



**HAL**  
open science

## Development of a new process for the selective rare earth recovery from used permanent magnets

D. Hartmann, M. Miguirditchian, V. Haquin, E. Andreiadis, J. Serp, R. Laucournet, R. Blank

### ► To cite this version:

D. Hartmann, M. Miguirditchian, V. Haquin, E. Andreiadis, J. Serp, et al.. Development of a new process for the selective rare earth recovery from used permanent magnets. Permanent Magnets and their applications (REPM 2016), Aug 2016, Darmstadt, Germany. cea-02438704

**HAL Id: cea-02438704**

**<https://cea.hal.science/cea-02438704>**

Submitted on 27 Feb 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DE LA RECHERCHE À L'INDUSTRIE



# Development of a new process for the selective rare earth recovery from used permanent magnets

**D. Hartmann**, M. Miguirditchian, V. Haquin,  
E. Andreiadis, J. Serp (1)  
R. Laucournet (2)  
R. Blank (3)

*(1): CEA, Atomic Energy and Alternative Energies Commission, DEN, DRCP, RadioChemistry and Processes Department, Marcoule, France*

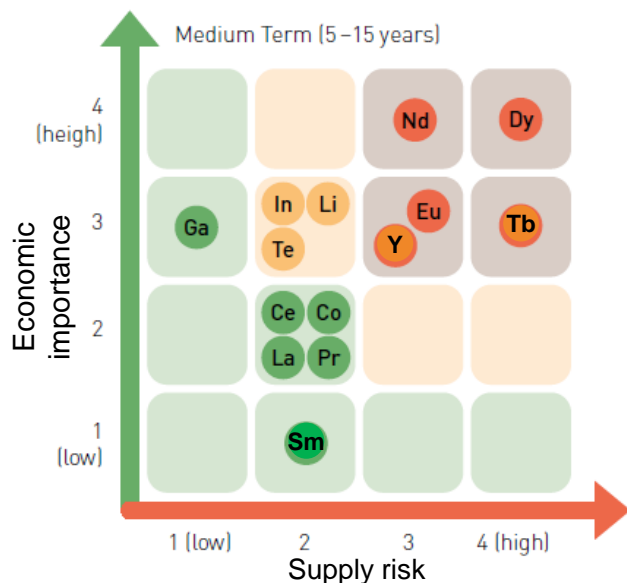
*(2): CEA, DRT, LITEN, Laboratory for Innovation in New Energy Technologies and Nanomaterials, Grenoble, France*

*(3): Vacuumschmelze, Permanent Magnets, Research & Development, Hanau, Germany*



- 1. Introduction: REE supply risk and need to recycle**
- 2. RE Separation Process Development**
- 3. Technical-economic assessment**
- 4. Conclusions and Outlook**

# 1. REE production, supply risk and applications



Source: report US Department of Energy 2010

- Rare earth elements (REE) = **Critical raw materials** for European economy
- 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 Kärr lease suspended until additional data are provided by TASMAN
  - ❖ Torrenueva project in Spain by QUANTUM faces opposition

- Most NET applications require **pure elements**, but REE extracted as a **group**
- Most abundant elements have **few applications**

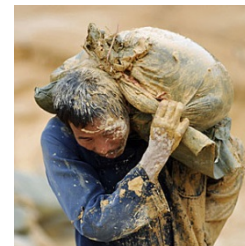
**Permanent magnets:  
35% of REE consumption in 2015**

**Need to diversify supply sources especially for most critical elements (Nd +Dy)**

# 1. 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 turbine

## Challenges

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

## Opportunities

- Competences and expertise of the **European recycling industry**
- Enhancing the use of the **urban mine** resource
- Economic and environmental **impact**

