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

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DE LA RECHERCHE À L'INDUSTRIE

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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

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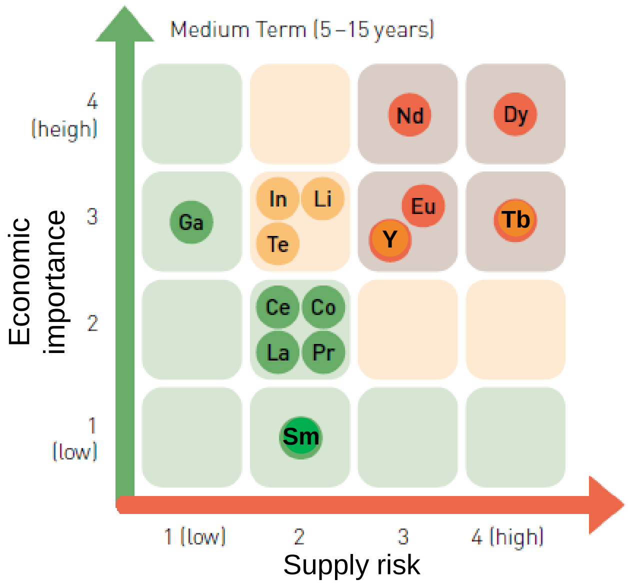


Source: report US Department of Energy 2010

- 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**

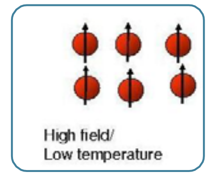
2. RE SEPARATION PROCESS DEVELOPMENT

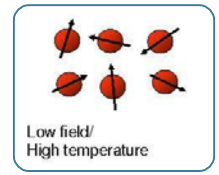
2. Scheme for REE recovery and purification

Magnet scraps

Waste containing magnets

Thermal treatment (demagnetization)





$T > T_c$

H_2 decrepitation and grinding

Mechanical treatment and dissolution

REE separation by solvent extraction

Fe+B+additives

Dy

Nd+Pr

Recovery > 99%
Purity > 99.5%

REE conversion to oxides

REE conversion to metal

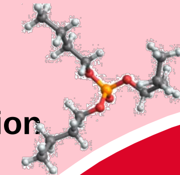
2. Advantages of the process

- 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 2nd cycle
- A full hydro/pyrometallurgical process adapted to oxidized scraps as well as EoL magnets, for which a simple decrepitation process is not efficient

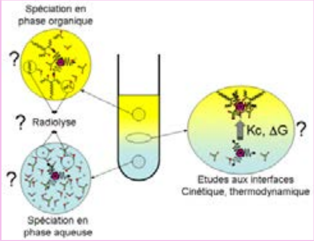
experts estimate around 20 % the proportion of magnets from WEEE amenable for a short way recycling (decrepitation)

