Process development for recycling rare earth from mining and urban waste materials

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Recycling targets

- **Direct recycling of pre-consumer manufacturing REE scrap/residues**
- **Landfill mining of historic residues**
- **Urban mining of post-consumer waste (complex multi-materials matrices)**
- **Reprocessing of mining and metallurgical waste**

Commercial recycling of REEs is extremely low
Less than 1% of the REEs were being recycled in 2011*

*Source: Binnemans et al. / J. of Cleaner Prod. 51 (2013), 1-22

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Rare earth elements: recycling opportunities*

- **Recycling is part of a threefold approach including also substitution & investment in primary mining**
- **REE are imported into the EU from a very limited number of producers**
- **Demand is high and steadily growing**
- **Recycling of REEs from spent products or mining/metallurgical waste, could provides a secondary supply**
- **However, closing the "REE loop" is a technical challenge, due to their specific uses and properties**

→ Recycling of REEs is still at an early stage

*European parliament (2015) Recovery of Rare Earths from Electronic Wastes: An opportunity for High-Tech SMEs

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Recycling REEs: specific challenges

> Development of dedicated techniques

- To prevent from “poor” REE recycling due to routine techniques designed for primary resources (ores) and/or standard metals
- To collect, sort and pre-treat WEEE specifically. Need for techniques focused on critical raw materials and particularly REEs

> Treatment

- Few mechanical pre-treatment and sorting processes are able to liberate and separate the complex intermix of materials
- Many components containing important resources are only partially sorted into the correct fractions. This leads to high losses of critical raw materials (dissipative processes)
- After shredding, losses of REE = 100% because brittle magnets end up as fine particles attached to large steel parts in the steel industry (EAF*) and are lost (in slags) for any recovery process

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*EAF : Electric Arc Furnace

REEs recovery technologies

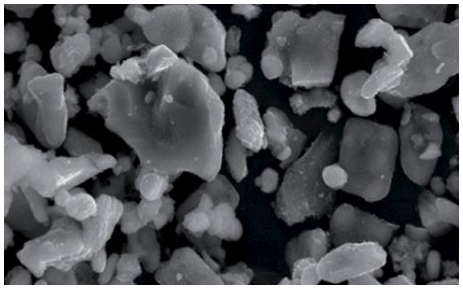
Sources of REEs	Process	Technology readiness level	Existing at industrial level
Lamp phosphors (Eu, Tb, Y)	Pre-processing + chemical attack of phosphors and recovery of REEs by precipitation or SX	Mature (still developing)	Yes (Solvay)
Cathode Ray Tube phosphors (Eu)	Chemical attack and solvent extraction	Limited research (declining interest ?)	No
Permanent Magnets (Nd, Pr Sm, Dy)	- Hydrometallurgy	Mature generally but still in lab scale	Investment project (Solvay)
	- Gas-phase extraction	Lab scale	No
	-Reprocessing of alloys to magnets after H_2 decrepitation	Lab scale	No
	-Biometallurgy	Lab-scale	Planned pilot in 2014
NiMH batteries (La, Ce, Pr, Nd)	Ultra High T°C smelting and hydro-pyro-metallurgy	Mature	Yes (UMICORE & SOLVAY)
Optical Glass (La)	Hydrometallurgy	Lab scale	No
Glass polishing powder (Ce)	Chemical process	Lab scale	No

Source: Binnemans et al. (2013)

REE recycling process development: BRGM R&D projects

> Urban waste

- VALOPLUS (achieved)
  - Supported by ANR*
  - Recycling the luminescent powders used in low-energy light lamps
- EXTRADE (ongoing)
  - Supported by ANR
  - Recovery of REEs from permanent magnets in WEEE



