SOLVAY latest developments in Rare Earth Recovery from Urban Mines

Exchange of good practices on metal by-products recovery

Technology and policy challenges

12-13 November 2015
Brussels, Belgium
Content

1. The RE market characteristics and the field of recycling

2. RE processing: Advantages and drawbacks of recycling

3. Recycling of RE at La Rochelle plant
   - From La Rochelle historical loss of yield
   - From NiMH batteries – A collaboration between Umicore and Solvay
   - From EOL lamps

11/13/2015
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CHEMICAL AND PHYSICAL PROPERTIES OF RARE EARTHS

RE separation is very difficult

Common external orbitals
5d1 6s2 valence electrons

Chemical properties

Internal orbital
progressival fillings 4f \( \rightarrow \) 0-14

Physical properties

RE have very specific
optical and magnetic
properties

Nucleus
RE are the salt and pepper of emerging technologies.

- Medical
- Lighting
- Catalysis
- Refinery
- Nuclear Industry
- DVD TV computers
- Communications
- Defense Industry
- Specialty alloys
- Energy
  - Batteries
  - Fuel Cells
- Car Industry
- Glass
- Ceramic jewelery
- GSM Ipod MP3
- Specialty alloys
- Industry
Most of the RE recycling projects have been launched during the RE crisis.

Since 2005 China has decided to limit its exports by a quotas policy …

…in 2010 a -40% cut in the quotas generated a major crisis impacting drastically the prices on the market.
Most of the RE recycling projects have been launched during the RE crisis.

This situation has led to a large number of recycling initiatives.

Now that RE are back to more normal prices most of these initiatives are unprofitable.

A major crisis impacting drastically the prices on the market.
The RE recycling projects must take into account the key RE market characteristics

What are they?
1st characteristic: RE are everywhere

The RE recycling should be focused on existing concentrated deposits.
2\textsuperscript{nd} characteristic: The RE prices are very different from one RE to another

China FOB prices – December 2014

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-The size of the market is different in value and volume
2nd characteristic:
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-The size of the market is different in value and volume

The End of Life RE recycling should be focused on the most valuable RE
The key criteria for a RE recycling project

• The recycling of RE should be focused:
  • on existing concentrated deposits:
    ➢ Existing tailings or losses from RE value chain
    ➢ Existing recycling loops for End of Life products
  • on the most valuable RE

Based on these criteria, **Solvay** decided in 2010 to recycle RE from:

➢ Solvay La Rochelle plant historical loss of yield (All RE)
➢ Production losses of Magnet manufacturers (Pr, Nd, Dy)
➢ 2 types of EOL products:
  - Low energy consumption lamps (La, Ce,Tb, Eu, Gd & Y).
  - NiMH batteries (La, Ce, Pr, Nd) in cooperation with **Umicore**
    who recycles the nickel.
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A long value chain from the ore to the pure RE oxides, RE separation is the key step.

Mining site → Ore concentrate → RE mix concentrate

Mining & concentration → Ore cracking

All RE applications use pure individual Rare Earths
This RE mix concentrate has no market.
A long value chain from the ore to the pure RE oxides, RE separation is the key step.

- Solvent Extraction is the only industrial process used nowadays for RE separation
- Solvay La Rochelle plant is the only facility outside of China able to separate all RE including HRE.
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A long value chain from the ore to the pure RE oxides, RE separation is the key step.

Solvay La Rochelle plant is the only facility outside of China able to separate all RE including HRE. In 2012 Solvay decided to restart main of its SX batteries for RE recycling.
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Rare Earths recycling at La Rochelle plant

• Taking the advantage of its existing separation facility at La Rochelle plant, Solvay decided in 2010 to launch a wide RE recycling project based on 3 pillars:

- RE recycling from La Rochelle historical loss of yield
- RE recycling from End Of life NiMH batteries – A collaboration between Umicore and Solvay
- RE recycling from End Of Life lamps
RE recycling from La Rochelle historical loss of yield

My God! A Rare Earth mine in La Rochelle!
RE recycling from La Rochelle historical loss of yield

My God! A Rare Earth mine in La Rochelle!

