

DE LA RECHERCHE À L'INDUSTRIE



# Innovative Coupled Hydrometallurgical and Pyrochemical Processes for Rare Earth Recycling

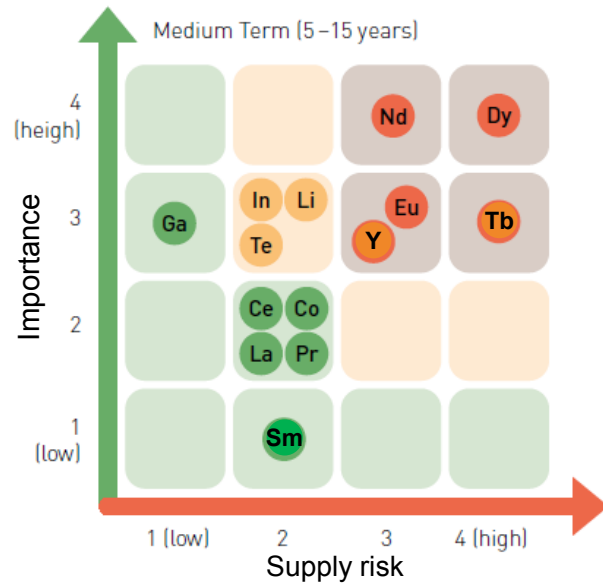
**E. Andreiadis, V. Blet, J. Serp, M. Miguirditchian**

*CEA, Atomic Energy and Alternative Energies Commission,  
Research Department on Mining and Fuel Recycling Processes,  
Marcoule, France*

*eugen.andreiadis @ cea.fr*

[www.cea.fr](http://www.cea.fr)





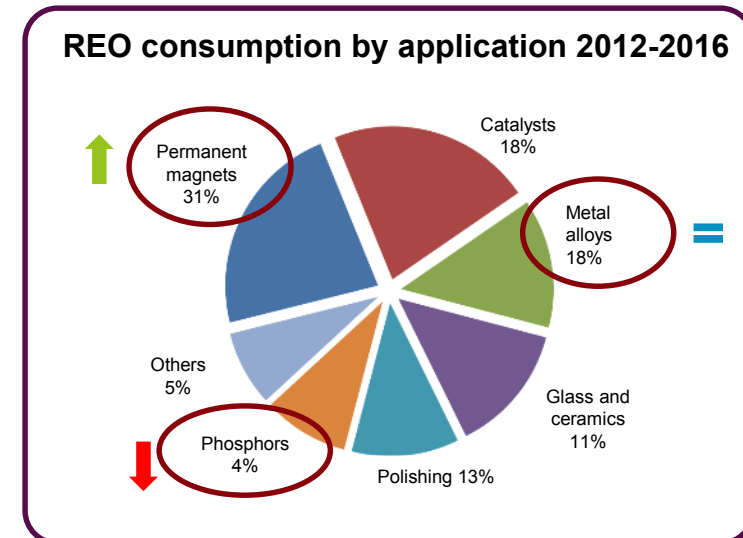
Source: report US Department of Energy 2010

## Rare earth elements are critical raw materials

- Demand growing, especially for magnets (> 7% per year for Nd)
- Accelerated growth of **HEV/EV market** (+30% in 2017)
- Global REO **production** in 2018 estimated at 175 kT/yr
- Production chain concentrated in China (mining, separation, downstream manufacturing, R&D capacity): **80% world REO supply**
- Currently **no European mine** in operation
- Significant **price volatility** during the last 10 years

## Possible solutions to decrease REE criticality

- **Reducing** consumption (shift in technology)
- **Substitution** by other non-critical metals
- **Diversifying** supply
  - Primary and secondary sources (new mines, tailings...)
  - **Recycling** (scraps, urban mine)



References: Roskill 2015, IMCOA 2017

## Advantages of recycling

- Target only the **most critical** rare earths
- No issues with **radioactive elements** (235U, 238U, 232Th)
- Lower environmental footprint (**public acceptance**)



500 kg Nd/MW in the magnet of a wind turbine

## Challenges

- Insufficient and untargeted **collection** of waste sources
- Difficult recovery of REE-containing fractions
- Difficult **separation of individual REE**
- No **regulatory incentives** for recycling WEEE
- **Low economic interest** in line with current market prices

Very low recycling rates  
6-7% in EU

Source: EU 2018 Report on CRM

## Opportunities

- Competences and expertise of the **European recycling industry**
- Leveraging on the **urban mine**
- **Development of a circular economy**
- Positive economic and environmental **impact**



## Recovering REE from NdFeB magnets and Ni-MH batteries

- **Magnets** are the most important REE application
- **Battery** recycling is regulated + immediate **availability**

# Flowchart for REE recovery from NdFeB magnets



High REE concentration  
(25% Nd, 5% Pr, 2-8% Dy)

Magnet scraps

EoL magnets



Thermal treatment  
H<sub>2</sub> decrepitation  
Mechanical treatment

Leaching

Selective precipitation

Fe(OH)<sub>3</sub>

REO mixed concentrate

R. Laucournet (CEA/DRT)  
Patent WO2014/06459

REE separation by solvent extraction

Fe + impurities

Dy

Nd+Pr

Recovery > 99%  
Purity > 99.5%



REO conversion

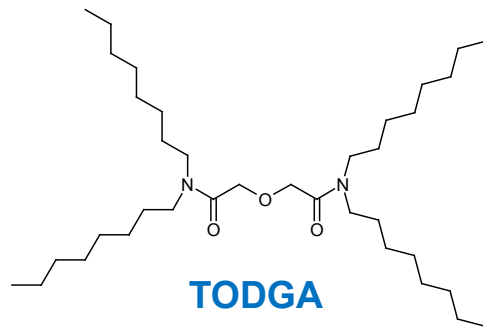
REE conversion to metal



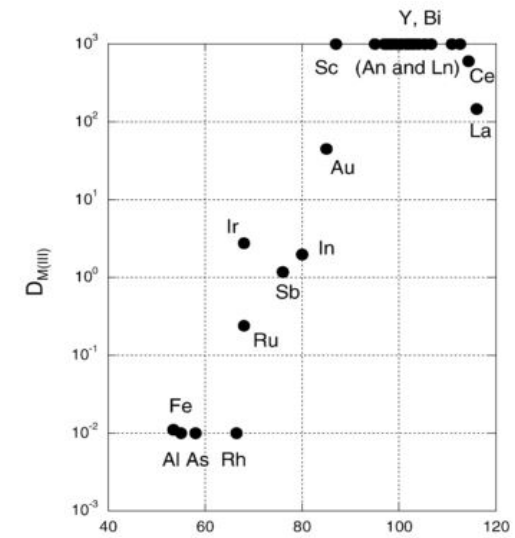
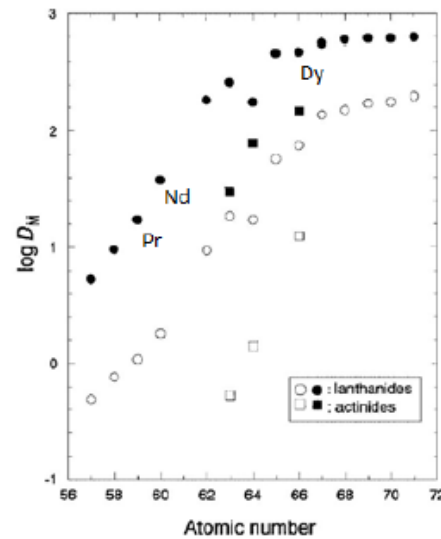
M. Miguiriditchian (CEA/DEN)  
Patent WO2016046179

# Selection and evaluation of the extractant system

- Challenge: excellent affinity and selectivity for REE in the presence of  $\text{Fe}^{3+}$
- Screening of several commercially-available extracting molecules
- Selection of **diglycolamides** (TODGA) class of solvating extractants



Sasaki et al, 2002



- Extraction capacity inversely proportional to  $\text{RE}^{3+}$  ionic radius
- Excellent extraction of heavy RE (Dy) and good intra-REE separation factor in nitric acid media
- Excellent selectivity with respect to boron and transition metals ( $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ )

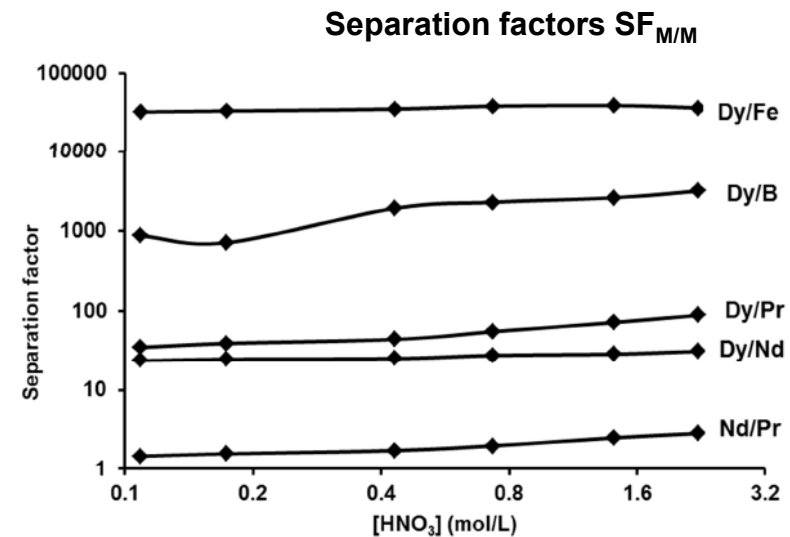
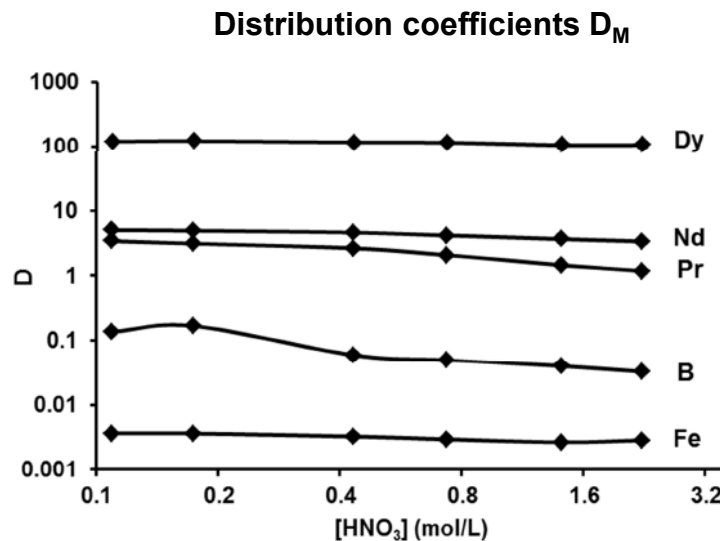
- Tests on synthetic and genuine magnet solutions in nitric acid
- **Quantitative extraction** of Dy ( $D > 100$ )
- **Efficient separation of RE** / transition metals (Fe, Co, Ni...) and RE/RE in a large range of acidity (0.4 to 5 M)
- **No 3<sup>rd</sup> phase** formation in process conditions
- **Quantitative stripping of Nd and Dy** at low acidity (pH 2-3)