> Mining waste

- ENVIREE (ongoing)
  - EU-ERAMIN call

*ANR: French National research Agency

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VALOPLUS

Valorization of used fluorescent powders

Contact point : Noureddine MENAD
n.menad@brgm.fr

SOLVAY asking more from chemistry®

VEOLIA

geoRessources

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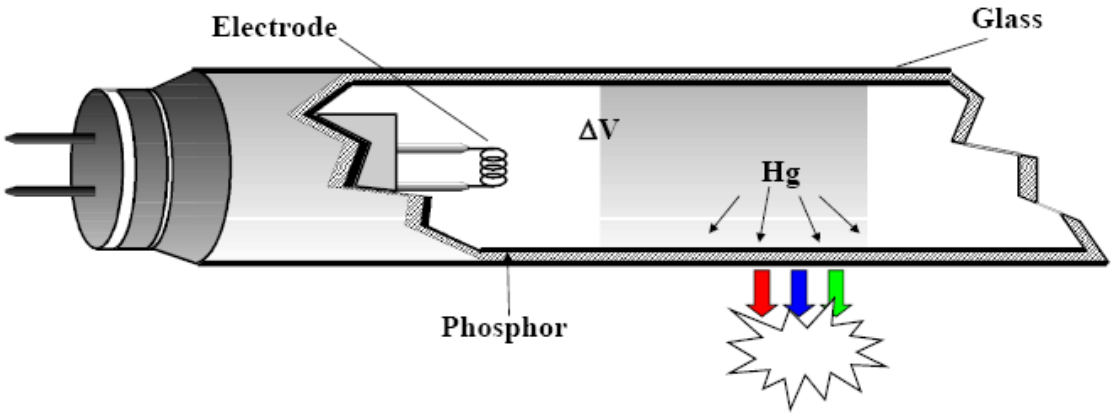
Low energy lamps

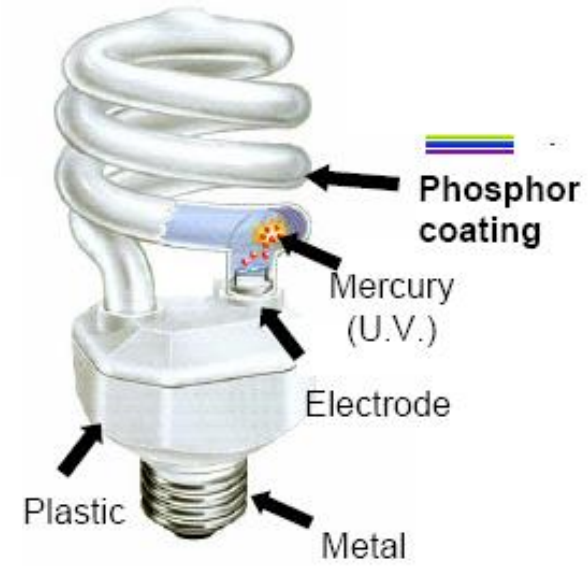
> Compared to filament lamps

- Energy consumption: 5 – 7 times lower
- Lifetime: 6 – 12 times longer

> How it works?



Compact Fluorescent Lamp (CFL)



