DE LA RECHERCHE À L'INDUSTRIE

Development of a selective Am separation process using TPAEN

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

CEA Marcoule, Nuclear Energy Division, Radiochemistry & Processes Department, France

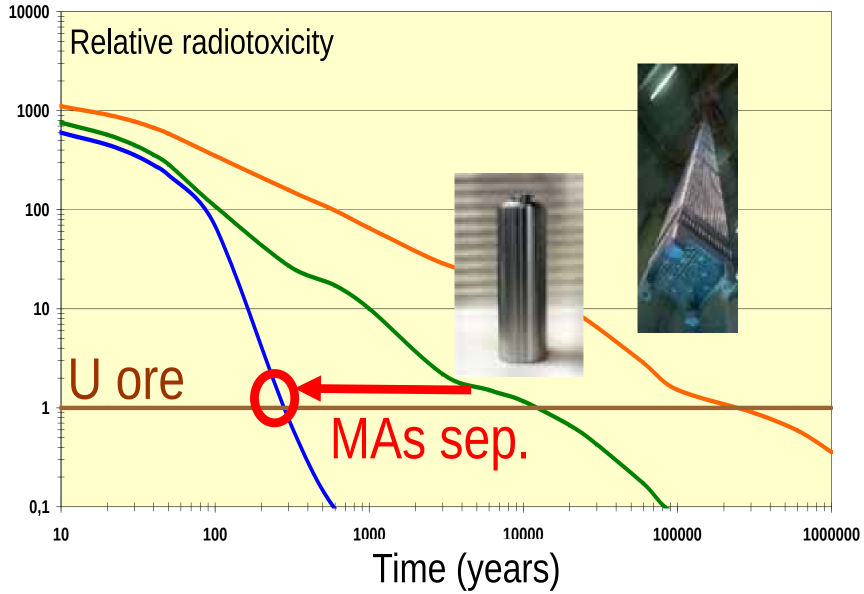
*Jülich Research Center GmbH, Institute of Energy and climate Research, Germany.

