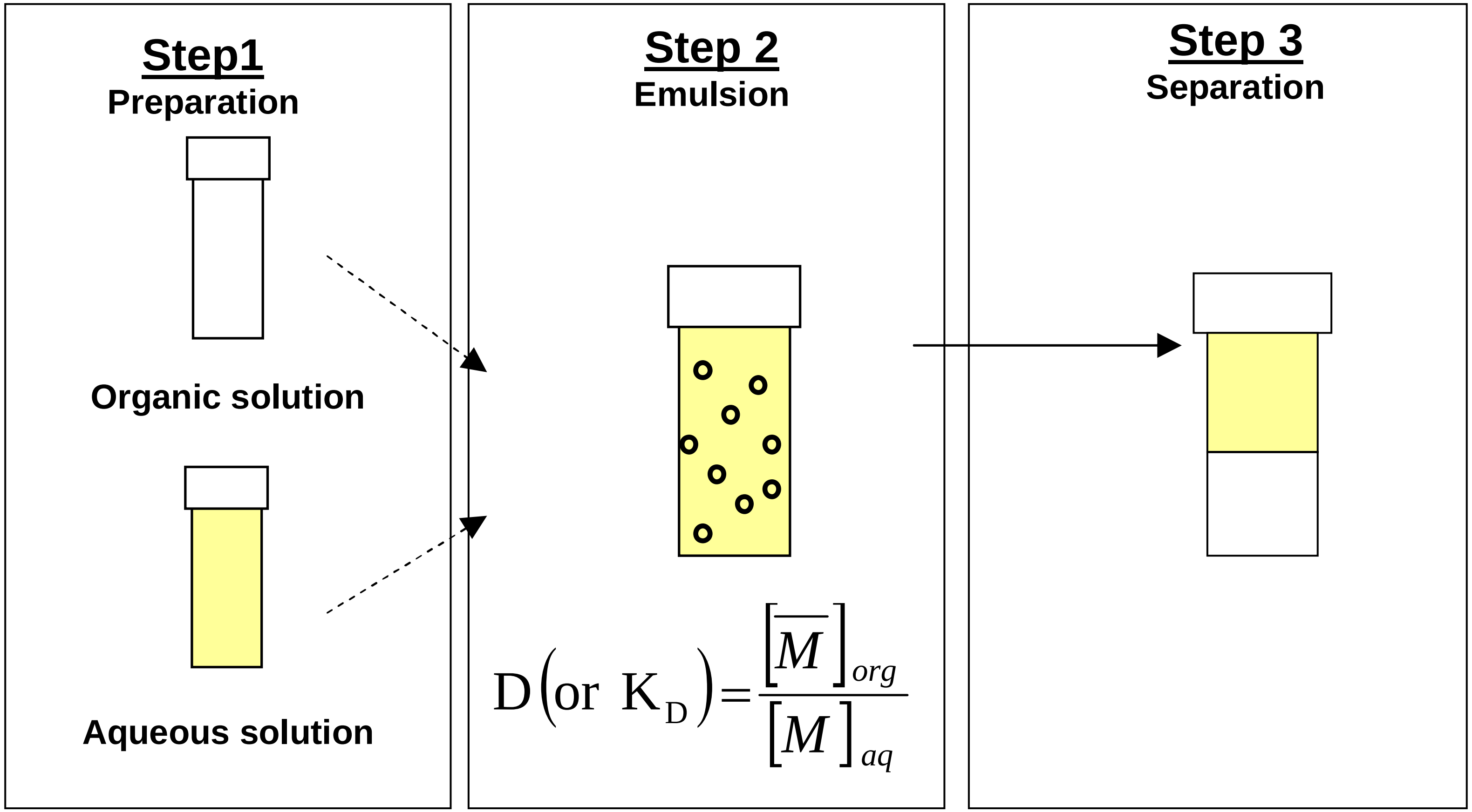
PUREX Volatile Radionuclides

➔ **Iodine**	(I_2)	[^{129}I]
➔ **Carbone**	(CO_2)	[^{14}C]
➔ **Tritium**	(HTO)	[^{3}H]
➔ **Krypton**	(Kr)	[^{85}Kr]

To be considered too :

- NO/NO_2

The principle of solvent extraction



Step1
Preparation

Organic solution

Aqueous solution

Step 2
Emulsion

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

Step 3
Separation

Extraction of a specie

$$(M)_{aq} \leftrightarrows (M)_{org}$$

Very diverse mechanisms:

- **solvatation (complexes)**
- **ion exchange (anions, cations)**
- **chelation**

(all organic species)

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

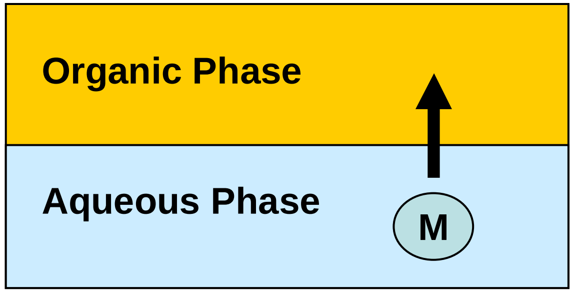
(all aqueous species)

For two elements, M_1 and M_2 to be separated :

$$FS_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}}$$

« Non compensated « extraction

- **« Passive extraction »,** solvation of a lipophilic compound in the organic phase

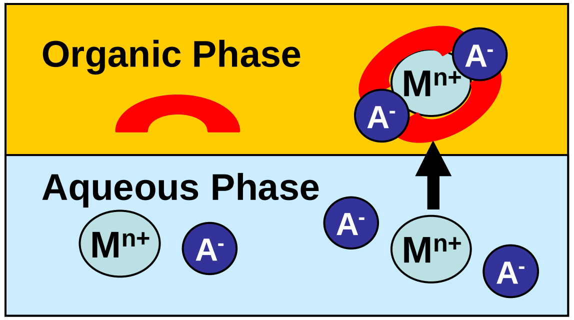


$$M \xrightleftharpoons{K_{ex}(M)} \overline{M}$$

« Non compensated « extraction

***Solvatation of a neutral complex*:**

(acid or metallic salt in the initial aqueous solution)



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

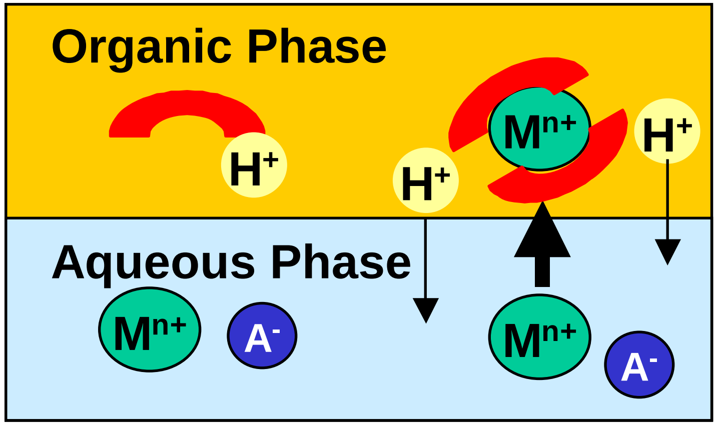
$$K_{ex}(M) = \frac{\left[\overline{MA_nE_e}\right]}{\left[M^{n+}\right]\cdot\left[\overline{E}\right]^e\cdot\left[A^-\right]^n} = \frac{D_M}{\left[\overline{E}\right]^e\cdot\left[A^-\right]^n}$$

- **Uranyl nitrate by TBP**

Ion Exchange extraction

- Cation exchange

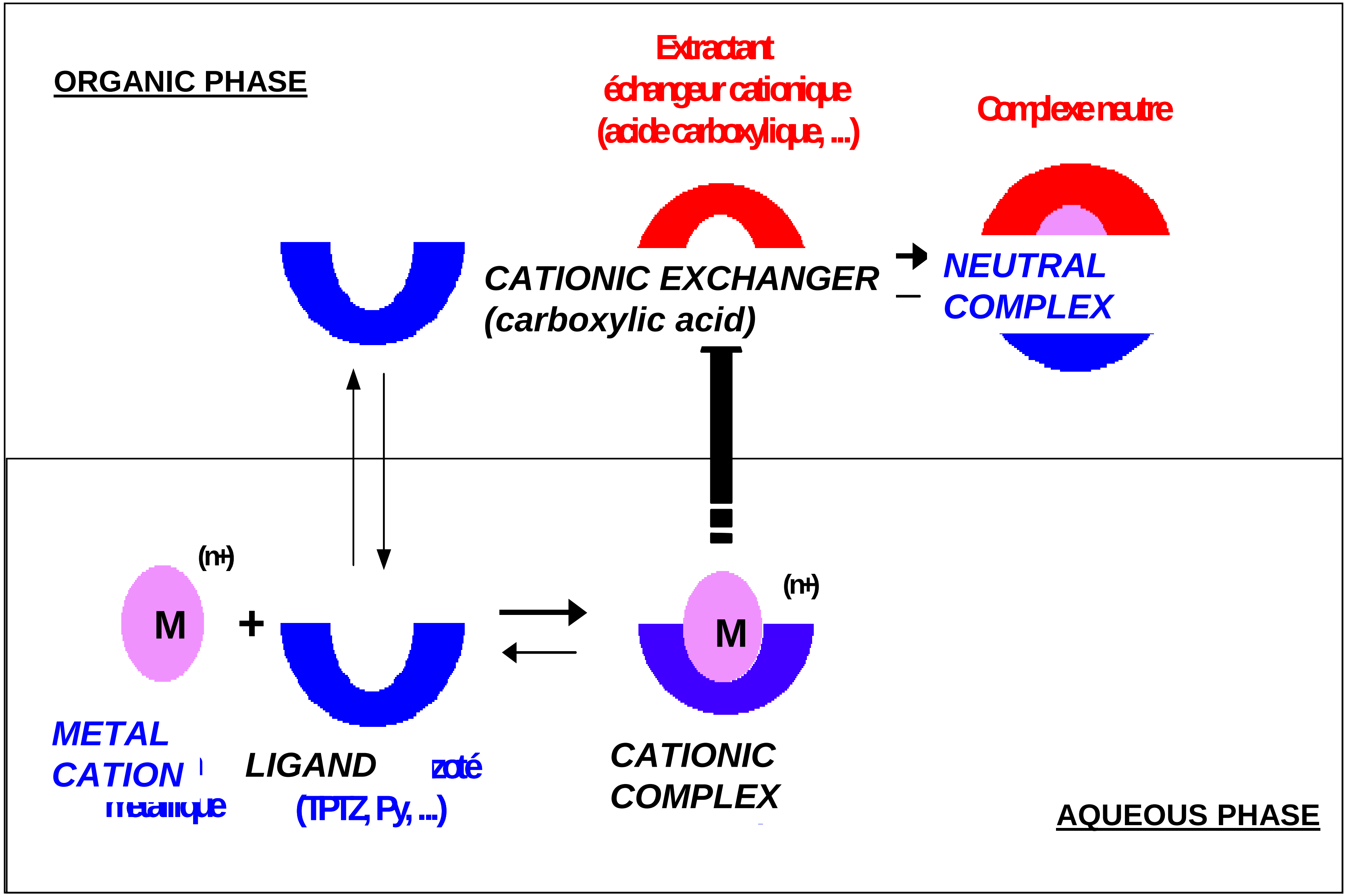
$$M^{n+} + m\,\overline{HA} \underset{K_{ex}}{\overset{}{\rightleftarrows}} \overline{MA_n(HA)_{m-n}} + n\,H^{+}$$



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

- ***Am^{3+} by HDEHP***

Synergistic extraction



ORGANIC PHASE

Extractant
échangeur cationique
(acide carboxylique, ...)

Complexe neutre

CATIONIC EXCHANGER
(carboxylic acid)

NEUTRAL
COMPLEX

METAL
CATION
métallique

LIGAND
zoté
(TPTZ, Py, ...)

CATIONIC
COMPLEX

AQUEOUS PHASE

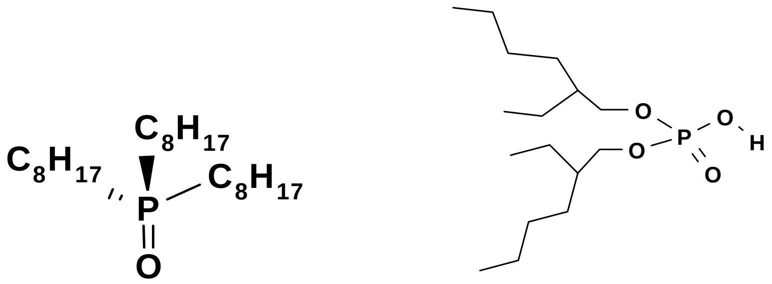
Synergistic extraction…

$$M^{n+} + e\overline{L} + m\overline{HA} \overset{K_{ex}}{\rightleftarrows} \overline{ML_eA_n(HA)_{m-n}} + nH^+$$

