



**SOLVAY**

asking more from chemistry®

# 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



Special Chem

# Content



The RE market characteristics and the field of recycling



RE processing: Advantages and drawbacks of recycling



Recycling of RE at La Rochelle plant

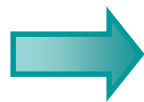
- From La Rochelle historical loss of yield
- From NiMH batteries – A collaboration between Umicore and Solvay
- From EOL lamps

Hydrogen 1 <b>H</b> 1.01	Periodic Table of the Chemical Elements Research School of Earth Sciences, ANU																Helium 2 <b>He</b> 4.00				
Lithium 3 <b>Li</b> 6.94	Beryllium 4 <b>Be</b> 9.01	You are														Boron 5 <b>B</b> 10.81	Carbon 6 <b>C</b> 12.01	Nitrogen 7 <b>N</b> 14.01	Oxygen 8 <b>O</b> 16.00	Fluorine 9 <b>F</b> 18.99	Neon 10 <b>Ne</b> 20.18
Sodium 11 <b>Na</b> 22.99	Magnesium 12 <b>Mg</b> 24.31	Here														Aluminum 13 <b>Al</b> 26.98	Silicon 14 <b>Si</b> 28.09	Phosphorus 15 <b>P</b> 30.97	Sulfur 16 <b>S</b> 32.07	Chlorine 17 <b>Cl</b> 35.45	Argon 18 <b>Ar</b> 39.95
Potassium 19 <b>K</b> 39.10	Calcium 20 <b>Ca</b> 40.08	Scandium 21 <b>Sc</b> 44.96	Titanium 22 <b>Ti</b> 47.87	Vanadium 23 <b>V</b> 50.94	Chromium 24 <b>Cr</b> 51.99	Manganese 25 <b>Mn</b> 54.94	Iron 26 <b>Fe</b> 55.85	Cobalt 27 <b>Co</b> 58.93	Nickel 28 <b>Ni</b> 58.69	Copper 29 <b>Cu</b> 63.55	Zinc 30 <b>Zn</b> 65.38	Gallium 31 <b>Ga</b> 69.72	Germanium 32 <b>Ge</b> 72.64	Arsenic 33 <b>As</b> 74.92	Selenium 34 <b>Se</b> 78.96	Bromine 35 <b>Br</b> 79.90	Krypton 36 <b>Kr</b> 83.80				
Rubidium 37 <b>Rb</b> 85.47	Sr 87.62	<b>Y</b> 88.91	Zr 91.22	Nb 92.91	Mo 95.94	Tc 98.91	Ru 101.07	Rh 102.91	Pd 106.42	Ag 107.87	Cd 112.41	In 114.82	Sn 118.71	Sb 121.76	Te 127.60	I 126.91	Xe 131.29				
Cesium 55 <b>Cs</b> 132.91	Ba 137.33			Hf 178.49	Ta 180.95	W 183.84	Re 186.21	Os 190.23	Ir 192.22	Pt 195.08	Au 196.97	Hg 200.59	Tl 204.38	Pb 207.20	Bi 208.98	Po 209.00	At 210.00	Rn 222.00			
Francium 87 <b>Fr</b> 223.00	Ra 226.00			Rf 261.10	Db 262.10	Sg 266.10	Bh 264.10	Hs 277.10	Mt 268.10												
		Lanthanum 57 <b>La</b> 138.91	Cerium 58 <b>Ce</b> 140.12	Praseodymium 59 <b>Pr</b> 140.91	Neodymium 60 <b>Nd</b> 144.24	Promethium 61 <b>Pm</b> 144.91	Samarium 62 <b>Sm</b> 150.36	Europium 63 <b>Eu</b> 151.96	Gadolinium 64 <b>Gd</b> 157.25	Terbium 65 <b>Tb</b> 158.93	Dysprosium 66 <b>Dy</b> 162.50	Holmium 67 <b>Ho</b> 164.93	Erbium 68 <b>Er</b> 167.26	Thulium 69 <b>Tm</b> 168.93	Ytterbium 70 <b>Yb</b> 173.04	Lutetium 71 <b>Lu</b> 174.97					
		Actinium 89 <b>Ac</b> 227.03	Thorium 90 <b>Th</b> 232.04	Protactinium 91 <b>Pa</b> 231.04	Uranium 92 <b>U</b> 238.03	Neptunium 93 <b>Np</b> 237.05	Plutonium 94 <b>Pu</b> 244.06	Americium 95 <b>Am</b> 243.06	Curium 96 <b>Cm</b> 247.07	Berkelium 97 <b>Bk</b> 247.07	Californium 98 <b>Cf</b> 251.08	Einsteinium 99 <b>Es</b> 252.08	Fermium 100 <b>Fm</b> 257.10	Mendelevium 101 <b>Md</b> 258.10	Nobelium 102 <b>No</b> 259.10	Lawrencium 103 <b>Lr</b> 260.10					

