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

C. Sorel, J.-M. Adnet, M.-C. Charbonnel

FROM RESEARCH TO INDUSTRY

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

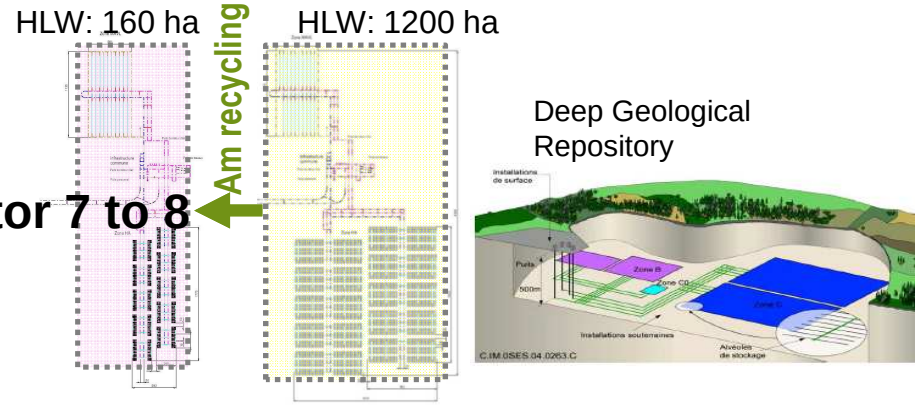
Christian Sorel, Jean-Marc Adnet, Marie-Christine Charbonnel

*CEA Marcoule / **N**uclear **E**nergy **D**ivision,*
RadioChemistry & Processes Department
Separation Process Chemistry and Modeling Service

INTRODUCTION

➢ Recycling Am alone

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



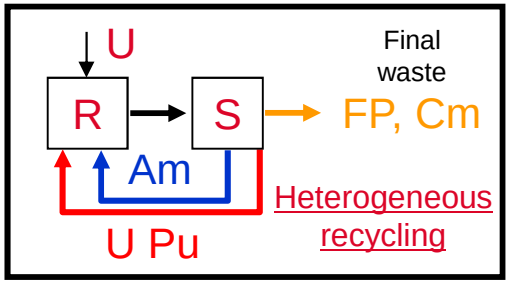
C. Poinssot, C. Rostaing, P. Baron, D. Warin, B. Boullis *Procedia Chem.* **7**, 358–366 (2012).
C. Poinssot, C. Rostaing, S. Grandjean, B. Boullis, *Procedia Chem.* **7**, 349–357 (2012).

➢ 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)

➢ Options

- Oxidation to Am(VI) and extraction (difficult to stabilize)
  Ex.: SESAME (CEA), $NaBiO_3$ (B. Mincher *et al.* INL)



PUREX
+
New process

- Without redox chemistry - With selective lipophilic or hydrophilic system
  Processes tested by CEA: DIAMEX 2 → DMDOHEMA (48 stages!)
  EXAm → DMDOHEMA + HDEHP / TEDGA
  TODGA / TPAEN

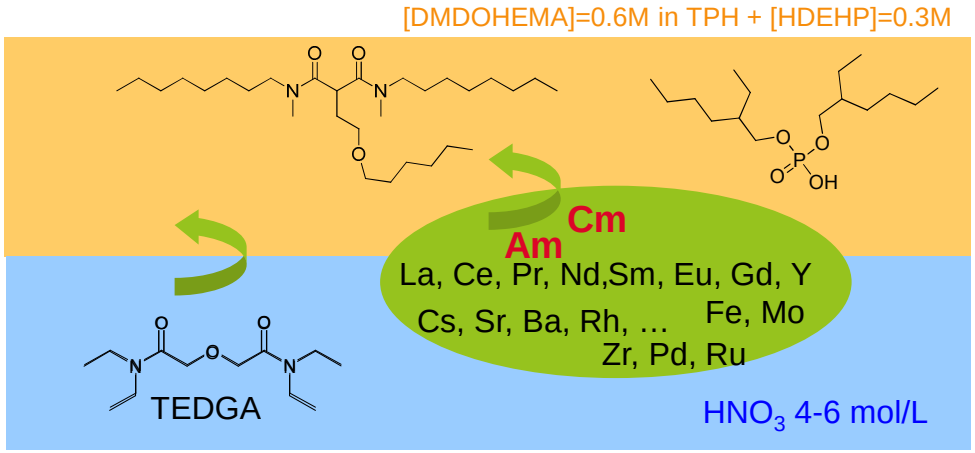
SACSESS Safety of actinide separation processes

EXAm - Principle

X. Heres, P. Baron, Patent FR2948384 (2011)

➢ 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)