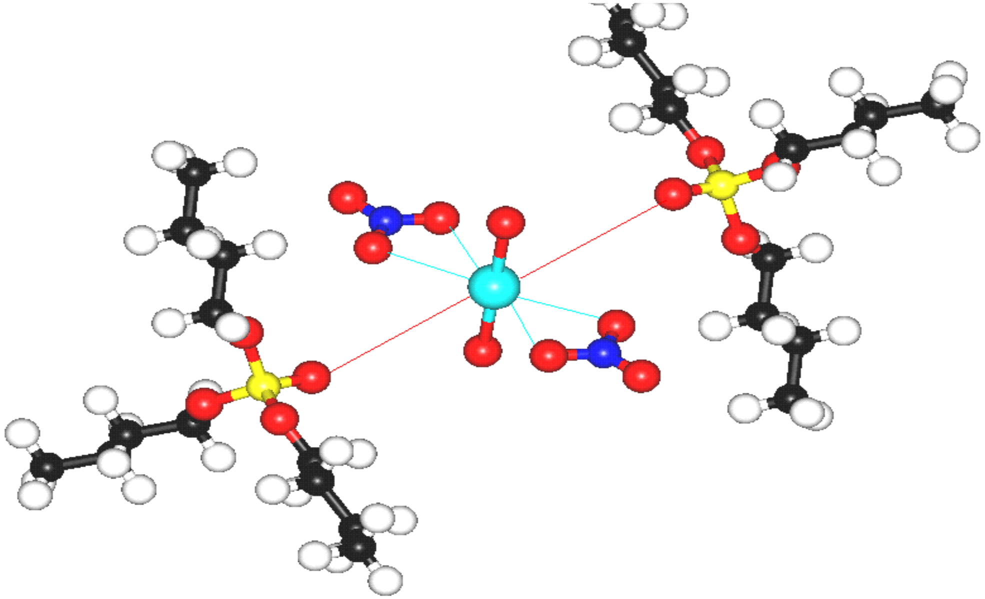
$$K_{ex} = \frac{\left[\overline{ML_eA_n(HA)_{m-n}}\right].\left[H^+\right]^n}{\left[M^{n+}\right].\left[\overline{HA}\right]^m \cdot \left[\overline{L}\right]^e} = \frac{D_M.\left[H^+\right]^n}{\left[\overline{HA}\right]^m \cdot \left[\overline{L}\right]^e}$$

UO_2^{2+} by

TOPO/HDEHP

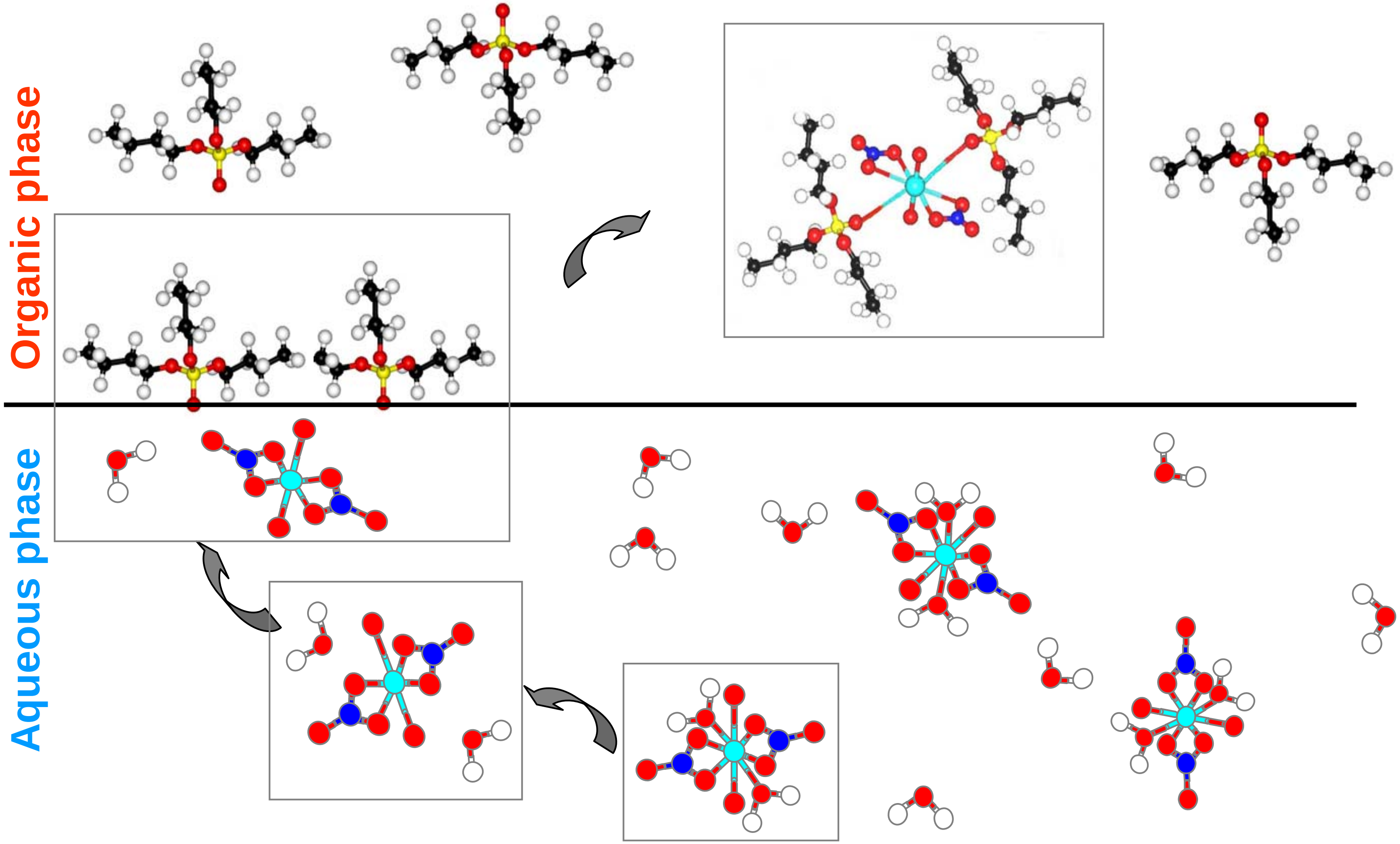


Uranyl Extraction by TBP



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

Uranyl Extraction by TBP

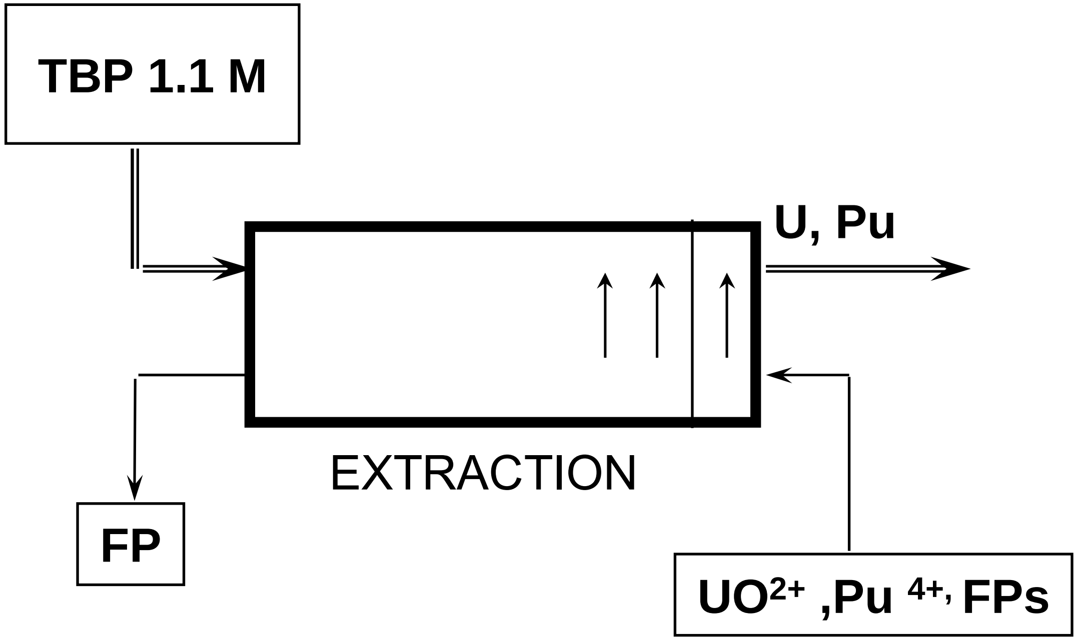


$$(UO_2^{2+})_{aq} + 2\,(NO_3^-)_{aq} + 2\,(TBP)_{org} \rightleftharpoons (UO_2(NO_3)_2\,,\,2TBP)_{org}$$

Actinide extraction by TBP

	OXIDATION STATE			
	III	IV	V	VI
U		X		●
Np		X	●	●
Pu	X	●		X
Am	X			
Cm	X			

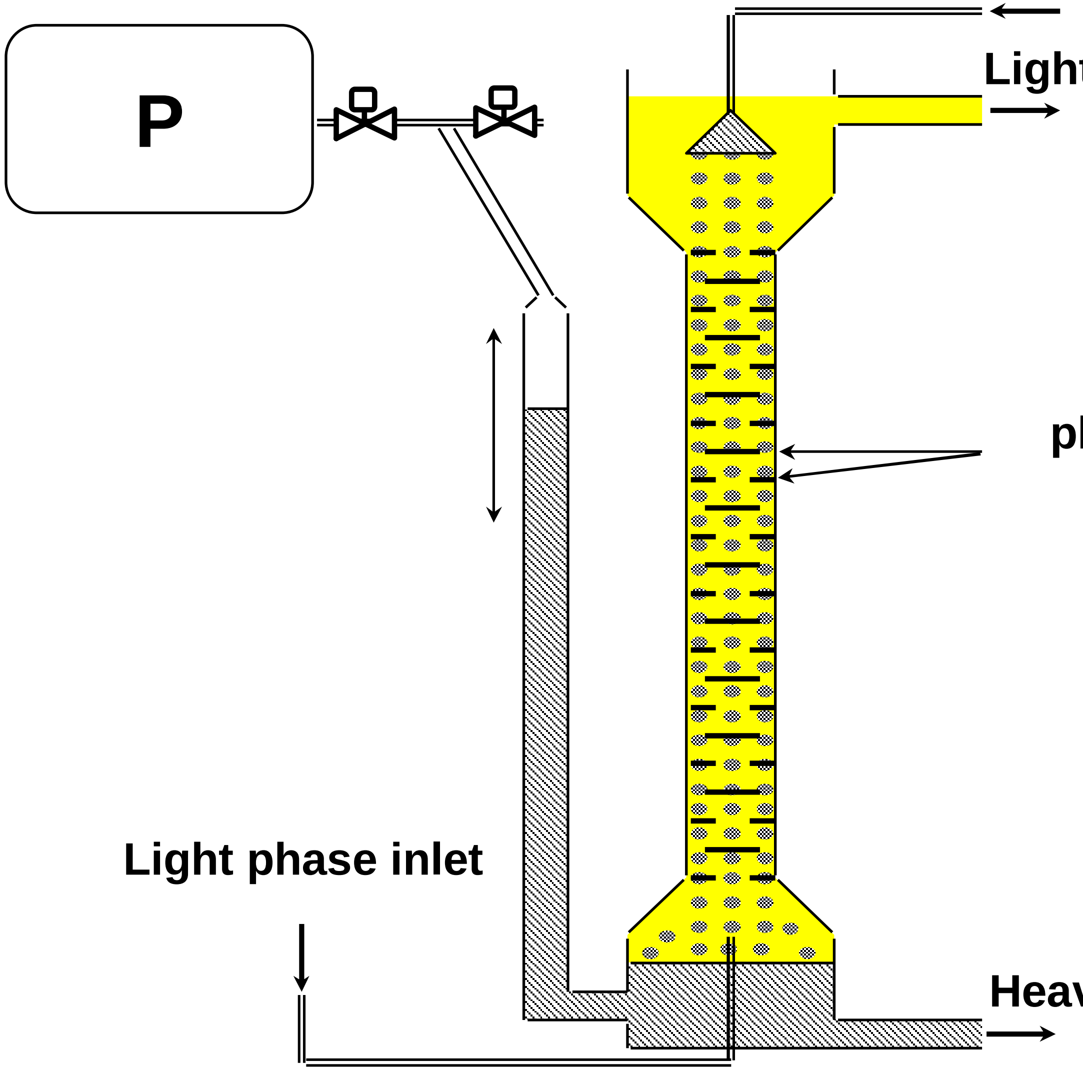
PUREX U-Pu Extraction operation



Operating conditions : $[HNO_3]$ **rather high**

$[U]_{org}$ **rather high**

PUREX with pulsed comumns : principle



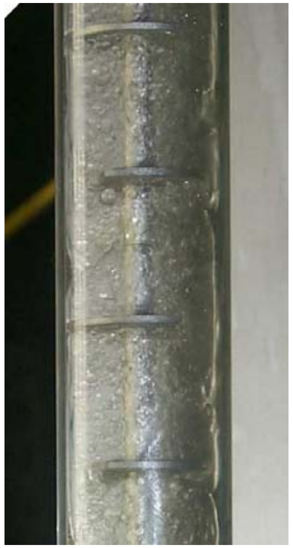
Heavy phase inlet

Light phase outlet

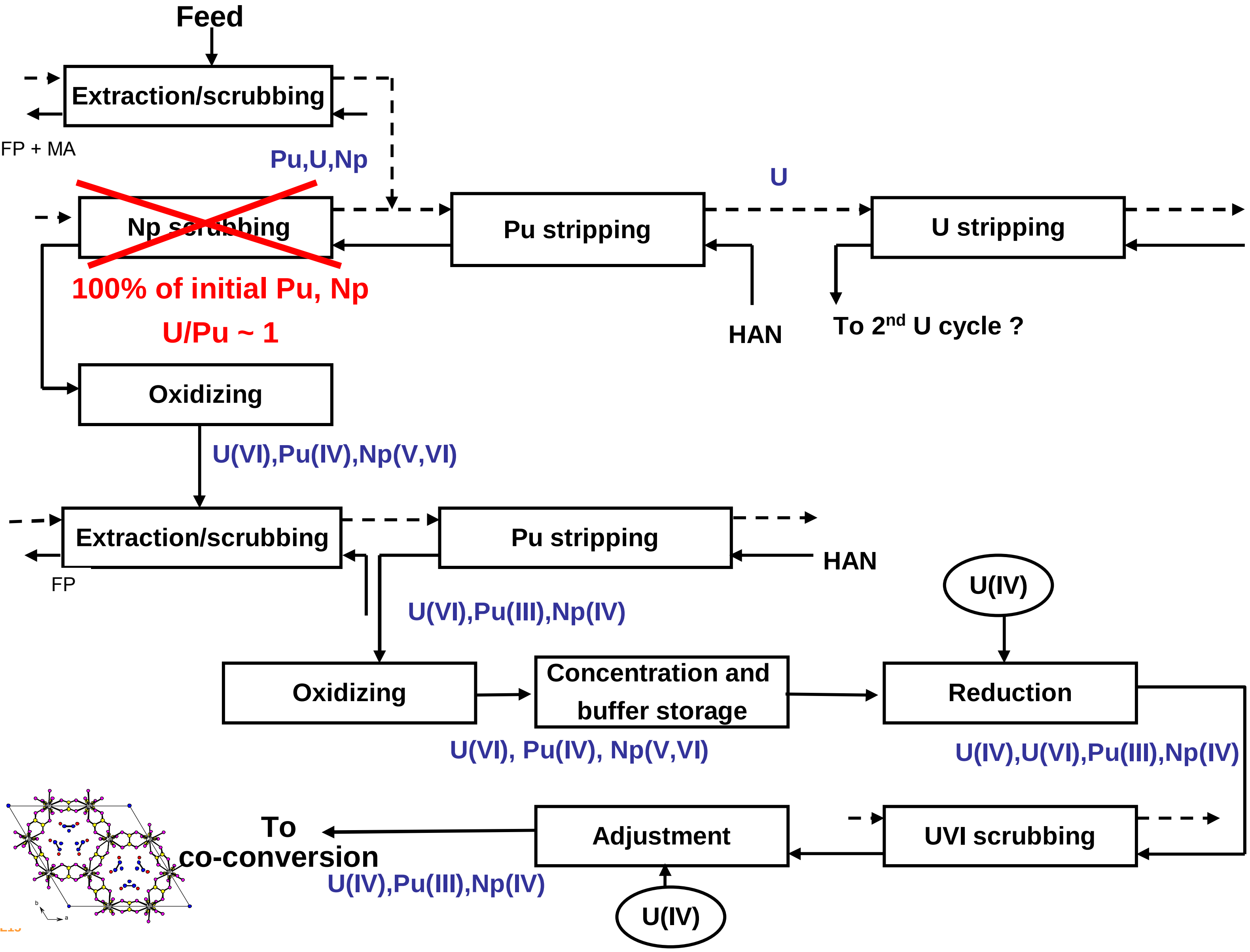
plates

Light phase inlet

Heavy phase outlet



From PUREX to COEX™: co-extraction principle (U-Pu-Np)



