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Development of a REE recycling process from used NdFeB magnets based on solvent extraction

***Vincent Blet*, M. Miguirditchian, V. Haquin, M-T Duchesne, V. Pacary, M. Montuir, J. Serp, L. Diaz, D. Hartmann**

CEA Marcoule

Nuclear Energy Division (DEN)
RadioChemistry & Processes Department (DRCP)

E. Bouyer, R. Laucournet

CEA Grenoble

Technological Research Division (DRT)
Innovation for new energies and nanomaterials technologies Laboratory (LITEN)

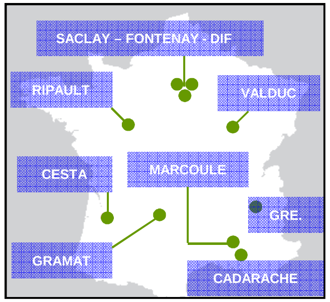
The CEA : atomic energy and alternative energies

Created in 1945 to give nuclear capacity to France,
in 2010 the CEA became :

cea energie atomique • energies alternatives

General Admin (CEO),
High Commissaire at Nuclear Energy

- Military Applications Division
- Nuclear Energy Division
- Technological Research Division
- Fundamental Research Division

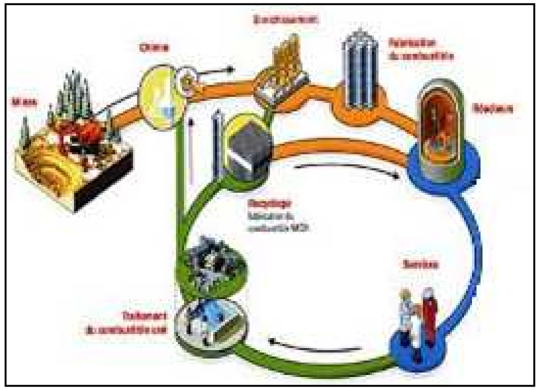


10 research centres

16110 employees – Annual budget : 4,4 billions € (2014)

It filed **751 (754) priority patent applications in 2014 (2013).**
Since 1984 it has created **120 companies** in the sector of innovative technologies

MARCOULE from yesterday to today



Marcoule was created in 1955

- De Gaulle's vision of a national nuclear detterence
- Strategical nuclear materials are needed.

3 reactors and a reprocessing plant were built

- Reactors G1 (1956), G2 (1958) and G3 (1959)
- UP1 reprocessing plant (1958) *& APM (1962)*

The path to civilian applications

- for the electronuclear industry (AREVA La Hague reprocesing plant) and the Nation's need (1991 & 2006 Acts on waste management)

- Marcoule became a world reference for waste management and nuclear spent fuel reprocessing-recycling :
  - **vitrification** (PIVER 1969, AVM 1978)
  - fuel cycle (ATALANTE 1992)
  - **Tomorrow's** Gen IV reactors