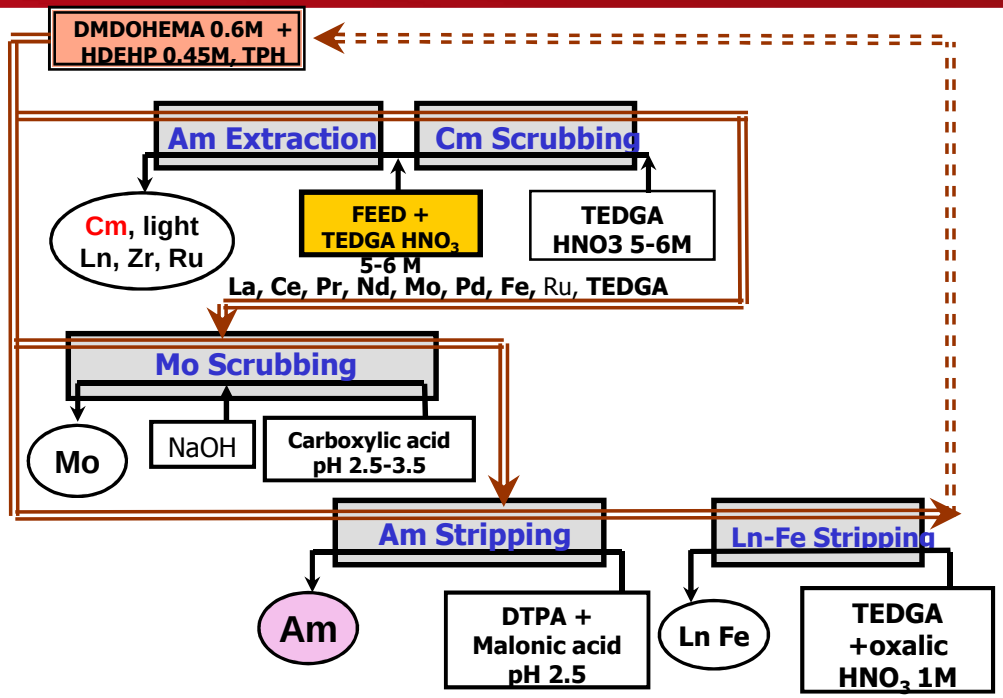
- **Complexed chemistry (example with Ln)**
  - **In the organic phase:** $Ln^{3+}(DEHP)_x$ and $Ln^{3+}(NO_3)_3(DMDOHEMA)_y$

but also $Ln^{3+}(NO_3)_x(HDEHP)_y(DEHP)_{3-x}$ $(DMDOHEMA)_z$, $LnNO_3)_3$ $(TEDGA)_n(DMDOHEMA)_y$

  - ***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. Mulller et al., SEIE 2016, 141-160, C. Marie, *et al. Proceedings ISEC,* **2014***,* 105-110.

EXAm – Process development



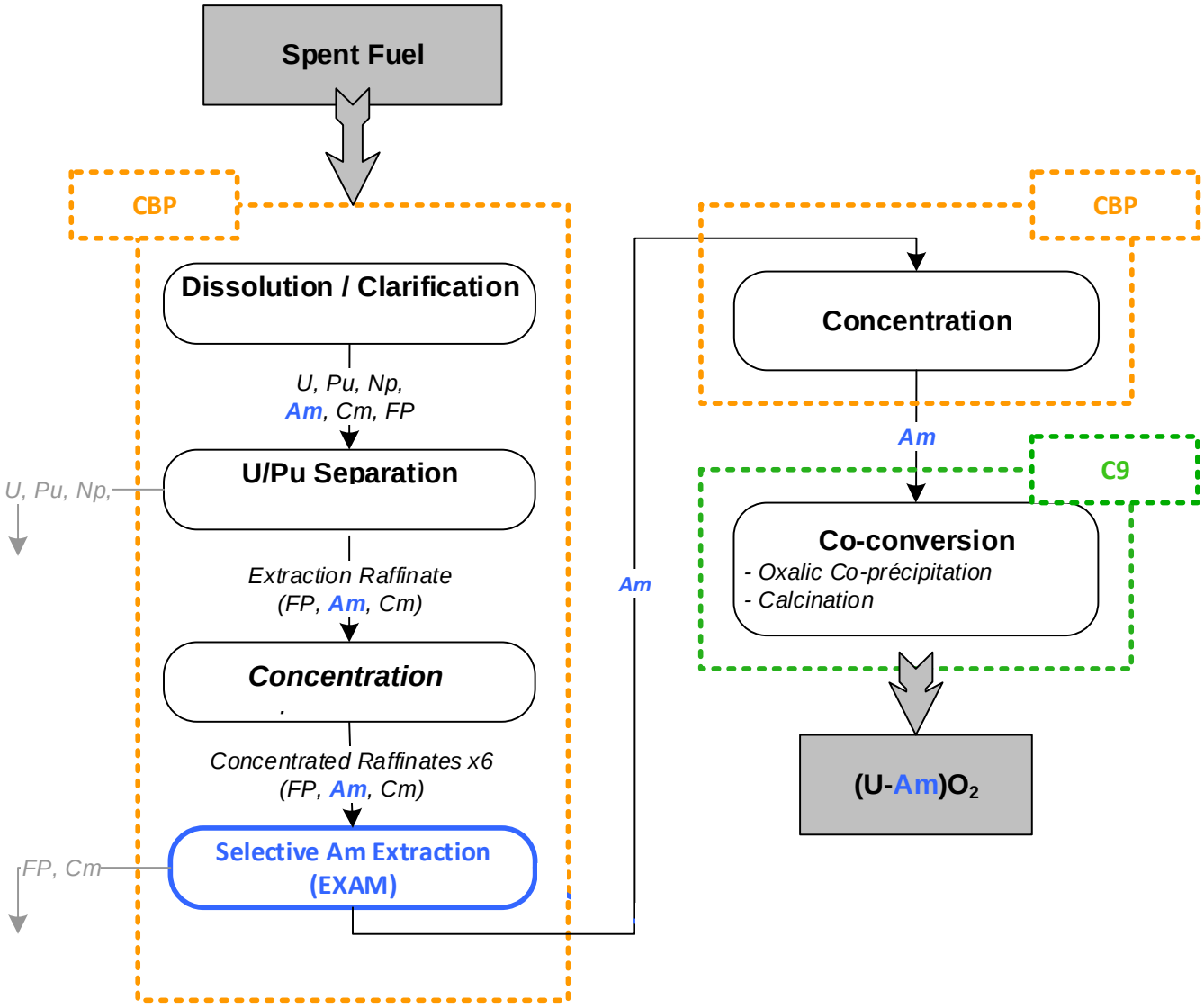
Demonstration of the faisability with a first hot test in ATALANTE facility in 2010