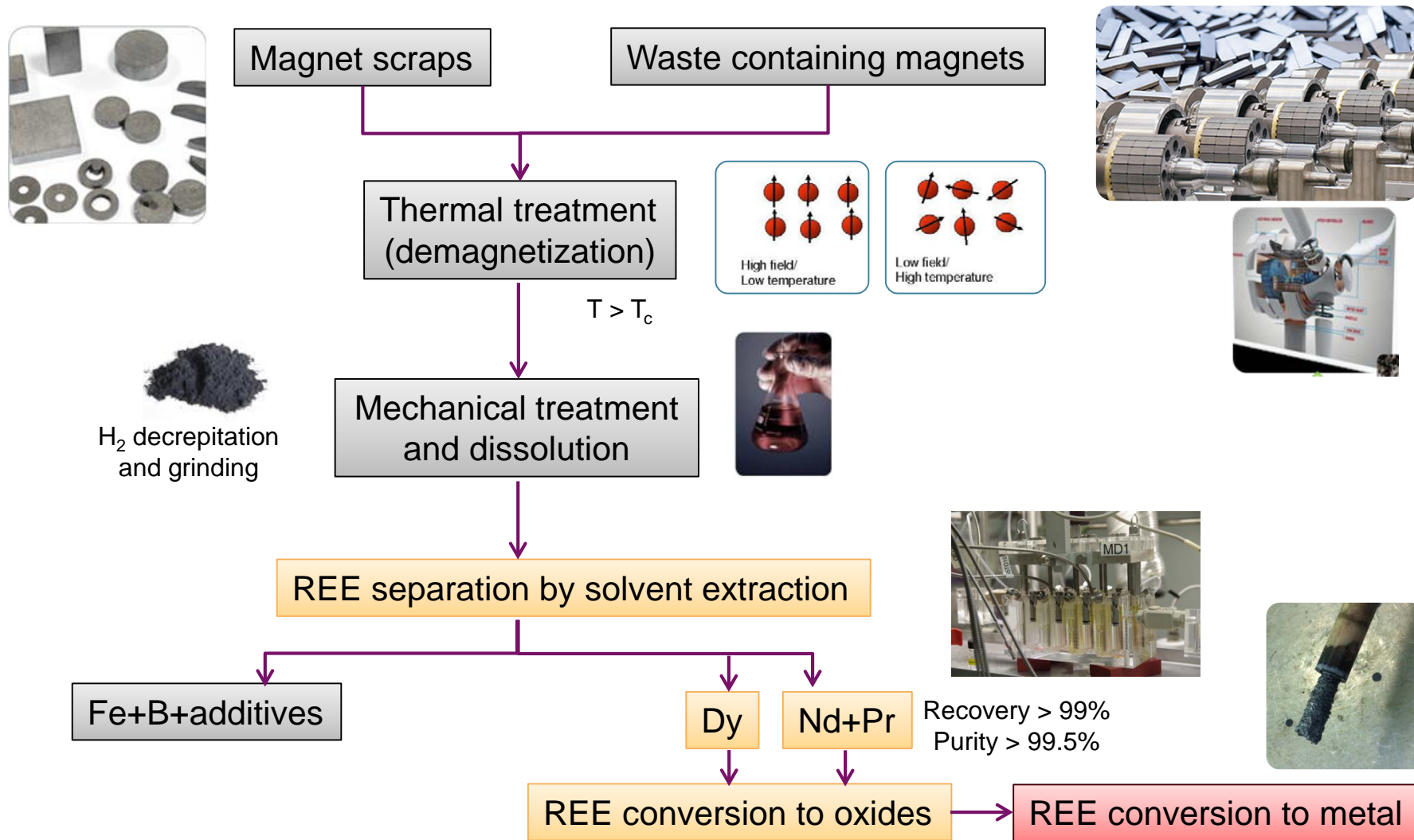


## Recycling NdFeB permanent magnets

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

## **2. RE SEPARATION PROCESS DEVELOPMENT**

# 2. Scheme for REE recovery and purification



## 2. Advantages of the process

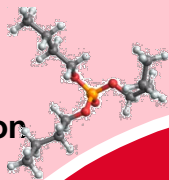
- ❑ Direct and selective extraction and purification of REE from the magnet solution
- ❑ No preliminary separations of Fe and transition elements by precipitation
- ❑ A flexible process:
  - **co-extraction of REE and further partitioning**
  - OR extraction of Dy in a 1st cycle, then Nd+Pr in a 2<sup>nd</sup> cycle
- ❑ A full hydro/pyrometallurgical process adapted to oxidized scraps as well as EoL magnets, for which a simple decrepitation process is not efficient

experts estimate around 20 % the proportion of magnets from WEEE amenable for a short way recycling (decrepitation)



