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

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DE LA RECHERCHE A L'INDUSTRIE

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

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A. Wilden, G. Modolo, N. Boubals, M. Miguirditchian

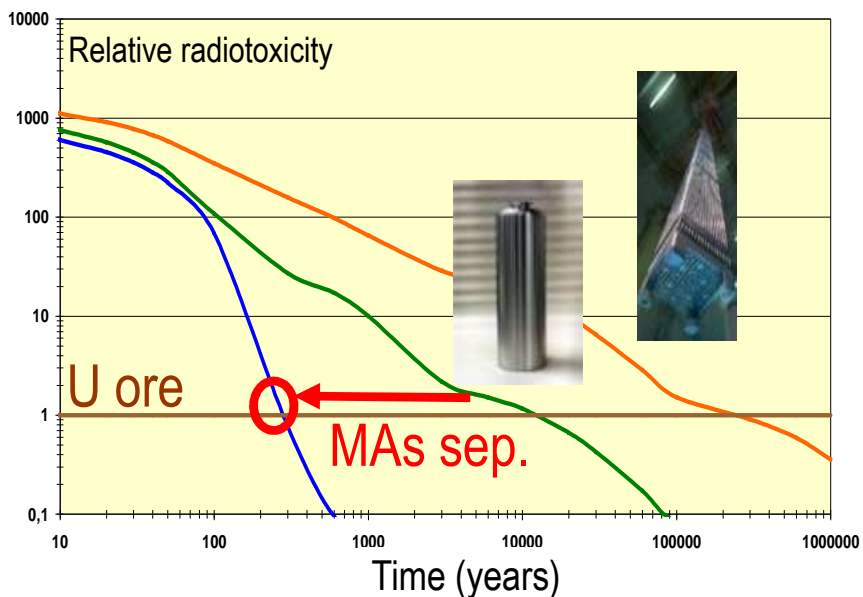
CEA Marcoule, Nuclear Energy Division, Radiochemistry  
& Processes Department, France



ACS NATIONAL MEETING & EXPOSITION

17th August 2015

Boston, US



## Recycling Am alone

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

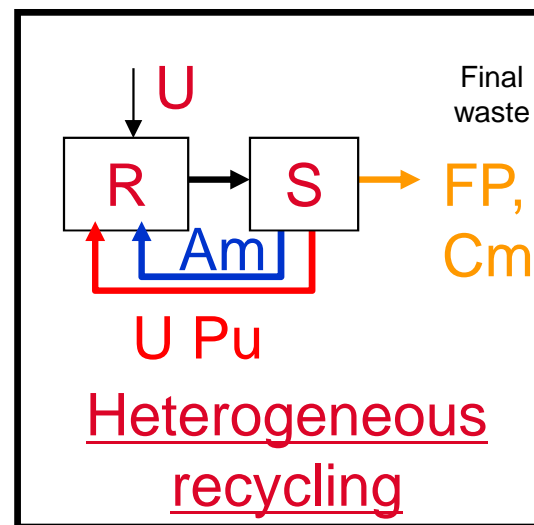
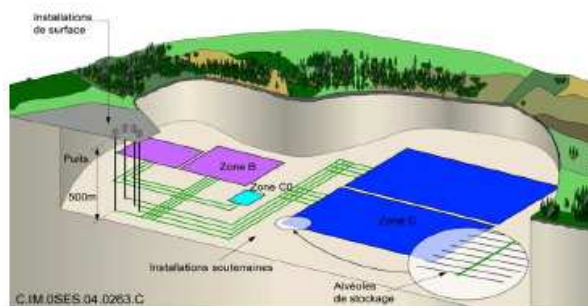
**With Am recycling, reduction of the repository surface by a factor up to 8**