Feed

Extraction/scrubbing

FP + MA

Pu,U,Np

~~Np scrubbing~~

100% of initial Pu, Np

U/Pu ~ 1

Pu stripping

HAN

U

U stripping

To 2^{nd} U cycle ?

Oxidizing

U(VI),Pu(IV),Np(V,VI)

Extraction/scrubbing

FP

Pu stripping

HAN

U(VI),Pu(III),Np(IV)

U(IV)

Oxidizing

Concentration and buffer storage

U(VI), Pu(IV), Np(V,VI)

Reduction

U(IV),U(VI),Pu(III),Np(IV)

To co-conversion

Adjustment

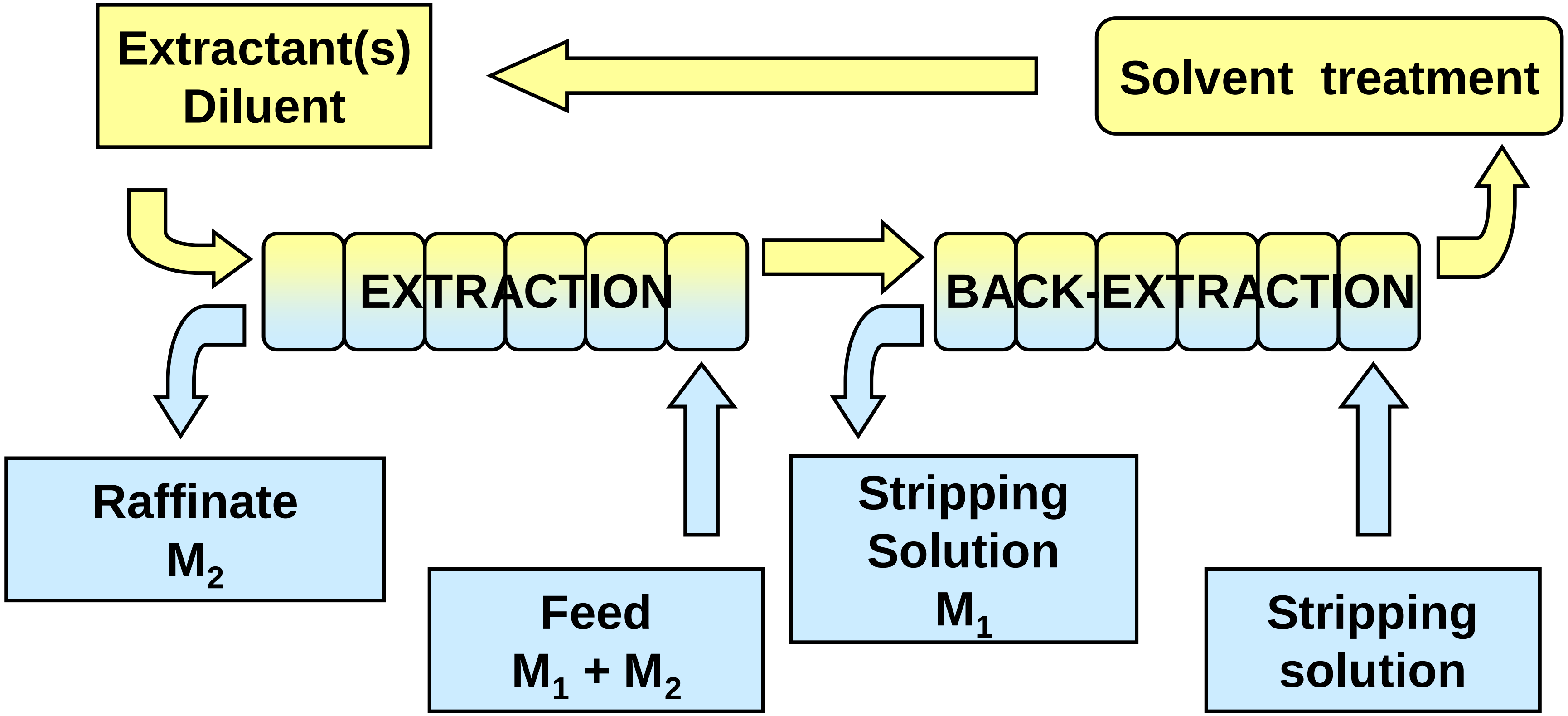
UVI scrubbing

U(IV),Pu(III),Np(IV)

U(IV)

Solvent extraction

- Counter-current separation process



Extractant(s)
Diluent

Solvent treatment

EXTRACTION

BACK-EXTRACTION

Raffinate
M_2

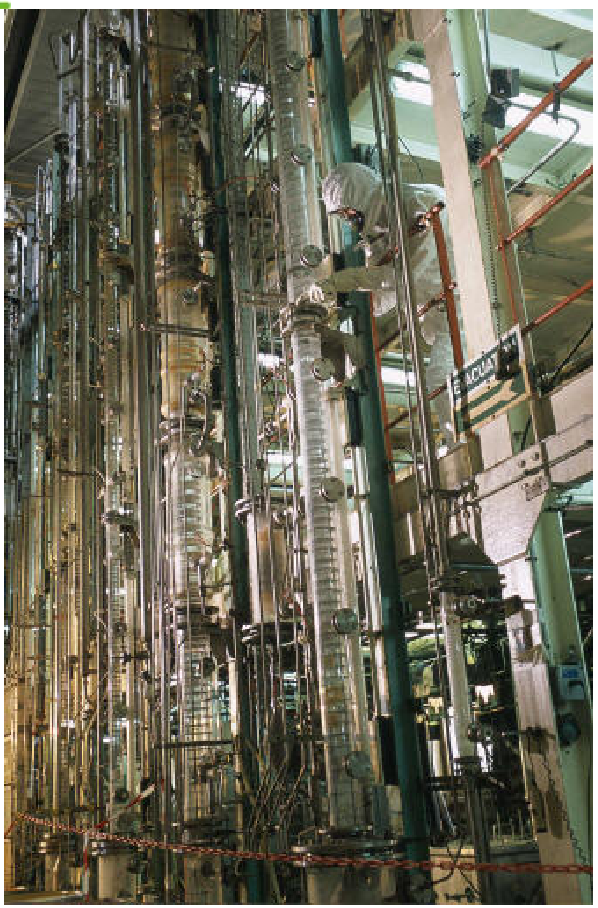
Feed
$M_1 + M_2$

Stripping
Solution
M_1

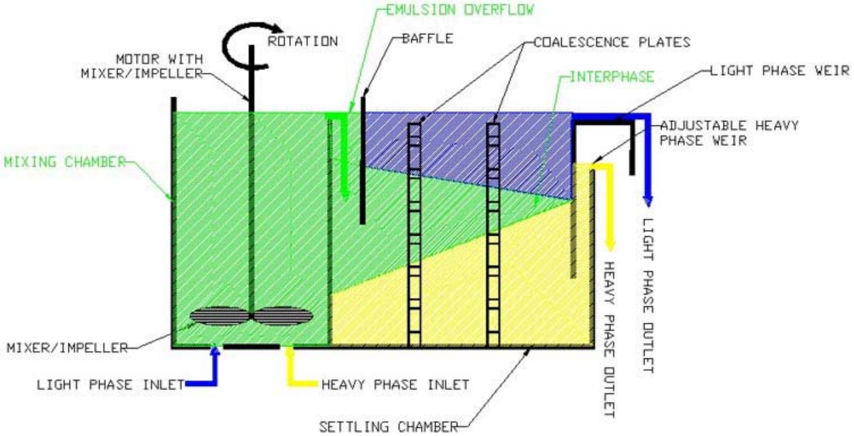
Stripping
solution

Industrial contactors

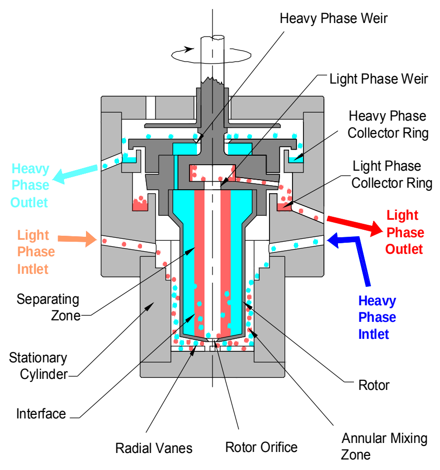
- Pulsed columns



- Mixer-settlers



- Centrifugal contactors



Requirements for process development

- Extraction efficiency
  - **Distribution ratios of separated elements**
    - **High distribution ratios at the extraction step**

$$D_M \times \frac{O}{A} >> 1 \Rightarrow E(\%) > 50\%$$

    - **Small distribution ratios at the stripping step**

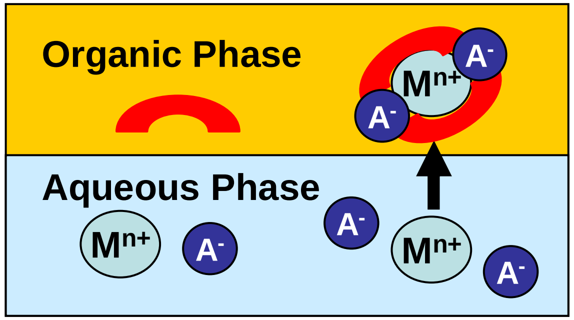
$$D_M \times \frac{O}{A} << 1 \Rightarrow E(\%) < 50\%$$

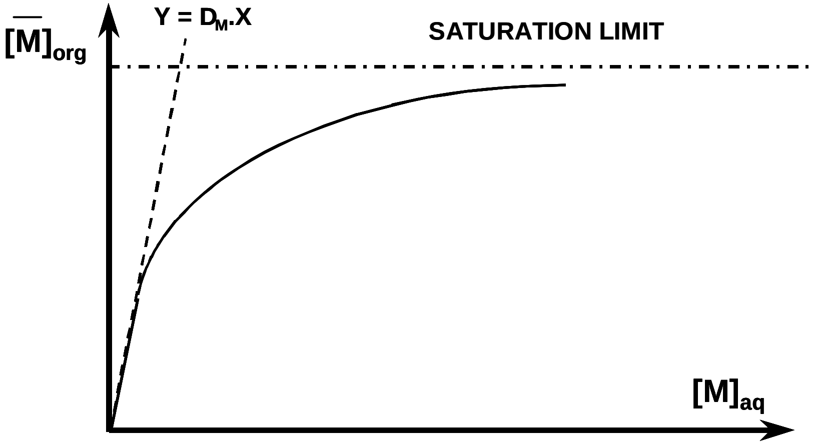
    - **High selectivity:** $FS_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}} >> 1$

- Fast kinetics of mass transfer
  - **Both at extraction and stripping steps**
    - **Implementation in short time contactors**

