

# A combined hydro- and pyrometallurgical process for REE recovery from used permanent magnets

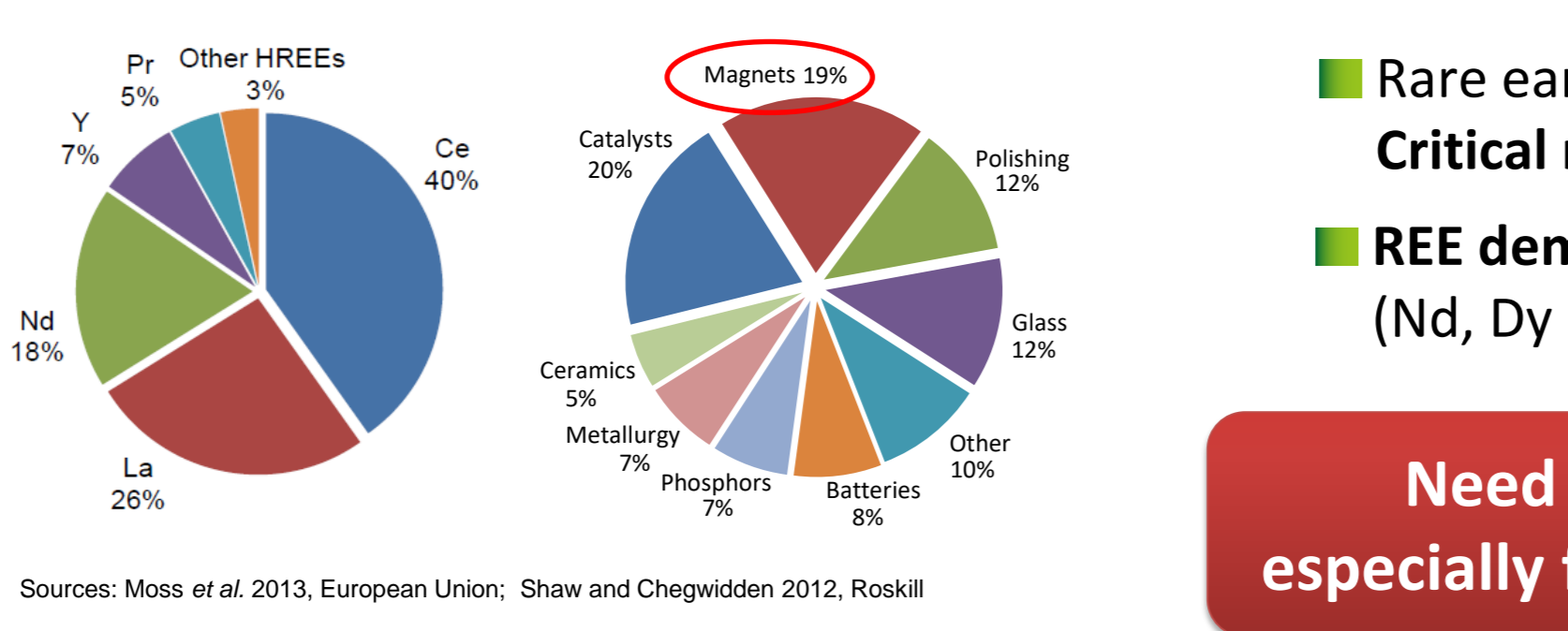
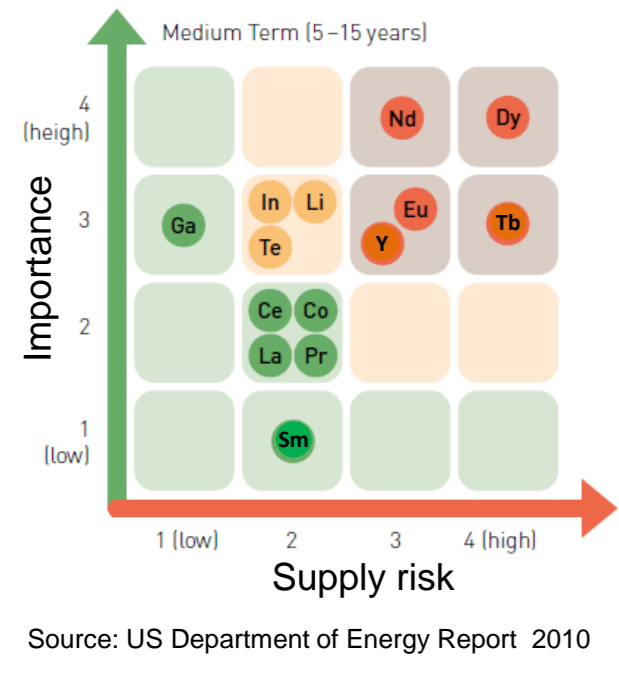
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## REE recycling: closing the materials loop



- Rare earth elements (REE) = **Critical raw materials** for European economy
- REE demand growing, especially for magnets (Nd, Dy most critical)

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

### Advantages of recycling

- Target the **most critical** rare earths
- No issues with **radioactive elements**
- Lower environmental footprint

### Challenges of recycling

- Low recycling rates** for REE (< 1%)
- Waste collection (such as WEEE)
- Individually separate REE**

