

DE LA RECHERCHE À L'INDUSTRIE



IMPORTANCE OF THERMOCHEMISTRY IN THE DEVELOPMENT OF ACTINIDES EXTRACTION PROCESSES

ISMEC 2017, June 12th-15th, 2017

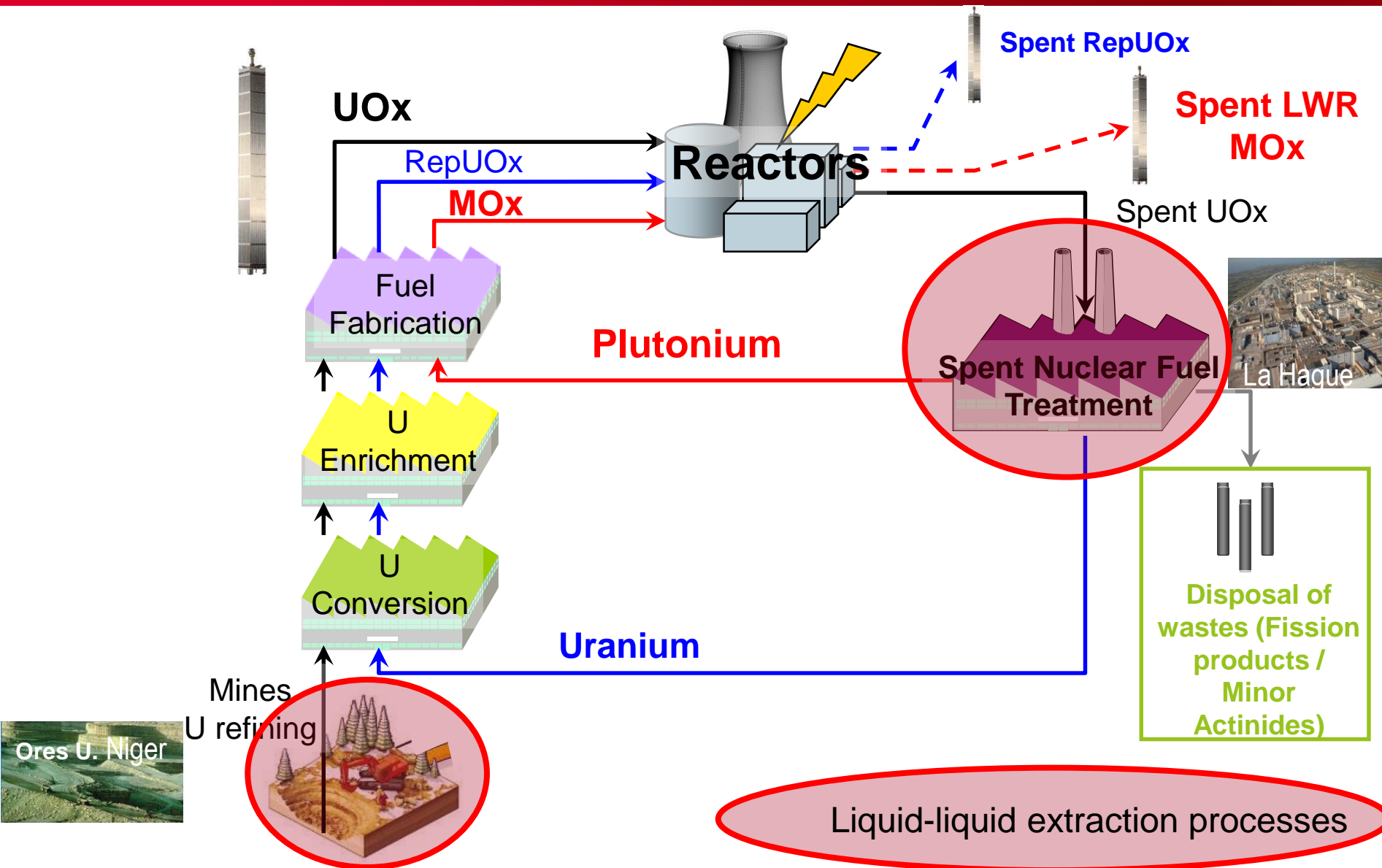
^a Marie-Christine Charbonnel, Nathalie Boubals, Olivia pecheur,
Dominique Guillaumont, Florian Rodrigues, C. Tamain, T. Dumas
Nuclear Energy Division/Resarch Department on Processes for
Mining and Fuel Recycling
Service of Dissolution and Separation processes

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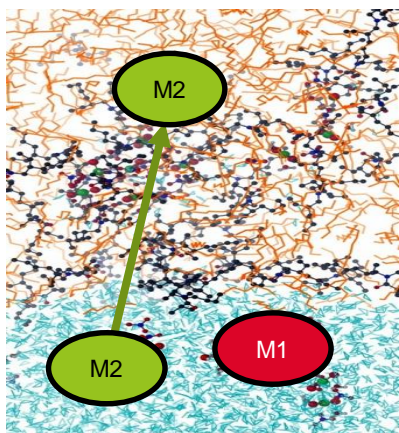
| PAGE 1

CURRENT NUCLEAR CLOSED FUEL CYCLE IN FRANCE



INTEREST OF LIQUID LIQUID EXTRACTION PROCESSES: SEPARATION AND PURIFICATION

One stage



$$D_M = \frac{c_M^{org}}{c_M^{aq}}$$

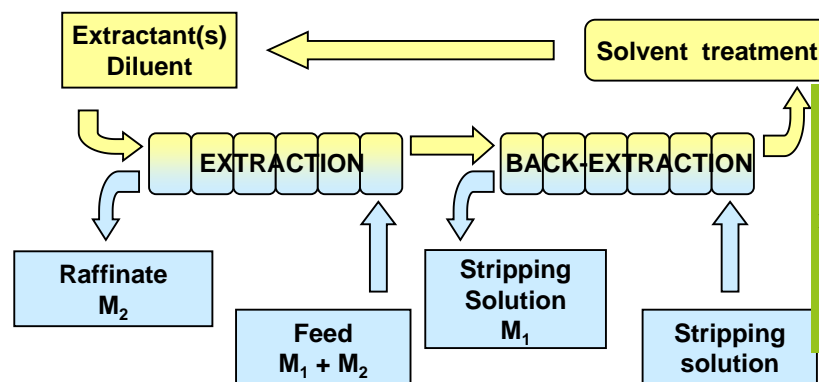
$$SF_{M/M'} = \frac{D_M}{D_{M'}}$$



Main advantages

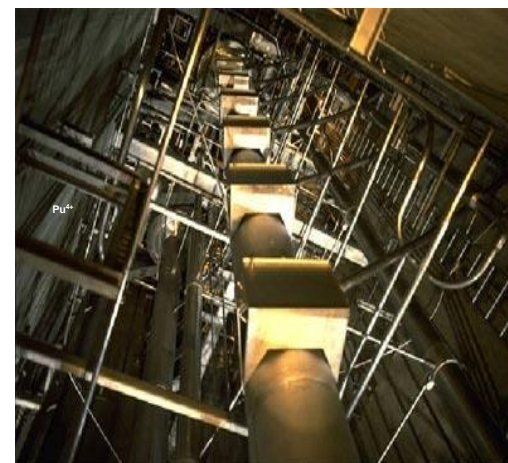
- Ability to operate in a continuous countercurrent mode,
- Multistage mode (to achieve high separation factors),
- High yield of recovery,
- Regeneration of solvent.