- Ligand stability
  - **Both *vs* acidic hydrolysis and radiolysis**

Distribution ratio





$$D_M = \frac{\sum[\overline{M}]}{\sum[M]}$$

Organic phase species

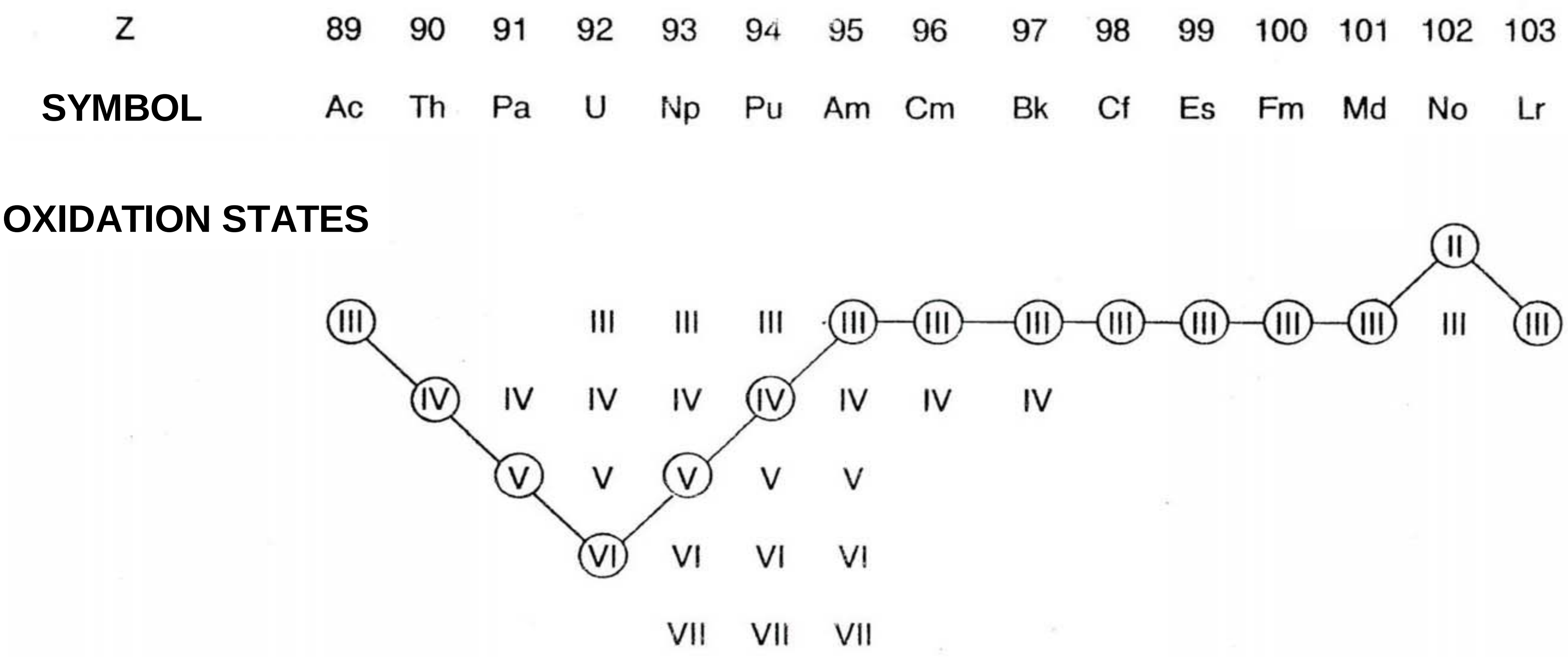
$$D_M = \frac{[\overline{M}] + [\overline{\text{complex}\ \ 1}] + [\overline{\text{complex}\ \ 2}] + \dots}{[M] + [\text{complex}\ \ 1] + [\text{complex}\ \ 2] + \dots}$$

Aqueous phase species

- D_M depends on **P, t°, [X], pH, *I* …**

$$E(\%) = 100 \cdot \frac{[\overline{M}]_{tot} \cdot V_{org}}{[M]_{tot} \cdot V_{aq} + [\overline{M}]_{tot} \cdot V_{org}} = 100 \cdot \frac{D_M}{D_M + \frac{V_{aq}}{V_{org}}}$$

Actinides properties



Z	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
SYMBOL	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
OXIDATION STATES														II	
	III			III	III	III	III	III	III	III	III	III	III	III	III
		IV	IV	IV	IV	IV	IV	IV	IV						
			V	V	V	V	V								
				VI	VI	VI	VI								
					VII	VII	VII								

<u>CHEMICAL BEHAVIOR</u>:

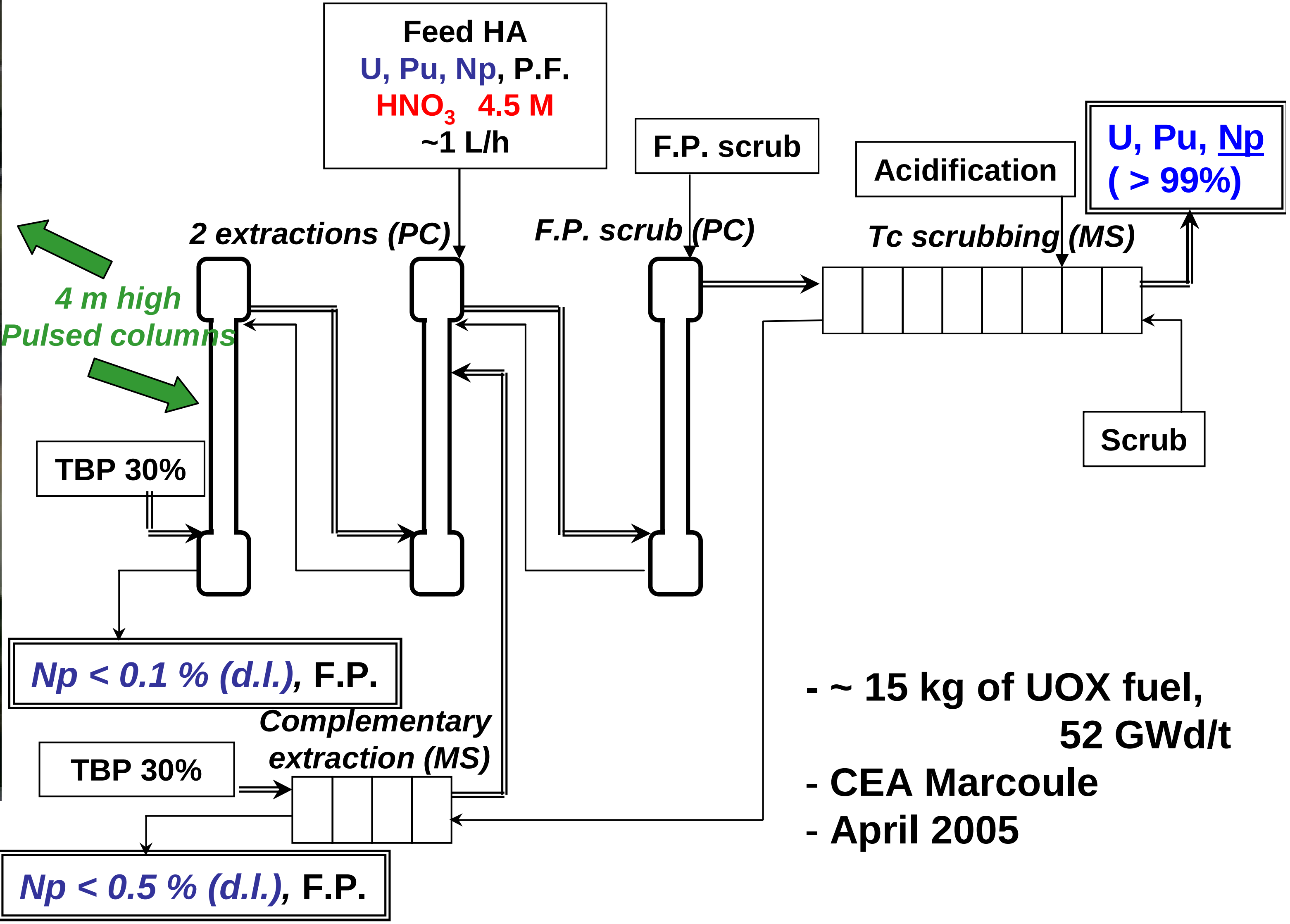
Light actinides (Th to Pu): *specific redox (PUREX basis*)

⇨ Np recovery is achievable by PUREX

Heavier actinides (from Am) *behave like lanthanides*

⇨ An(III) recovery requires new separation processes

Np Extraction demonstration hot run



4 m high
Pulsed columns

Feed HA
U, Pu, Np, P.F.
HNO_3 4.5 M
~1 L/h

F.P. scrub

Acidification

U, Pu, Np
(> 99%)

2 extractions (PC)

F.P. scrub (PC)

Tc scrubbing (MS)

TBP 30%

Scrub

***Np < 0.1 % (d.l.)*, F.P.**

Complementary extraction (MS)

TBP 30%

***Np < 0.5 % (d.l.)*, F.P.**

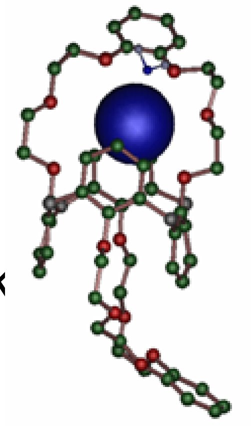
- **~ 15 kg of UOX fuel, 52 GWd/t**
- **CEA Marcoule**
- **April 2005**

Partitioning research steps

⇨ A true challenge : a sophisticated partitioning chemistry under highly radioactive conditions

⇨ Fundamental research : a wide co-operative framework

- exploration : new extracting systems
- fundamentals : in-depth study of mechanisms at work



A few hundreds

of new molecules

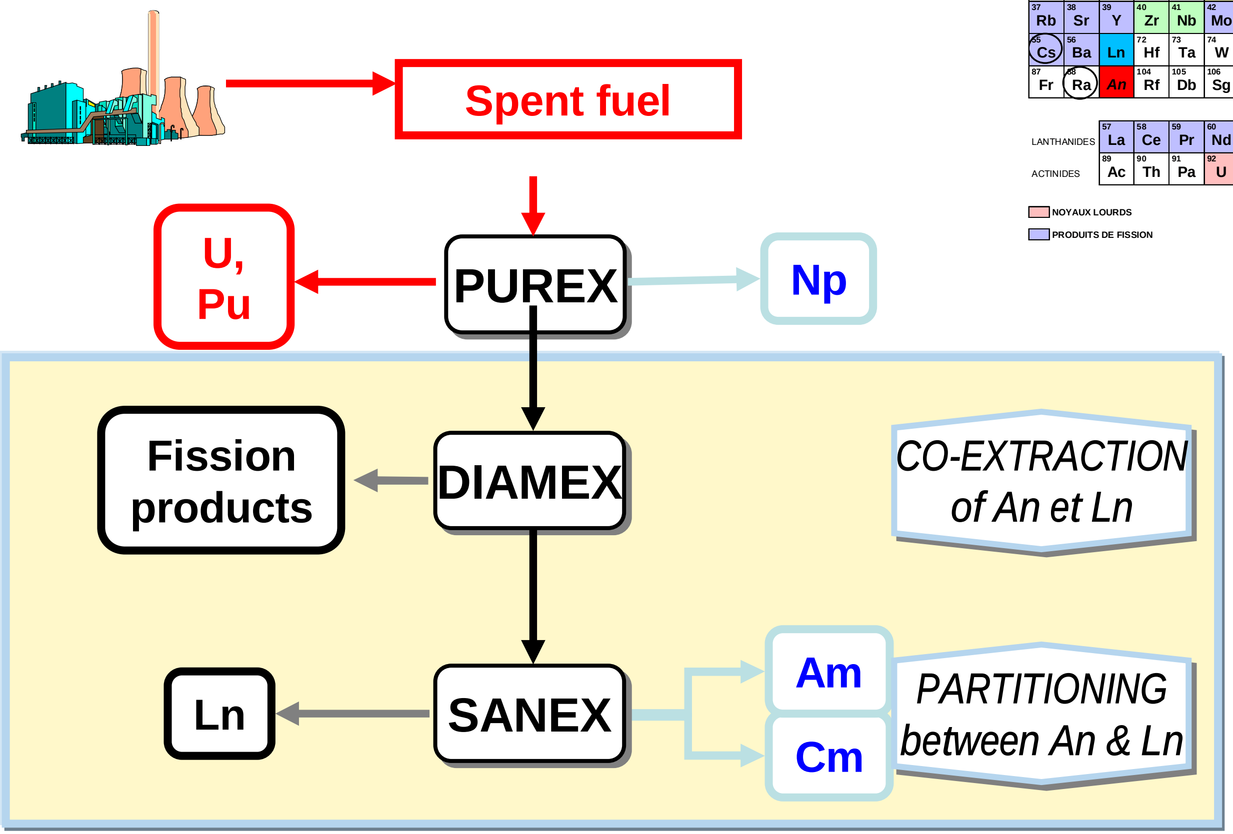
⇨ Applied research :

- process design
- lab experiments on actual spent fuel material
- « demonstration » experiments :
  integration, representativeness, long-lasting performance

Scale : 1/10000

Scale : 1/100 à 1/1000

Actinides Partitioning : the research path used



Spent fuel

PUREX

U, Pu

Np

DIAMEX

Fission products

CO-EXTRACTION of An et Ln

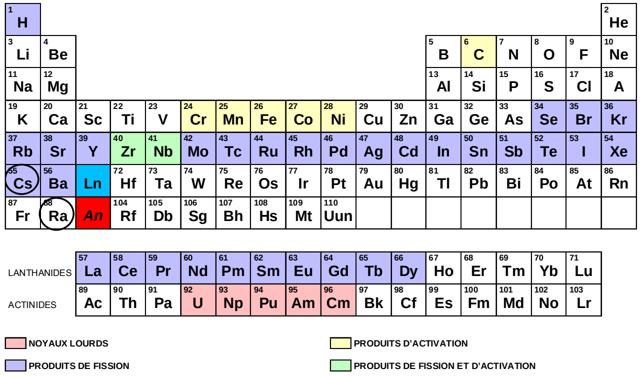
SANEX

Ln

Am

Cm

PARTITIONING between An & Ln



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 A
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	Ln	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	*An*	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun								

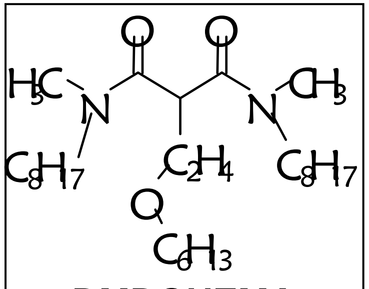
LANTHANIDES	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
ACTINIDES	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

