

FROM RESEARCH TO INDUSTRY

cea den

Separation of Americium alone from a Concentrated Raffinate by Liquid-Liquid Extraction (EXAm)

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➤ Recycling Am alone

- ↘ waste lifetime and radiotoxicity
- ↘ long term waste heat power → save repository resource

➤ Am and Cm chemistry

- Hard acids (HSAB theory)
- Ionic radius: Am 1.106 Å / Cm 1.094 Å
- Redox: Am(III) → Am(IV), (V), (VI)

57 La 138.9	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [144.91]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05
89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 244.06	95 Am 243.06	96 Cm 247.07	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.11]	102 No [259.10]

➤ Options

- Oxidation to Am(VI) and extraction (difficult to stabilize)
Ex.: SESAME (CEA), NaBiO₃ (B. Mincher *et al.* INL)
- Without redox chemistry - With selective lipophilic or hydrophilic system

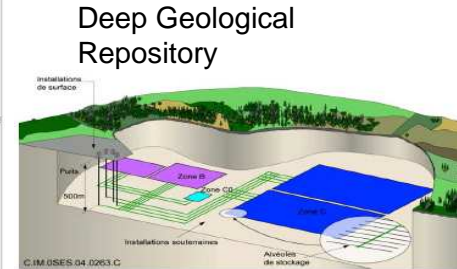
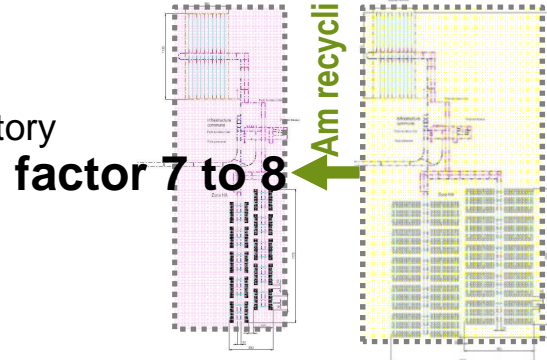
Processes tested by CEA: DIAMEX 2 → DMDOHEMA (48 stages!)

EXAm → DMDOHEMA + HDEHP / TEDGA

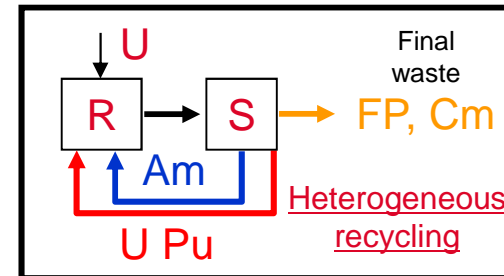
TODGA / TPAEN



HLW: 160 ha HLW: 1200 ha



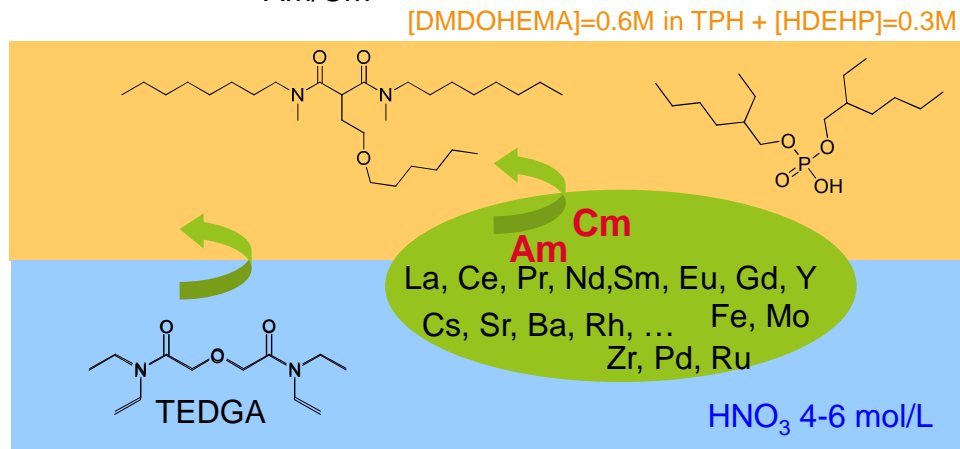
C. Poinssot, C. Rostaing, P. Baron, D. Warin, B. Boullis *Procedia Chem.* **7**, 358–366 (2012).
C. Poinssot, C. Rostaing, S. Grandjean, B. Boullis, *Procedia Chem.* **7**, 349–357 (2012).



PUREX
+
New process

➤ Selective Recovery of Americium alone from a PUREX raffinate in 1-cycle

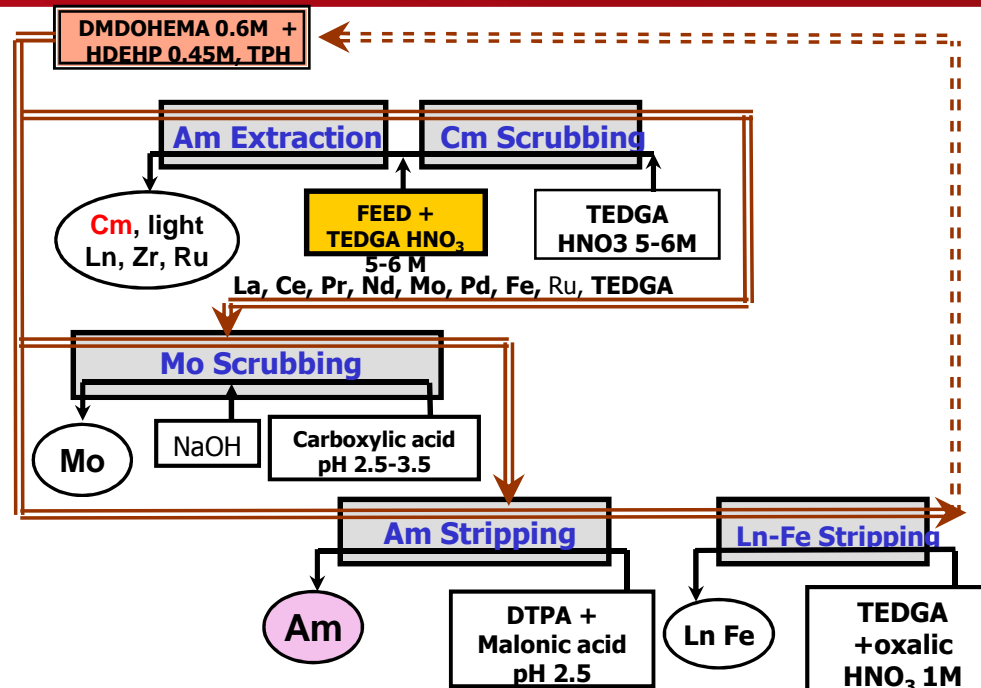
- Feed solution already cleared from U, Pu and Np
- Extractants alone → very low Am/Cm selectivity ($SF_{Am/Cm} = 1.6$)
- with TEDGA → $SF_{Am/Cm} = 2.5$ (32 stages)



■ Complexed chemistry (example with Ln)

- ❖ In the organic phase: $Ln^{3+}(DEHP)_x$ and $Ln^{3+}(NO_3)_3(DMDOHEMA)_y$
but also $Ln^{3+}(NO_3)_x(HDEHP)_y(DEHP)_{3-x}(DMDOHEMA)_z$, $Ln(NO_3)_3(TEDGA)_n(DMDOHEMA)_y$
- ❖ In the aqueous phase: $Ln(TEDGA)_n^{3+}$ (n=1,2 and 3)

M.-C. Charbonnel *et al.*, *Procedia Chem.* **2012**, 7, 20–26. V. Pacary *et al.*, *Procedia Chem.* **2012**, 7, 328–333. J. Muller *et al.*, *SEIE* 2016, 141-160, C. Marie, *et al. Proceedings ISEC*, **2014**, 105-110.