SACSESS Safety of actinide separation processes

April 23, 2015

Warsaw, Poland

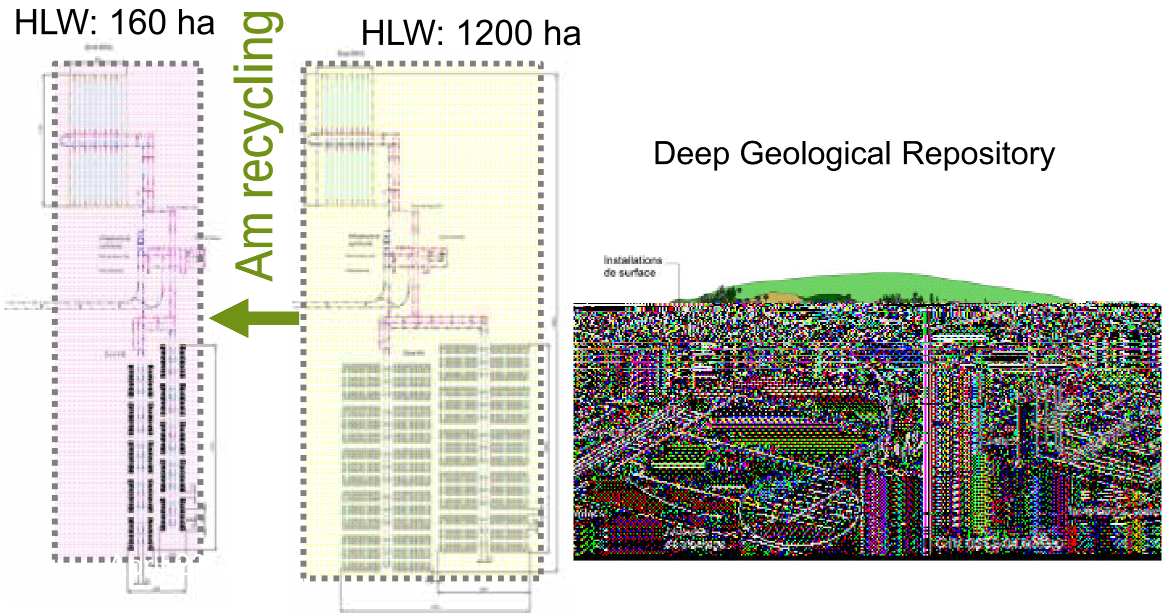
April 23, 2015

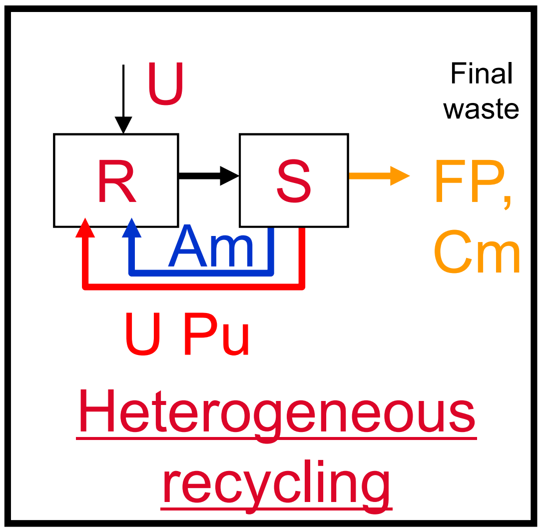


Recycling Am alone

- ↘ 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



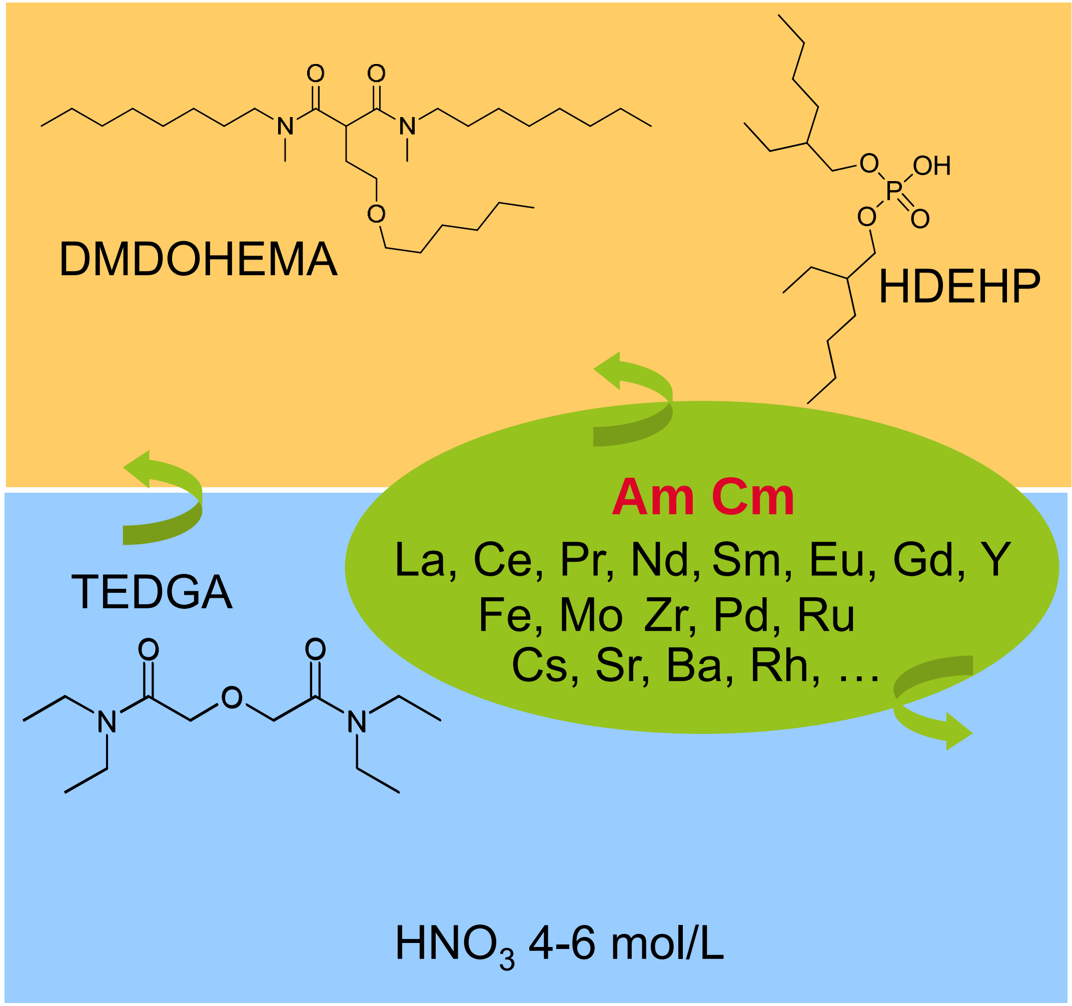


PUREX + EXAm

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 AT HIGH ACIDITY



Model: 62 equilibria (V. Pacary, M. Montuir, LMPR)

Complex Chemistry

- DMDOHEMA alone → very low Am/Cm selectivity ($SF_{Am/Cm}$ = 1.6)
  with TEDGA → $SF_{Am/Cm}$ = 2.5
- Org. Phase: Ternary complexes
  $Ln^{3+}(HDEHP)_x(DMDOHEMA)_y$
- 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)

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

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

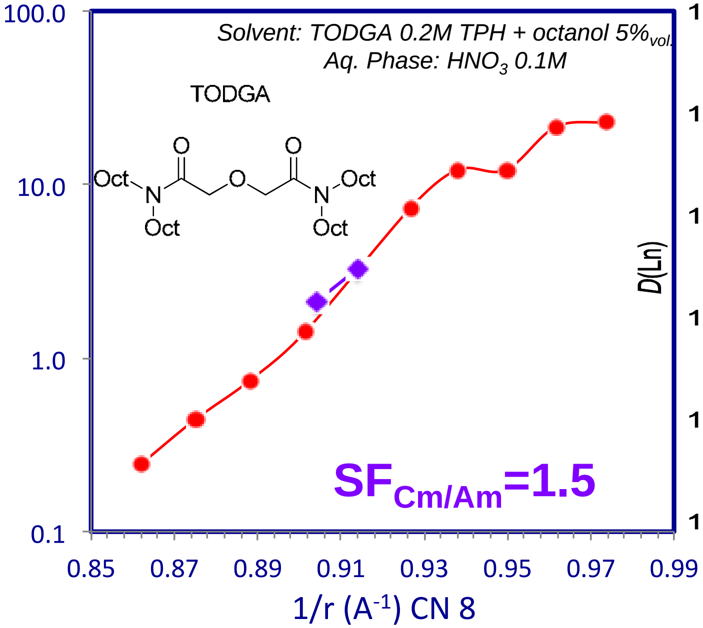
Am/Cm Separation by Liquid-Liquid Extraction

How to select a new extracting system?