🟥 NOYAUX LOURDS

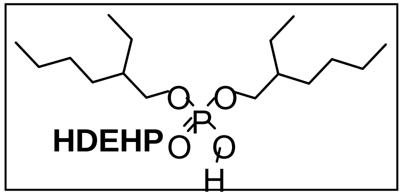
🟦 PRODUITS DE FISSION

🟨 PRODUITS D'ACTIVATION

🟩 PRODUITS DE FISSION ET D'ACTIVATION

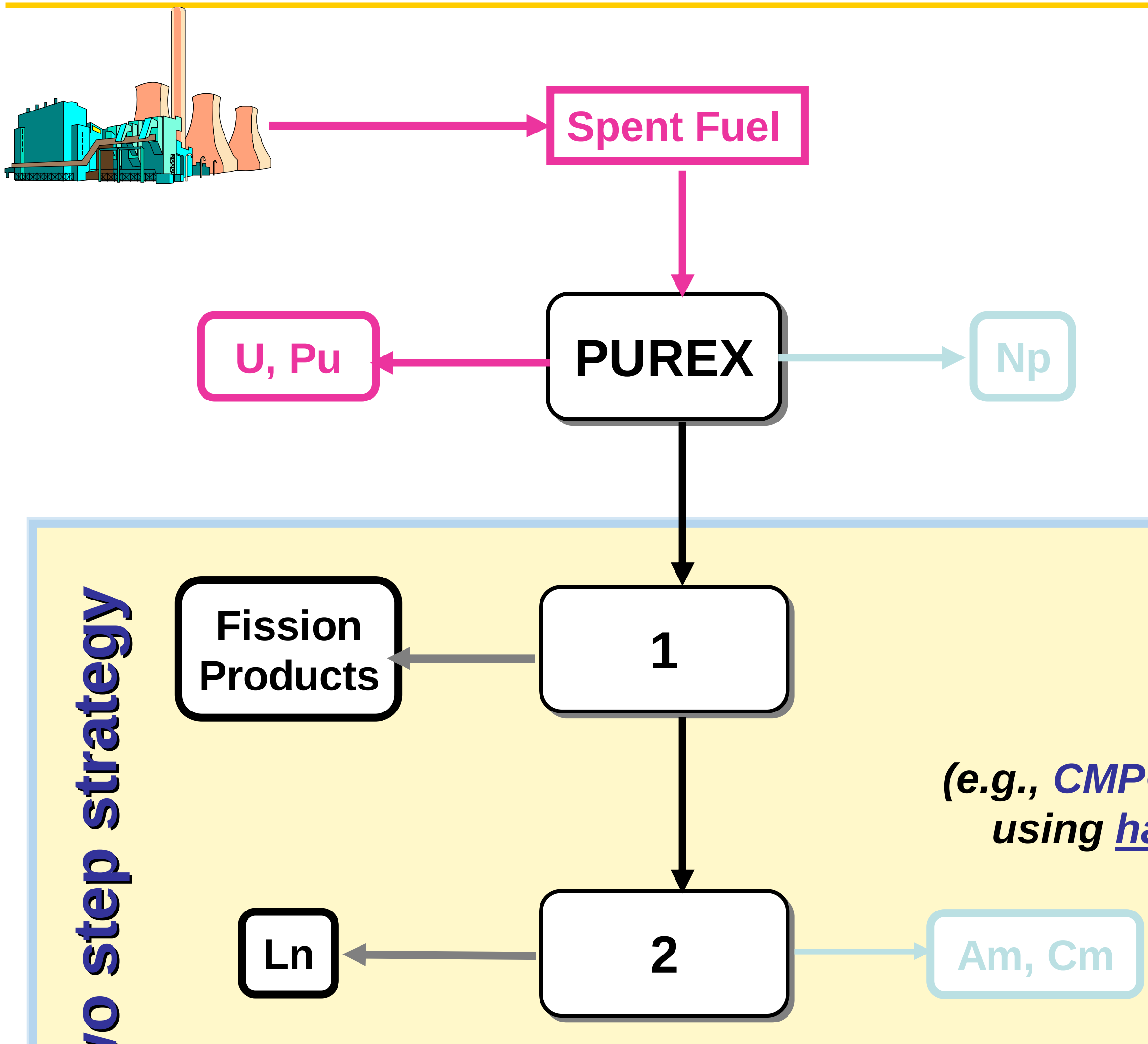


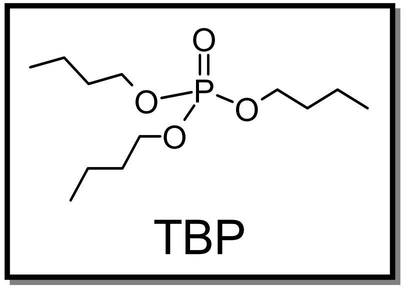
DMDOHEMA



HDEHP

Am^{3+} and Cm^{3+} recovery : a 2-step strategy





CO-EXTRACTION of MAs and Ln

(e.g., CMPO, TRUEX processes using hard-donor ligands)

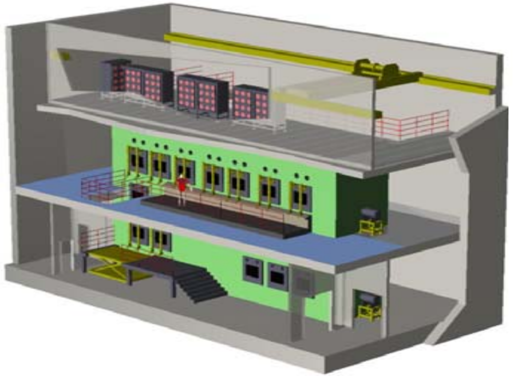
SEPARATION of MAs from Ln

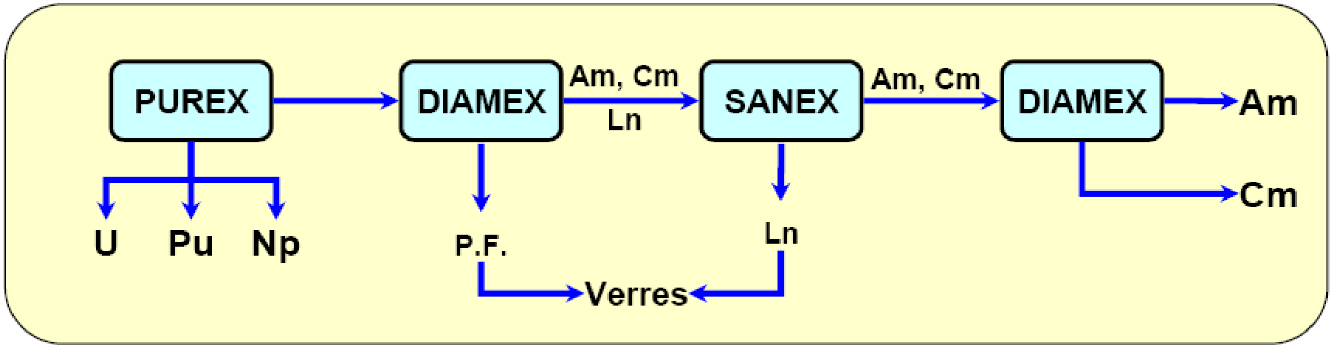
(e.g. SANEX, TALSPEAK processes using soft-donor ligands)

1991-2006 : Partitioning results

⇨ The results :

  - ⇨ Neptunium: recovery up to 99%, with modified PUREX
  - ⇨ Americium and Curium: recovery up to 99.9%, with DIAMEX-SANEX



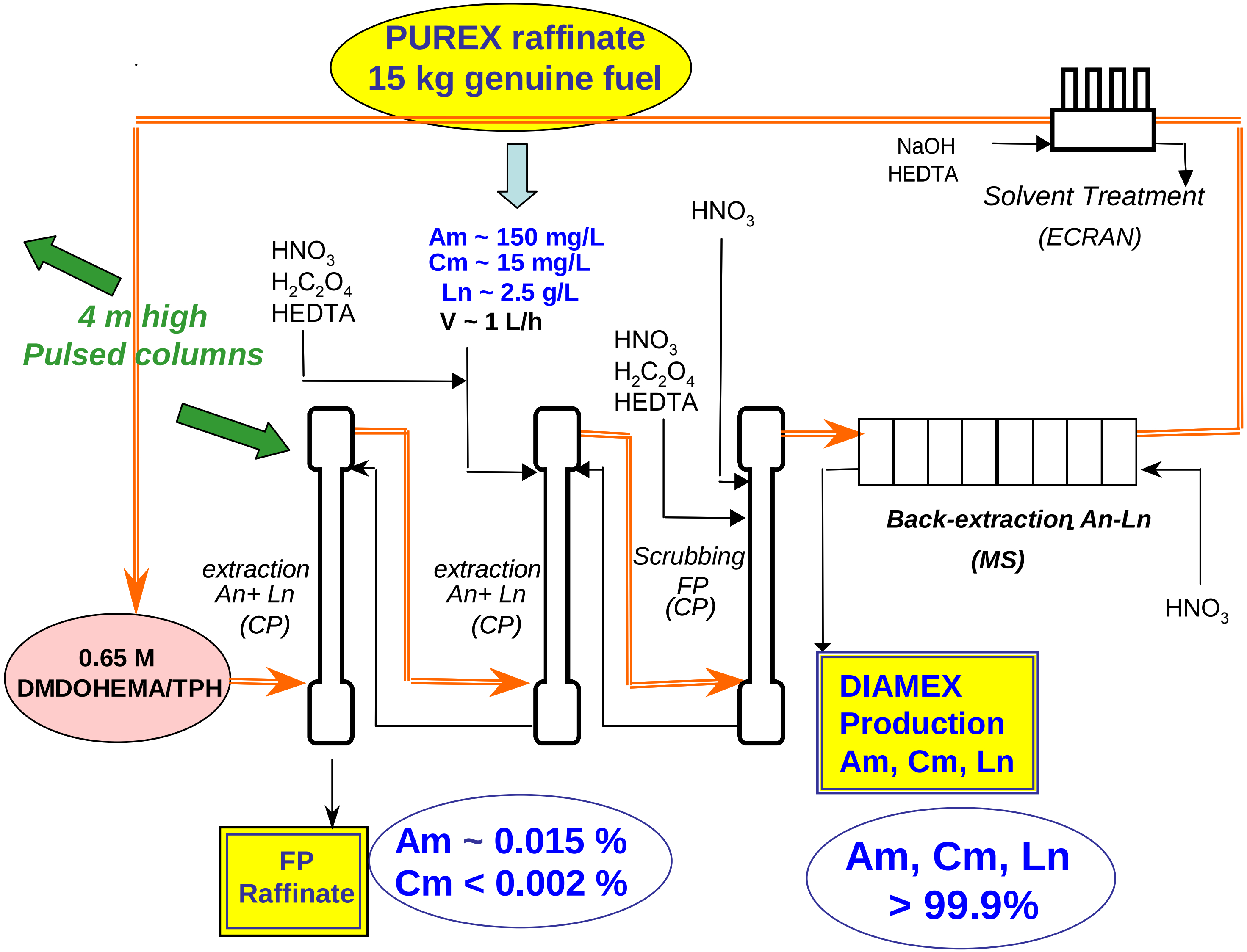


Tested at CEA Atalante Marcoule hot labs on 15 kgs of EDF UOx spent fuel

⇨ Proven processes and technologies which can be applied to other partitioning schemes

⇨ Further steps will be required prior to any industrial implementation

DIAMEX demonstrative hot run, November 2005



PUREX raffinate
15 kg genuine fuel

Am ~ 150 mg/L
Cm ~ 15 mg/L
Ln ~ 2.5 g/L
V ~ 1 L/h

4 m high
Pulsed columns

HNO_3
$H_2C_2O_4$
HEDTA

extraction
An+ Ln
(CP)

extraction
An+ Ln
(CP)

HNO_3
$H_2C_2O_4$
HEDTA

HNO_3

Scrubbing
FP
(CP)

NaOH
HEDTA

Solvent Treatment
(ECRAN)

Back-extraction An-Ln
(MS)

HNO_3

0.65 M
DMDOHEMA/TPH

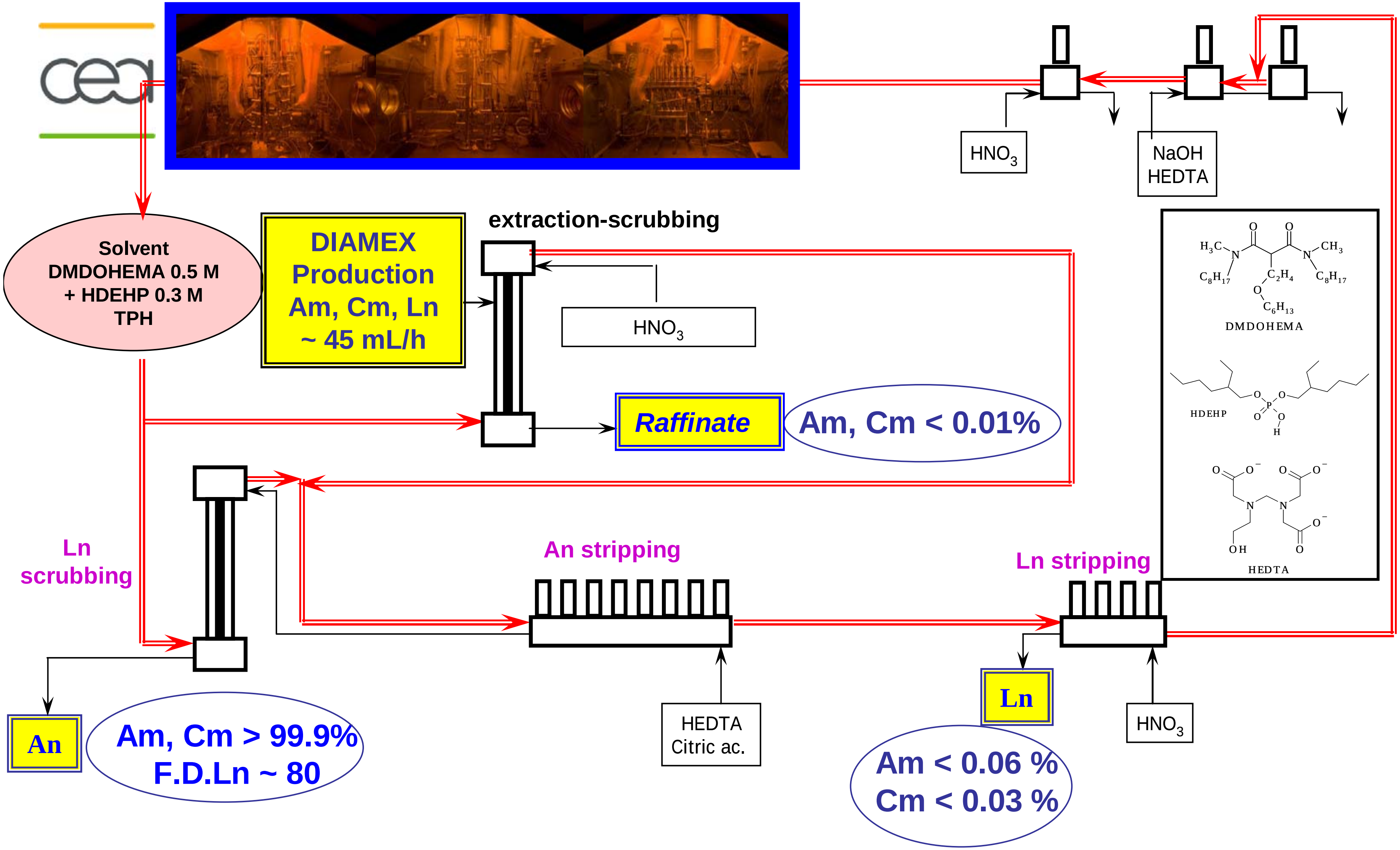
FP
Raffinate

Am ~ 0.015 %
Cm < 0.002 %

DIAMEX
Production
Am, Cm, Ln

Am, Cm, Ln
> 99.9%

SANEX demonstrative hot run, December 2005



Solvent
DMDOHEMA 0.5 M
+ HDEHP 0.3 M
TPH

DIAMEX
Production
Am, Cm, Ln
~ 45 mL/h

extraction-scrubbing

HNO_3

Raffinate

Am, Cm < 0.01%

Ln
scrubbing

An stripping

Ln stripping

HEDTA
Citric ac.