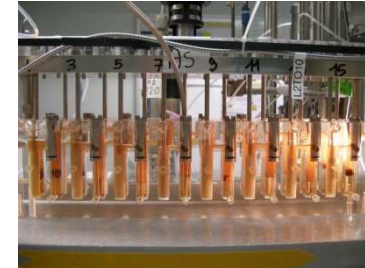
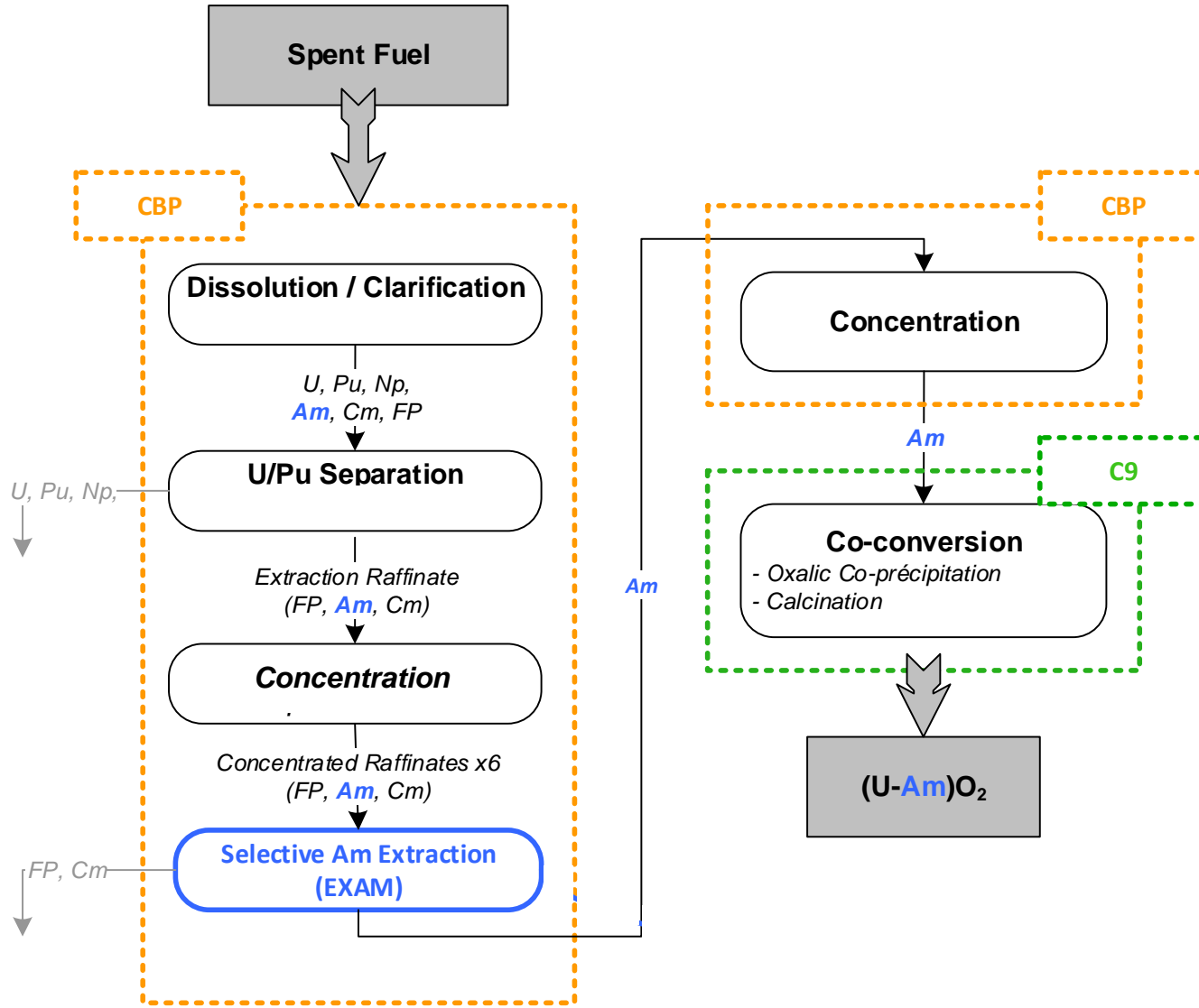


Demonstration of the faisability with a first hot test in ATALANTE facility in 2010

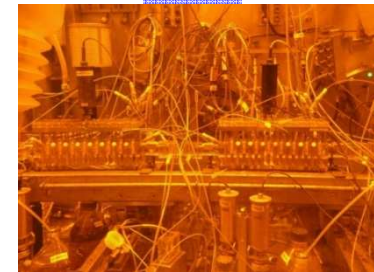
→ Am recovery \approx 98.5% with $DF_{Am/Cm} = 500$

Improvement suggested : increase the compactness of the process (to reduce industrial contactors size and quantity of side streams)

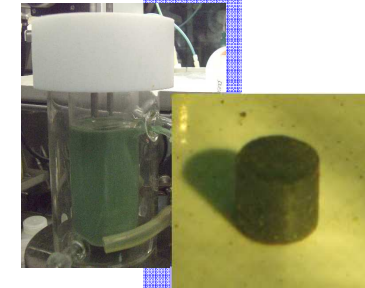
Next step: Hot Test on genuine PUREX raffinate after concentration



Cold and spiked tests



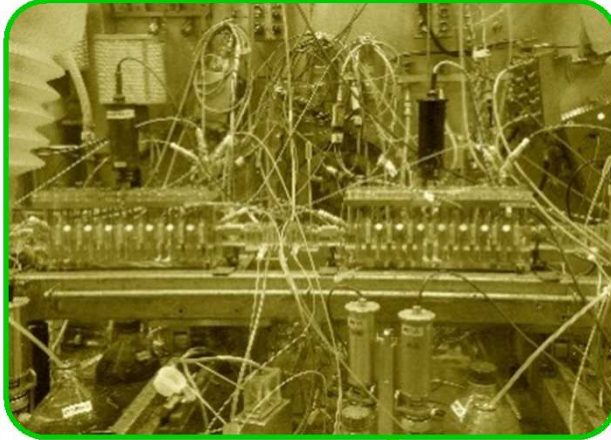
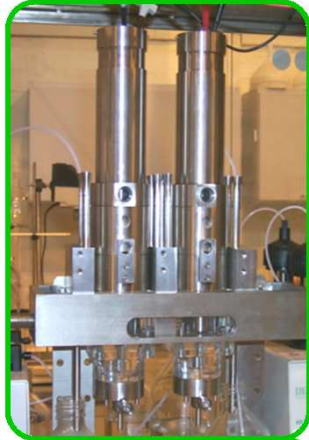
Hot test



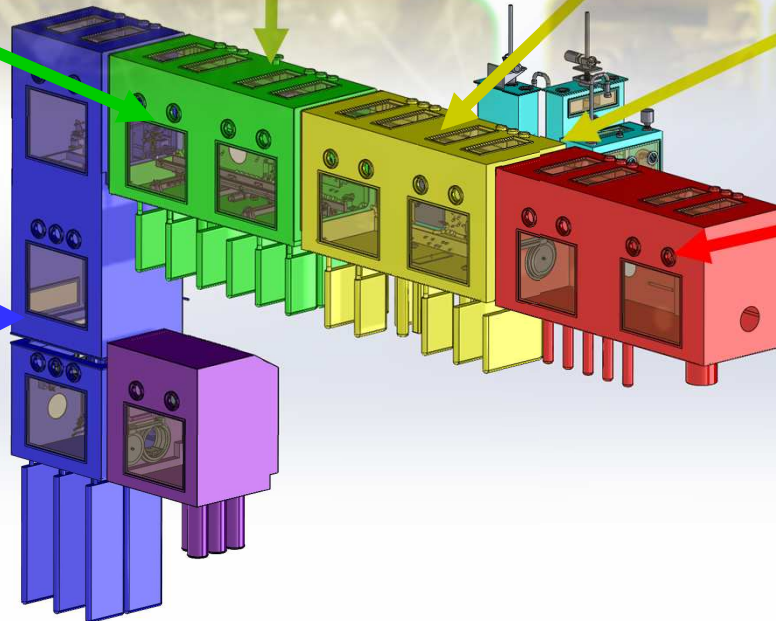
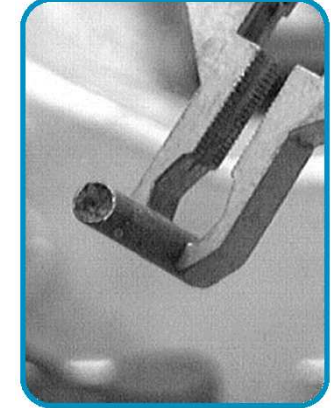
Oxalic co-conversion and U-Am oxide fabrication