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



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



Extractant system selection

Molecular scale chemistry

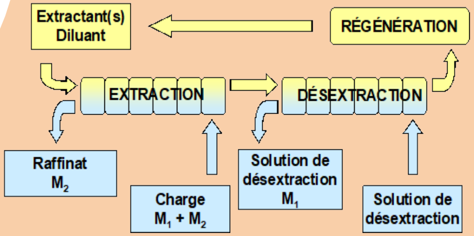
Specific objectives, D, SF, % Recovery

Integrated experiments

Process modelling

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

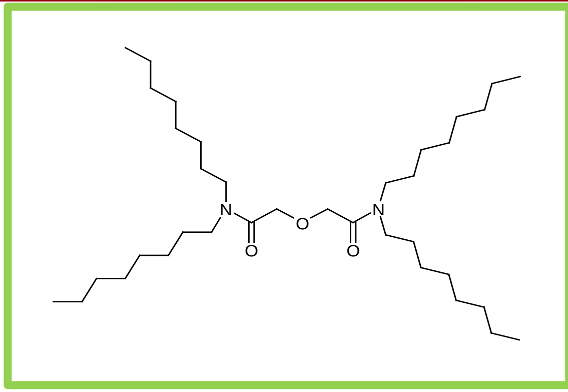
PAREX simulation code



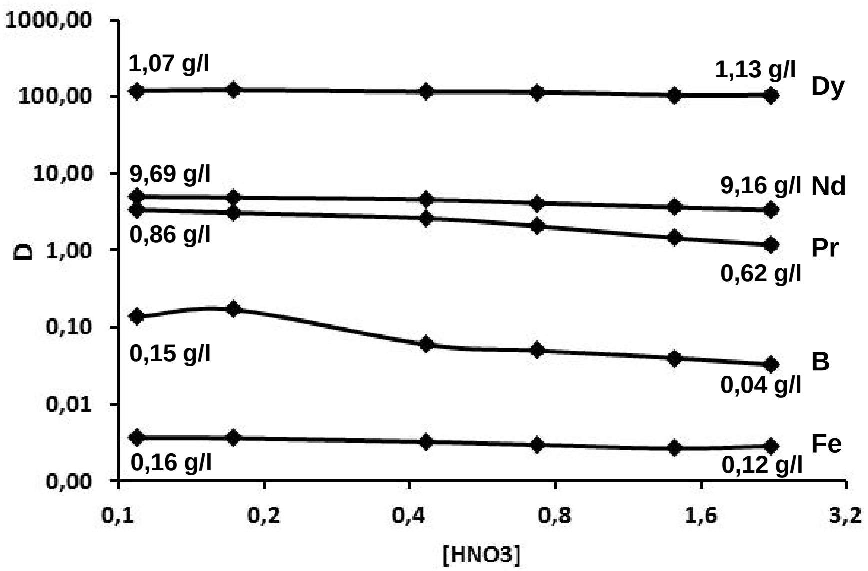
- Development of extraction models and specific flowsheet
- Optimization of the separation