### Opportunities

- Expertise of **European recycling actors**
- 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

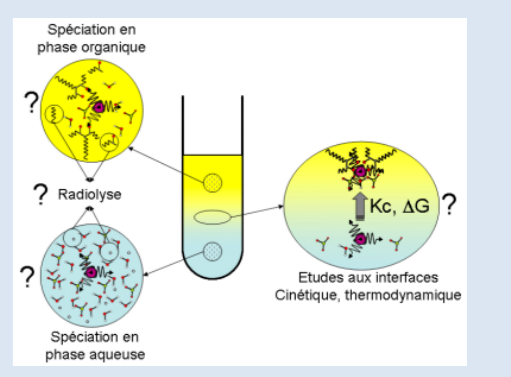


## Our approach to process development

- Ligand design
- Synthesis of extracting molecules
- Optimization of extractant formulation



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



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

**Extractant system selection**

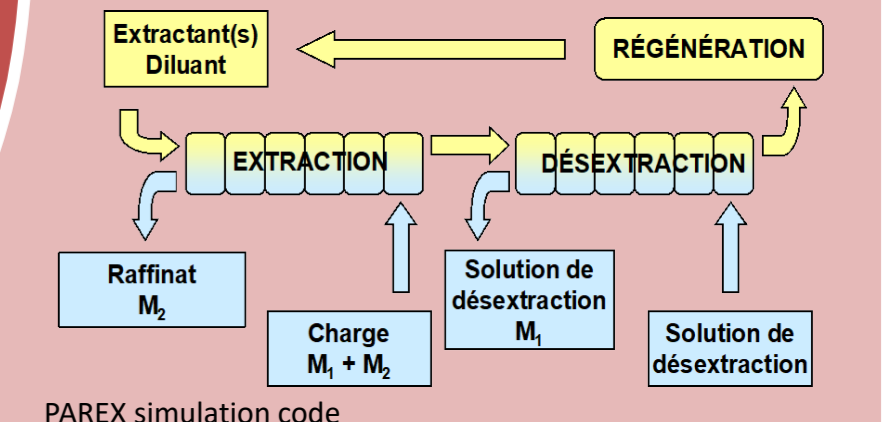
**Molecular scale chemistry**



**Integrated experiments**

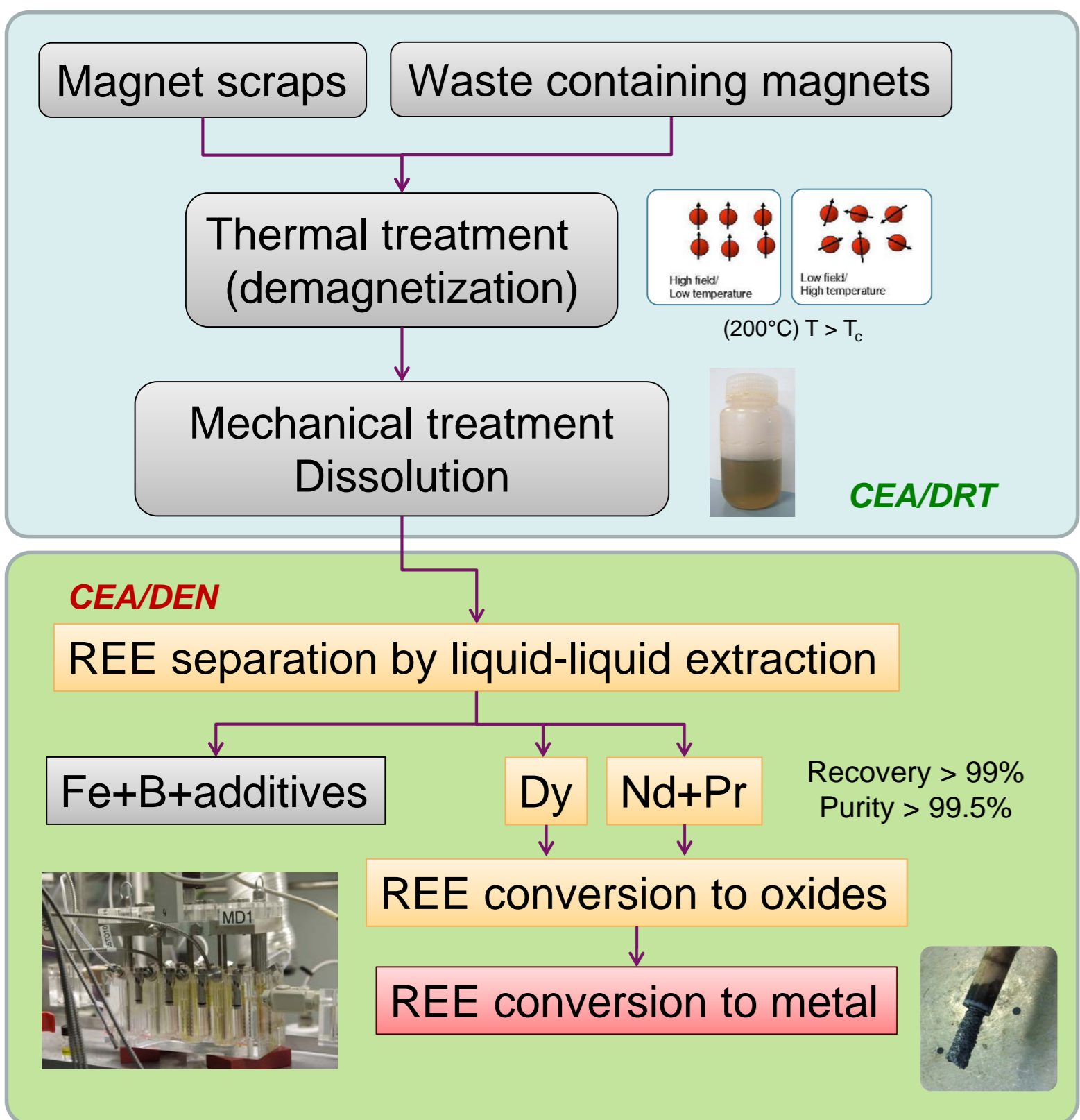
**Process modelling**

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



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

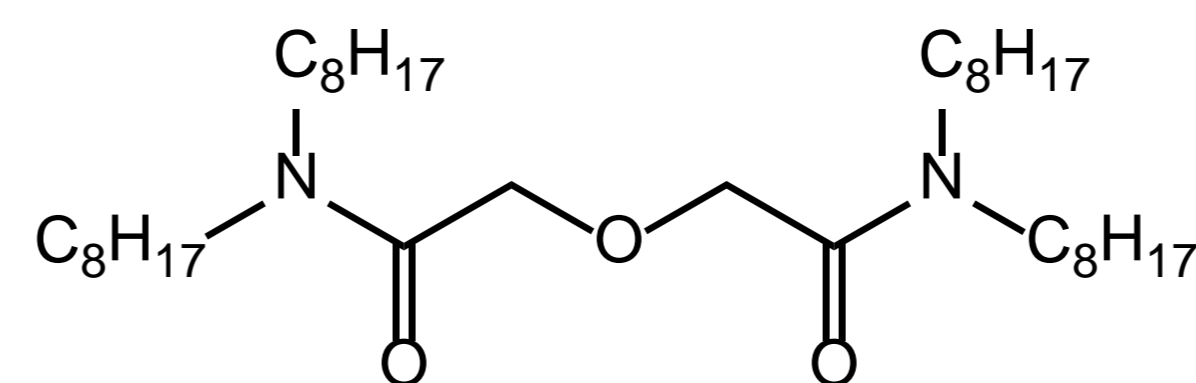
## The RECAPE process



- Direct and selective extraction and purification of heavy REE (Dy)** from the magnet solution
- No preliminary separation of Fe and transition elements by precipitation**