Overview of the CBP Shielded Process Line

Solvent extraction



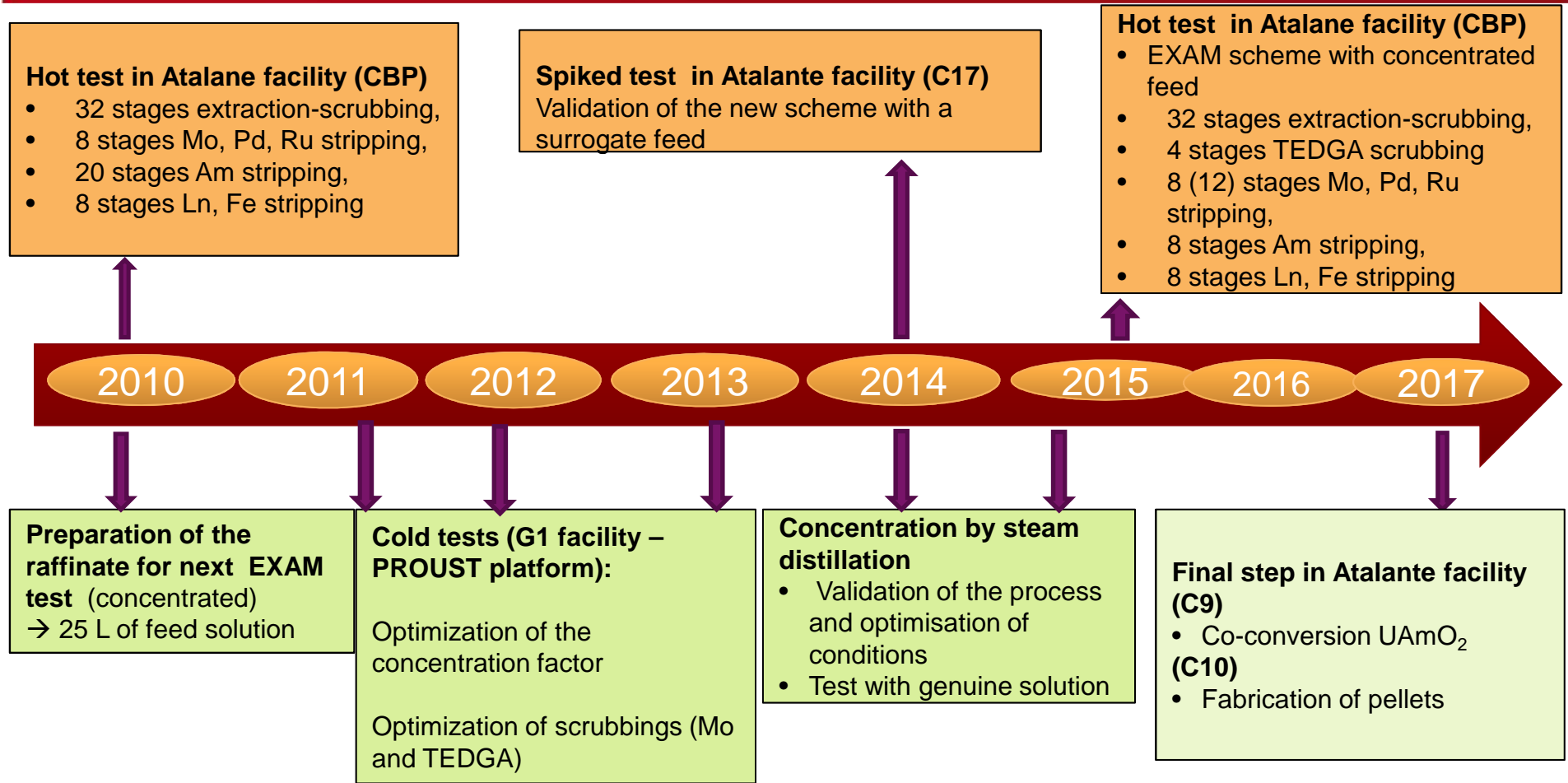
Dissolution and clarification



SNF reception

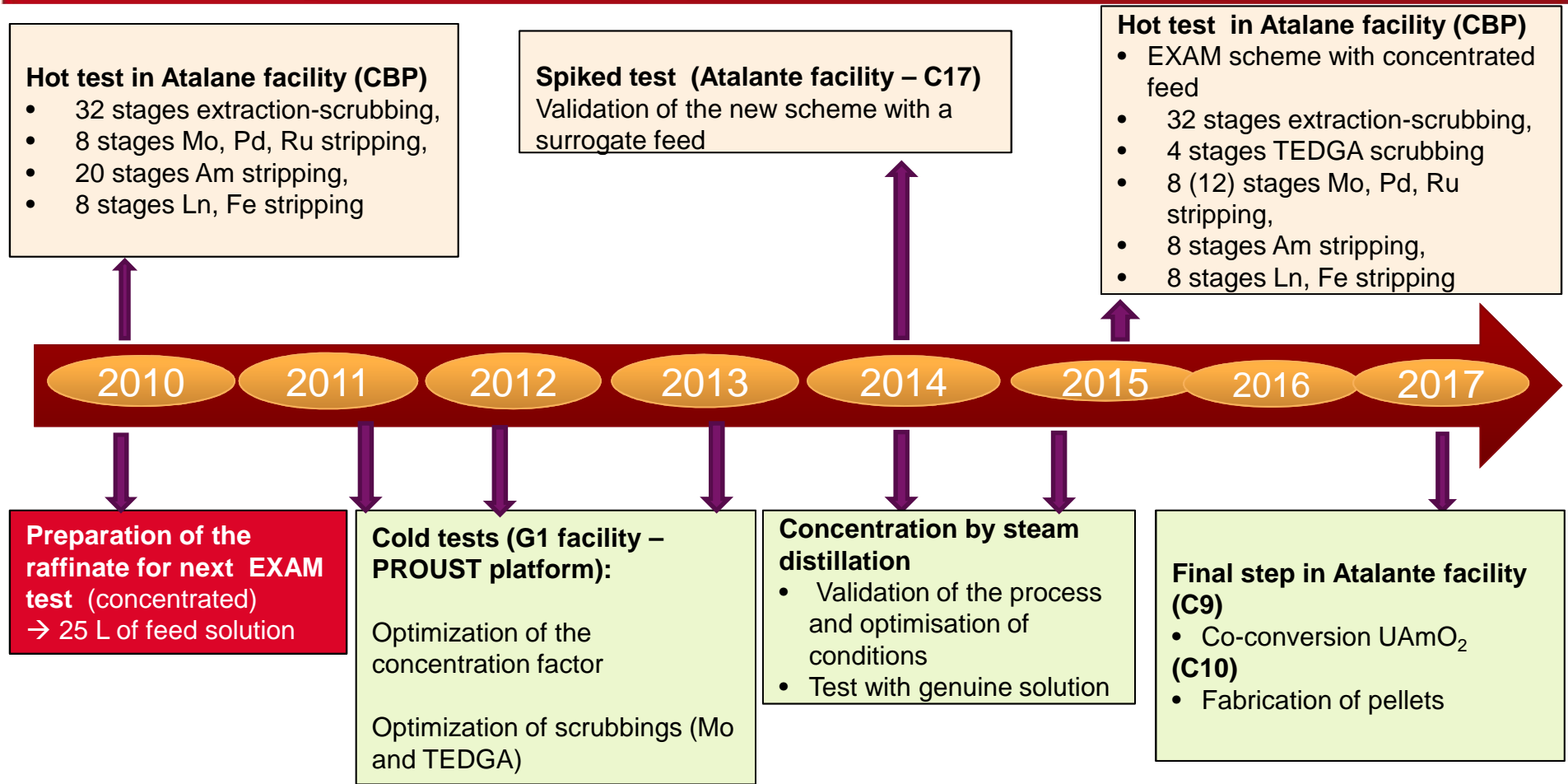


EXAM – Process Development



Tests at laboratory scale

Modelling



Tests at laboratory scale

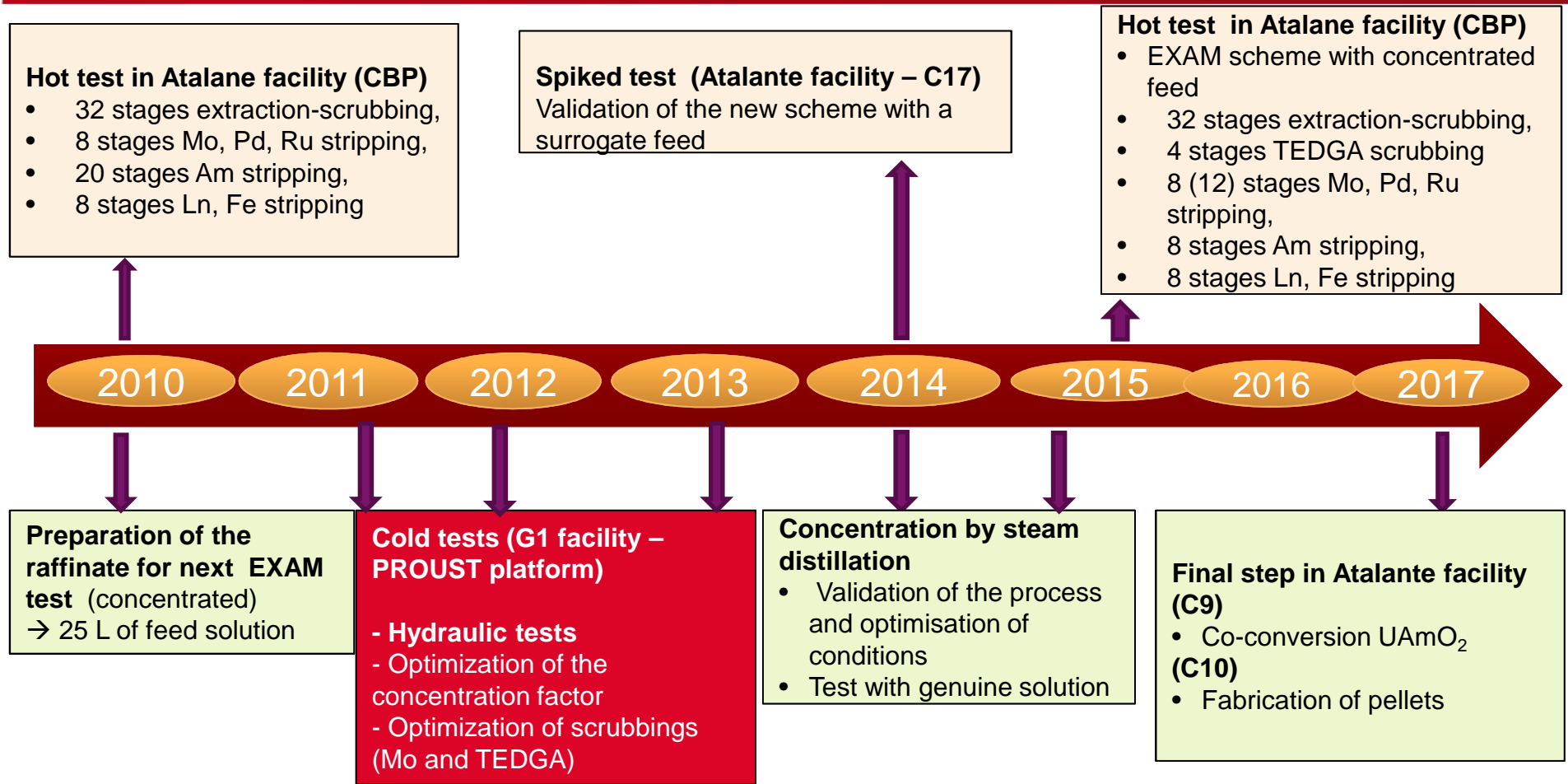
Modelling

- 3 dissolution batches
 - Dissolution of 3 kg of UOX and 1.6 kg of MOX fuel

- Total volume : 22 L

- Main characteristics of the dissolution solution
 - $C_{\text{HNO}_3} = 4.3\text{M}$,
 - $c_{\text{U}} = 160\text{ g/L}$,
 - $c_{\text{Pu}} = 4.4\text{ g/L}$,
 - $c_{\text{Np}} = 49\text{ mg/L}$,
 - $c_{\text{Am}} = 160\text{ mg/L}$
 - $c_{\text{Cm}} = 50\text{ mg/L}$
 - Total $\beta\gamma$ activity: $1.9 \cdot 10^{12}\text{ Bq/L}$ (02/2011),
 - ^{106}Ru activity: $1.35 \cdot 10^{11}\text{ Bq/L}$ (02/2011).