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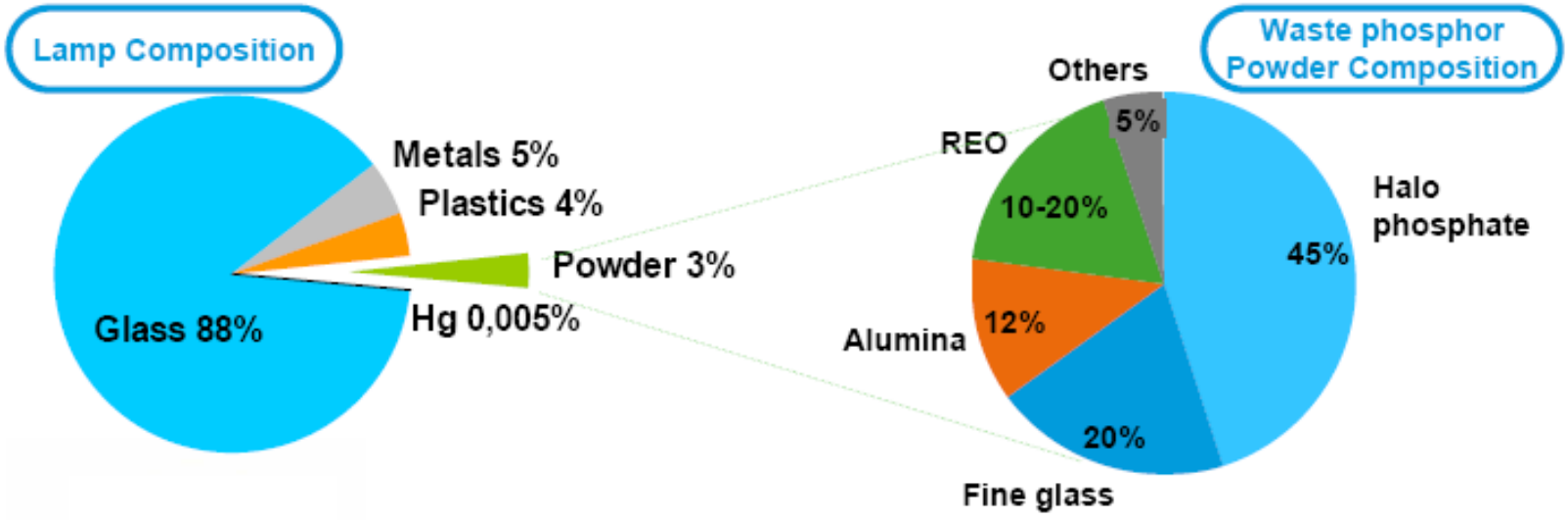
Low energy lamps

> Composition



> Old generation

White phosphor => halophosphate

> New generation:

Red, blue and green phosphors
=> white light emission

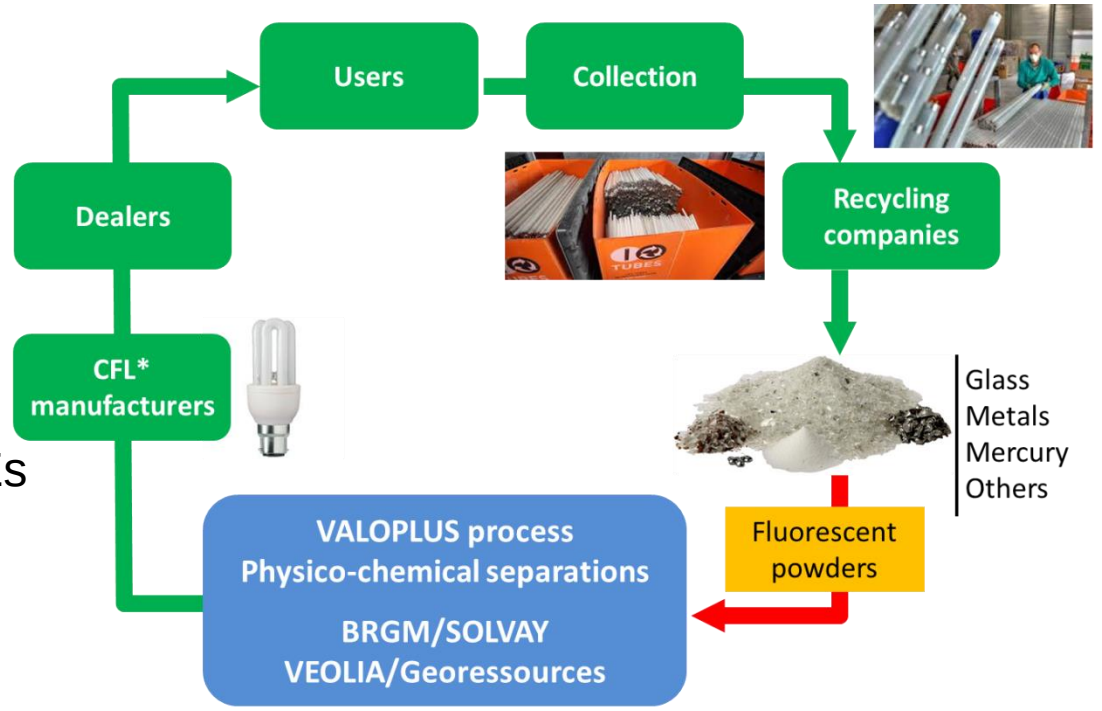
RE based phosphors

BAM	$BaMgAl_{10}O_{17} : Eu^{2+}$
CAT	$(Ce, Tb)MgAl_{11}O_{19}$
CBT	$(GdMg)B_5O_{10}:Ce^{3+},Tb^{3+}$
LAP	$LaPO4:Ce^{3+},Tb^{3+}$
YOX	$Y_2O_3:Eu^{3+}$

Objectives

> To develop innovative processes for the valorization of the phosphors throughout 2 approaches:

- Recovery of the pure phosphors
- Assessment of their performances for making new lamps
- Recovery of the REEs



*CFL: Compact Fluorescent Lamp

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VALOPLUS Process scheme

Element	Value (in %)
Halophosphate	67
BAM	4
CAT	4
LAP	4
CBT	5
Y-Eu	15

Element	Value (in %)	Recovery rate (in %)
Halophosphate	68	60.1
BAM	3.5	80.8
CAT	4	78.3
LAP	4	78.3
CBT	4	61.6
Y-Eu	16.5	78.8

Element	Value (in %)	Recovery rate (in % of < 10µm)
Halophosphate	68	36.2
BAM	4	27.2
CAT	3	35.9
LAP	10	84.8
CBT	4	69.1
Y-Eu	11	21.9

Element	Value (in %)	Recovery rate (in % of < 10µm)
Halophosphate	39	11.1
BAM	2	7.5
CAT	14	48.6
LAP	17	66.3
CBT	23	80.0
Y-Eu	4	4.1

Feed → **Classification (hydrocyclone)** → < 10 µm → **Magnetic separation 1** → Mag. → **Magnetic separation 2** → Mag → **Purification**

Classification (hydrocyclone) → > 10 µm

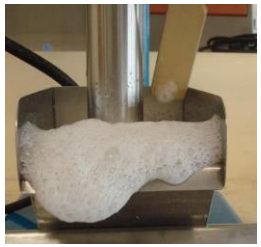
Element	Value (in %)	Recovery rate (in %)
Halophosphate	81.5	39.9
BAM	1.5	19.2
CAT	2	21.7
LAP	2	21.7
CBT	4.5	38.4
Y-Eu	8	21.2

Magnetic separation 1 → Non Magnetic YOX + BAM + Halophosphates

Element	Value (in %)	Recovery rate (in % of < 10µm)
Halophosphate	67	63.8
BAM	6	72.8
CAT	3	64.1
LAP	1	15.2
CBT	1	30.9
Y-Eu	22	78.1

Magnetic separation 2 → Non Magnetic YOX + BAM + LAP + Halophosphates

Element	Value (in %)	Recovery rate (in % of < 10µm)
Halophosphate	70	20.2
BAM	3	11.4
CAT	4	14.0
LAP	5	19.7
CBT	2	7.2
Y-Eu	14	14.6



Flotation → YOX concentrate / Halo / BAM concetrate

Flotation → YOX concentrate / Halo / BAM concetrate

Doctoral thesis in progress BRGM/University of Lorraine – Flotation of ultrafine particles

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Main results

- **Sampling of 6 sites and characterization of the collected samples**
  - Phosphors are contained in the fine fraction
- **Study on separation processes both on mechanisms and on experimental tests**
  - Definition of a flowsheet for the separation and concentration of the phosphors/rare earth
- **Evaluation of the quality of the recovered products**
  - Positive results
- **Patent pending (BRGM, SOLVAY, VEOLIA, University of Lorraine – 10/07/2014)**

