

# The REPUTER project for Ni-MH battery recycling

***Eugen Andreiadis***

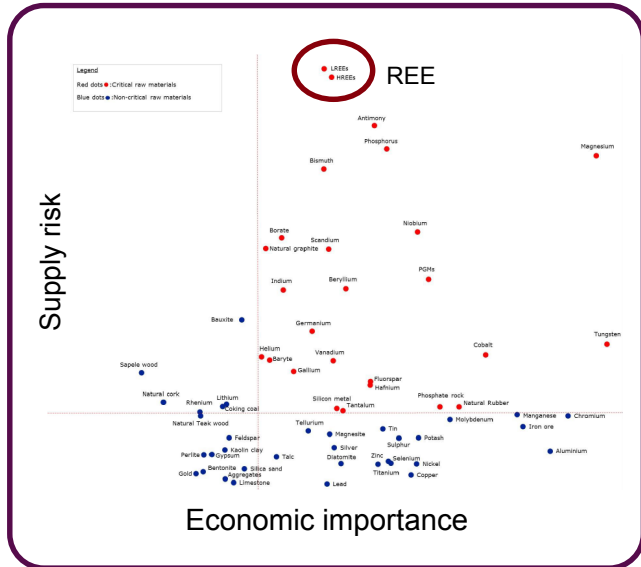
*Project Coordinator*

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

*eugen.andreiadis @ cea.fr*



# Critical supply of (some) rare earth elements

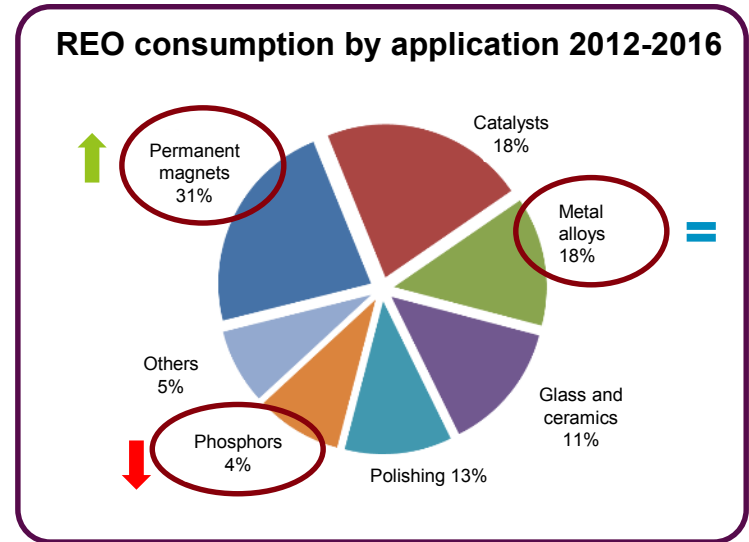


Source: EU report 2017

- **Demand growing**, especially for magnets (> 7% per year for Nd)
- Accelerated growth of **HEV/EV market** (+30% in 2017)
- Market driven by **Nd** and **Dy** demand
- 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**
- Significant **price volatility** during the last 10 years
- Currently **no European mine** in operation

## Possible ways to alleviate REE supply risk

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

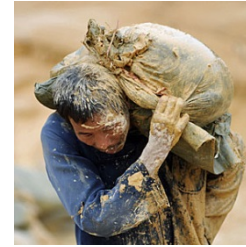


References: Roskill 2015, IMCOA 2017

# REE recycling: closing the materials loop

## Advantages of recycling

- Target only the **most critical** rare earths (balance problem)
- No issues with **radioactive elements** ( $^{235}\text{U}$ ,  $^{238}\text{U}$ ,  $^{232}\text{Th}$ )
- Lower environmental footprint (**public acceptance**)



**Very low  
recycling rates\*  
average 7% in EU**

\*very disparate values in the REE series  
Source: JRC, EC Report on CRM 2018

## Challenges

- Insufficient and untargeted **collection** of waste sources
- Difficult recovery of REE-containing fractions
- Difficult **separation of individual REE in pure form**
- **Low economic interest** in line with current market prices

## Opportunities

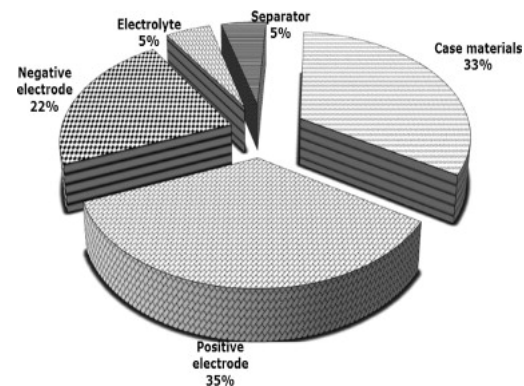
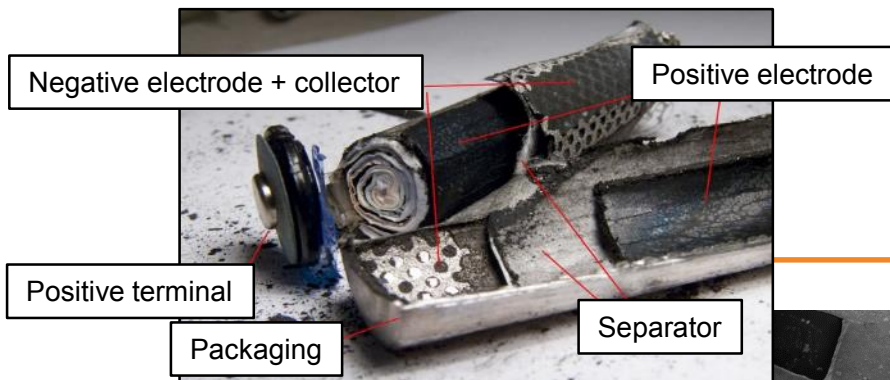
- Competences and expertise of the **European recycling industry**
- **Development of a circular economy**
- Positive economic and environmental **impact**



## Recovering REE from Ni-MH batteries

- **Battery** recycling is an obligation
- Immediate **availability** of the supply
- Battery recycling processes already implemented

# Ni-MH battery composition



Al-Thyabat, Minerals Engineering 2013

**Anode (-)**

Active material  
 $MmB_5$  & ( $Y_2O_3$ ,  $Yb_2O_3$ , additives)

$Mm = La_{0,62}Ce_{0,27}Pr_{0,03}Nd_{0,08}$   
 $B_5 = Ni_{3,55}Co_{0,75}Mn_{0,4}Al_{0,3}$

**Composition cylindrical Ni-MH battery**

Component	Percentage
Ni	40%
Fe	22%
REE	10%
Other	25%
Co	3%

**Cathode (+)**

Active material  
 $Ni(OH)_2$  & (Ni, Co, Zn, Y)

Interest for the integration of a REE recovery step in the process of Ni-MH battery recycling

“Recovery, purification and elaboration of rare earth elements for Ni-MH battery recycling”

## Overall project goal:

Develop an efficient, eco-conceived rare earth recovery and separation process flowsheet from used Ni-MH batteries, starting from collection down to the formulation of REE as pure metals or oxide materials ready to be used in various applications

## Objectives:

- Reinforce through common goals the **expertise** and **competences** gained in France in hydrometallurgy and in pyrometallurgy;
- Remove some of the **scientific and technical barriers** currently affecting the REE recycling
- Evaluate different flowsheets for **producing recycled rare earths** in the form of oxides or purified metals for industrial applications (catalytic materials, battery grade alloys, etc.);
- Evaluate the **impact** of the recycling process using a **technical-economic and life cycle analysis**.