# CHEMICAL AND PHYSICAL PROPERTIES OF RARE EARTHS

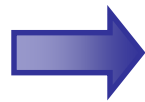
RE separation is very difficult

Common external orbitals  
5d1 6s2 valence electrons



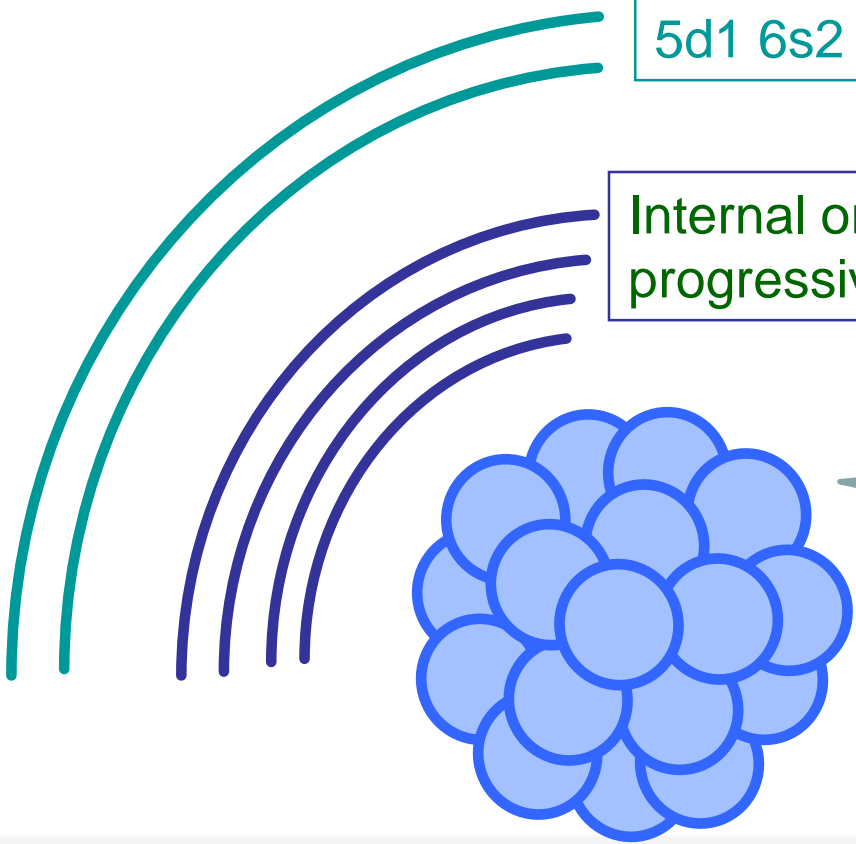
Chemical properties

Internal orbital  
progressivall fillings 4f → 0-14



Physical properties

RE have very specific  
optical and magnetic  
properties



Nucleus

# ➤ RE are the salt and pepper of emerging technologies



**Defense Industry**

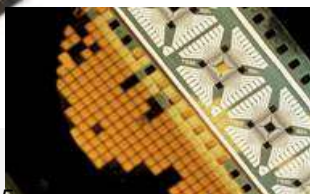