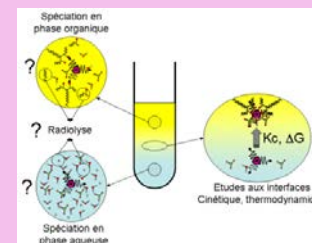
## 2. A well-tried approach to separation process development at CEA

- 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



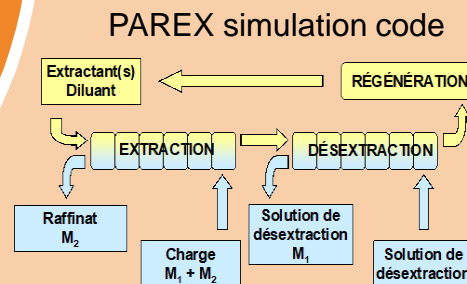
**Specific objectives, D, SF, % Recovery**

**Integrated experiments**



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

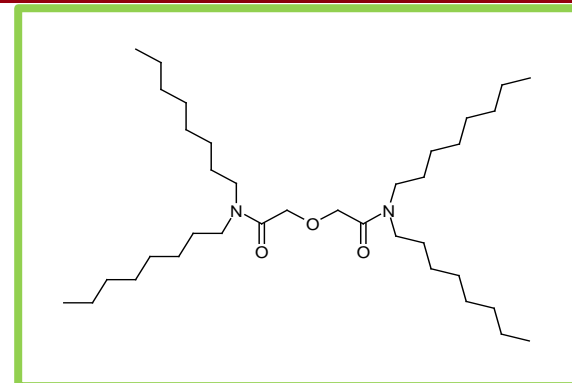
**Process modelling**



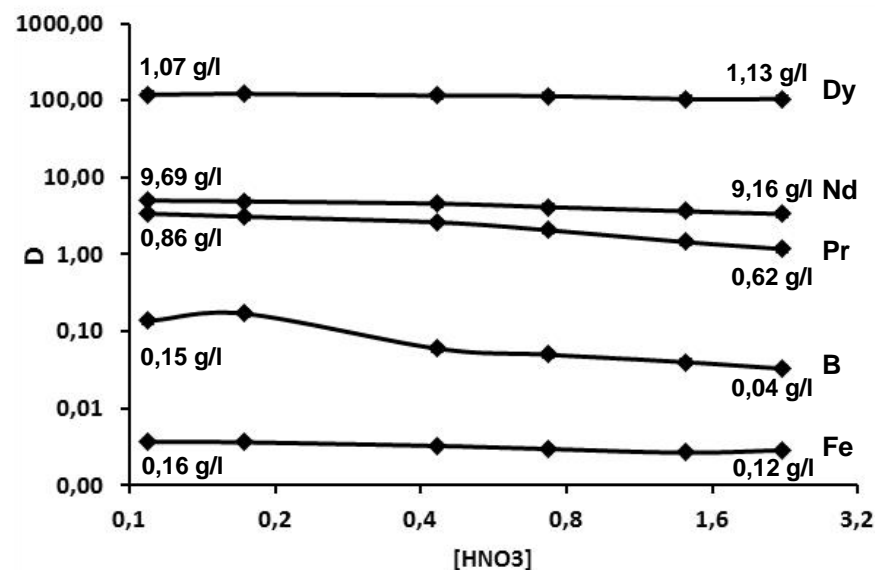
- Development of extraction models and specific flowsheet
- Optimization of the separation

## 2. Selection and evaluation of the extracting 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** as extractant
- Solvent composition: 0.2 M TODGA + 5% octanol / kerosene
- Tests on synthetic and genuine magnet solutions in nitric acid
- **Quantitative extraction** of REE
- **Efficient separation of RE** / transition metals (Fe, Co, Ni...) and heavy RE / light RE in a large range of acidity (0.4 to 5 M)
- **Quantitative stripping of Dy** at low acidity (pH 3) and "high" temperature (45-50°C)
- Confirmation of the potential of TODGA for selective RE recovery and grouped separation from permanent magnet solutions



Sasaki, Y.; Tachimori, S., Solvent extraction and Ion exchange **2002**, 20(1)