# The REPUTER project

## ■ Consortium of 5 partners



**liten**



- **SNAM** - Physical and mechanical battery treatment
- **CEA DRT (LITEN)** - Leaching and precipitation, TE+LCA
- **CEA DEN** - coordination, extraction, cermet conversion, molten salt electrolysis, TE+LCA
- **LGC** - molten salt electrolysis
- **ICMPE** - metal alloy purification (vacuum fusion)

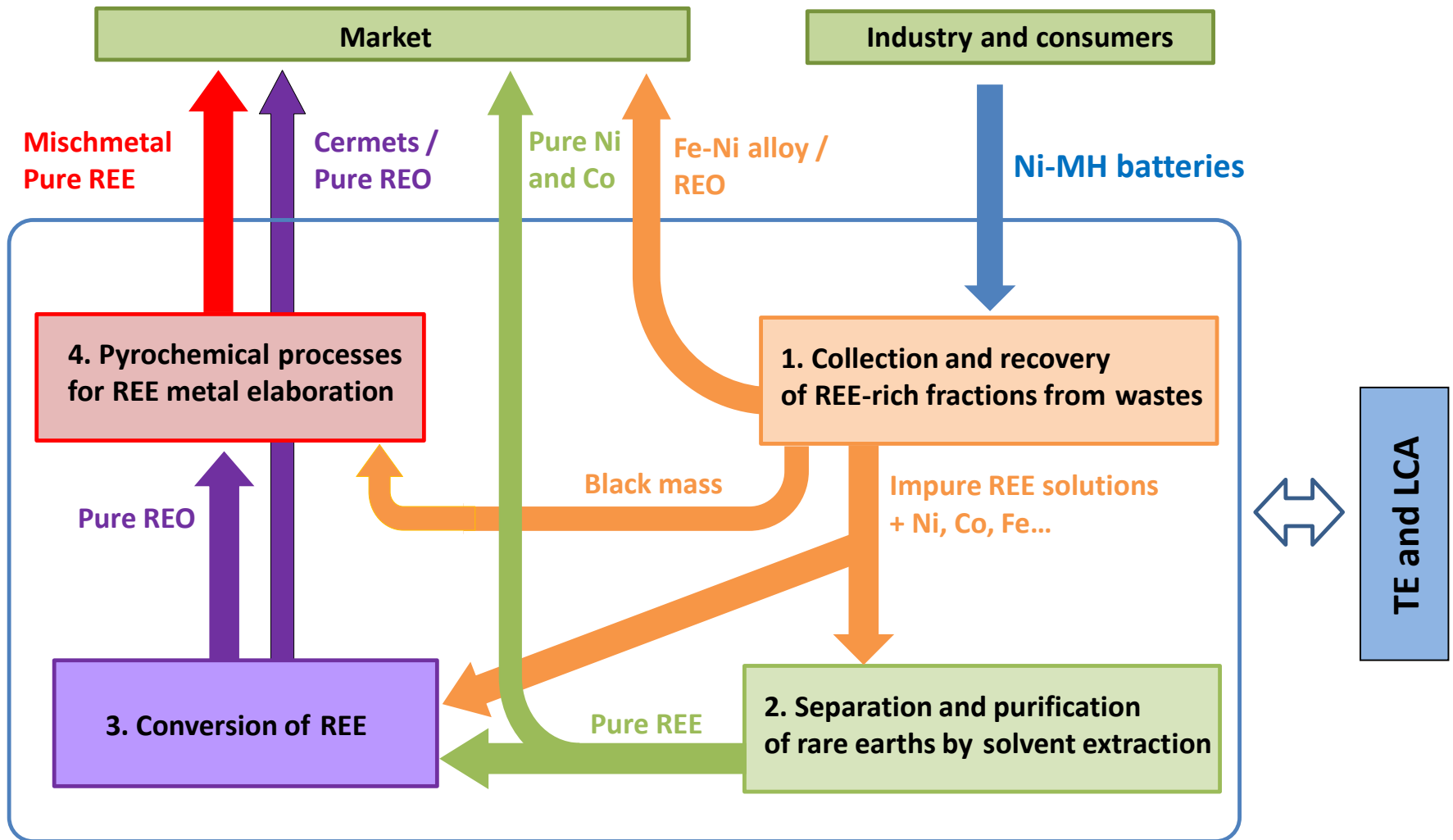
■ Total budget 2 M€ (ANR funding: 750 k€)

■ Start 2016 pour 49 months (→ end 2019)

■ Labelling by 3 competitive poles:



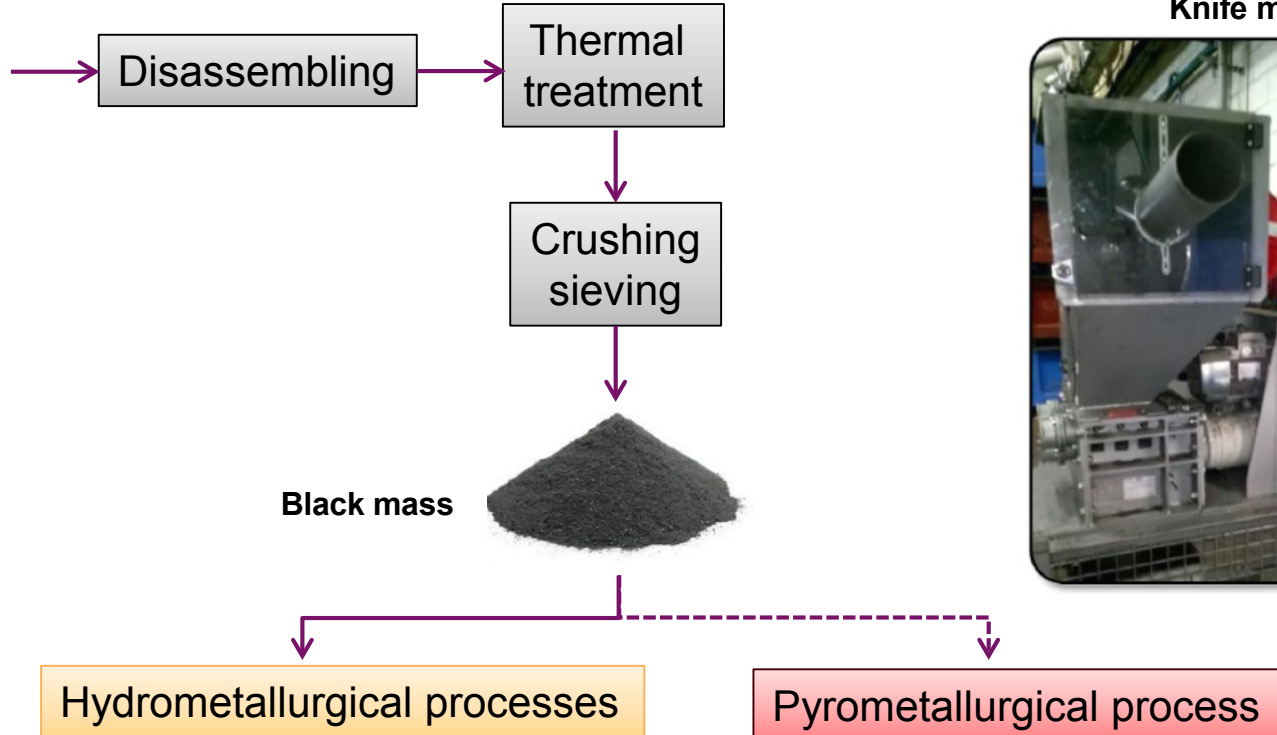
# Various flowsheets for REE recycling



# Recovery of REE-rich fractions

## ➤ Physical and mechanical treatment of batteries

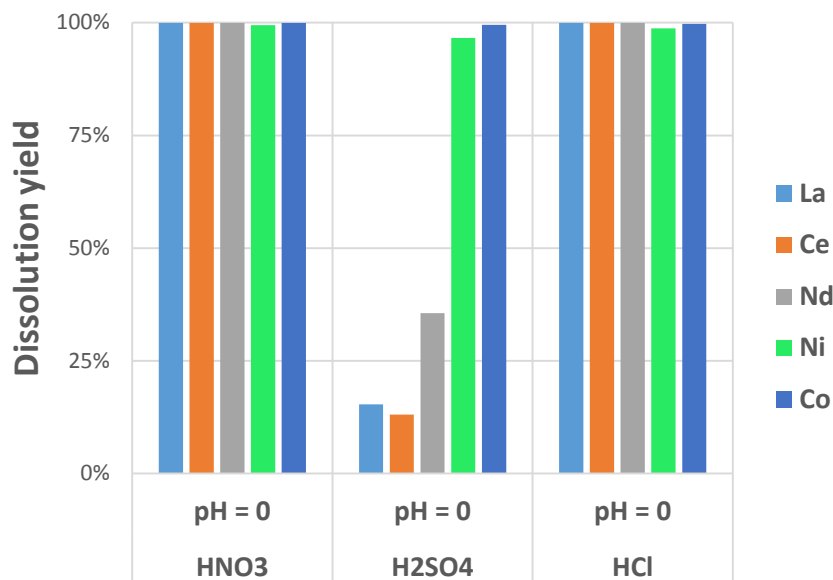
- Adapting the existing NiMH recycling process for the recovery of RE-rich fractions:
  - Selection of battery cell types (origin, condition, composition...)
  - Optimization of crushing and sieving operations
  - Choosing the ideal conditions for a size based separation REE/Fe





## ➤ Total digestion (REE + Ni, Co...)

- Choice of acids and leaching conditions compatible with an industrial approach
  - Excellent yield for HNO<sub>3</sub> and HCl acid solutions at controlled pH
  - Optimization of S/L ratio
  - Scale-up to a 5 L reactor



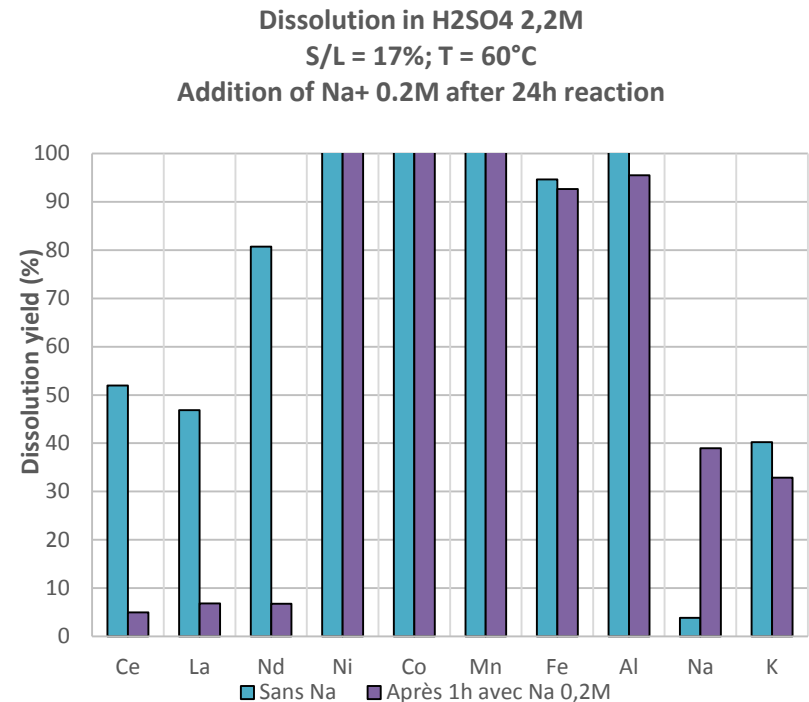
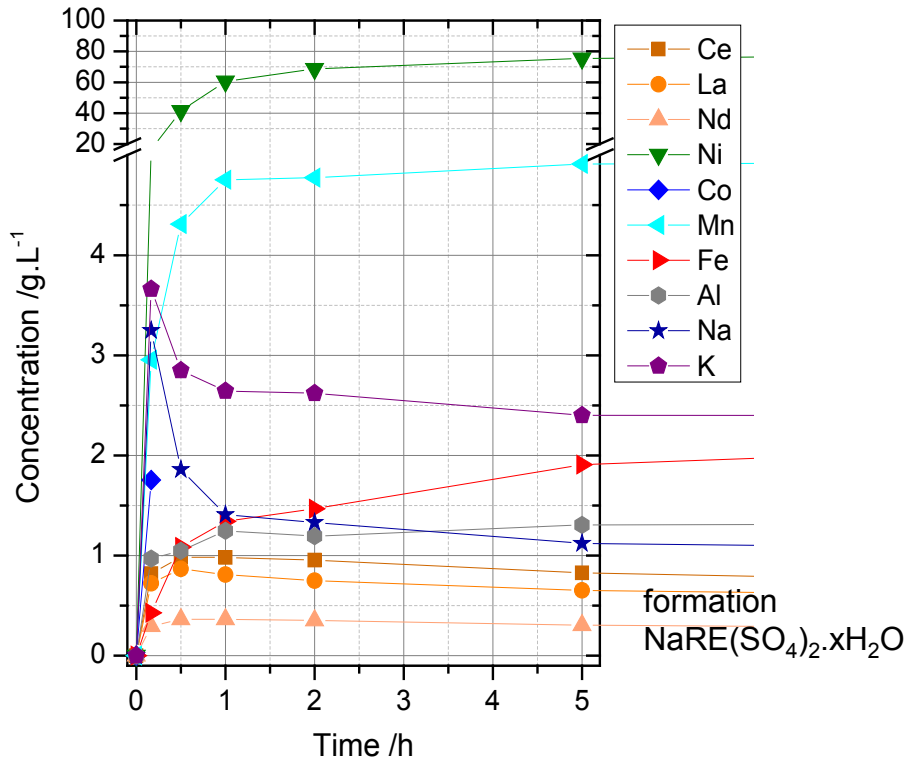
### Lixiviation solution composition (g/L)

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

## ➤ Selective leaching

- Precipitation of REE in sulfuric acid solution as double sulfate
- Optimization of REE precipitation by  $\text{Na}^+$  addition
- Redissolution of double sulfate precipitate ( $\text{HCl}$ ,  $\text{HNO}_3$ ) and conversion to oxide



