# Development of a selective Americium Separation Process by Liquid-Liquid Extraction

C. Marie, M.-T. Duchesne, E. Russello, P. Kaufholz, A. Wilden, G. Modolo, N. Boubals, M. Miguirditchian

DE LA RECHERCHE À L'INDUSTRIE

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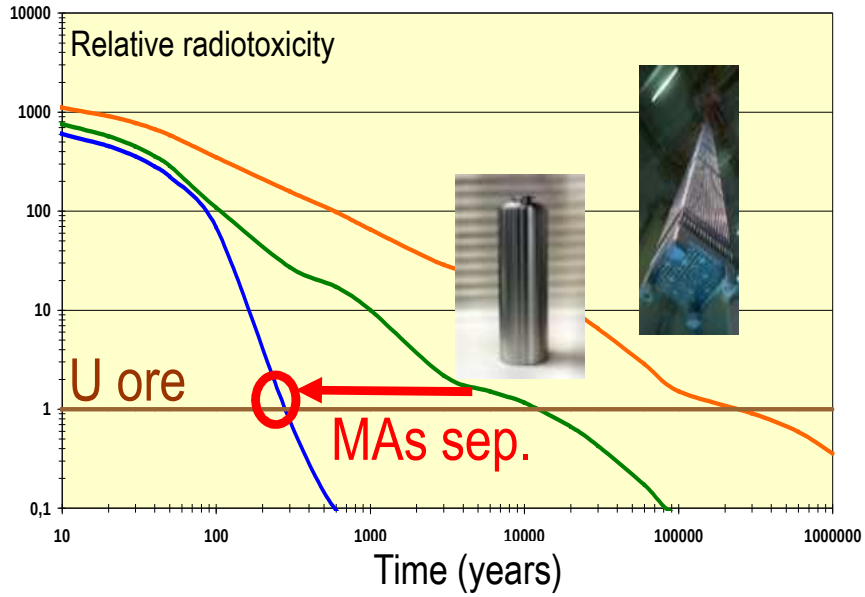
**ACS NATIONAL MEETING & EXPOSITION**

17th August 2015 Boston, US

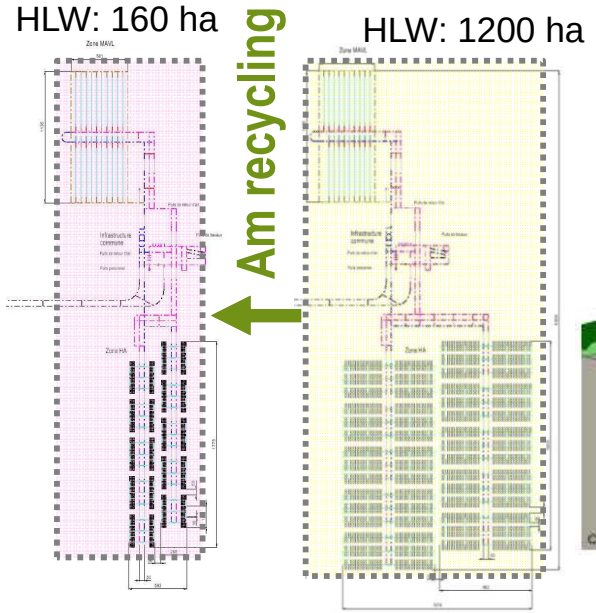
# INTRODUCTION

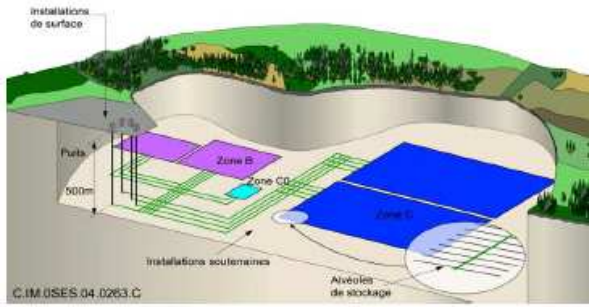


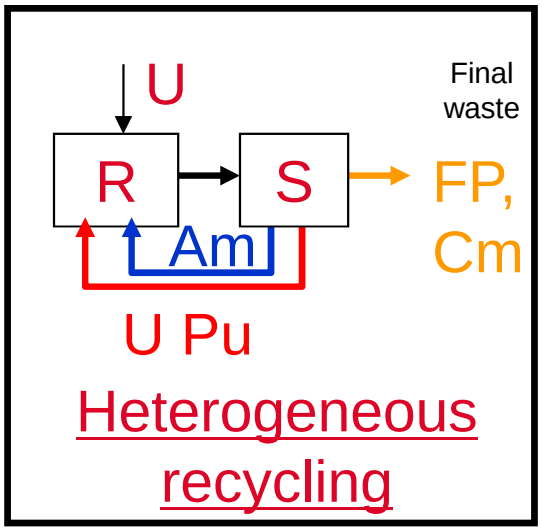

## Recycling Am alone

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

**With Am recycling, reduction of the repository surface by a factor up to 8**




PUREX + EXAm

R = reactor S = separation FP = fission products

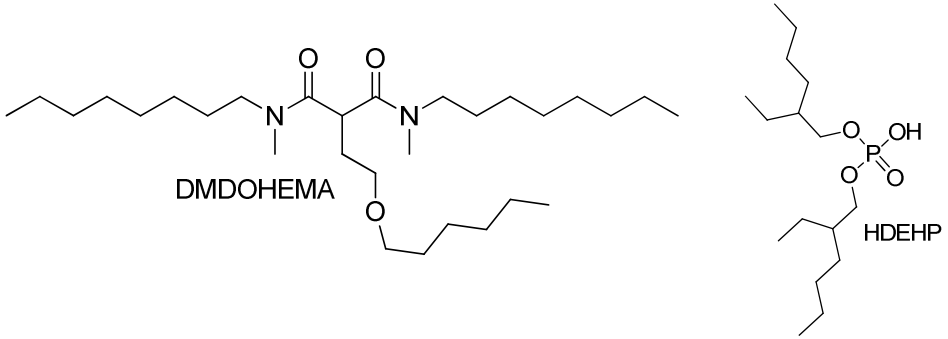

C. Poinssot, C. Rostaing, P. Baron, D. Warin, B. Boullis *Procedia Chem.* **7**, 358–366 (2012).
C. Poinssot, C. Rostaing, S. Grandjean, B. Boullis, *Procedia Chem.* **7**, 349–357 (2012).