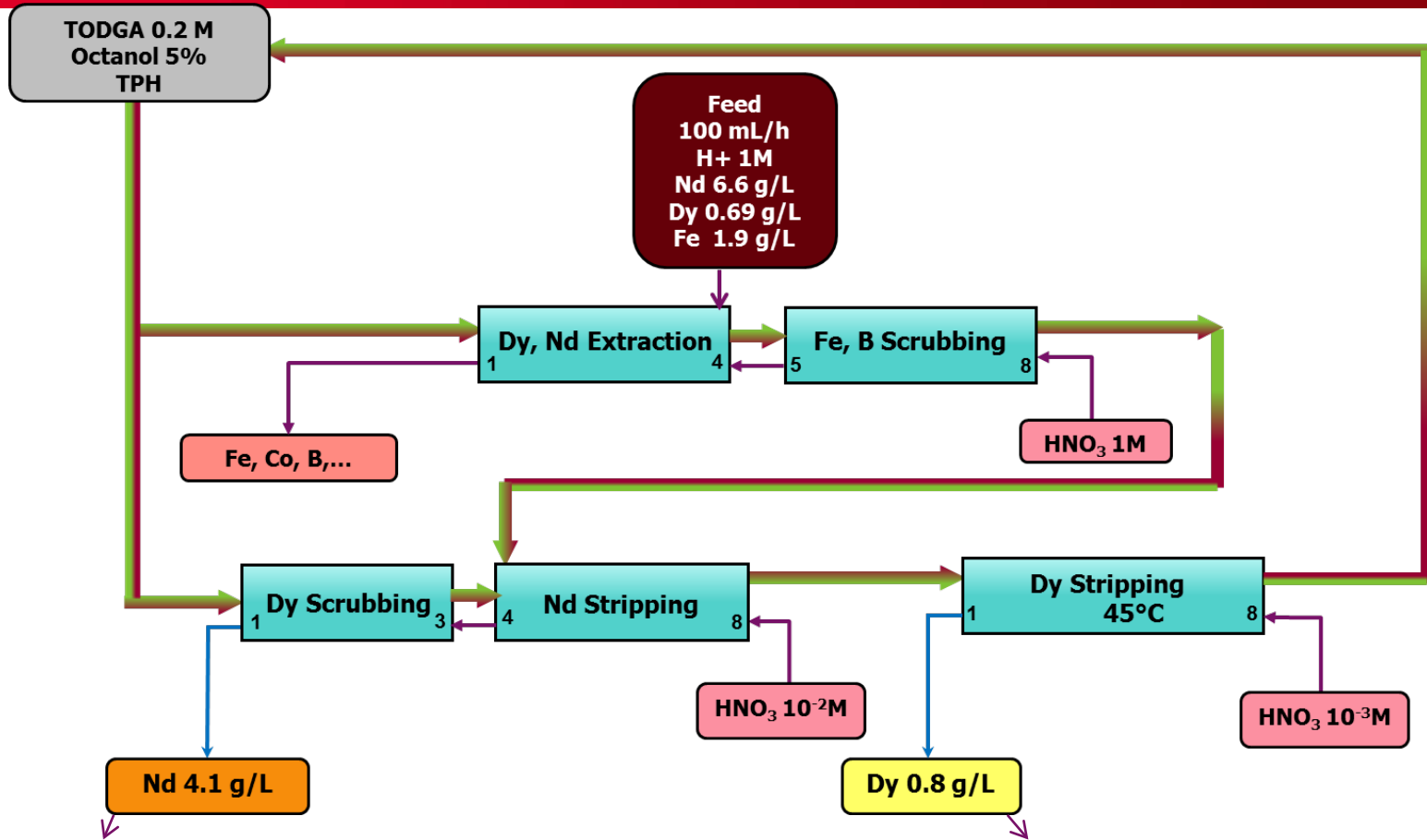


## 2. Development of the separation process flowsheet

- **CEA PAREX simulation code** → calculation of flowsheets to recover Dy and Nd+Pr with theoretical purities > 99.5% in a limited number of stages
- Effective and compact process
- **Patent application** FR 1459023 (March 2014): « *Processes of selective recovery of rare earths from acidic aqueous phases stemming from the processing of end-of-life permanent magnets or scraps* » (PCT/EP2015/071679)
- **Pilot tests**
  - ✓ 20 h duration (steady state)
  - ✓ 100 mL/h (lab-scale mixer settlers)



