

DE LA RECHERCHE À L'INDUSTRIE



# A combined process for the selective rare earth recovery and separation from used permanent magnets

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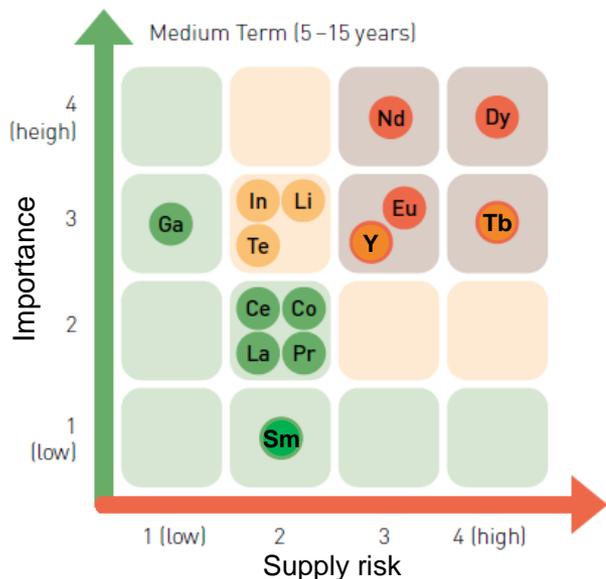
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# REE production, supply risk and applications

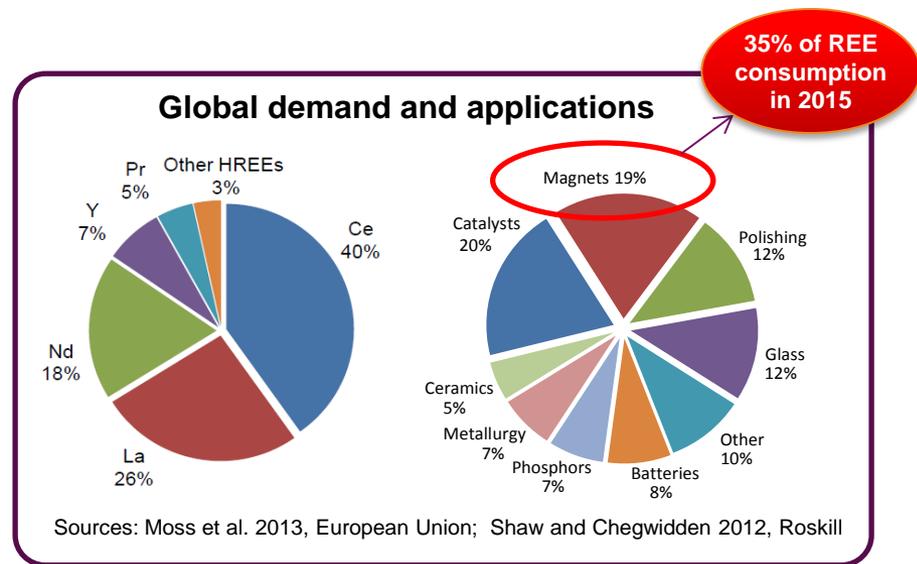


Source: report US Department of Energy 2010

- Rare earth elements (REE) = **Critical raw materials** for European economy ?
- Global REO production 125 000 T/yr
- Significant **price drop** in 2015 (excess supply, illegal mining)
- RE **demand growing**, especially for magnets (**Nd, Dy most critical**)
- Production chain concentrated in China (mining, separation, downstream manufacturing, R&D capacity): **85% world REO supply**
- All **heavy REE production** controlled by China
- Currently **no European mine** in operation (Norra Karr lease cancelled)

- Most NTE applications require **pure elements**, but REE extracted as a **group**
- Earth **abundance decreases** along the series
- Most abundant elements have **few applications**

**Need to diversify supply sources especially for heavy, critical elements (Dy)**



# REE recycling: closing the materials loop

## Advantages of recycling

- Target the **most critical** rare earths and address the balance problem
- No issues with **radioactive elements** (235U, 238U, 232Th)
- Lower environmental footprint



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

## Challenges

- Very low **recycling rates** for REE
- Insufficient and untargeted **collection** of waste sources (such as WEEE)
- Difficult recovery of REE-containing fractions (design, coatings, adhesives)
- Difficult **separation of individual REE**
- Optimization of re-processing technologies
- **Economic incentive**