# Am/Cm Separation

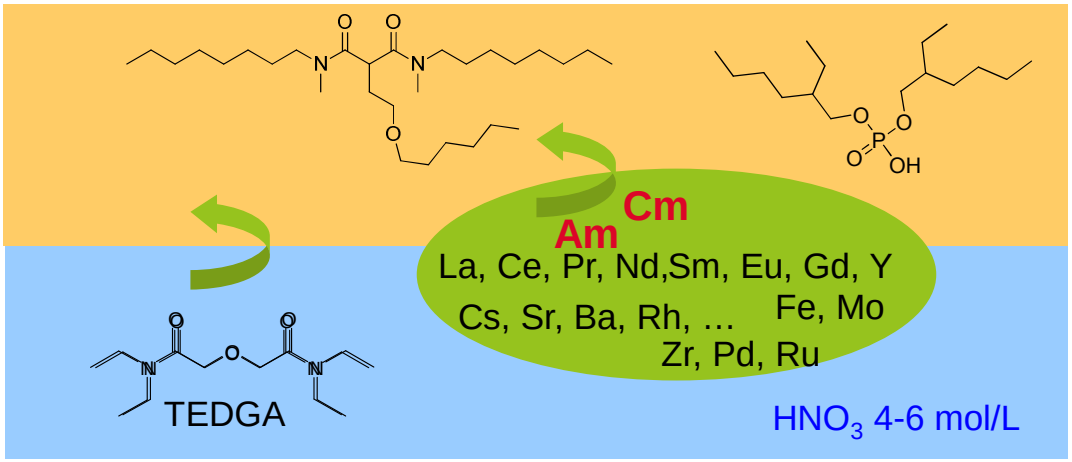
*M.-C. Charbonnel *et al*., *Procedia Chem.* **2012**, *7*, 20–26.
**V. Pacary *et al.*, *Procedia Chem.* **2012**, *7*, 328–333.

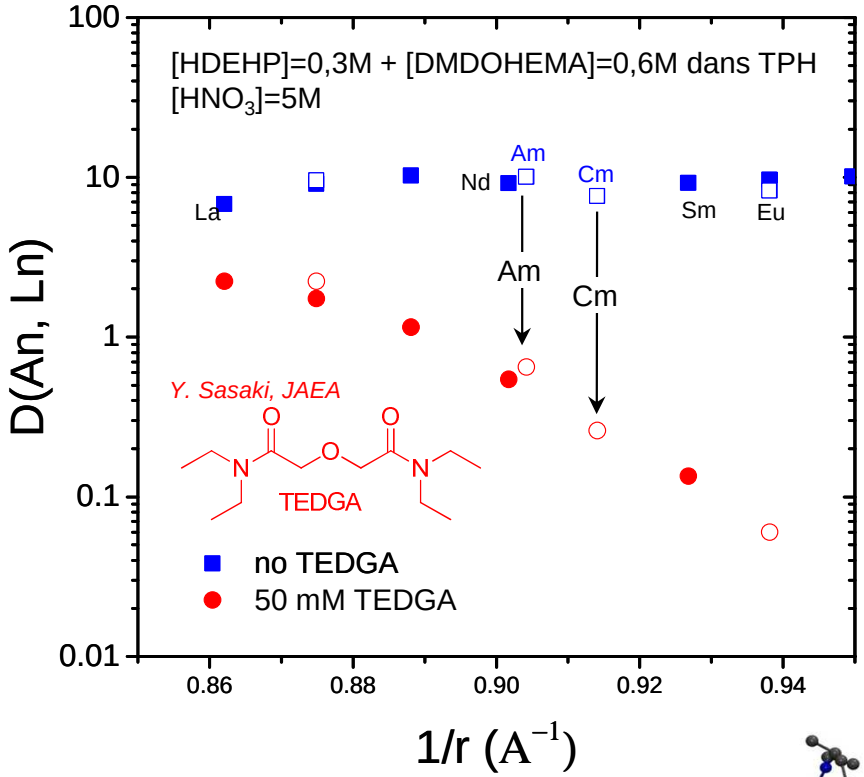
## EXAm Liquid/Liquid Extraction Process

Selective Recovery of Americium alone from a PUREX raffinate (already cleared from U, Pu and Np).

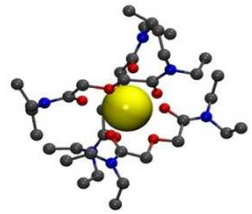



- Extractants alone → very low Am/Cm selectivity ($SF_{Am/Cm}$ = 1.6)
- with TEDGA → $SF_{Am/Cm}$ = 2.5