Solvent formulation:

0.2 M TODGA + 5% octanol / HTP

Synthetic aqueous solution composition:

Elément	B	Fe	Co	Ni	Cu	Pr	Nd	Dy
g/l	0.5	35	0.2	0.8	0.5	3.1	12.5	0.3



- **Confirmation** of the potential of TODGA for selective Dy recovery from NdFeB magnet solutions

- Elaboration of a phenomenological model from experimental batch data

- Representation of distribution equilibria

HNO<sub>3</sub>-Oct, HNO<sub>3</sub>-TODGA, Ln-NO<sub>3</sub>-TODGA

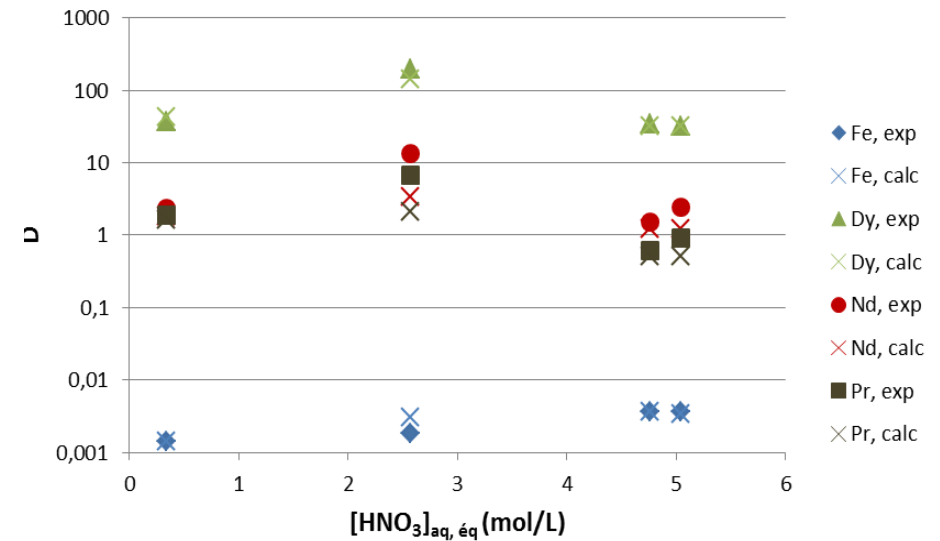
- (HNO<sub>3</sub>)(octanol)<sub>2</sub>
- (HNO<sub>3</sub>)<sub>m</sub>(TODGA) with m = 1 to 3
- M(NO<sub>3</sub>)<sub>3</sub>(TODGA)<sub>n</sub> with n = 3 for Dy, Nd, Pr, Fe

$$K'_n = \frac{[TR(NO_3)_3, TODGA_n]}{\gamma_{TR(NO_3)_3} \cdot [TR(NO_3)_3] \cdot [TODGA]^n}$$

- Activity coefficients taken into account in aqueous phase

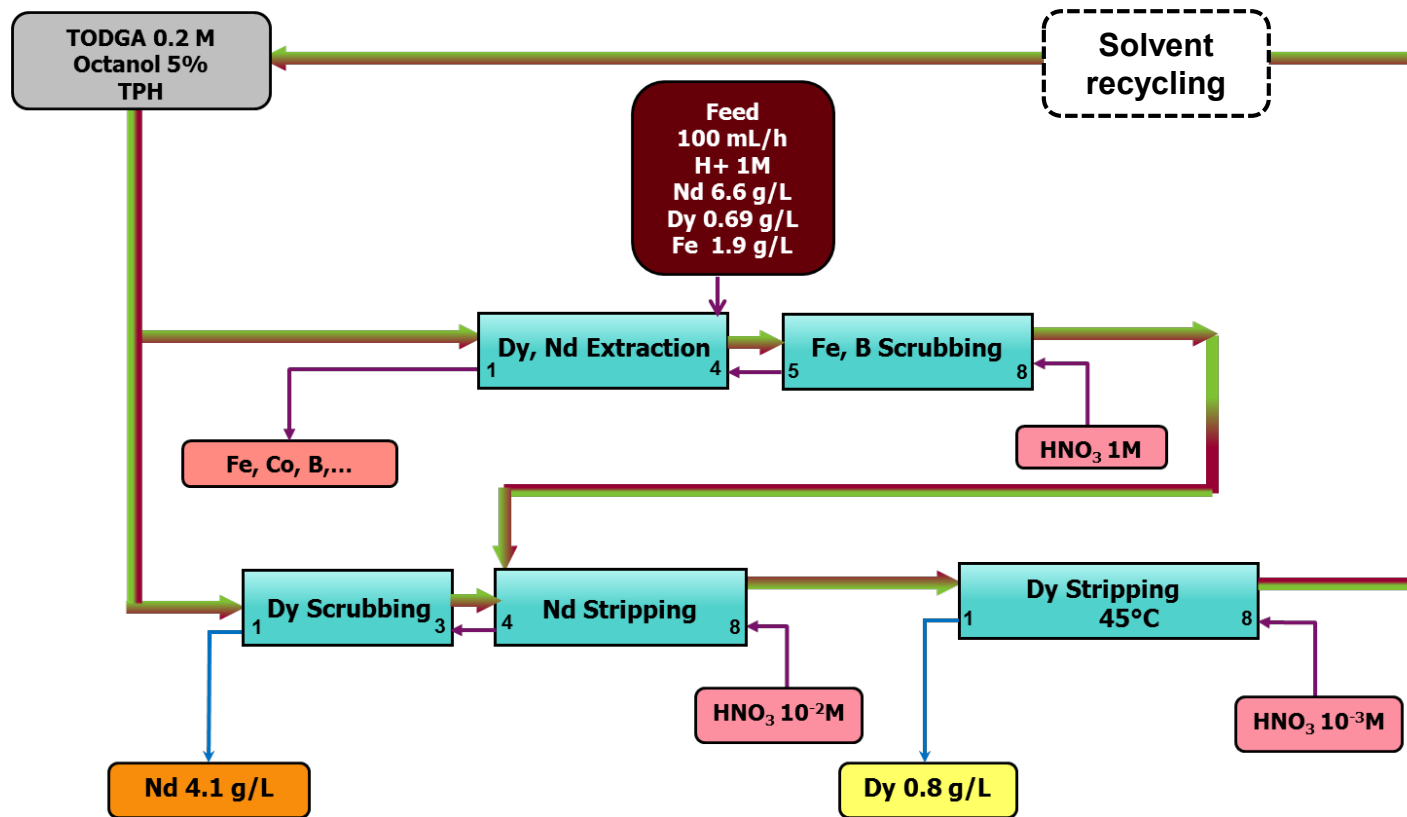
- **Good agreement** between extraction experiments and calculated values for both synthetic and real solutions

- Implementation of the model in the **CEA PAREX simulation code** and calculation of flowsheets