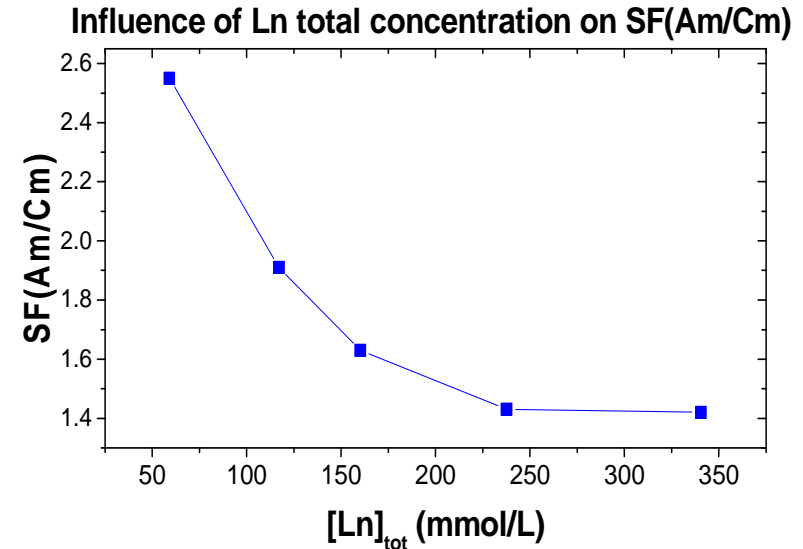
Tests at laboratory scale

Modelling

EXAM (Concentrated flowsheet) Which concentration factor?

- Keep a good Am/Cm separation factor

	UO ₃ (PUREX raffinate)	5x
Σ Ln (mM)	25	125
Σ Cations (mM)	52	260

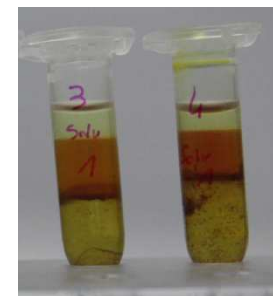


- Main modifications

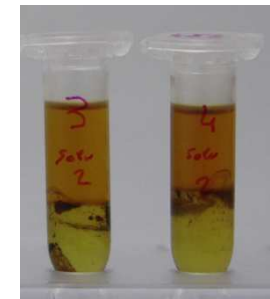
Increase of c_{Ln}^{aq} ---→ **increase c_{TEDGA}**

But c_{TEDGA}^{org} ↗ and then the loading capacity ↘

Avoid 3rd phase formation ---→ **increase c_{HDEHP}**



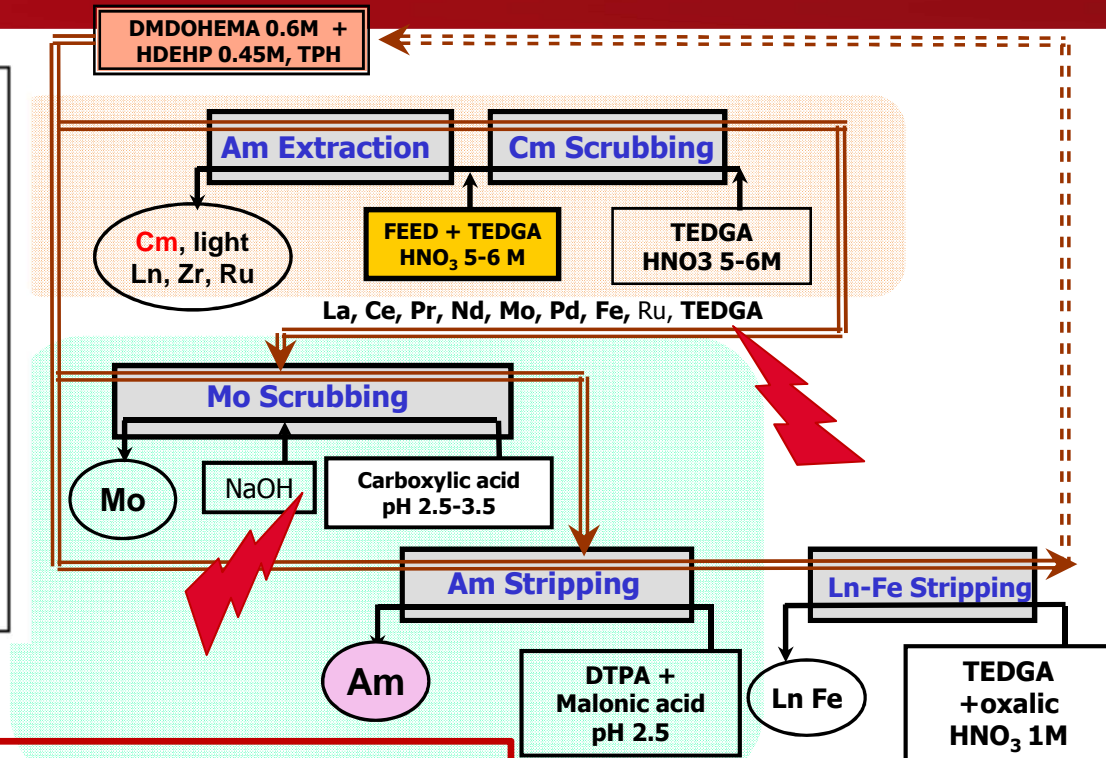
DMDOHEMA 0.6M
HDEHP 0.30 M



DMDOHEMA 0.6M
HDEHP 0.45 M

- Highest Concentration Factor reasonably achievable is **3.5**

EXAM (concentrated flowsheet) Which influence on stripping steps?

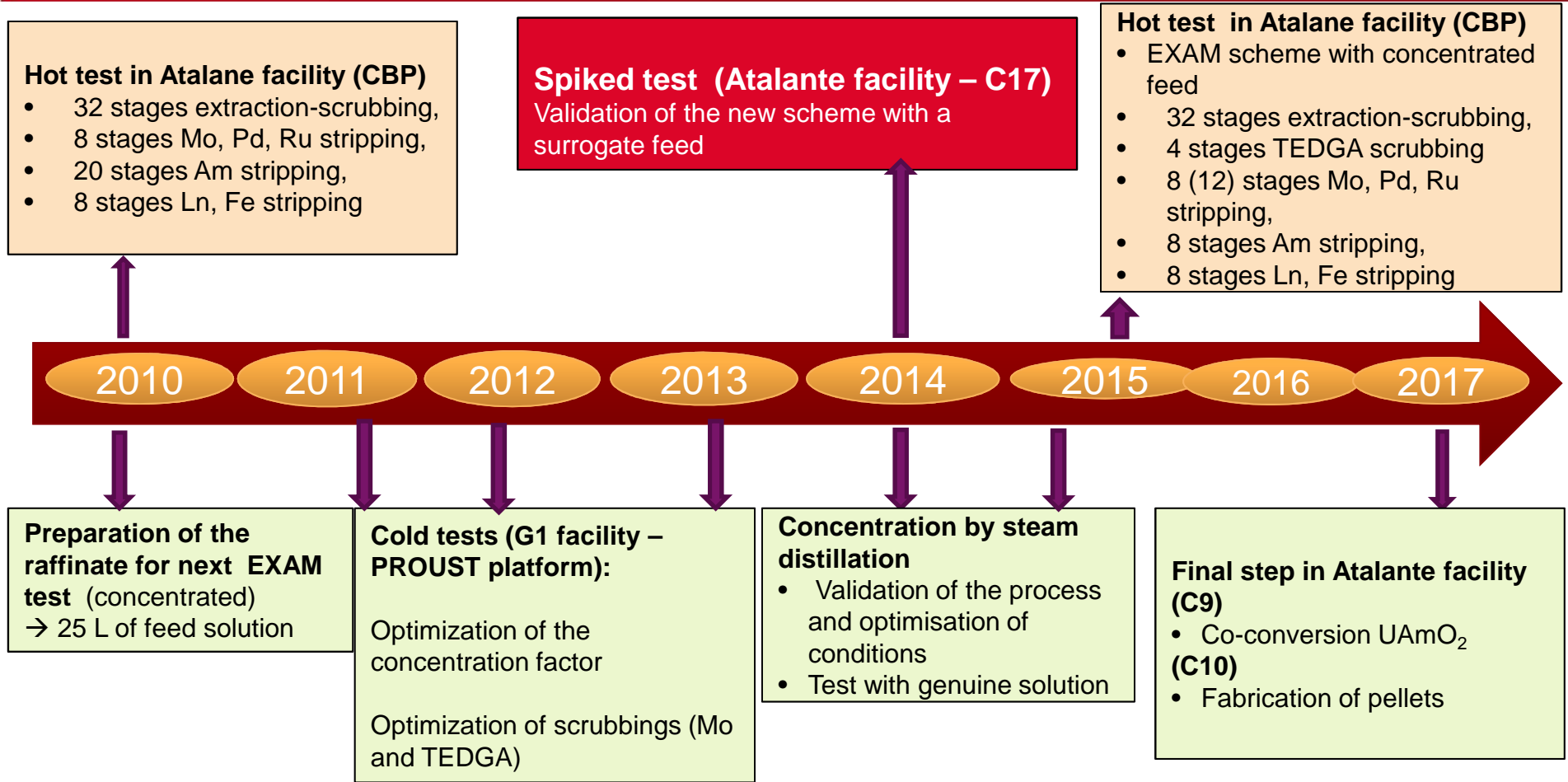


2 main issues with a concentrated flowsheet:

- c_{TEDGA} in the organic phase increases
 - Leak of Am during Mo scrubbing
 - Competition with DTPA during the Am stripping
- pH stabilization in Mo scrubbing steps more difficult
 - Study of others buffering/complexing molecules

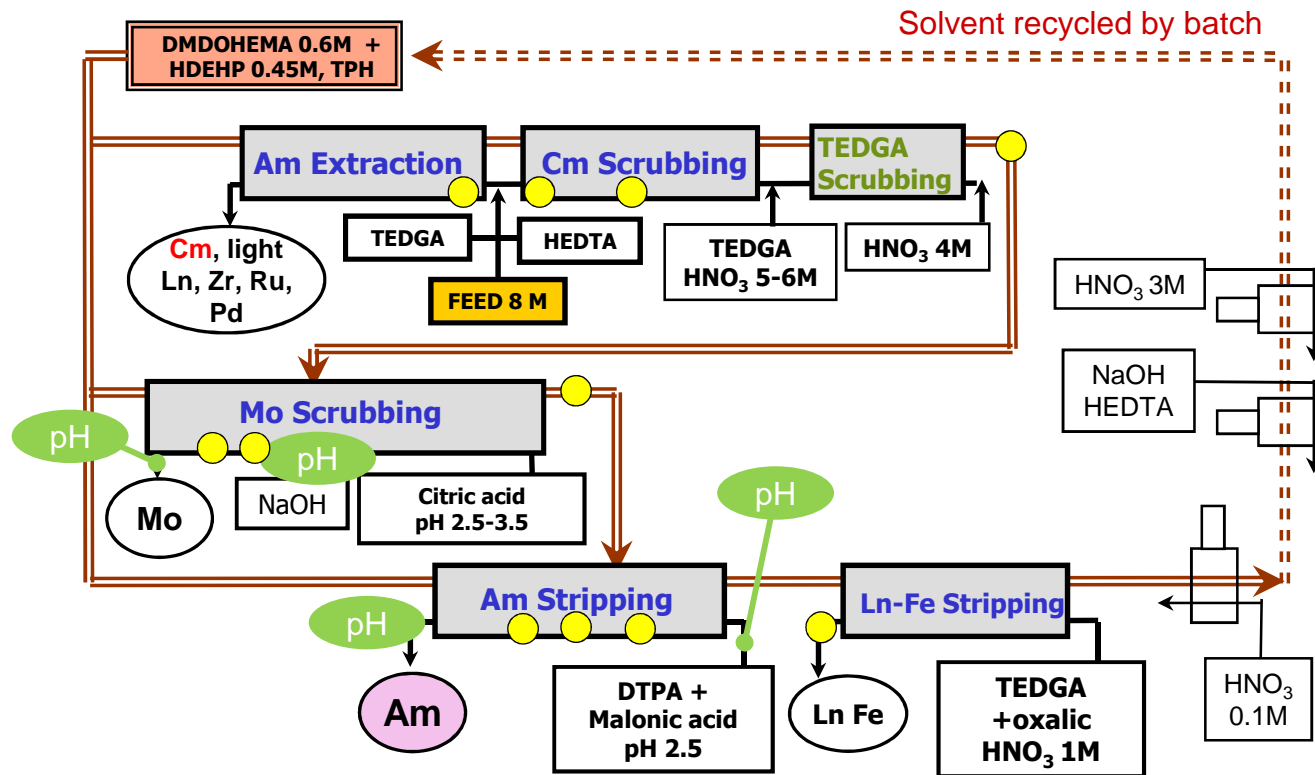
➔ **Additional TEDGA scrubbing** to maintain $c_{\text{TEDGA}}^{\text{org}} < 10 \text{ mM}$

➔ **Citric acid (instead glycolic acid) in Mo scrubbing test**



Tests at laboratory scale

Modelling



Simulated Feed
Concentration factor = 3 UO₃

Element	g/L
La	1.6
Ce	2.6
Pr	1.2
Nd	4.9
Sm	1.2
Eu	0.17
Gd	0.22
Y	0.56
Zr	1.8
Pd	2.2
Mo	2.2
Fe	1.1
Ru	1.7

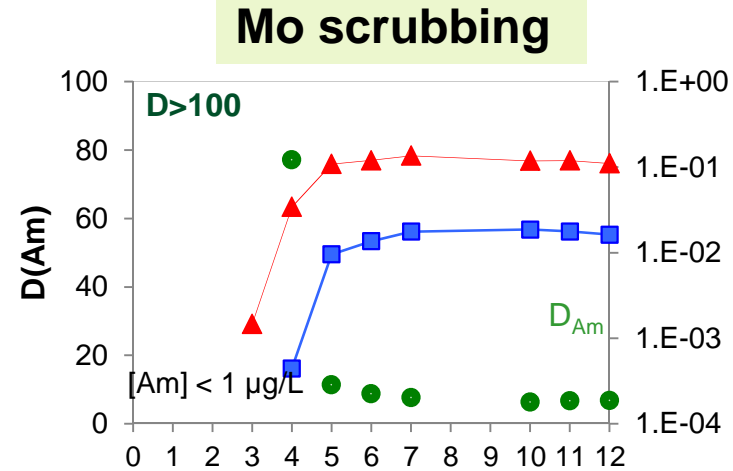
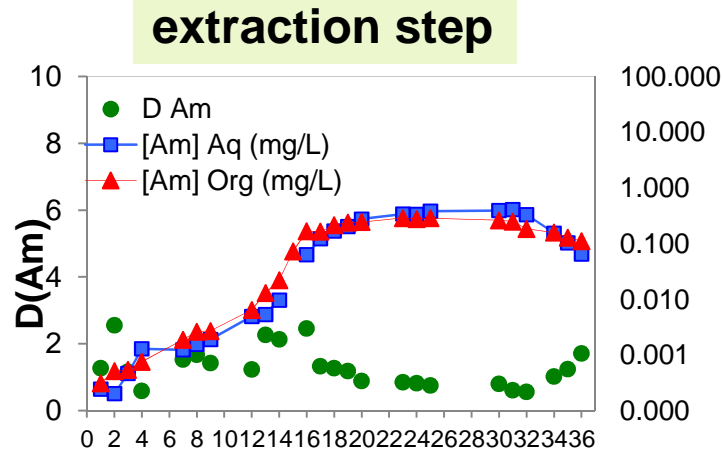
²⁴¹Am
0.4 mg/L

²⁴⁴Cm
0.2 mg/L

- Addition of HEDTA as Pd masking agent (limit the saturation)
- TEDGA Scrubbing
- pH control, online spectrophotometry ●
- Solvent recycled by batch (after analysis c and re-adjustment)

