The REPUTER project for Ni-MH battery recycling

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Critical supply of (some) rare earth elements

- **Demand growing**, especially for magnets (> 7% per year for Nd)
- Accelerated growth of **HEV/EV market** (+30% in 2017)
- Market driven by **Nd** and **Dy** demand
- Global REO production in 2018 estimated at 175 kT/yr
- Production chain concentrated in China (mining, separation, downstream manufacturing, R&D capacity): **80% world REO supply**
- Significant **price volatility** during the last 10 years
- Currently **no European mine** in operation

Possible ways to alleviate REE supply risk

- **Reducing** consumption (shift in technology)
- **Substitution** by other non-critical metals (La, Ce)
- **Diversifying** supply
  - Primary and secondary sources (new mines, tailings…)
  - **Recycling** (scraps, urban mine)

References: Roskill 2015, IMCOA 2017

REO consumption by application 2012-2016

- Permanent magnets 31%
- Metal alloys 18%
- Catalysts 18%
- Phosphors 4%
- Polishing 13%
- Glass and ceramics 11%
- Others 5%

Source: EU report 2017
REE recycling: closing the materials loop

Advantages of recycling

- Target only the **most critical** rare earths (balance problem)
- No issues with **radioactive elements** \( ^{235}\text{U}, ^{238}\text{U}, ^{232}\text{Th} \)
- Lower environmental footprint (**public acceptance**)

Challenges

- Insufficient and untargeted **collection** of waste sources
- Difficult recovery of REE-containing fractions
- Difficult **separation of individual REE in pure form**
- **Low economic interest** in line with current market prices

Very low recycling rates*
average 7% in EU

*very disparate values in the REE series
Source: JRC, EC Report on CRM 2018

Opportunities

- Competences and expertise of the **European recycling industry**
- Development of a circular economy
- Positive economic and environmental **impact**

Recovering REE from Ni-MH batteries

- **Battery** recycling is an obligation
- Immediate **availability** of the supply
- Battery recycling processes already implemented
Ni-MH battery composition

Negative electrode + collector
Positive electrode
Positive terminal
Packaging
Separator

Active material
MmB₅ & (Y₂O₃, Yb₂O₃, additives)

Anode (-)
Mm = La₀.₆₂Ce₀.₂⁷Pr₀.⁰₈Nd₀.₀₈
B₅ = Ni₃.₅₅Co₀.₇₅Mn₀.₄Al₀.₃

Cathode (+)
Active material
Ni(OH)₂ & (Ni, Co, Zn, Y)

Interest for the integration of a REE recovery step in the process of Ni-MH battery recycling

Al-Thyabat, Minerals Engineering 2013

Composition cylindrical Ni-MH battery

Ni 40%
Fe 22%
REE 10%
Co 3%
Other 25%
The REPUTER project

“Recovery, purification and elaboration of rare earth elements for Ni-MH battery recycling”

Overall project goal:

Develop an efficient, eco-conceived rare earth recovery and separation process flowsheet from used Ni-MH batteries, starting from collection down to the formulation of REE as pure metals or oxide materials ready to be used in various applications.

Objectives:

- Reinforce through common goals the expertise and competences gained in France in hydrometallurgy and in pyrometallurgy;
- Remove some of the scientific and technical barriers currently affecting the REE recycling;
- Evaluate different flowsheets for producing recycled rare earths in the form of oxides or purified metals for industrial applications (catalytic materials, battery grade alloys, etc.);
- Evaluate the impact of the recycling process using a technical-economic and life cycle analysis.
The REPUTER project

Consortium of 5 partners

- **SNAM** - Physical and mechanical battery treatment
- **CEA DRT (LITEN)** - Leaching and precipitation, TE+LCA
- **CEA DEN** - coordination, extraction, cermet conversion, molten salt electrolysis, TE+LCA
- **LGC** - molten salt electrolysis
- **ICMPE** - metal alloy purification (vacuum fusion)

- Total budget 2 M€ (ANR funding: 750 k€)
- Start 2016 pour 49 months (→ end 2019)