➔ **Am recovery ≈ 98.5% with $DF_{Am/Cm}$ = 500**

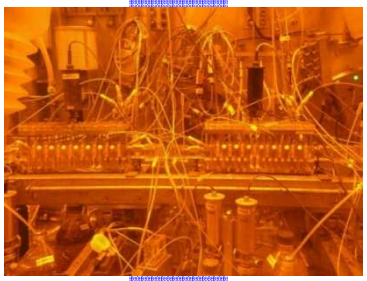
Improvement suggested : increase the compactness of the process (to reduce industrial contactors size and quantity of side streams)

Next step: Hot Test on genuine PUREX raffinate after concentration

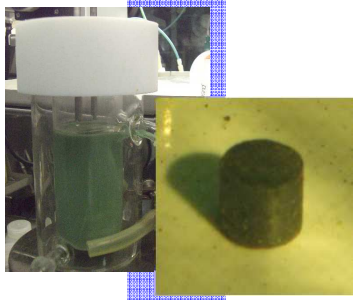
EXAM integral experience



Cold and spiked tests



Hot test

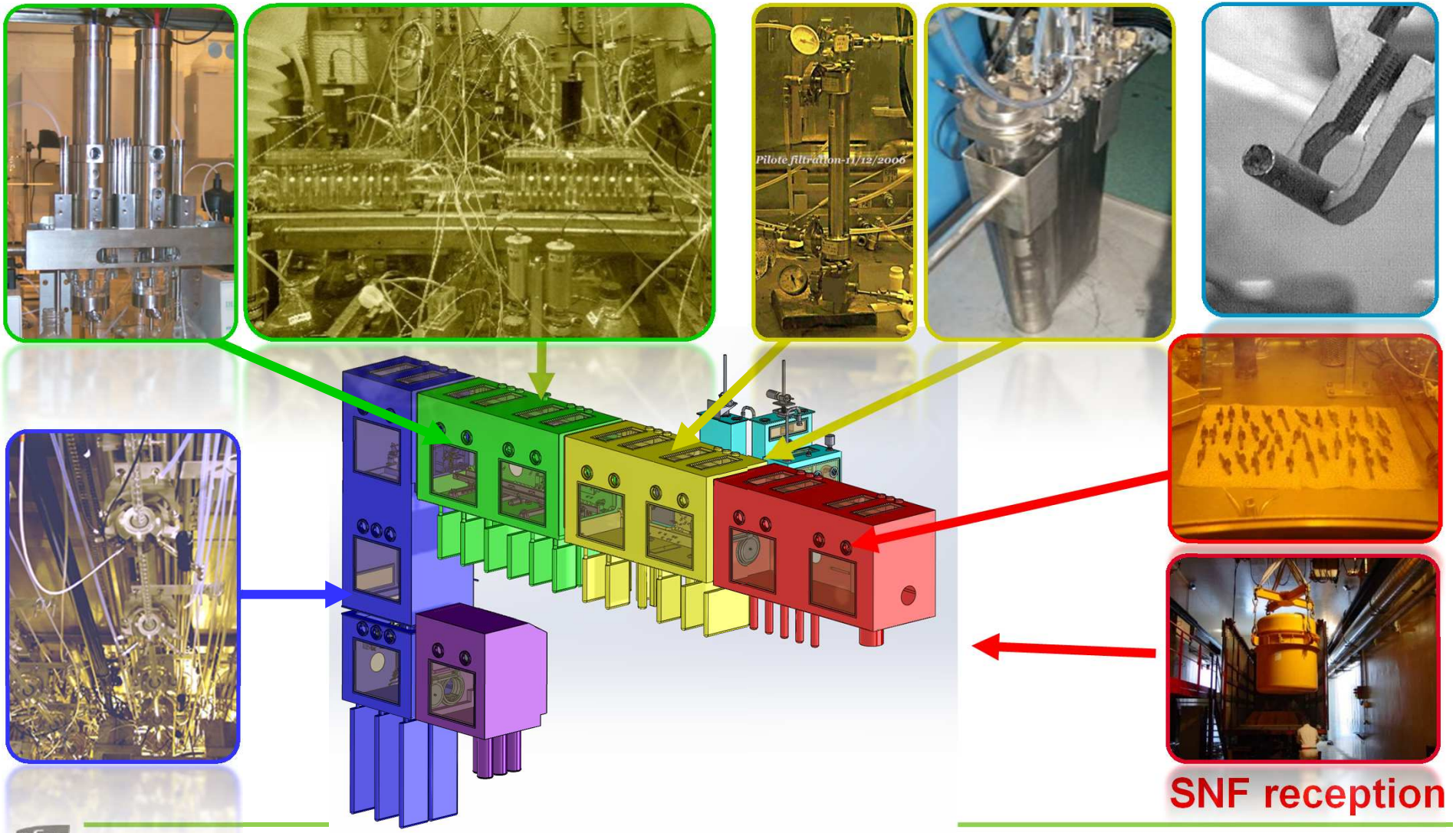


Oxalic co-conversion and U-Am oxide fabrication

Overview of the CBP Shielded Process Line

Solvent extraction

Dissolution and clarification



SNF reception

EXAM – Process Development

Hot test in Atalane facility (CBP)
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Spiked test in Atalante facility (C17)
Validation of the new scheme with a surrogate feed