## Selection and evaluation of the extractant system

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

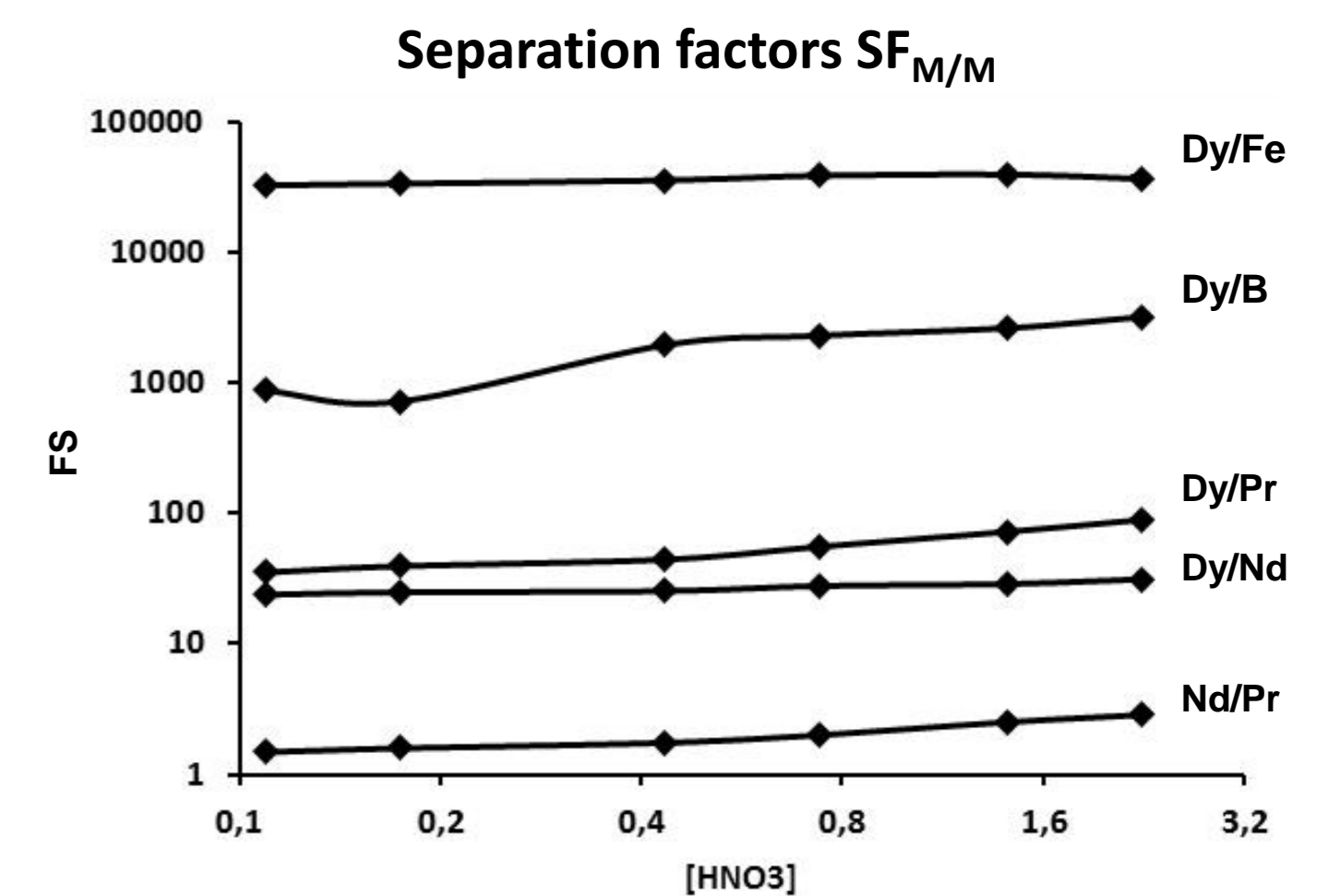
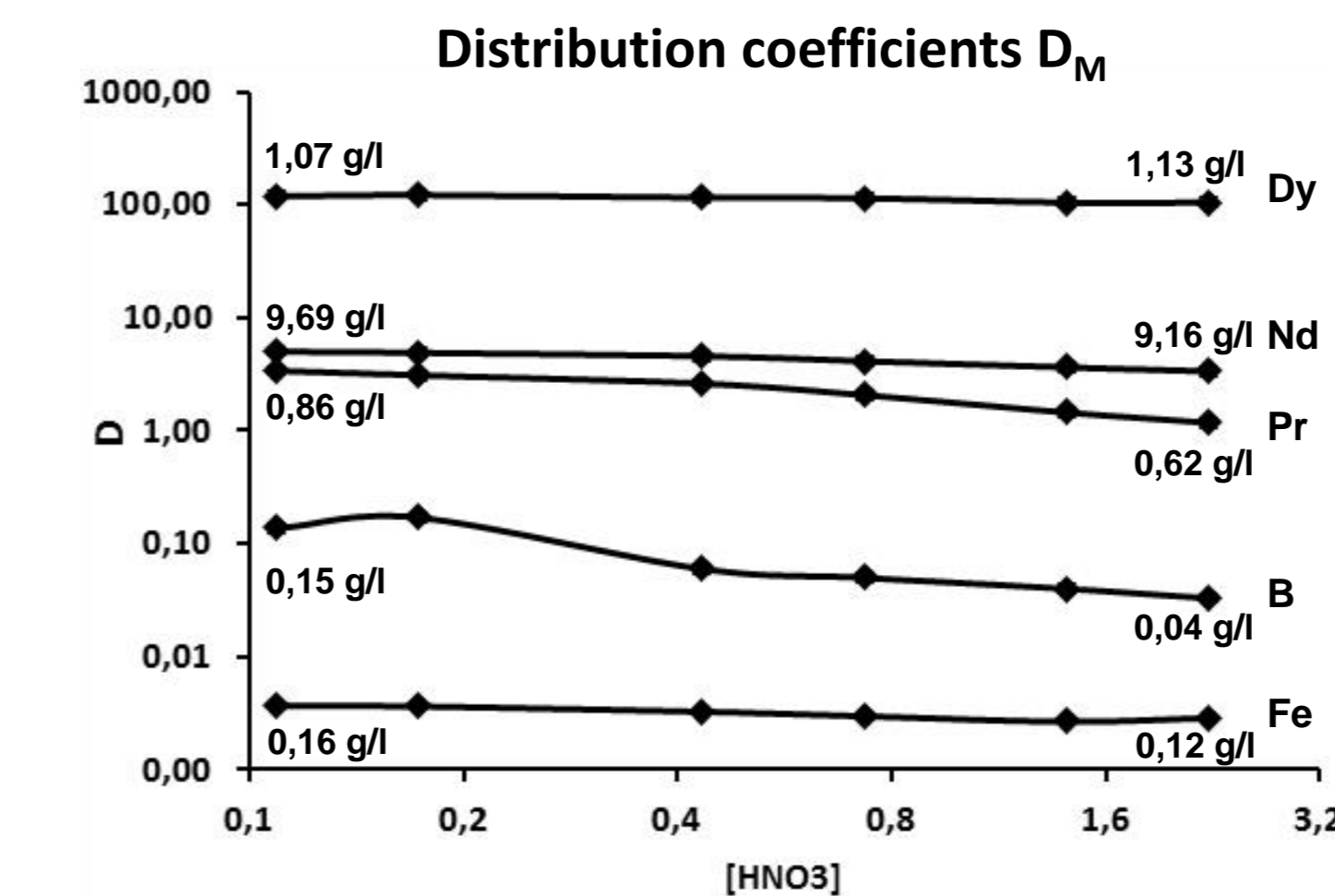