HLW: 160 ha

HLW: 1200 ha

Am recycling

Deep Geological Repository

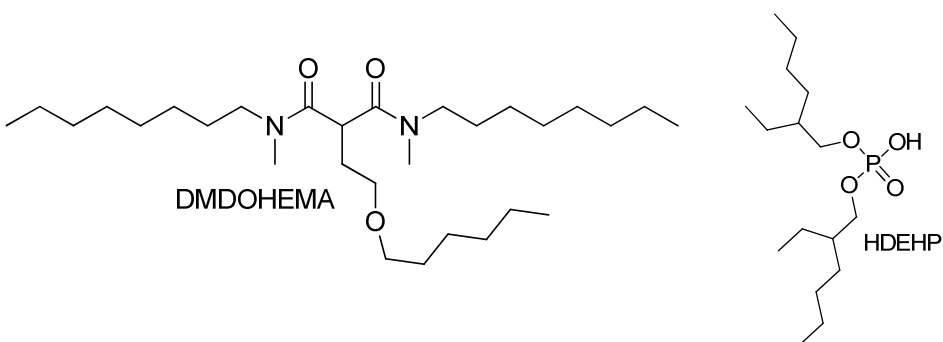


PUREX  
+  
EXAm

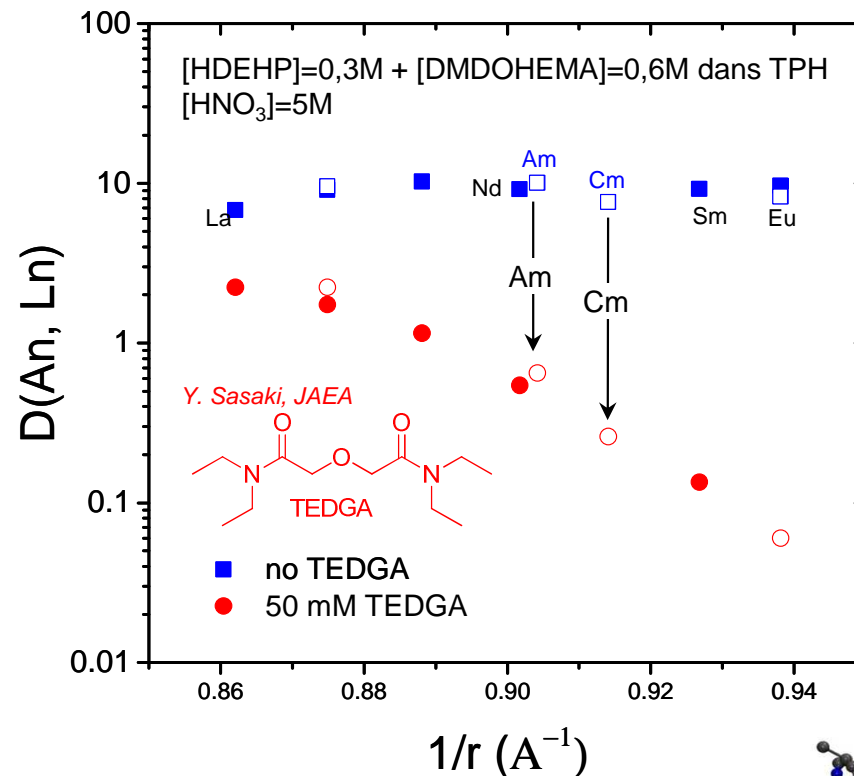
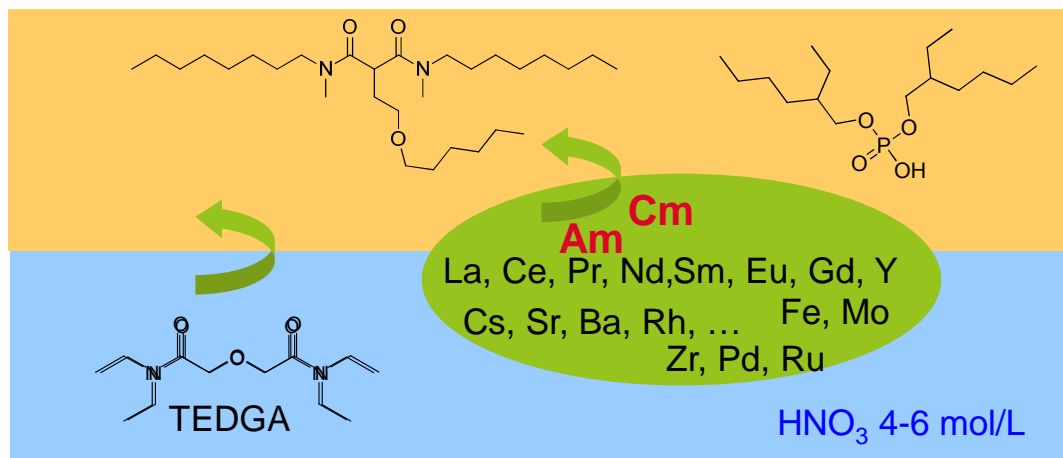
R = reactor S = separation FP = fission products

## EXAm Liquid/Liquid Extraction Process

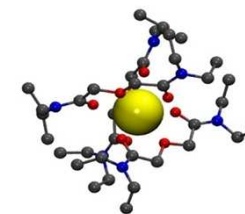
Selective Recovery of Americium alone from a PUREX raffinate (already cleared from U, Pu and Np).



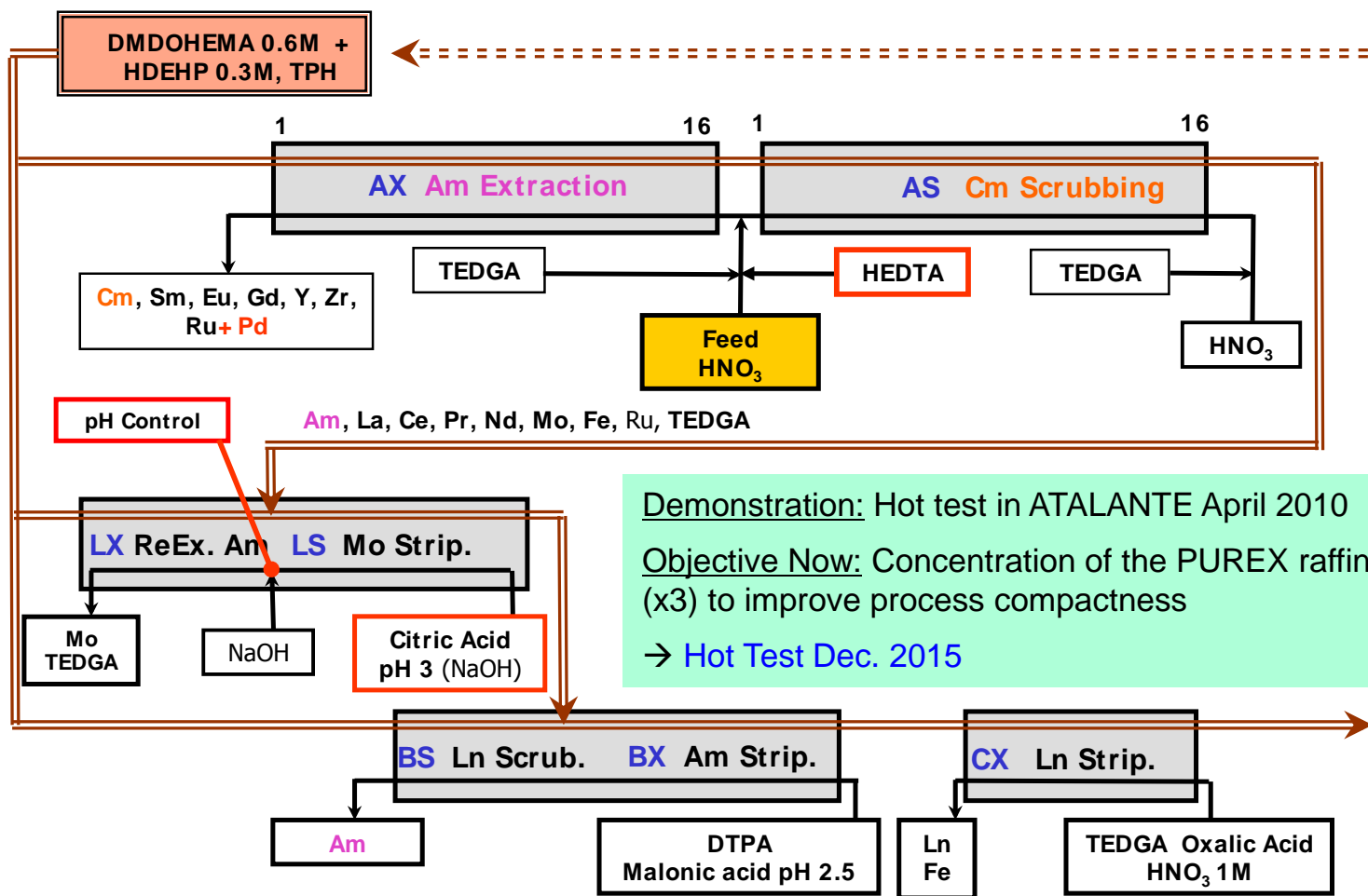
- Extractants alone → very low Am/Cm selectivity ( $SF_{Am/Cm} = 1.6$ )
- with TEDGA →  $SF_{Am/Cm} = 2.5$