Hot test in Atalane facility (CBP)
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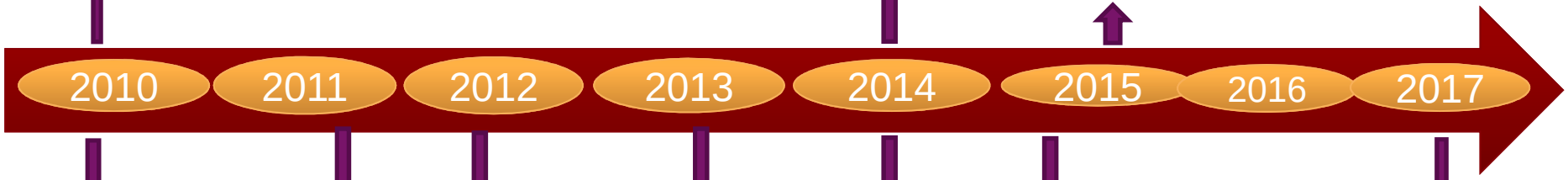

Preparation of the raffinate for next EXAM test (concentrated)
→ 25 L of feed solution

Cold tests (G1 facility – PROUST platform):

Optimization of the concentration factor

Optimization of scrubbings (Mo and TEDGA)

Concentration by steam distillation
- Validation of the process and optimisation of conditions
- Test with genuine solution

Final step in Atalante facility (C9)
- Co-conversion $UAmO_2$

(C10)
- Fabrication of pellets

Tests at laboratory scale

Modelling

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2010 2011 2012 2013 2014 2015 2016 2017

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Tests at laboratory scale

Modelling

Spent fuel dissolution

- 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_{HNO3} = 4.3M,
  - c_U = 160 g/L,
  - c_{Pu} = 4.4 g/L,
  - c_{Np} = 49 mg/L,
  - c_{Am} = 160 mg/L
  - c_{Cm} = 50 mg/L
  - Total βγ activity: $1.9.10^{12}$ Bq/L (02/2011),
  - ^{106}Ru activity: $1.35.10^{11}$ Bq/L (02/2011).

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- Hydraulic tests
- Optimization of the concentration factor
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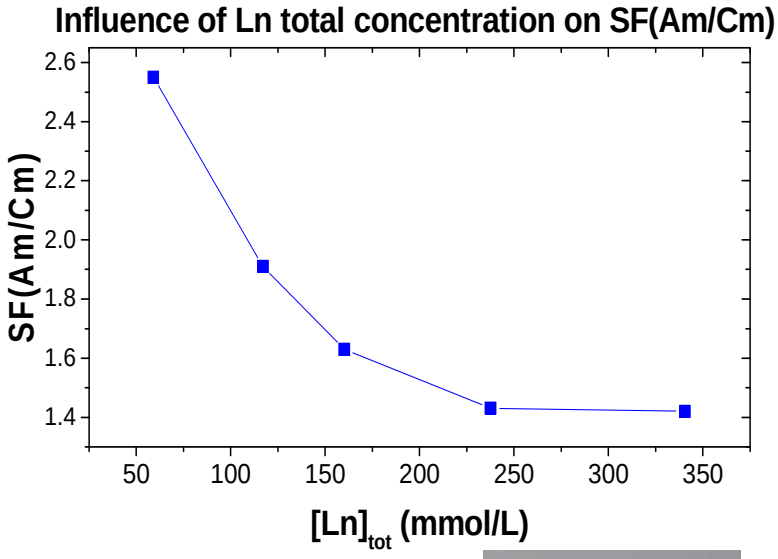
Tests at laboratory scale

Modelling

EXAM (Concentrated flowsheet)
Which concentration factor?