## Opportunities

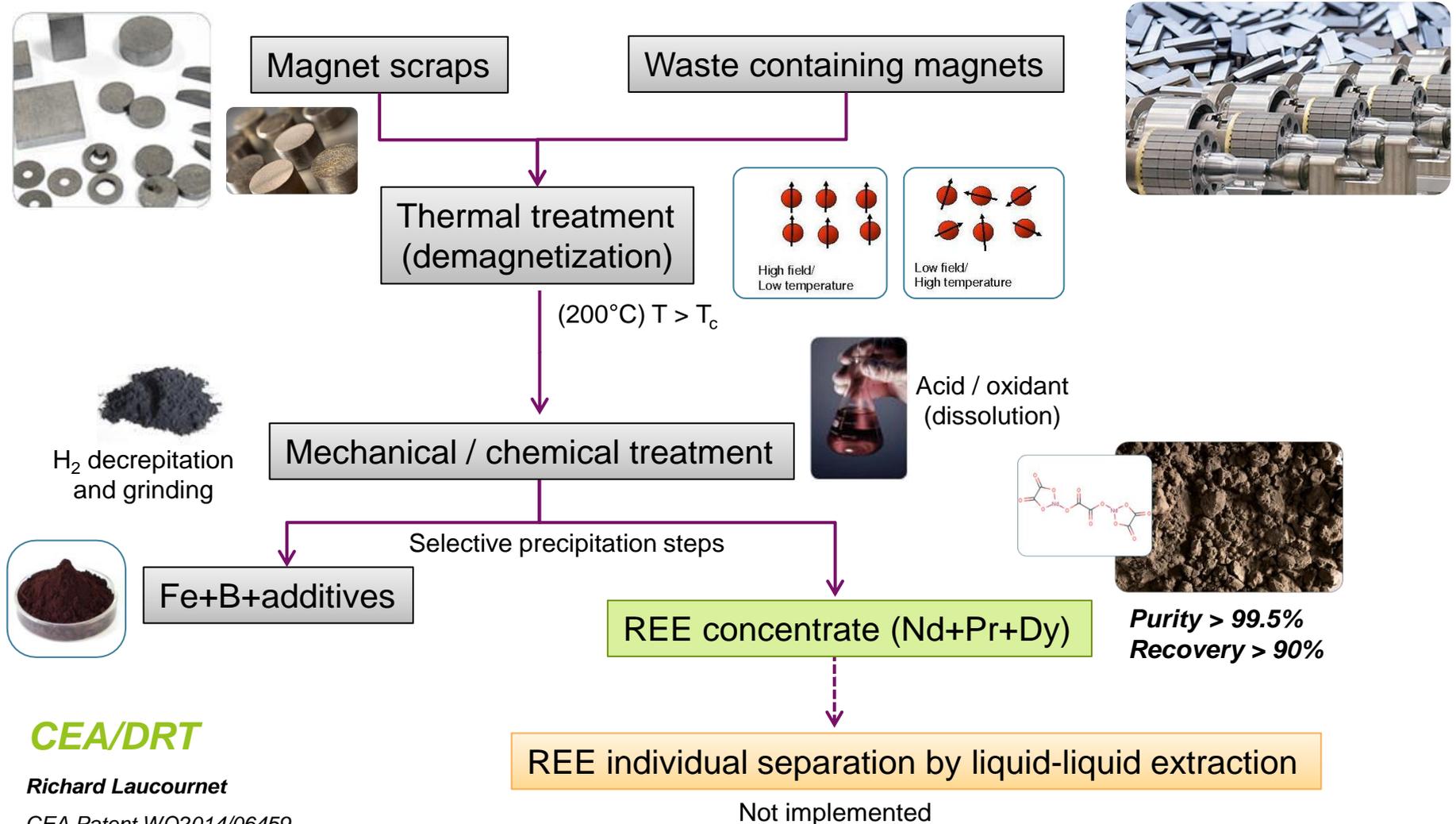
- Competences and expertise of the **European recycling industry**
- Leveraging on the **urban mine**
- Economic and environmental **impact**



## Recycling NdFeB permanent magnets

- Most important market, driving REE demand (NTE)
- **High REE concentration** (25% Nd, 5% Pr, 2-8% Dy)
- Immediate **availability**