Solvent formulation: **0,2M TODGA + 5% octanol / TPH**

- Tests on **synthetic and genuine magnet solutions** in nitric acid

Élément	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

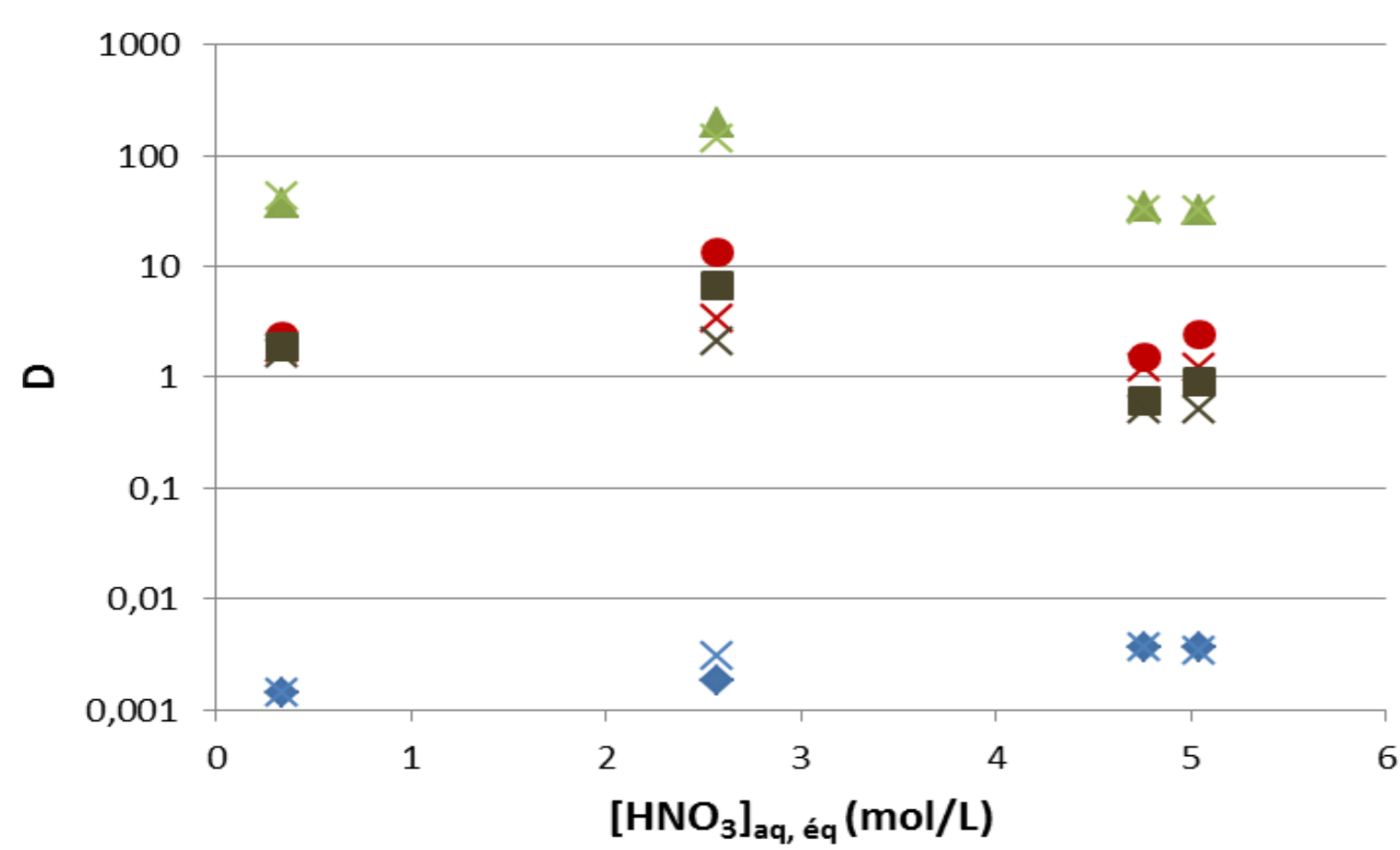
- Quantitative extraction of Dy (D>100)**
- Efficient separations of REs / transition metals (Fe, Co, Ni...)** and RE/RE in a large range of acidity (0.4 to 5M)
- No 3<sup>rd</sup> phase formation** in processes conditions
- Quantitative stripping of REE** at low acidity (pH 3) and high temperature (45-50°C)



## Process modelling

- Elaboration of a **phenomenological model** from experimental batch data
- Representation of distribution equilibria  $\text{HNO}_3\text{-Oct}$ ,  $\text{HNO}_3\text{-TODGA}$ ,  $\text{Ln-NO}_3\text{-TODGA}$

