Recycling of REE and Strategic Metals from Wastes of Electrical and Electronic Equipments

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PROMETIA 28-29 November 2017, Barcelona
OUTLINE

- Introduction on Strategic Metals
- Strategic Metals in WEEE
- Case study (Extrade Project)
- Case study (Valoplus Project)
- Conclusions
INTRODUCTION

The developed countries deal with a persistent concern about the supply of strategic metals. These strategic metals are essential to the development of innovative high-tech industries, and particularly those associated with green energy.

These metals are found mainly in the following EEE-components and EEE-product groups: Mobile phones; Personal Computers (desktop computers), Laptops and notebooks; TV and flat screen monitors, Rechargeable batteries, wind turbines and photovoltaic cells.

The political crisis caused by China towards Japan with REE supply in balance (95% of the world's needs) did that amplify those concerns.

In this context, in 2011, 2014 and 2017, the European Union published a list of 14, 20 and 27 Strategic Raw Materials respectively.

At the French level, the roadmap to improve the productivity of the resources is marked by the installation in April 2010 strategic metals Plan and the creation of the COMES (Committee for strategic metals) in January 2011.

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What is a critical metal

- Base metals vs critical metals
- Two criteria:
  - The needs of our industry for a given metal
  - The worldwide availability of this metal

- A material will be critical in an industry but not in another, in one country but not in another, and it evolves over time.
### EU CRMs 2017

<table>
<thead>
<tr>
<th>CRMs (27)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
</tr>
<tr>
<td>Fluorspar</td>
</tr>
<tr>
<td>LREEs</td>
</tr>
<tr>
<td>Phosphorus</td>
</tr>
<tr>
<td>Baryte</td>
</tr>
<tr>
<td>Gallium</td>
</tr>
<tr>
<td>Magnesium</td>
</tr>
<tr>
<td>Scandium</td>
</tr>
<tr>
<td>Beryllium</td>
</tr>
<tr>
<td>Germanium</td>
</tr>
<tr>
<td>Natural graphite</td>
</tr>
<tr>
<td>Silicon metal</td>
</tr>
<tr>
<td>Bismuth</td>
</tr>
<tr>
<td>Hafnium</td>
</tr>
<tr>
<td>Natural rubber</td>
</tr>
<tr>
<td>Tantalum</td>
</tr>
<tr>
<td>Borate</td>
</tr>
<tr>
<td>Helium</td>
</tr>
<tr>
<td>Niobium</td>
</tr>
<tr>
<td>Tungsten</td>
</tr>
<tr>
<td>Cobalt</td>
</tr>
<tr>
<td>HREEs</td>
</tr>
<tr>
<td>PGMs</td>
</tr>
<tr>
<td>Vanadium</td>
</tr>
<tr>
<td>Coking coal</td>
</tr>
<tr>
<td>Indium</td>
</tr>
<tr>
<td>Phosphate rock</td>
</tr>
</tbody>
</table>
Countries accounting for largest share of global supply of CRMs

China is the major supplier of critical raw materials (70% of their global supply and 62% of their supply to the EU)
Brazil (niobium), USA (beryllium and helium), Russia (palladium) and South Africa (iridium, platinum, rhodium and ruthenium) are also important producers of critical raw materials


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Generally the critical metals are used in small proportions but their application for mass-market products makes that the world demand quickly increases.
Global EOL recycling rates for 60 metals (Graedel et al 2011°)

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Clean energy
Wind energy in particular, permanent magnets of the electric generators mobilizing several rare earths

TRANSPORT
Production of lithium for hybrid and electric vehicles - Alloys very high-performance

PHOTOVOLTAIC
PHOTOVOLTAIC Cells with layers CIGS (Cu, In, Ga and Se), cells in the cadmium telluride and cells in the germanium

Electronic devices
Alloys silicone-germanium, hafnium, GaAs for new transistors

GEOLOCALISATION
Gallium nitride

Screen (LCD-LED)
Indium, Galium

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Permanent magnets in standard vehicle

Normal car today may contain hundreds of magnets

Christian Jönsson Magnets in art (and design, EUREAN, EU FP7, Marie Curie Initial training, Network

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Wind turbines

By MW installed production capacity:

- +/- 600kg of Nd/Fe/B type permanent magnets

- 4.1% Dy = 24.6 kg per MW about +/- 40t Dy used in 2013 (worldwide production +/- 1600t)

- 31% Nd = 186 kg Nd per MW

(General Electric, given: US DEPARTMENT OF ENERGY)

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Printed circuit boards

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Chemical composition of a Smartphone

**ELEMENTS OF A SMARTPHONE**

**SCREEN**
- Indium tin oxide is a mixture of indium oxide and tin oxide, used in a transparent film in the screen that conducts electricity. This allows the screen to function as a touch screen.
- The glass used on the majority of smartphones is an aluminosilicate glass, composed of a mix of alumina ($\text{Al}_2\text{O}_3$) and silica ($\text{SiO}_2$). This glass also contains potassium ions, which help to strengthen it.
- A variety of Rare Earth Element compounds are used in small quantities to produce the colours in the smartphone's screen. Some compounds are also used to reduce UV light penetration into the phone.