## Complex Chemistry

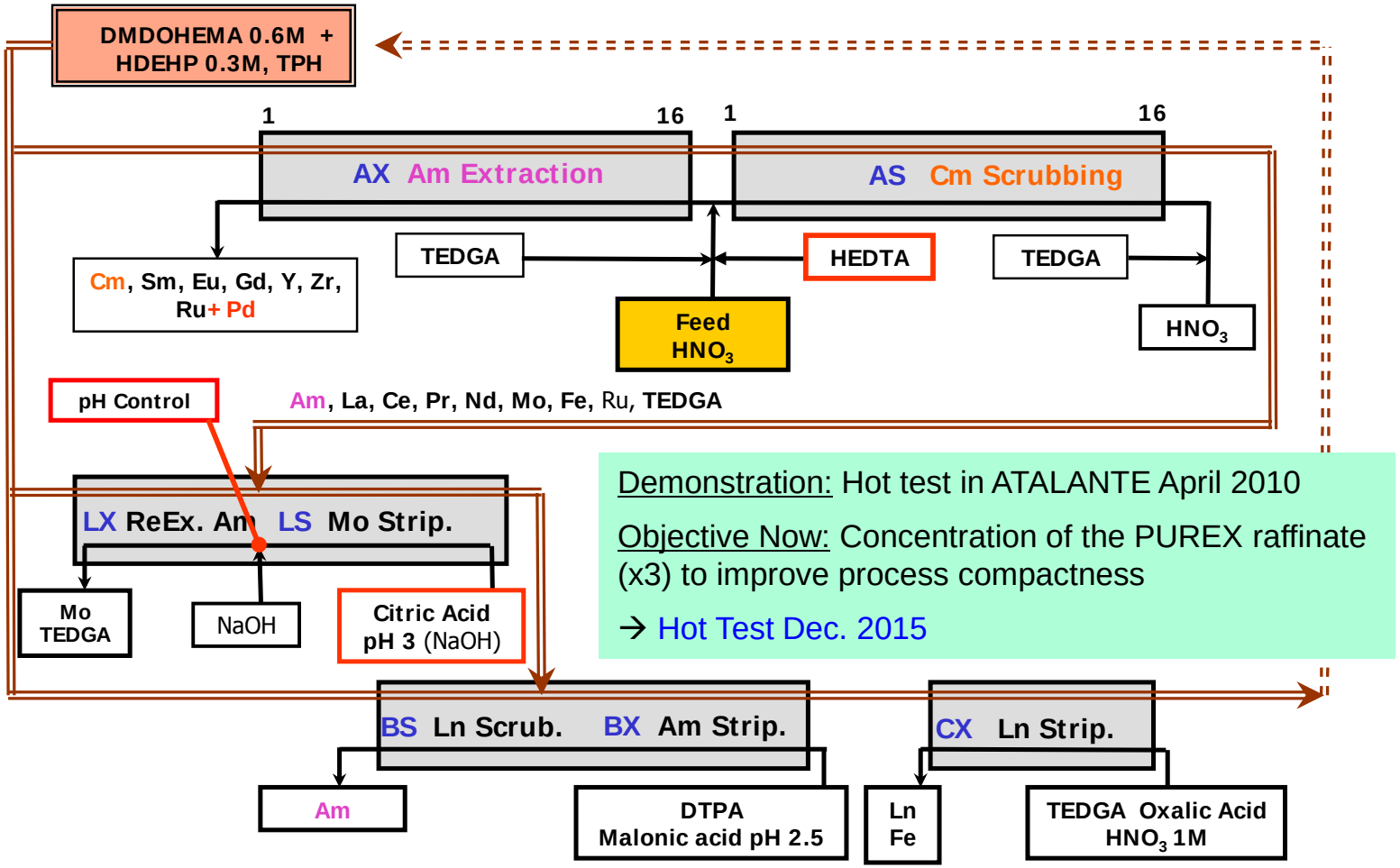


- Org. Phase: Ternary complexes $Ln(HDEHP)_x(DMDOHEMA)_y$ *J. Muller Thesis*
- Aq. Phase: $Ln(TEDGA)_n^{3+}$ (n=1,2,3) Stability constants (Ln, Am)*

→ $Ln(TEDGA)_n(D)_y$ in the Org. Phase (n= 1,2)

# EXAm

C. Marie, *et al. Proceedings ISEC*, 105-110(2014)

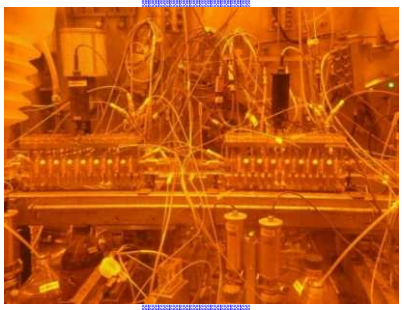



Demonstration: Hot test in ATALANTE April 2010

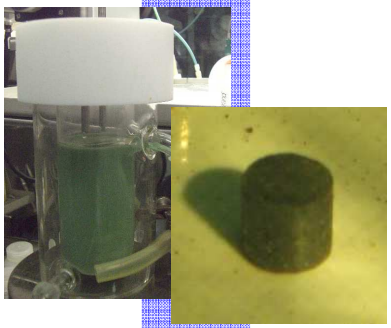
Objective Now: Concentration of the PUREX raffinate (x3) to improve process compactness

→ Hot Test Dec. 2015

Cold and spiked tests



Hot test



**Oxalic co-conversion and U-Am oxide fabrication**

## Axis of improvment:

- Lower partitionning of the ligand
- Complexing agent with higher Am/Cm selectivity
- Complexing agent with both Am/Cm AND Am/Ln selectivity

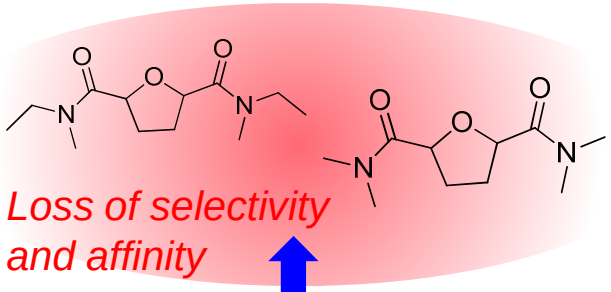
# Synthesis of new TEDGA Analogs

S. Chapron PhD

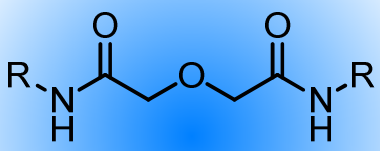
S. Chapron *et al.* SXIX (33) 236-248, 2015