**Communications**



**Energy**  
Batteries  
Fuel Cells



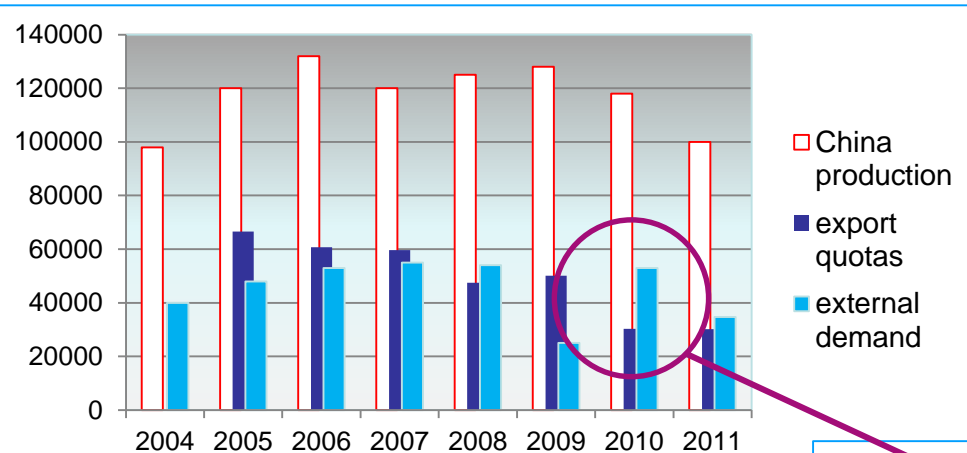
**DVD TV computers**



**jewelery**

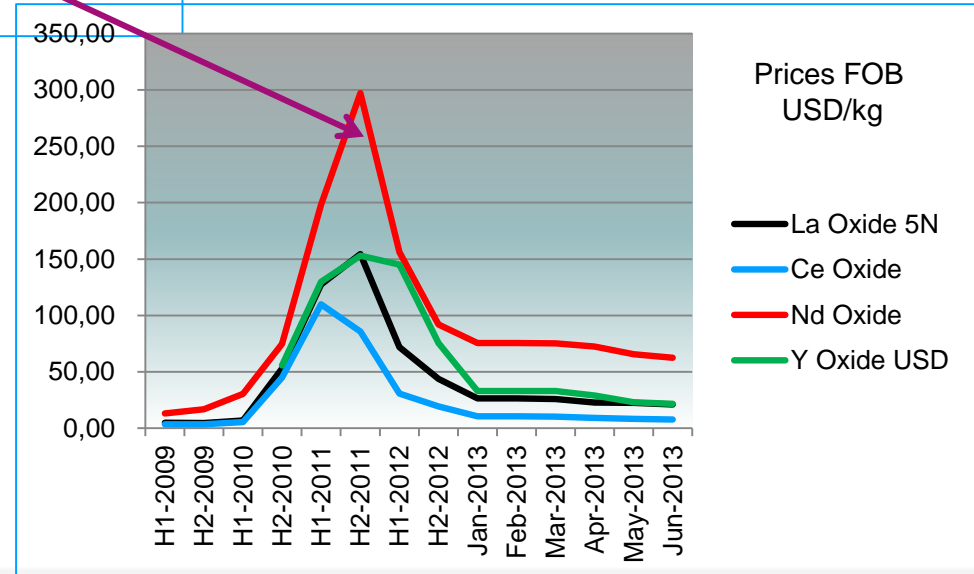


# Most of the RE recycling projects have been launched during the RE crisis



*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

140000

12

10

8

6

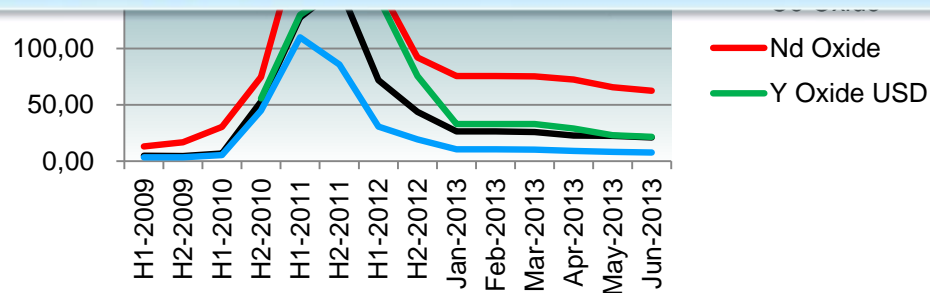
4

2

**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?**



➤ **1<sup>st</sup> characteristic: RE are everywhere**