**ELECTRONICS**
- Copper is used for wiring in the phone, whilst copper, gold and silver are the major metals from which microelectrical components are fashioned. Tantalum is the major component of micro-capacitors.
- Nickel is used in the microphone as well as for other electrical connections. Alloys including the elements praseodymium, gadolinium and neodymium are used in the magnets in the speaker and microphone. Neodymium, terbium and dysprosium are used in the vibration unit.
- Pure silicon is used to manufacture the chip in the phone. It is oxidised to produce non-conducting regions, then other elements are added in order to allow the chip to conduct electricity.
- Tin & lead are used to solder electronics in the phone. Newer lead-free solders use a mix of tin, copper and silver.

**BATTERY**
- The majority of phones use lithium ion batteries, which are composed of lithium cobalt oxide as a positive electrode and graphite (carbon) as the negative electrode. Some batteries use other metals, such as manganese, in place of cobalt. The battery's casing is made of aluminium.

**CASING**
- Magnesium compounds are alloyed to make some phone cases, whilst many are made of plastics. Plastics will also include flame retardant compounds, some of which contain bromine, whilst nickel can be included to reduce electromagnetic interference.
Available for recycling: smartphones

**REEs:** 64 532 423 853 smartphones * 309,24 mg /smartphone = 19 956 tonnes

**Indium:** 64 532 423 853 smartphones * 27,75 mg /smartphone = 1791 tonnes

**Lithium:** 64 532 423 853 smartphones * 0,84 g / smartphone = 54 207 tonnes

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Airbus A380 contains 530 km of conductor wires, 40 300 connectors; 2,9 million of contacts. The contacts are almost all alloys Cu/Be (+/- 2% Be)

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Recovery of strategic metals

REPARTITION OF PROJECTS BY TYPE OF WASTE IN FRANCE

REPARTITION OF PROJECTS BY TYPE OF METALS IN FRANCE

Définition d’orientations prioritaires de recherche –développement pour le développement de compétences françaises de recyclage des métaux critiques, Report, Ademe, Juin 2017

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Permanent magnet containing REE in WEEE

<table>
<thead>
<tr>
<th>REE application</th>
<th>Estimated REE stocks in 2020 (tons)</th>
<th>Estimated average lifetime (years)</th>
<th>Estimated REE old scrap in 2020 (tons)</th>
<th>Pessimistic scenario: recycled REE in 2020 (tons)</th>
<th>Optimistic scenario: recycled REE in 2020 (tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnets</td>
<td>300,000</td>
<td>15</td>
<td>20,000</td>
<td>3300</td>
<td>6600</td>
</tr>
<tr>
<td>Lamp Phosphors</td>
<td>25,000</td>
<td>6</td>
<td>4167</td>
<td>1333</td>
<td>2333</td>
</tr>
<tr>
<td>Nickel-metal-hydride batteries</td>
<td>50,000</td>
<td>10</td>
<td>5000</td>
<td>1000</td>
<td>1750</td>
</tr>
<tr>
<td>Total</td>
<td>375,000</td>
<td></td>
<td>29,167</td>
<td>5633</td>
<td>10,683</td>
</tr>
</tbody>
</table>
Recovery of REE from permanent magnets

2014: More than 80 processes

- Hydrogen decrepitation
- Magnesium liquid
- Extraction in gas phase
- Extraction by solvent
- Electrolysis
- Pyrometallurgy
- Ionic liquid
- Acid leaching
WEEE
- Depollution
  - Recovery of components containing magnets
- Shredding
  - Thermal treatment
  - Fragmentation
  - Magnetic separation
    - Eddy current Separation
    - Manual sorting
  - Demagnetized magnets
- Shredding
- Milling
- Powder purification
- Selective extraction of REE
- Magnetization
- New magnets

Routine Process
EXTRADE
EXTRADE PROJECT

REEs containing components in WEEE

Hard Disk Drives

Loudspeakers

Small electric motors

Metallic support

Magnet
Rare earth permanent magnets

Rare earths: 17 elements

Nd - Neodymium 144.24
Pr - Praseodymium
Dy - Dysprosium
Fe - Iron
B - Boron

Comparative table of maximum energy product for different permanent magnets

Nd-Fe-B ingot produced by arc-melting
Nd-Fe-B magnets with nickel plating

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**EXTRADE PROJECT (Characterization)**