## ➤ Implementation of a hydrometallurgical pilot unit

- Integrated to the SNAM site in Viviez (France): logistics, SEVESO environment, QA...
- Dissolution / precipitation / filtration / calcination units
- Scalable towards an increased capacity production



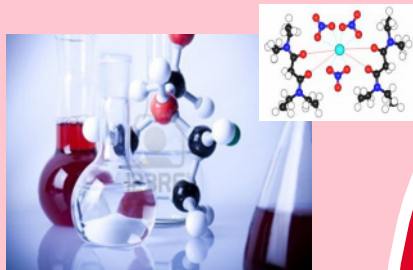
10 L reactor

1 m<sup>2</sup> press filter



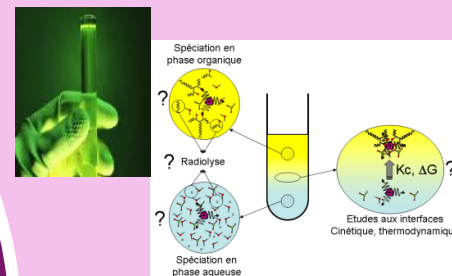
# Integrated approach to SX process development

- Design and synthesis of extracting molecules
- Optimization of extractant formulation



**Extractant system selection**

- Measurement of batch data
- Understanding the extraction mechanisms (affinity, selectivity)
- Structure-activity relations



**Molecular scale chemistry**

**Specific objectives**

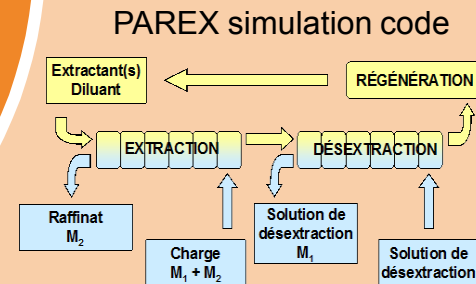
**Integrated experiments**



- Qualification of the process on real solutions
- Industrial extrapolation using simulation

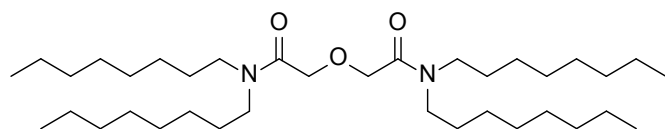
**Process modelling**

- Development of extraction models and flowsheets
- Optimization



# Selection and evaluation of a REE extractant system

- Goal: extract the REE from the leaching solutions while allowing the recovery of pure Ni and Co
- Challenge: Need an extractant with excellent affinity and selectivity for REE **in the presence of Fe<sup>3+</sup>**
- Screening of several commercially-available extracting molecules
- Selection of **diglycolamides** (TODGA) class of solvating extractants

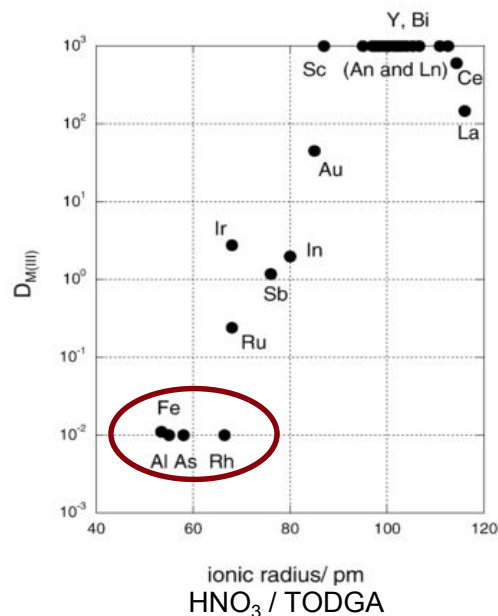
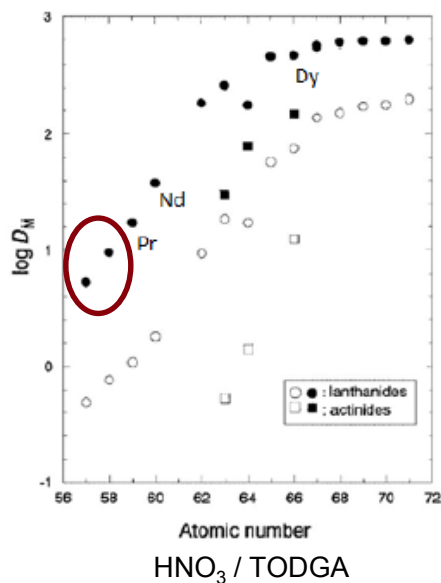


TODGA

Sasaki et al, 2002

$$D_M = \frac{[M^{n+}]_{org}}{[M^{n+}]_{aq}}$$

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

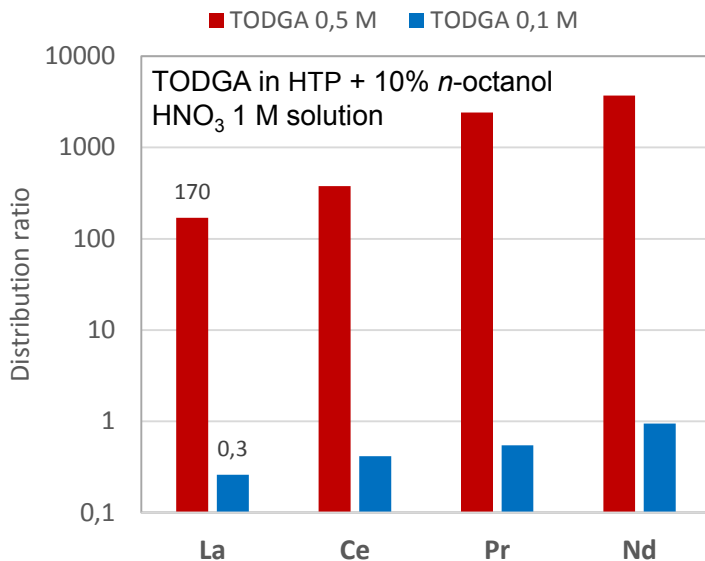


- Extraction capacity inversely proportional to REE<sup>3+</sup> ionic radius
- Preference for heavy RE and good intra-REE separation factors in nitric acid media
- Excellent selectivity with respect to transition metals (Fe<sup>3+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>)