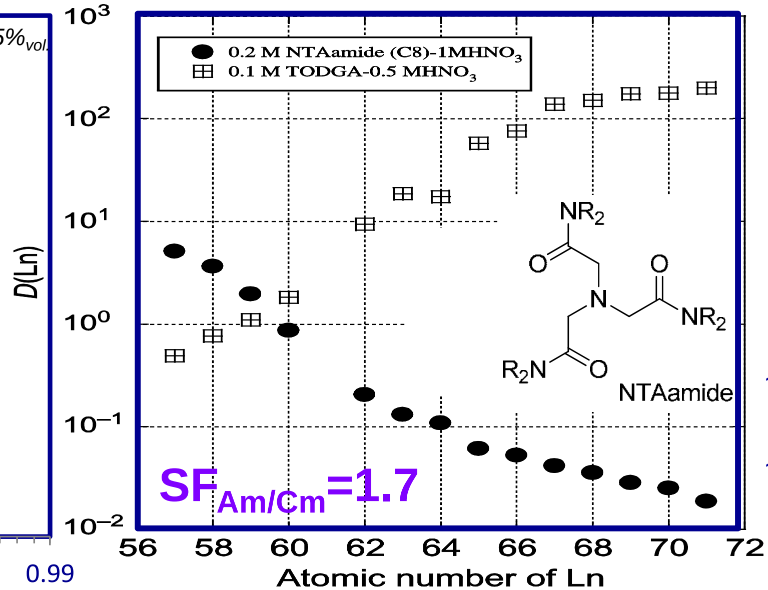
without redox chemistry

An(III), Ln(III) extractants ➔ $SF_{Cm/Am\ or\ Am/Cm} \leq 2$

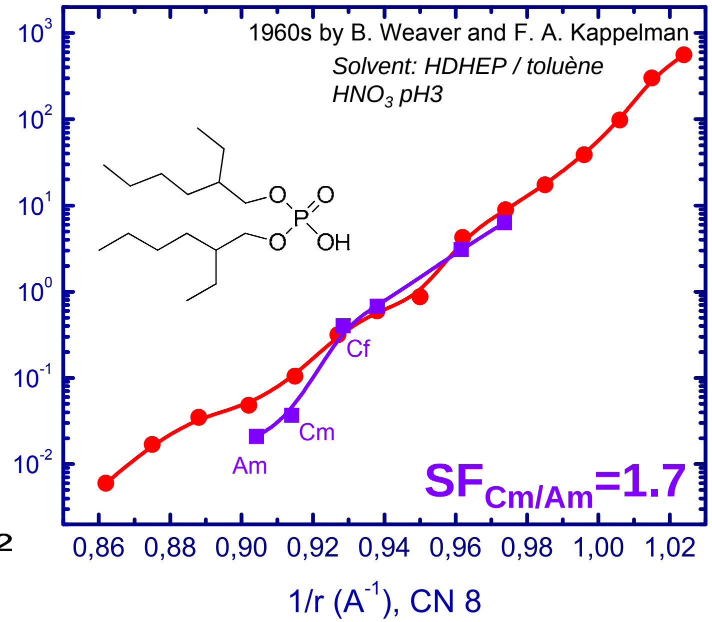
TODGA



NTA-Amide (C8)



HDEHP



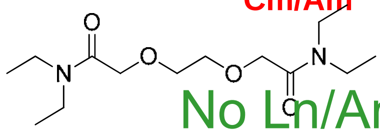
➔ Extractant + complexing agent in the aqueous phase

Sazaki et al.

TDdDGA

+TEDOODA

$SF_{Cm/Am} = 3.3$

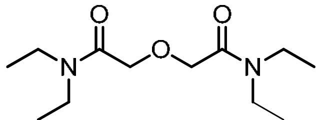


No Ln/Am sep.

Sazaki et al.

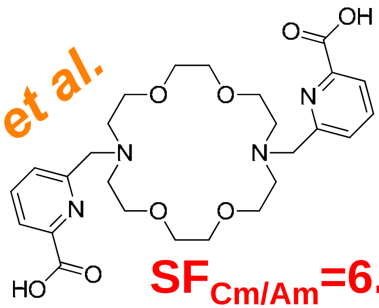
+ TEDGA

$SF_{Am/Cm}=6.5$



Am/Ln Sep. OK

Jensen et al.