- **Nd$_2$Fe$_{14}$B magnet**
- **Coating (Ni or Ni/Cu) thickness 28µm**

### Elements and Weight Percentages

<table>
<thead>
<tr>
<th>Elem</th>
<th>Weight %</th>
<th>Nd$<em>2$Fe$</em>{14}$B Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fek</td>
<td>69.6</td>
<td>72.0</td>
</tr>
<tr>
<td>NdL</td>
<td>28.1</td>
<td>27.0</td>
</tr>
<tr>
<td>DyL</td>
<td>2.3</td>
<td>1.0 (B)</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Thermal treatment (demagnetization)

Electrical (high-voltage electric pulses) and Mechanical treatment to recover magnets from the computer system unit

Route 1 – elaboration of new magnets with recycled magnets powder (short loop)

- Separation of Ni coating from NdFeB magnets
  - Mechanical treatment
  - Chemical treatment: solvo-thermal decrepitation
- Press-molding in magnetic field / sintering / magnetization

Route 2 – extraction of REE using innovative hydrometallurgical techniques

- Weak & cheap acid selective dissolution
- Selective recovery of REE using biomaterials
- Selective precipitation

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Manual dismantling

HDD
- Disque dur
- Magnet

Loudspeakers
- Metallic support
- Magnet

Small electrical motors
- Composite Magnet
Quantification of magnet in electronic devices

<table>
<thead>
<tr>
<th>Sources</th>
<th>Weight % of magnet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computer loudspeakers</td>
<td>4 – 6</td>
</tr>
<tr>
<td>HDD from central unit computer</td>
<td>2.5 – 2.8</td>
</tr>
<tr>
<td>HDD from Laptop</td>
<td>2 - 3</td>
</tr>
<tr>
<td>Small electric motors (A)</td>
<td>22 – 26</td>
</tr>
<tr>
<td>Small electric motors (B)</td>
<td>0.8 – 2</td>
</tr>
</tbody>
</table>
Composition of HDD

- Magnet: 3%
- Plastics: 1%
- Other metals: 1%
- Iron scrap: 8%
- PCB: 7%
- Aluminum: 80%

EXTRADE PROJECT (Characterization)

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EXTRADE PROCESS (Recovery of magnets from HDD)

1. Demagnetisation
2. Screening
3. Liberation of magnets
   - Mechanical/Electro-fragmentation

HDD

HDD free of magnets to metallurgy

Permanent magnets

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Route 2 – extraction of REE using innovative hydrometallurgical techniques

Selective leaching

Precipitation (NaOH)
Route 2 – extraction of REE using innovative hydrometallurgical techniques

Selective sorption of REE using biomaterials

Remaining metals in solution, %

Bio materials

xA  xB  xC  xD  xE  xF

Nd  Dy  Fe

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Precipitation (oxalic acid)

Rare earth oxalates

XRD

Nd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_{10}$

Rare earth oxides

XRD

(Nd$_{0.9}$Dy$_{0.1}$)$_2$O$_3$
EXTRADE PROCESS (Recovery of magnets from HDD)

1000 kg
30 kg d'aimants

Traitement thermique, 350°C, 30 mn

1000 kg
30 kg d'aimants

Broyage autogène, 45 mm

970.62 kg
0.69 Kg

Classification

229.41 kg
30 kg

20 - 5 mm

FM1

144.78 kg
26.63 kg

140.88 kg
24.94 kg

Séparation magnétique BI

FN2

FN1

4.37 kg
10.12 kg

FM2

4.37 kg
3.90 kg

FM1

SN2

SN1

FM

Séparation magnétique BI

FN

Concassage

151 kg
29.31 kg

Fe+B

Nd, Dy, Pr

Lixivation

Ni

20.01 kg
9.0 kg

29.31 kg
0.29 kg
ANR project - Valoplus

Valorisation of Fluorescent Powders of used CFL

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Objectives

Users → Collection → Recycling companies

Dealers

CFL manufacturers

VALOPLUS process
Physico-chemical separations

BRGM / SOLVAY/VEOLIA / Georessources

Fluorescent powder

Glass
Metals
Mercury
Others

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Composition of Fluorescent Lamps

- **Atomes de Mercure** (Mercury atoms)
- **Ballast** (Ballast)
- **Électrodes** (Electrodes)
- **UV** (UV)
- **Verre** (Glass)
- **Couche de luminophores** (Phosphor Coating)
- **Neutral gas**
- **Mercury atoms**
- **Electrode**
- **Screw Cap**
- **Electrical contact**