# REE separation by solvent extraction

- Tested TODGA 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



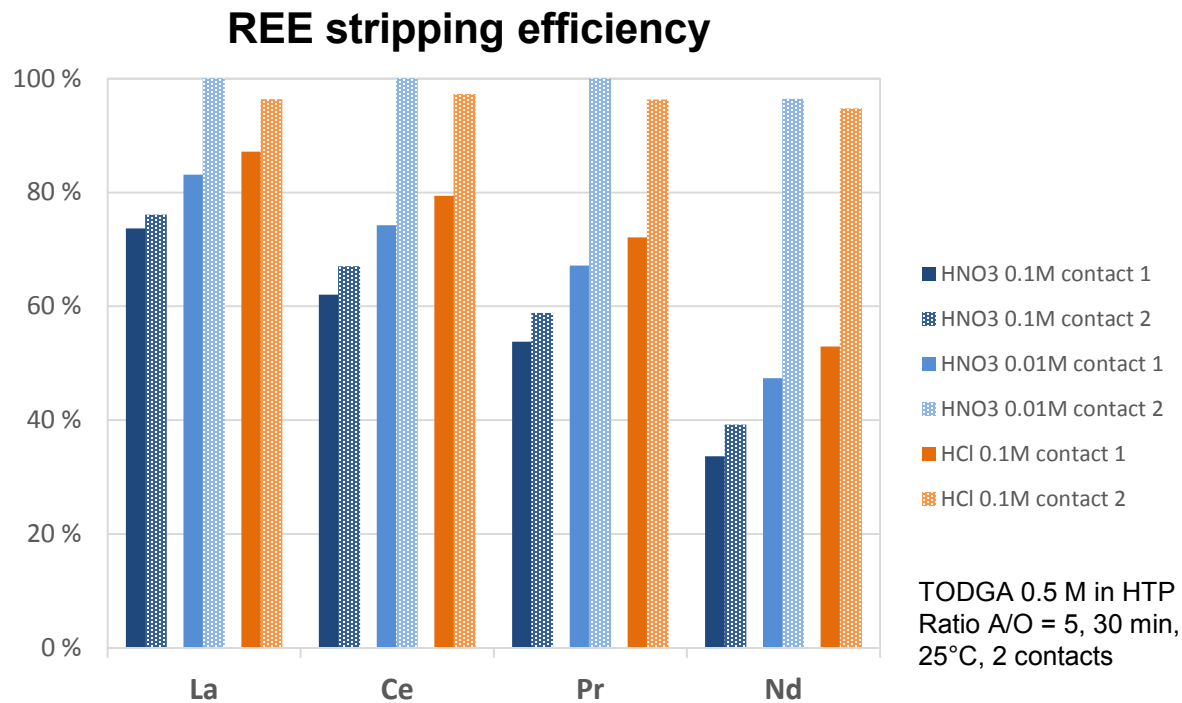
## Composition of aqueous and organic phases

Element	Initial aqueous phase (ppm)	Aqueous phase after extraction (ppm)	Organic phase after extraction (ppm)	Mass balance (%)	D
La	7 159	167,0	6608,6	94,6	<b>40</b>
Ce	9 180	80,6	8707,4	95,7	<b>108</b>
Pr	1 385	2,0	1357,6	98,2	<b>679</b>
Nd	2 768	2,4	2760,0	99,8	<b>1150</b>
Ni	62 622	63761,8	1,2	101,8	0,00
Co	8 136	8508,6	3,0	104,6	0,00
Mn	3 421	3498,0	24,4	103,0	0,01
Fe	4 358	4423,4	105,0	103,9	0,02

- 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% (1 contact, before scrubbing and stripping)

# REE separation by solvent extraction

- Tested TODGA on simulated and real solutions in HNO<sub>3</sub> and HCl media
- Optimisation of extraction and stripping conditions



- Near-quantitative stripping of REE in 2 contacts with dilute acid at room temperature (HNO<sub>3</sub> 0.01M or HCl 0.1M)

■ 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

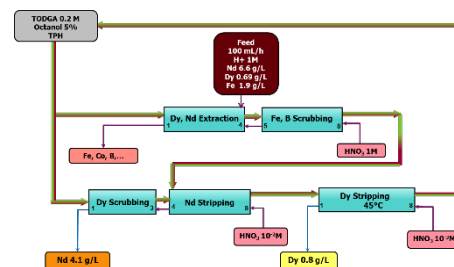
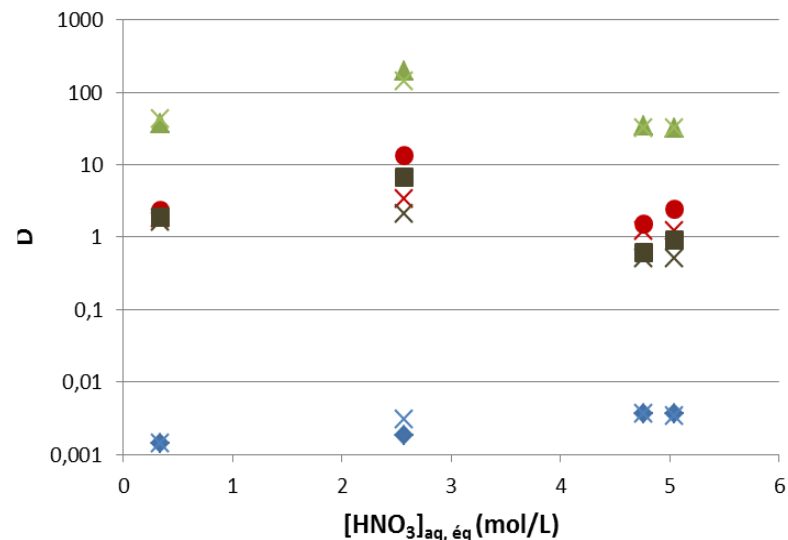
- (HNO<sub>3</sub>)(octanol)<sub>2</sub>
- (HNO<sub>3</sub>)<sub>m</sub>(TODGA) with m = 1 to 3
- M(NO<sub>3</sub>)<sub>3</sub>(TODGA)<sub>n</sub> with n = 1 to 3 for La, Nd, Ni, Fe

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

■ Activity coefficients taken into account in aqueous phase

- Implementation of the model in the **CEA PAREX+ simulation code** and calculation of flowsheets
- Pilot demonstration on real solutions

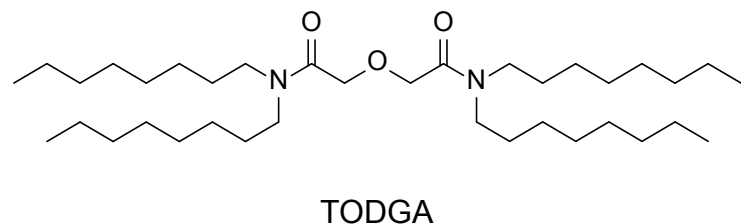
Example of model fit of experimental data



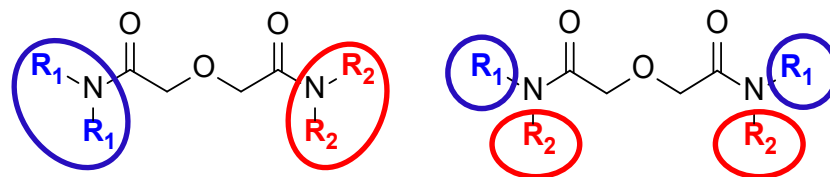


## Objectives:

- Improving the extraction of **light REE**
- Reducing the extractant **concentration** in the organic phase (OPEX)
- Increasing the **selectivity** towards transition metals (e.g. Fe, Ni, Co)
- Improving the REE extraction in **sulfuric** and **hydrochloric** acid media