➤ Main results

- Very good adequation between data calculated and measurements

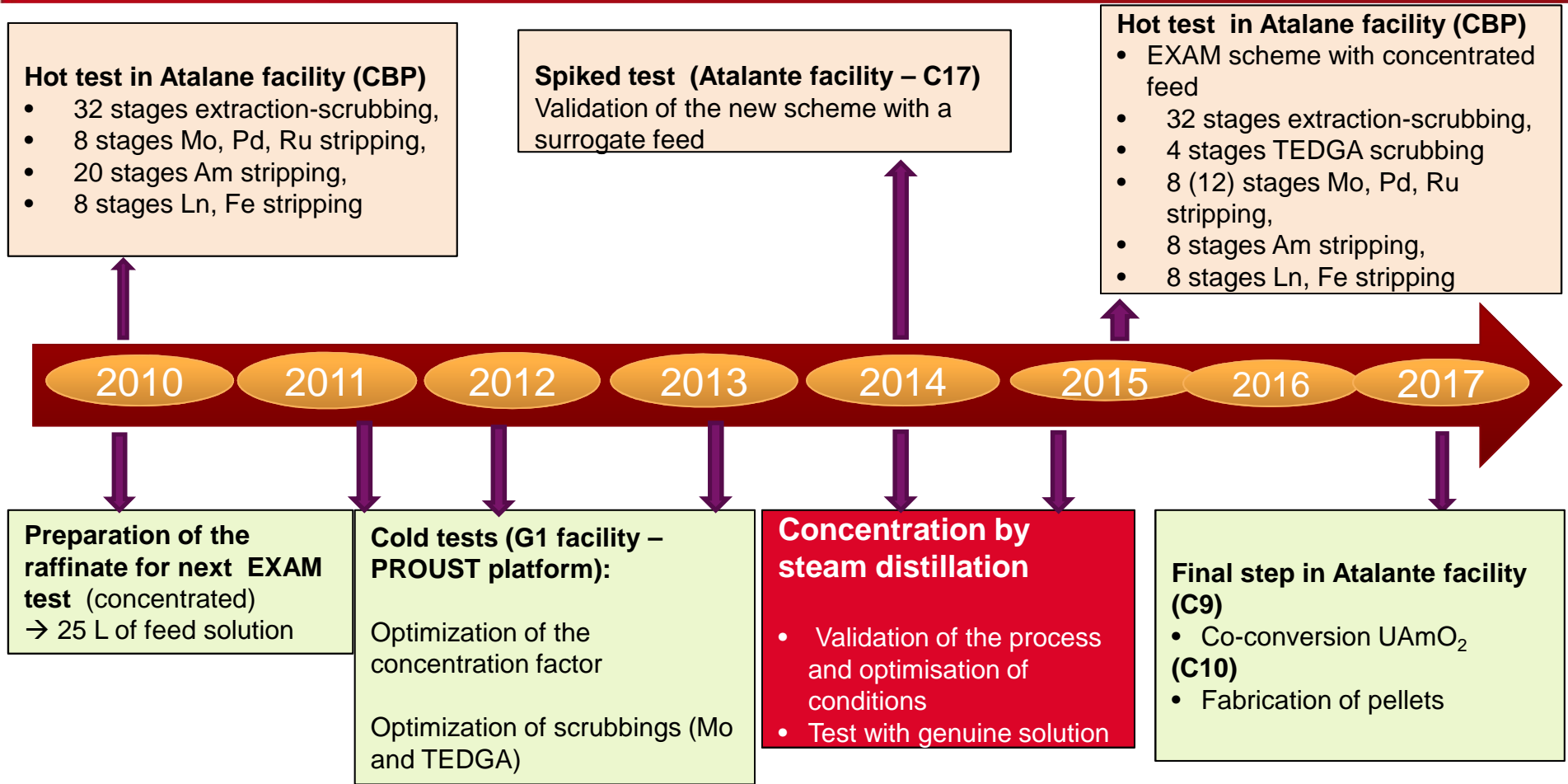


➤ Performances

Step	Am Recovery	Decontamination factor
Am Extraction Cm Scrubbing	~ 98.4%	DF(Am/Cm) ~ 40 Efficient TEDGA scrubbing ($C_{TEDGA}^{org} < 10mM$)
Mo Scrubbing	$C_{Am}^{raffinat} < 0.1\%$	Quantitative recovery of Mo (< 0.1%)
Am Stripping	> 99.87%	DF(Am/Nd) = 100

Technical problems
Equilibrium not reached

pH well controlled



Tests at laboratory scale

Modelling

➤ Choice of steam distillation instead of classical formic denitration

- safety regulation at Atalante facility
- acidity very high

➤ Goals of the steam distillation

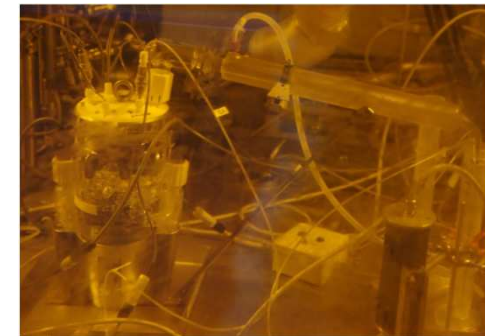
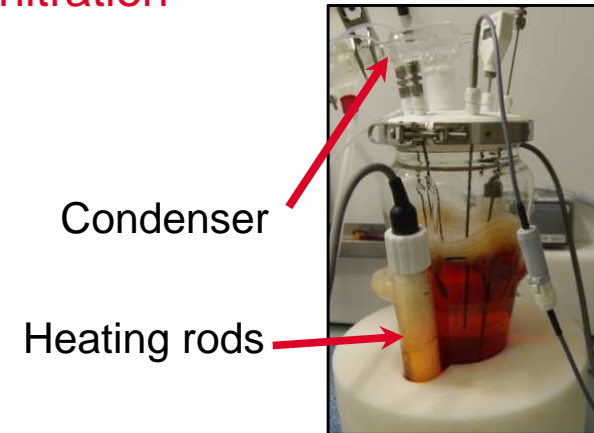
- Increase the salts concentrations by a factor of 6
- Maintaining the nitric acid concentration around 8 M

➤ Preliminary optimization of operational conditions: (C17 cell)

- Low acidity of the feed solution: $[H^+]_{\text{feed}} = 3,4 \text{ M}$
- High acidity in the reactor: $8 \text{ M} \Rightarrow [H^+]_{\text{distillate}} = 1,8 \text{ M}$
- Minimization of effluent volumes
- Absence of precipitates (only RuO_2 and small quantity of Zr/phosphates)

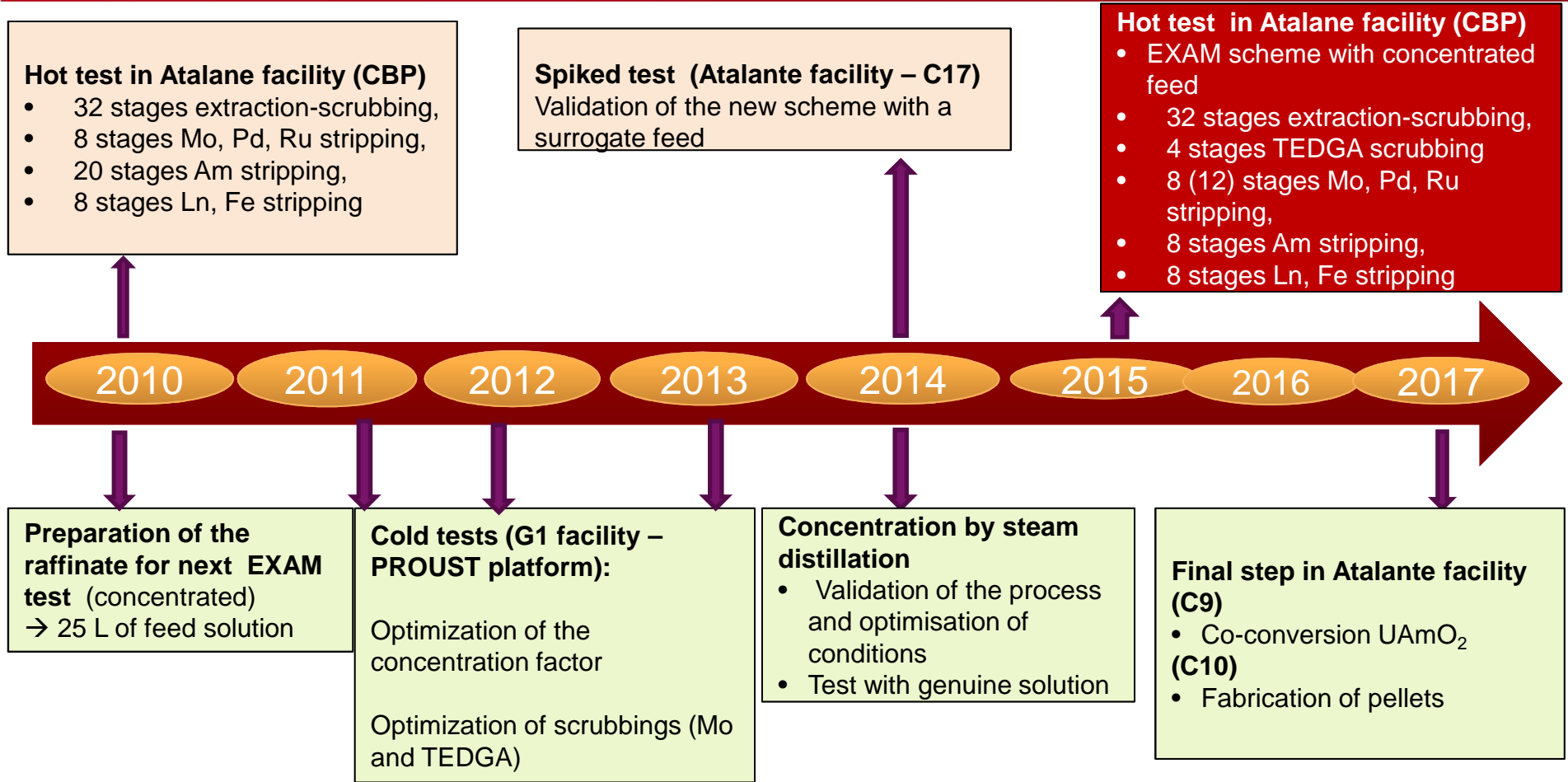
➤ Concentration of the active solution (CBP)

- Test of the cooling system, determination of the maximum heating power and of the optimum flowrates
- Concentration in two batches of 11 L (duration of 3 shifts)