HNO_3

NaOH
HEDTA

HNO_3

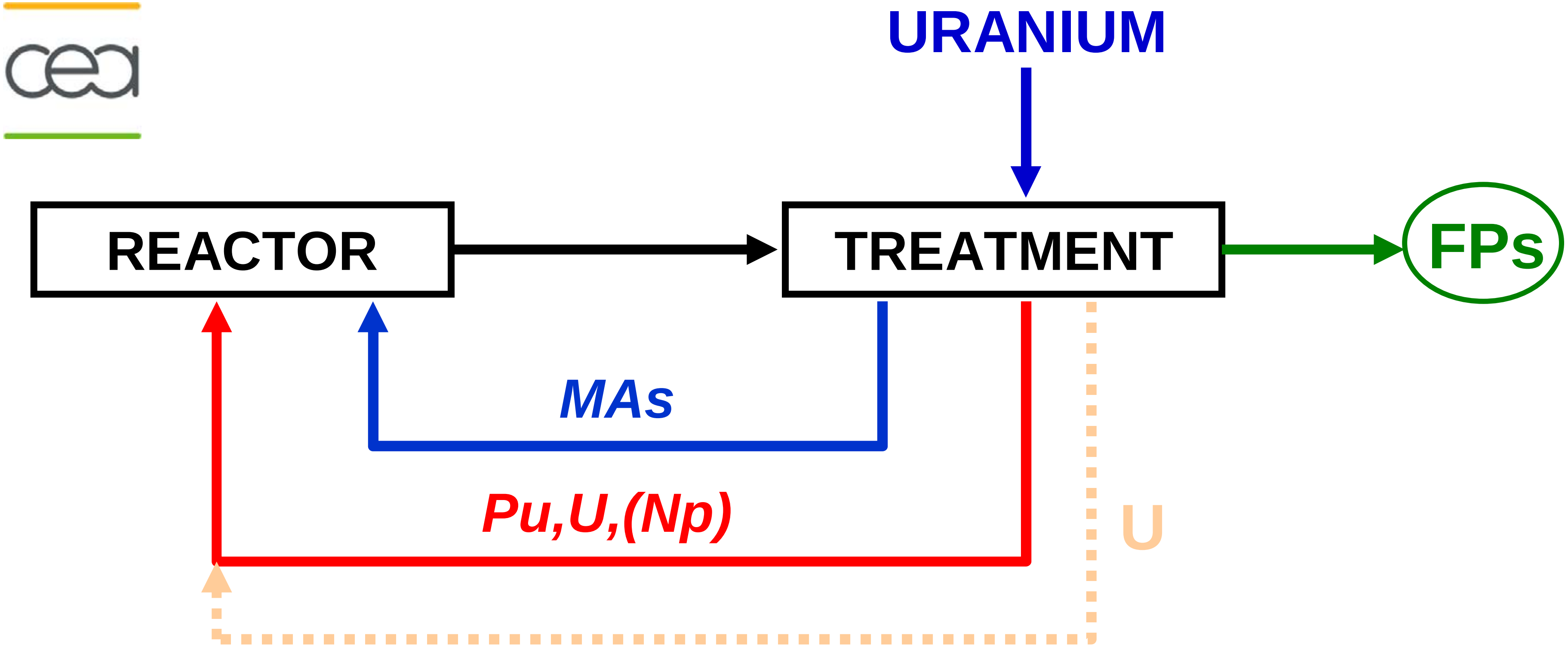
An

Am, Cm > 99.9%
F.D.Ln ~ 80

Ln

Am < 0.06 %
Cm < 0.03 %

Fuel cycle, the MA heterogeneous recycling option



URANIUM

REACTOR

TREATMENT

FPs

MAs

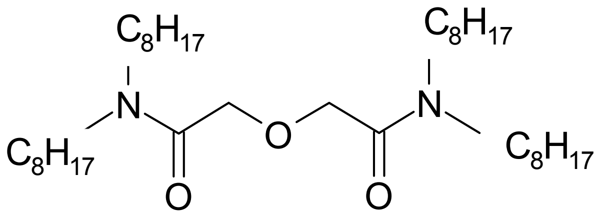
Pu,U,(Np)

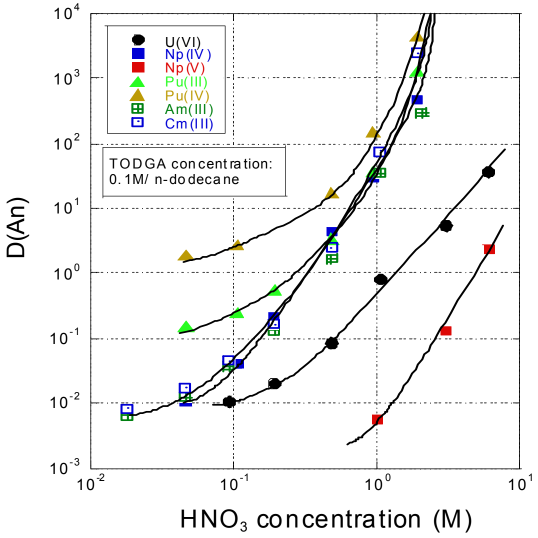
U

- U, Pu, Np by COEX™
- Am (and Cm) separation : simplified DIAMEX-SANEX,…
- Am (and Cm) recycled on dedicated « targets-blankets »

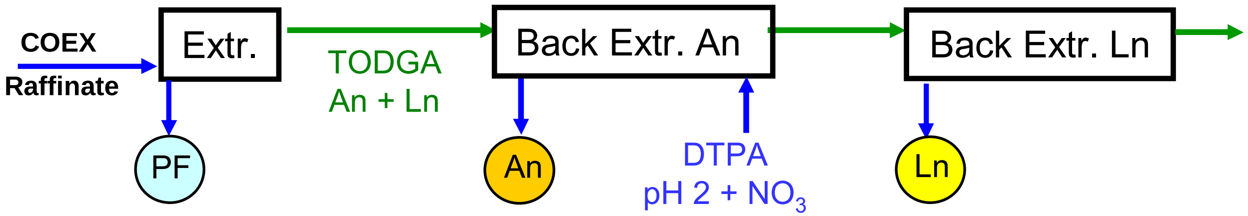
Simplified TODGA-SANEX process

- Co-extraction An (III) and Ln (III) with TODGA, using HNO_3 4N



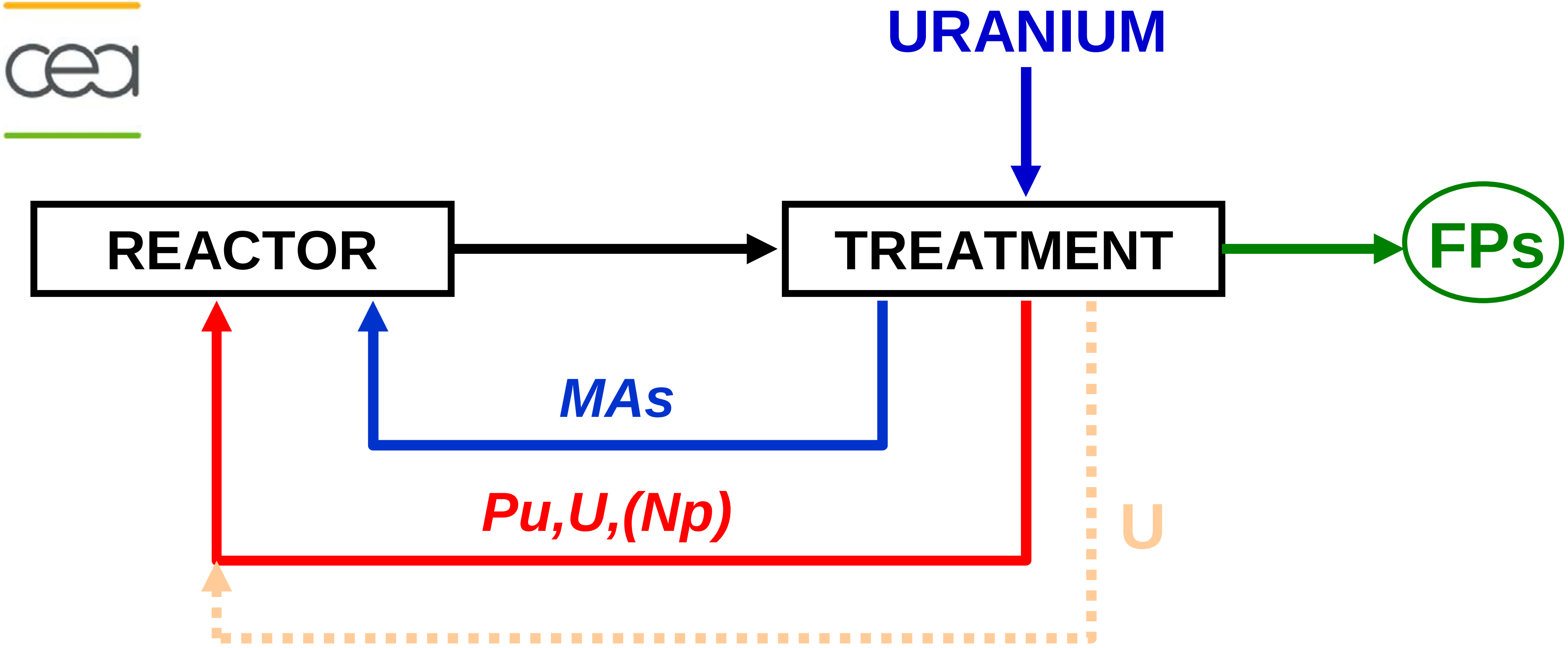


- **Selective back-extraction of An (III)**
  - **With polyamino-carboxylic hydrophile complexing agent**



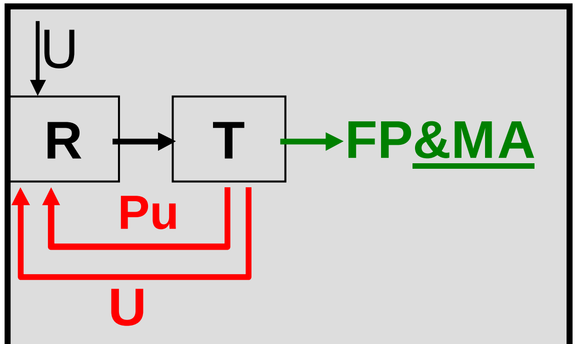
- **<u>Advantages</u> : simple scheme, TODGA synthesis low cost**
- **<u>Drawbacks</u> : high sensitivity of the Am-Cm back extraction step to pH and temperature**

Fuel cycle, the MA heterogeneous recycling option

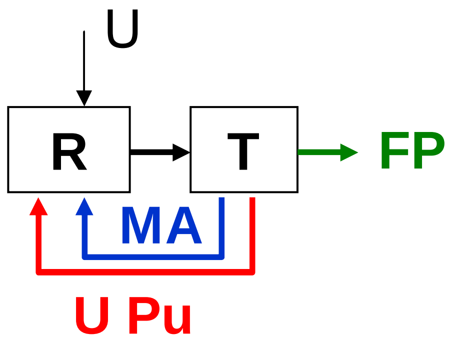


- U, Pu, Np by COEX™
- Am (and Cm) separation : (DIAMEX-SANEX), (SANEX-TODGA)…
- Am (and Cm) recycled on dedicated « targets-blankets »

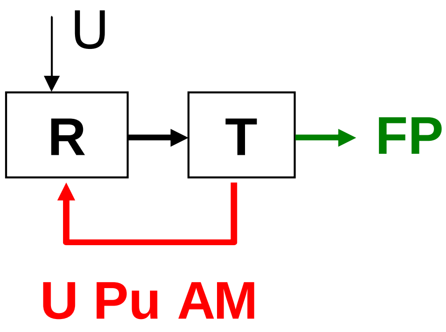
Actinide recycling : what fuel cycle option ?