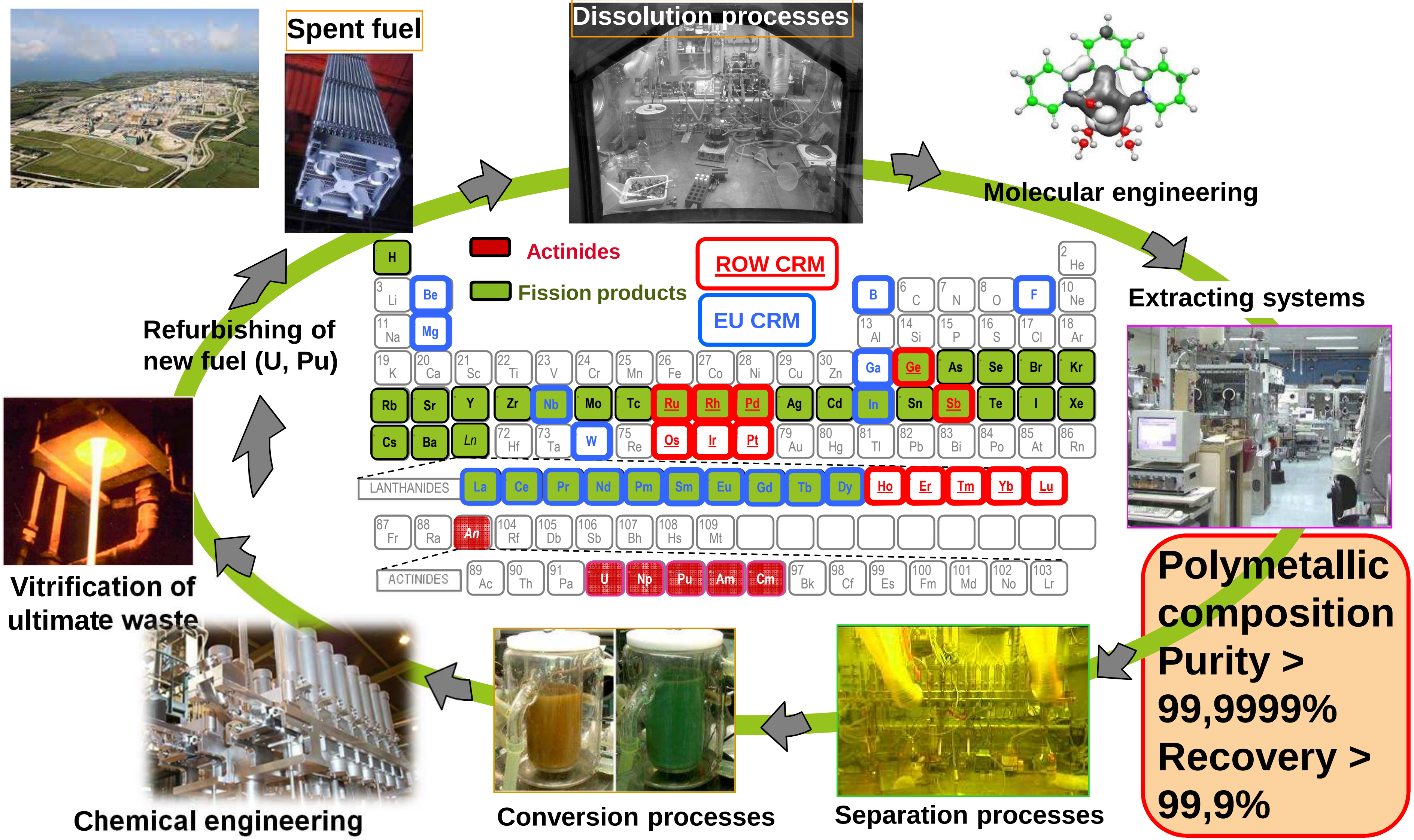
- **cleanup & dismantling**

Extracthive PROCESS DESIGNERS

- and **valorisation** : transfer of technology, start-up

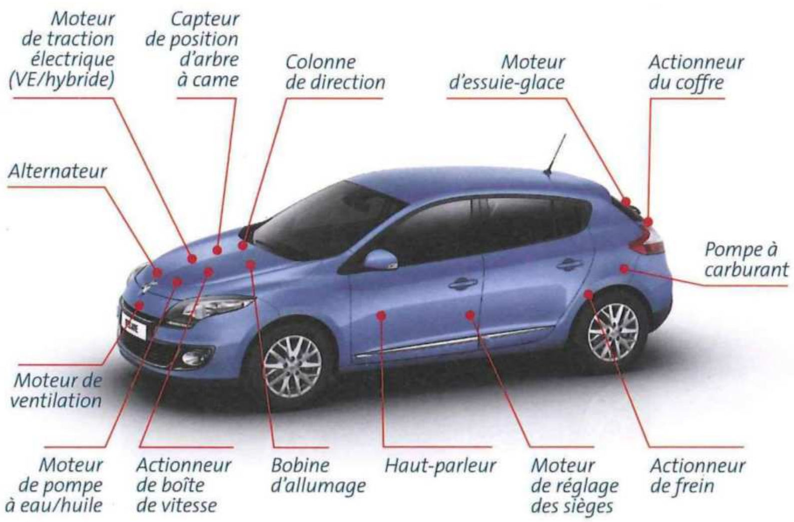
5000 persons – 1520 CEA staff – 300 M€ in local economy

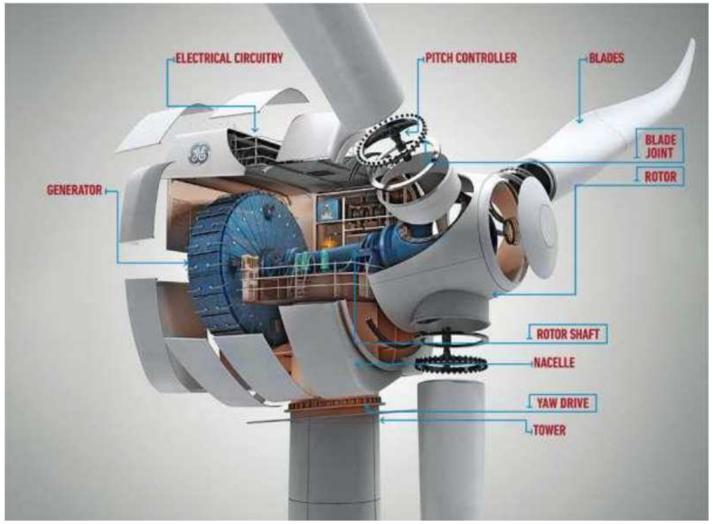
French nuclear fuel cycle and critical raw materials circular economy



Recycling of NdFeB permanent magnets

➢ Use of NdFeB permanent magnets is growing up :





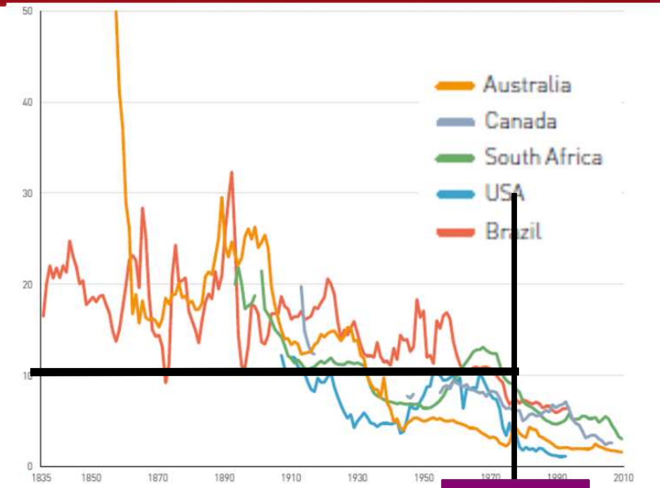
➢ 88% of world production of REE in 2014 come from China

CRM recycling : a way to secure the supply but also a response to the….

➢ Decline of old primary mines

➢ Ex. : Gold ore grades (g/t Au) between1830 and 2010

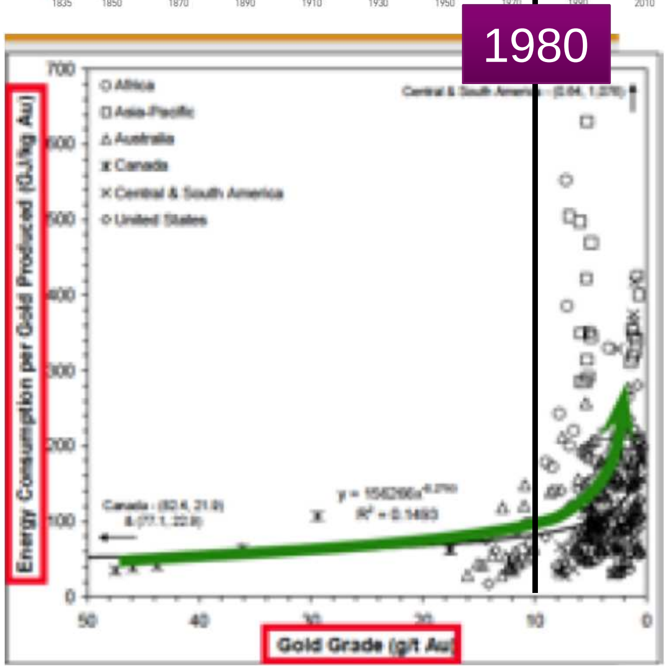
Metal recycling, UNEP, 2013



Increase in the environmental impact

Ex. : Energy required for producing gold as a function of ore grade

Ressources minérales et énergie, ANCRE (2015)



Recycling rates REE < 1% !