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

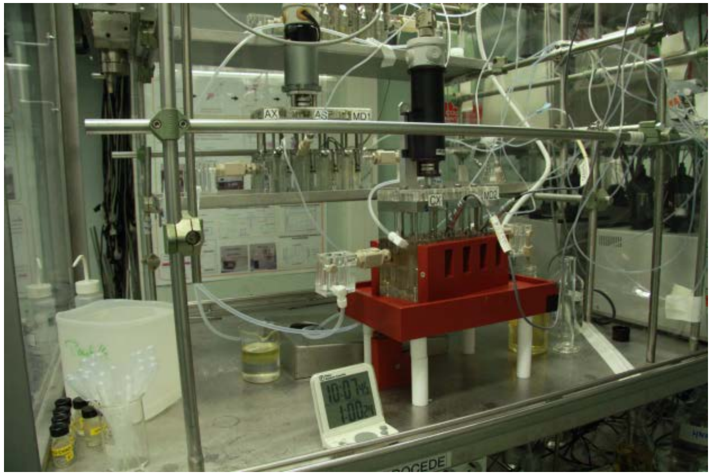


Sasaki, Y.; Tachimori, S., Solvent extraction and Ion exchange **2002**, *20(1)*

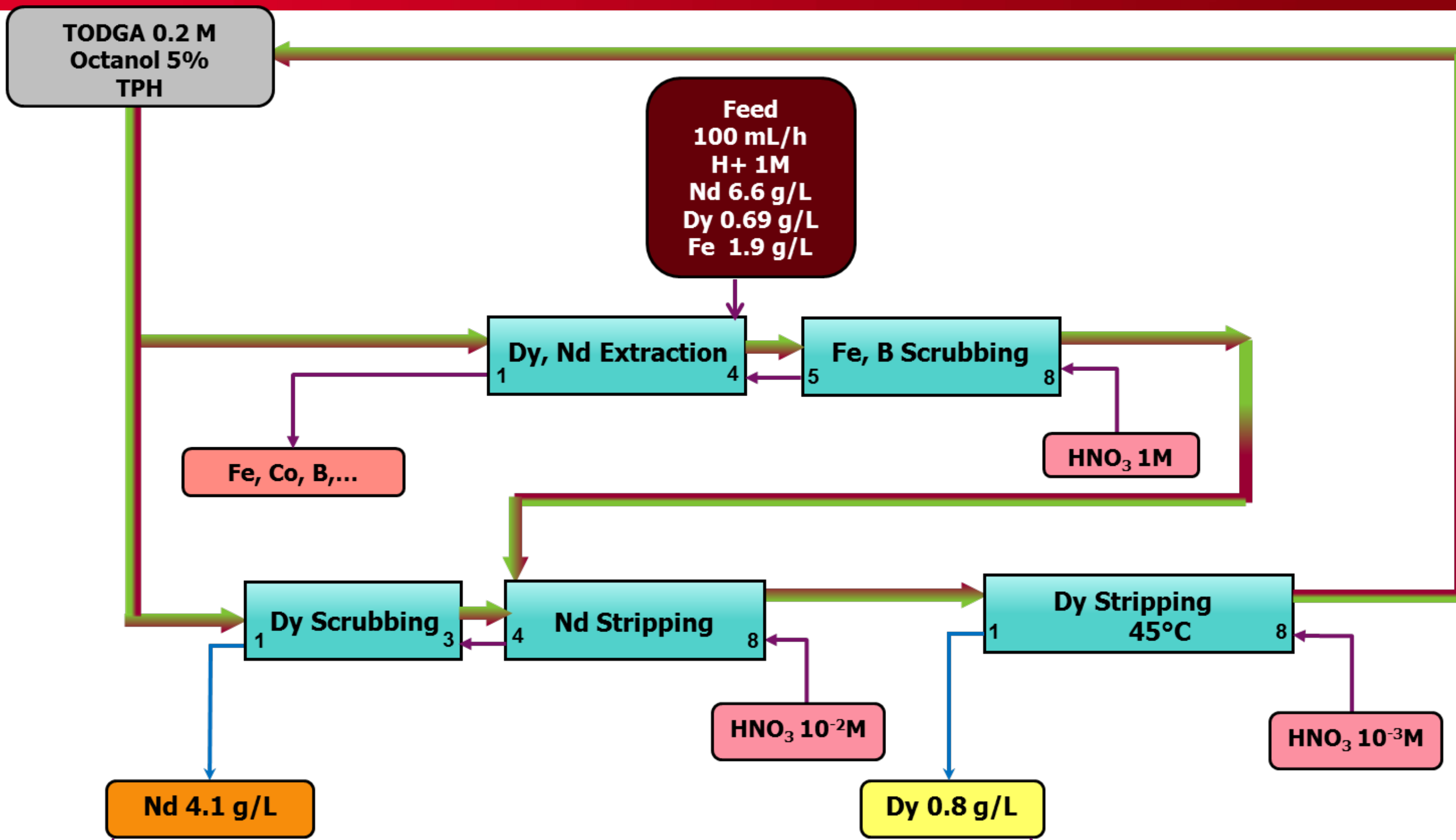


2. Development of the separation process flowsheet

- **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	**$3.5.10^{-4}$**	< 5.10^{-6} each	> **99.99**	**99.97**

Nd (g/L)	Pr (g/L)	Fe and other impurities (g/L)	Purity Dy (%)	Recovery (%)
$5.6.10^{-5}$	8.10^{-6}	< 5.10^{-6} each	**> 99.96**	**99.5**