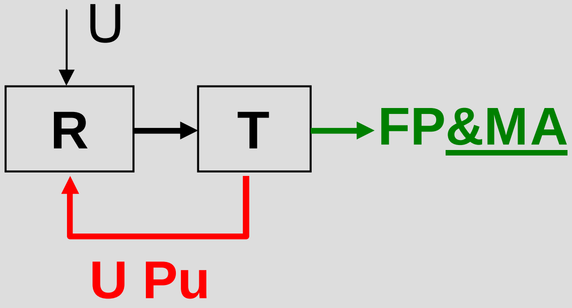
U and Pu recycled,
PUREX



MA heterogeneous recycling

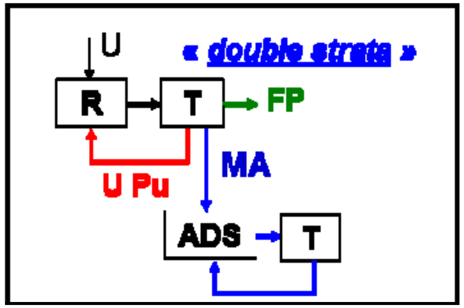


MA homogeneous recycling



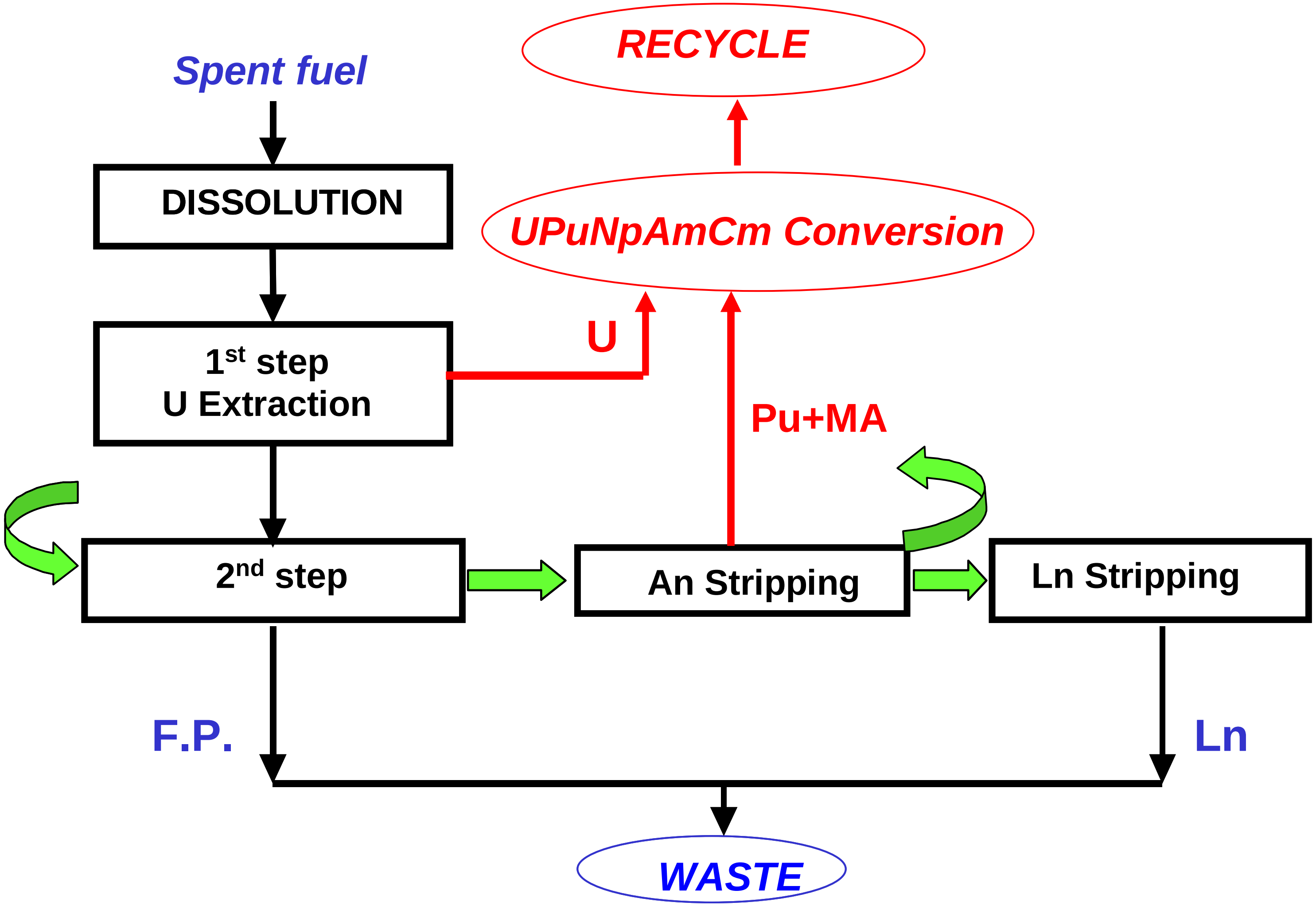
U and Pu recycled,
COEX

MA : Np, Am, Cm

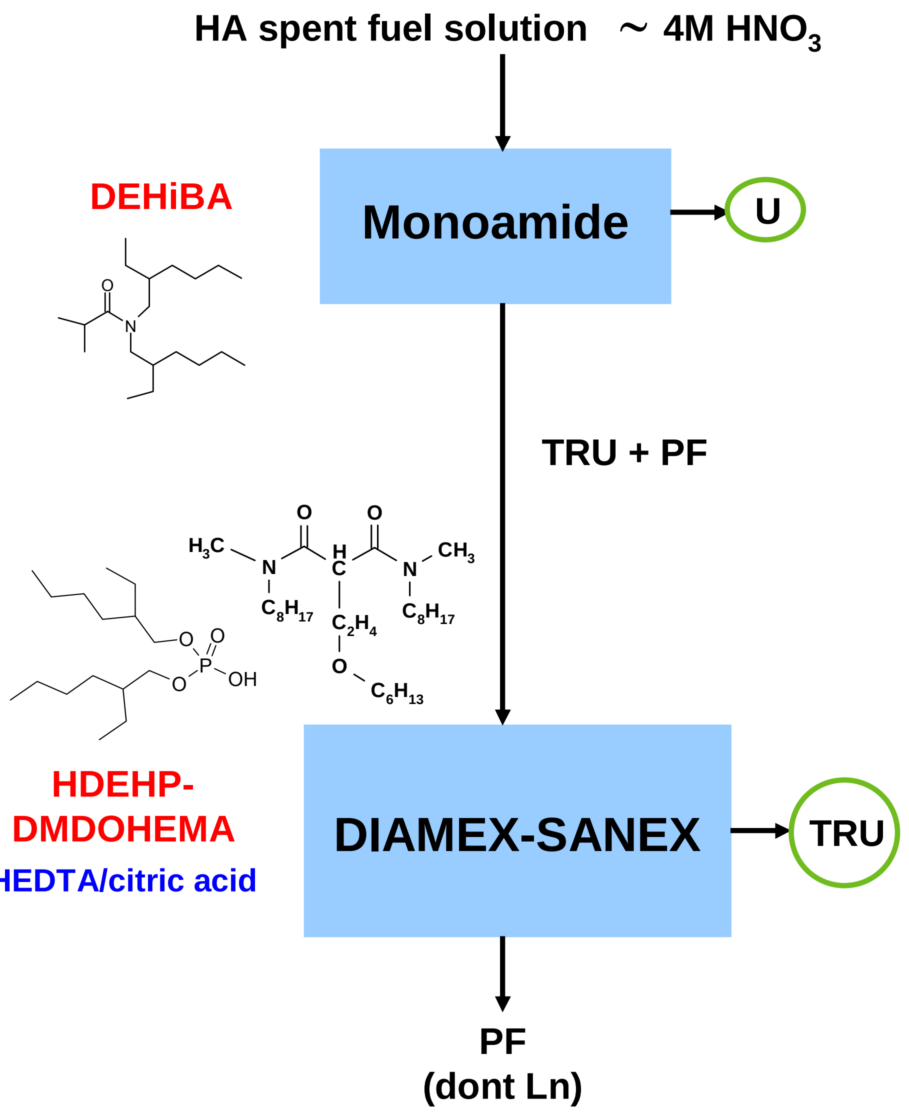


Fuel cycle, the MA homogeneous recycling option

The grouped actinide GANEX concept



The GANEX process



HA spent fuel solution ~ 4M HNO_3

Monoamide → U

DEHiBA

TRU + PF

HDEHP-DMDOHEMA

HEDTA/citric acid

DIAMEX-SANEX → TRU

PF
(dont Ln)

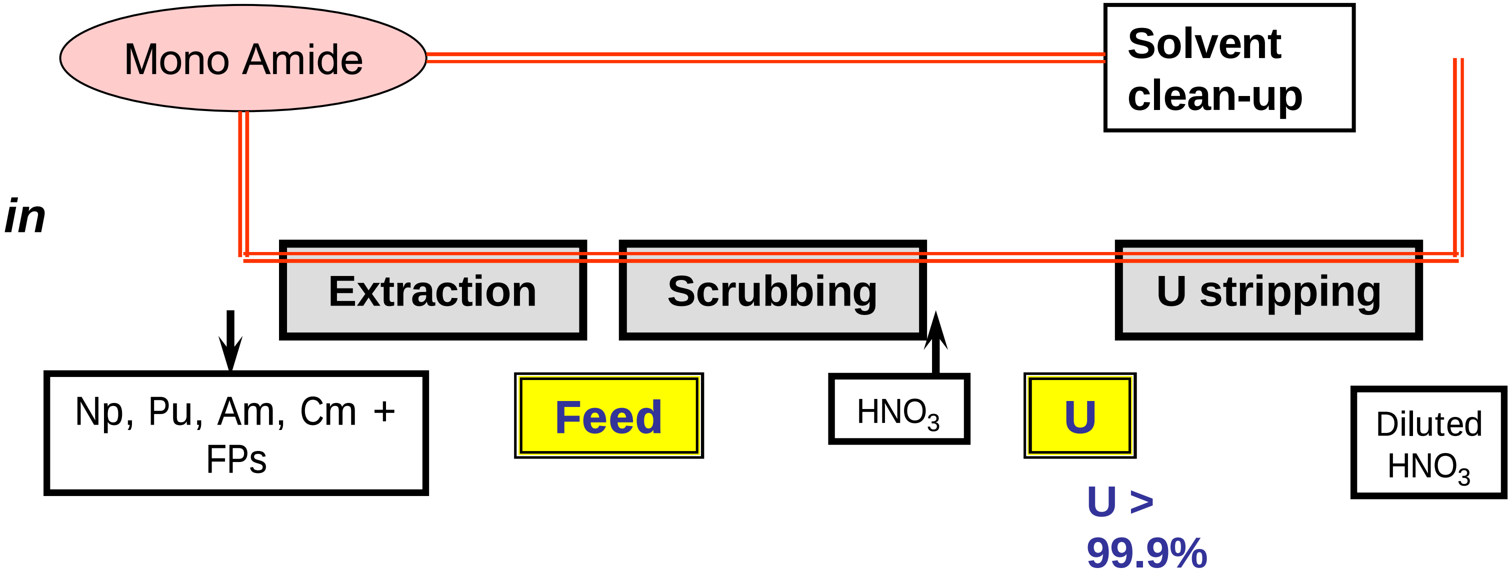
Excellent compromise between complete Uranium extraction, and good U(VI)/Pu(IV) selectivity

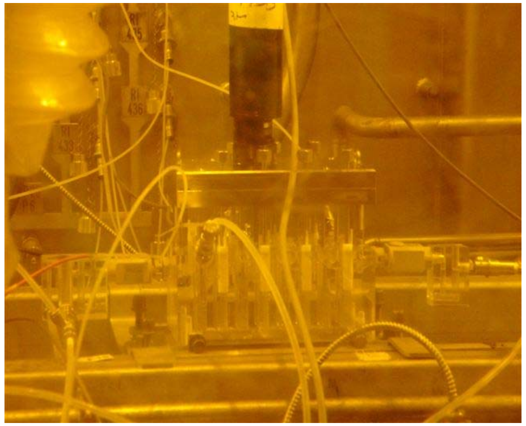
Adaptation of the process already demonstrated in 2005

GANEX demonstrative hot runs, 2008

1st step : *U selective extraction*

(performed successfully in June 2008)





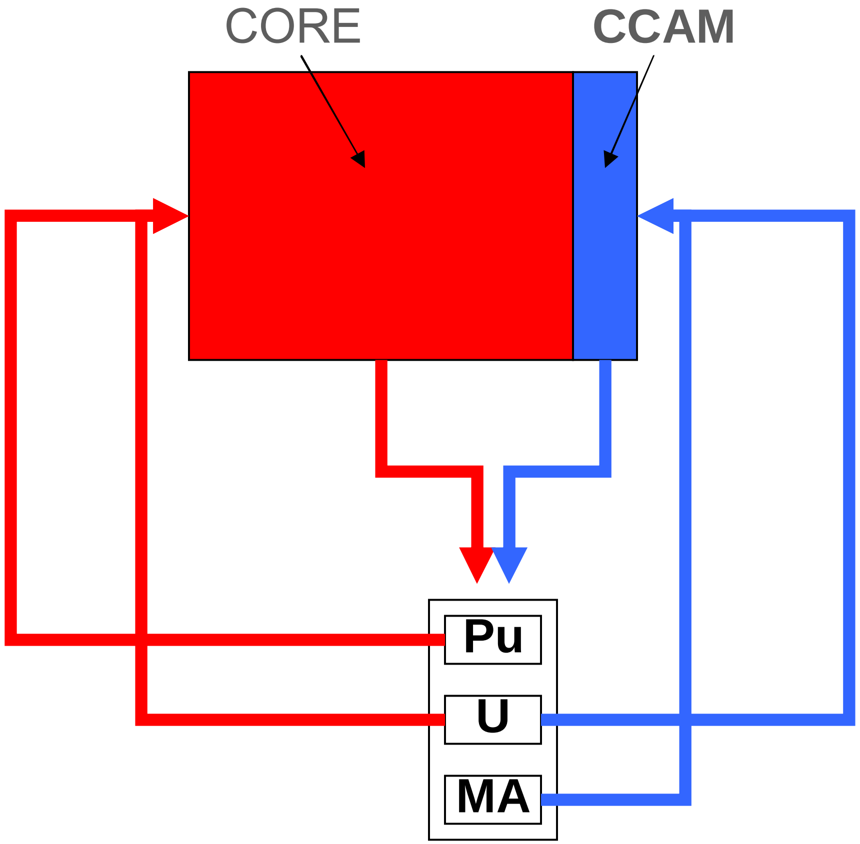
2nd step :