# Scheme for REE recovery and purification

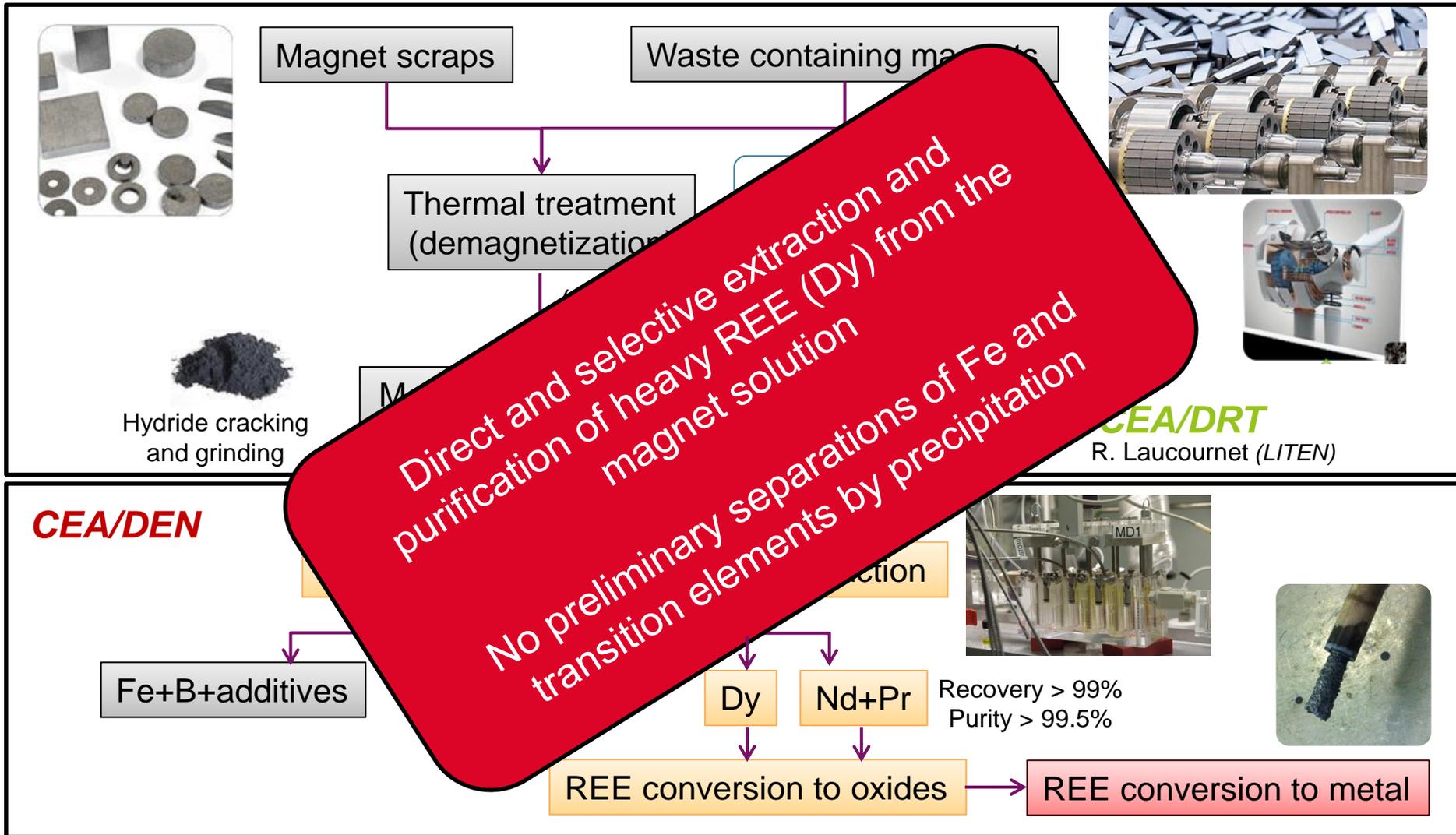


**CEA/DRT**

Richard Laucournet

CEA Patent WO2014/06459

# RECAPE Process

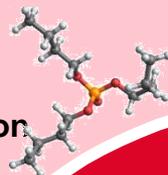


Direct and selective extraction and purification of heavy REE (Dy) from the magnet solution

No preliminary separations of Fe and transition elements by precipitation

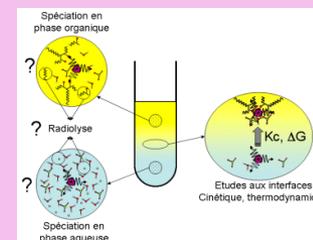
# A well-tries approach to process development

- Ligand design
- Computational chemistry
- Synthesis and characterization of extracting molecules
- Optimization of extractant formulation



**Extractant system selection**

- Measurement of distribution coefficients
- Understanding of extraction mechanisms (affinity, selectivity)
- Structure-activity relations



**Specific objectives,  $D$ ,  $SF$ , % Recovery**

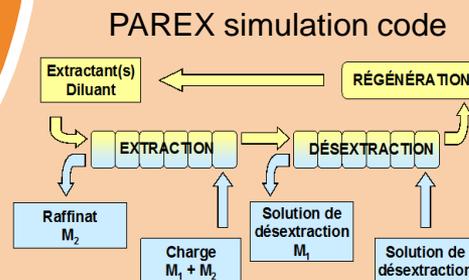
**Molecular scale chemistry**

**Integrated experiments**



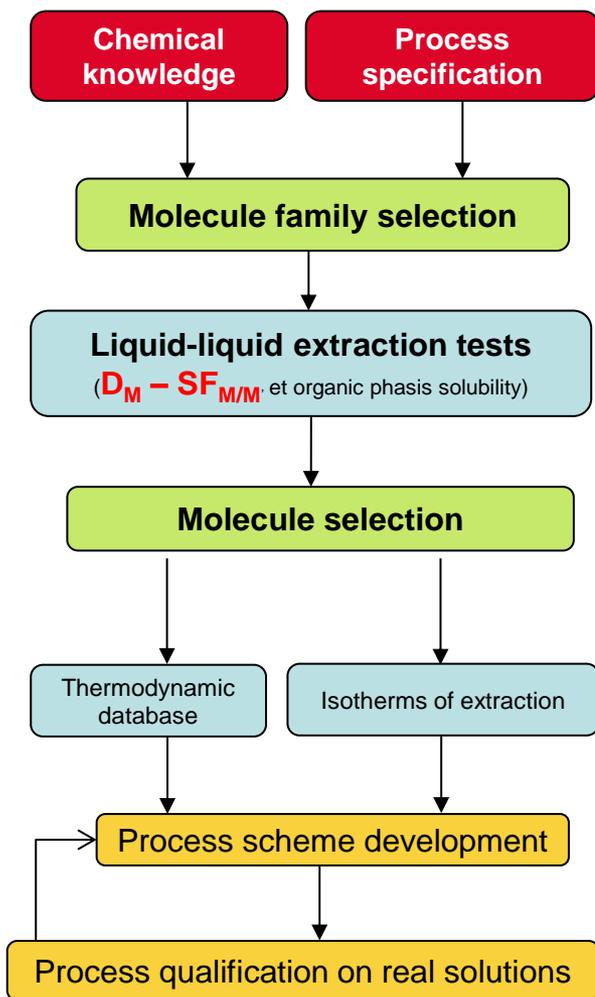
- Qualification of the process on real solutions
- Industrial extrapolation using simulation