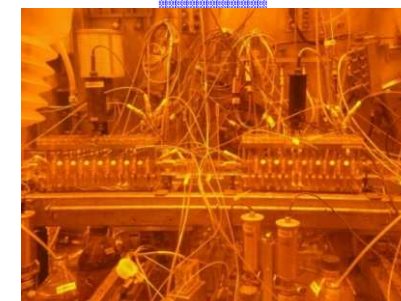
## Complex Chemistry



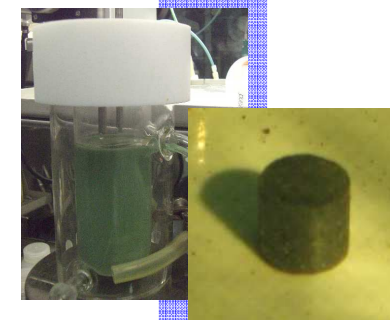
- Org. Phase: Ternary complexes  $Ln(HDEHP)_x(DMDOHEMA)_y$  *J. Muller Thesis*
  - Aq. Phase:  $Ln(TEDGA)_n^{3+}$  ( $n=1,2,3$ ) Stability constants ( $Ln, Am$ )\*
- $Ln(TEDGA)_n(D)_y$  in the Org. Phase ( $n=1,2$ )



Cold and spiked tests



Hot test

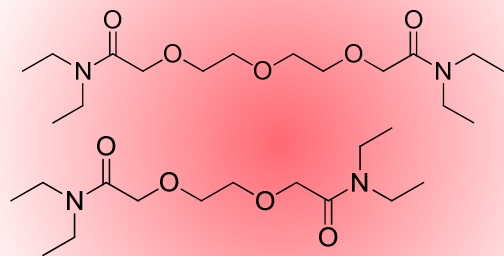


Oxalic co-conversion and U-Am oxide fabrication

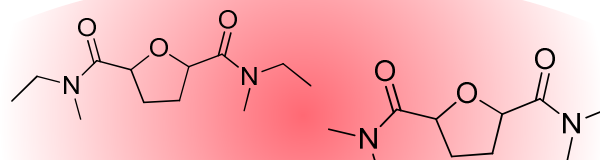
## Axis of improvement:

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

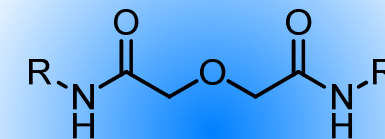
## Spacer



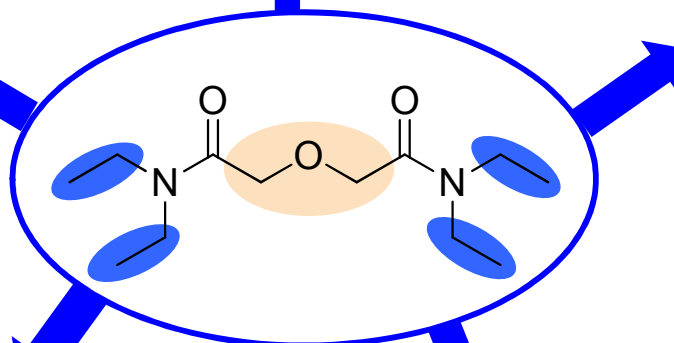
*Inversion of selectivity*



*Loss of selectivity and affinity*

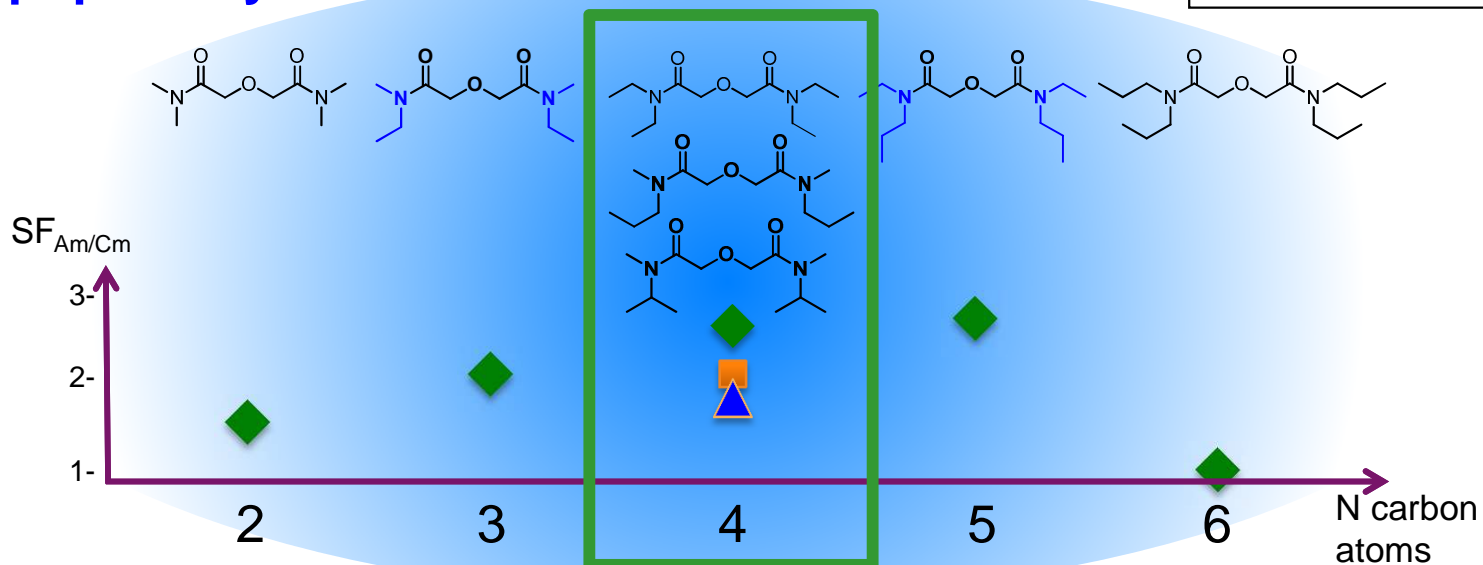


*High affinity with extractants in the organic phase*



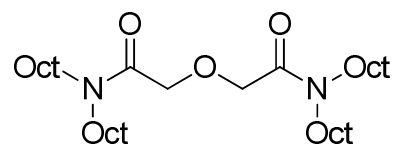
**TEDGA = best compromise between selectivity and partitioning**