## Spacer

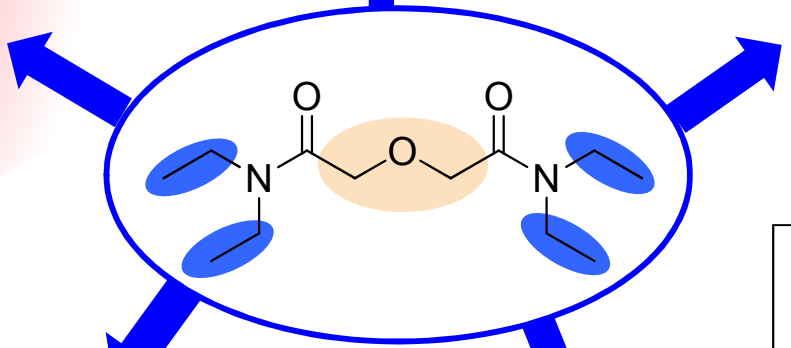
*Inversion of selectivity*



*Loss of selectivity and affinity*

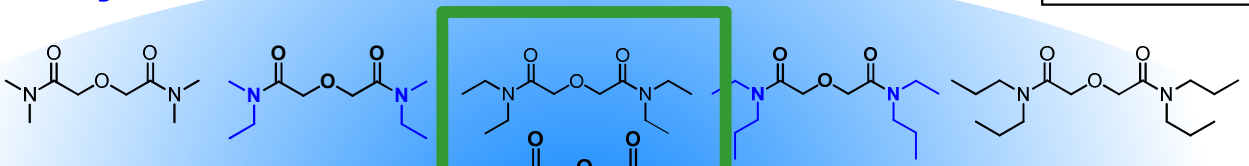


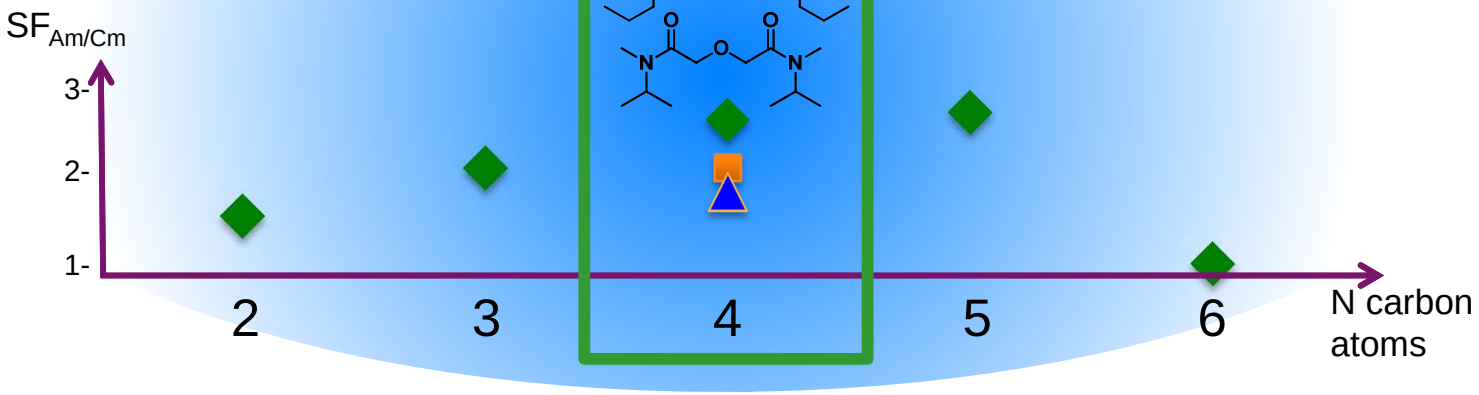
*High affinity with extractants in the organic phase*



**TEDGA = best compromise between selectivity and partitionning**

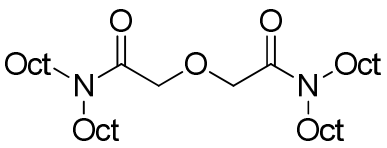
## Lipophilicity





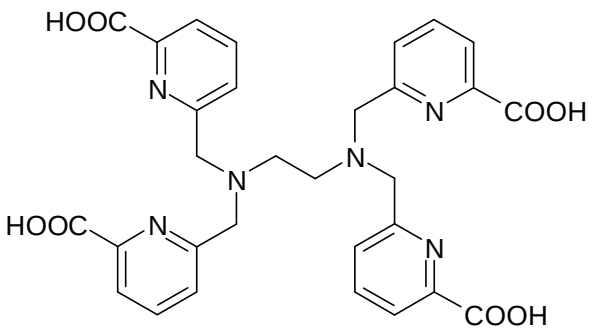
# TODGA / TPAEN SYSTEM

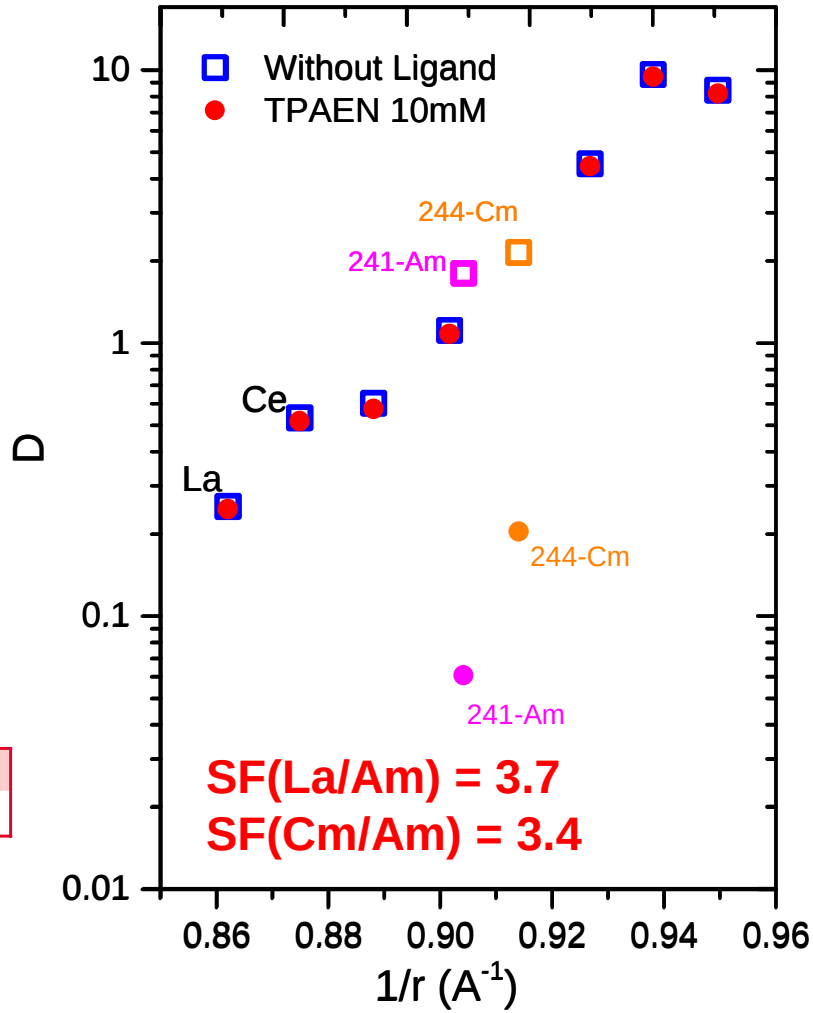
TODGA




\+

TPAEN




**TPAEN = Am stripping agent**

**Solvent = 0.2M TODGA + 5% vol. octanol in TPH**

1) Ln + Am and Cm loading at 1M $HNO_3$

| Element | La | Ce | Pr | Nd | Sm | Eu | Gd | Y | total |
|---|---|---|---|---|---|---|---|---|---|
| [ ] mmol/L | 3.8 | 0.35 | 0.29 | 1.5 | 8.3 | 2.1 | 1.7 | 1.6 | **20** |