Labelling by 3 competitive poles:
Various flowsheets for REE recycling

1. Collection and recovery of REE-rich fractions from wastes

2. Separation and purification of rare earths by solvent extraction

3. Conversion of REE

4. Pyrochemical processes for REE metal elaboration

Market

Industry and consumers

Ni-MH batteries

Mischmetal

Pure REE

Cermets / Pure REO

Pure Ni and Co

Fe-Ni alloy / REO

Impure REE solutions + Ni, Co, Fe…

Black mass

Pure REE

Pure REO

Ni-MH batteries
Recovery of REE-rich fractions

- Physical and mechanical treatment of batteries
  - Adapting the existing NiMH recycling process for the recovery of RE-rich fractions:
    - Selection of battery cell types (origin, condition, composition…)
    - Optimization of crushing and sieving operations
    - Choosing the ideal conditions for a size based separation REE/Fe

- Disassembling
- Thermal treatment
- Crushing sieving
- Black mass
- Hydrometallurgical processes
- Pyrometallurgical process

Knife mill
Hydrometallurgical treatment of the black mass

- **Total digestion (REE + Ni, Co...)**
  - Choice of acids and leaching conditions compatible with an industrial approach
    - Excellent yield for HNO₃ and HCl acid solutions at controlled pH
    - Optimization of S/L ratio
    - Scale-up to a 5 L reactor

**Lixiviation solution composition (g/L)**
HNO₃ 1 M (pH = 0), rt, S/L = 10%

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>4.6</td>
</tr>
<tr>
<td>Ce</td>
<td>7.7</td>
</tr>
<tr>
<td>Pr</td>
<td>0.5</td>
</tr>
<tr>
<td>Nd</td>
<td>2.0</td>
</tr>
<tr>
<td>Ni</td>
<td>40.0</td>
</tr>
<tr>
<td>Co</td>
<td>5.2</td>
</tr>
<tr>
<td>Mn</td>
<td>2.1</td>
</tr>
<tr>
<td>Fe</td>
<td>3.3</td>
</tr>
</tbody>
</table>
Hydrometallurgical treatment of the black mass

- **Selective leaching**
  - Precipitation of REE in sulfuric acid solution as double sulfate
  - Optimization of REE precipitation by Na\(^+\) addition
  - Redissolution of double sulfate precipitate (HCl, HNO\(_3\)) and conversion to oxide

[Graph showing concentration over time for various elements.]
Hydrometallurgical treatment of the black mass

- Implementation of a hydrometallurgical pilot unit
  - Integrated to the SNAM site in Viviez (France): logistics, SEVESO environment, QA…
  - Dissolution / precipitation / filtration / calcination units
  - Scalable towards an increased capacity production

10 L reactor

1 m² press filter
Integrated approach to SX process development

Specific objectives

- Design and synthesis of extracting molecules
- Optimization of extractant formulation
- Development of extraction models and flowsheets
- Optimization

Extractant system selection
- Molecular scale chemistry
- Measurement of batch data
- Understanding the extraction mechanisms (affinity, selectivity)
- Structure-activity relations

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

Process modelling
- Development of extraction models and flowsheets

PAREX simulation code

Goal: extract the REE from the leaching solutions while allowing the recovery of pure Ni and Co

Challenge: Need an extractant with excellent affinity and selectivity for REE in the presence of Fe$^{3+}$

Screening of several commercially-available extracting molecules

Selection of diglycolamides (TODGA) class of solvating extractants

Extraction capacity inversely proportional to REE$^{3+}$ ionic radius

Preference for heavy RE and good intra-REE separation factors in nitric acid media

Excellent selectivity with respect to transition metals (Fe$^{3+}$, Ni$^{2+}$, Co$^{2+}$)

\[
D_M = \frac{[M^{n+}]_{org}}{[M^{n+}]_{aq}}
\]

\[
FS_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}}
\]

\[
N\ O\ \ N
\]

TODGA

Sasaki et al, 2002
REE separation by solvent extraction

- Tested TODGA on simulated and real solutions in HNO₃ and HCl media
- Optimisation of extraction and stripping conditions