Innovative RE-use and Recycling VALue Chain for High-Power Magnets

Bonded magnets
Sintered magnets

Waste Resources → Used magnets Collection & Analysis → Reuse / Recycling → Magnets conditioning / Magnets remanufacturing / REEs extraction → Magnets Market / REEs market

Pyrometallurgy
Electroreduction in molten salt
Hydrometallurgy processes
Bioleaching

cea tech · ARELEC · BASF The Chemical Company · VEOLIA PROPRETÉ · BOSCH Technik fürs Leben · Fraunhofer

Magnet platform : semi industrial scale for NdFeB manufacturing

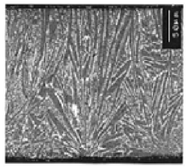
EQUIPMENTS

PROCESS

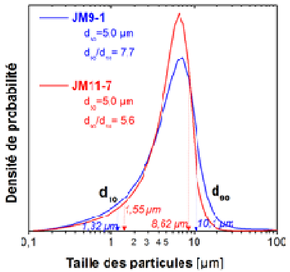
Alloying by Strip casting → Decrepitation → Milling → Powders alignment → pressing → Sintering Annealing → Machining → Motor integration

KNOW HOW

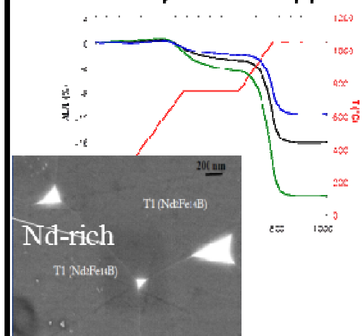
Control of ribbon microstructure



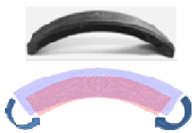
Control of particle size distribution



Thermodynamics approch

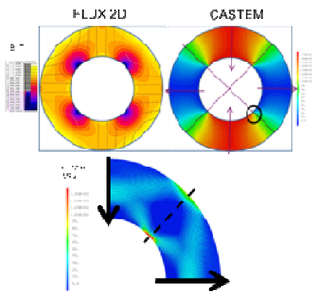


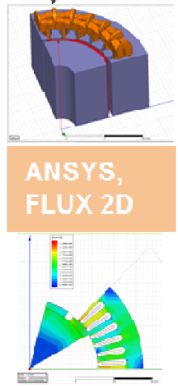
Viscoplastic approch



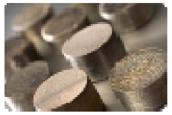
Simulation of geometrical distortions of anisotropic magnets during sintering

Thermomechanical approch





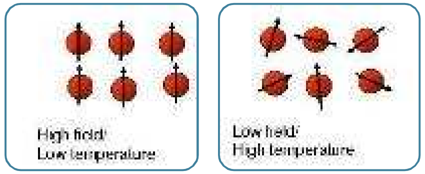
A first scheme for REE recovery and purification

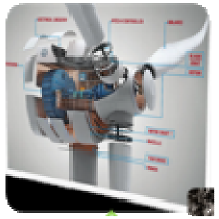



Magnet scraps

Waste containing magnets

Thermal treatment (demagnetization)



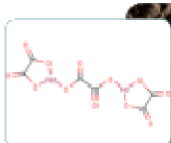


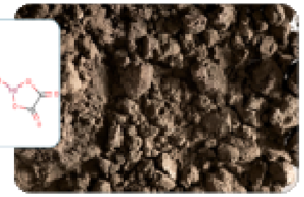
(200℃) T > T_c

Hydride cracking and grinding

Mechanical/chemical treatment

Acid / oxidant (dissolution)





Selective precipitation steps

Fe+B+additives

REE concentrate (Nd+Pr+Dy)

Purity > 99.5%
Recovery > 90%

Patented process

REE individual separation by liquid-liquid extraction

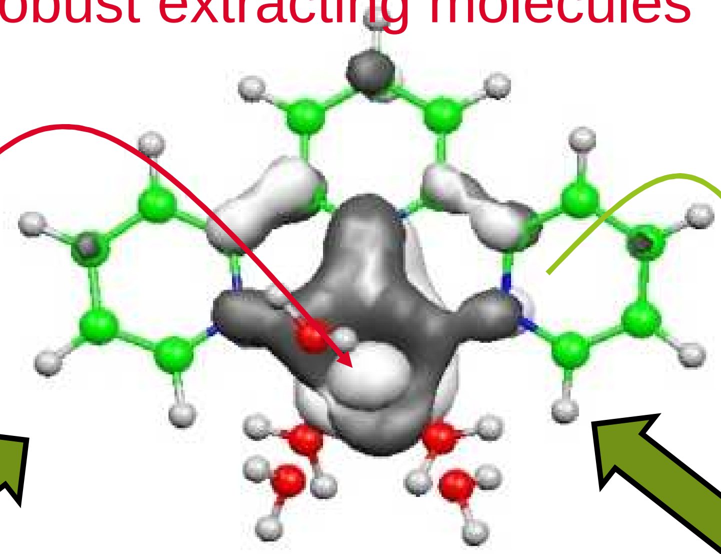
REE purification

Molecular engineering (*coll ICSM)*

Understanding the basic mechanisms to design efficient, selective and robust extracting molecules

Active site

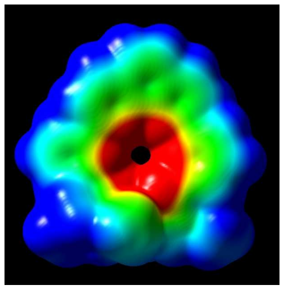
- Nature of the donnor atoms
- Chemical functions
- Organization : number, spacing