## ➤ Pilot test n°1

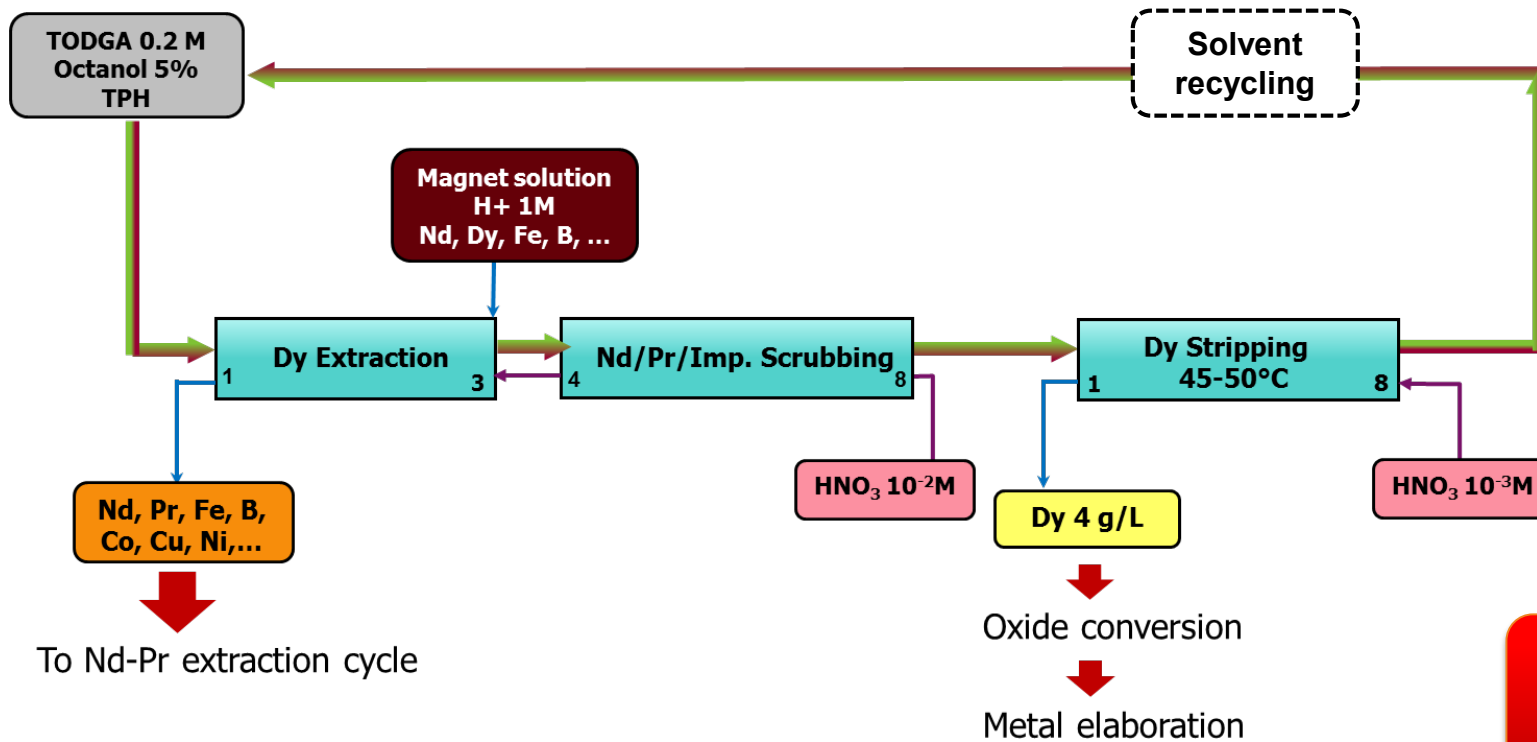
- Selective extraction of all REE followed by Dy/Nd partitioning
- Compact 24-stage lab-scale mixer-settler setup at 100 mL/h



- Test runned for 32 h
- Very good hydrodynamic behavior
- UV-vis on-line analysis (for Nd) and ICP-AES measurements for Dy, Nd, Fe
- **Excellent recovery of REE** with very high purity
  - Nd+Pr recovery > 99.98% with purity > 99.99%
  - Dy recovery 96.7% with purity 99.96%

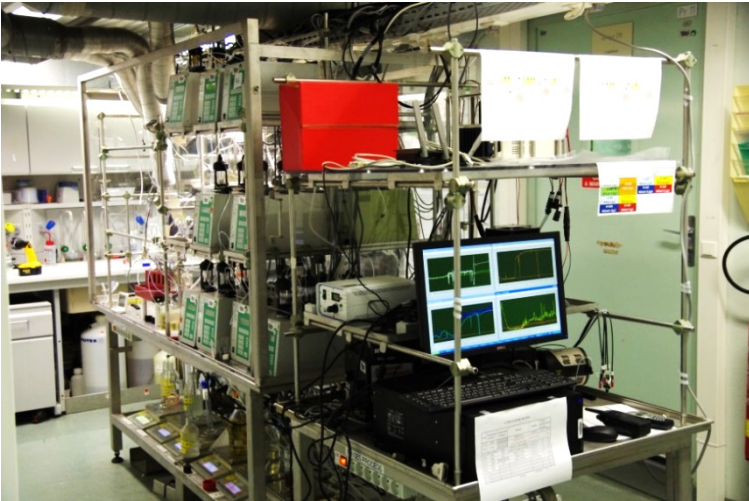
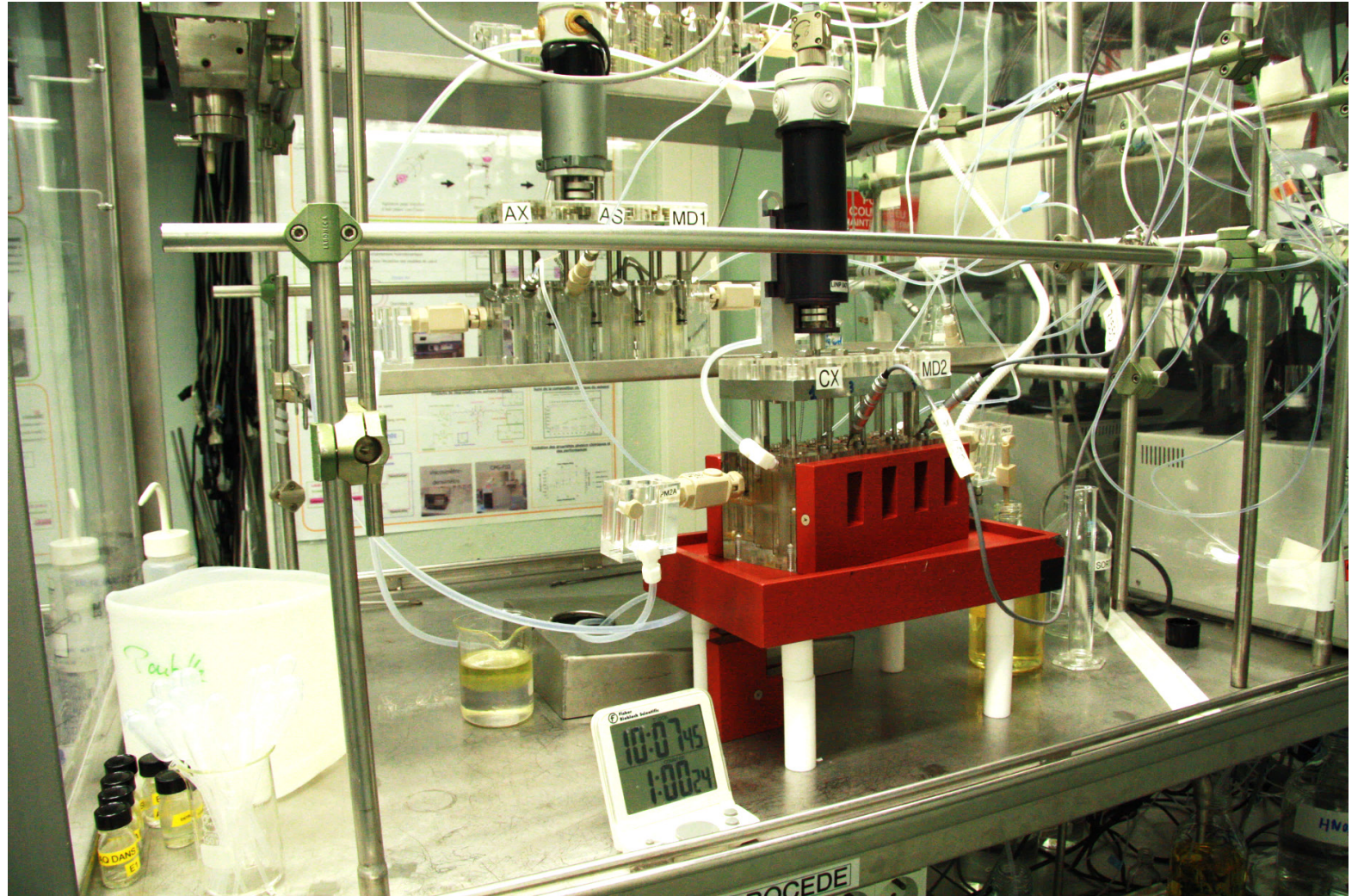
## ➤ Pilot test n°2

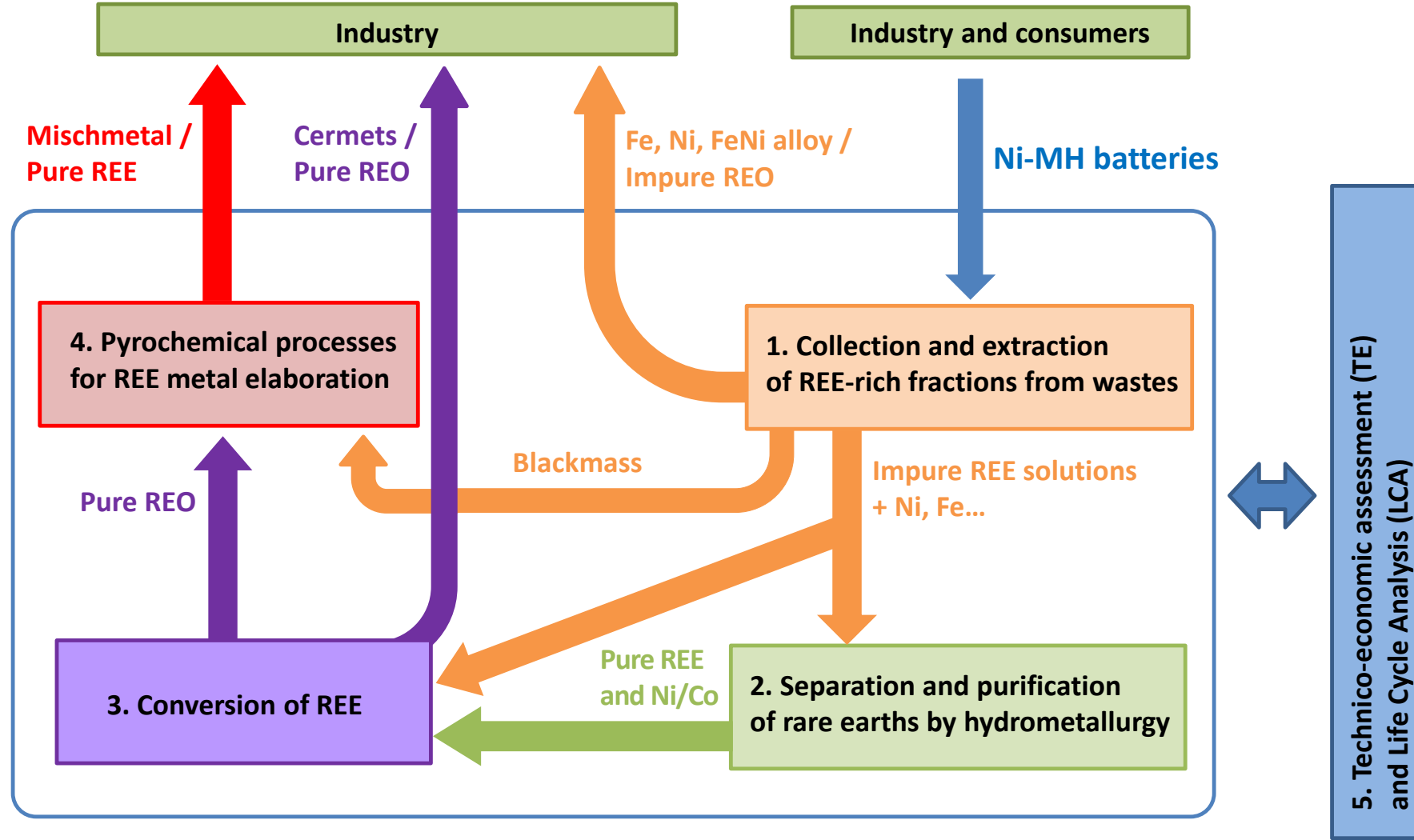
- Selective extraction of only Dy followed by stripping
- Nd & Pr collected in the raffinate for further 2<sup>nd</sup> cycle process
- Compact 16-stage lab-scale mixer-settler setup at 200 mL/h