Process flow sheet



$$DF_M = \frac{\left(\frac{[impurity]}{[product]} \right)_{initial}}{\left(\frac{[impurity]}{[product]} \right)_{final}}$$

PUREX process

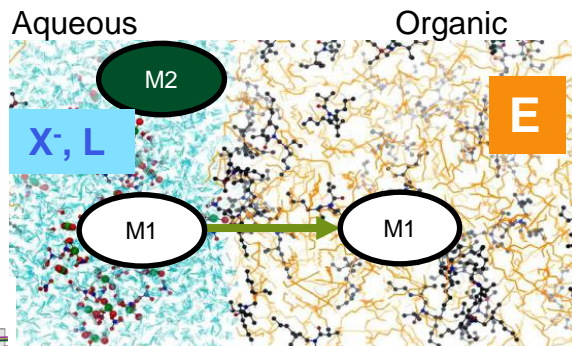
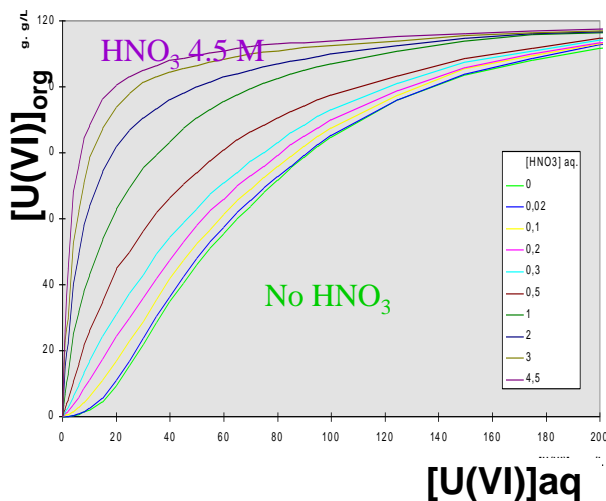


La Hague. Areva

➤ Performances of a process characterized by

Affinity

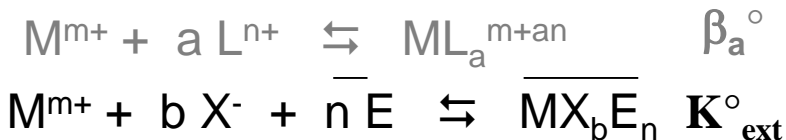
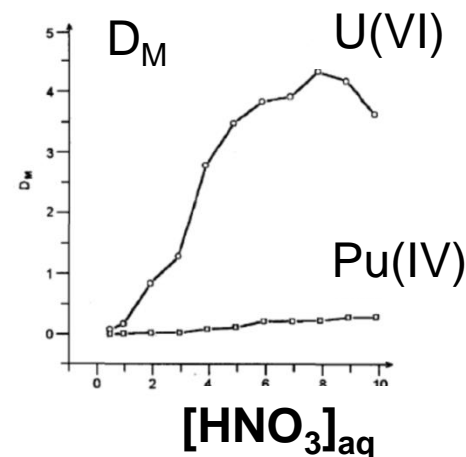
$$D_{M_1} = \frac{C_{M_1}^{org}}{C_{M_1}^{aq}}$$



Competition between complexation in aqueous phase and transfer into organic phase

Selectivity

$$SF_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}}$$



$$(\Delta_{ext} G^\circ)_M = f(K_{ext}^\circ M, \beta_a^\circ M)$$

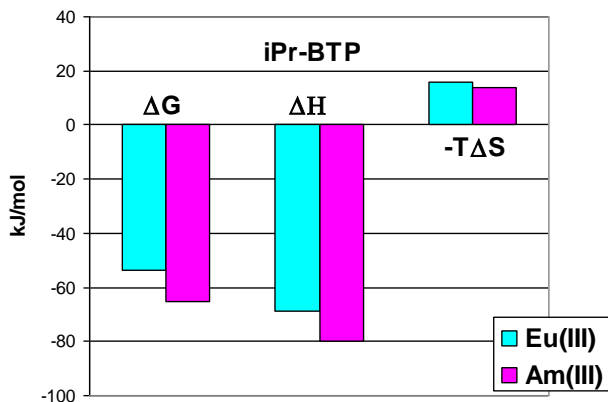
$$\Delta(\Delta_{ext} G^\circ)_{M_2/M_1} = (\Delta_{ext} G^\circ)_{M_2} - (\Delta_{ext} G^\circ)_{M_1}$$

$$= f(K_{ext}^\circ M_2, \beta_a^\circ M_2, K_{ext}^\circ M_1, \beta_a^\circ M_1)$$

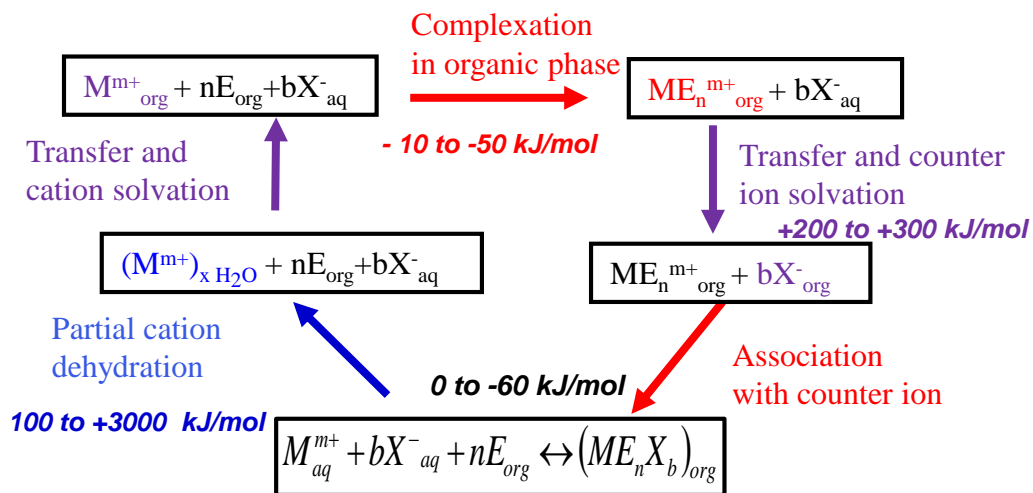
➤ Difficulty to predict the efficiency of the separation (affinity and selectivity)

□ Sum of contributions

Enthalpy/entropy



Binding / solvation / transfer



□ Global effect with low energy effects

$$SF_{M2/M1} = 100 \quad \Delta(\Delta_{\text{ext}} G)_{M2/M1} = -11.5 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1} \quad (-2.7 \text{ kcal}\cdot\text{mol}^{-1})$$

SPECIFICATIONS OF THE LIQUID-LIQUID SEPARATION

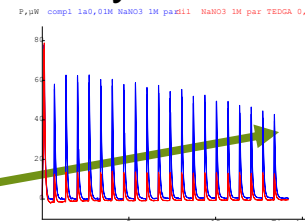
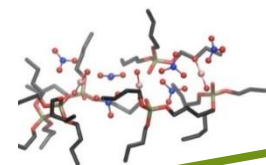
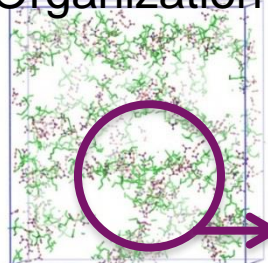
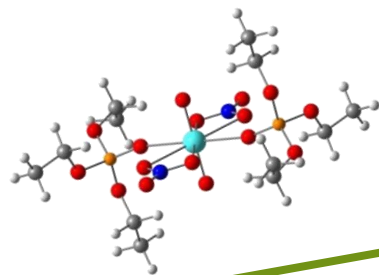
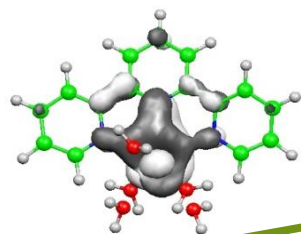
Understand the driven force of affinity and selectivity