- **Keep a good Am/Cm separation factor**

	UOx3 (PUREX raffinate)	5x
Σ Ln (mM)	25	125
Σ Cations (mM)	52	260



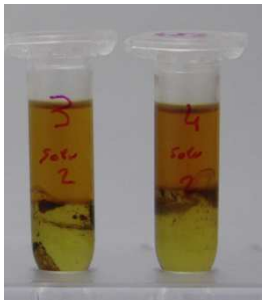
- **Main modifications**

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

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

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

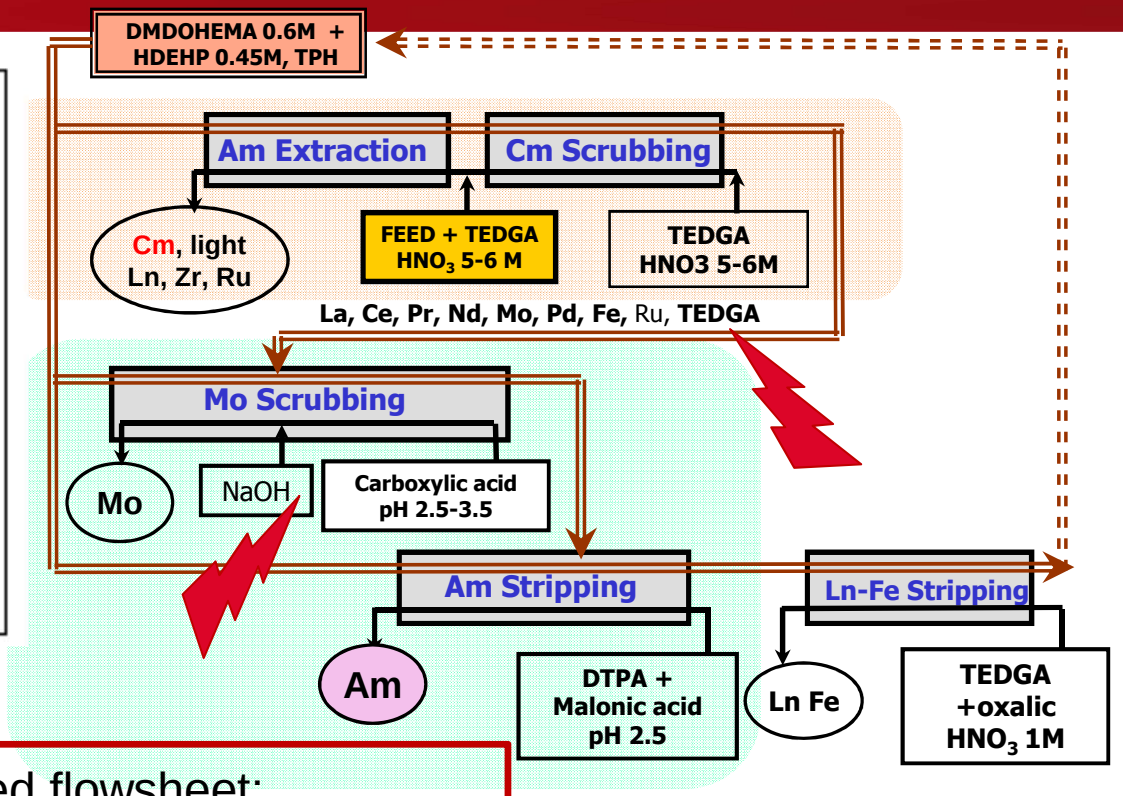
DMDOHEMA 0.6M
HDEHP 0.30 M



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

  → **Additional TEDGA scrubbing** to maintain c_{TEDGA}^{org} < 10 mM

- pH stabilization in Mo scrubbing steps more difficult

  Study of others buffering/complexing molecules → **Citric acid (instead glycolic acid) in Mo scrubbing test**

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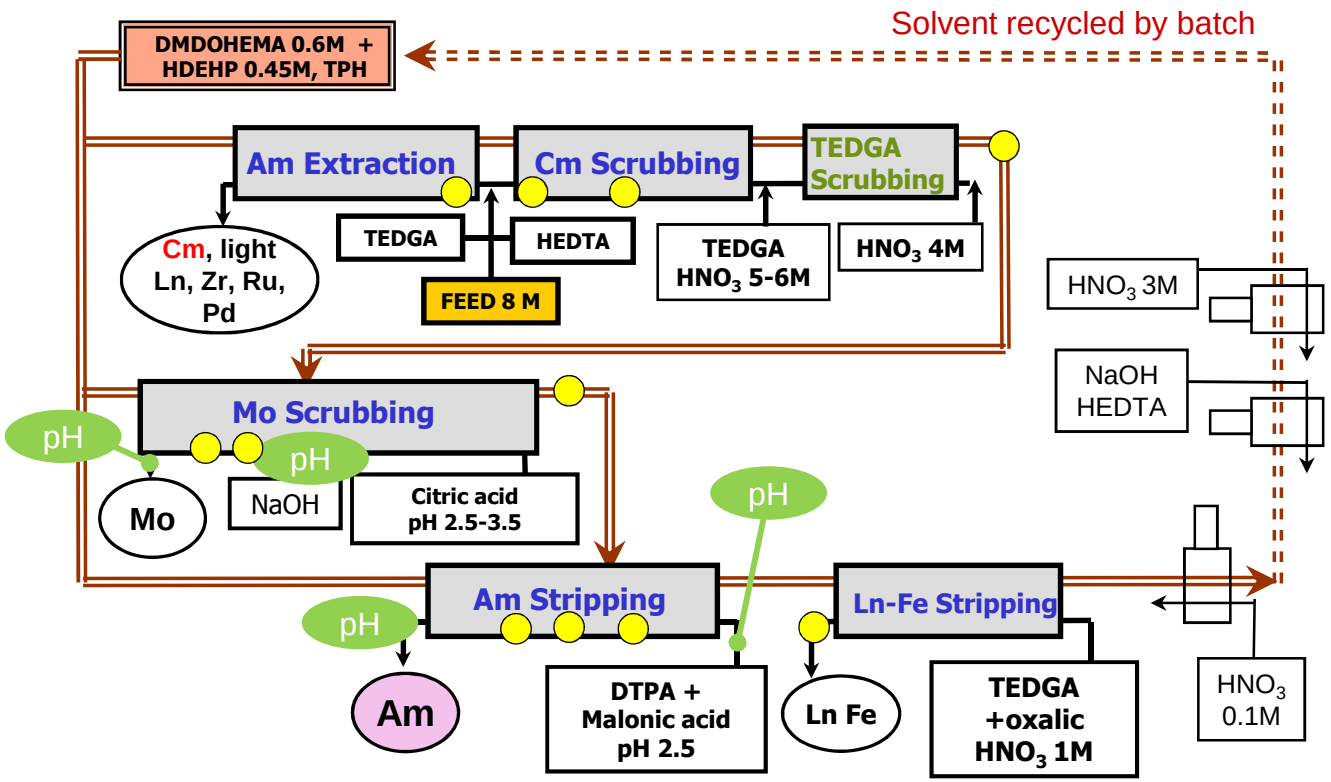
Tests at laboratory scale

Modelling

Spiked test april 2014

Atalante C17



- 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)