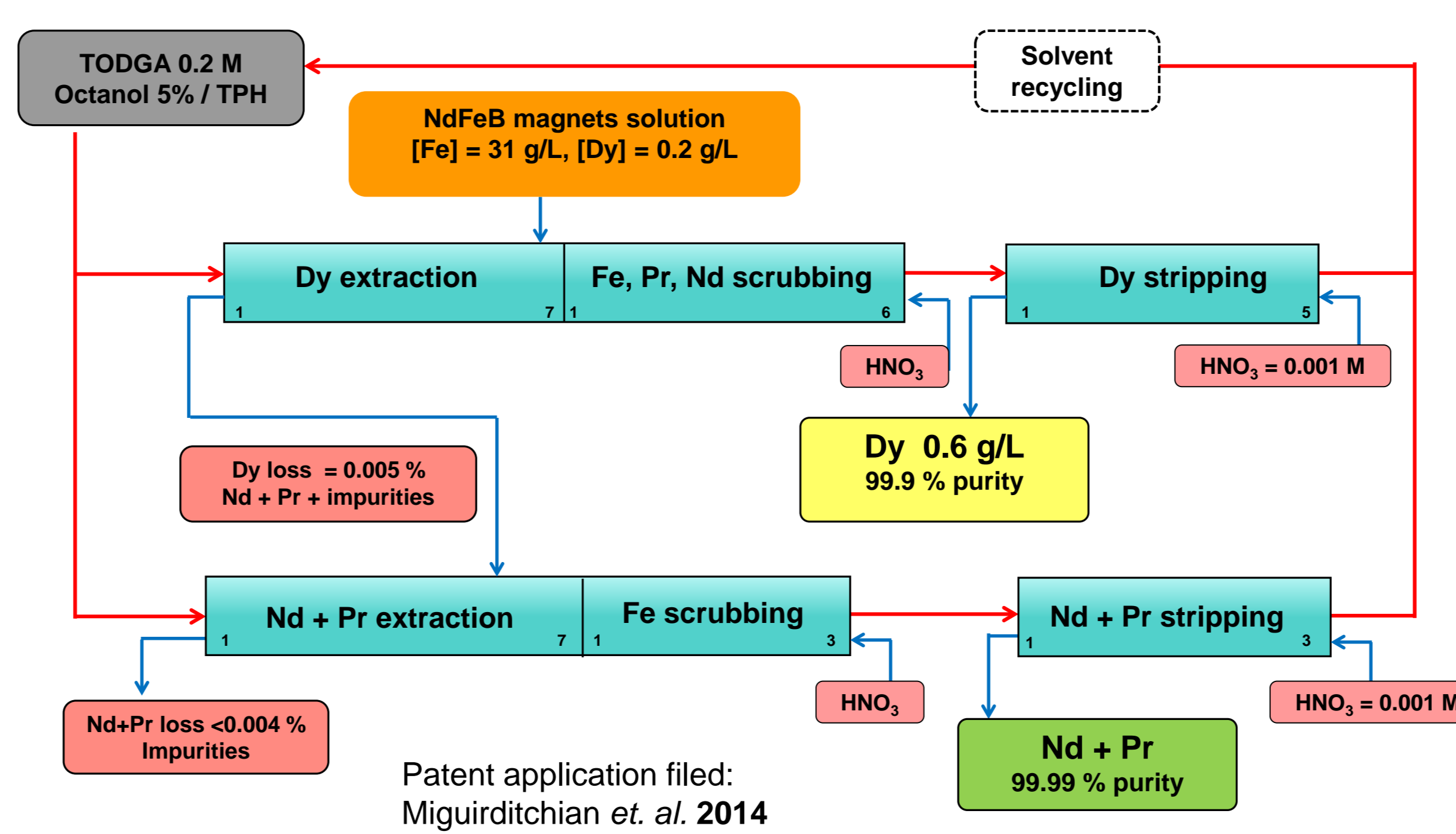
$$K'_n = \frac{[TR(NO_3)_3, TODGA_n]}{Y_{TR(NO_3)_3} \cdot [TR(NO_3)_3]^3 \cdot [TODGA]^n}$$