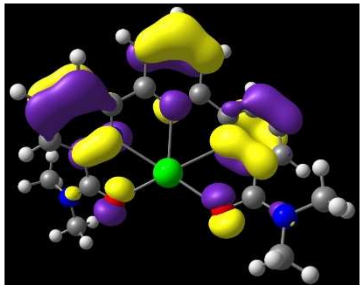
Molecular structure

- Nature
- Length of the chains
- Size of the cycle
- Chemical resistivity

Theoretical chemistry

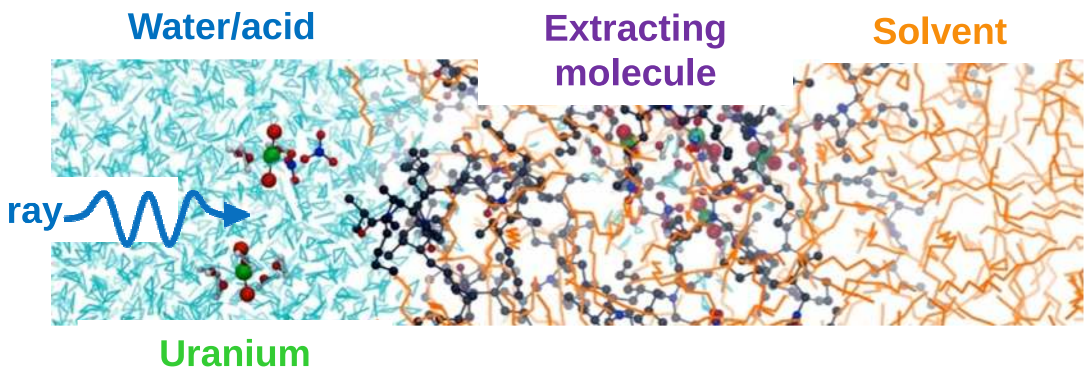


Potentiel électrostatique

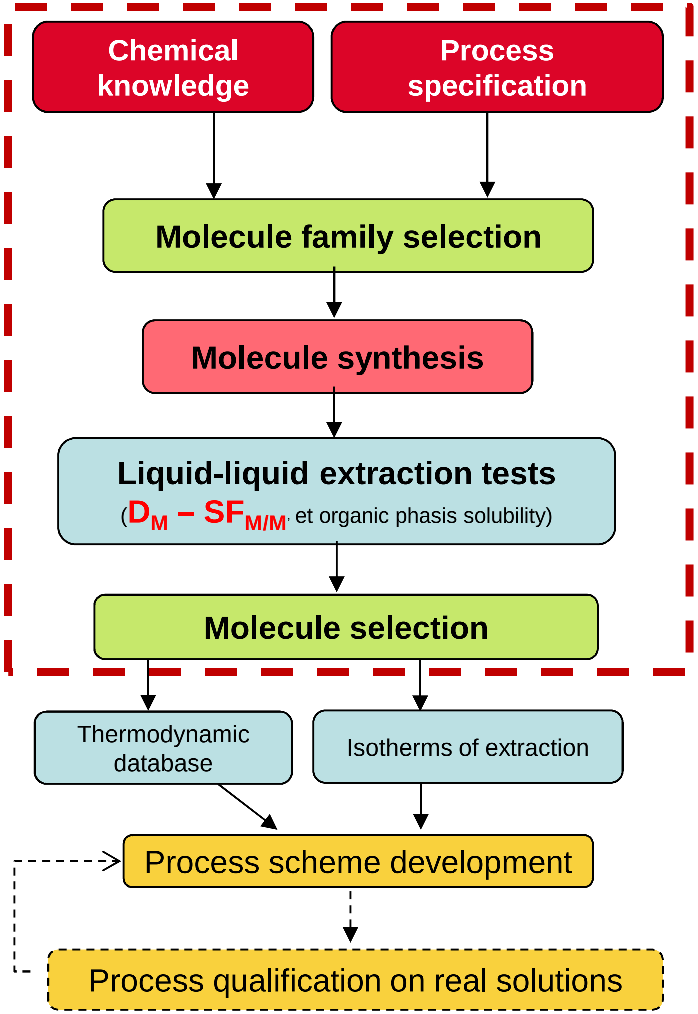


Orbitales moléculaires

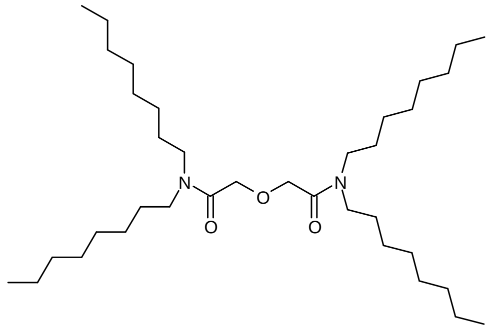
supramolecular mechanisms



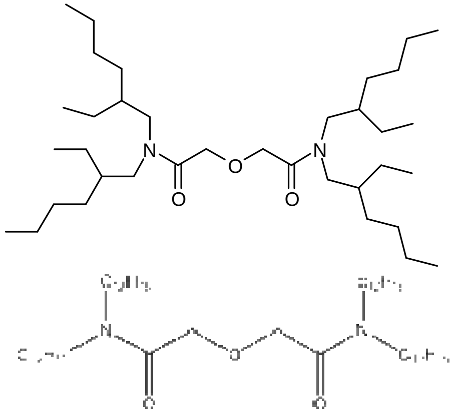
Selection and evaluation of the extractant system



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



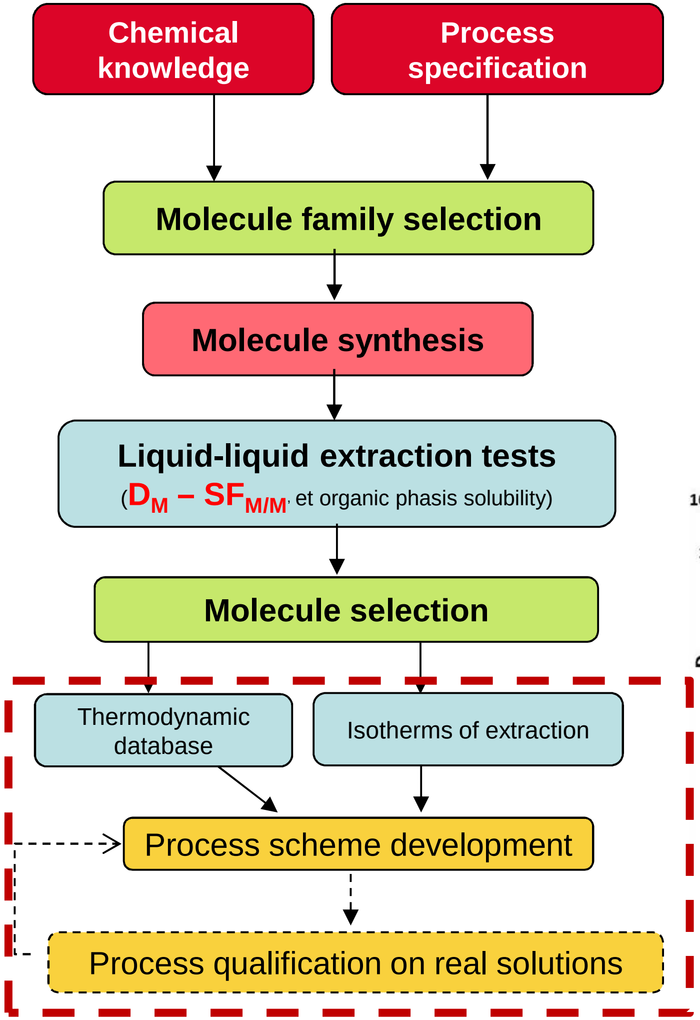
Sasaki et al, 2002



- Selection of **TODGA/TPH** as solvent
- Addition of 5% octanol to prevent 3rd phase formation at high REE loading