Nature of bonds

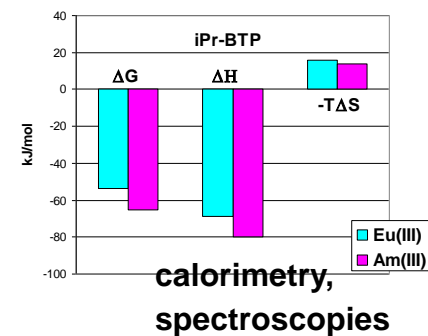
Speciation

Organization

Thermodynamics



From atomic scale to thermodynamics



DFT calculations

Spectroscopies (FTIR, UV-visible, NMR, TRLIFS, EXAFS, ESI-MS), calorimetry

Molecular dynamics SAXS, SANS, osmometry

calorimetry, spectroscopies

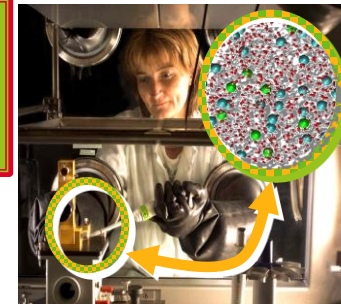
Classical approach in metal complexation chemistry but with high acidity and radioactive elements (not at trace levels): dedicated techniques connected with glove boxes

Selectivity between similar ions

An(III)/Ln(III) – Am(III)/Cm(III)

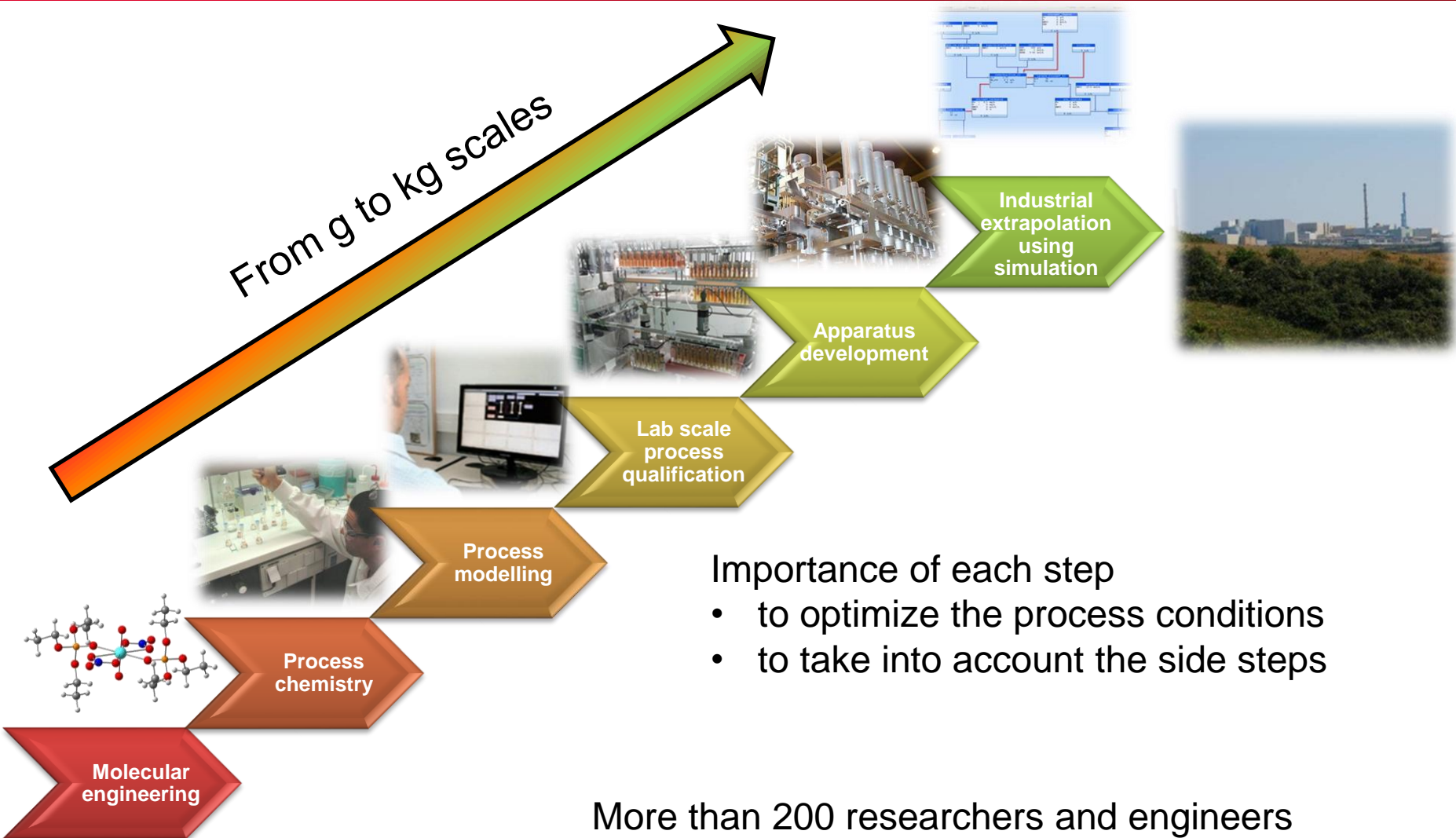
Selectivity between different ions (charge and/or size)

(U(VI)/Fission products, U(VI)/Fe(III), U(VI)/Pu(IV)



AN INTEGRATED APPROACH: THE KEY OF A SUCCESSFUL INDUSTRIAL SOLUTION

From g to kg scales



Importance of each step

- to optimize the process conditions
- to take into account the side steps

More than 200 researchers and engineers
at DMRC-Marcoule

MAIN STEPS WHERE SPECIATION AND THERMOCHEMISTRY IS IMPORTANT

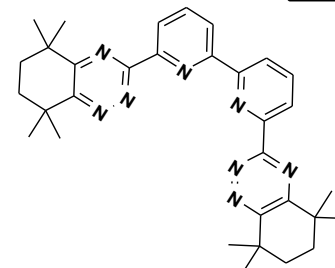
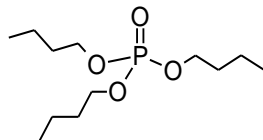
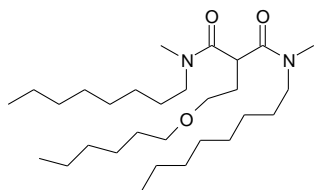
Molecular engineering

❑ Molecular design (organic extractants, aqueous complexants)

Fundamental knowledge of chemistry to design efficient molecules

- New ideas tested followed by comprehensive studies to describe the chemical system
- Establishment of structure-activity relations to propose new molecules

Speciation, $\Delta\Delta G$, $\Delta\Delta H$



Process chemistry

❑ Process chemistry and modelling

Provide speciation and thermodynamic data

Equilibria in homogeneous phases and between phases and related K , ΔH

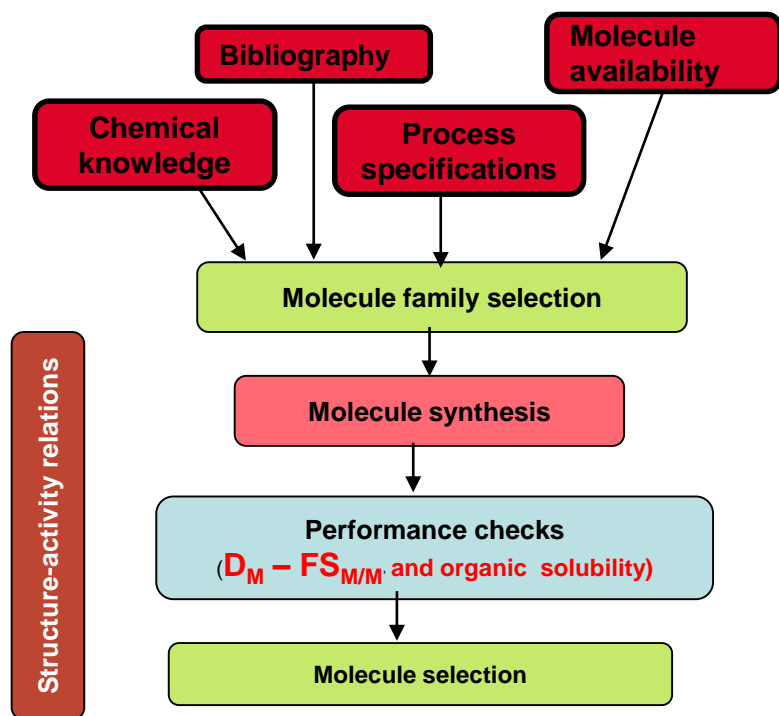
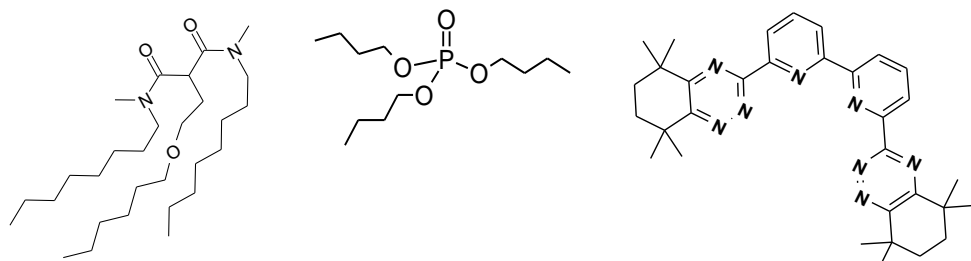
Process modelling