$SF_{Cm/Am}=6.5$

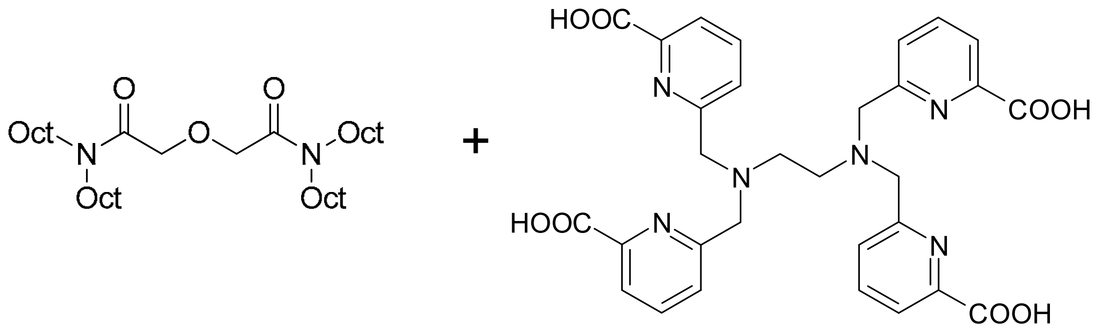
pH 3, no light Ln/Am sep.

Y. Sasakii *et al. Solvent Extr. Res. Dev. Jpn.* **2011**, *18*, 93–101.

Sasaki, Solv. Ext. Ion Exch. **2013** 31(4), 401-415

Mark P. Jensen et al. *Inorg. Chem.*, **2014**, *53* (12), 6003–6012

TODGA TPAEN



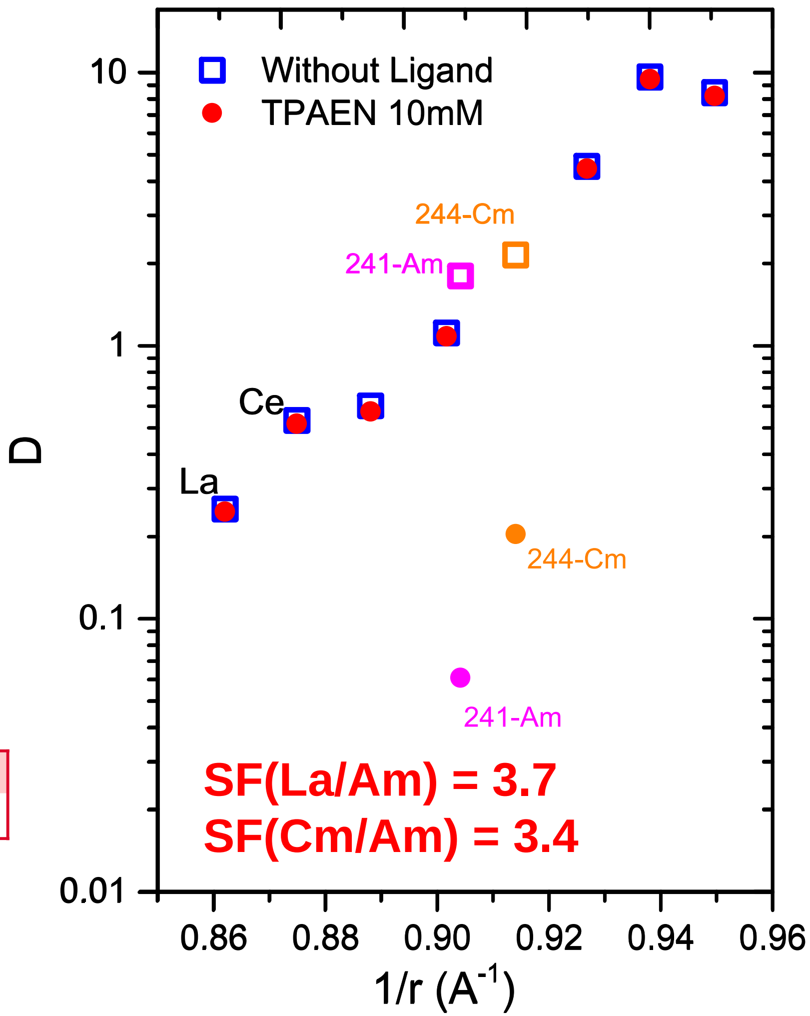
Am Stripping Tests

- Solvent = 0.2M TODGA + 5% vol. octanol in TPH
  Loaded with Ln (from La to Gd) 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

- **Stripping: TPAEN 10 mM at pH 1 (pH$_{eq.}$ = 0.8)**
  Stirring 30min at 25° C