Pu-Np-Am-Cm co-recovery *(diamide-based process)*

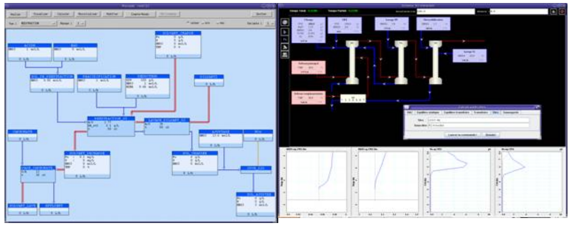
(performed successfully in November 2008)

Heterogeneous multi-recycling

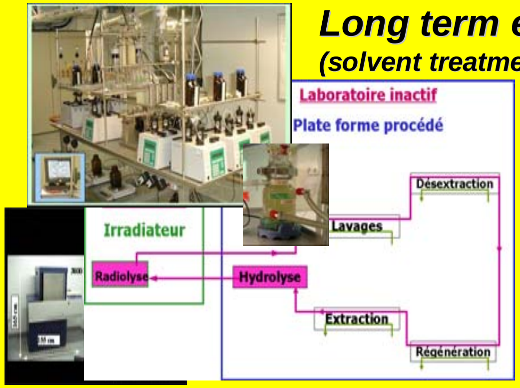
- **Core : $UPuO_2$**
- **"CCAM" : U<u>AM</u>O_2 (<u>*AM*</u> =Np/Am/Cm)**
  (minor actinide-loaded blankets)



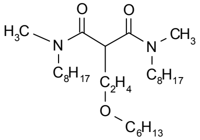
Recycling process : consolidation towards industrialization



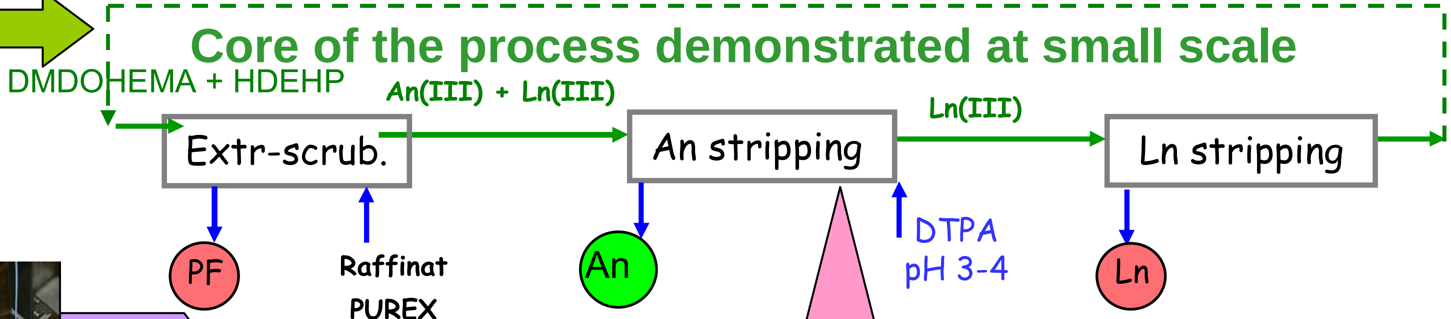
Modeling
(flowsheet, sensitivity, operation)



Long term effects
(solvent treatment)



Extractant synthesis



Core of the process demonstrated at small scale

DMDOHEMA + HDEHP

An(III) + Ln(III)

Ln(III)

Extr-scrub.

An stripping

Ln stripping

PF

Raffinat
PUREX

An

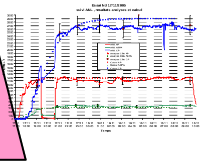
DTPA
pH 3-4

Ln

Equipments
(Implementation, extrapolation)

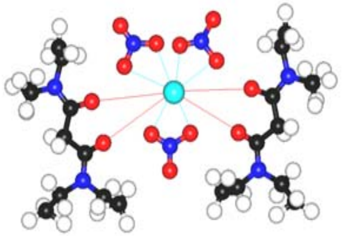
Interface
Co-conversion

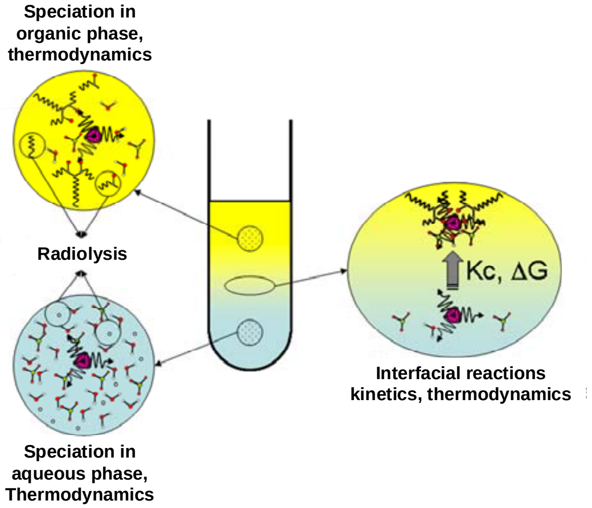
In situ analysis
(cations, pH…)



FP solution adapted to vitrification
(Concent. Calcination)

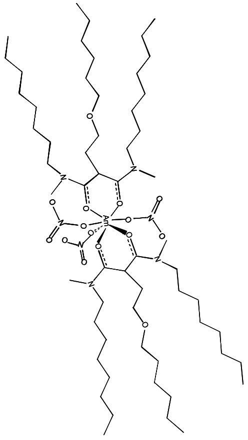
Modelling





- For what?
  - Reliable Calculation Codes
    - Draft flowsheets in industrial scale
    - Minimise number of experimental tests, steps and measuremer
    - Carry out operating analysis and transitory calculations

- How?
  - Phenomenological representation
    - Main equilibria during MA selective stripping



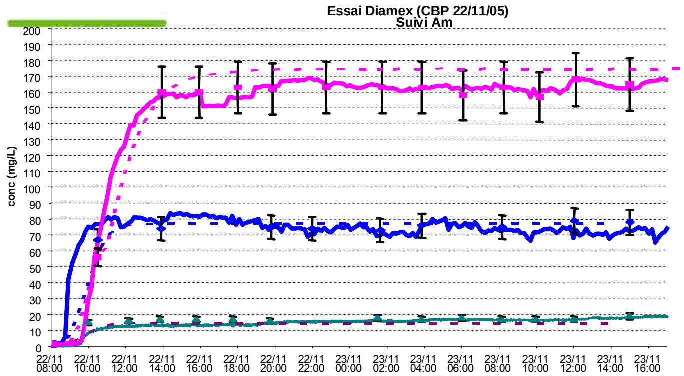
DIAMEX-SANEX:

- Extraction: M^{3+} + n (HDEHP) $\Leftrightarrow$ [M, 3DEHP,HDEHP] + 3 H^+
- Complexation: M^{3+} + HEDTA $\Leftrightarrow$ (M,HEDTA) + 3 H^+

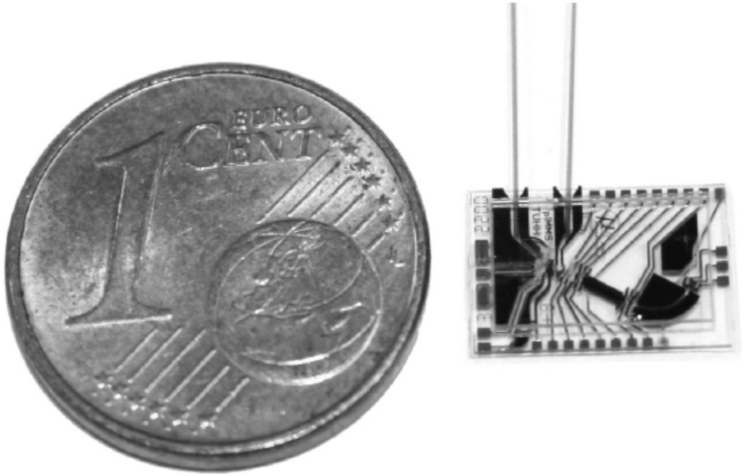
SANEX-TODGA:

- Extraction: M^{3+} + 3 NO_3^- + 3 TODGA $\Leftrightarrow$ [$M(NO_3)_3$,3 TODGA]
- Complexation: M^{3+} + HEDTA $\Leftrightarrow$ (M,HEDTA) + 3 H^+

Piloting process and in-situ analysis



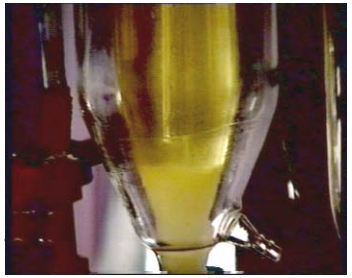
- Piloting process
  - Identifying sensitive parameters via sensitivity analysis and transient calculations
    - pH, flowrate, temperature…
  - Determine relevant points to be followed to detect serious malfunctioning
    - [cation]



- In-situ measurements
  - Am and Nd
    - Spectrophotometry adapted to « high activity »
  - Solvent
    - Assessment of miniaturized mass spectrometers

Apparatus: adaptation

- To each step specificity
  - **Solid Presence**
  - **Slow kinetics**

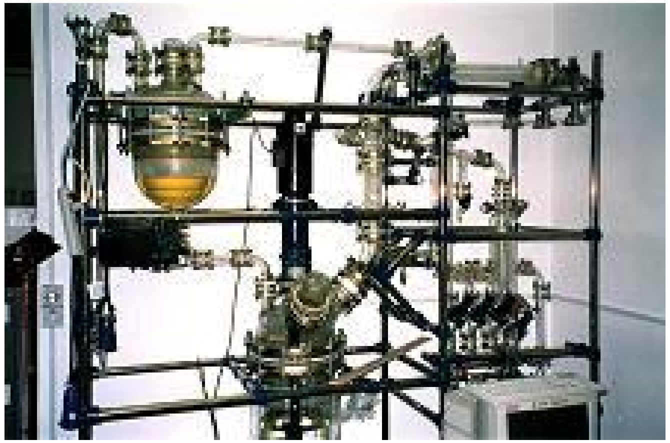


- Implementing conditions
  - **Example: comparison between DMDODHEMA**
    - Lower interfacial Tension
    - Higher Viscosity
    - Phase density difference, ajustable via extractant concentration

- Hydrodynamics tests to perform in pulsed columns (small diameter)
  - **DMDOHEMA/HDEHP/TPH**
  - **TODGA/TBP/TPH**

Extractant Synthesis

- **New extractants: DMDOHEMA, TODGA, DEHiBA…**
  - **Identify malonamides capable of being synthetized at large scale (tons)**
  - **Cost assessment**
  - **Required purity**



from kg to ton…

Solvent clean up

- **Objective : assessment of long term solvent behaviour**
  - **Clean up efficiency destined to remove acidic degradation products issued from hydrolysis/radiolysis**

Continuous long term runs

Simulating 1-2 years of industrial operation

⇨ **No significant impact on Hydraulic and Recovery performances**

Solvent studied:

- **DMDOHEMA/TPH**
- **DMDOHEMA/HDEHP/TPH**

Yet to be tested:

⇨ **TODGA**

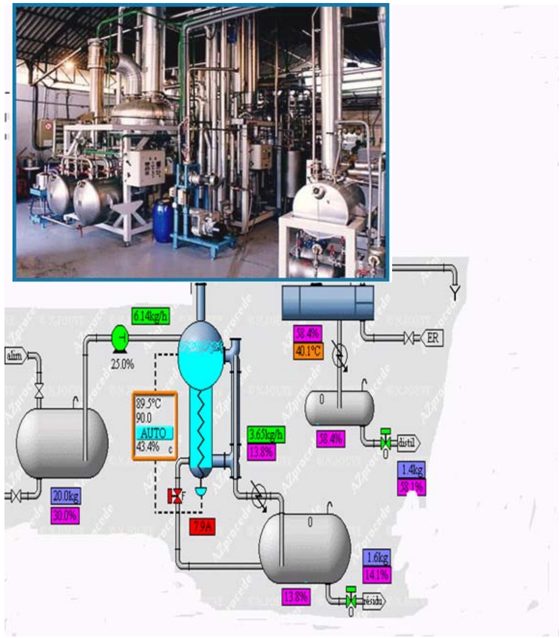
⇨ **DIAMEX-SANEX**

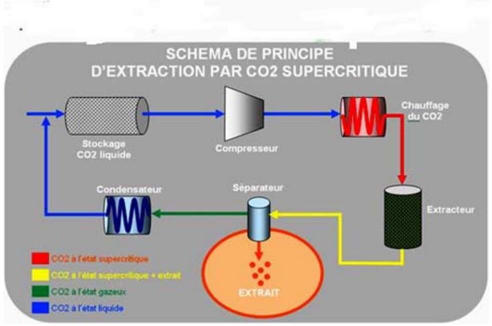
MARCOULE γ-Irradiation loop

Solvent clean up

- **Need of solvent purification step**
  - **Recover pure diluent**
  - **Extractant concentration**
  - **Decontamination/some degradation products**
  - ☹ **Thermosensitive molecules**

- **Assessment**
  - **Evaporation under vacuum**
  - **Flash distillation**
  - **Supercritical carbon dioxide extraction**





Innovative process : results to be obtained for 2012

1993

Exploratory Research

Several hundreds of molecules assessed

2001

Concepts selected
and validated

Scale 1/10000

2005

Demonstration experiments

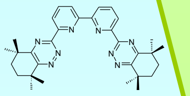
Scale 1/1000

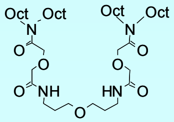
2008

Simplification

« **Consolidation** »

integration,
long-lasting performance
representativeness,





2012

Towards potential industrialization

Program in progress…