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

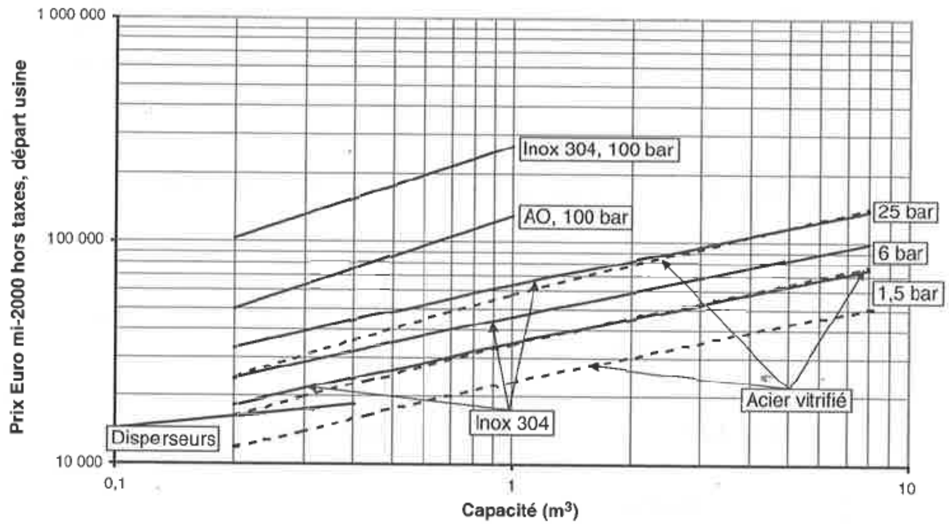
1g and 5g Dy deposits

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

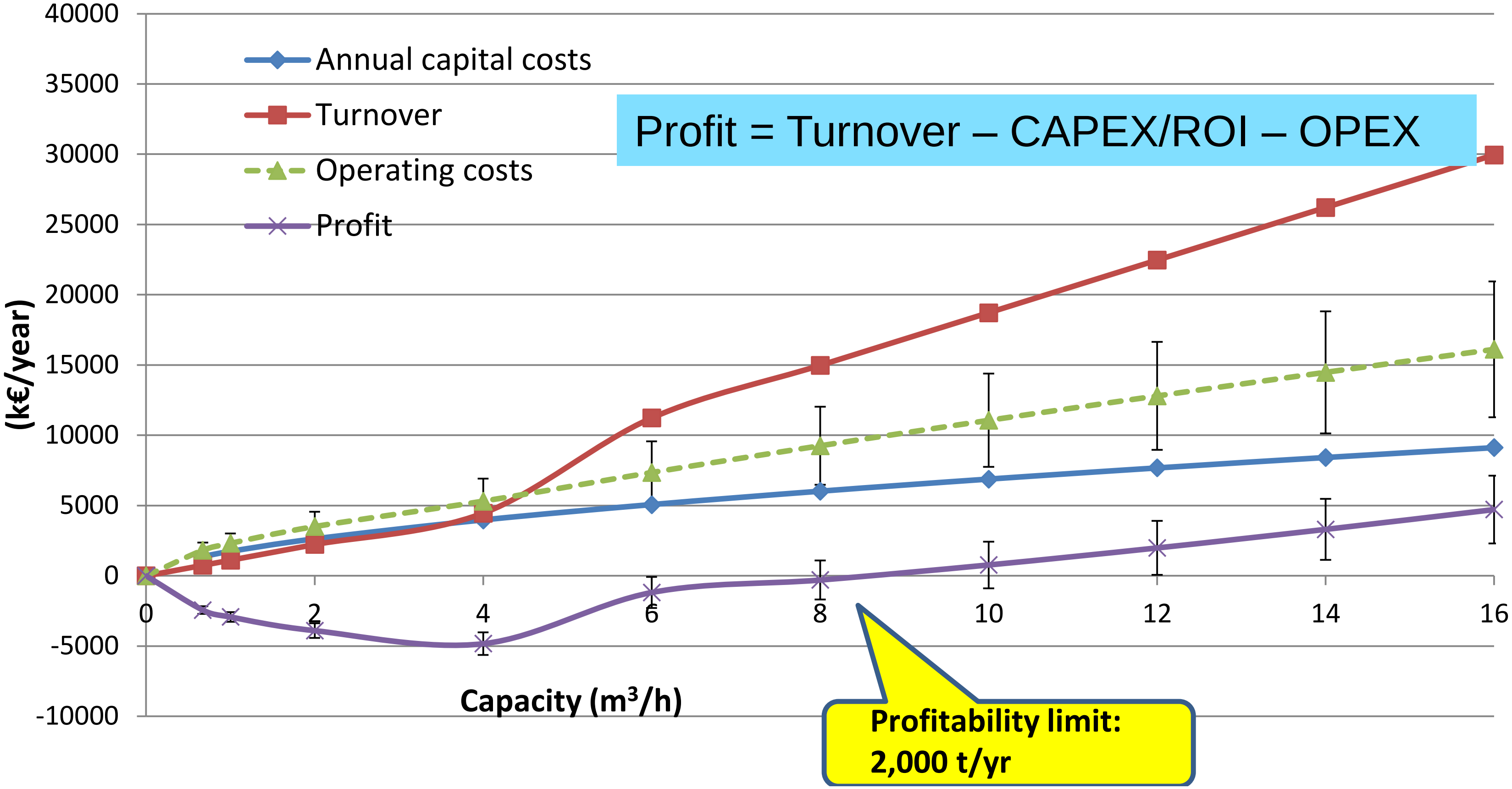


Price of agitated reactors

3. Influence of throughput on economy

- **Non optimised conditions**
- RoI = 3 years
- Careful hypothesis for REEs prices
- Work in 5 shifts for throughput > 5 m³/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: Nd_2O_3 /Pr_2O_3= 51 US $/kg – Dy_2O_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 NO_3^- is strictly supervised)