Simulated Feed

Concentration factor = 3 UOX_3

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

^{241}Am 0.4 mg/L

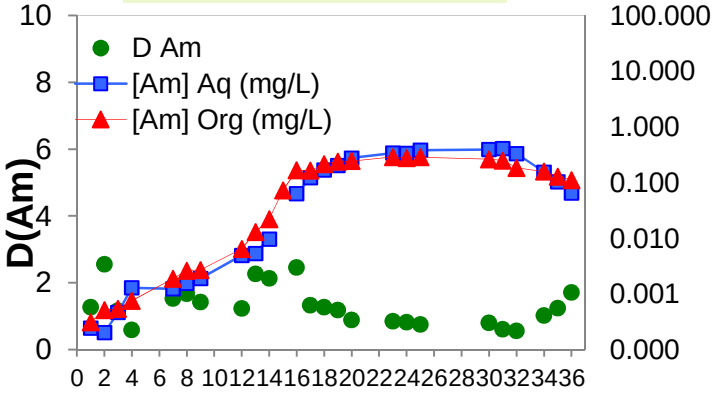
^{244}Cm 0.2 mg/L

Spiked tests april 2014 Atalante C17

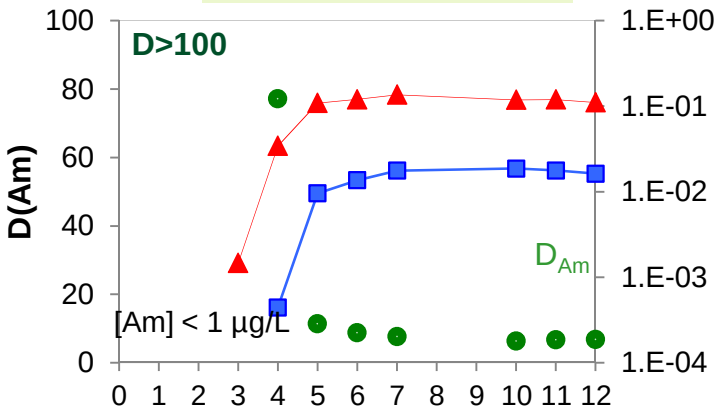
➢ Main results

- Very good adequation between data calculated and measurements

extraction step



Mo scrubbing



➢ 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

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(C10)
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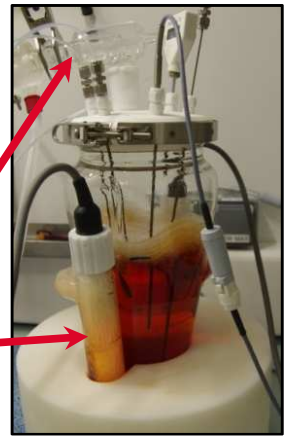
Tests at laboratory scale

Modelling

Concentration of PUREX raffinate

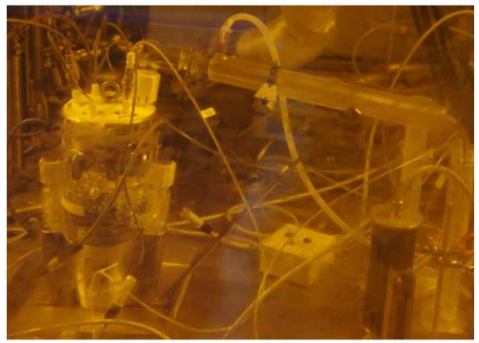
- Choice of steam distillation instead of classical formic denitration
  - safety regulation at Atalante facility
  - acidity very high



- **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: $[H^+]_{feed}$ = 3,4 M
  - High acidity in the reactor: 8 M => $[H^+]_{distillate}$ = 1,8 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