## Lipophilicity

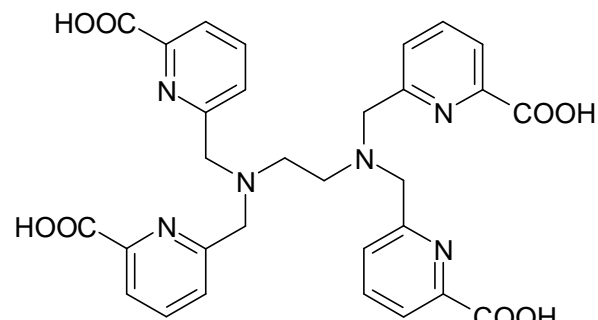




TODGA



TPAEN



**TPAEN = Am stripping agent**

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

1) Ln + Am and Cm loading at 1M HNO<sub>3</sub>

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

+ <sup>241</sup>Am, <sup>244</sup>Cm

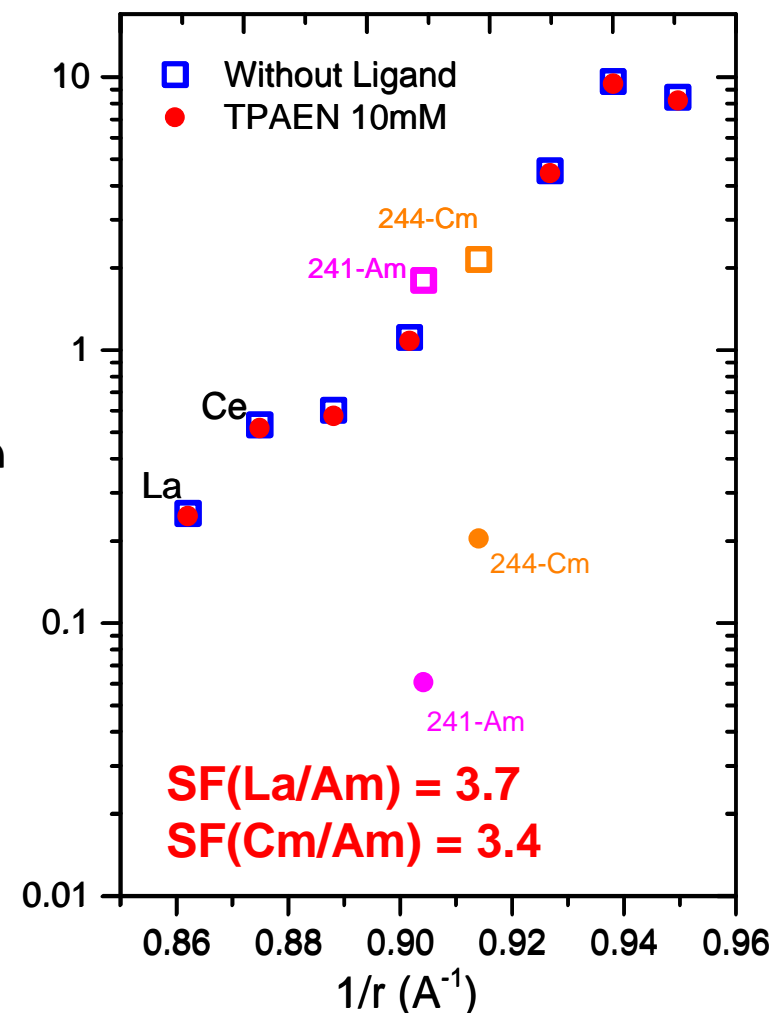
2) Stripping: TPAEN 10 mM at pH 1

Stirring 30min at 25° C

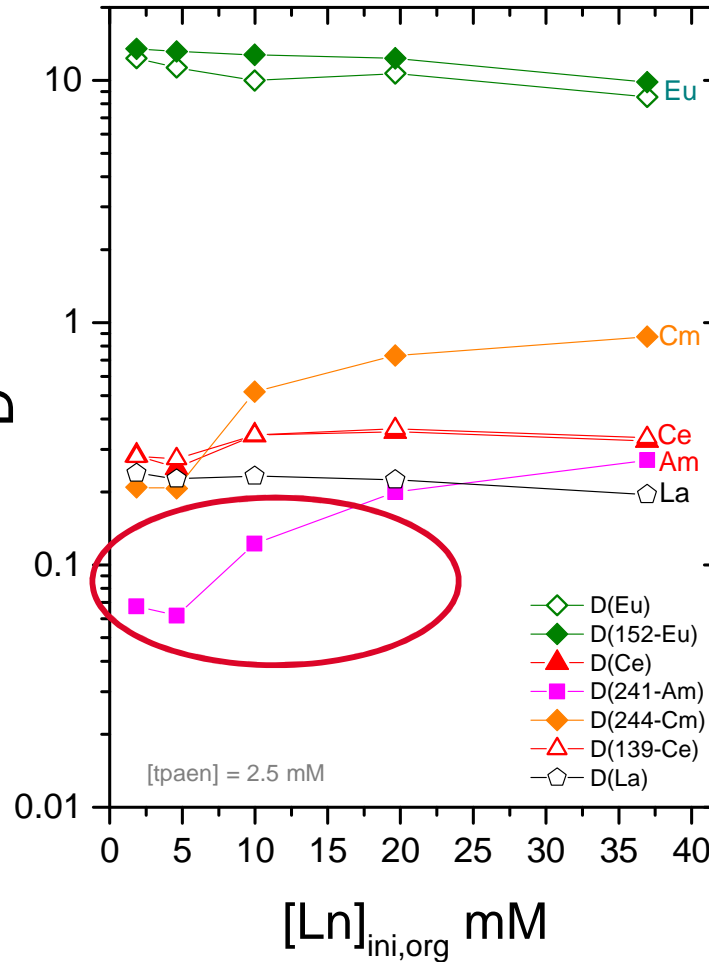
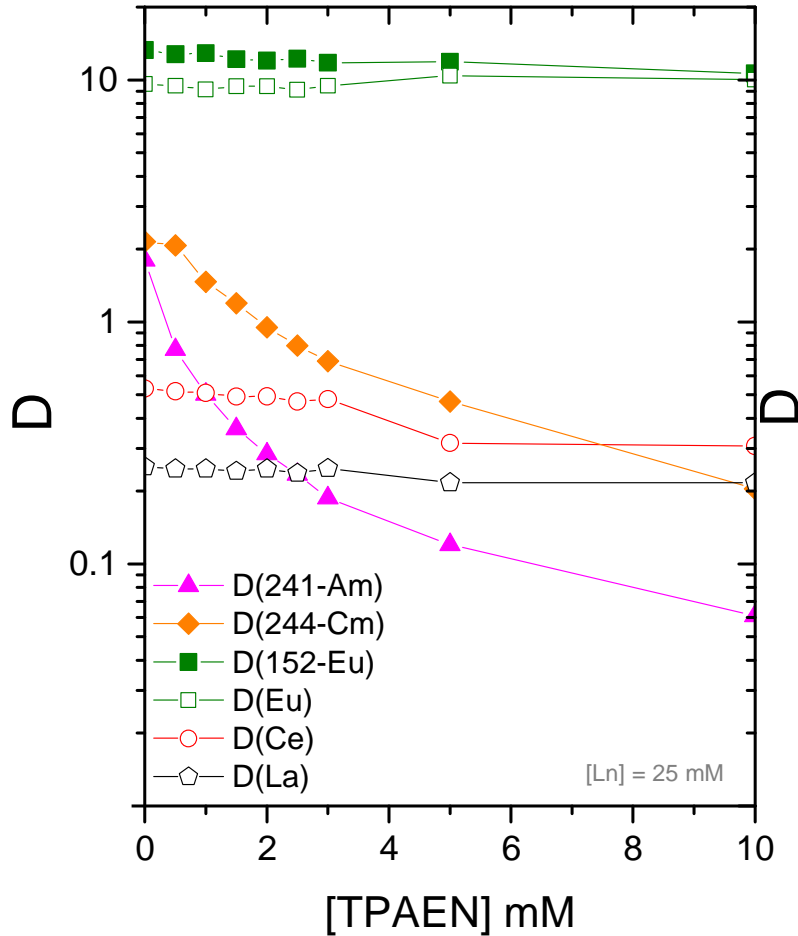
 **Light Ln/Am + Cm/Am separation**

 **Low solubility of TPAEN (2.5 mM in HNO<sub>3</sub> 0.1M)**

D



# EFFECT OF TPAEN AND Ln CONCENTRATIONS



**Experimental Conditions:**

- Solvent = 0.2M TODGA + 5% vol. octanol in TPH, loaded with Ln (from La to Gd) <sup>241</sup>Am, <sup>244</sup>Cm, <sup>152</sup>Eu, <sup>139</sup>Ce traces at 1M HNO<sub>3</sub>
- 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<sub>éq</sub>=0.8)
- Separation La/Am more limiting than Cm/Am
- SF<sub>Ln/Am</sub> ↗ with [TPAEN]

- No effect of Ln concentration on Ln distribution → far from saturation of the solvent
- SF<sub>Ln/Am</sub> ↘ with [Ln] (strong dependence)