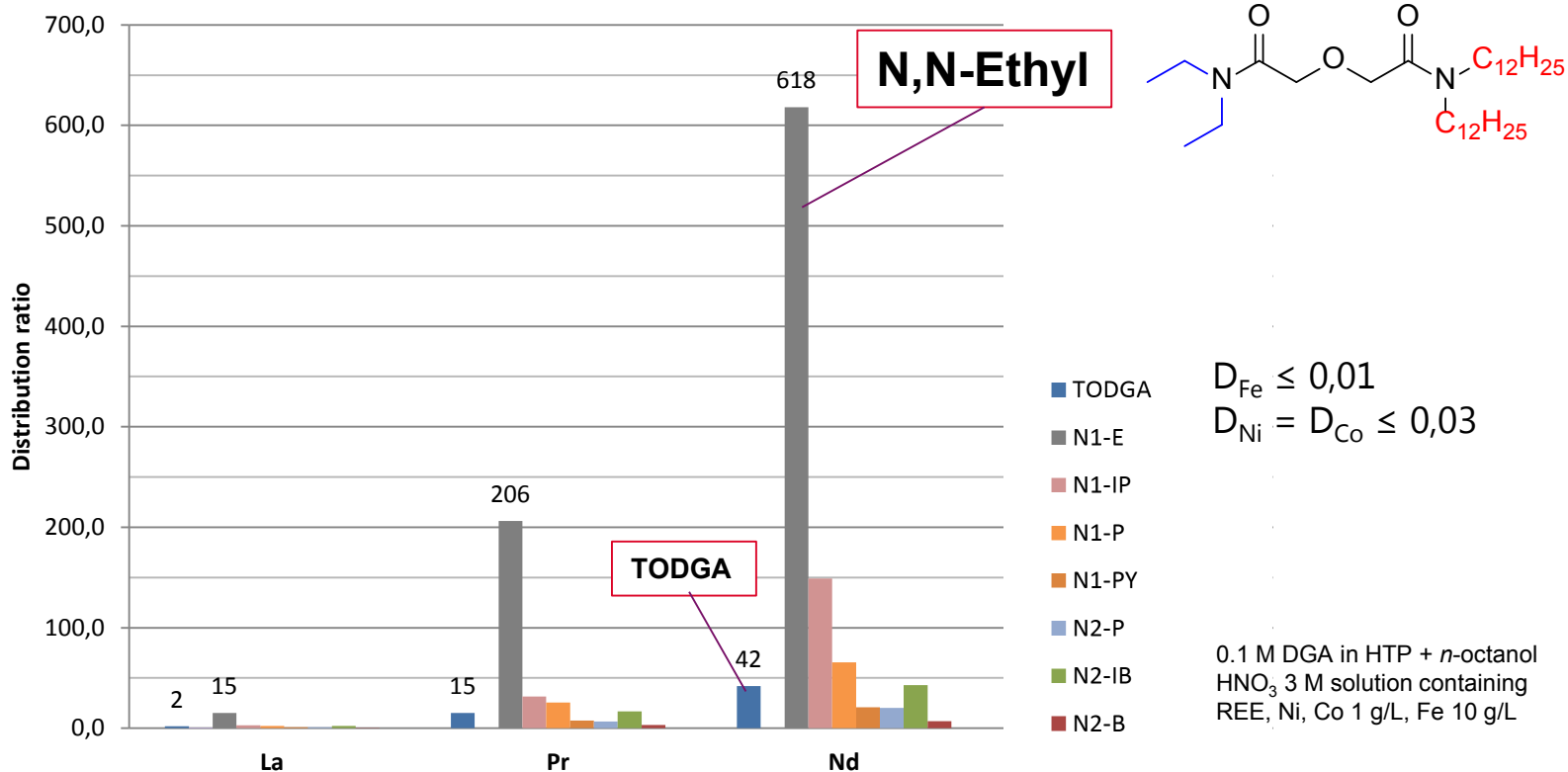
## 7 new DGAs synthesized



## Increase the amphiphilic character

- Short (hydrophilic) alkyl chains: R<sub>1</sub>
- Long (lipophilic) alkyl chains: R<sub>2</sub>

# Solvent extraction by DGA in nitric acid solution



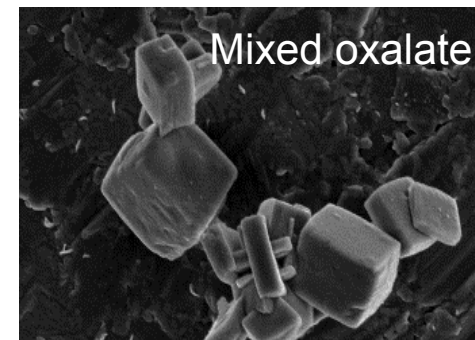
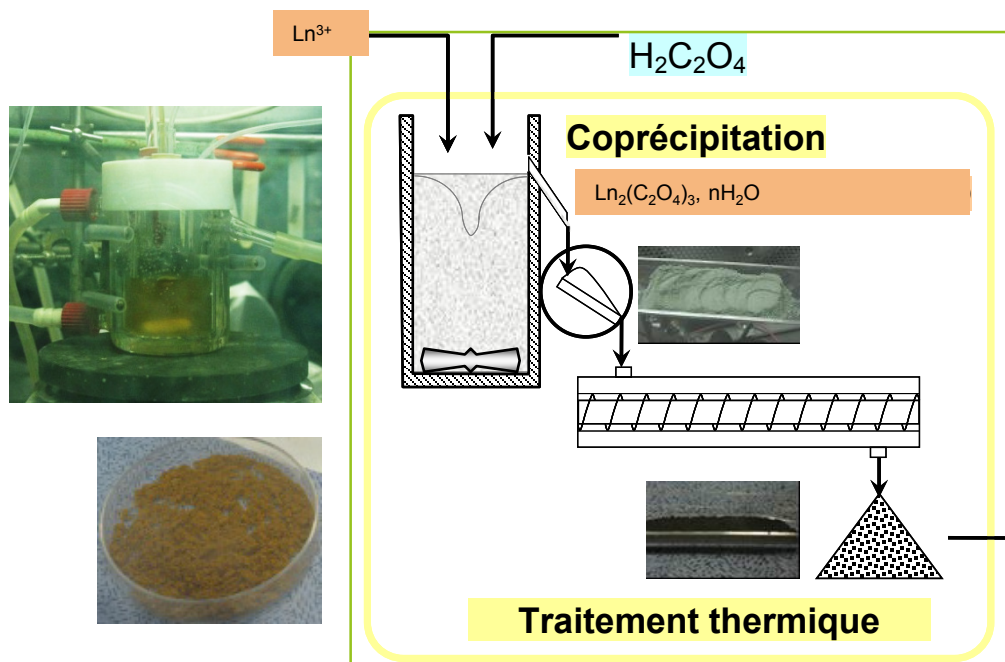
- Increased extraction (x 15) of light REE for **N,N-Ethyl** compared to TODGA
- Excellent selectivity REE / impurities (Fe, Co, Ni)
- Working on understanding the **influence of minor chain variations** on the extraction properties

Andreiadis, patent FR1853263

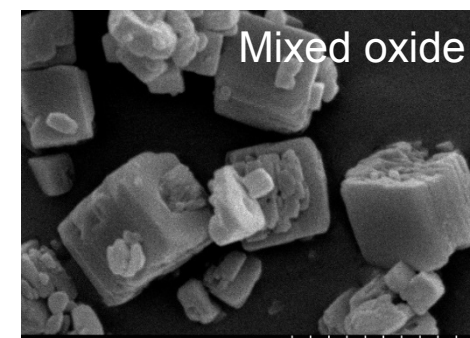
# Conversion of REE into oxides

## ➤ Conversion of purified REE into a oxides

- Production of a highly homogeneous powder by **oxalic precipitation**
- Thermal treatment by calcination leading to oxides