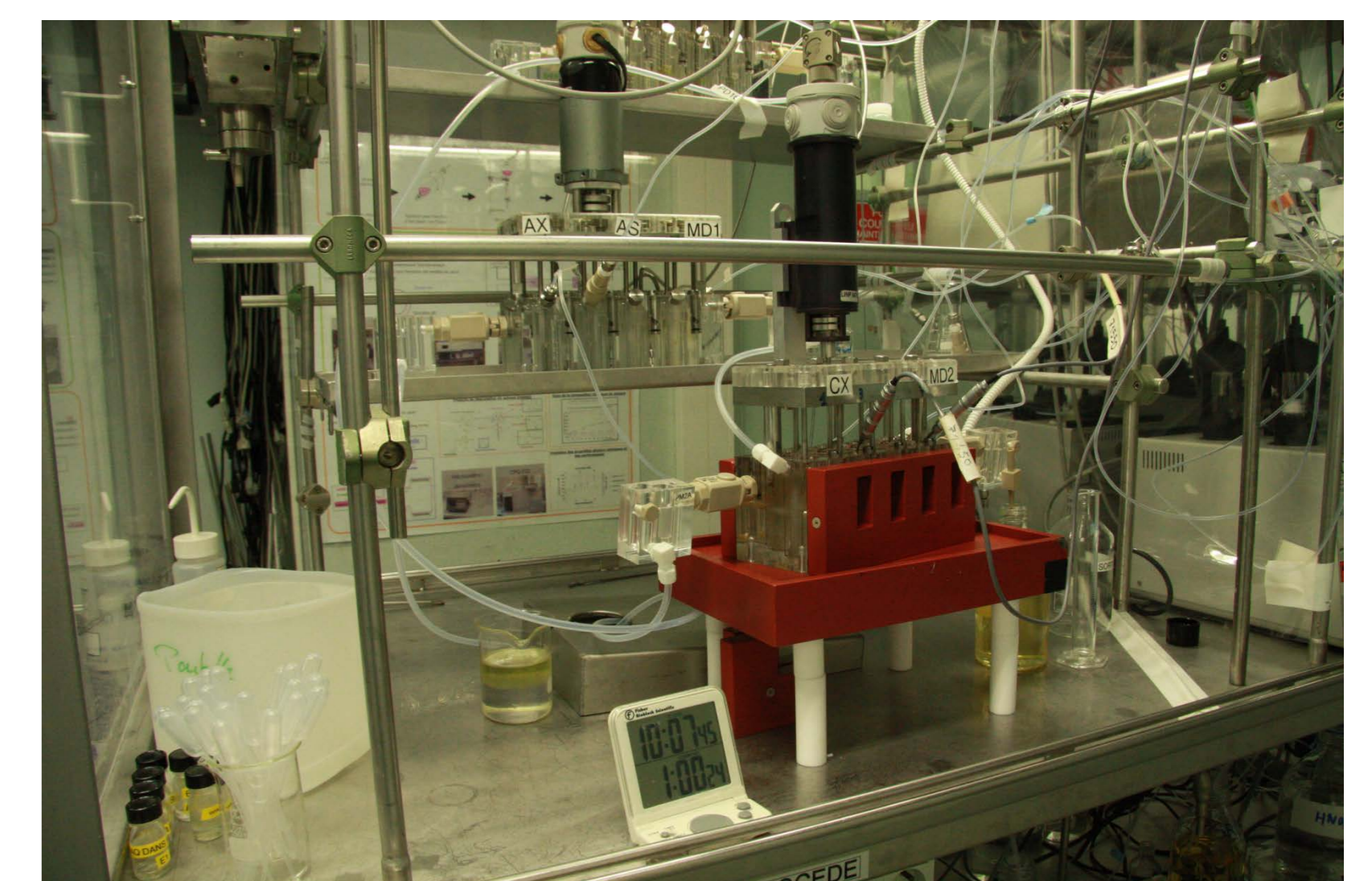
- Activity coefficients** taken into account in aqueous phase
- Good agreement** between extraction experiments and calculated values for both synthetic and real solutions
- Implementation of the model in the **CEA PAREX simulation code** and calculation of flow-sheets