Light Ln/Am + Cm/Am separation

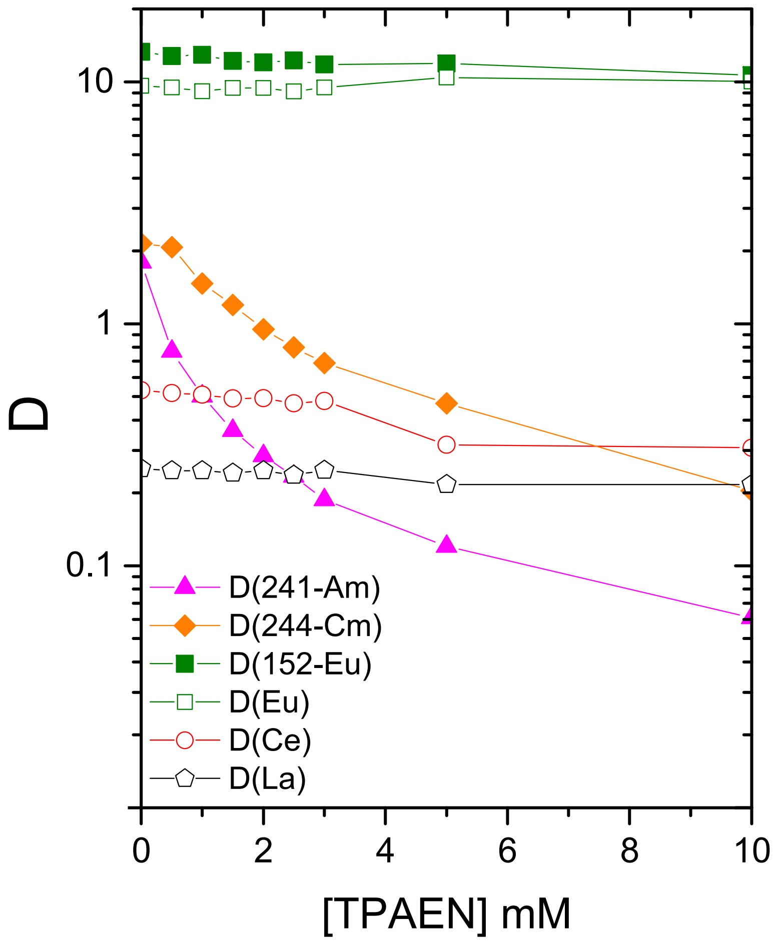
Solubility in water = 5-20 mM (2.5 mM in HNO_3 0.1M)

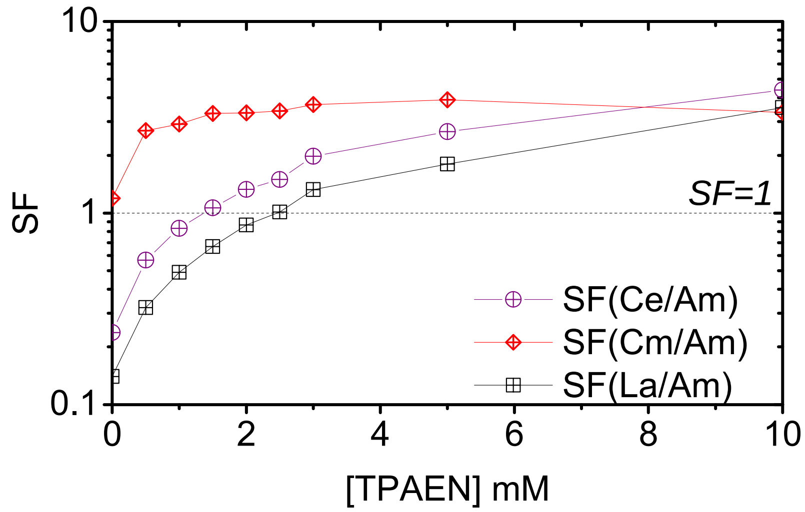
EFFECT OF TPAEN CONCENTRATION (2)

Stripping Conditions:

+ Ln data by ICP-AES

- **Solvent = 0.2M TODGA + 5% vol. octanol in TPH**, loaded with **Ln (from La to Gd) 25 mM** ^{241}Am, ^{244}Cm, ^{152} Eu, ^{139}Ce traces at 1M HNO_3
- **Stripping: TPAEN 1 to 10 mM at p**H1, *Stirring 30min at 25° C*





- No effect of TPAEN concentration on Ln distribution (at this acidity, $pH_{éq}=0.8$)
- Separation La/Am AND Ce/Am more limiting than Cm/Am
- $SF_{Ln/Am}$ ↗ with [TPAEN]

Effect of high concentration of Ln?…

Am STRIPPING WITH TPAEN
Am MACROCONCENTRATION

Stripping Conditions:

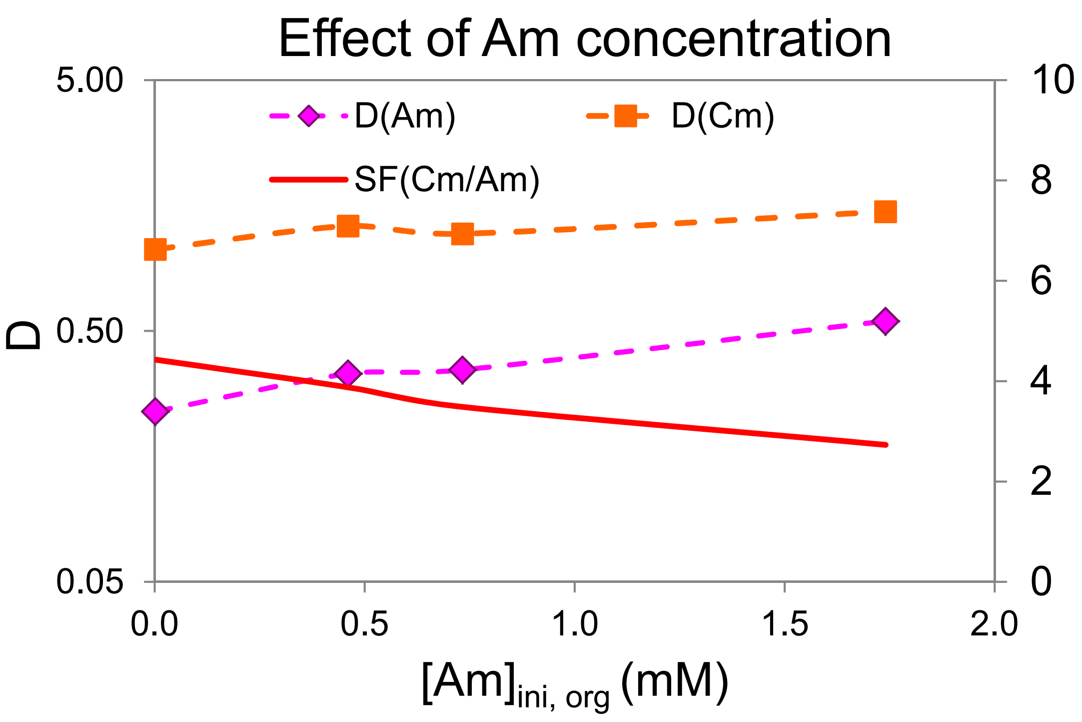
- Solvent = 0.2M TODGA + 5% vol. octanol in TPH
- Loaded with Ln (from La to Gd) 20 mM ^{241}Am 0.5 to 1.5 mM + ^{244}Cm 5µM (at 1M HNO_3)
- Stripping: TPAEN 1 - 2.5 mM at pH1

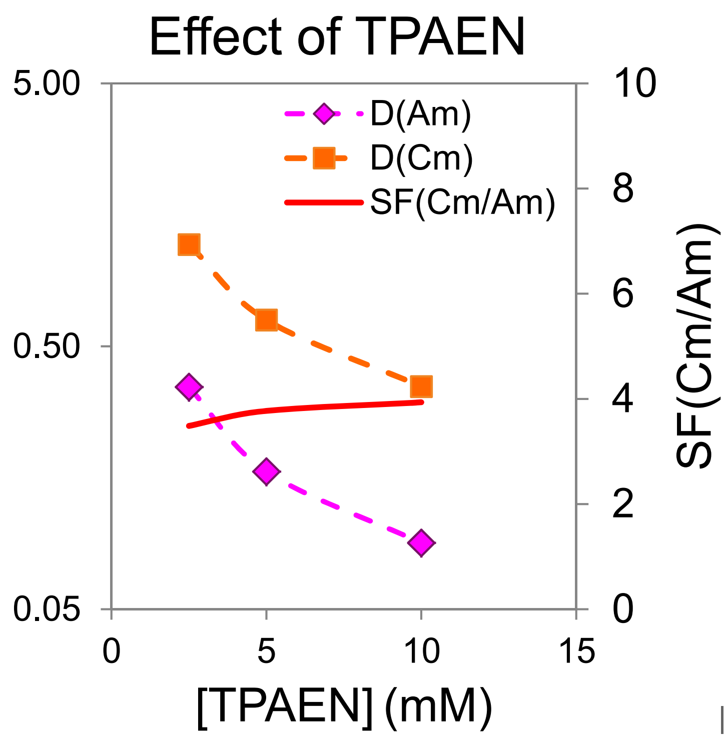
Stirring 30min at 25° C

- Slight decrease of $SF_{Cm/Am}$ when concentration of ^{241}Am ↗
- Slight increase of $SF_{Cm/Am}$ when concentration of TPAEN ↗