### Fluorescent powders:
- **Mixture of several phosphors,**
- **Containing of complex compounds and expensive to elaborate,**
  - a. Non direct reusable as lamps
  - b. Only components not yet recycled

### Acronym | Phosphor lamps
--- | ---
BAM | $\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}^{2+}$
CAT | $(\text{Ce},\text{Tb})\text{MgAl}_{11}\text{O}_{19}$
CBT | $(\text{GdMg})\text{B}_{2}\text{O}_{10} : \text{Ce}^{3+},\text{Tb}^{3+}$
LAP | $\text{LaPO}_{4} : \text{Ce}^{3+},\text{Tb}^{3+}$
YOX | $\text{Y}_{2}\text{O}_{3} : \text{Eu}^{3+}$
Halo-phosphates | $(\text{Sr},\text{Ca})_{10}(\text{PO}_{4})_{6}(\text{Cl},\text{F})_{2} : \text{Sb}^{3+},\text{Mn}^{2+}$

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Recycling Methods of CFLs

**1. Crushing + Classification**

- Metals
- mixture of fluorescent powder with glass and Hg
- Elimination and deposit

**2. End cut**

- Metals
- Glass
- Ceramics
- Fluorescent powders

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Crushing</th>
<th>End cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 40 µm</td>
<td>28.89</td>
<td>0.3</td>
</tr>
<tr>
<td>+20 - 40 µm</td>
<td>6.95</td>
<td>0.8</td>
</tr>
<tr>
<td>10-20 µm</td>
<td>64.16</td>
<td>19.4</td>
</tr>
<tr>
<td>10 µm</td>
<td>64.16</td>
<td>79.4</td>
</tr>
</tbody>
</table>
Results

- Used fluorescent lamps
- Dismantling
  - Powders containing Hg
- Thermal treatment
  - Powders Free of Hg
  - Urban water
- Hydro-cyclone
  - Urban water
  - Magnetic separation 10A
    - Magnetic fraction 10A
      - LAP, BAM, CAT, CBT Less YOX
  - Magnetic separation 5A
    - Magnetic fraction 5A
      - LAP, BAM, CAT, CBT Less YOX and Halo-Ph
  - Urban water
  - Reagent AC-3
- Flotation
  - Non Magnetic 10A
    - Non Magnetic 5A
      - LAP, BAM, CAT, CBT Less YOX and Halo-Ph
  - Float
    - YOX, Less Halo-Ph, and less BAM, LAP, and CBT
  - Sink
    - Halo-Ph, and less BAM, LAP, and CBT
  - Magnetic fraction 10A
    - LAP, BAM, CAT, CBT Less YOX and Halo-Ph
  - Magnetic fraction 5A
    - LAP, BAM, CAT, CBT Less YOX and Halo-Ph
  - Reused glass Halo-phosphates and fluorescent powders
- Purification
  - H$_2$O+HCl+H$_3$PO$_4$
  - Halo-Ph and aLAP, CAT, BAM and less CBT

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Results

Classification by hydro-cyclone: very efficient to produce fraction -10µm (Fluorescent powder)

Magnetic separation to 18000 Gauss:

✓ For the Non-magnetic fraction
  • Recovery of > 75% of the Halo-phosphates
  • Recovery rate of the YOX and BAM > 95% (OF hydro cyclone)

✓ For the magnetic fraction
  • Recovery rate of the LAP and CBT > 80%

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Solvay/Rhodia factory at Saint-Fons (Rhône) for recovery of REEs from CFLs
First unit of recycling of rare earths in Europe from CFLs.
40 employes

1 000 tonnes of Fluorescent Powder / year in both units (Saint-Fons (Rhône) and La Rochelle to extract 200 tonnes of REEs. About 10% of Solvay/Rhodia production


From 1 100 - 1 500 t of waste / year, where 1 000 t fluorescent powders and 100-500 t of glass, the process produces:
- 188 t of REEs as oxides (430 t as nitrates),
- 100 - 500 t of glass (by-products to be valorised),
- 800 t of phosphates (by-product to be valorised),
- 150 t of banal wastes.

Conclusions

- Recovery of Strategic metals from secondary materials complements the primary mining of REE ores.
- The recycling of permanent magnets: an ecological solution to the difficulties of supply in rare earths.
- Waste stream of REE was identified and Amount of deposit was estimated.
- Recovery of Strategic metals from WEEE is challenging and possible.

Recycling of Strategic Metals is recommended for:
- Efficient use of natural resources
- Supply of critical raw materials
- Balance problem.
THANK YOU FOR YOUR ATTENTION

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