## Development of the separation process flowsheet and pilot demonstration

- 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 in two steps for Dy (step 1) and Nd+Pr (step 2) separation from REE solutions**



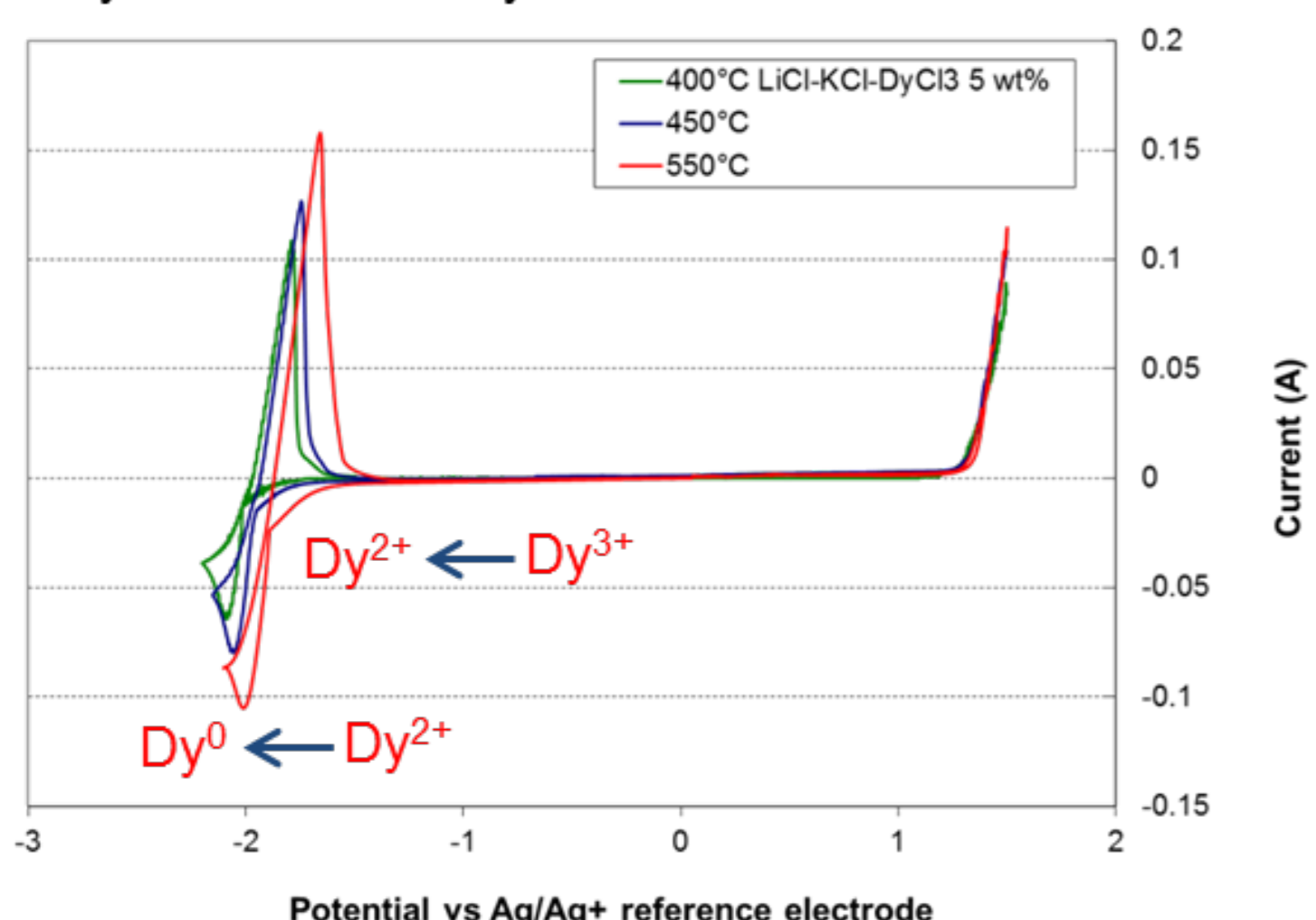
- Very good hydrodynamic behavior
- UV-vis on-line analysis (for Nd) and ICP-AES measurements for Dy, Pr, Nd, Fe
- Production of gram-scale Dy at **4.2 g/L**