**Process modelling**

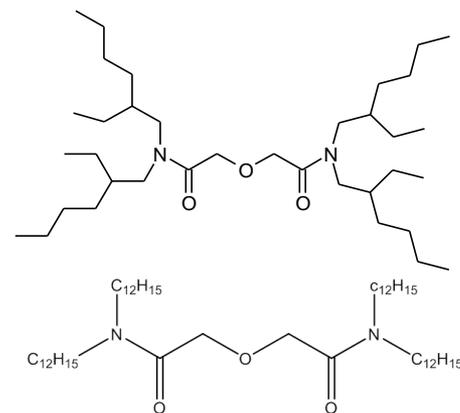
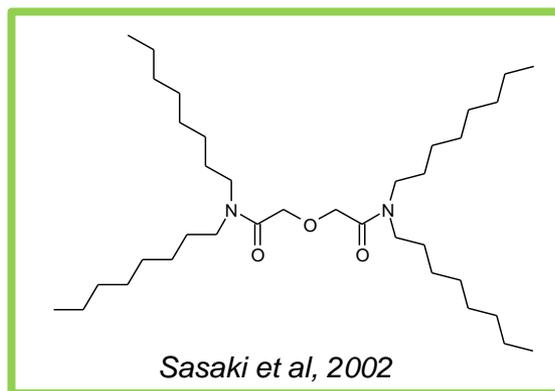


- Development of extraction models and specific flowsheet
- Optimization of the separation

# Selection and evaluation of the extractant system



- Screening of several extracting molecules available at the laboratory
- Selection of diglycolamide (DGA) extractants for selective Dy extraction versus Fe, B, Ni, Co and light REE

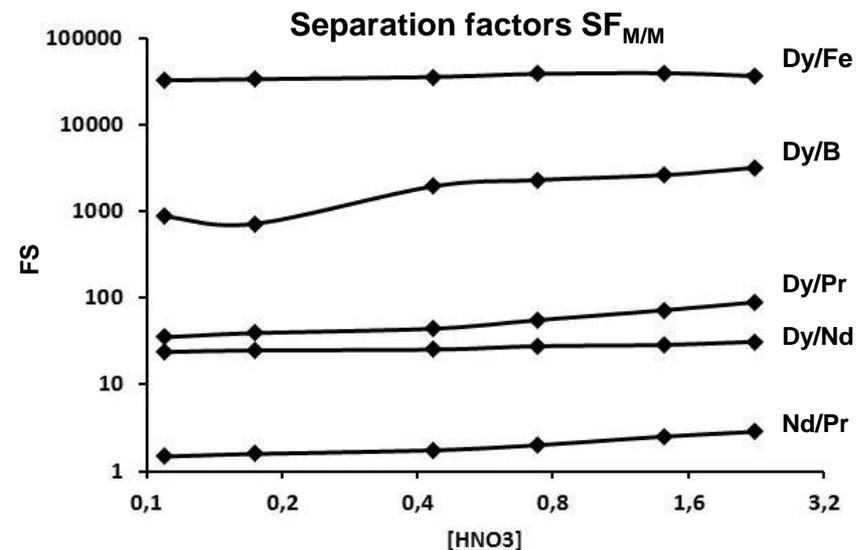
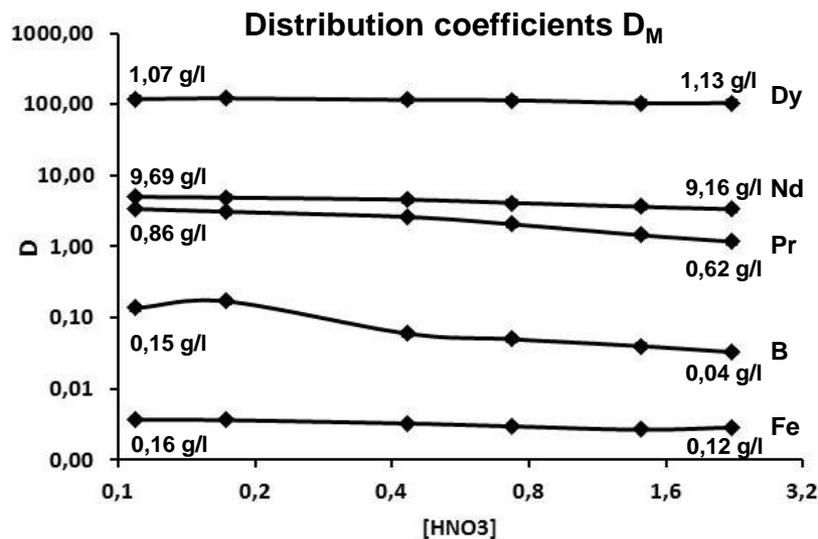