## 2. Pilot demonstration test on VAC scraps



Pr (g/L)	Dy (g/L)	Fe and other impurities (g/L)	Purity Nd+Pr (%)	Recovery (%)
0.012	$3.5 \cdot 10^{-4}$	$< 5 \cdot 10^{-6}$ each	<b>&gt; 99.99</b>	<b>99.97</b>

Nd (g/L)	Pr (g/L)	Fe and other impurities (g/L)	Purity Dy (%)	Recovery (%)
$5.6 \cdot 10^{-5}$	$8 \cdot 10^{-6}$	$< 5 \cdot 10^{-6}$ each	<b>&gt; 99.96</b>	<b>99.5</b>

## 2. Pyrometallurgical process for metal elaboration

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

Use of **transient electroanalytical techniques** (voltammetry reversal chronopotentiometry, chronoamperometry...) to optimize experimental conditions:

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

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

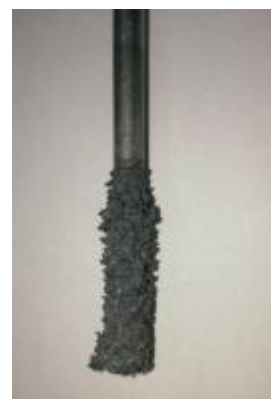
- Metal adherence
- Faradic yield
- Product purity
- Cell materials compatibility

*Patent pending*

**Glovebox setup**



**Metal deposition tests on gram scale**



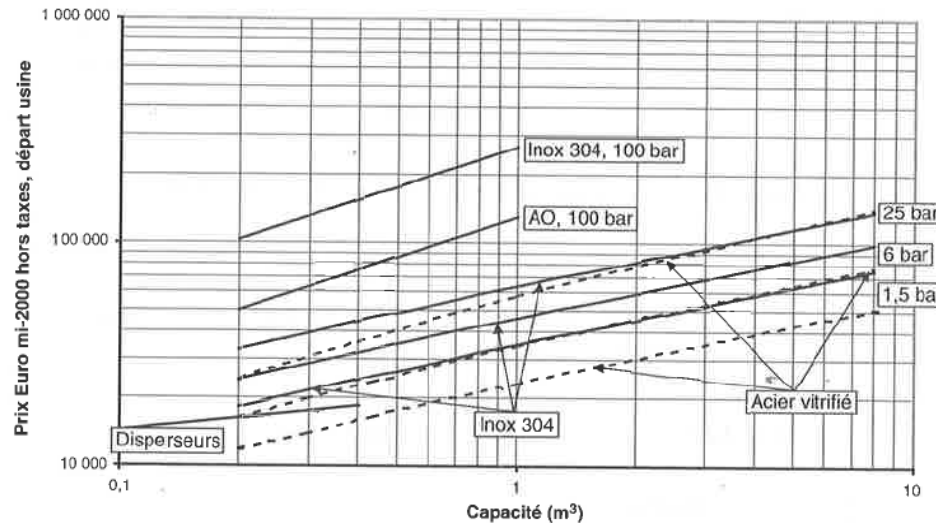
**1g and 5g Dy deposits**

### **3. TECHNICAL-ECONOMIC ASSESSMENT**

### 3. Methodology of economic assessment

- ❖ Technically based approach on detailed knowledge of the process
- ❖ Choice of a given capacity (in relation with market analysis or customer requirements)
- ❖ Step by step capital and operating costs calculations, with assessment of uncertainties at often as necessary
- ❖ Application of security factors, according to the state of the art

Reference: A. Chauvel, G. Fournier, C. Raimbault « Manuel d'évaluation économique des procédés » (Handbook of process economic evaluation), ed. TECHNIP 2001