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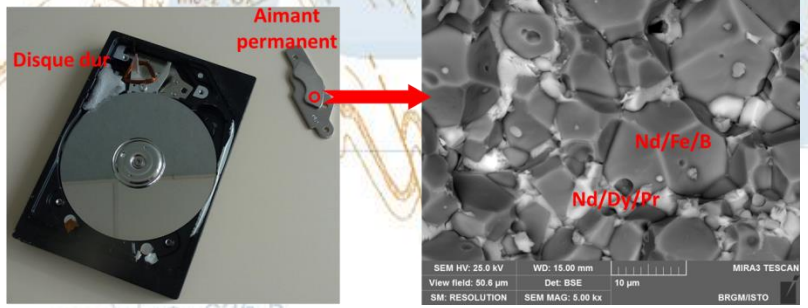
EXTRADE

Recovery of REEs from permanent magnets in WEEE

Contact point : Noureddine MENAD
n.menad@brgm.fr

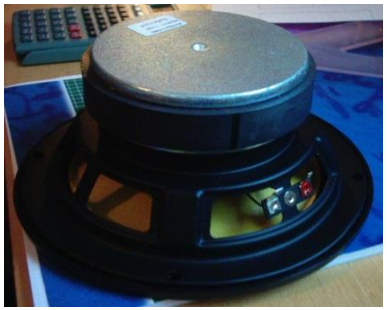


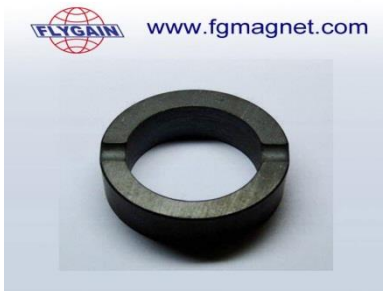
http://extrade.brgm.fr

REEs containing components in WEEE