- Selection of **TODGA / TPH** as solvent
- Addition of 5% octanol to prevent 3<sup>rd</sup> phase formation at high REE loading
- ➡ **0.2M TODGA + 5% octanol / TPH**

# RE Separation Process Development

- 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 Dy** at low acidity (pH 3) and high temperature (45-50°C)

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

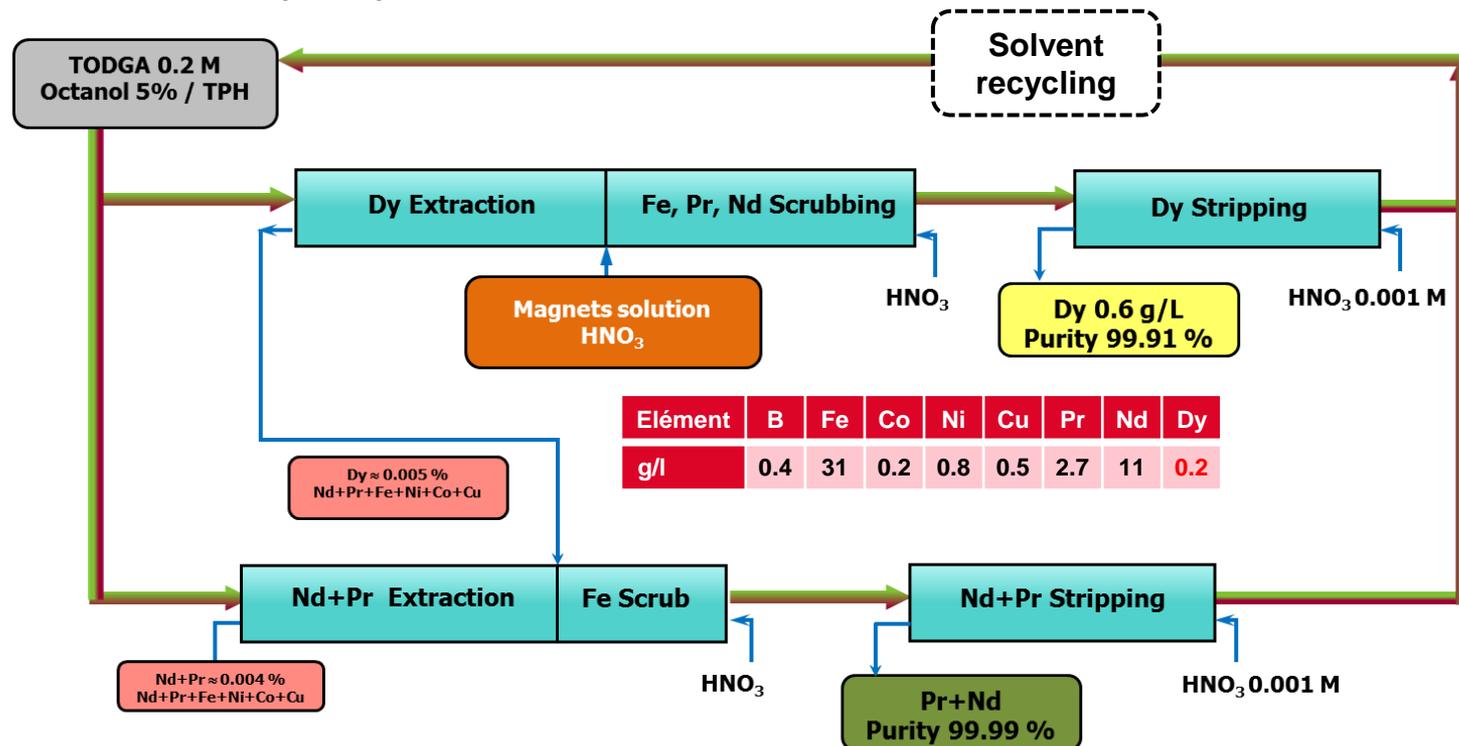


- **Confirmation** of the potential of TODGA for selective Dy recovery from NdFeB magnet solutions