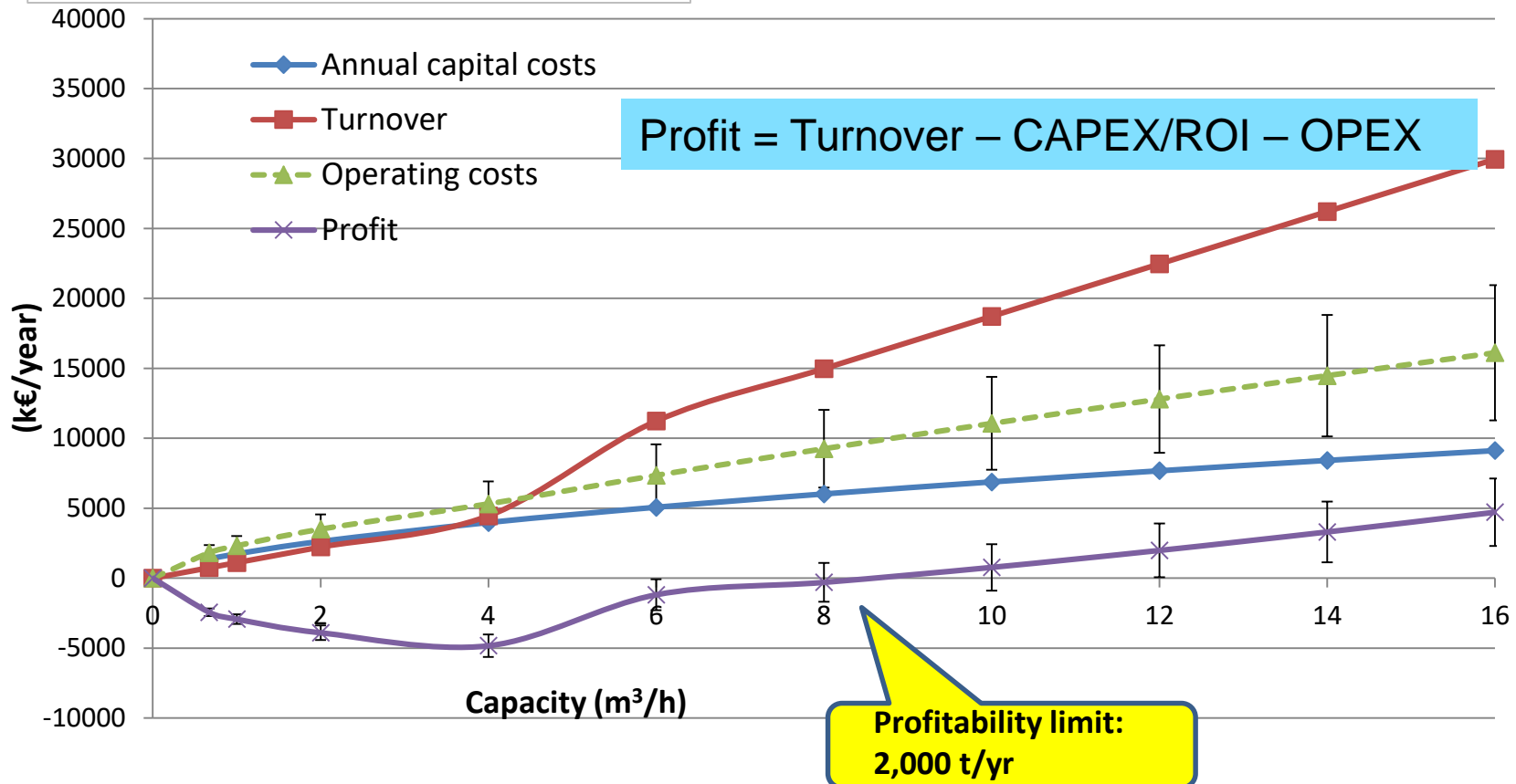


Price of agitated reactors

### 3. Influence of throughput on economy

- Non optimised conditions
- RoI = 3 years
- Careful hypothesis for REEs prices
- Work in 5 shifts for throughput > 5 m<sup>3</sup>/h
- 15% uncertainty on operating costs

**CONCLUSION :**  
The profitability limit will be shifted to a lower capacity with an optimised process





### 3. Results of technical-economic assessment

❑ Solution composition:

Element	Nd	Pr	Dy
Leach solution (g/L)	4.30	1.10	0.44

❑ Market prices:  $\text{Nd}_2\text{O}_3 / \text{Pr}_2\text{O}_3 = 51$  US \$/kg –  $\text{Dy}_2\text{O}_3 = 310$  US \$/kg (2015)