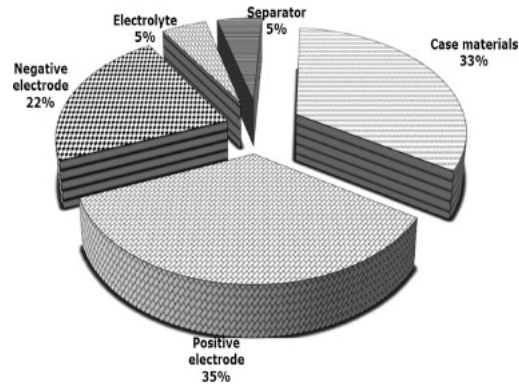
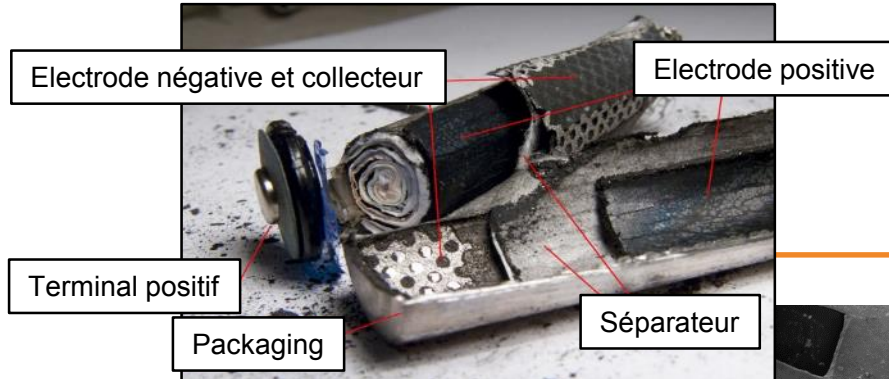
- Test runned for 20 h
- Very good hydrodynamic behavior
- UV-vis on-line analysis (for Nd) and ICP-AES measurements for Dy, Nd, Fe
- ➔ **Excellent recovery of Dy (99.7%)** with very high purity
- Upgrade Dy from 0.69 to 4.05 g/L (×6)

Validation of hydrometallurgical process flowsheets at TRL 5 level

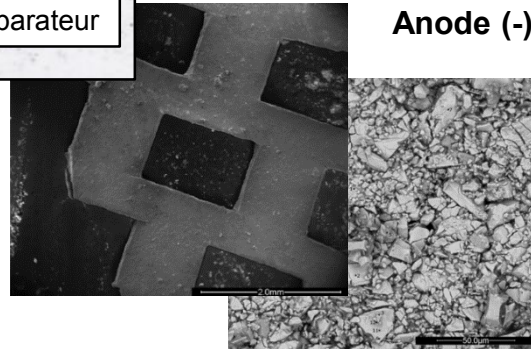




# Ni-MH battery composition

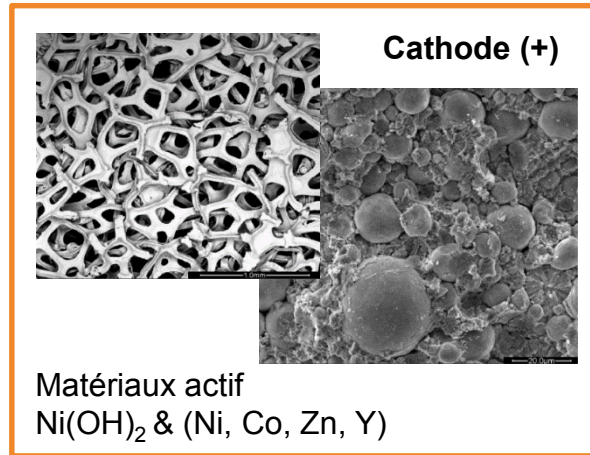
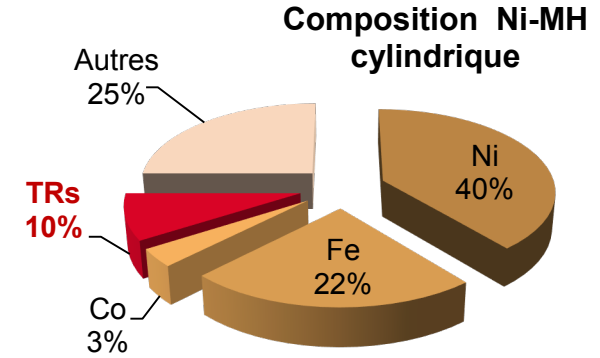
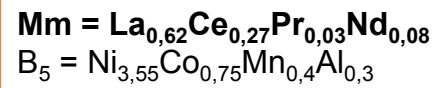


Al-Thyabat, Minerals Engineering 2013



Anode (-)

Matériaux actif  
 $MmB_5$  & ( $Y_2O_3$ ,  $Yb_2O_3$ , liants)

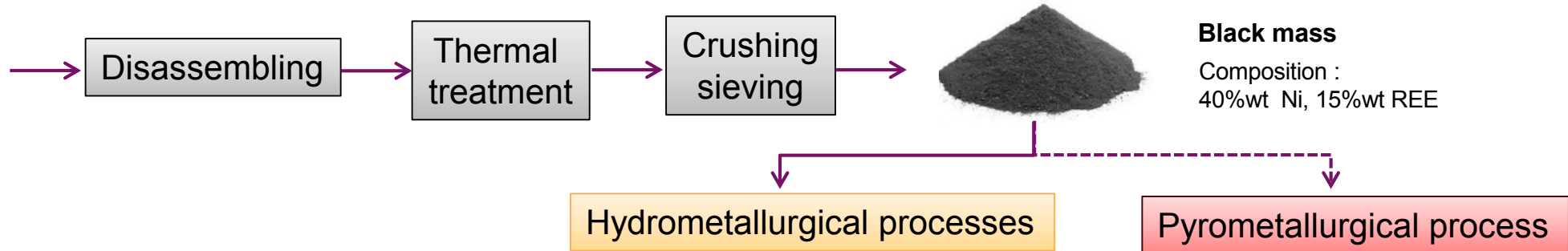


Cathode (+)

Matériaux actif  
 $Ni(OH)_2$  & (Ni, Co, Zn, Y)

## ➤ Physical and mechanical treatment of batteries

- Adapting an existing NiMH recycling process for the recovery of RE-rich fractions
- Production of a 10 kg final sample



## ➤ Hydrometallurgical treatment of the black mass

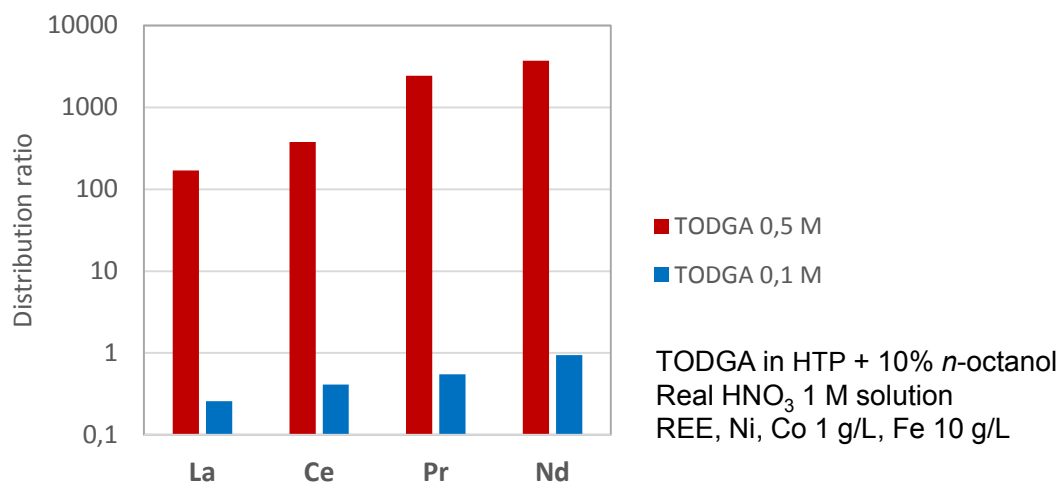
- Choice of acids and leaching conditions compatible with an industrial approach
- Total digestion (REE + Ni, Co...)
  - Excellent yield for HNO<sub>3</sub> and HCl acid solutions at controlled pH
- Selective leaching (only Ni, Co...)
  - Precipitation of REE in sulfuric acid solution
  - Redissolution of sulfate precipitates and further conversion