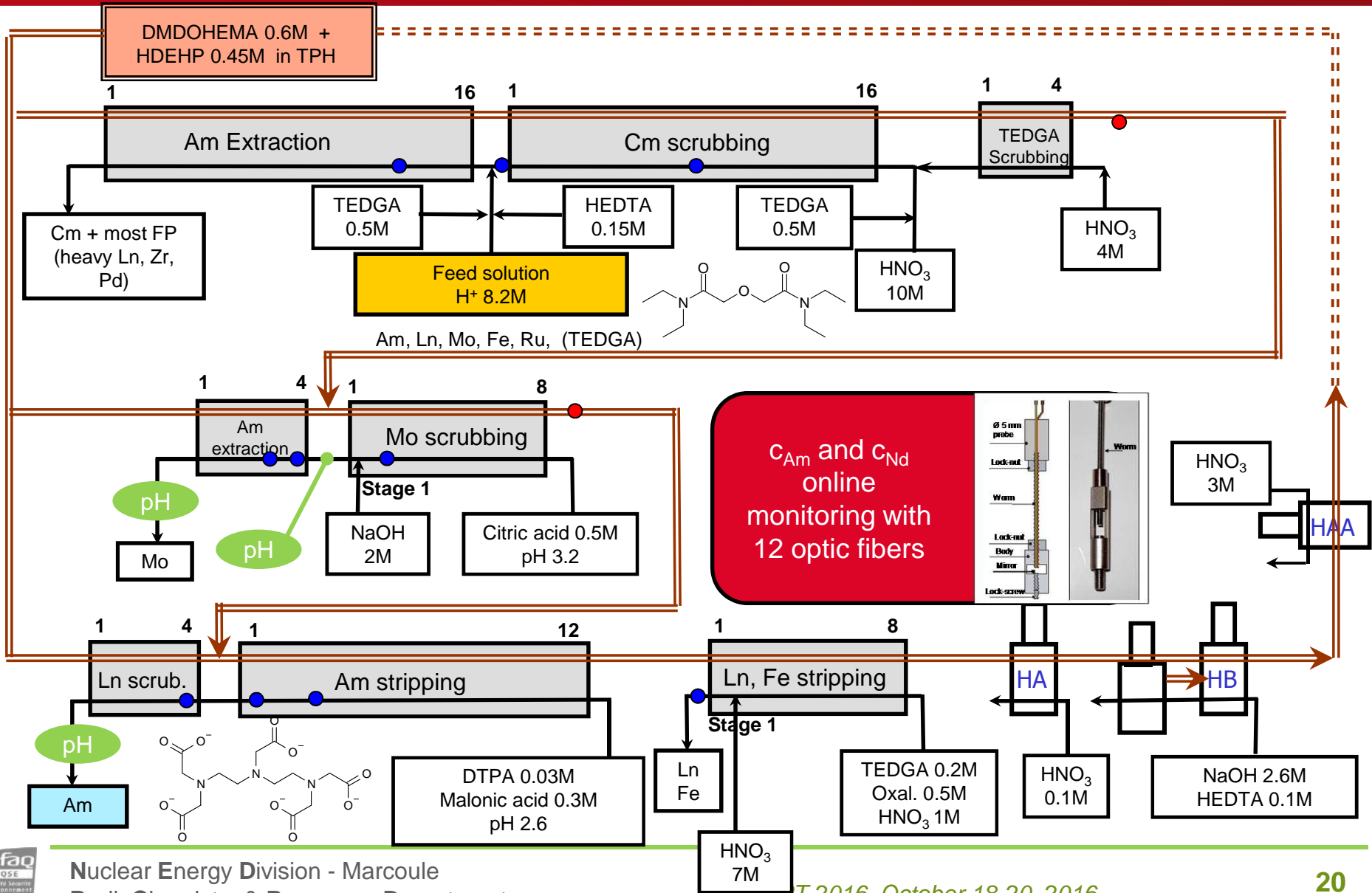
Composition of PUREX raffinates

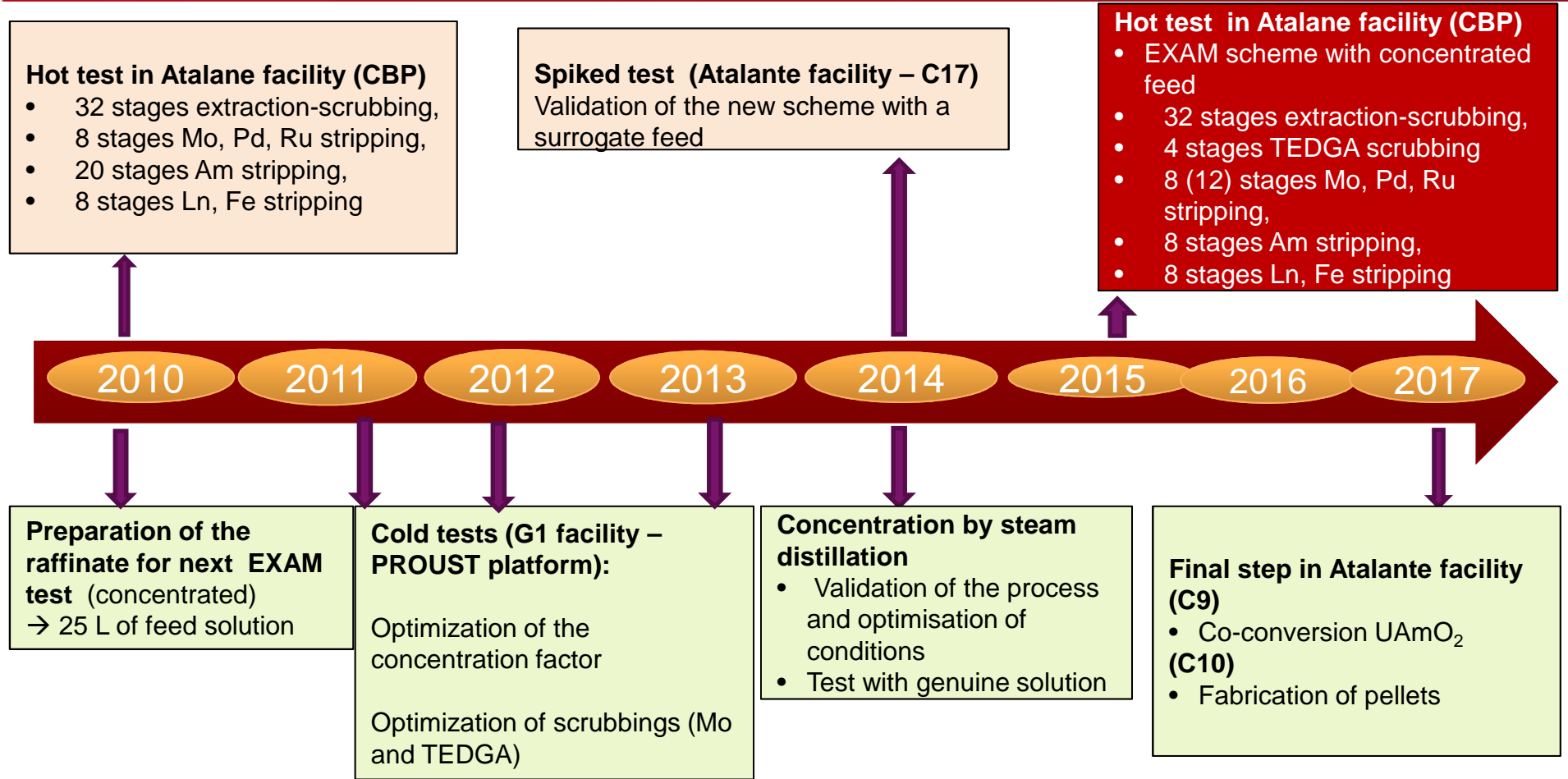
Elements	Before concentration	After concentration
HNO ₃ (mol/L)	3.4	8.2
Am (mg/L)	155	1197
Cm (mg/L)	-	323
Nd (mg/L)	740	3269
Ce (mg/L)	440	2169
Pr (mg/L)	200	956
La (mg/L)	240	1245
Sm (mg/L)	156	917
Eu (mg/L)	29	151
Gd (mg/L)	38	376
Zr (mg/L)	276	900
Mo (mg/L)	405	1186
Pd (mg/L)	138	617



Tests at laboratory scale

Modelling





Tests at laboratory scale

Modeling

High capacity of the PAREX code

- ① Thermodynamic of acid and metals extraction
- ② Mass transfer kinetic
- ③ Hydrodynamic in contactors

□ Before the test

- design the entire flowsheet according the required performances,
- carry out sensitivity studies towards operating parameters,
- identify relevant status parameters for process monitoring,
- propose a flowsheet correction procedure,



□ During the test

- help experimenters to modify flowsheet (flows, stage...),
- simulate all operating condition changes by transient calculations,



□ After the test

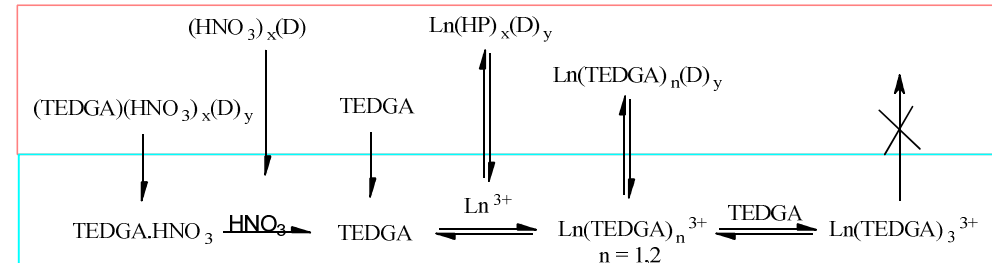
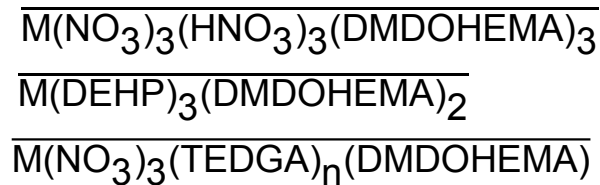
- compare the calculated and measured concentrations to assess the accuracy of the model.