# Development of the separation process flowsheet

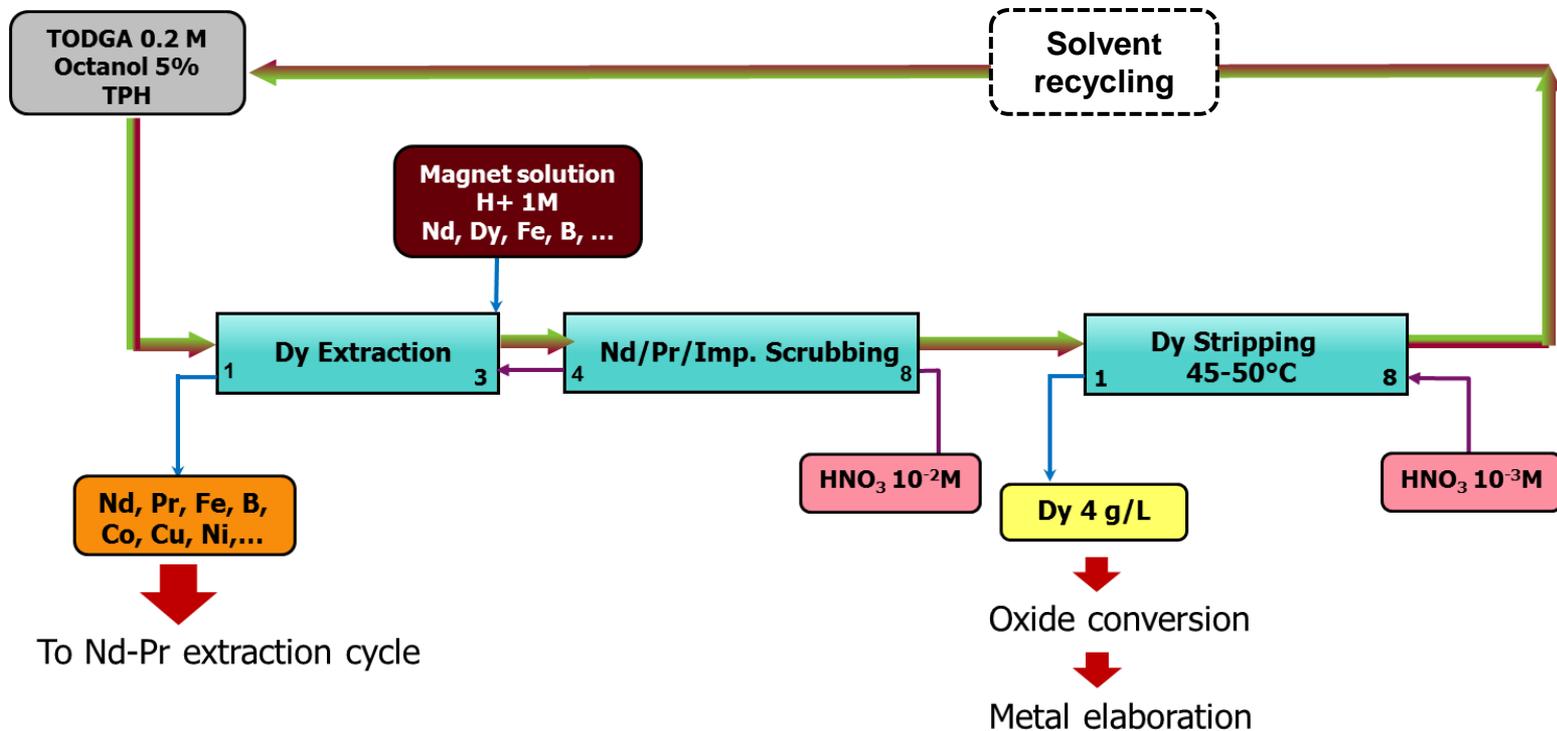
- Calculation of flow sheets in 1 or 2 cycles to recover Dy and Nd+Pr with theoretical purities > 99.5% in a limited number of stages
- Effective and compact process