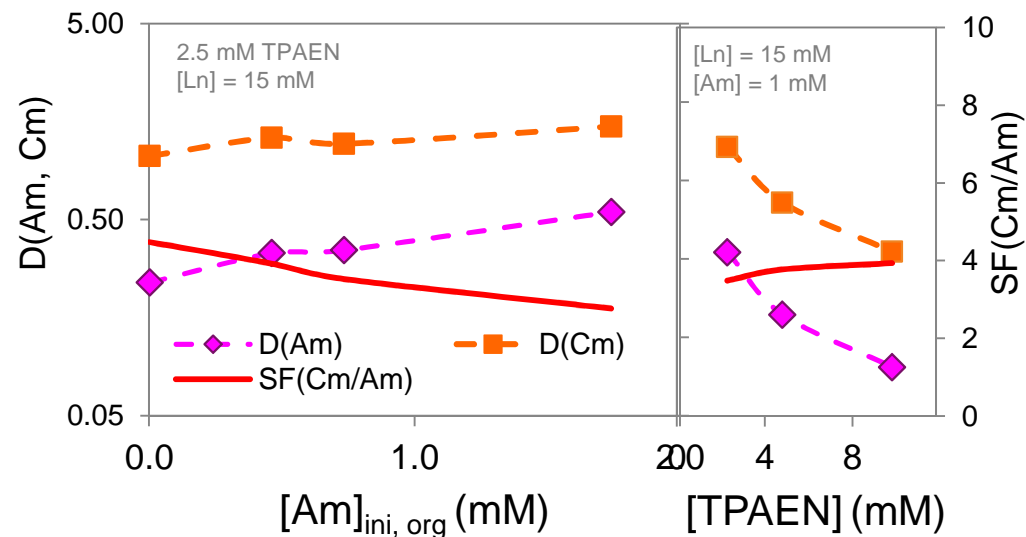
## Experimental conditions

- Solvent = 0.2M TODGA + 5% vol. octanol in TPH
  - Loaded with Ln (up to 20 mM), <sup>241</sup>Am (up to 2 mM), <sup>244</sup>Cm 7 μM (at 1M HNO<sub>3</sub>)
  - Stripping: TPAEN at pH1 *Stirring 30min at 25° C*
- Parameters studied: [Ln], [Am], [TPAEN], Temp.**

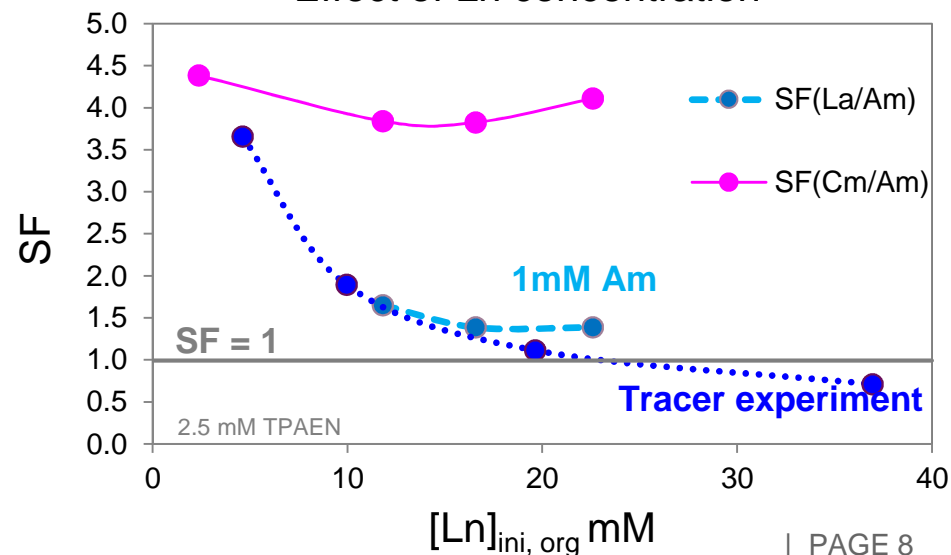
## Results

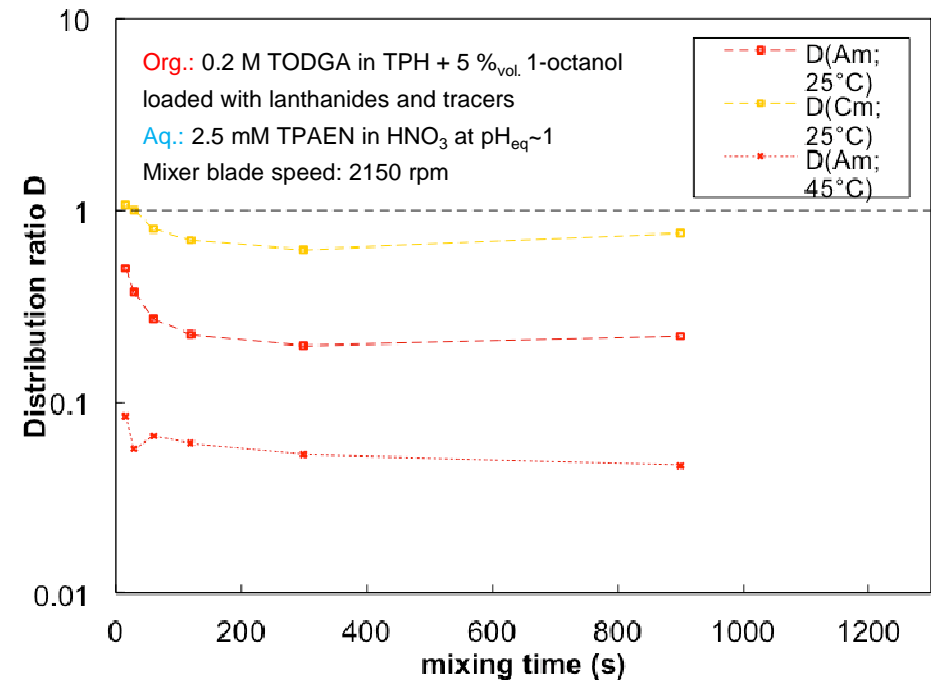
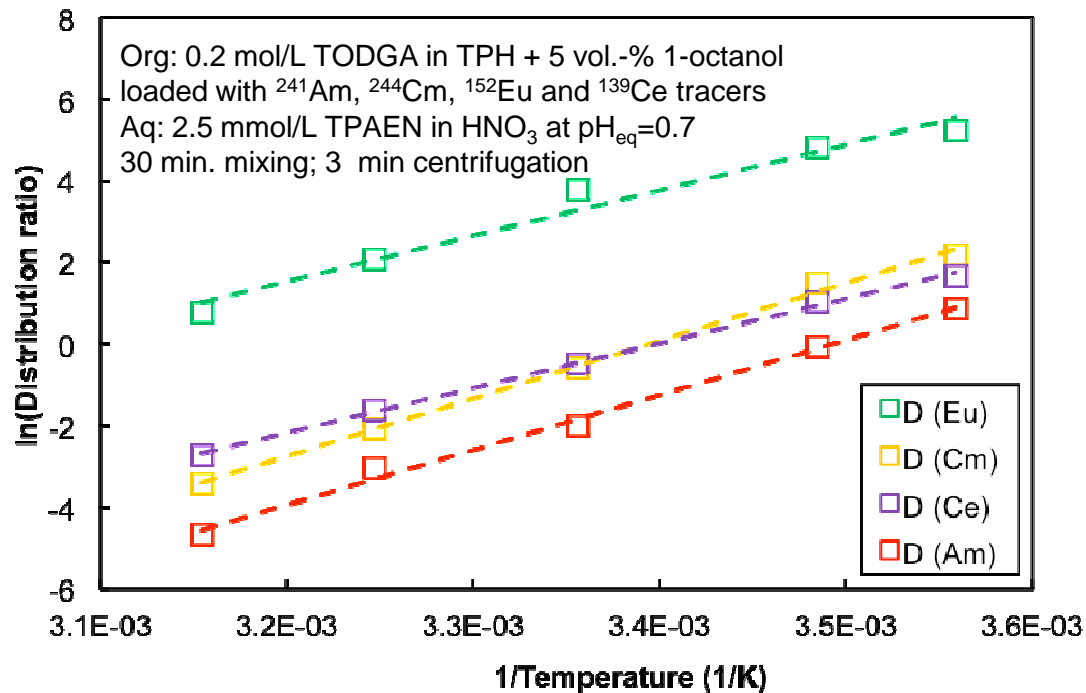
- Important complexation capacity of Am  
 $\rightarrow [TPAEN]/[Am]_{Aq} = 2$
- Slight decrease of SF<sub>Cm/Am</sub> when **[<sup>241</sup>Am]** ↗
- Slight increase of SF<sub>Cm/Am</sub> when **[TPAEN]** ↗
- SF<sub>Ln/Am</sub> ↘ with **[Ln]** (strong dependance)
- SF(La/Am) ↗ with **[TPAEN]** and **Temperature**