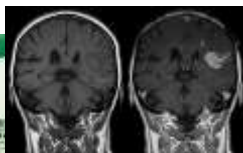
**Communications**



**Energy**  
**Batteries**  
**Fuel Cells**



**Defense**  
**Industry**



**Medical**



**The RE recycling should be  
focused on existing  
concentrated deposits.**



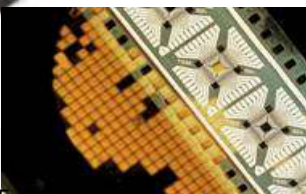
**Nuclear**  
**Industry**



**Glass**



**DVD TV**  
**computers**



**GSM Ipod MP3**



**Ceramic**

**jewelery**



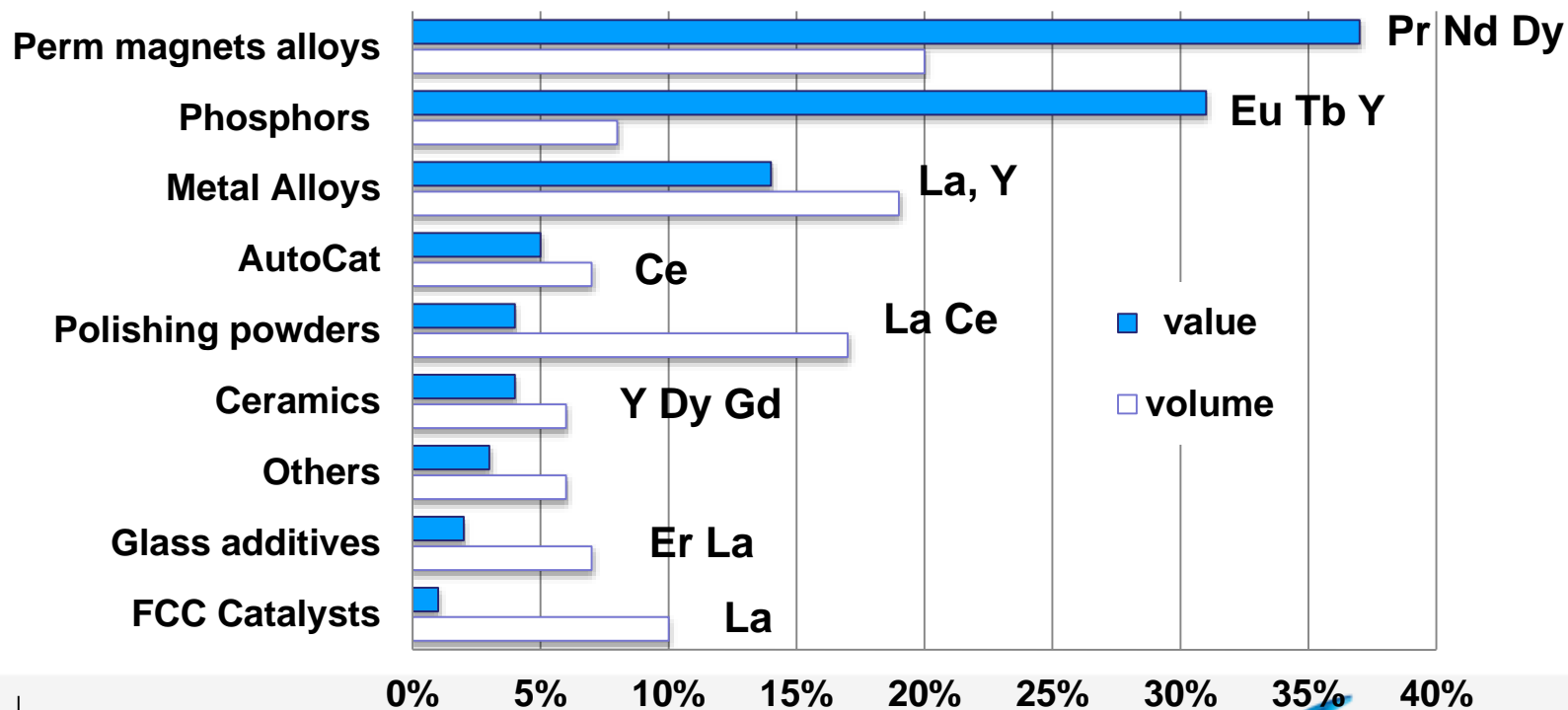
## ➤ 2<sup>nd</sup> characteristic:

The RE prices are very different from one RE to another

China FOB prices – December 2014

USD/kg	La	Ce	Pr	Nd	Eu	Tb	Dy	Y
oxide	4.1	3.7	98	56	545	555	295	11

*-The size of the market is different in value and volume*



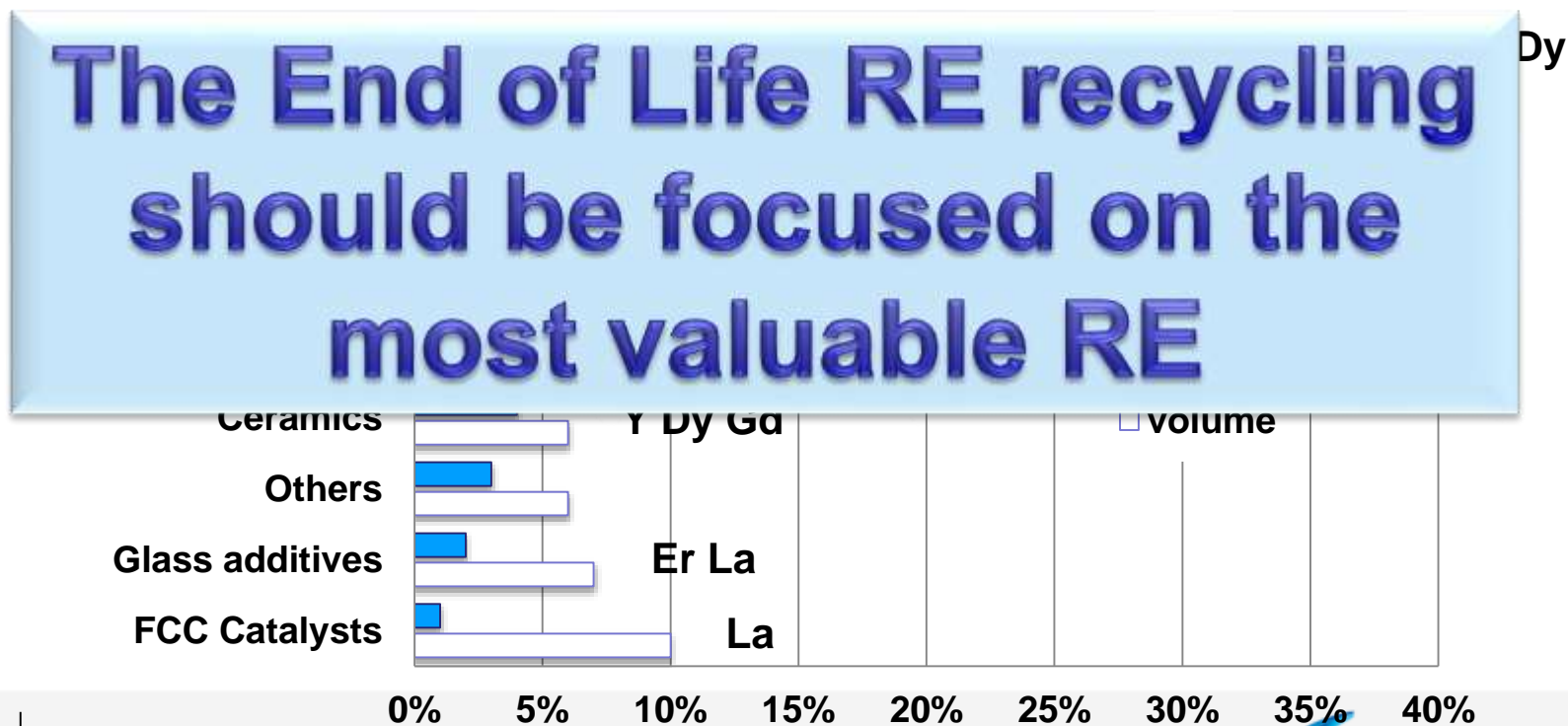
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# The key criteria for a RE recycling project

- 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



Mining &  
concentration

Ore concentrate



Ore cracking

RE mix concentrate



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.