Measurment of Ln by ICP-OES on-going…

Effect of [Ln], Temperature…





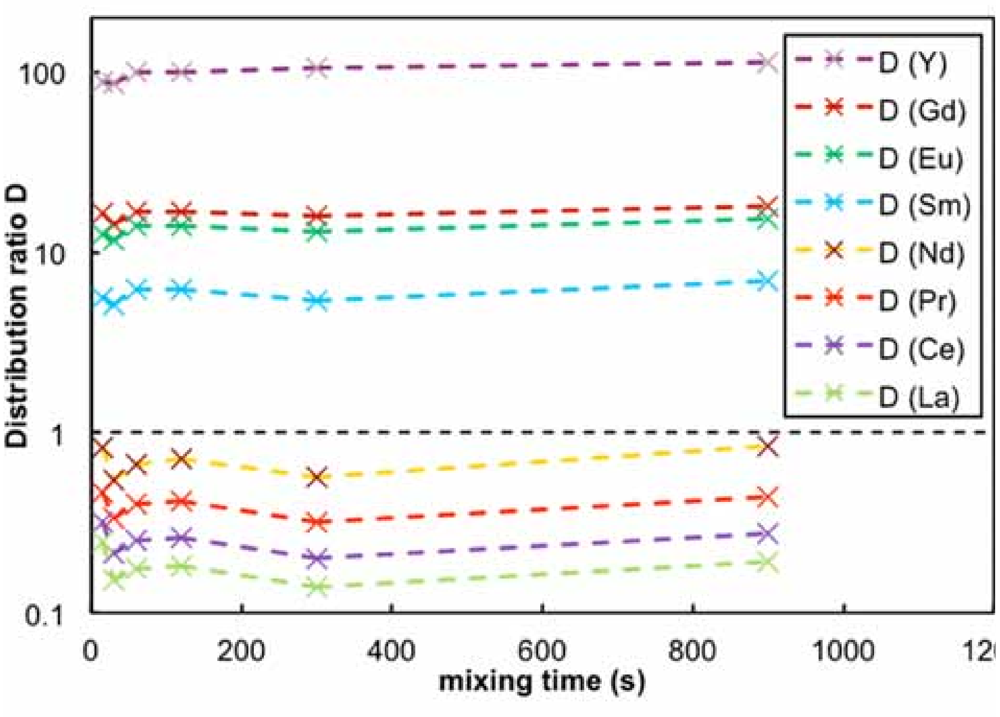
BATCH KINETICS

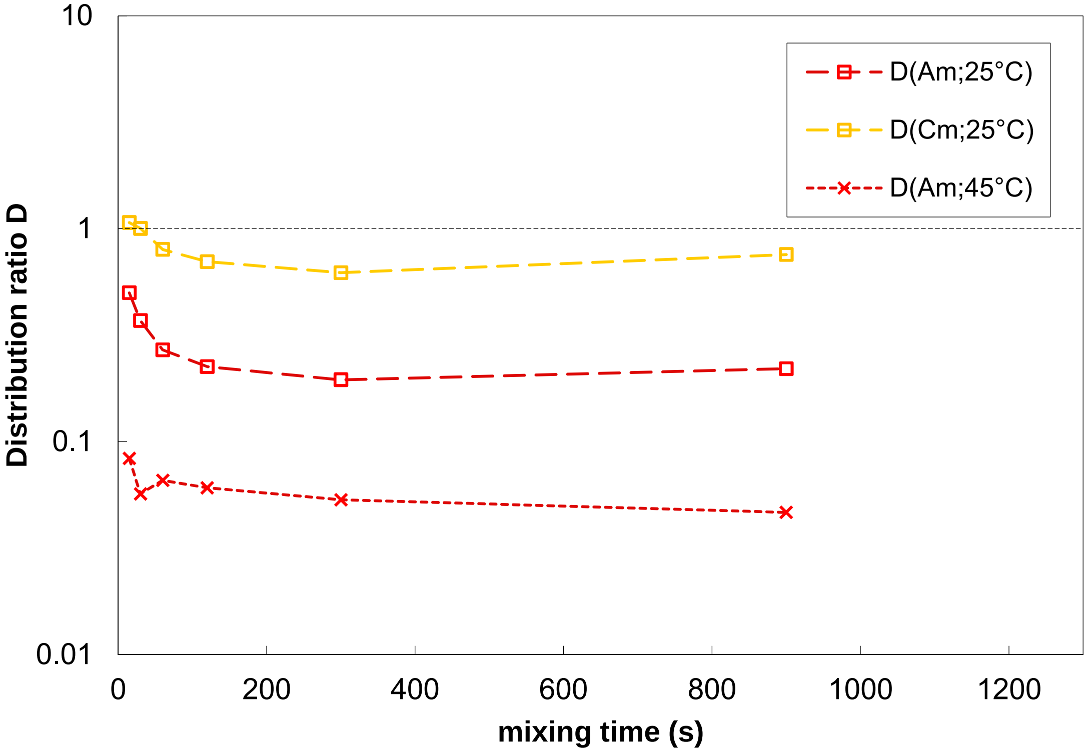
P. Kaufholz

Organic phase: 0.2 mol/L TODGA in TPH + 5 vol.-% 1-octanol loaded with lanthanides and tracers