**Quantitative recovery of Dy with very high purity**  
Dy recovery > 99% with purity > 99.9%

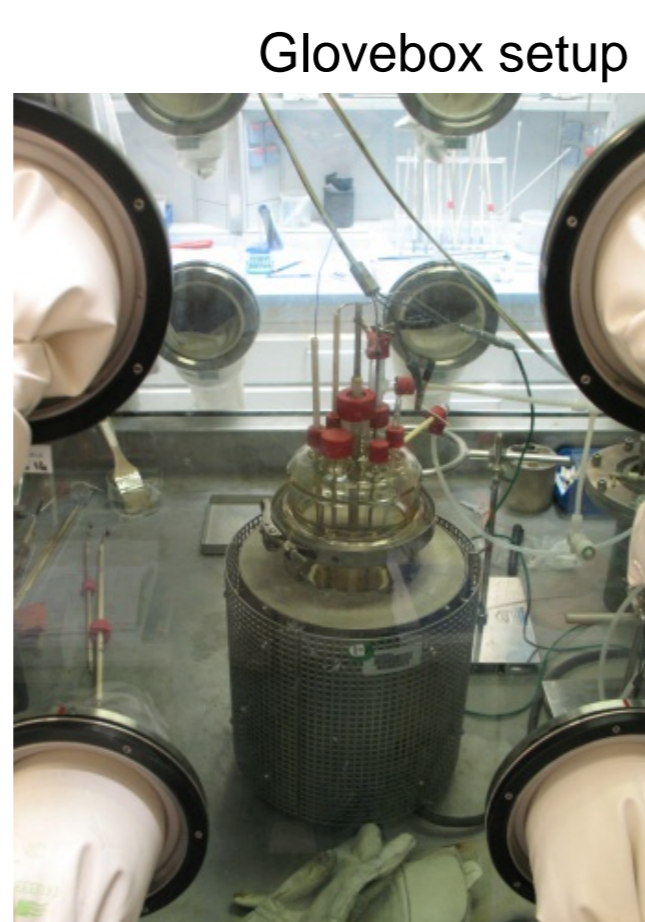
## Pyrometallurgical process for metal elaboration

- Pyrometallurgical conversion of the separated REE into high purity RE metals
- Use of transient electroanalytical techniques (voltammetry reversal chronopotentiometry, chronoamperometry...) to optimize the conditions
- Metal deposition tests to evaluate the process efficiency

Cyclic voltammetry in molten chloride salt



- Shiny metallic deposits
- Faradic efficiency ≈ 80%



## Conclusions

- Development of a **full RE separation process** from used permanent magnets
  - Collaboration between **CEA/DRT** (magnet fabrication, front-end recycling process) and **CEA/DEN** (SX separation, RE conversion) in the frame of the **NTE programme**
- Demonstration of the **scientific feasibility of Dy recovery by SX** without preliminary separation of Fe, B and the coating elements by precipitation
- Production of **pure Dy from real used magnets** during the pilot tests
  - Experiments in progress on Dy and Nd-Pr conversion to oxides (oxalic precipitation) and to metals (electrolysis in molten salts)
  - Analysis on RE oxides and Dy metal to check the purity of the final products
- Optimization of the model and the process flow-sheet
- Scale-up** of the process and **techno-economic study** are in progress to evaluate the cost of such process at an industrial scale