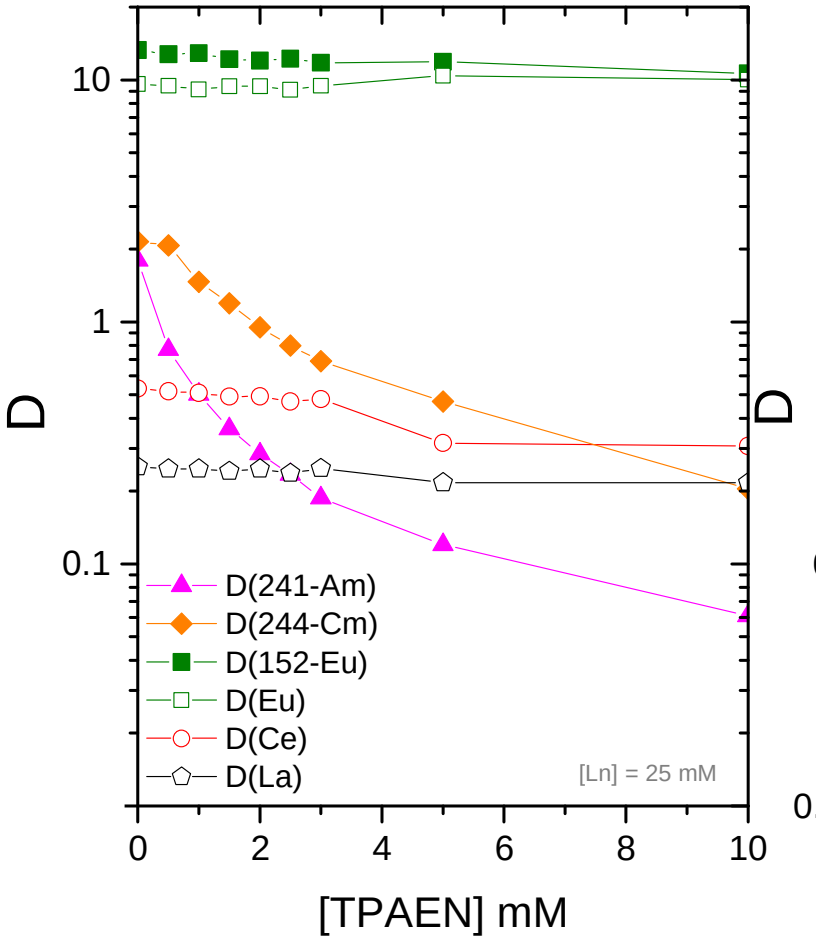
\+ $^{241}Am$, $^{244}Cm$

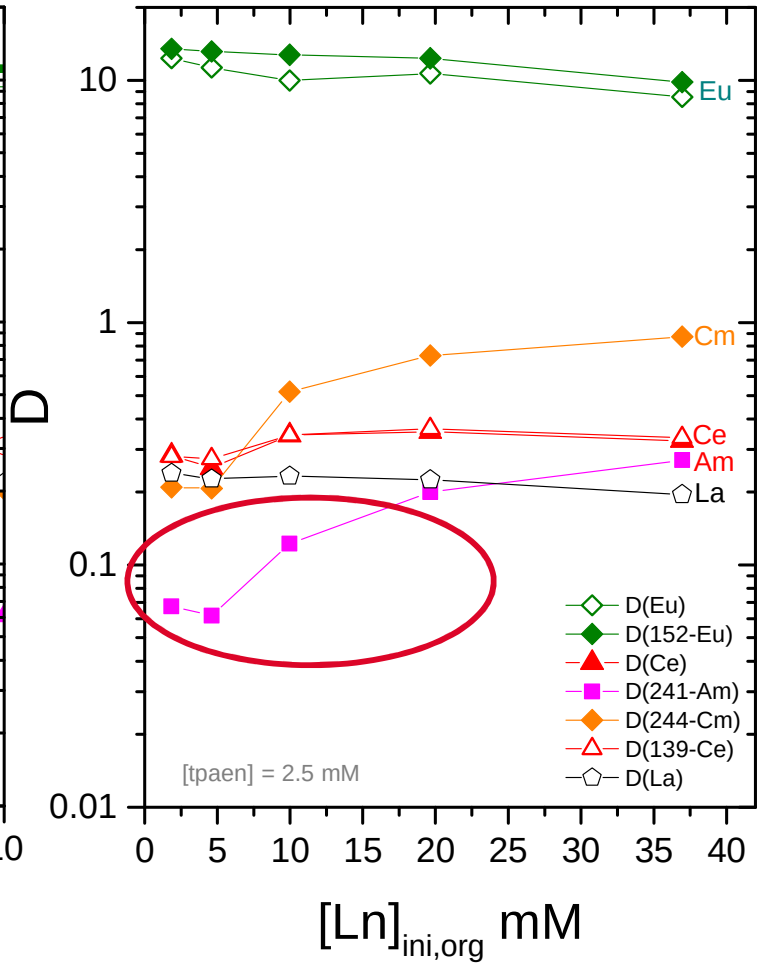
**2) Stripping: TPAEN 10 mM at pH 1**

*Stirring 30min at 25° C*

- ***Light Ln/Am + Cm/Am separation***
- ***Low solubility of TPAEN (2.5 mM in $HNO_3$ 0.1M)***

# EFFECT OF TPAEN AND Ln CONCENTRATIONS




**Experimental Conditions:**

- **Solvent = 0.2M TODGA + 5% vol. octanol in TPH**, loaded with **Ln (from La to Gd)** $^{241}$Am, $^{244}$Cm, $^{152}$ Eu, $^{139}$Ce traces at 1M $HNO_3$
- **Stripping:**