➲ ***0.2M TODGA + 5% octanol / TPH***

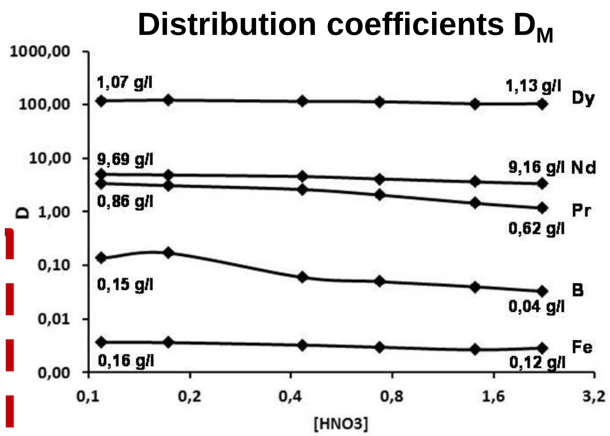
RE Separation Process Development

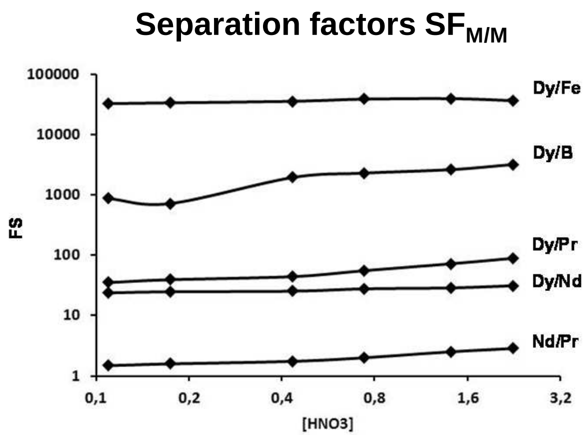


- Tests on synthetic and genuine magnet solutions in nitric acid

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

- **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 3rd phase** formation in processes conditions

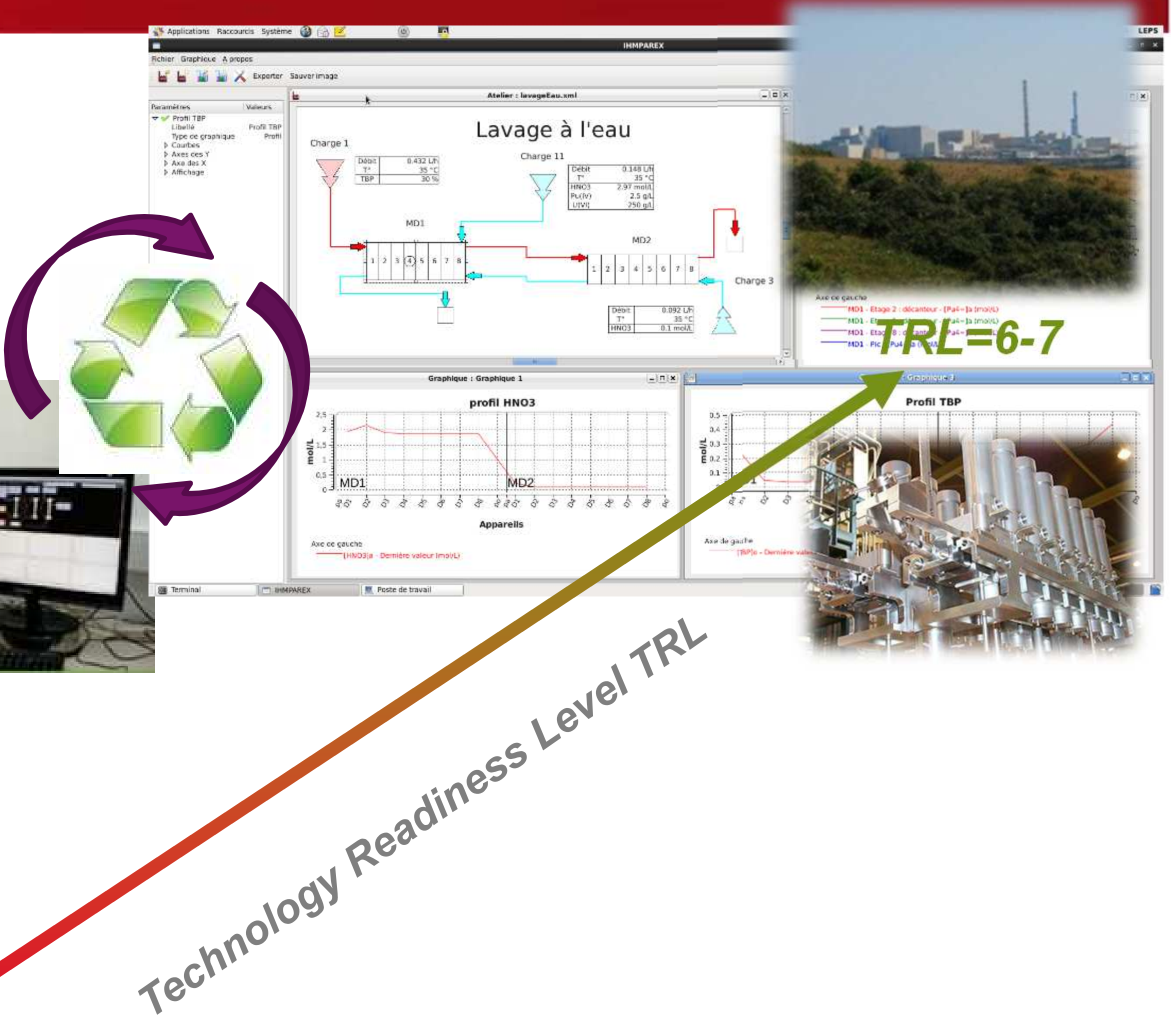


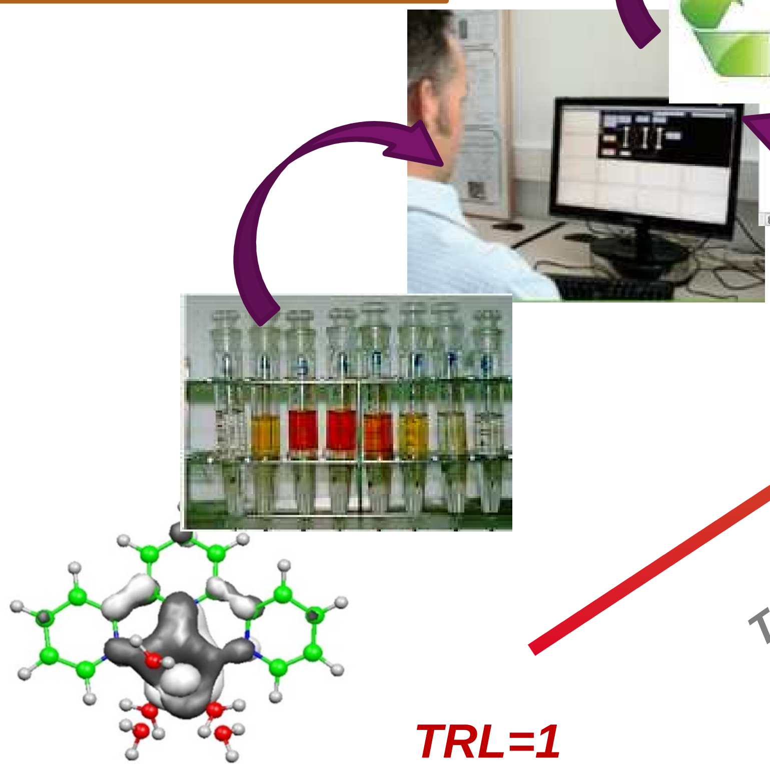


- **Quantitative stripping of REE** at low acidity (pH 3) and high temperature (45-50°C)