❑ Industrial operation

Non classical industrial behaviors (dysfonctionment, shift,...): comprehensive chemistry studies to give explanation and propose solutions

Speciation, stability constants

APPROACH TO DESIGN A NEW CHEMICAL SYSTEM



Performances

- High affinity towards the target element,
- Reversibility,
- High selectivity / other solutes and impurities

Effects of media

- Stability (hydrolysis in acidic media, oxydation....) and low influence of degradation products,
- Solubility of the extractant (low in the aqueous phase, high in the organic phase even in presence of the target element)

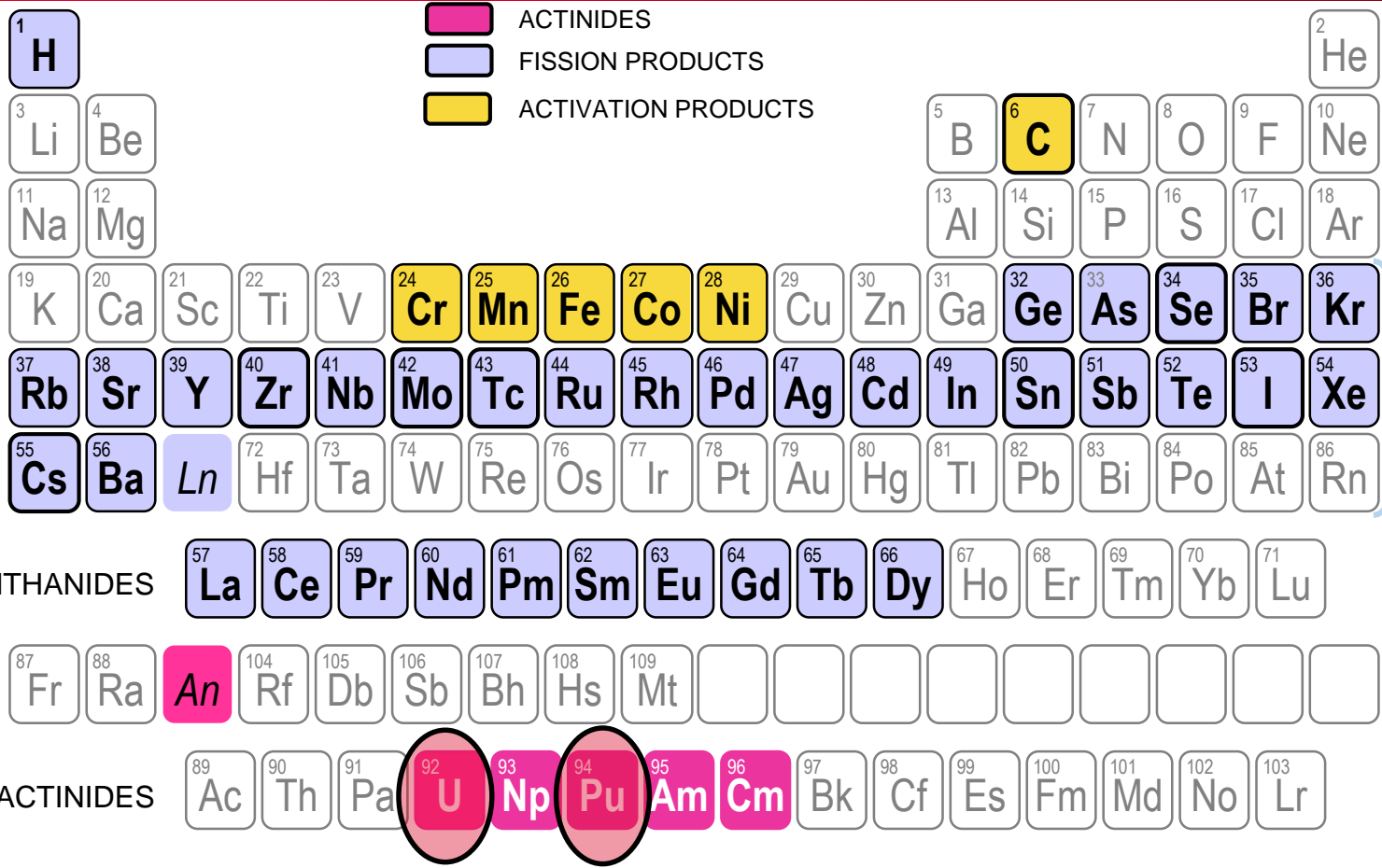
Industrialisation

- Kinetics of reactions and hydrodynamic properties (viscosity, densities, interfacial tensions....) compatible with industrial contactors,
- Cost of the reactants and synthesis,
- Chemical hazards and respect of REACH regulations

Environmental footprint

- Good recoverability of reactants,
- Incinerable reactants (CHON)

CHEMICAL ELEMENTS IN NUCLEAR SPENT FUELS



For 1 t of spent fuel
(standard fuel, irradiation : 3 years)



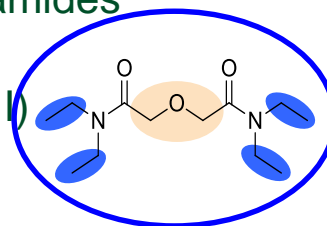
**PFs (without Ln):
24 kg**

**Lanthanides:
10.2 kg**

**U 955 kg
Pu 9.6 kg
Minors actinides 0.78 kg**

Molecular design

- Extraction of U(VI) from phosphate rocks
- Separation U/Pu for future plants by N,N-dialkylamides
- Hydrophilic diglycolamides to separate Am/Cm(III)



P08 N. Boubals

Process chemistry and modelling

- Kinetics data (extraction of U(VI) and Pu(IV) by N,N-dialkylamides)

OC31 A. Lelias

Industrial exploitation

- Impact of γ -irradiation on the palladium behavior in the PUREX process
- Speciation of ruthenium in the PUREX process with coupled spectroscopic techniques

P69 B. Simon

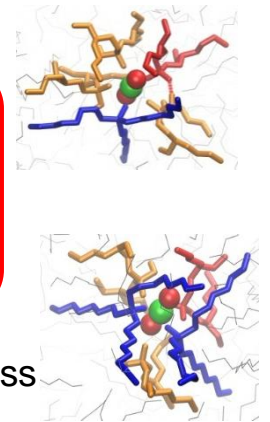
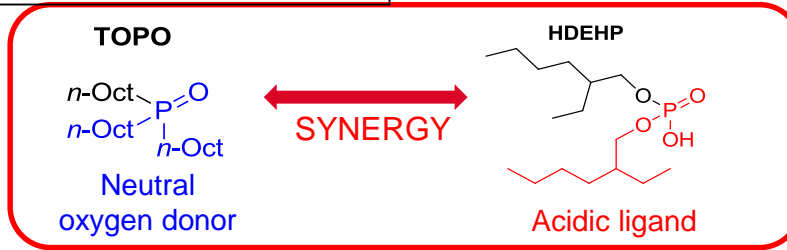
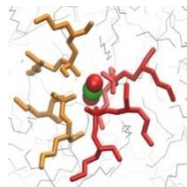
OC9 C. Lefebvre