**TPAEN at pH1**, *Stirring 30min at 25° C*

*+ Ln data by ICP-AES*

**It is not possible to separate Am from light Ln if [Ln] > 15 mM**

- No effect of TPAEN concentration on Ln distribution (at this acidity, $pH_{éq}$=0.8)
- Separation La/Am more limiting than Cm/Am
- $SF_{Ln/Am}$ ↗ with [TPAEN]
- No effect of Ln concentration on Ln distribution → far from saturation of the solvent
- $SF_{Ln/Am}$ ↘ with [Ln] (strong dependance)

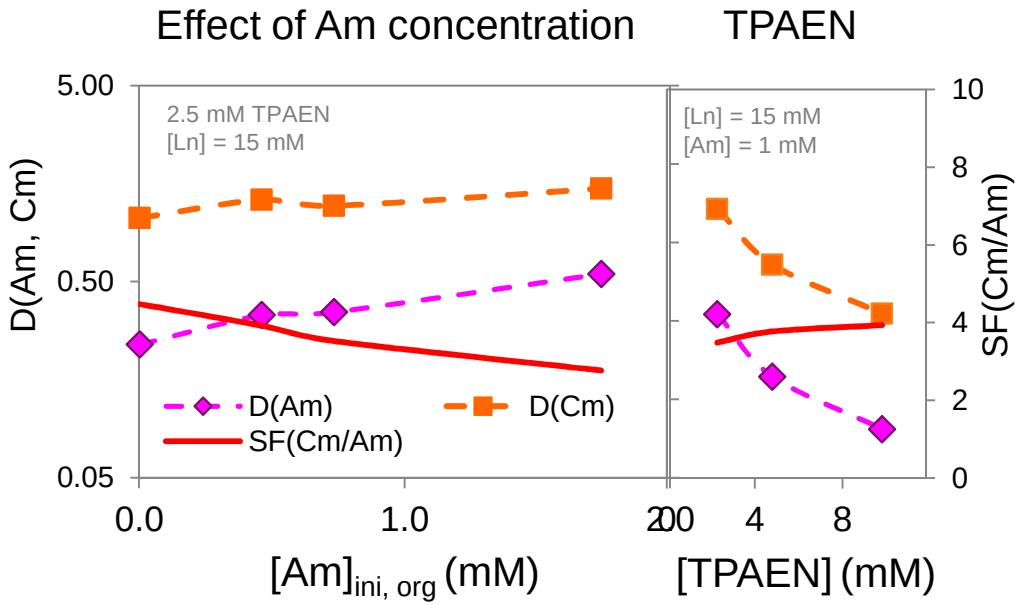
# MACRO Am EXPERIMENTS

P. Kaufholz, Jülich

**Experimental conditions**

- Solvent = 0.2M TODGA + 5% vol. octanol in TPH
- Loaded with Ln (up to 20 mM), $^{241}$Am (up to 2 mM), $^{244}$Cm 7 µM (at 1M $HNO_3$)
- Stripping: TPAEN at pH1 *Stirring 30min at 25° C*