Mining site



Mining &  
concentration

Ore concentrate



Ore cracking

RE mix concentrate



Pure RE salts  
or oxides



RE  
finishing

Pure RE solutions

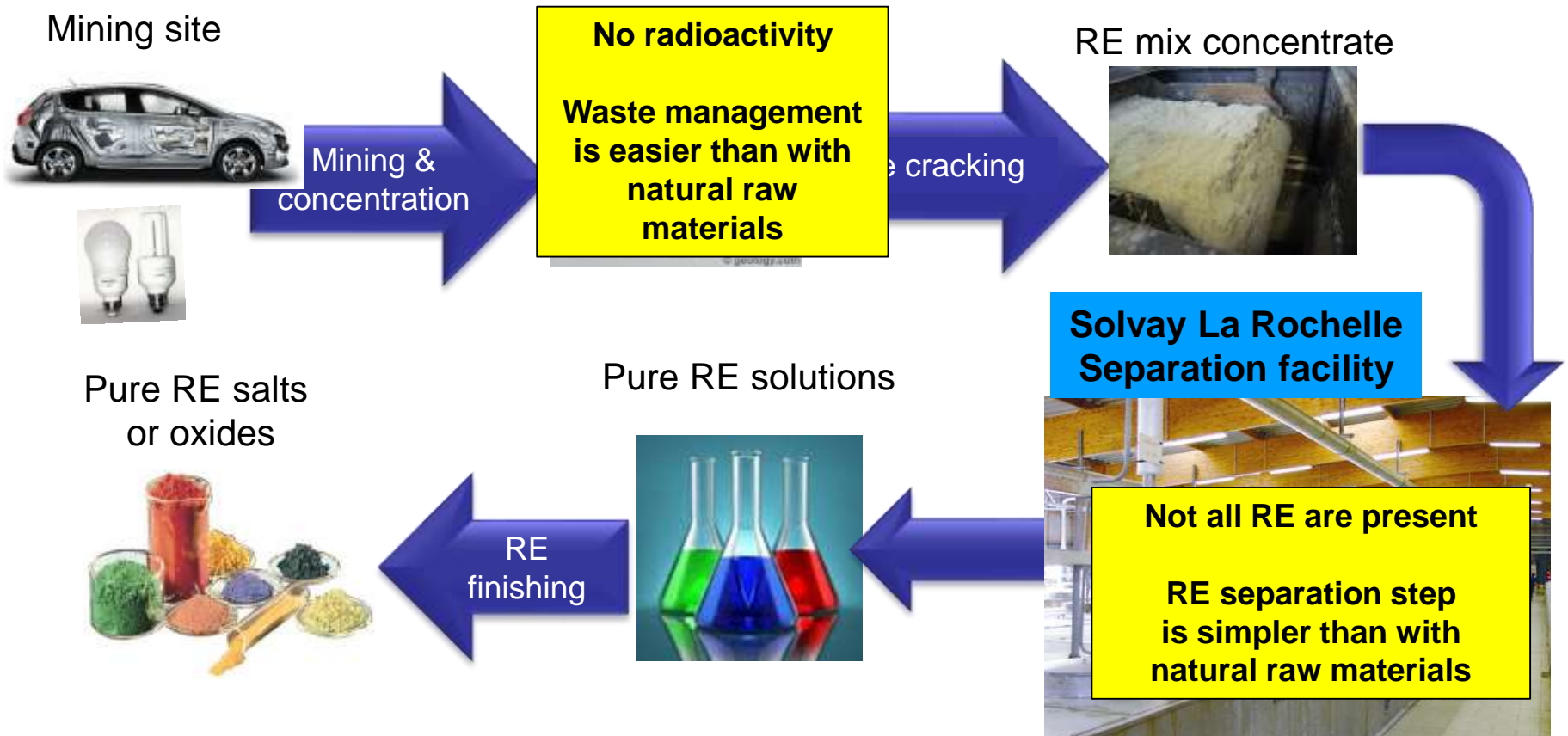


**Solvay La Rochelle  
Separation facility**



- 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.