EXAMPLE 1: OPTIMISATION OF URANIUM EXTRACTION FROM PHOSPHATES (1)

Context: Extraction of uranium from phosphates ores

Aim of the study: Research of new extractant system

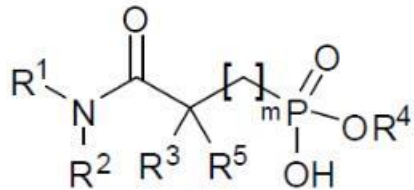
Reference system: synergistic mixture



Limitations due to

- affinity to U(VI) (not enough to improve the process compactness)
- affinity to Fe(III) slightly too high (insoluble cruds - U stripping)

Extracting moiety – Family of molecules

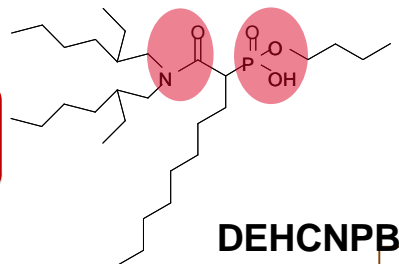


Bifunctional molecules: **Amido-phosphonates**

Molecules of interest

Synthesis of 10-12 molecules

Extracting system



Chemical system (in dodecane)	C (mol/L)	D _U	SF _{U/Fe}
TOPO + HDEHP (1:4)	0.1	0.8	200
DEHCNPB	0.1	70	8 700

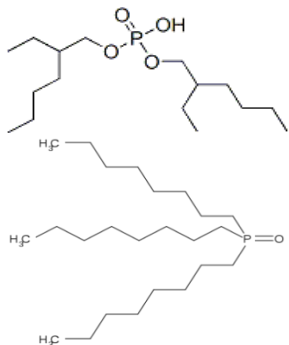
D_U x 20
SF_{U/Fe} x 35

R. Turgis et al. SX-IX, 2014 - R. Turgis et al., Procedia Eng., 2016
 Patent WO 2013/167516 A1 6/5/2013 (national) and 14/11/2013 (international)

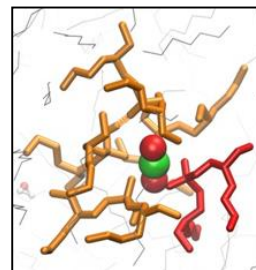
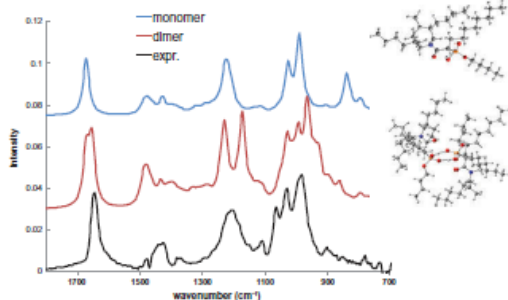
EXAMPLE 1: OPTIMISATION OF URANIUM EXTRACTION FROM PHOSPHATES (2)

- Comprehensive studies** to describe and understand the origin of higher performances uranium extraction (FTIR-EXAFS-DFT calculations-MD-SAXS-SANS)

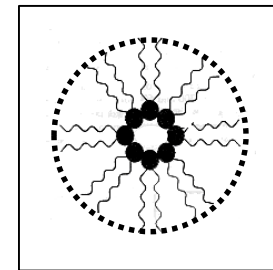
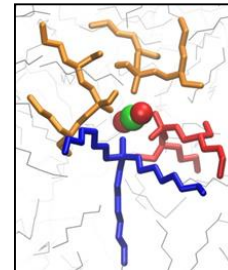
Synergistic system



Synergism with 4HDEHP-1TOPO



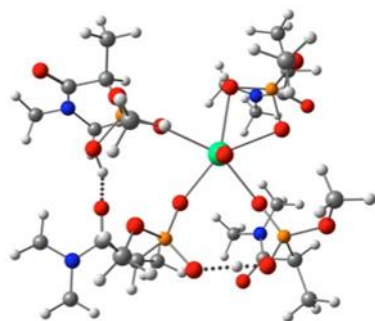
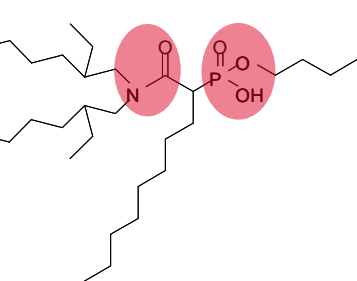
HDEHP; DEHP; TOPO



Numerous aggregates (from 2 to 6)

S. Dourdain, I. Hofmeister, O. Pecheur, et al. *Langmuir* (2012)
O. Pecheur, *Solv.Extr. Ion Exch.*(2016)
O. Pecheur et al., *J;Phys.Chem.* (2016)
O. Pecheur, PhD Montpellier (2014)

Bifunctional molecule

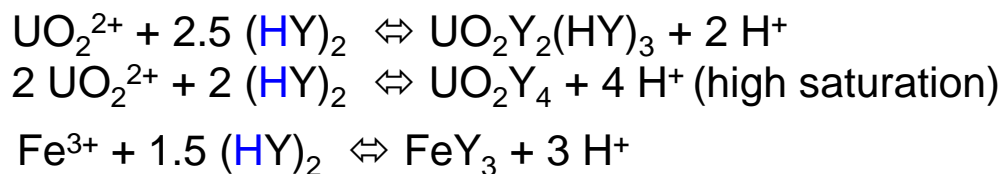


Best fit for EXAFS spectra

- 4 DEHCNPB **linked to U with P=O bonds**
- 1 DEHCNPB bidentate
- Coordination number : 5

Neutral fonction (N)CO (less basic) in the outer sphere

From slope analysis (batch experiments)

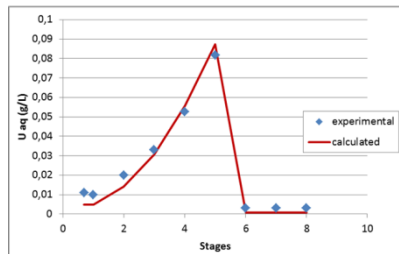
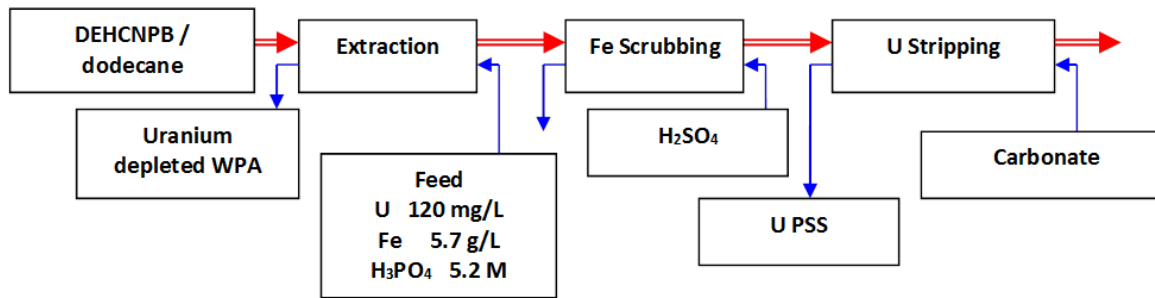


M. Miguiditchian, *Solv.Extr. Ion Exch.*(2016)

Complex	Log K	ΔH (kJ/mol)
UO ₂ Y ₂ (HY) ₃	8.22	-51.5
UO ₂ Y ₄	11.86	-51.5
FeY ₃	6.1	-49.4

EXAMPLE 1: OPTIMISATION OF URANIUM EXTRACTION FROM PHOSPHATES (3)

- Design of a flowsheet with 3 main steps tested on a genuine industrial phosphoric acid solution (Counter-current test runned in mixer-settlers)



good agreement between experimental and calculated concentrations profiles which validates the extraction model