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(C10)
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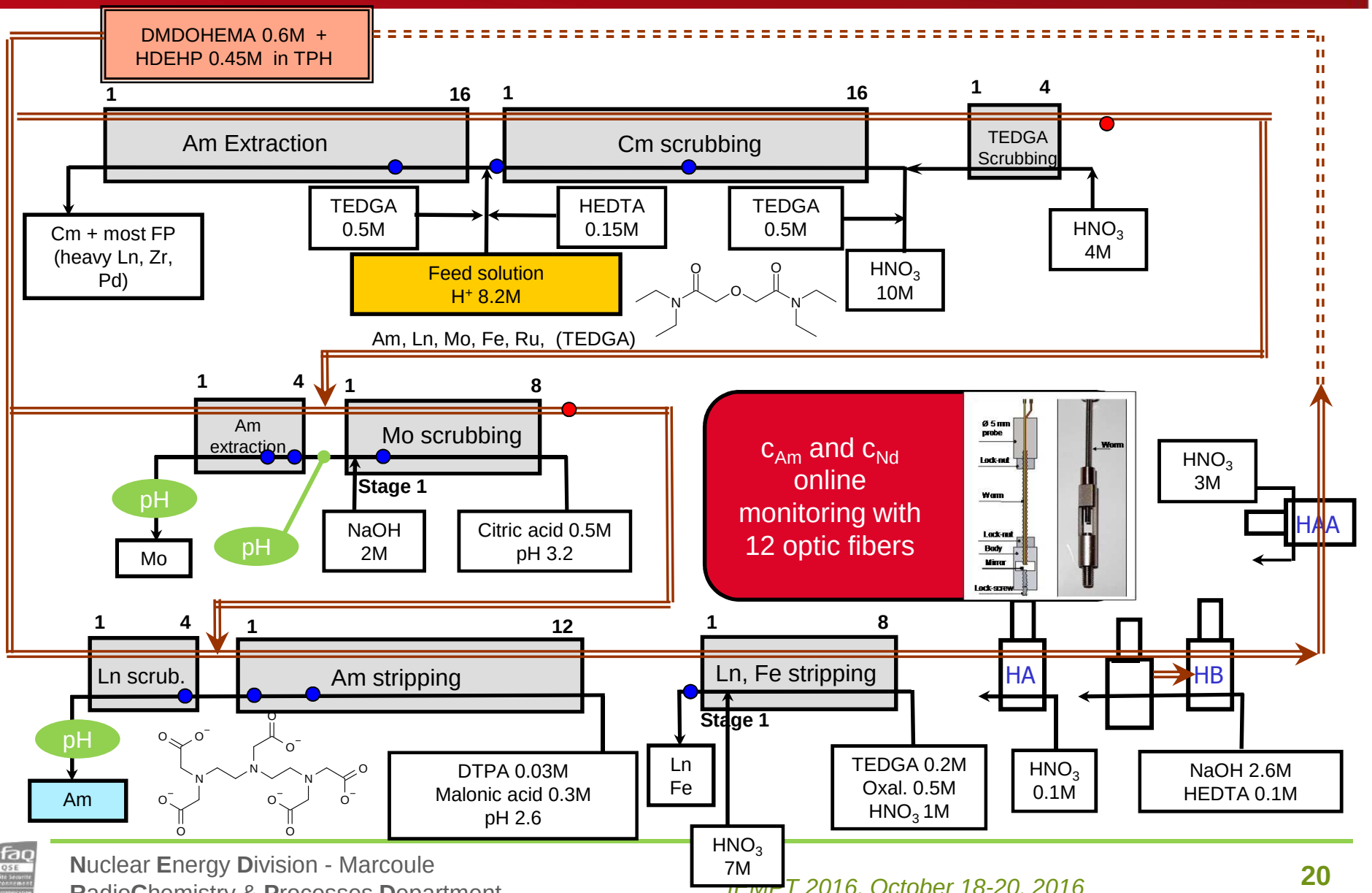
Tests at laboratory scale

Modelling

Flowsheet of the EXAm process



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Modeling

Interest of modeling during a pilot test

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.**

Development of the model with laboratory data

➢ Extraction step (high acidity)

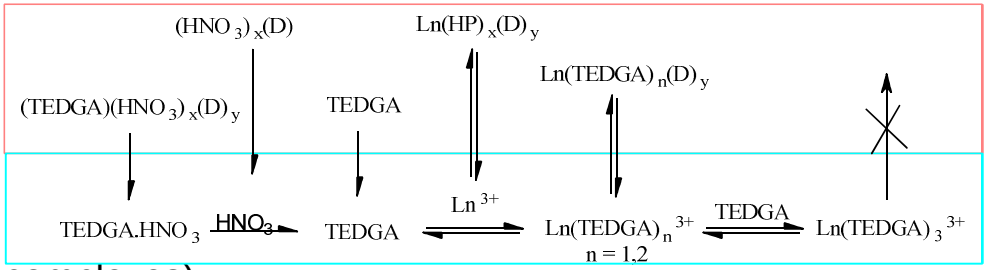
15 extractable elements **taken into account (HNO_3,** Am, Cm, rare earths, Fe, Mo, Pd, Zr)

- **Ln and An(III)**

$$\overline{M(NO_3)_3(HNO_3)_3(DMDOHEMA)_3}$$

$$\overline{M(DEHP)_3(DMDOHEMA)_2}$$

$$\overline{M(NO_3)_3(TEDGA)_n(DMDOHEMA)}$$



- **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)

$\overline{(DMDOHEMA)(DEHP)}$ $M(DMDOHEMA)(DEHP)_3$

Low pH (D_{Mo} increases with pH): $MoO_2^{2+} + 2\overline{HDEHP_2} \Leftrightarrow \overline{(MoO_2)(DEHP)_2(HDEHP)_2} + 2H^+$