systemic modelling using PAREX

Dynamic simulation code PAREX

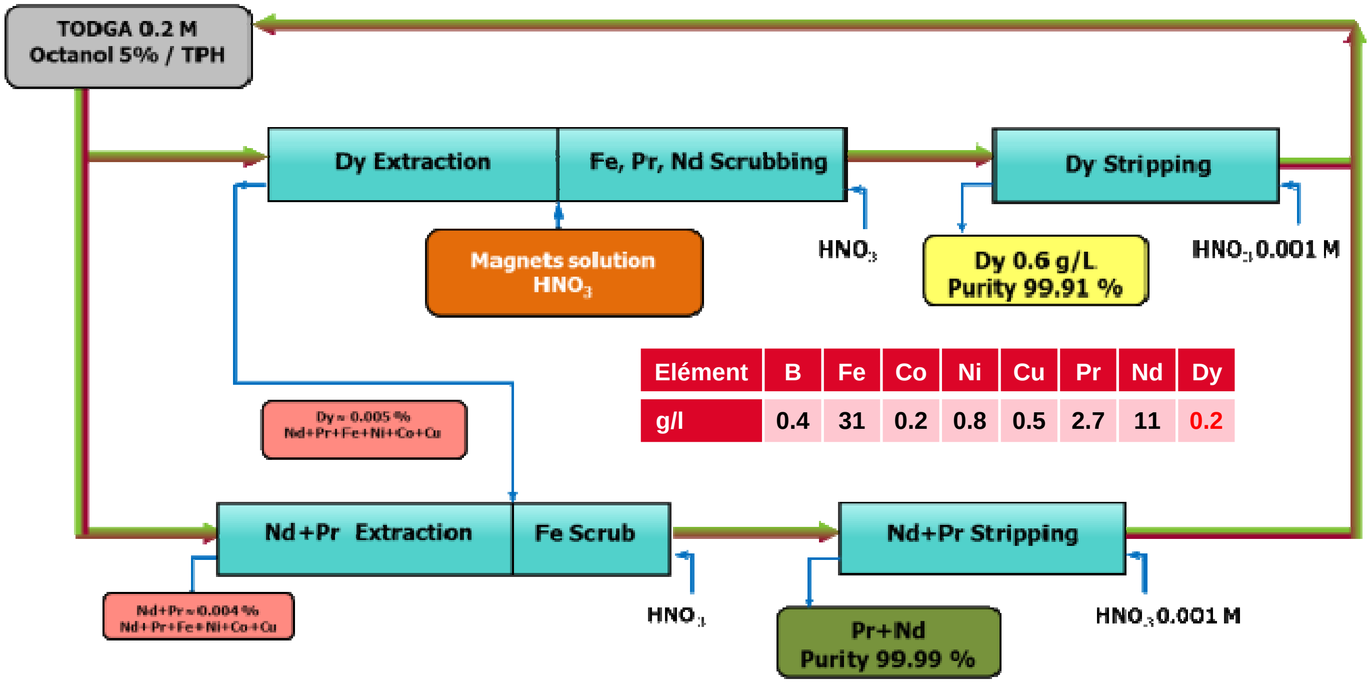




Development of the separation process flowsheet

➢ Flow sheet simulation

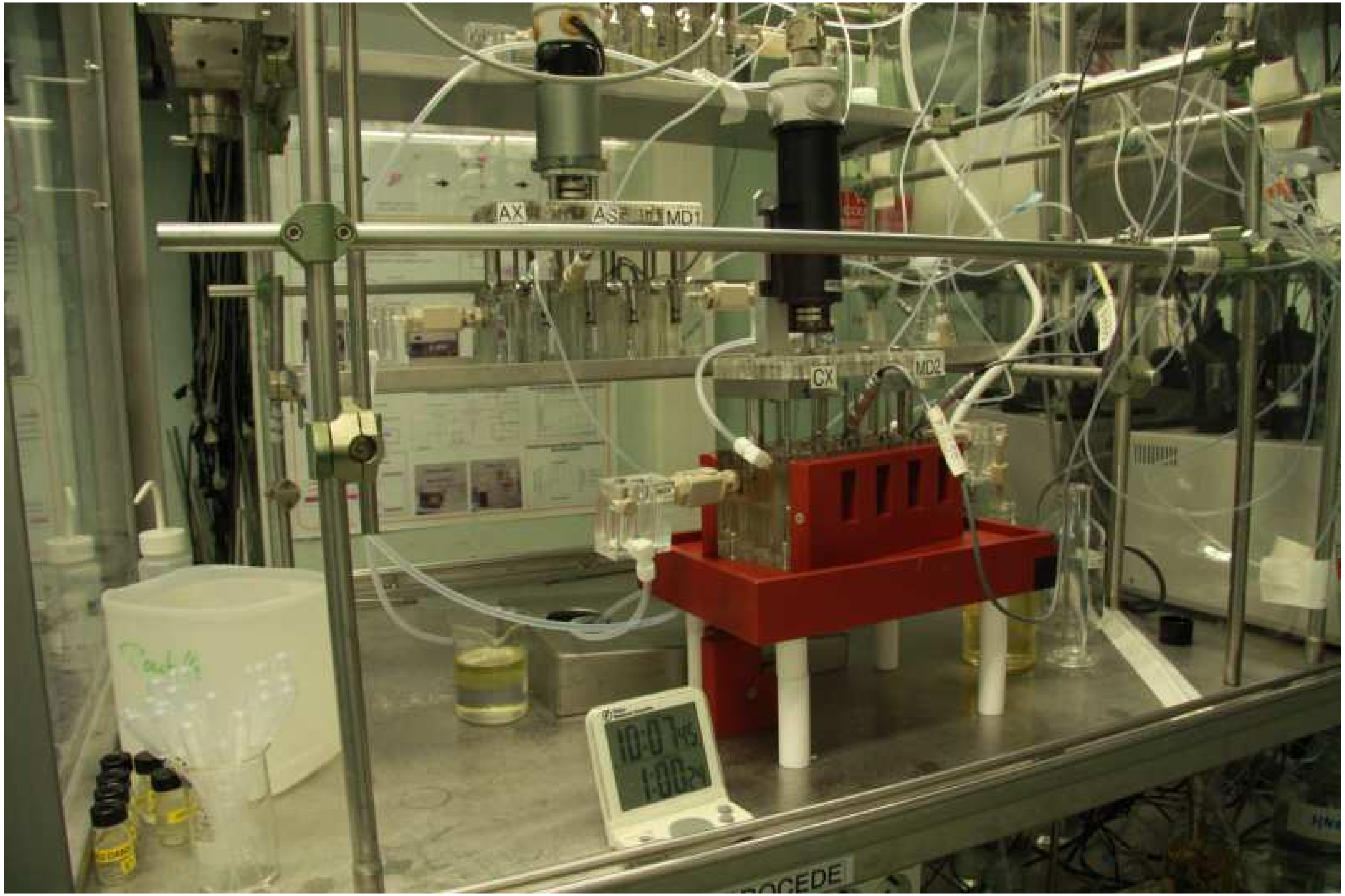
- Simulation of flow sheets to recover Dy and Nd+Pr with theoritical purities > 99.5% in a limited number of stages