Aqueous phase: 2.5 mM TPAEN in HNO_3 at pH_{eq}~1

Mixer blade speed: 2150 rpm; T=20˚C samples from emulsion



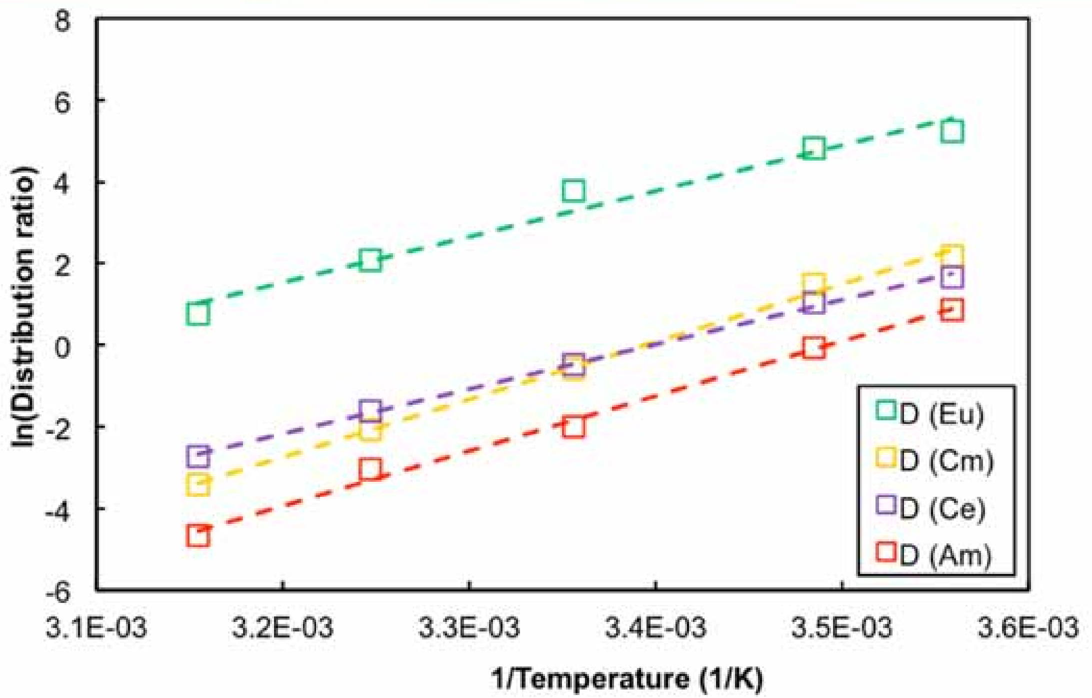


Results:

- Kinetics of An(III) significantly slower than Ln
- An close to D_{eq} after 120 s
- Experiment at 45˚C shows an increase in kinetics for An

Separation factors at diff. temperatures

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



Org: 0.2 mol/L TODGA in TPH + 5 vol.-% 1-octanol loaded with ^{241}Am, ^{244}Cm, ^{152}Eu and ^{139}Ce tracers
Aq: 2.5 mmol/L TPAEN in HNO_3 at pH_{eq}=0.7
30 minutes mixing; 3 min centrifugation

Results:

- Strongly exothermic extraction system
- TPAEN complexation endothermic in aqueous phase
- Different slopes for the Ln and for the An but similar within the group
- Separation factors are influenced by temperature

$SF_{Ce/Am}$ ↗ with Temperature but D ↘

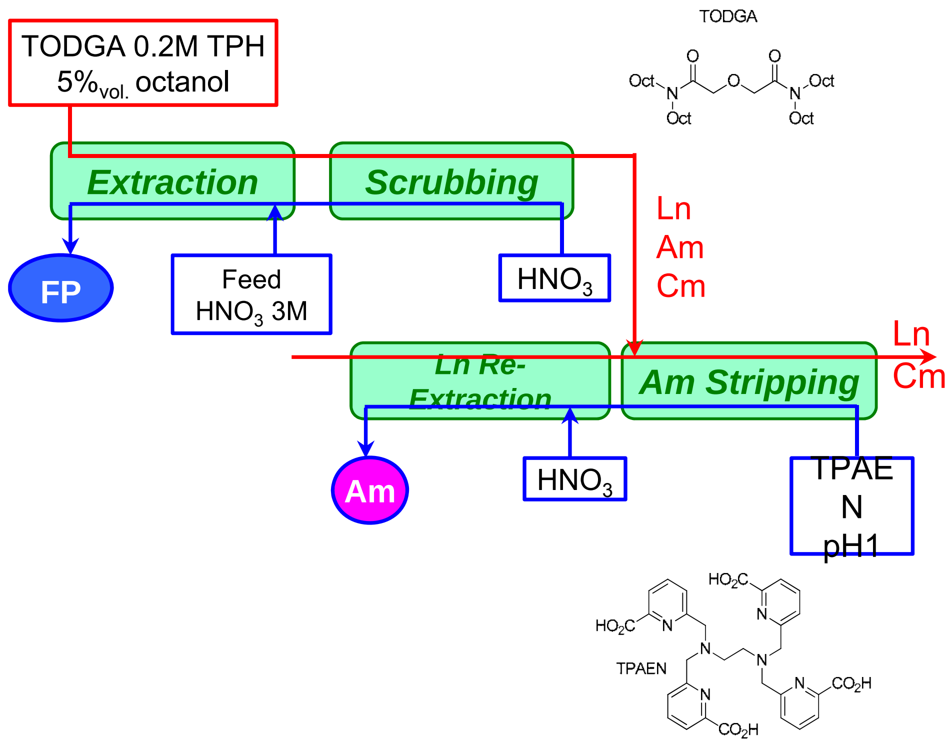
CONCLUSION

- TODGA + TPAEN ➔ stripping of Am selectively from Cm AND light Ln
- SF(Cm/Am) and (La/Am) ↗ with TPAEN conc.
- TPAEN concentration can be increased up to 2.5 mM at pH 1
- Am stripping slow but ↗ with temperature
- Light Ln / Am separation cannot be achieved at high concentrations of Ln

  Solutions: 1) Increase [TPAEN]

  2) Re-extraction steps?

  3) Temperature



- Experiments with macroconcentrations of ^{241}Am ➔ high complexation capacity of TPAEN
- Perspectives:
  - Additional data acquisition (CEA + Jülich) to develop a thermodynamical model (V. Vanel, CEA)
  - Spiked test at Jülich in September 2015
  - Hot test at ITU at the end of 2015 on genuine PUREX raffinate
  - *Understand impact of synthesis impurities (UNIPR)*
  - *Synthesis of new derivatives with higher water solubility (UNIPR)*