Recovery of U > 91% (U losses (raffinate and recycled solvent) \leq 5 mg/L)

Concentration of U from 0.12 to 5.6 g/L

High DF of U from Fe and other impurities

Fe/U = 0.043% < ASTM specifications (0.15%)

- Increased efficiency of an industrial process obtained from molecular design
- The studies on speciation are in progress (diff. spectroscopic methods): with U, but mainly with Fe

EXAMPLE 2 – EXTRACTION OF U(VI) AND PU(IV) BY N,N-DI-ALKYLAMIDES (1)

Context: Pu multi-recycling (towards GEN(IV) fuel cycle)

Aim: Research of a new extracting system with high U/Pu selectivity

Litterature

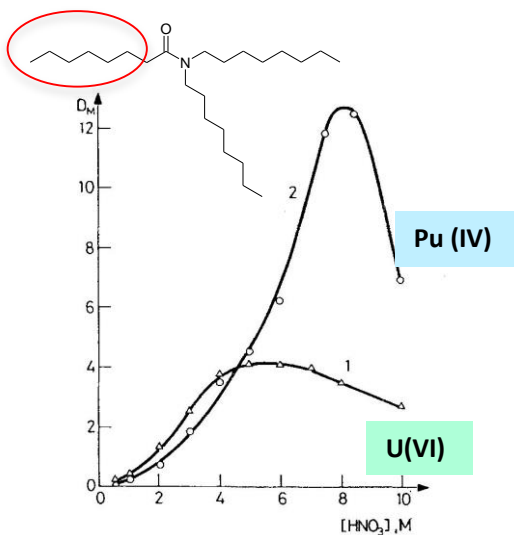
Database

Chemical
knowledge

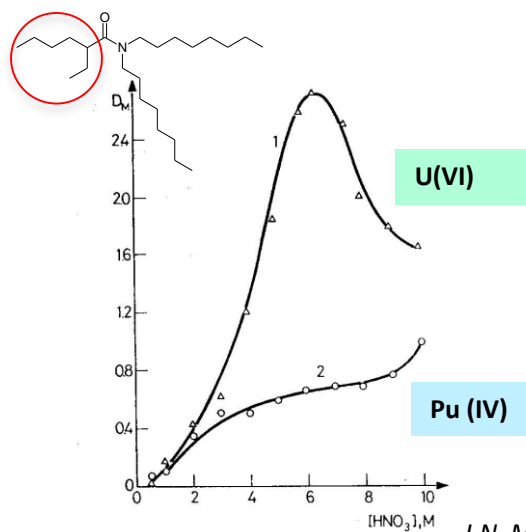
Process
specifications

Extracting moiety –
Family of molecules

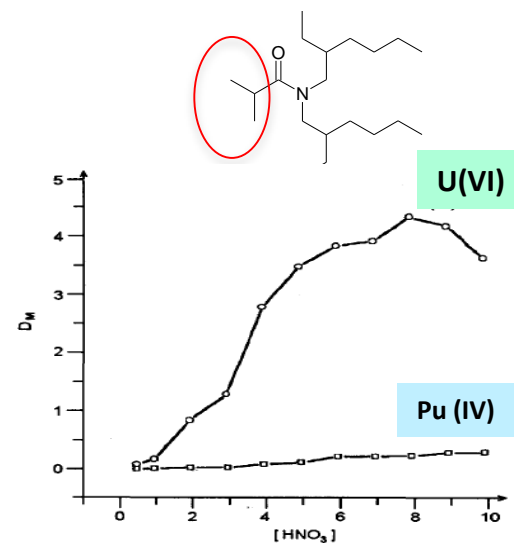
Family of N,N-dialkylamides



G.M. Nair et al., J.Radioanal.Nuc.Chem., 1995, 191. 323.



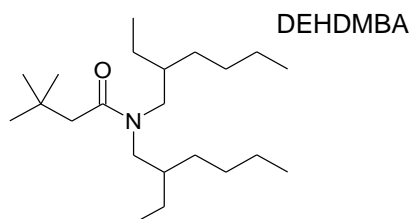
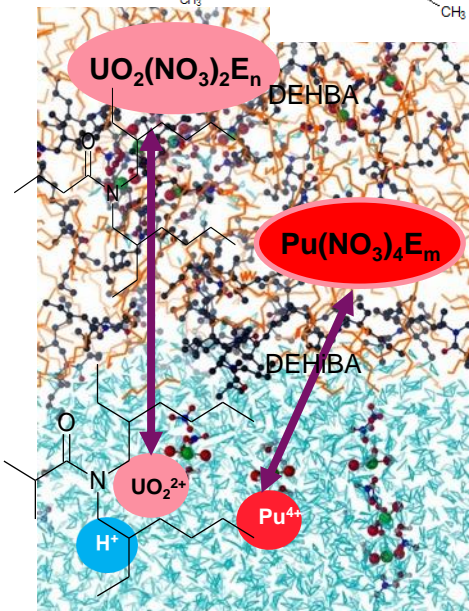
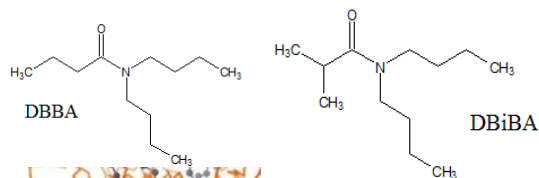
J.N. Mathur. J.N, Radiochim. Acta, 1996 and Prabhu, D.R. J. Inorg. Nucl. Chem., 1997



How explain the important effect of the alkyl chains on the selectivity U(VI)/Pu(IV)?

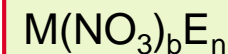
EXAMPLE 2 – NEW INVESTIGATIONS ON THE SELECTIVITY U(VI)-PU(IV)

Objective: Better knowledge about the influence of the ramification of alkyl chains



Speciation and structural information

- Geometry around the cation
 - Crystals (XRD)
 - In solution (EXAFS)
- Stoichiometry of complexes (ESI-MS, slope analysis)



Thermodynamic properties related to the extraction

Describe **the distribution** of a solute as a single net equilibrium and application of classical mass balance



$$D_M = \frac{c_M^{org}}{c_M^{aq}}$$

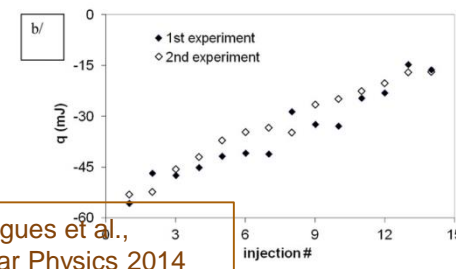
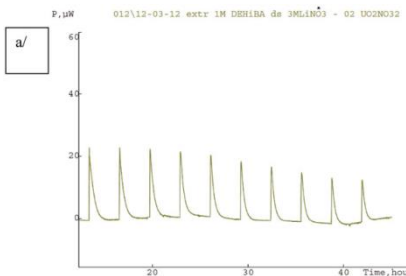
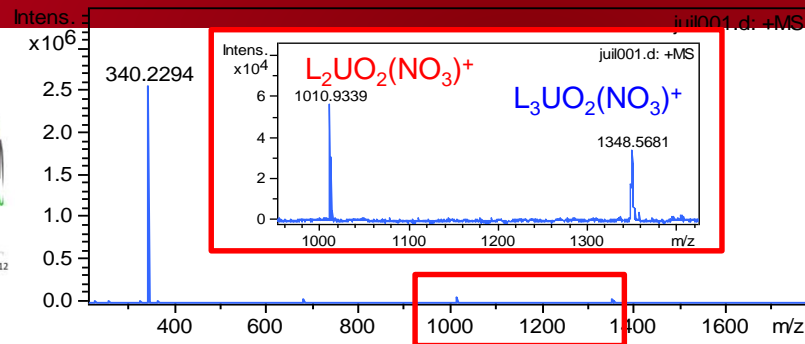
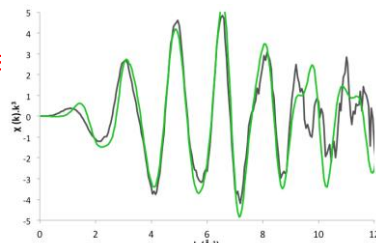
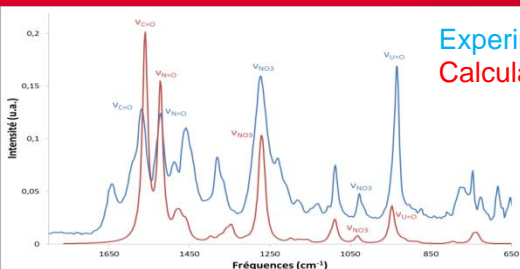
Stability constant