Effect of Am concentration



Effect of Ln concentration





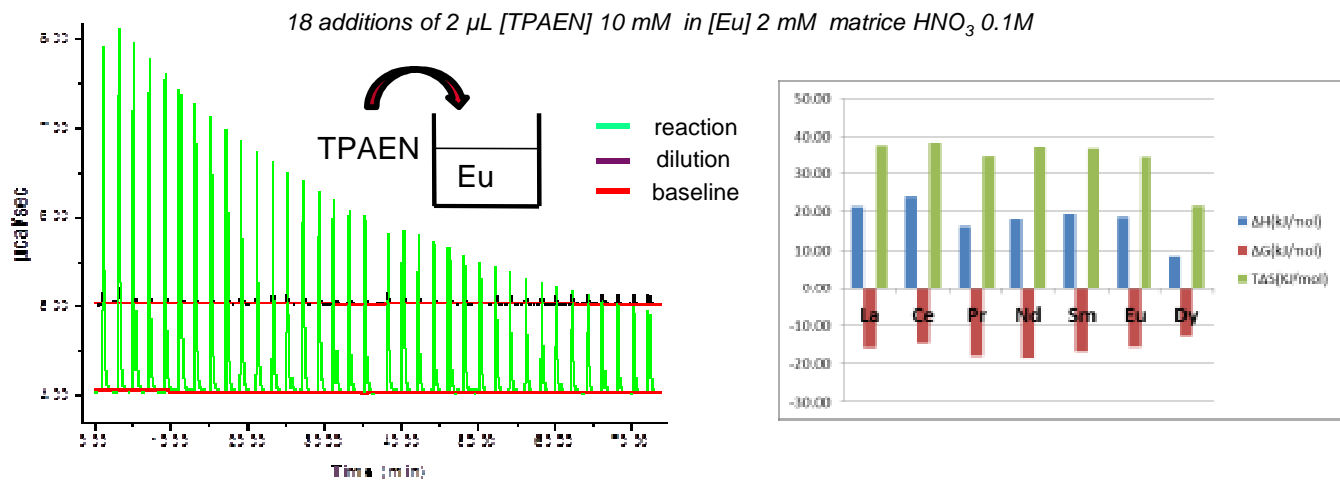
## Results:

- 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

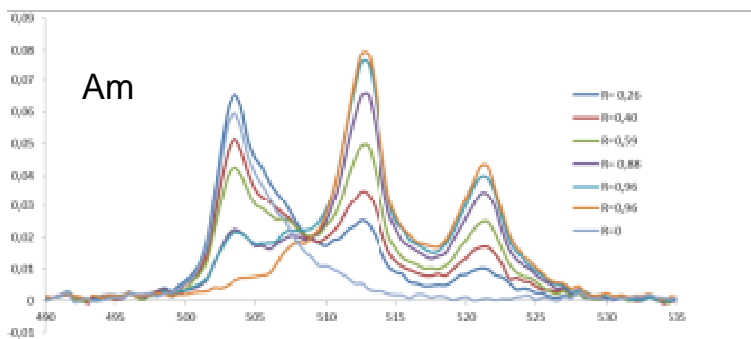
$\text{SF}_{\text{Ce/Am}}$   $\nearrow$  with Temperature