**Parameters studied: [Ln], [Am], [TPAEN], Temp.**

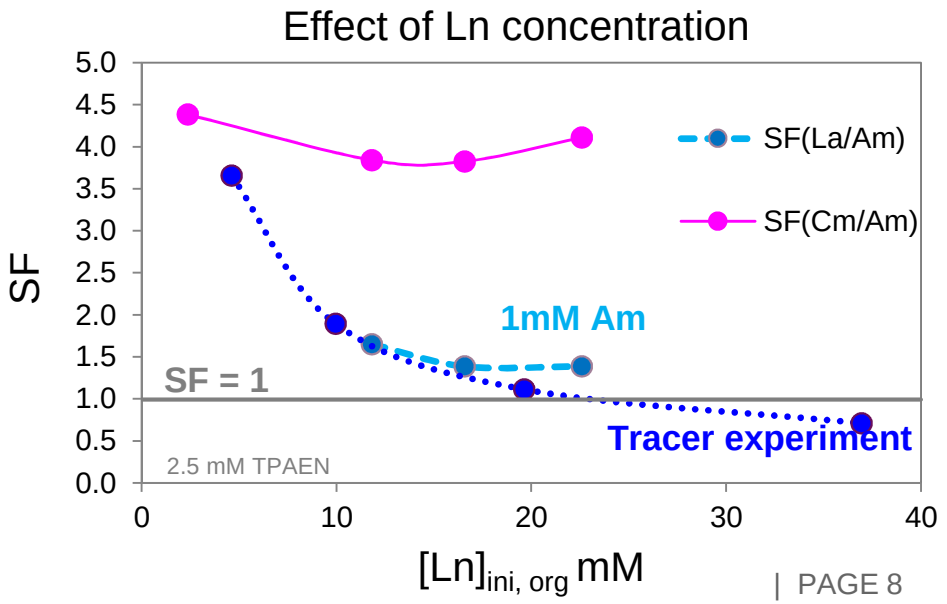



## Results

- Important complexation capacity of Am

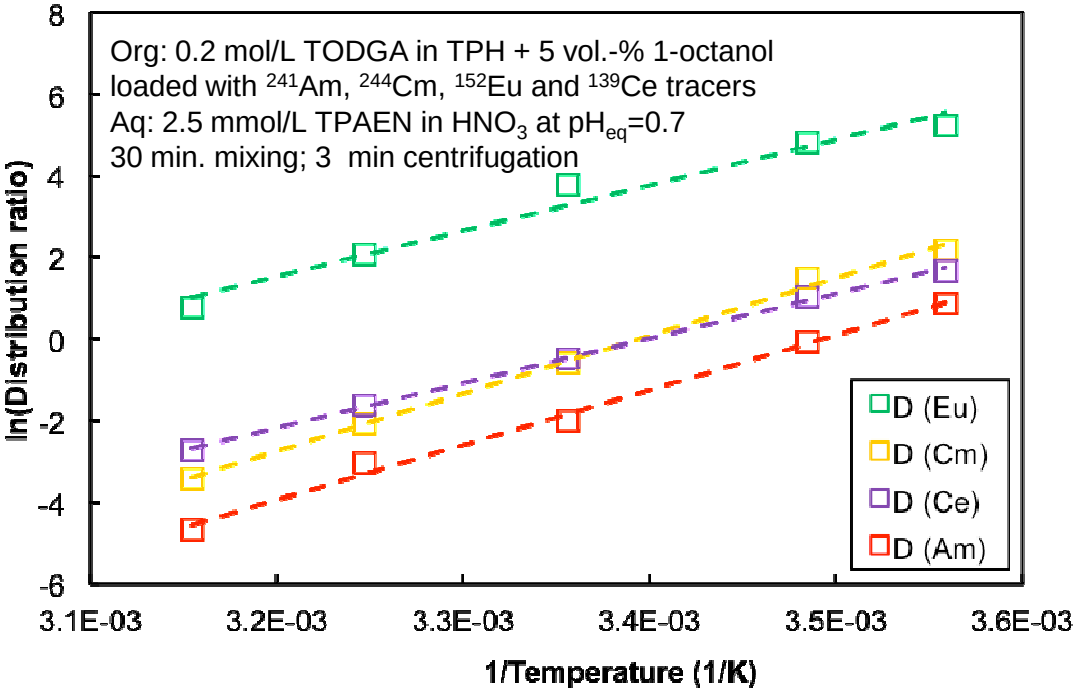
  ➔[TPAEN]/$[Am]_{Aq}$ = 2

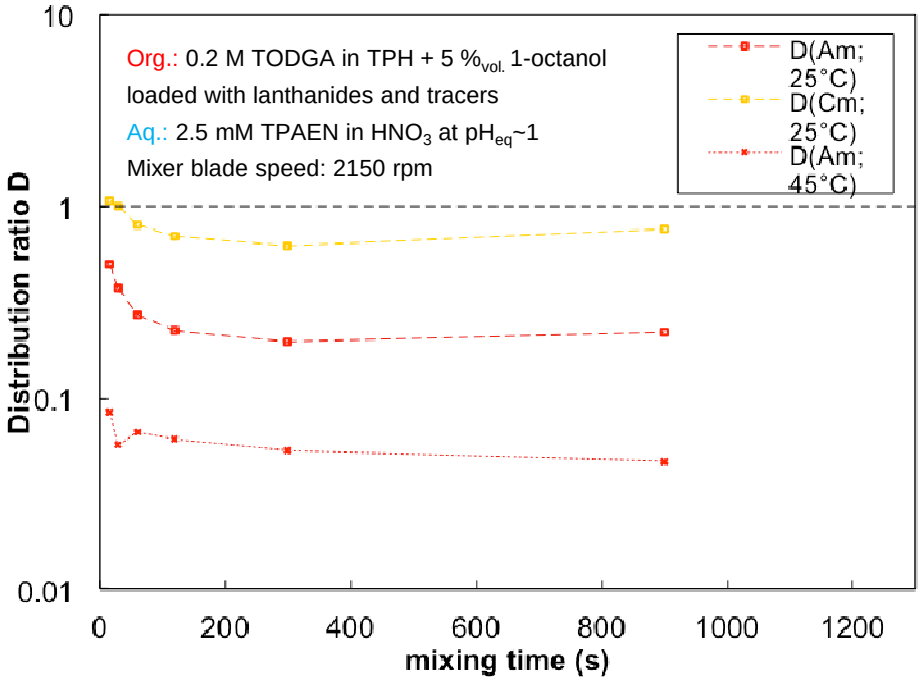
- Slight decrease of $SF_{Cm/Am}$ when **[$^{241}$Am]** ↗
- Slight increase of $SF_{Cm/Am}$ when **[TPAEN]** ↗
- $SF_{Ln/Am}$ ↘ with [Ln] (strong dependance)
- SF(La/Am) ↗ with **[TPAEN] and Temperature**



# BATCH KINETICS AND EFFECT OF TEMPERATURE

P. Kaufholz




## Results:

- Strongly exothermic extraction system
- Different slopes for Ln and An but similar within the group
- Separation factors are influenced by temperature
- Kinetics of An(III) significantly slower than Ln
- Faster Am stripping at high Temperature

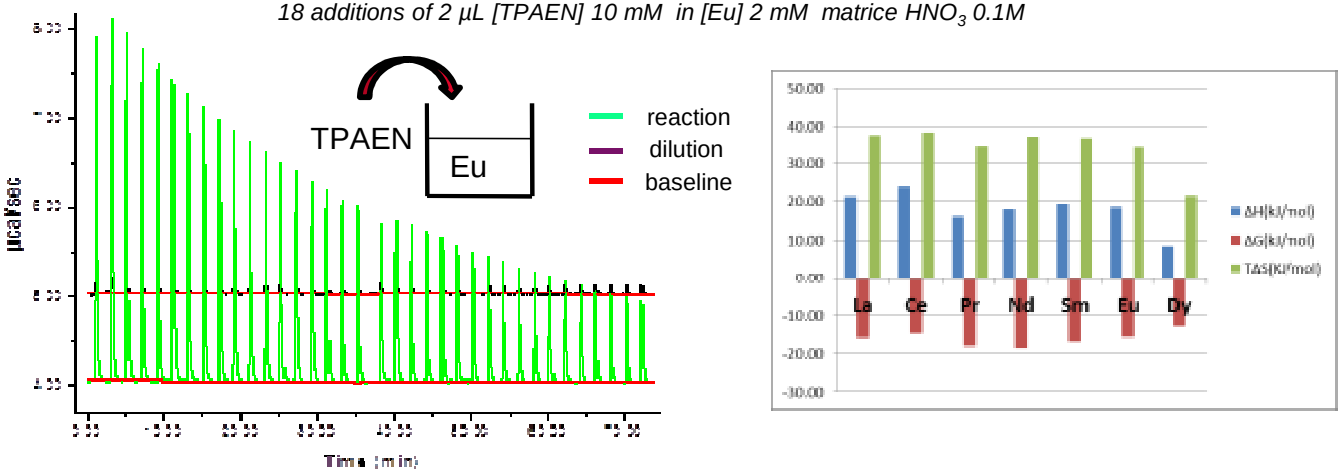
| T (° C) | SF(Cm/Am) | SF(Ce/Am) |
|---|---|---|
| 8 | 3.5 | 2.2 |
| 14 | 4.7 | 3.0 |
| 25 | 4.0 | 4.7 |
| 44 | 3.6 | 7.1 |