Elément	B	Fe	Co	Ni	Cu	Pr	Nd	Dy
g/l	0.4	31	0.2	0.8	0.5	2.7	11	0.2

Effective and compact process in two steps for Dy (step 1) and Nd+Pr (step 2) separation from REE solutions

Pilot demonstration test on used magnets



Pilot demonstration tests on used magnets

➢ Pilot test

- ✓ UV-vis on-line analysis (for Nd) and ICP-AES measurements for Dy, Nd, Fe
- ✓ 20hrs duration (steady stade)
- ✓ 100 ml/h

➢Results for 1-step (Dy recovery)

- ✓ **Dy recovery > 99.7% with purity > 99.99%**
- ✓ Production of Dy concentrated from 0.7 to 4.1 g/L

➢Results for 2-steps (Dy and Nd recovery)

- ✓ **Dy recovery > 99.5% with purity > 99.95%**
- ✓ **Nd recovery > 99.97% with purity > 99.99% (without Pr) or 99.7% (with Pr)**

Pyrometallurgical process for metal elaboration

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

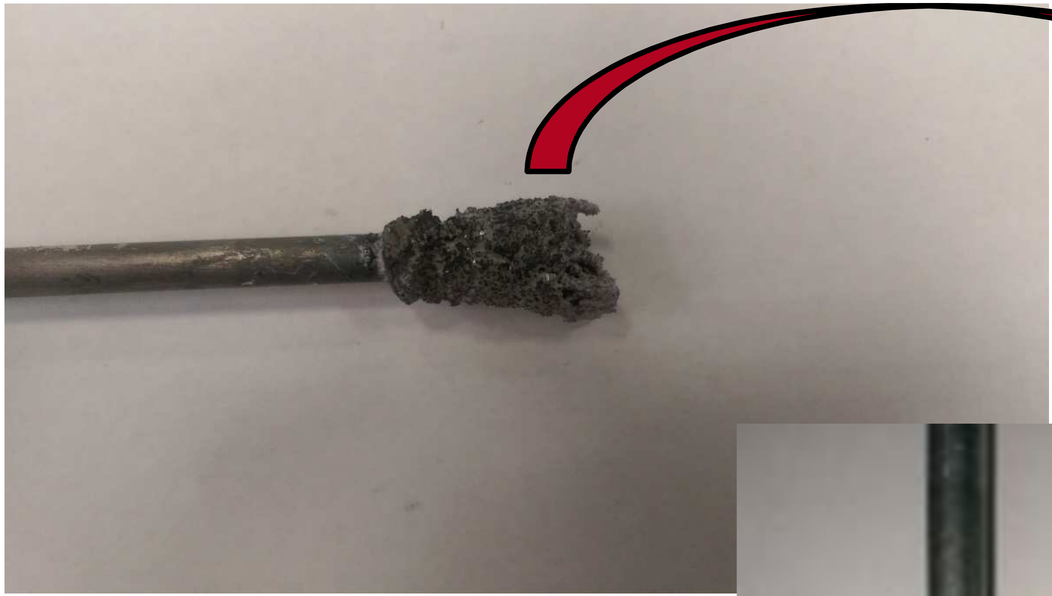
Use of **transient electroanalytical techniques** (voltammetry reversal chronopotentiometry, chronoamperometry…) to optimize the experimental conditions:

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

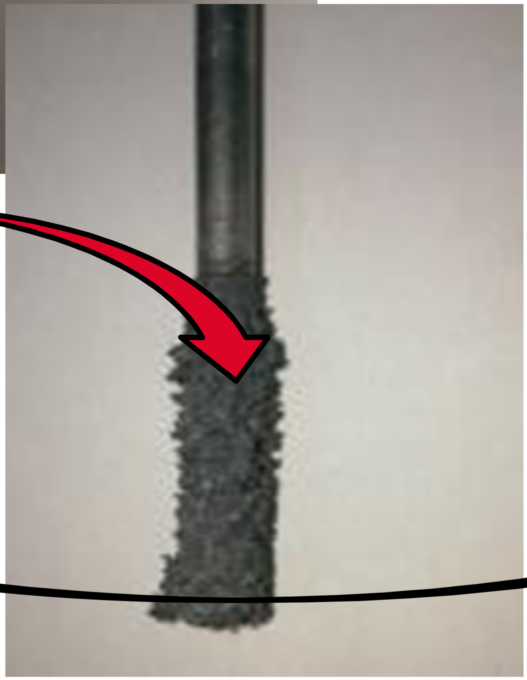
Metal deposition tests to evaluate the process efficiency:

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

Nd and Dy deposits…



1g Nd deposit



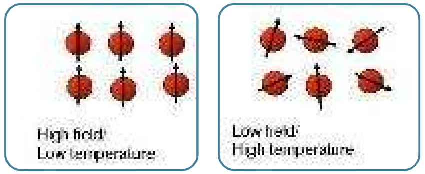
1g and 5g Dy deposits

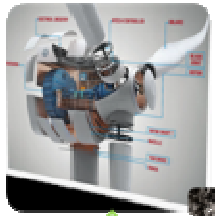
RECAPE Process

Magnet scraps

Waste containing magnets

Thermal treatment (demagnetization)