## Calorimetry



**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

$\log\beta$  (Am-TPAEN) =  $6.1 \pm 0.2$  at 25 ° C

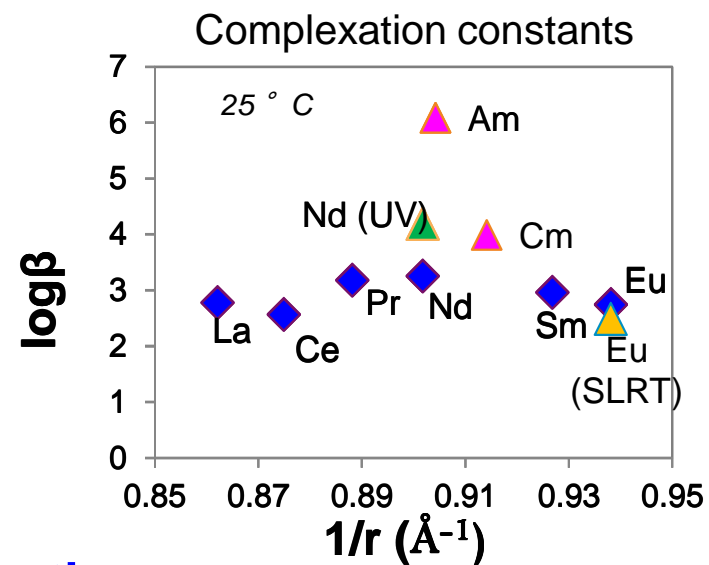
$\log\beta$  (Nd-TPAEN) =  $4.2 \pm 0.1$  at 25 ° C

## TRFLS

[Eu] =  $1 \cdot 10^{-3}M$  and [TPAEN] = 0 to  $1.17 \cdot 10^{-2}M$  matrice  $\text{HNO}_3$  0.1M

$\log\beta$  (Eu-TPAEN) = 2.5 at 25 ° C      2.4 (KIT)

Log $\beta$  (Cm-TPAEN) = 4.0 at RT      4.3 (KIT)



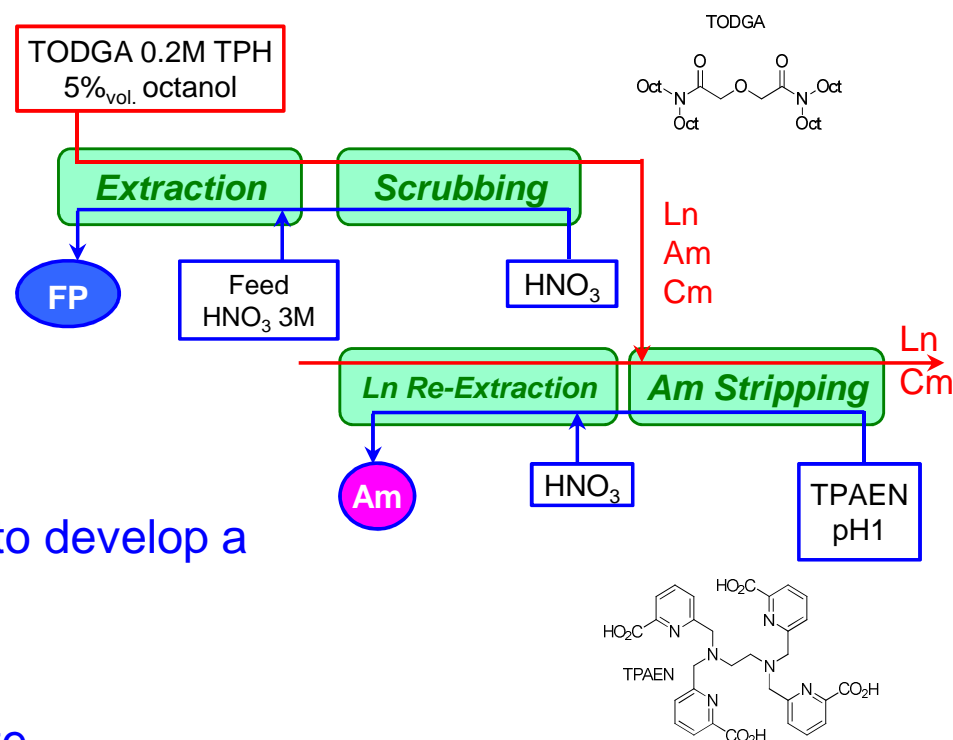
## EXAm Process

- Demonstration of the scientific feasibility of the sole Americium separation from a PUREX raffinate in 1-cycle
- Process adapted to a concentrated raffinate ( $\times 3$ ) 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

DE LA RECHERCHE A L'INDUSTRIE

cea den



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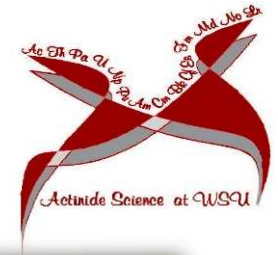
A. Casnati



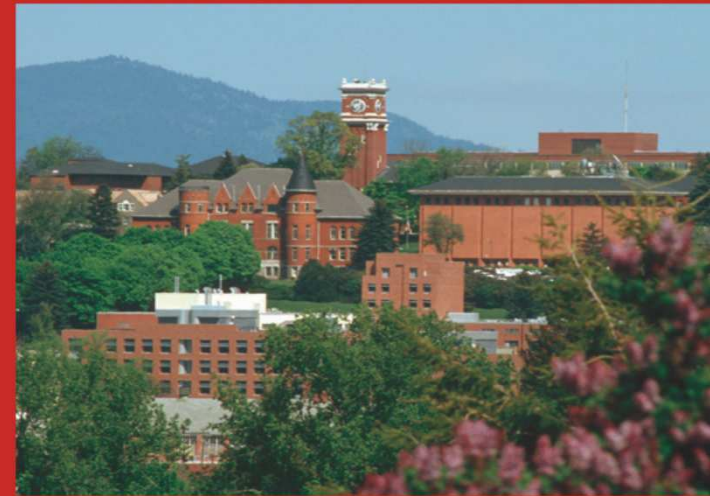
A. Geist



# Acknowledgments



Ken Nash group



**THANK YOU FOR YOUR  
ATTENTION !**