**$SF_{Ce/Am}$ ↗ with Temperature**

# COMPLEXATION STUDIES N. Boubals, P. Guilbaud (LILA)

## Calorimetry

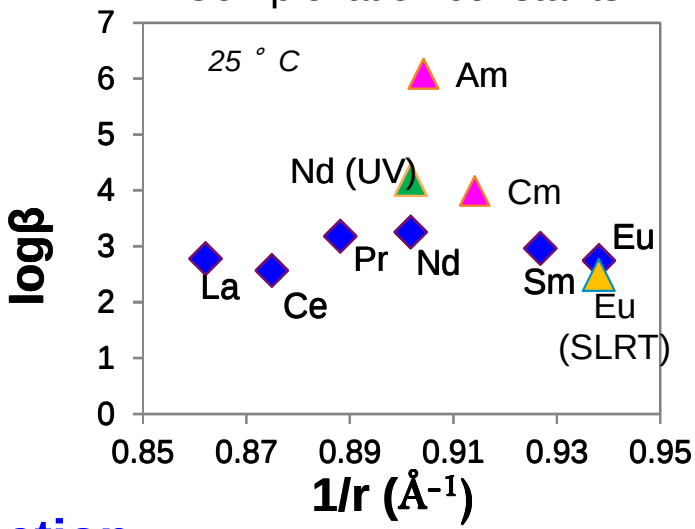
*18 additions of 2 µL [TPAEN] 10 mM in [Eu] 2 mM matrice $HNO_3$ 0.1M*





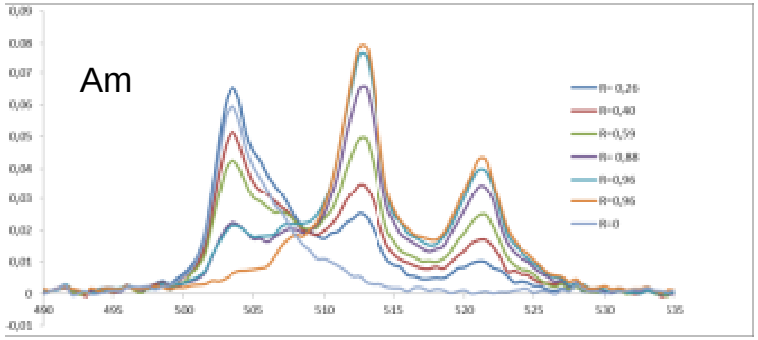


Complexation constants




**Endothermic complexation reaction**

## UV-visible spectrophotometry → complexation constants




*[Am] = 1.9 E-4M ; [TPAEN] 0 to 2.5 E-4M ; matrice HCl 0.1M [TPAEN]/ [Am] = 1.33*

***logβ (Am-TPAEN) = 6.1 ± 0.2 at 25° C***

***logβ (Nd-TPAEN) = 4.2 ± 0.1 at 25° C***

## TRFLS

*[Eu] =1 $10^{-3}$M and [TPAEN] = 0 to 1.17 $10^{-2}$M matrice $HNO_3$ 0.1M*

***logβ (Eu-TPAEN) = 2.5 at 25° C*** *2.4 (KIT)*

***Logβ (Cm-TPAEN) = 4.0 at RT*** *4.3 (KIT)*

# CONCLUSION

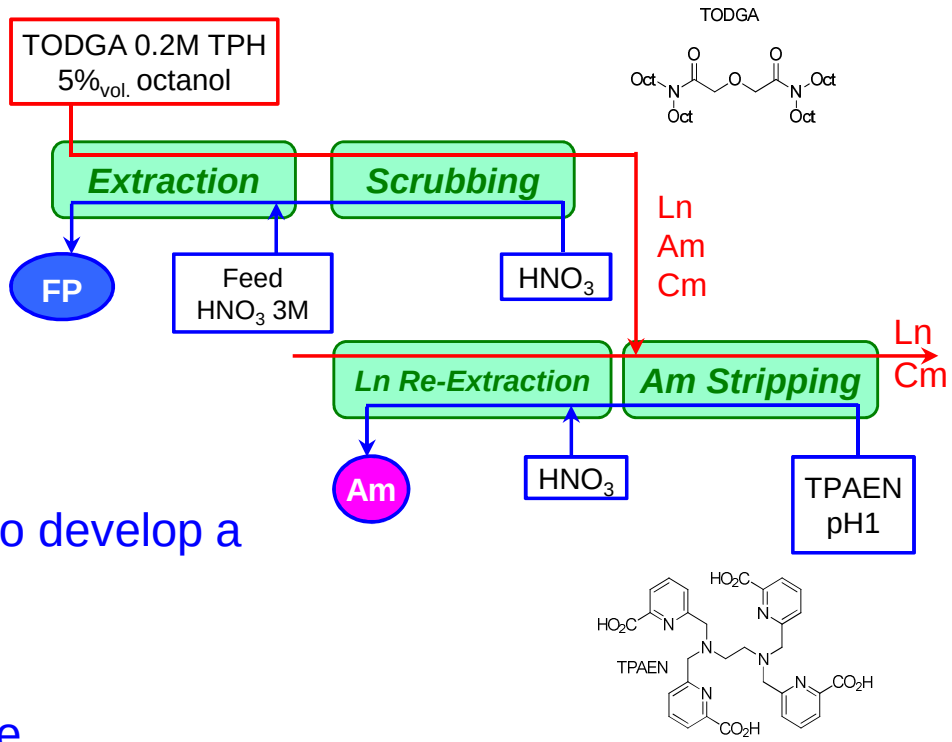
## EXAm Process

- Demonstration of the scientific feasibility of the sole Americium separation from a PUREX raffinate in 1-cyle
- Process adapted to a concentrated raffinate (×3) in order to reduce contactors size
- Objective now = Recovery of Am for $(U,Am)O_2$ pellets fabrication

➔ Last step = hot test on a concentrated raffinate in ATLANTE

## TODGA + TPAEN

- Stripping of Am selectively from Cm and light Ln
- Light Ln / Am separation is difficult to achieve at high concentrations of Ln




- Perspectives:
  - Additional data acquisition (CEA + Jülich) to develop a thermodynamical model
  - Spiked test at Jülich in October 2015
  - Hot test at ITU on genuine PUREX raffinate
  - *Complexation studies: NMR, ESI-MS (Jessica Drader)*

# Acknowledgments

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SACSESS
Safety of actinide separation processes

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