↓ Thermal conversion



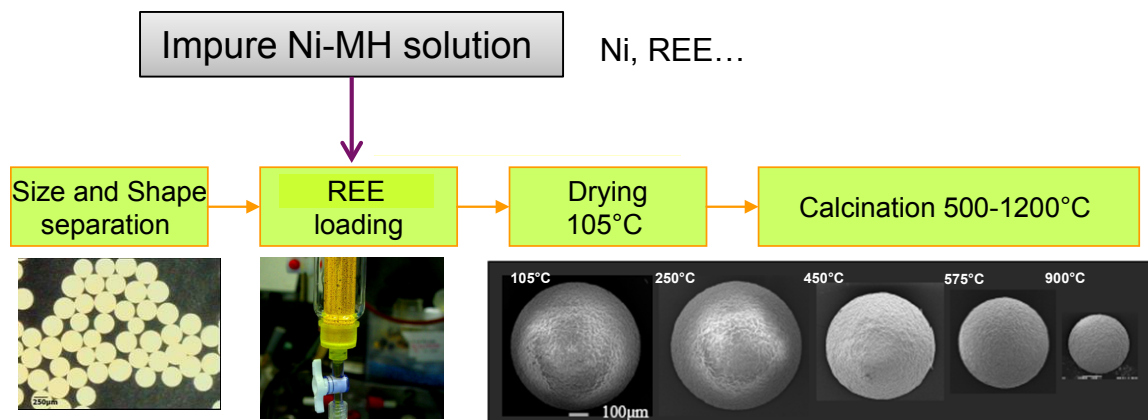
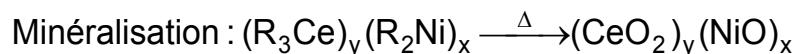
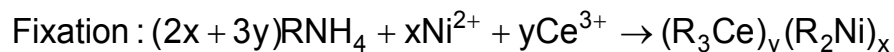
- Robust process exploited for Pu conversion
- Affords supplemental purification with respect to other metal impurities

# Conversion of REE into cermets

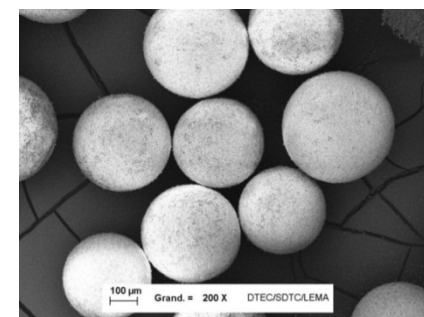
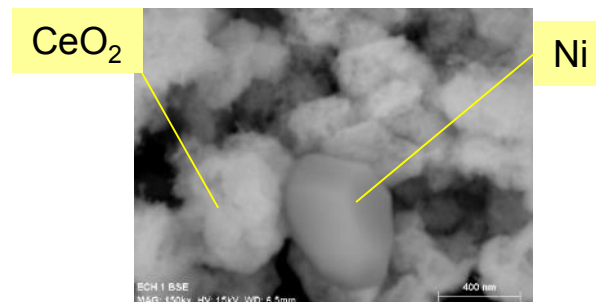
## ➤ Conversion of Ni and REE into cermets Ni-Ce(Ln)O<sub>2</sub> (WAR process)

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

### Straight-forward synthetic process (CEA patent)



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



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

Electroreduction in molten chloride of Nd suffers from **low faradic yields** (<40%) due to the presence of  $M^{2+}$  species (disproportionation reaction  $Nd^0 + Nd^{3+} \rightarrow Nd^{2+}$ )

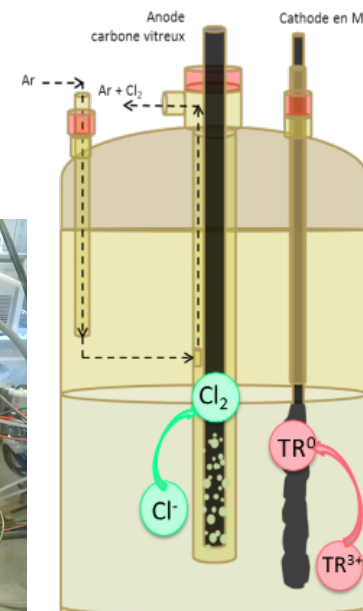
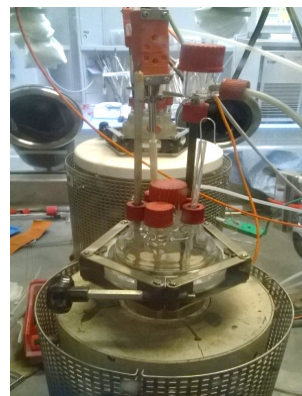
Use of **transient electroanalytical techniques** (voltammetry reversal chronopotentiometry, chronoamperometry...)

to optimize the experimental conditions:

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

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

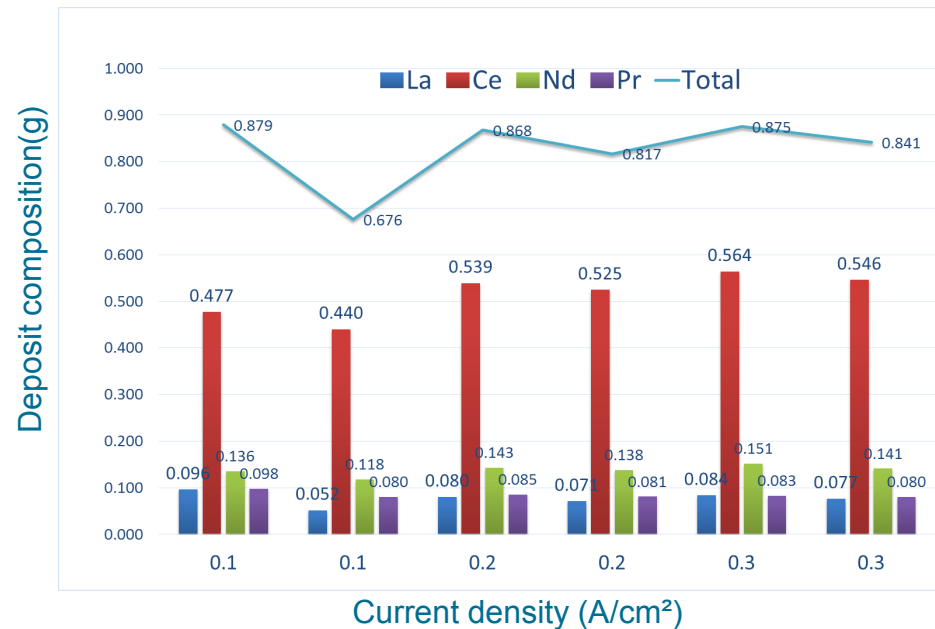
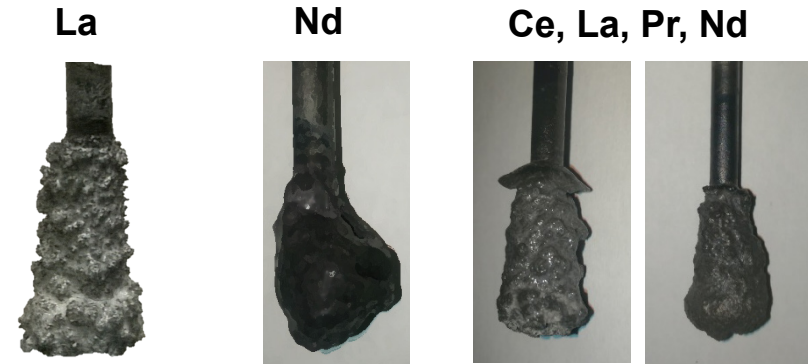
- Faradic yield, product purity, cell materials compatibility
- Operating conditions:
  - 500 g salt bath
  - Constant current electrolysis
  - 4 wt% < TR<sup>3+</sup> < 7 wt%
  - 0.1 A/cm<sup>2</sup> < Cathodic current density < 0.3 A/cm<sup>2</sup>
  - 2000 s < Electrolysis time < 10000 s for 1 g RE metal