$$\Delta_{extr} X (G-H-S)$$

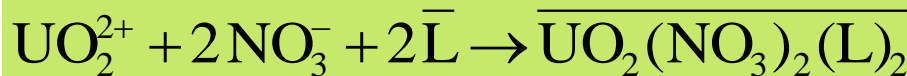
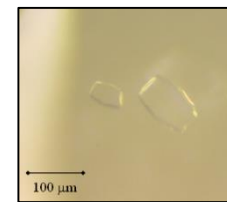
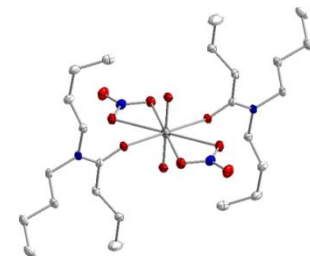
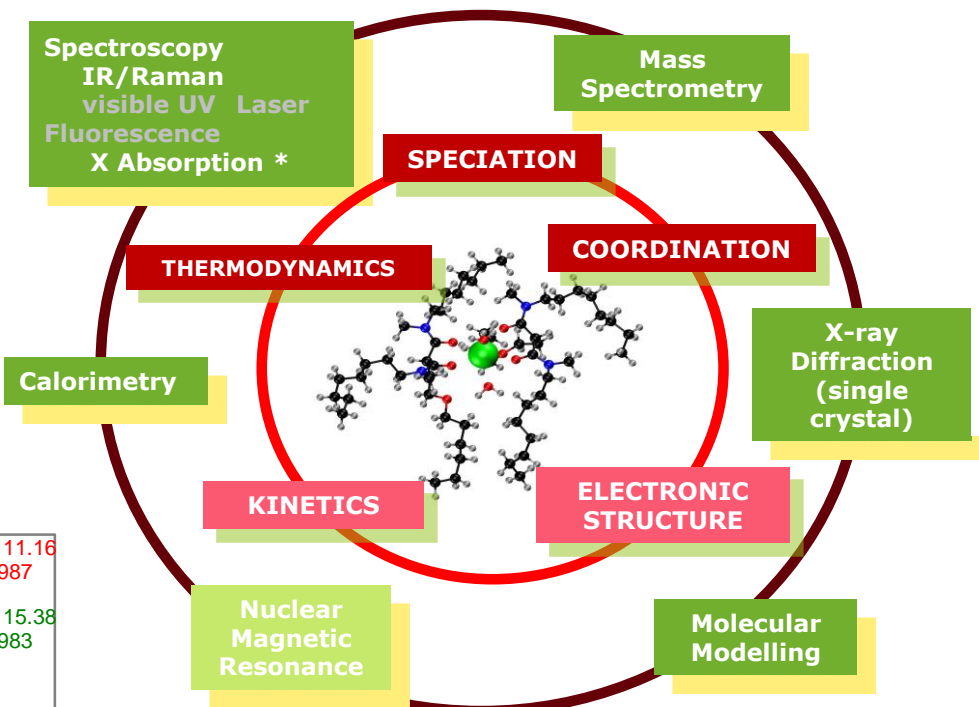
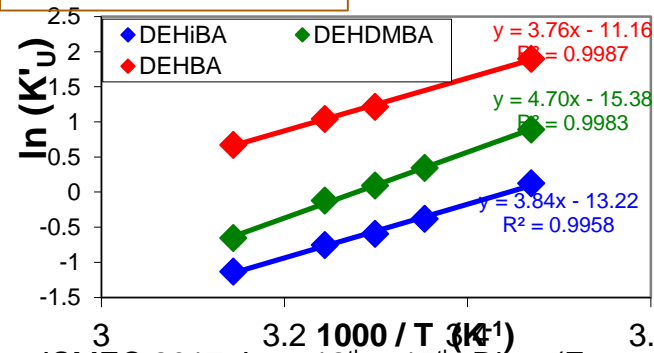
Ligand	DEHBA	DEHDMBA	DEHiBA
D_U	4.2	3.3	1.5
D_{Pu}	3.1	0.90	0.07
$SF_{U/Pu}$	0.7	3.6	20.7

$C_L=1\text{mol.l}^{-1}$ in dodecane- $[HNO_3] = 3\text{mol.l}^{-1}$

EXAMPLE 2 : MOLECULAR APPROACH TO DESCRIBE U(VI) EXTRACTION BY N,N-DIALKYLAMIDES

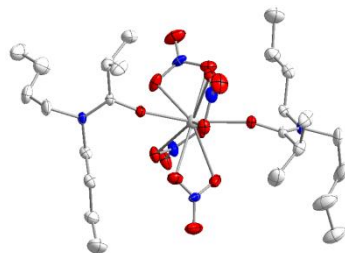
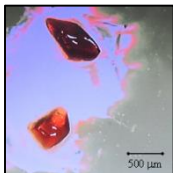
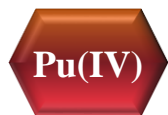


F. Rodrigues et al.,
Molecular Physics 2014



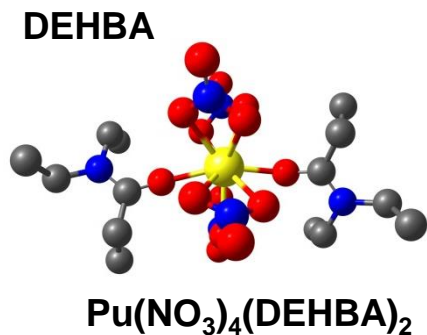
EXAMPLE 2 : MOLECULAR APPROACH TO DESCRIBE PU(IV) EXTRACTION BY N,N-DIALKYLAMIDES

Coordination (DRX, EXAFS, DFT)

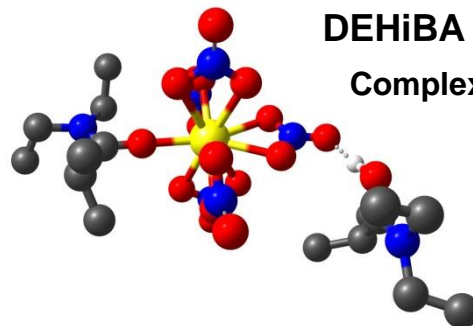


C. Tamain et al, 9th international conference on f-elements, Oxford, 6-9 Sept 2015

Coordination in solution (EXAFS, DFT)

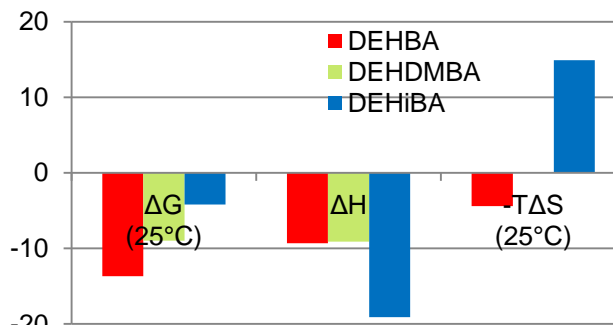
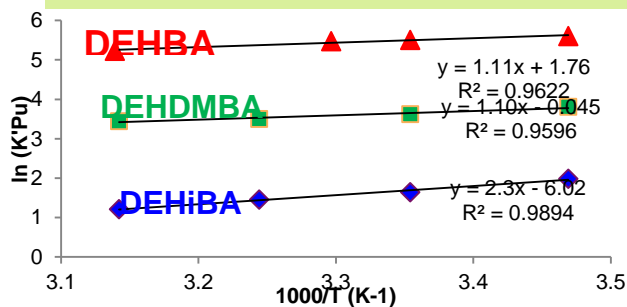