**Lixiviation solution composition (g/L)**  
HNO<sub>3</sub> 1 M (pH = 0), rt, S/L = 10%

La	4.6
Ce	7.7
Pr	0.5
Nd	2.0
Ni	40.0
Co	5.2
Mn	2.1
Fe	3.3

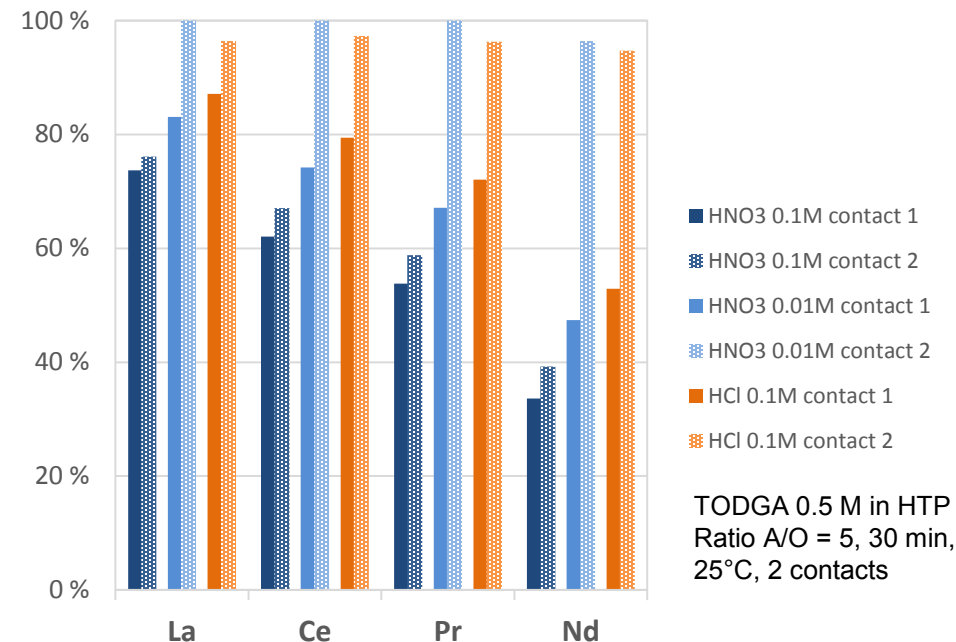
- Choice of TODGA extractant for selective REE extraction
- Tests on simulated and real solutions in HNO<sub>3</sub> and HCl media
- Optimisation of extraction and stripping conditions

## REE extraction function of TODGA concentration



- Excellent extraction of light REE upon increasing TODGA concentration
- Very high selectivity (Ni, Co, Mn, Fe not extracted)
- Very high REE purity in the extract >99% (after 1 contact, before scrubbing and stripping)

## REE stripping efficiency

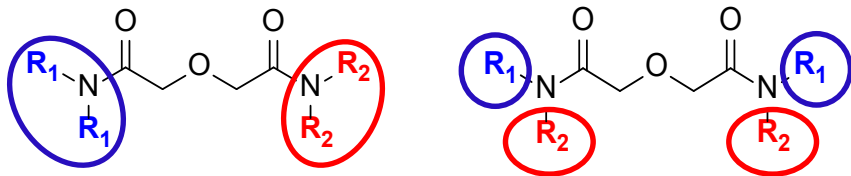


- Near-quantitative stripping of REE in 2 contacts with dilute acid at rt (HNO<sub>3</sub> 0.01M or HCl 0.1M)
- Flowsheet calculation for the recovery of a purified mixed-REE solution in progress...

## Increase the amphiphilic character

- Short (hydrophilic) alkyl chains:  $R_1$
- Long (lipophilic) alkyl chains:  $R_2$

- Improving the extraction of light REE
- Increasing the selectivity towards transition metals (e.g. Fe, Ni)
- Improving the REE extraction in sulfuric and hydrochloric acid media

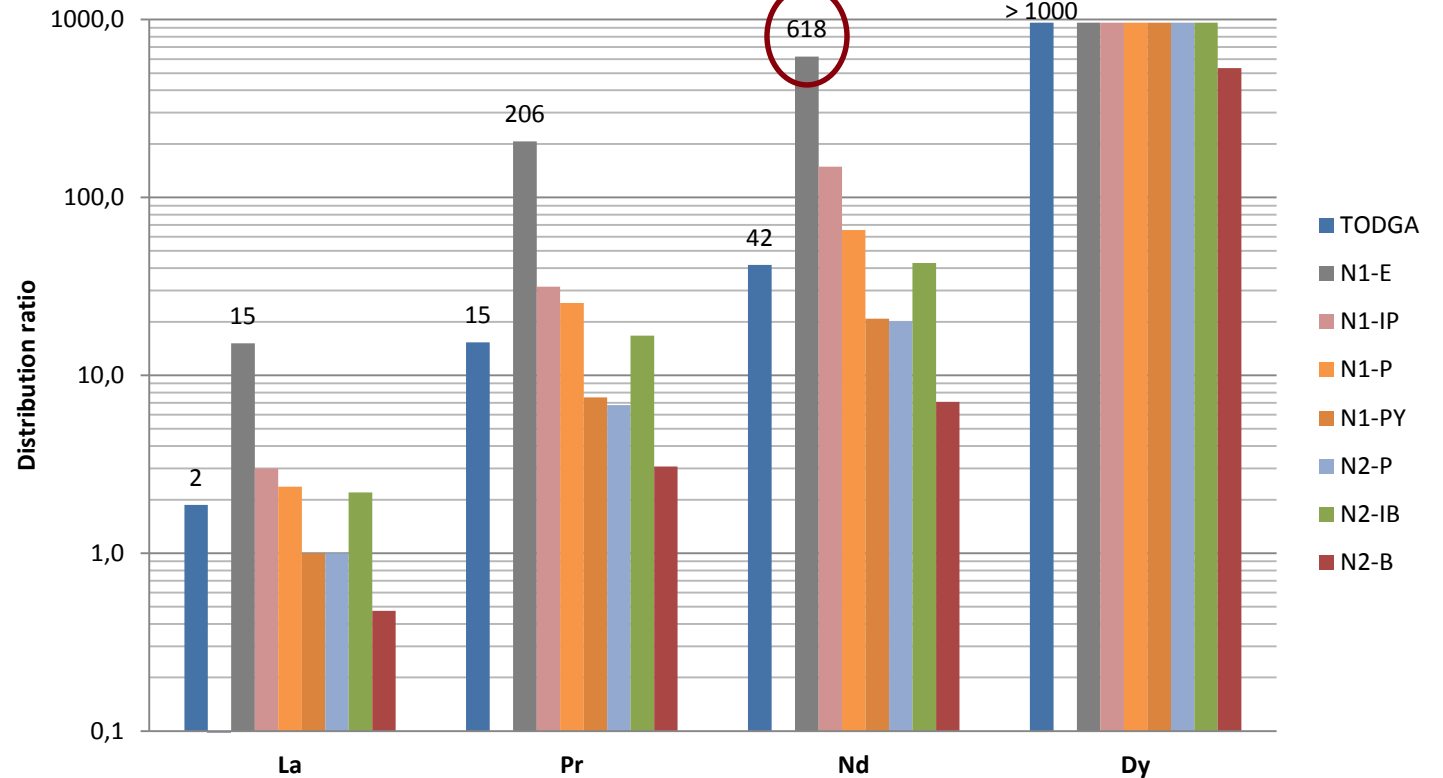


7 new DGAs synthesized

## Distribution ratios

**(N1-E)-DGA**

0.1 M DGA in HTP + 10% *n*-octanol  
HNO<sub>3</sub> 3 M solution containing  
REE, Ni, Co 1 g/L, Fe 10 g/L

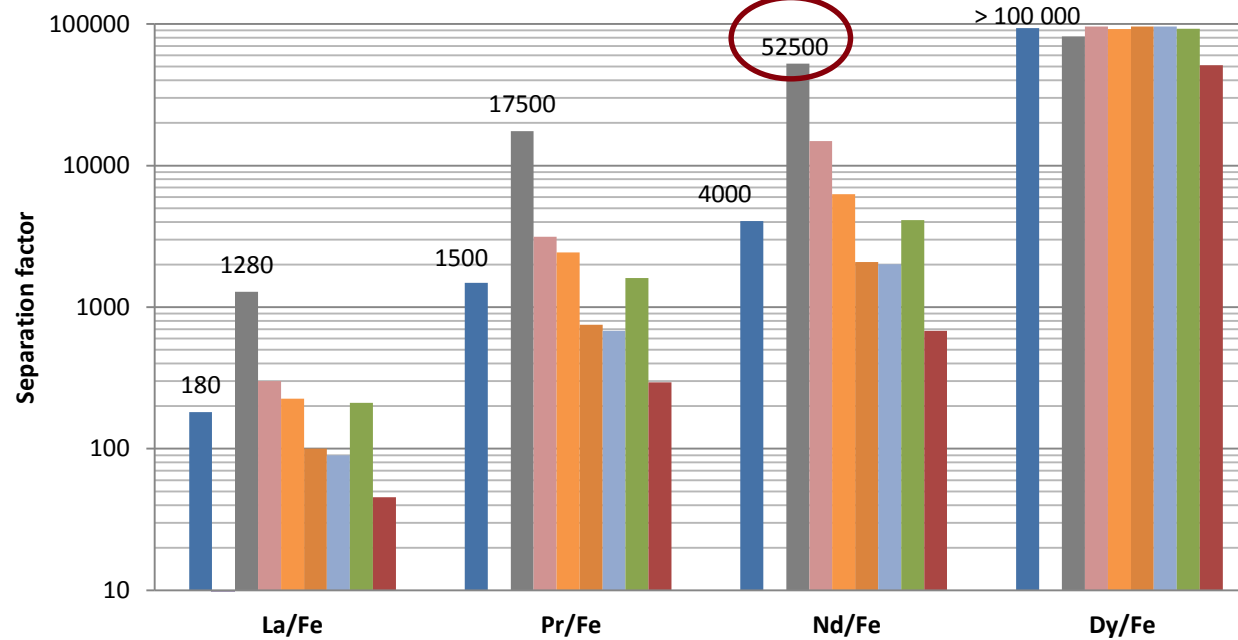


- Excellent extraction of heavy REE ( $D_{Dy} > 1000$ )
- Increased extraction (x 15) of light REE for **(N1-E)-DGA** compared to TODGA