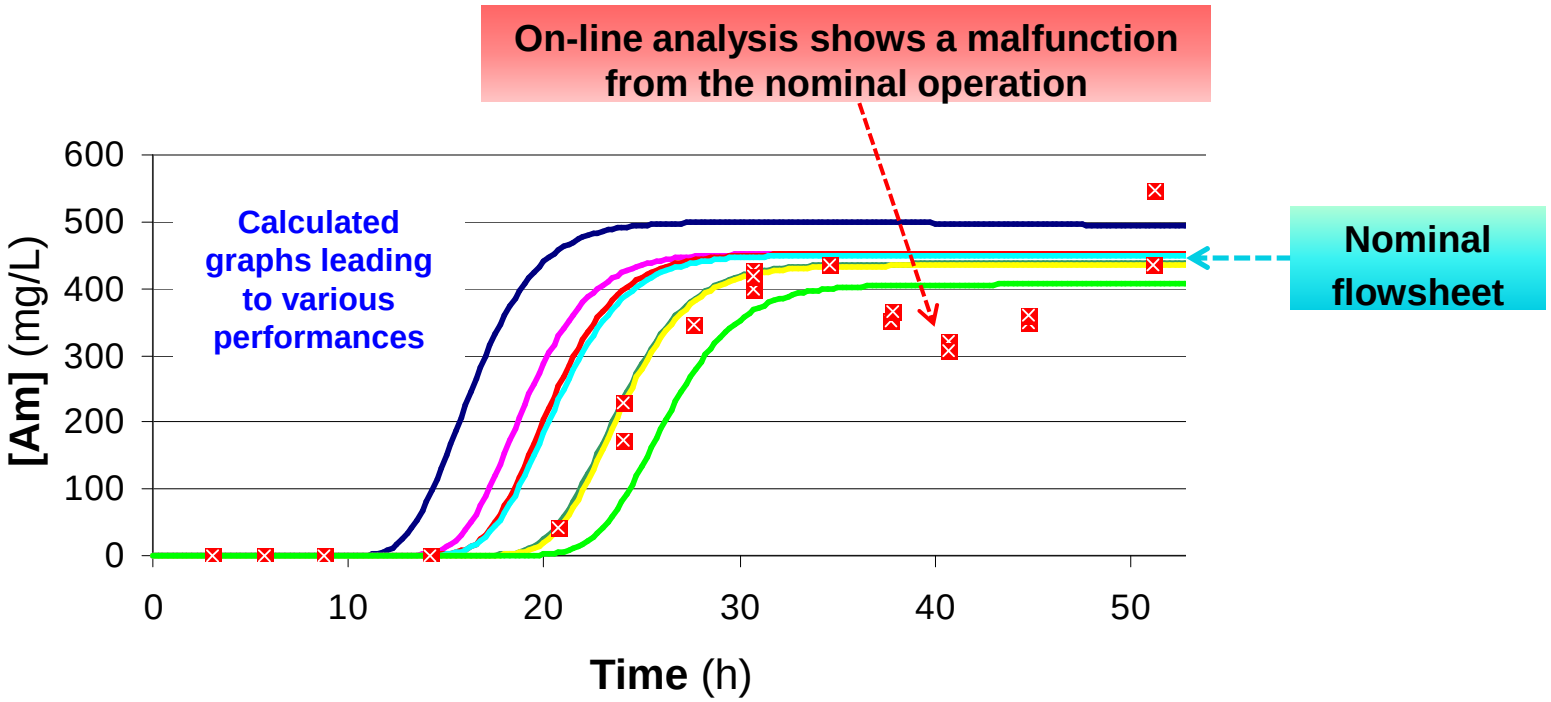
Moderate pH (pH independent): $MoO_3 + 2\overline{HDEHP_2} \Leftrightarrow \overline{(MoO_3)(HDEHP)_4}$

High pH (D_{Mo} decreases with pH): $MoO_4^{2-} + 2\overline{HDEHP_2} + 2H^+ \Leftrightarrow \overline{(MoO_2)(DEHP)_2(HDEHP)_2}$

Marie C., SOLVENT EXTRACTION AND ION EXCHANGE 2016, 34 (5), 407–421

PAREX to help in conducting the pilot test

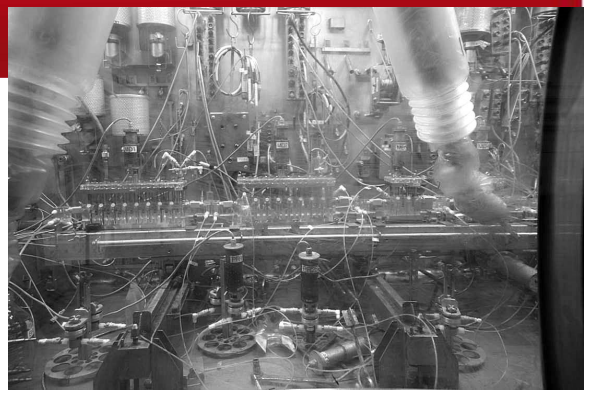
On-line measurement of Am concentration during an EXAm pilot test



- 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,…)

EXAM test with a concentrated scheme



➢ 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	$c_{Am}^{raffinate}$ 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%)**	**$DF_{Am/Cm}$ ~ 54** (target 500) With Am: less than 1.7% lanthanides, 0.3% Fe, 0.05% Mo, 0.7% Pd and 1.1% Ru

Conclusions

➢ 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%^{241}Am-40.9%^{243}Am-0.5%^{242}Am**)**, 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} 7g/L (Atalante CBP)] Mi 2017
  Co-conversion of Am (Atalante C9) ,
  Production of Am pellets
  Transfer to ATR for irradiation experiments

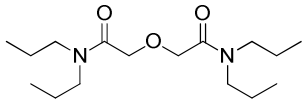
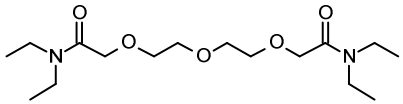
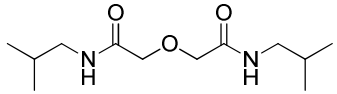
Perspectives

➢ **Further studies** (small effort, mainly laboratory studies)

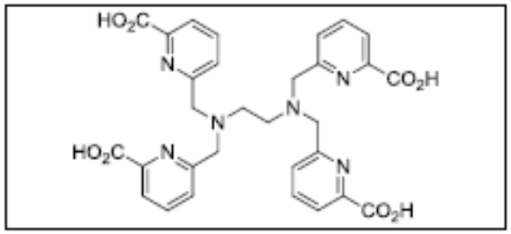
- EXAM process
  - Complete the study of Cm chemistry (stability constants with TEDGA estimated from extraction tests and from Sm behavior)

  - 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 partitionning 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)



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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

Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Marcoule | 30207 Bagnols-Sur-Cèze Cedex
T. +33 (0)4 66 79 61 69 | F. +33 (0)4 66 79 63 39

Etablissement public à caractère industriel et commercial | R.C.S Paris B 775 685 019

Direction de l'Energie Nucléaire
Département RadioChimie et Procédés
Service de Modélisation et Chimie des procédés de Séparation