# 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
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# A long value chain from the ore to the pure RE oxides, RE separation is the key step.

Mining site



Mining &  
concentration

No radioactivity

Waste management  
is easier than with  
natural raw  
materials

Cracking

RE mix concentrate



**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

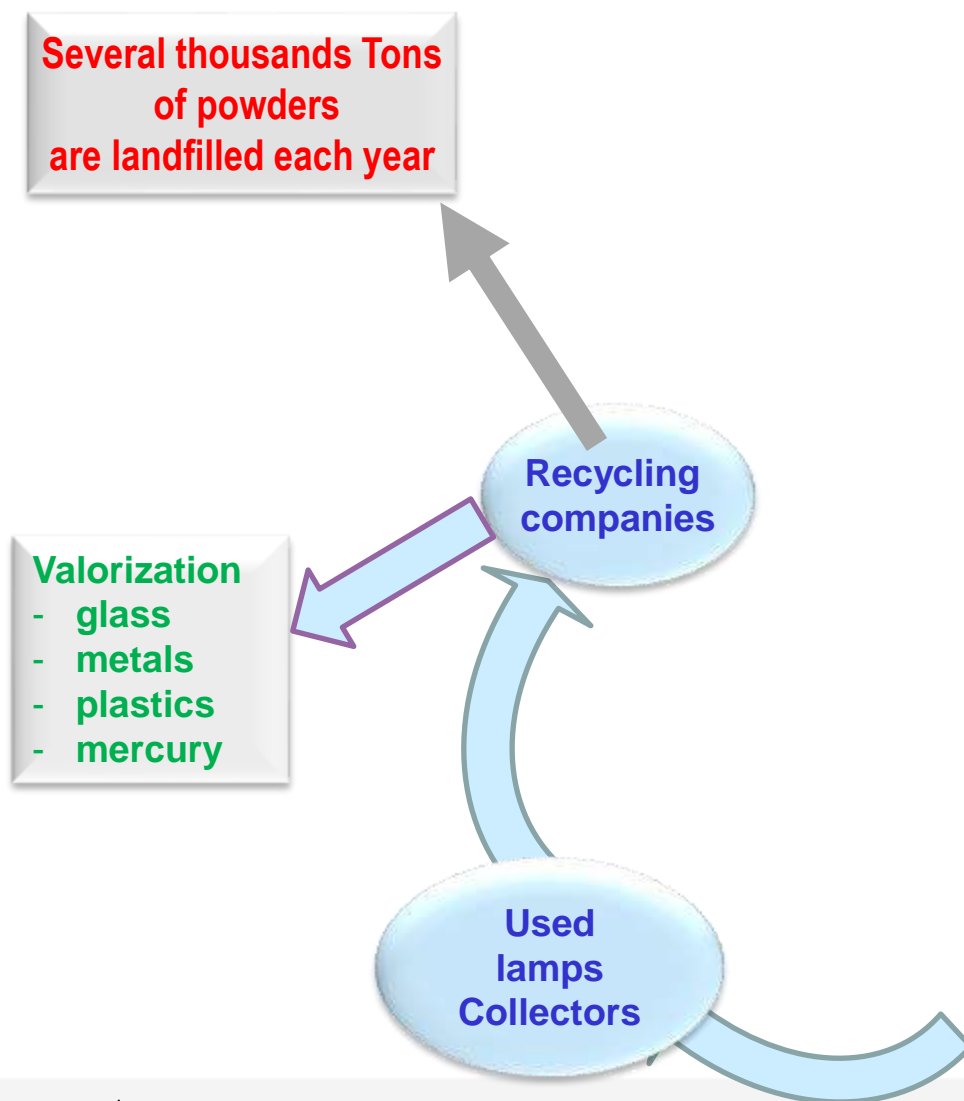
# Recycling of RE from NiMH batteries

## A collaboration between Umicore and Solvay



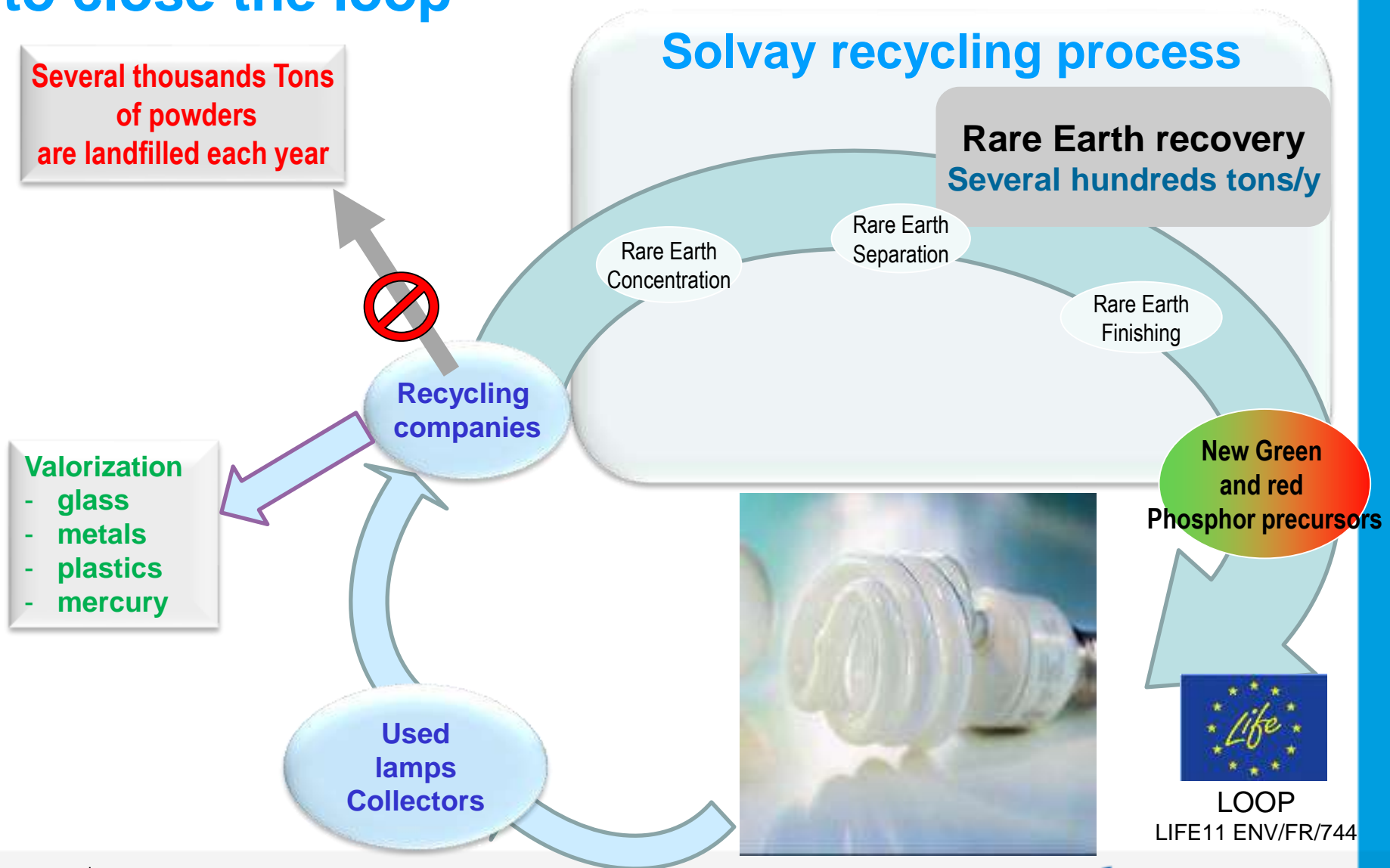
- Umicore started the recycling of Ni from NiMH with a specific process leading to a RE concentrate (M = La rich mishmetal)
- Solvay can recycle this RE concentrate at La Rochelle plant, producing RE specialties belonging to regular Solvay product portfolio

# RE recycling from end of life lamps.. to close the loop



LOOP  
LIFE11 ENV/FR/744

# RE recycling from end of life lamps.. to close the loop



# 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



LOOP  
LIFE11 ENV/FR/744



# Solvay Strategy to guaranty the security of RE Supply outside of China

- 1<sup>st</sup> 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<sup>nd</sup> 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