Ramification of the alkyle chain



E. Acher et al., Inorg. Chem., 2016, 55, 5558-5569

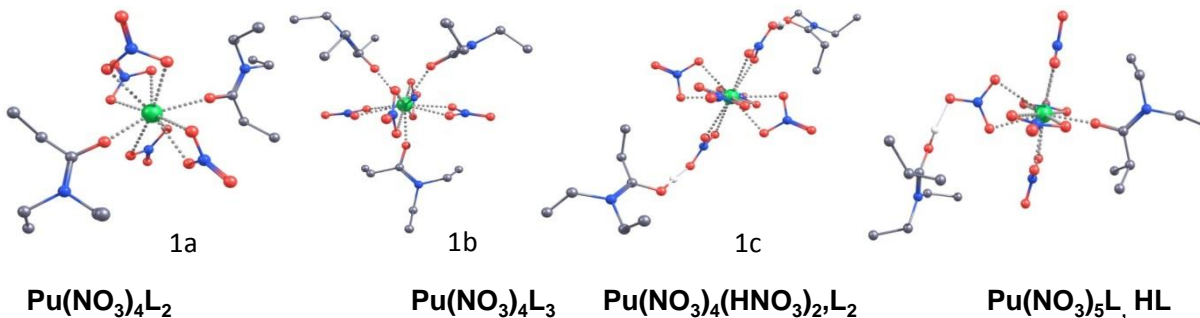
Extraction to the organic phase



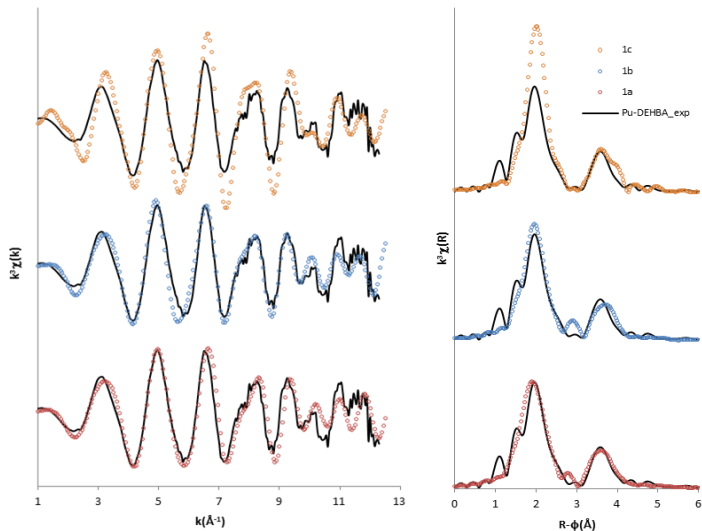
NATURE OF PU(IV)-AMIDES COMPLEXES IN SOLUTION (2)

EXAFS spectra
+ simulation with FEFF and
DFT (atomic positions)

Synchrotron SOLEIL, Saclay, Mars
Synchrotron ESRF, Grenoble, ROBL

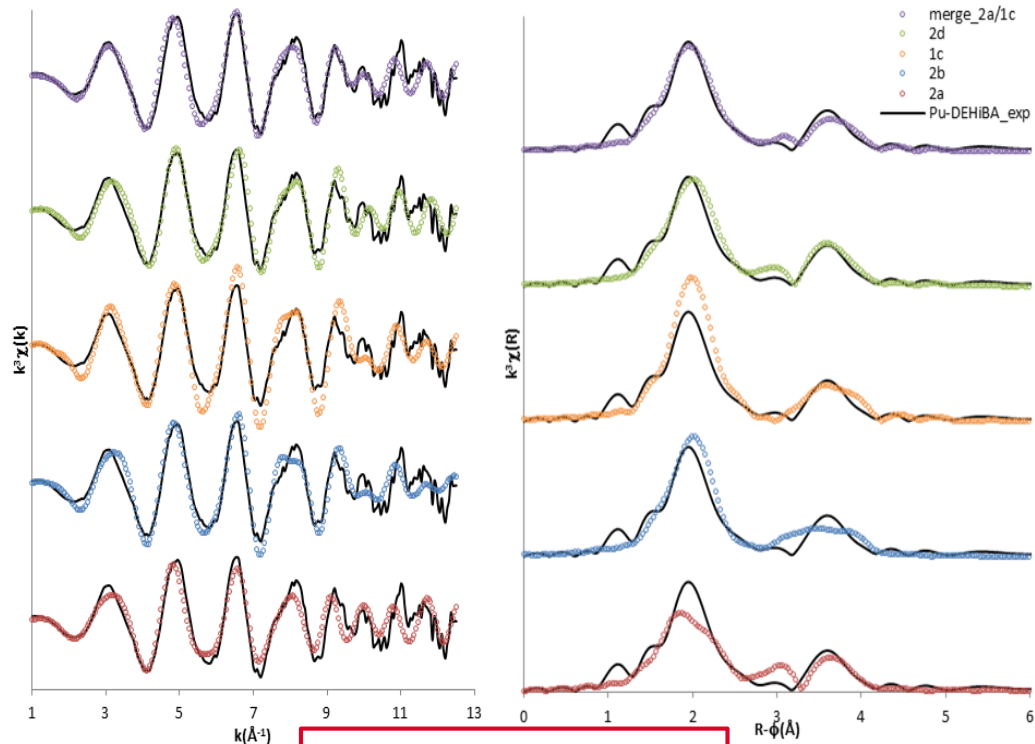


DEHBA



Experimental (Pu(IV) extracted from HNO_3
3M by amide 0.5M-dodecane)

Best fit: $\text{Pu}(\text{NO}_3)_4\text{L}_2$



Best fit: $\text{Pu}(\text{NO}_3)_5\text{L, HL}$

E. Acher et al., Inorg. Chem., 2016,
55, 5558-5569

❑ The development of liquid-liquid extraction processes is efficient

With a good modeling of extraction at each step: data base

Speciation: identification of complexes, coordination

Thermodynamic properties: equilibria, stability constants and related ΔG - ΔH - ΔS

❑ Improvement of the methodology to design new molecules in progress (objective: to reduce the number of synthesis)

Structure-activity relations with help of basic knowledge, speciation and thermodynamic properties ($\Delta\Delta G$ - $\Delta\Delta H$ - $\Delta\Delta S$)

Not obvious with radioelements **and** biphasic systems

Efficient methodology if combined with spectroscopic techniques and DFT calculations.

Detailed analysis to identify the driving force

$$1/ \Delta(\Delta_{\text{ext}} G^\circ)_{L2/L1} = \Delta(\Delta_{\text{dehydration}} G^\circ)_{L2/L1} + \Delta(\Delta_{\text{coordination}} G^\circ)_{L2/L1} + \Delta(\Delta_{\text{solvation}} G^\circ)_{L2/L1}$$

$$2/ \Delta(\Delta_{\text{ext}} G^\circ)_{Pu/U} = \Delta(\Delta_{\text{ext}} H^\circ)_{Pu/U} - T \Delta(\Delta_{\text{ext}} S^\circ)_{Pu/U}$$

PhD studies

O. Pecheur, B. Fries
F. Rodrigue, E. Acher

Calorimetry and thermodynamic
in solution

N. Boubals

EXAFS T. Dumas, P. Solari
(Mars synchrotron)

DRX C. Tamain

ESI-MS L. Berthon

DFT calculations D. Guillaumont
Molecular dynamics P. Guilbaud

Process development C.Sorel,
M. Miguirditchian

SAXS, SANS S. Dourdain
(ICSM)



Thank you for your attention



FROM RESEARCH TO INDUSTRY



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de Dissolution et de Séparation