NdFeB magnet Flowrate (t/yr)	REO Production (t/yr)	CAPEX (M€)	OPEX (M€/yr)	Turnover (M€/yr)
15,000 t/yr (easily recoverable EoL magnets in EU) * 27 % = 4,000 t/yr	Nd = 344 Dy = 35	21 (SX)	15 (raw materials)	35
100 t/yr (scraps)	Nd = 8.6 Dy = 0.88	4 (SX)	2 (staff costs)	0.7

- ❖ For 4,000 t/yr , ROI of 3 yrs, the benefit would be positive
- ❖ For 100 t/yr, **the process is unprofitable**

Liquid waste treatment cost has to be further assessed, depending on local regulations (discharge of  $\text{NO}_3^-$  is strictly supervised)



## 4. Conclusions and outlook

### 1. Conclusions

- Development of a **full RE separation process** from used permanent magnets
  - Fruitful collaboration between different CEA research teams
  - Process patented for Dy and Nd recovery from permanent magnets
- Demonstration of the **scientific feasibility of Dy and Nd/Pr recovery by SX** without preliminary separation of Fe, B and coating elements by precipitation
- **Pilot scale production** of highly pure Dy from real used magnets and scraps
  - Experiments in progress on Dy and Nd-Pr conversion to oxides 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

### 2. Outlook

- **Life Cycle Assessment** (LCA) is in progress for different options of the process
- Generic process → can be adapted for other WEEE or valuable materials

■ **We are open to collaboration for scaling-up** of recycling processes based on technical-economic assessment (TEA) and LCA