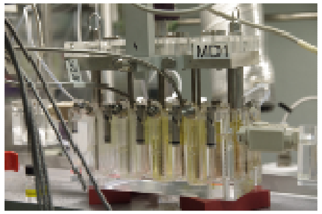


(200℃) T > T_c

Hydride cracking and grinding

Mechanical treatment
Dissolution

REE separation by liquid-liquid extraction



Fe+B+additives

Dy

Nd+Pr

Recovery > 99%
Purity > 99.5%

Patented process

REE conversion to oxides → REE conversion to metal

First preliminary techno-économics evaluations

Waste effluent treatment cost has to be further assessed

Nd_2O_3 = 51 \$/kg – Dy_2O_3 = 310 \$/kg (2016)

NdFeB magnet Flowrate (t/yr)	REO Production (t/yr)	Investment cost (M€)	Operational cost (M€/yr)	Turnover (M€/yr)
15000 t/yr (EoL, Europe) * 27 % = 4000 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 (personal)	0,7

For 4000 t/yr , ROI of 3 yrs, the benefit would be positive
For 100 t/yr, the process is unprofitable

A novel TriNox process avoiding SX

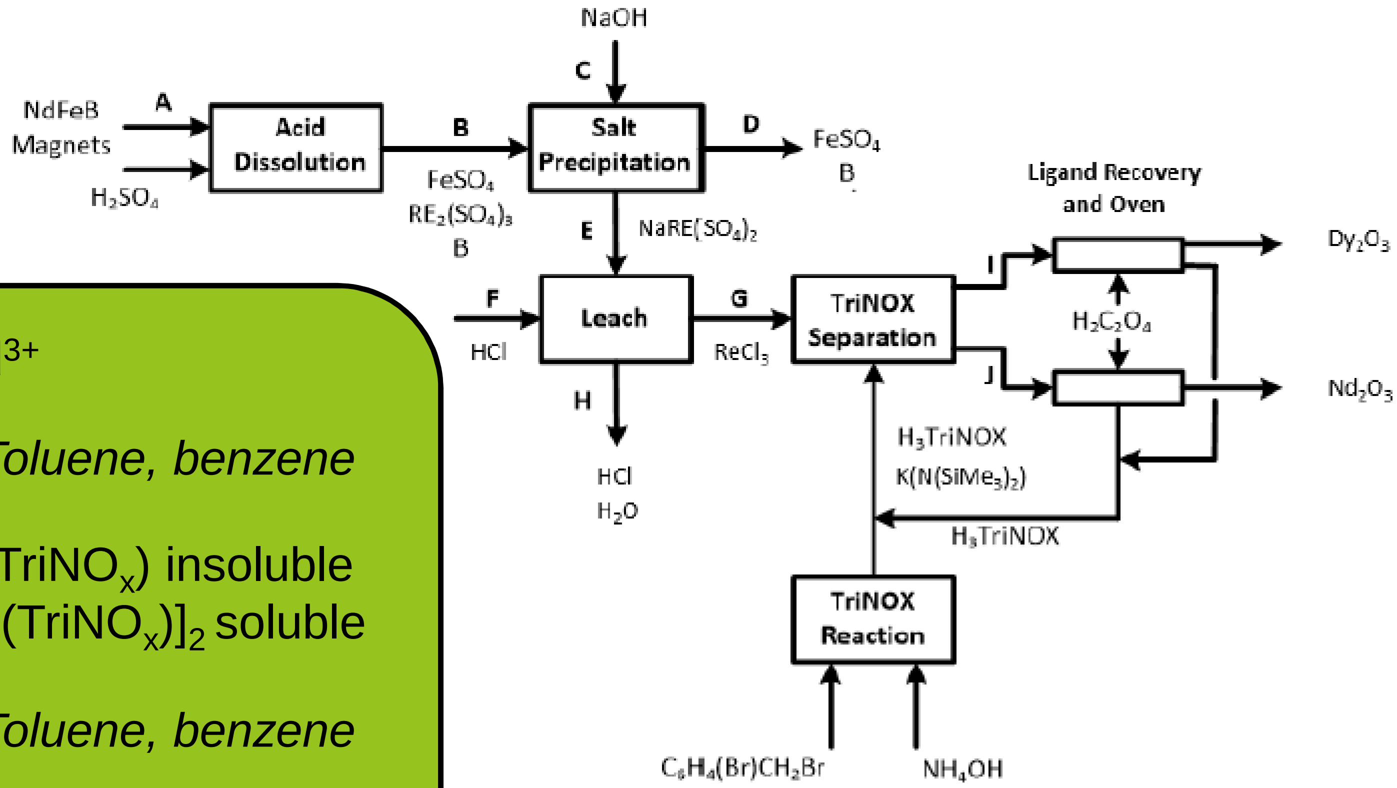
$Dy^{3+} << Nd^{3+}$

Toluene, benzene

$Dy^{3+} \rightarrow Dy(TriNO_x)$ insoluble
$Nd^{3+} \rightarrow [Nd(TriNO_x)]_2$ soluble

Toluene, benzene

$S_{Nd/Dy} = 359$ (benzene)



E.J. Schelter, J.A. Bogart, Simple chemical method for the separation of rare earth metals, Patent WO2016019044 A1

Some techno-economics considerations on theTriNox Process

USA : 7000 t REE in magnets in 2020 * 2% (recycling rate) → Production of 126 t/yr of Nd_2O_3 and 14 t/yr Dy_2O_3 from scraps

2016 / kg Nd_2O_3

Rare Earth Oxide Price	Raw Materials Cost: $ 109.65	$ 219.29	$ 328.94	$ 438.58
$ 42.00	Negative IRR	Negative IRR	Negative IRR	Negative IRR
$ 84.00	Negative IRR	Negative IRR	Negative IRR	Negative IRR
$ 126.00	14.09%	Negative IRR	Negative IRR	Negative IRR
$ 168.00	45.97%	Negative IRR	Negative IRR	Negative IRR
$ 210.00	71.98%	23.41%	Negative IRR	Negative IRR
$ 252.00	95.62%	53.20%	Negative IRR	Negative IRR
$ 294.00	117.62%	78.73%	31.82%	Negative IRR
$ 336.00	138.33%	102.12%	60.35%	1.19%

IRR : Internal Rate Of Return → **No mid term profitability**

Dai, Alan X.; Lippincott, Connor A.; Nissan, Michael E.; and Shim, Richard, "Recycling of Neodymium and Dysprosium from Permanent Magnets" (2016). Senior Design Reports (CBE). Paper 81.,

Conclusions and outlooks

- A full REE separation process from used permanent magnets (RECAPE) has been developed :
  - efficient with recovery of highly pure Dy and Nd
  - **compact** with a limited number of unit operation

- Process patented in 2014 with a TRL of 5

- This is a generic process adaptable for other WEEE or valuable materials

- We are open to collaboration for the scaling-up of the process based on techno-economics evaluation and Life Cycle Assesment.

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