4. Conclusions and outlook

1. <u>Conclusions</u>

- 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. <u>Outlook</u>

- **Life Cycle Assessment** (LCA) is in progress for different options of the process

- Generic process → can be adapted for other WEEE or valuable materials

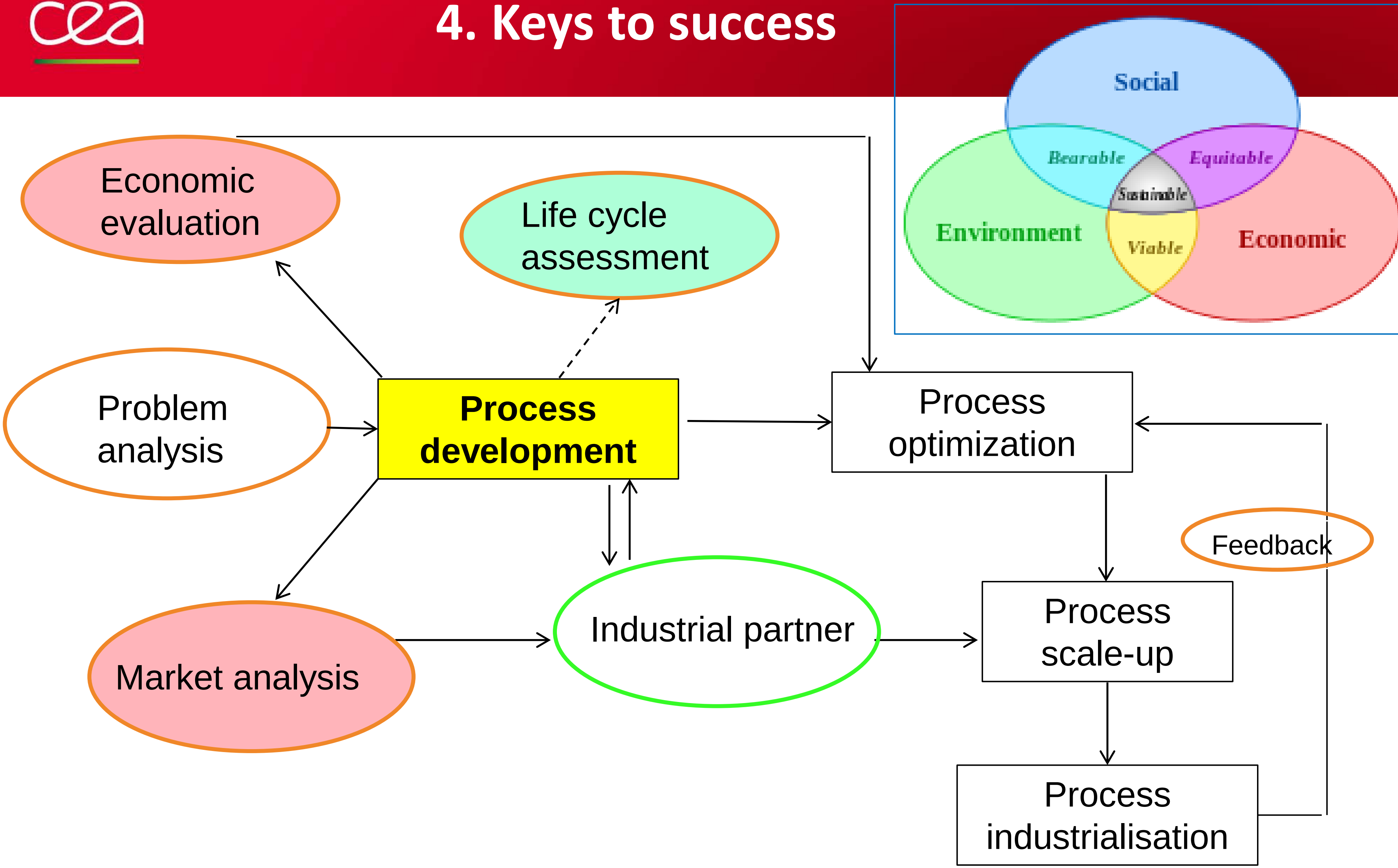
- **We are open to collaboration for scaling-up** of recycling processes based on technical-economic assessment (TEA) and LCA

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

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

- $Nd_2Fe_{14}B$ 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 2nd 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
  - Semi-quantitative for minor elements by ICP-MS

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

> 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