Andreiadis, patent pending FR1853263

## Separation factors REE / Fe(III) HNO<sub>3</sub> 3 M

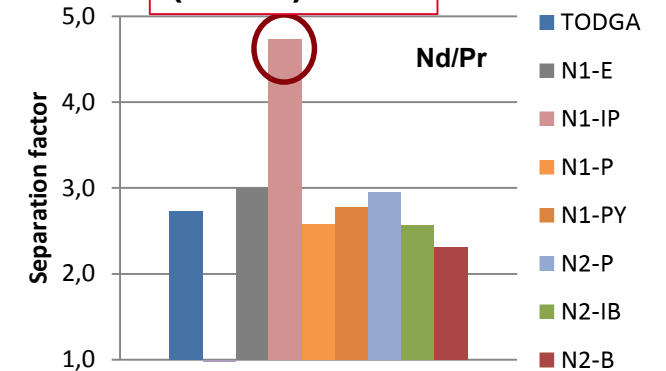
**(N1-E)-DGA**



Novel DGAs

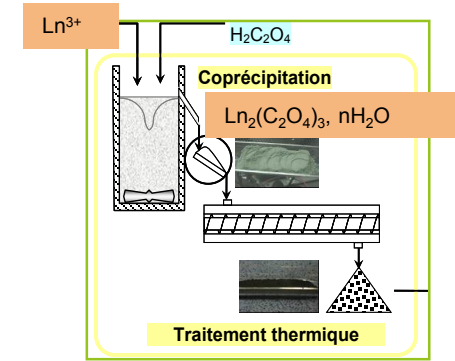
- Excellent selectivity REE / impurities (Fe, Co, Ni)
- **(N1-E)-DGA** is 6-15 times more selective than TODGA
- Increased intra-REE selectivity (Nd/Pr) for **(N1-IP)-DGA**
- Working on understanding the **influence of minor chain variations** on the extraction properties

**(N1-IP)-DGA**



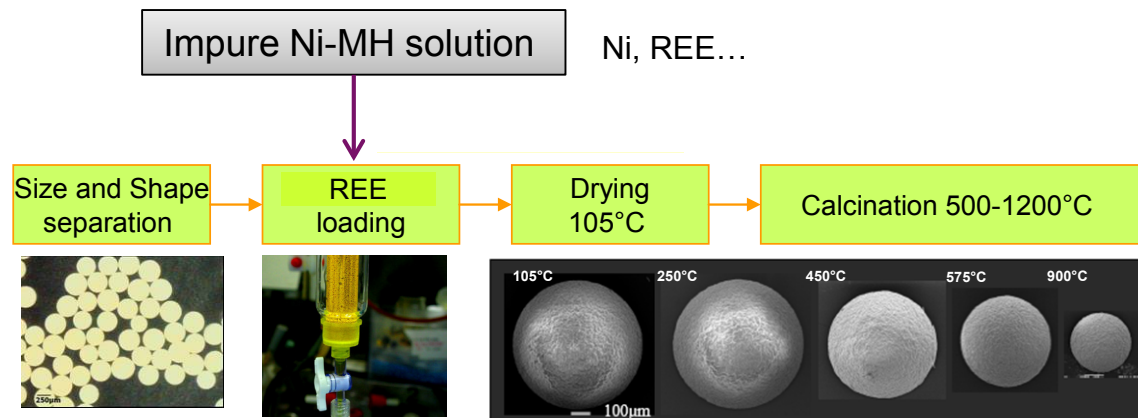
## ➤ Conversion of purified REE into a oxides

- Both for magnet or battery recycling, after the solvent extraction step
- Production of a highly homogeneous powder by **oxalic precipitation**

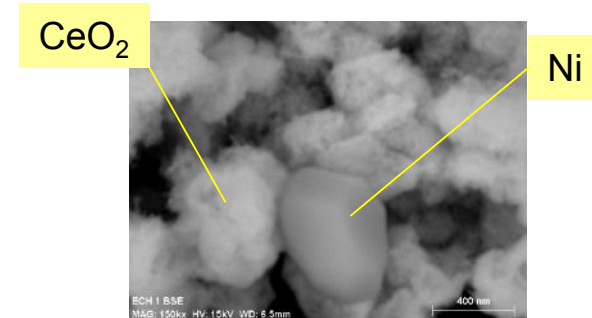


## ➤ Conversion of Ni and REE into cermets Ni-Ce(Ln)O<sub>2</sub> (WAR process)

- CERMET = porous microspheres of cerium oxide incorporating other REO and metallic Ni
- Numerous applications replacing PGM in **catalysis** (steam methane reforming, hydrogenation)
- Straight-forward synthetic process (CEA patent)
- No need for SX purification of input leaching solutions



CERMET particles with controlled parameters (size, porosity, exchange area)



Caravaca, *Catalysts*, 2017, 7(12), 368  
T. Delahaye, patent EP3034209

Electroreduction in molten chloride of Nd or Dy suffers from **low faradic yields** (<40%) due to the presence of  $M^{2+}$  species

Use of **transient electroanalytical techniques**

(voltammetry reversal chronopotentiometry, chronoamperometry...)

to optimize the experimental conditions:

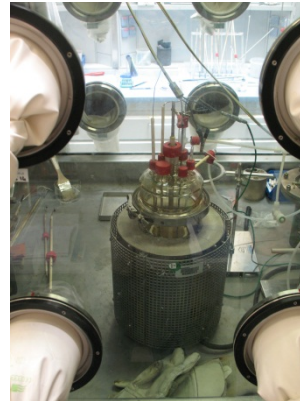
- Salt composition (chloride / fluoride)
- Temperature
- RE concentration
- Current and current density

**Metal deposition tests** to evaluate the process efficiency:

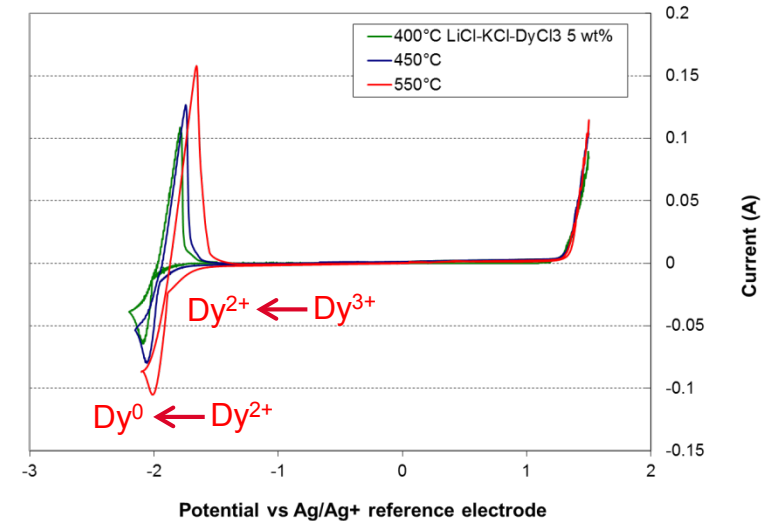
- Faradic yield
- Product purity
- Cell materials compatibility

Gram-scale production of pure or mixed metallic REE with Faradic efficiency  $\approx 80\%$