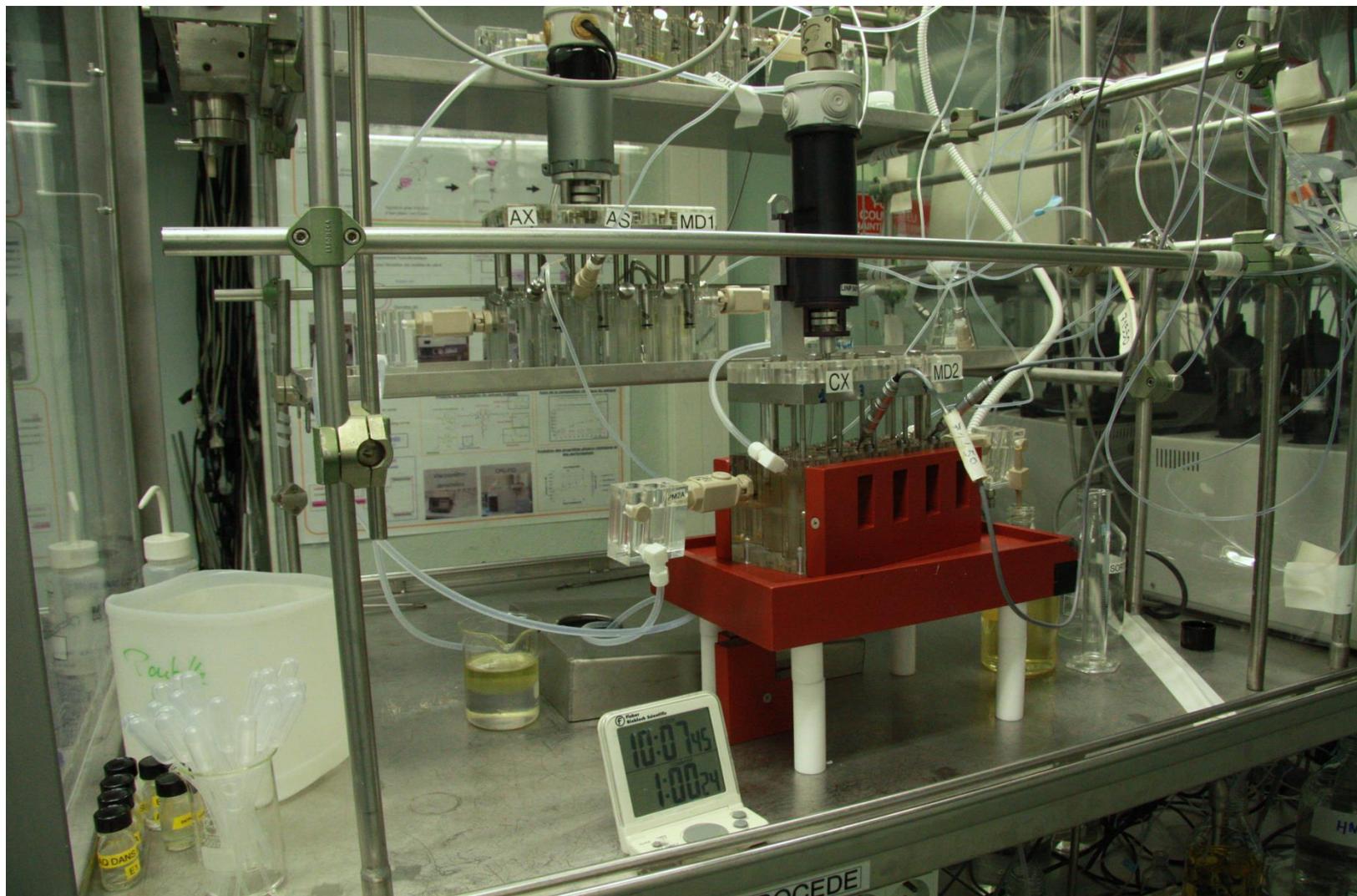
■ Patent application 1459023: *Procédés de récupération sélective de terres rares présentes dans des phases aqueuses acides issues du traitement d'aimants permanents usagés ou rebutés* »

# Pilot demonstration test on used magnets

- Solution of NdFeB magnets in  $\text{HNO}_3$  provided by CEA/DRT/LITEN
- Test in 16 stages of lab-scale mixer-settlers on PROUST platform (CEA / Marcoule)
- 1-cycle flowsheet for selective Dy recovery
- Nd & Pr collected in the raffinate for further 2<sup>nd</sup> cycle process

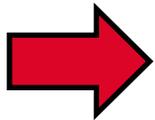


# Pilot demonstration test on used magnets



# Pilot demonstration test on used magnets

- Test runned for 20 hours with solvent recycling (steady state reached)
- Very good hydrodynamic behavior
- UV-vis on-line analysis (for Nd) and ICP-AES measurements for Dy, Nd, Fe
- ➔ **Quantitative recovery of Dy** with very high purity
  - **Dy recovery > 99.7% with purity > 99.99%**
    - Loss of only 1.7 mg/L of Dy in the raffinate
  - Production of Dy concentrated from 0.69 to 4.05 g/L (×6)



**Dy 4.1 g/L**  
 Nd  $\approx$  0.2 mg/L  
 Al  $\approx$  0.2 mg/L  
 Fe  $\approx$  0.03 mg/L  
 Co, Cu, B, ... < 0.03 mg/L

- Conversion of Dy to REO and metals in progress



**Objective:** pyrometallurgical conversion of the separated REE into high purity RE metals.

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

to optimize the experimental condition:

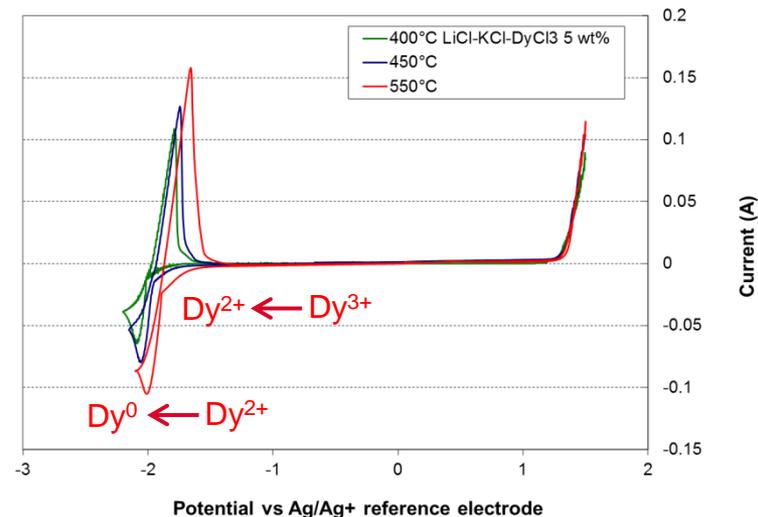
- Salt composition
- Temperature
- Dy concentration
- Current and current density