Recycling started in October 2010
RE recycling from La Rochelle historical loss of yield

• Very complex stockpile with a large spectrum of individual compounds

• The process developed should be able to treat various types of minerals (oxides, phosphates, oxalates, silicates…)

• From 2010 until now this «deposit» represent an key part of La Rochelle raw materials
Recycling of RE from NiMH batteries
A collaboration between Umicore and Solvay

- Umicore started the recycling of Ni from NiMH with a specific process leading to a RE concentrate (M = La rich mishmetal)

- Solvay can recycle this RE concentrate at La Rochelle plant, producing RE specialties belonging to regular Solvay product portfolio
RE recycling from end of life lamps to close the loop

Several thousands Tons of powders are landfilled each year

Valorization
- glass
- metals
- plastics
- mercury

Recycling companies

Used lamps Collectors

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RE recycling from end of life lamps to close the loop

Several thousands Tons of powders are landfilled each year.

Valorization - glass - metals - plastics - mercury

Recycling companies

Solvay recycling process

Rare Earth recovery
Several hundreds tons/y

Rare Earth Concentration
Rare Earth Separation
Rare Earth Finishing

New Green and red Phosphor precursors

Used lamps Collectors

 LOOP
LIFE11 ENV/FR/744

11/13/2015
RE recycling from end of life lamps

- The mineralogical composition of phosphor powders is very complex:
  - Halophosphates: \((\text{Sr, Ca})_{10}(\text{PO}_4)_6(\text{Cl, F})_2:\text{Sb}^{3+},\text{Mn}^{2+}\) (halophosphates)
  - RE oxide: \(\text{Y}_2\text{O}_3:\text{Eu}^{3+}\)
  - RE phosphates \((\text{La, Ce, Tb})\text{PO}_4\)
  - RE aluminates: BAM: \((\text{Ba, Sr})\text{MgAl}_{10}\text{O}_{17}\):\text{Eu}^{2+},\text{Mn}^{2+}\)
    CAT: \((\text{Ce, Tb})\text{MgAl}_{11}\text{O}_{19}\)

- The process is done in 2 sites:
  - Saint Fons (Lyon) for halophosphates removal
  - La Rochelle for RE minerals dissolution, RE separations and new phosphor precursor production
Solvay Strategy to guaranty the security of RE Supply outside of China

- 1\textsuperscript{st} step: Recycling
  - Recycling of production La Rochelle wastes. La Rochelle plant started in 2010 to recycle wastes
  - Recycling of production wastes from magnet manufacturers
  - Recycling of End of Life Equipment.
    - From NiMH batteries – A collaboration between Umicore and Solvay
    - From EOL lamps

- 2\textsuperscript{nd} step: Partnerships with key mining players outside of China
  - Solvay is offering tolling for heavy rare earths separation outside of China to key partners

- More globally, on Mining related industry: leverage Solvay Novecare product portfolio of solvents and organic additives to offer a wide range of products & services to global mining industry
Business model for Solvay mining business activity

A 3 pillars approach

- **Sales of existing products:**
  - Flotation collectors
  - Liquid-liquid extraction solvents:
    - Amines based, Phosphorous based
  - Emulsifiers

- **Develop a Service offer to mining company**
  - Accompany development of projects
  - Help mining companies to solve their operating problems (eg: operation of liquid/liquid extraction unit, radioactive impurities removal…)

- **New products development**
  - Ion Exchange resins for specific applications
  - Flotation
    - Amine based formulations for non sulfide ores: Iron, Potash and phosphates
  - New generation of emulsifiers
Conclusions

• The RE recycling can be a part of the RE sourcing outside of China, but due to the RE market dynamics this will remain a small portion of RE raw materials,

• The technologies developed by Solvay for RE recycling are similar to mining process adapted to the specific characteristics of urban mines

• The profitability of the RE recycling is mostly dependent on RE prices and in the current situation of low RE prices the economics are difficult

• SOLVAY can leverage its own know how and product portfolio to address more general mining industry challenges
Thank you for your attention