➤ Extraction step (high acidity)

15 extractable elements taken into account (HNO_3 , Am, Cm, rare earths, Fe, Mo, Pd, Zr)

■ Ln and An(III)

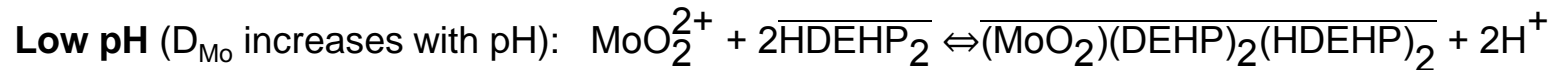


■ Pd and Ru → extraction by DMDOHEMA (1:1 complexes)

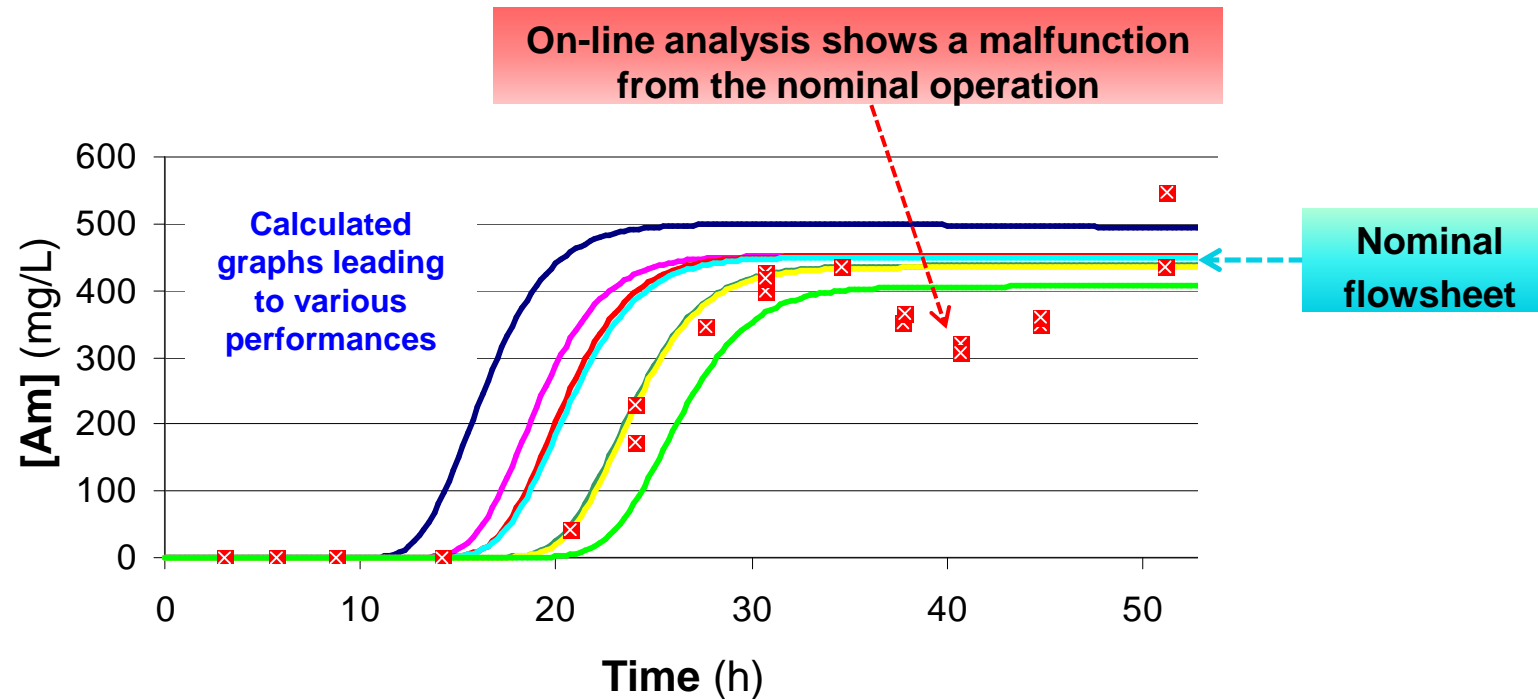
■ Fe and Mo → Quantitatively extracted by HDEHP ($D > 30$)

■ Zr → 1:3 non-extractable complex with TEDGA

➤ Mo stripping (low acidity)



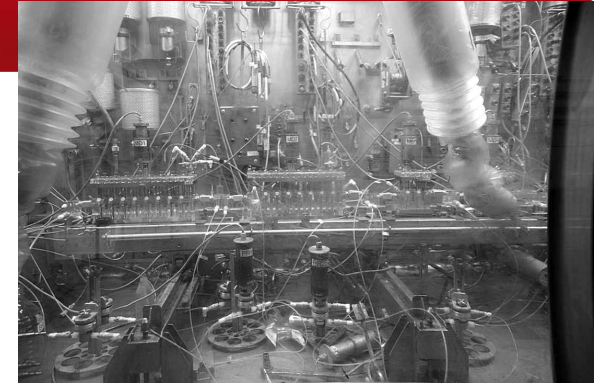
On-line measurement of Am concentration during an EXAm pilot test



- PAREX can rapidly calculate transient curves (live acceleration factor > 100) to correct the flowsheet during a pilot test

The main issue during the test : keep important Am recovery and high DF
(↗TEDGA, ↗agitation, ↘flowrates,...)





➤ Main results

- Operating parameters optimized during three successive tests (acid, surrogate, HA)
- Good hydrodynamic behavior
- Efficient monitoring thanks to online analysis with laboratory support
- Flowsheet optimization during the test

➤ Performances

Step	Am Recovery	Decontamination factor
Mo Scrubbing	$C_{Am}^{\text{raffinate}}$ from 0.01 to 0.02% (Target 0.1%)	Quantitative recovery of Mo
Am Stripping Ln Scubbing		$DF_{Am/Nd} = 2800$ (target value = 400)
Global	2.46 g of Am (96.5%)	$DF_{Am/Cm} \sim 54$ (target 500) With Am: less than 1.7% lanthanides, 0.3% Fe, 0.05% Mo, 0.7% Pd and 1.1% Ru

➤ Demonstration of the feasibility of a concentrated scheme with real raffinate

- Flowsheet adaptations were implemented and consolidated by successive tests: laboratory scale data, tests on inactive feed solution and spiked test with trace amounts of americium and curium.
- Production of **2.4 grams of americium** (58.5%²⁴¹Am-40.9%²⁴³Am-0.5%²⁴²Am), well decontaminated from lanthanides and molybdenum.
But lower DF_{Am/Cm} than expected may be understood
- Reduction of liquid waste volume and improvement of compactness, in parallel first evaluation of feasibility to manage all effluents with classical outlets (study to continue)
- Ultimate steps of the integral experience will be performed next years
 - Concentration of the 2.7L of Am solution to obtain $c_{Am} \text{ 7g/L}$ (Atalante CBP)
 - Co-conversion of Am (Atalante C9) ,
 - Production of Am pellets
 - Transfer to ATR for irradiation experiments

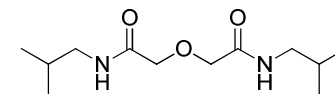
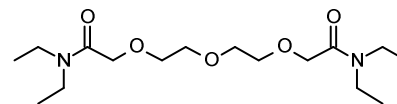
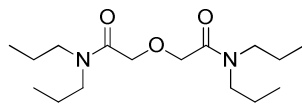
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➤ Further studies (small effort, mainly laboratory studies)

■ EXAM process

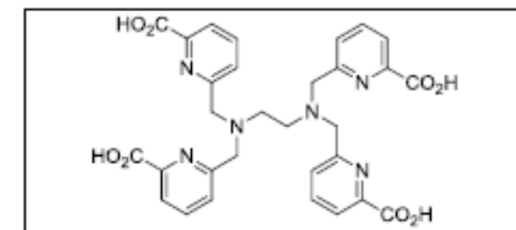
- ❖ Complete the study of Cm chemistry (stability constants with TEDGA estimated from extraction tests and from Sm behavior)
 - Recent results from KIT (A. Geist): TRLIFS data, soon published,
 - Extraction tests to perform
 - Modification of the model in progress

- ❖ Design of new ligands with lower partitioning and with higher Am/Cm AND Am/Ln selectivity, following of S. Chapron thesis (SEIE, 2015, 33(3), 236-248)



■ TPAEN process

- Some tests (mixer settlers) with representative solution
- Design of new ligands (increase the solubility)



Aknowledgments

CBP team

Frédéric Antégnard, Marie-Jordane Bollesteros, Sylvain Costenoble, Marc Montuir,

Modeling team

Vincent Vanel, Vincent Pacary, B. Dinh

Process development

Cécile Marie, Xavier Heres, M. Miguirditchian

Analytical team of CBA

Atalante

Thank you

for your attention

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