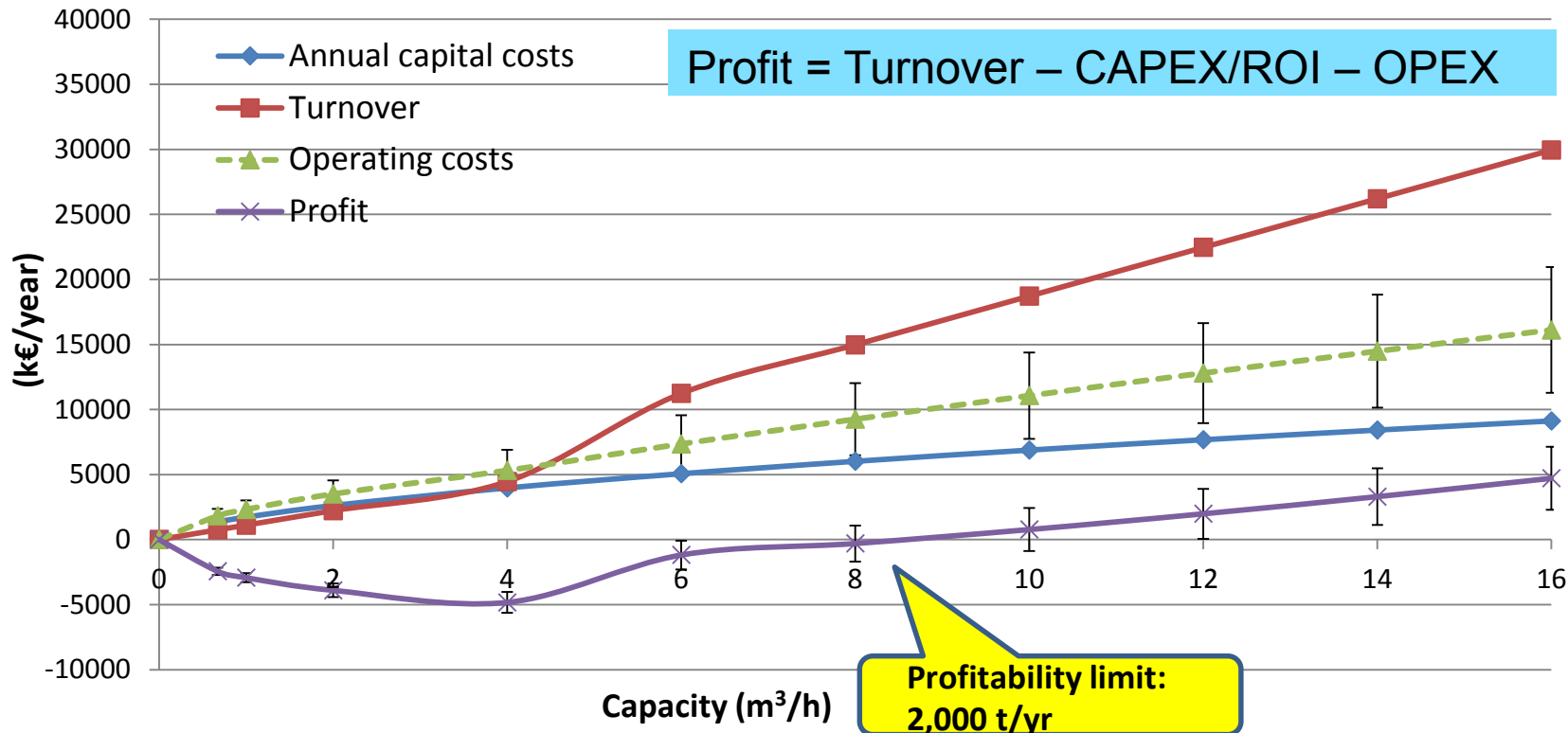
Glovebox setup



Cyclic voltammetry in molten chloride salt



Hydrometallurgical recovery of REO from NdFeB magnet scraps (excluding pyrometallurgical steps)



- The profitability limit can be shifted to a lower capacity (**300 t/yr**) with an **optimised process**
- Liquid waste treatment cost has to be further assessed, depending on local regulations (discharge of NO<sup>3-</sup> is strictly supervised)

- **Non optimised conditions**
- RoI = 3 years
- Careful hypothesis for REEs prices  
Nd<sub>2</sub>O<sub>3</sub> 50 US \$/kg; Dy<sub>2</sub>O<sub>3</sub> = 300 US \$/kg
- Work in 5 shifts for throughput > 5 m<sup>3</sup>/h
- 15% uncertainty on operating costs

- Development of two **REE separation process** from permanent magnets and spent NiMH batteries
- Demonstration of the **scientific feasibility of REE recovery by SX** without preliminary separation of transition metal impurities by precipitation
- **Pilot scale production (TRL 5)** of highly pure Dy and Nd/Pr solutions from used magnets
  - Experiments in progress on NiMH battery flowsheet process
- **REE conversion** to oxides (oxalic precipitation) and CERMETS
- **Molten salt electrolysis** for producing pure or mixed metallic REE
- **Technical-economic study** of the process for cost and rentability evaluation
- REE recycling from **magnets** involving hydrometallurgy and SX **doesn't seem currently profitable**
  - Low volume of small magnets from available, easily dismantled WEEE
  - High lifetime of larger magnet-containing products (wind turbines, HEV motors)
- REE recycling from spent **NiMH batteries might be interesting**
  - Simple, compact flowsheet integrated in existing battery recycling process
  - Production of value-added products (cermet...)
  - TEA needed to confirm these hypotheses

## Acknowledgments

### **CEA / DEN**

V. Haquin  
M-T. Duchesne  
V. Pacary  
M. Montuir  
D. Rinsant  
G. Mossand  
D. Hartmann  
L. Diaz

### **CEA / DRT**

E. Billy  
P. Feydi  
R. Laucournet

### **SNAM**

N. Coppey

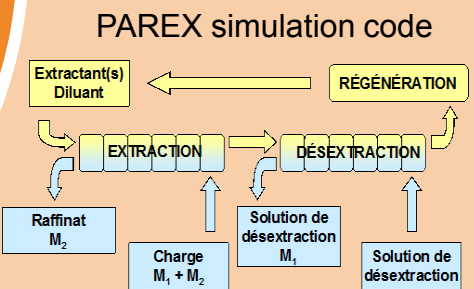
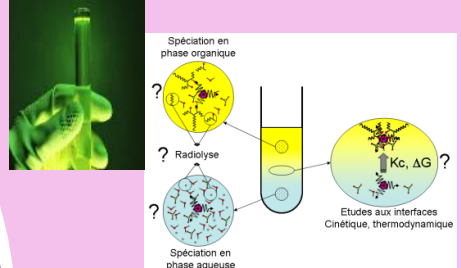
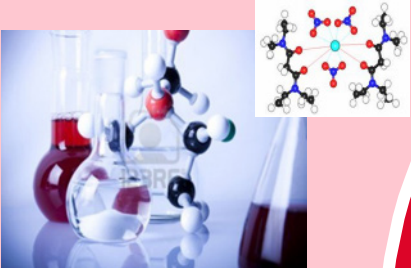
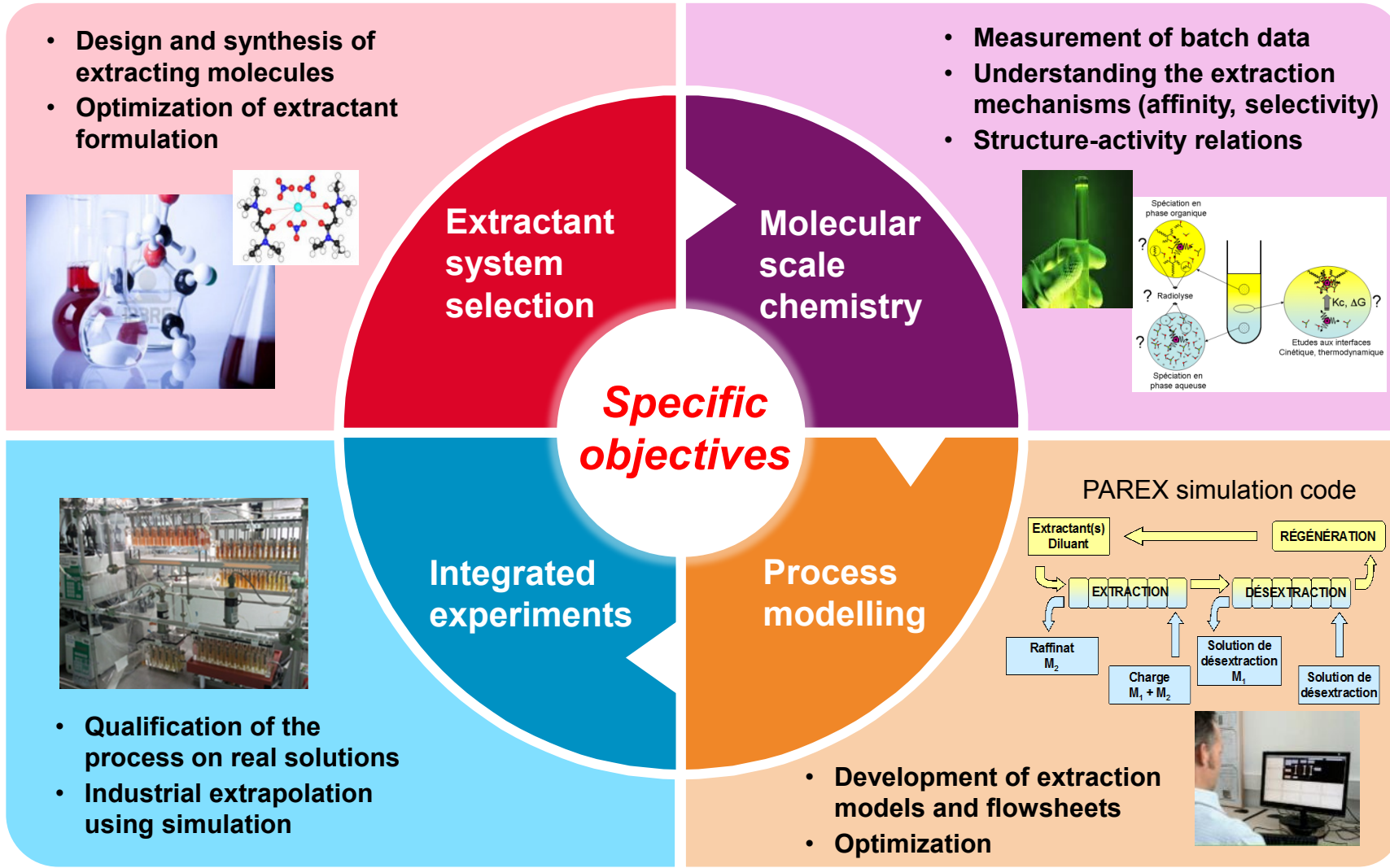


ANR REPUTER project  
grant 15-CE08-0017-01

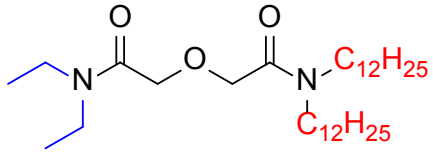
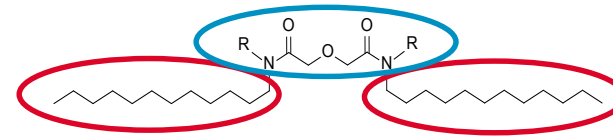
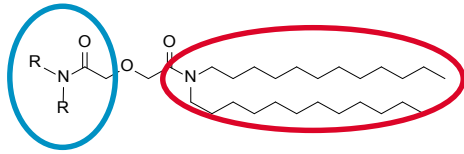
# Thank you for your attention

Commissariat à l'énergie atomique et aux énergies alternatives  
Centre de Marcoule | BP17171 | 30207 Bagnols-sur-Cèze Cedex  
[eugen.andreiadis @ cea.fr](mailto:eugen.andreiadis@cea.fr)

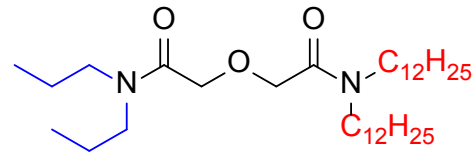
Nuclear Energy Division  
Research Department on Mining and Fuel Recycling Processes