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

- Metal adherence
- Faradic yield
- Product purity
- Cell materials compatibility

Cyclic voltammetry in molten chloride salt

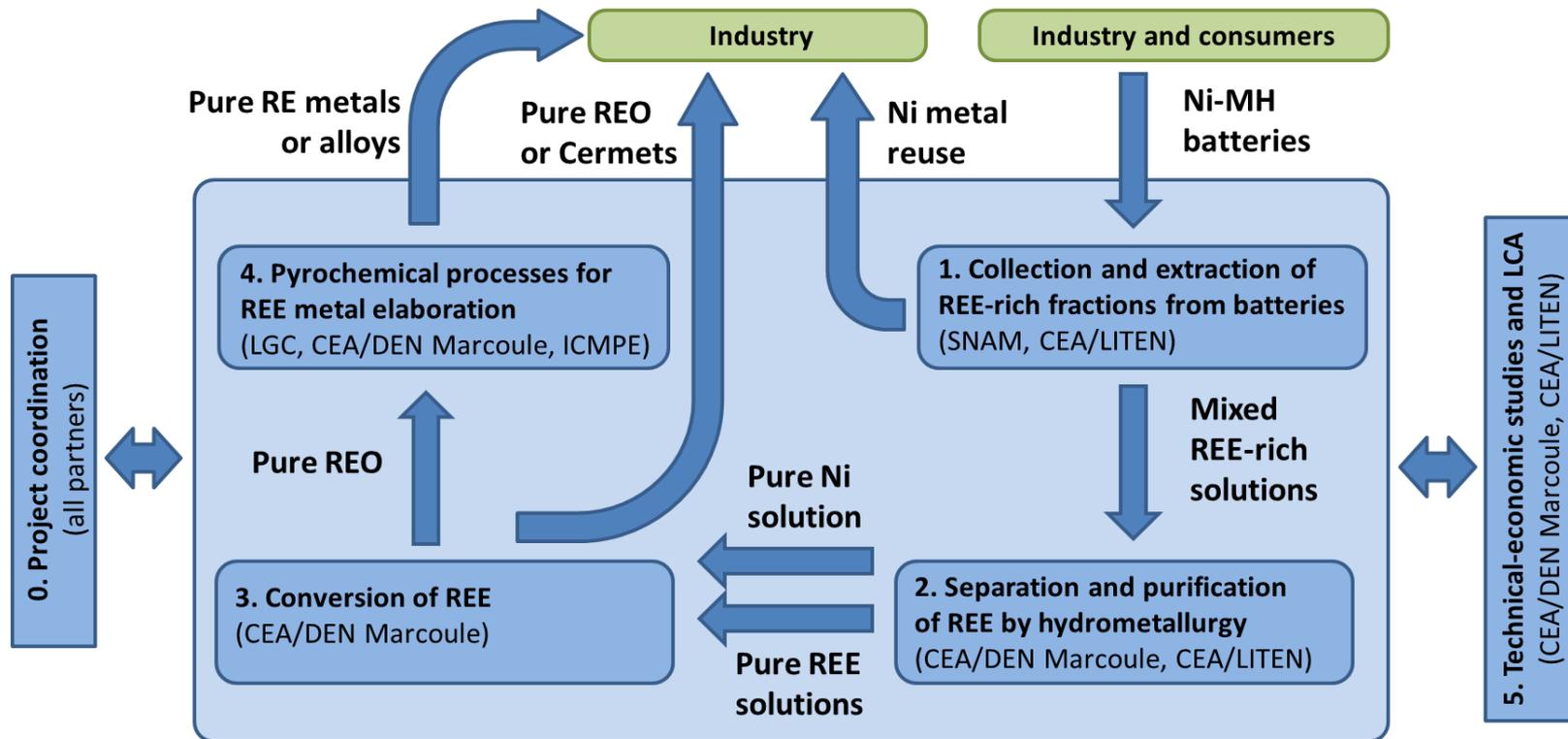


**Gram-scale production of metallic Dy**  
Faradic efficiency ≈ 80%

# Conclusions and outlook

- Development of a **full RE separation process** from used permanent magnets
  - Fruitful collaboration between CEA / DRT (magnet fabrication, front-end recycling process) and CEA / DEN (SX separation, RE conversion)
  - Process patented for Dy and Nd recovery from permanent magnets
- Demonstration of the **scientific feasibility of Dy recovery by SX** without preliminary separation of Fe, B and the coating elements by precipitation
- **Pilot scale production** of highly pure Dy from real used magnets
  - Experiments in progress on Dy and Nd-Pr conversion to oxides (oxalic precipitation) and to metals (electrolysis in molten salts)
- Scale-up and **technical-economic study** of the process allowed the evaluation of the process cost at an industrial scale
- Development of recycling processes for other WEEE or valuable materials
  - ANR « REPUTER » project on the recycling of REE from **spent Ni-MH batteries**

## 2 M€ budget REPUTER project started in 2016



## Acknowledgments

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# THANK YOU FOR ATTENTION

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