# Molten salt electroreduction for metal elaboration

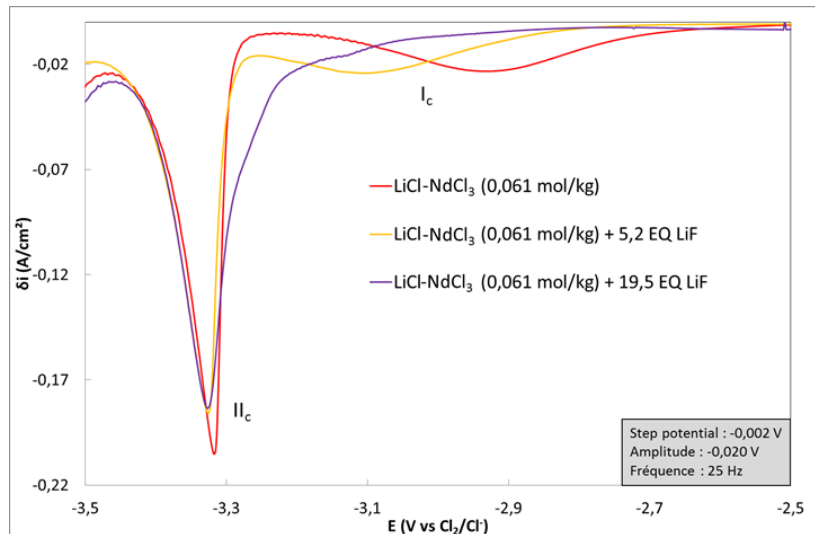
## ➤ Rare earth (RE) chloride electrolysis in LiCl-KCl (450-500°C)

- La deposition : dendritic deposit with high current efficiency (CE)
- Nd deposition : powder deposition with low CE 40%
- Grouped La, Ce, Pr, Nd electrolysis according to black mass composition
- ➔ Co-deposition allows the quantitative recovery of Nd (stabilisation effect)
- ➔ Reproducible results
- ➔ Composition stable on 6 successive deposits
- ➔ La recovery is more difficult (the lowest reduction potential)



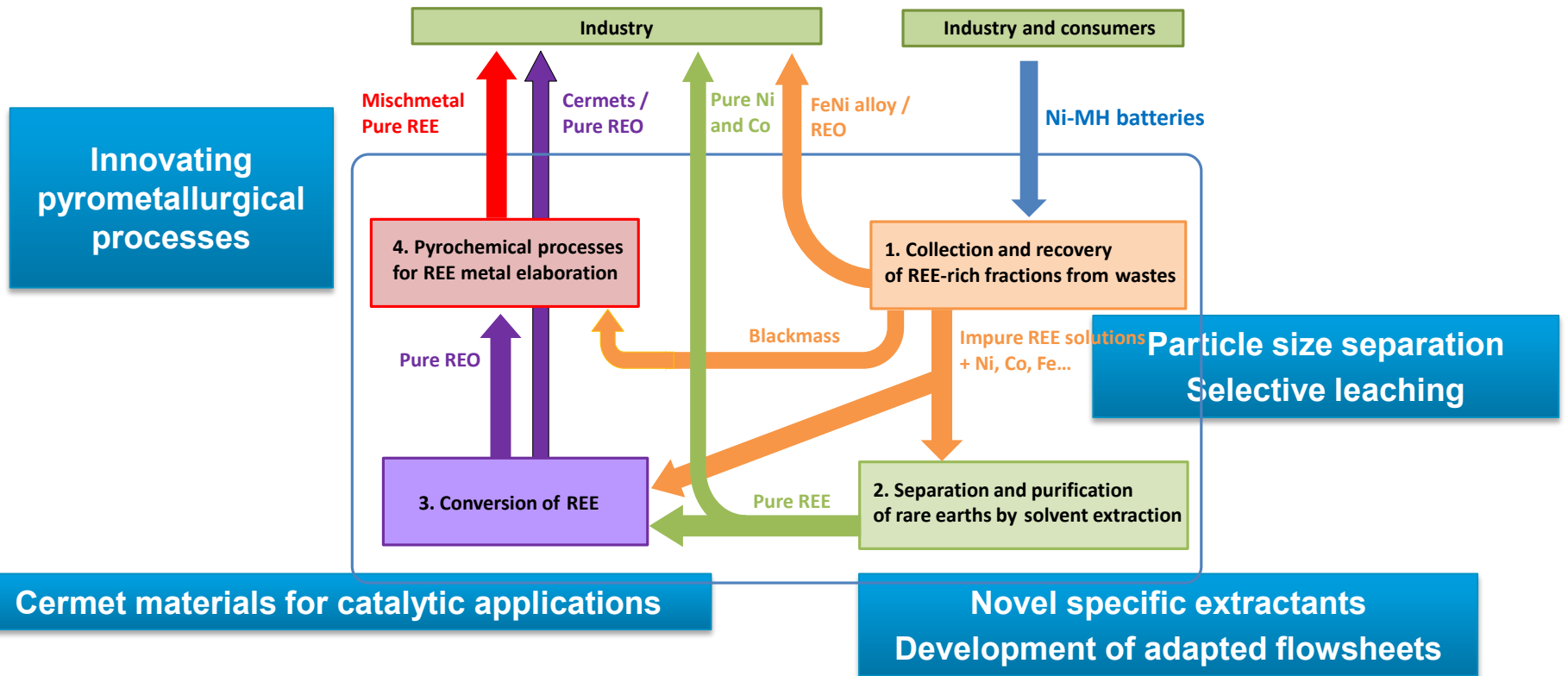
## ➤ Neodymium electrochemical behaviour in LiCl-LiF (550°C-650°C)

- Addition of LiF in LiCl stabilizes  $\text{Nd}^{3+}$
- $\text{Nd}^{2+}/\text{Nd}^0$  transition tends to disappear (not completely)
- Electrolysis tests show that Nd deposition in LiCl-LiF give dendritic deposition with higher CE than LiCl-KCl ( $70 < \text{CE} < 90$ )
- Best CE are obtained at 550°C ( $4\text{wt}\% < \text{Nd}^{3+} < 6\text{ wt}\%$ )



**Nd deposit**

# Innovative solutions for REE recycling from Ni-MH batteries



**Integration of the REE recovery step in the global battery recycling process**  
Simple, compact flowsheets producing value-added products (cermet, mischmetal...)



## Acknowledgments

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### **LGC**

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# Thank you for your attention

Commissariat à l'énergie atomique et aux énergies alternatives  
Nuclear Energy Division  
Research Department on Mining and Fuel Recycling Processes  
Centre de Marcoule | BP17171 | 30207 Bagnols-sur-Cèze Cedex

[eugen.andreiadis @ cea.fr](mailto:eugen.andreiadis@cea.fr)

Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019



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