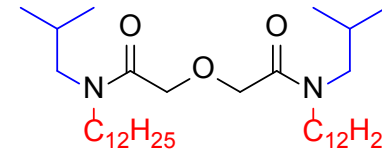
# Novel dissymmetrical DGA extractants



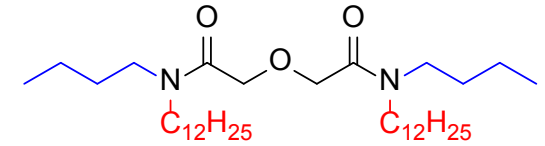
N,N,-diethyl-N',N'-didodecyl DGA  
(N,N-E)



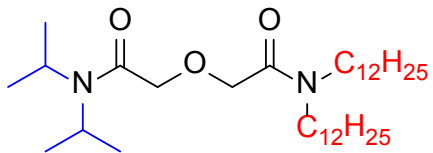
N,N,-dipropyl-N',N'-didodecyl DGA  
(N,N-P)



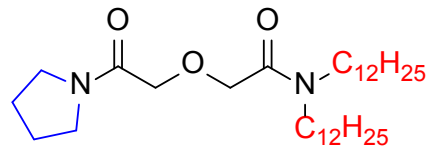
N,N',-diisobutyl-N',N'-didodecyl DGA  
(N,N'-iB)



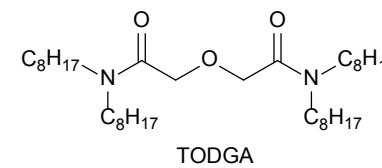
N,N',-dibutyl-N',N'-didodecyl DGA  
(N,N'-B)



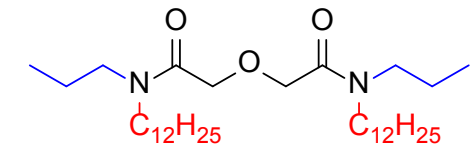
N,N,-diisopropyl-N',N'-didodecyl DGA  
(N,N-iP)



N-pyrrolidinyl-N',N'-didodecyl DGA  
(N-Py)

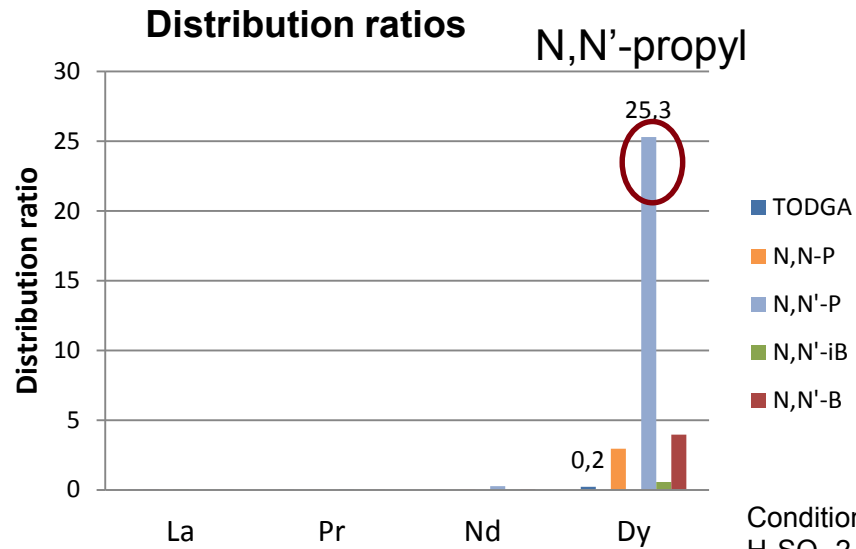


TODGA  
Reference extractant

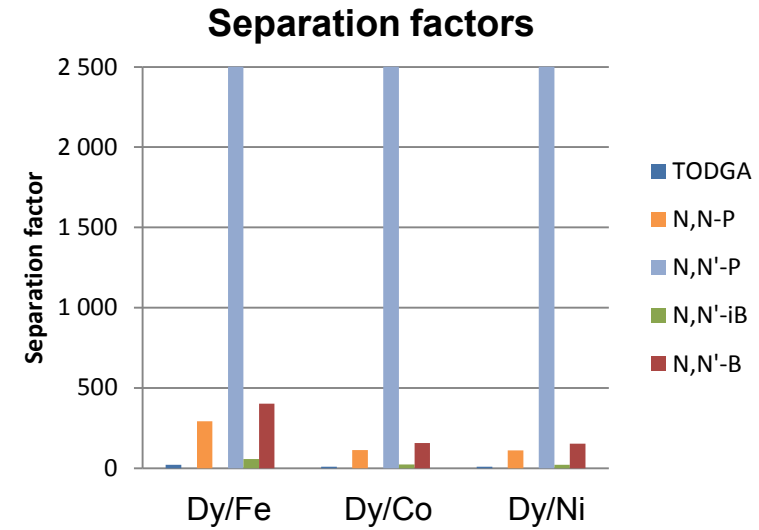


N,N',-dipropyl-N',N'-didodecyl DGA  
(N,N'-P)

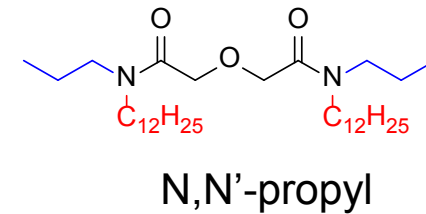
# Solvent extraction by DGA in H<sub>2</sub>SO<sub>4</sub> solution

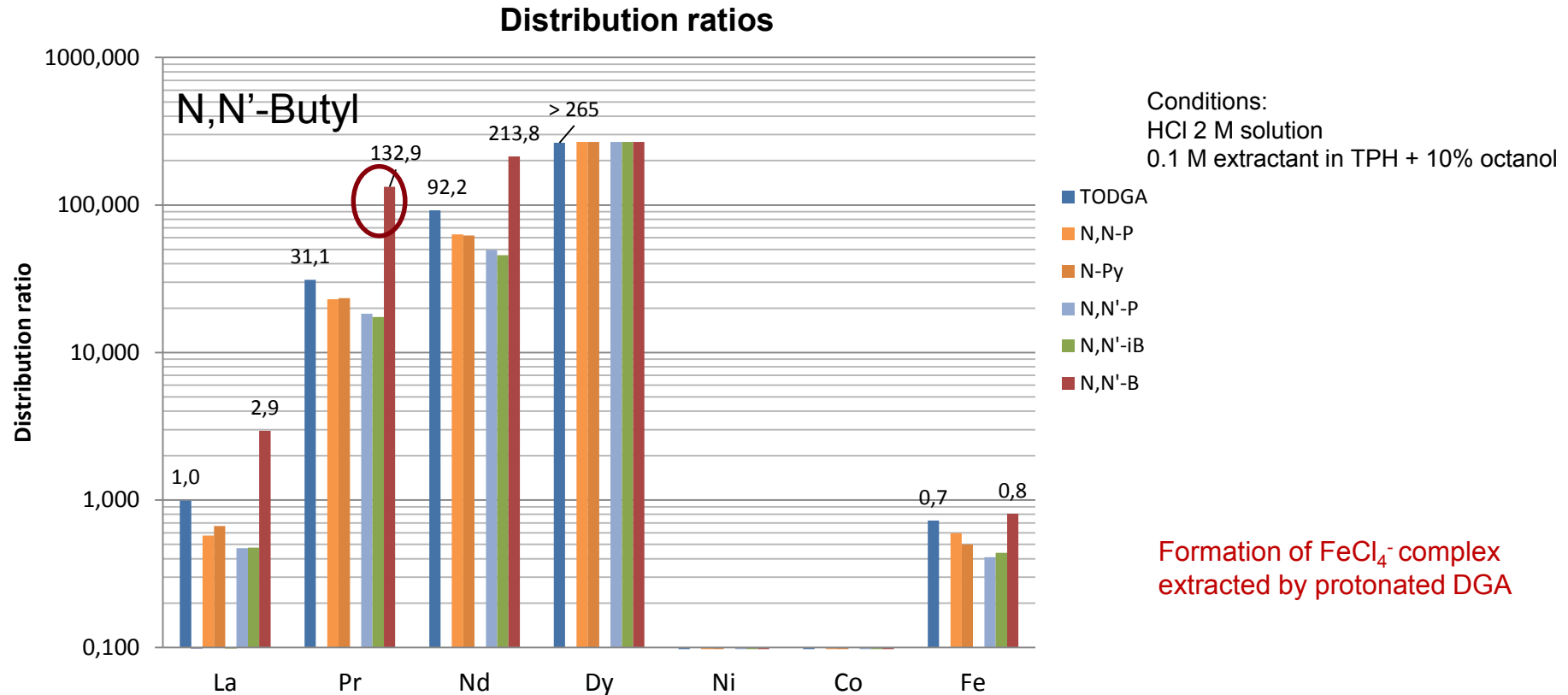


Conditions:  
H<sub>2</sub>SO<sub>4</sub> 2 M solution;  
REE, Ni, Co 1g/L, Fe<sup>3+</sup> 10 g/L  
0.1 M extractant in TPH + 10% octanol



- Much lower extraction in 2 M sulfuric acid compared to 3 M nitric acid solutions
- Only heavy REE can be selectively extracted, no light-REE extraction
- Remarkable improvement of extraction compared to TODGA (x 100) for N,N'-propyl DGA ( $D_{Dy} = 25$  for N,N'-propyl DGA)
- Excellent separation factors Dy / Fe, Co, Ni





Formation of  $\text{FeCl}_4^-$  complex extracted by protonated DGA

- Low La extraction but good (Nd, Pr) or excellent (Dy) extraction of heavier REE
- Increased extraction ability (2-4 x) for N,N'-Butyl DGA compared to TODGA
- No extraction of Ni or Co however 40% of Fe is extracted
- We need to improve the selectivity with respect to  $\text{Fe}^{3+}$