REE extraction function of TODGA concentration

<table>
<thead>
<tr>
<th>Element</th>
<th>Initial aqueous phase (ppm)</th>
<th>Aqueous phase after extraction (ppm)</th>
<th>Organic phase after extraction (ppm)</th>
<th>Mass balance (%)</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>7 159</td>
<td>167,0</td>
<td>6608,6</td>
<td>94,6</td>
<td>40</td>
</tr>
<tr>
<td>Ce</td>
<td>9 180</td>
<td>80,6</td>
<td>8707,4</td>
<td>95,7</td>
<td>108</td>
</tr>
<tr>
<td>Pr</td>
<td>1 385</td>
<td>2,0</td>
<td>1357,6</td>
<td>98,2</td>
<td>679</td>
</tr>
<tr>
<td>Nd</td>
<td>2 768</td>
<td>2,4</td>
<td>2760,0</td>
<td>99,8</td>
<td>1150</td>
</tr>
<tr>
<td>Ni</td>
<td>62 622</td>
<td>63761,8</td>
<td>1,2</td>
<td>101,8</td>
<td>0,00</td>
</tr>
<tr>
<td>Co</td>
<td>8 136</td>
<td>8508,6</td>
<td>3,0</td>
<td>104,6</td>
<td>0,00</td>
</tr>
<tr>
<td>Mn</td>
<td>3 421</td>
<td>3498,0</td>
<td>24,4</td>
<td>103,0</td>
<td>0,01</td>
</tr>
<tr>
<td>Fe</td>
<td>4 358</td>
<td>4423,4</td>
<td>105,0</td>
<td>103,9</td>
<td>0,02</td>
</tr>
</tbody>
</table>

- Excellent extraction of light REE upon increasing TODGA concentration
- Very high selectivity (Ni, Co, Mn, Fe not extracted)
- Very high REE purity in the extract >99% (1 contact, before scrubbing and stripping)
REE separation by solvent extraction

- Tested TODGA on simulated and real solutions in HNO₃ and HCl media
- Optimisation of extraction and stripping conditions

Near-quantitative stripping of REE in 2 contacts with dilute acid at room temperature (HNO₃ 0.01M or HCl 0.1M)
Elaboration of a **phenomenological model** from experimental batch data

**Representation of distribution equilibria**

HNO$_3$-Oct, HNO$_3$-TODGA, Ln-NO$_3$-TODGA

- (HNO$_3$)(octanol)$_2$
- (HNO$_3$)$_m$(TODGA) with $m = 1$ to 3
- M(NO$_3$)$_3$(TODGA)$_n$ with $n = 1$ to 3 for La, Nd, Ni, Fe

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

**Activity coefficients taken into account in aqueous phase**

- Implementation of the model in the **CEA PAREX+ simulation code** and calculation of flowsheets
- Pilot demonstration on real solutions
Objectives:
- Improving the extraction of light REE
- Reducing the extractant concentration in the organic phase (OPEX)
- Increasing the selectivity towards transition metals (e.g. Fe, Ni, Co)
- Improving the REE extraction in sulfuric and hydrochloric acid media

7 new DGAs synthesized

Increase the amphiphilic character
- Short (hydrophilic) alkyl chains: $R_1$
- Long (lipophilic) alkyl chains: $R_2$
Solvent extraction by DGA in nitric acid solution

- Increased extraction (x 15) of light REE for **N,N-Ethyl** compared to TODGA
- Excellent selectivity REE / impurities (Fe, Co, Ni)
- Working on understanding the influence of **minor chain variations** on the extraction properties

Andreadias, patent FR1853263

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**Graph Explanation:**
- **Distribution ratio**
- **Elements:** La, Pr, Nd
- **Extraction systems:** TODGA, N1-E, N1-IP, N1-P, N1-PY, N2-P, N2-IB, N2-B
- **Conditions:** 0.1 M DGA in HTP + n-octanol HNO₃ 3 M solution containing REE, Ni, Co 1 g/L, Fe 10 g/L
- **Results:**
  - \( D_{Fe} \leq 0.01 \)
  - \( D_{Ni} = D_{Co} \leq 0.03 \)
Conversion of purified REE into oxides

- Production of a highly homogeneous powder by **oxalic precipitation**
- Thermal treatment by calcination leading to oxides