# THANK YOU FOR ATTENTION

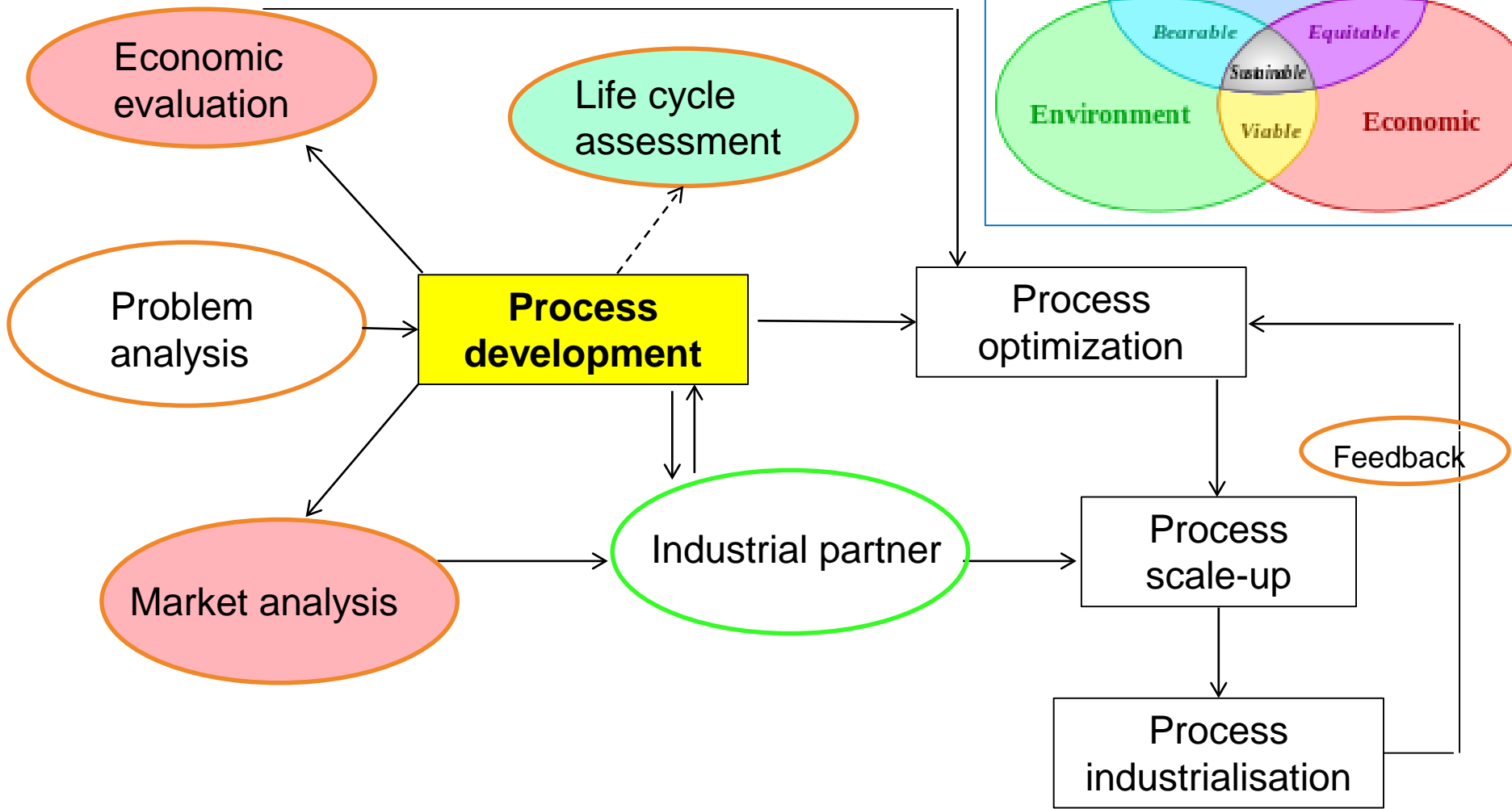
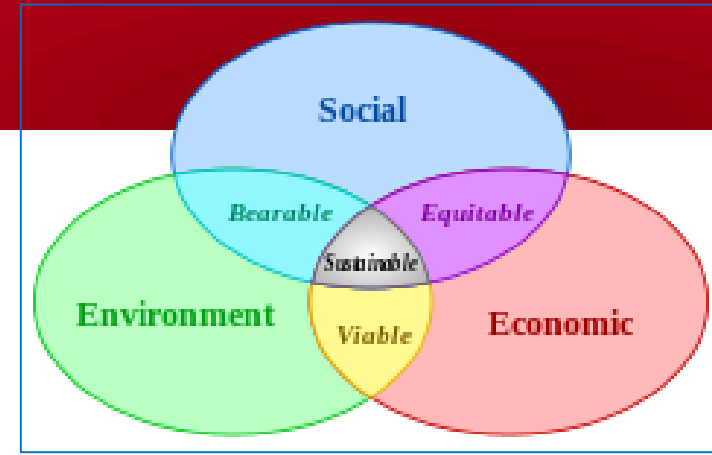
---

Commissariat à l'énergie atomique et aux énergies alternatives  
Centre de Marcoule | BP17171 | 30207 Bagnols-sur-Cèze Cedex  
**didier.hartmann @ cea.fr**

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

Direction de l'énergie nucléaire  
Département de radiochimie des procédés  
Service de modélisation et de chimie des  
procédés de séparation

# 4. Keys to success



The 4 pillars of a successful development

# COMPOSITION OF VAC'S SCRAPS

## ❖ Nd<sub>2</sub>Fe<sub>14</sub>B alloy composition

For applications in temperature, Nd is partially substituted by Dy (or Tb)

	%
Fe	72.3
Nd	26.7
B	1.0

❖ Analysis of the 2<sup>nd</sup> VAC sample « partially oxidized NdFeB material produced from sludge » (500 g received in Nov 2014, analyzed for new experiments in May-July 2015)

➤ Quantitative determination for major elements by ICP-AES after digestion

↓

Elements	%
Fe	54.3
Nd	22.4
Dy	2.23
Co	1.61
B	0.73
Cu	0.11
Pr	0.07

➤ Semi-quantitative for minor elements by ICP-MS

↓

> 0.3 mg/g	Al-Er-Tb
0.05 < < 0.3 mg/g	Mg-Ti-Cr-Mn-Ni-Zn-As-Gd-Hf-W
< 0.05 mg/g (50 ppm)	Li-Be-V-Ge-Se-Y-Nb-Mo-Pd-Sn-Sb-Te-La-Ce-Sm-Ho-Tm-Yb-Lu-Ta-Re-Pt-Hg-Th-Ru