**Coprécipitation**

\[ \text{Ln}^{2+} + 3\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Ln}_2(\text{C}_2\text{O}_4)_3, n\text{H}_2\text{O} \]

Robust process exploited for Pu conversion

Affords supplemental purification with respect to other metal impurities
Conversion of REE into cermets

- **Conversion of Ni and REE into cermets Ni-Ce(Ln)O₂ (WAR process)**
  - CERMET = porous microspheres of cerium oxide incorporating other REO and metallic Ni
  - Numerous applications replacing PGM in **catalysis** (steam methane reforming, hydrogenation)
  - **No need for SX purification** of input leaching solutions

**Straight-forward synthetic process (CEA patent)**

Fixation: \((2x + 3y)RNH₄ + xNi^{2+} + yCe^{3+} \rightarrow (R₃Ce)ₙ(R₂Ni)ₓ\)

Minéralisation: \((R₃Ce)ₙ(R₂Ni)ₓ \xrightarrow{Δ} (CeO₂)ₙ(NiO)ₓ\)

Réduction: \((CeO₂)ₙ(NiO)ₓ \xrightarrow{H₂} (CeO₂)ₙ/Niₓ\)

- **CERMET particles with controlled parameters** (size, porosity, exchange area)

- **Impure Ni-MH solution**
  - Ni, REE...

- **Size and Shape separation** → **REE loading** → **Drying 105°C** → **Calcination 500-1200°C**

- **Caisso, JACS 2017**
  - Caravaca, **Catalysts, 2017, 7(12), 368**
  - T. Delahaye, patent EP3034209
Electroreduction in molten chloride of Nd suffers from low faradic yields (<40%) due to the presence of M²⁺ species (disproportionation reaction Nd⁰ + Nd³⁺ → Nd²⁺)

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

- Salt composition (chloride / fluoride)
- Temperature
- RE concentration
- Current and current density

Metal deposition tests to evaluate the process efficiency:

- Faradic yield, product purity, cell materials compatibility
- Operating conditions:
  - 500 g salt bath
  - Constant current electrolysis
  - 4 wt% < TR³⁺ < 7 wt%
  - 0.1 A/cm² < Cathodic current density < 0.3 A/cm²
  - 2000 s < Electrolysis time < 10000 s for 1 g RE metal
Rare earth (RE) chloride electrolysis in LiCl-KCl (450-500°C)

- La deposition: dendritic deposit with high current efficiency (CE)
- Nd deposition: powder deposition with low CE 40%

- Grouped La, Ce, Pr, Nd electrolysis according to black mass composition
- Co-deposition allows the quantitative recovery of Nd (stabilisation effect)
- Reproducible results
- Composition stable on 6 successive deposits
- La recovery is more difficult (the lowest reduction potential)
Molten salt electroreduction for metal elaboration

- Neodymium electrochemical behavior in LiCl-LiF (550°C-650°C)
  - Addition of LiF in LiCl stabilizes Nd³⁺
  - Nd²⁺/Nd⁰ transition tends to disappear (not completely)
  - Electrolysis tests show that Nd deposition in LiCl-LiF give dendritic deposition with higher CE than LiCl-KCl (70< CE <90)
  - Best CE are obtained at 550°C (4wt%< Nd³⁺ <6 wt%)

![Nd deposit]
Innovative solutions for REE recycling from Ni-MH batteries

Integration of the REE recovery step in the global battery recycling process
Simple, compact flowsheets producing value-added products (cermet, mischmetal...)

Innovating pyrometallurgical processes

Cermet materials for catalytic applications

Novel specific extractants
Development of adapted flowsheets

1. Collection and recovery of REE-rich fractions from wastes

2. Separation and purification of rare earths by solvent extraction

3. Conversion of REE

4. Pyrochemical processes for REE metal elaboration

Particle size separation
Selective leaching

Mischmetal
Pure REE

Cermet / Pure REO

Pure Ni
and Co

FeNi alloy /
REE

Ni-MH batteries

Industry

Industry and consumers

Pure REO

Blackmass

Impure REE solutions
+ Ni, Co, Fe...

Industry and consumers

FeNi alloy /
REE

Pure REO

Cermets / Pure REO

Industry
Thank you for your attention

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