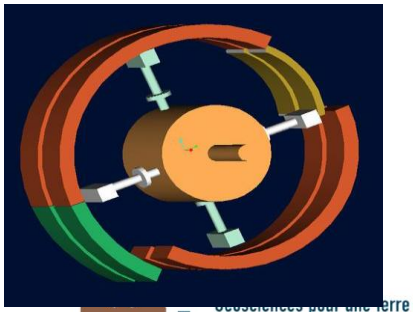
Hard Disk Drives

Loudspeakers





Small electric motors



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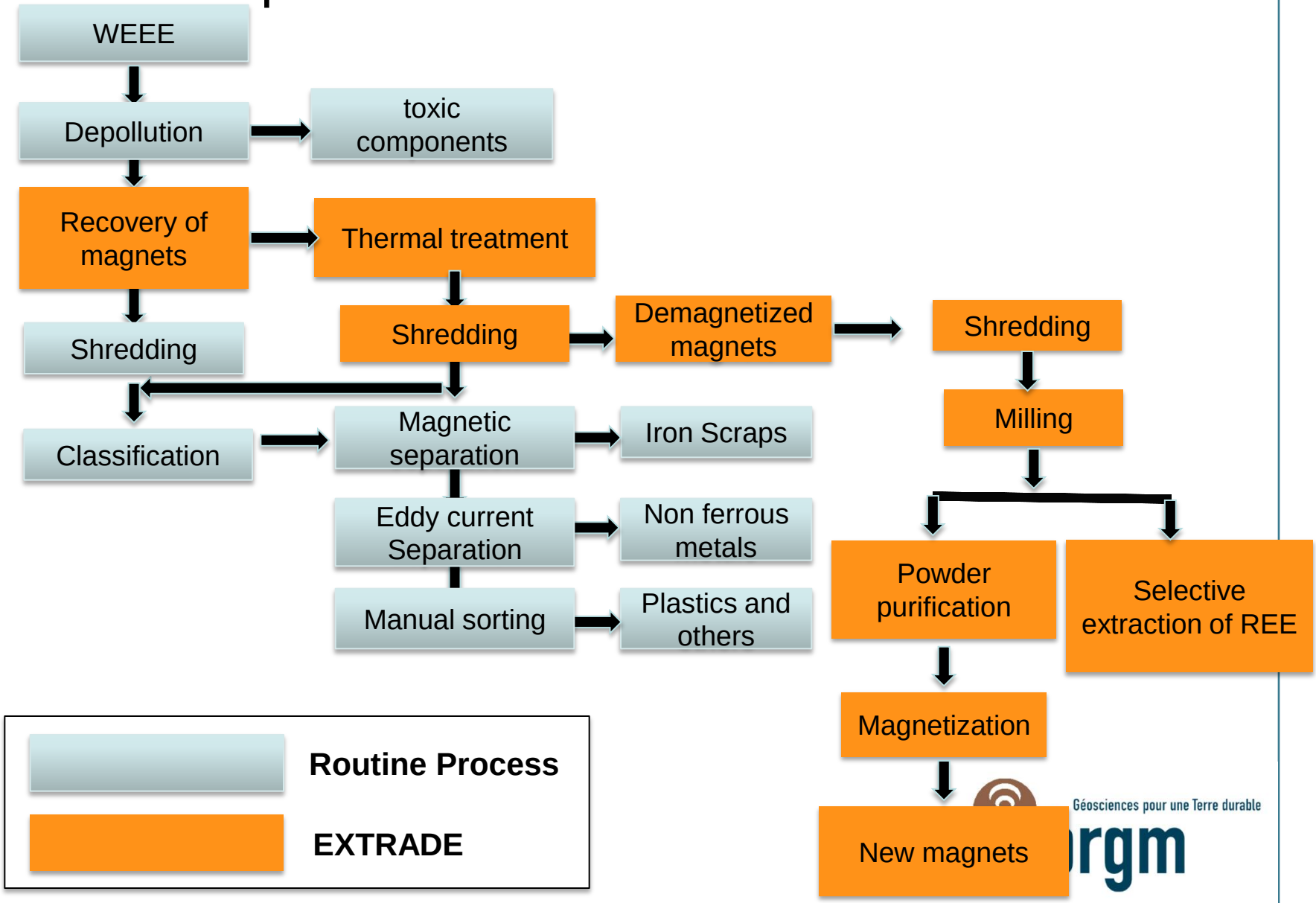
EXTRADE process



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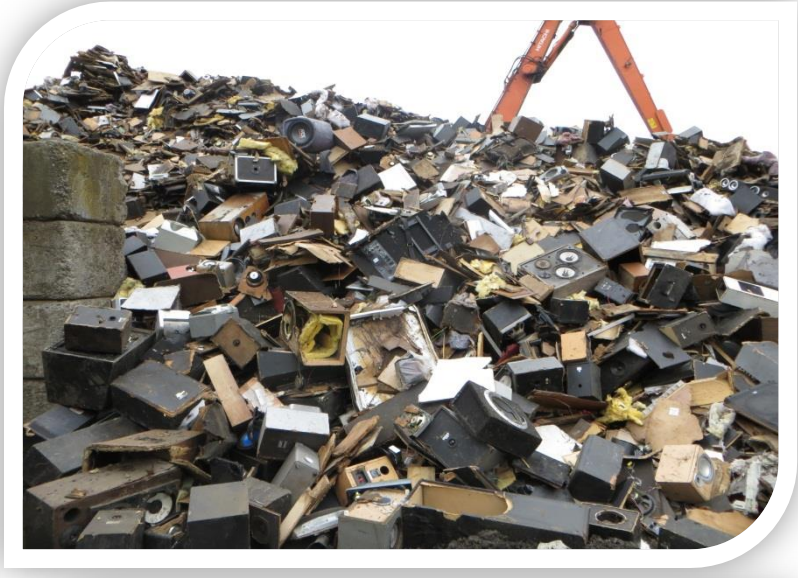
Sampling of WEEE

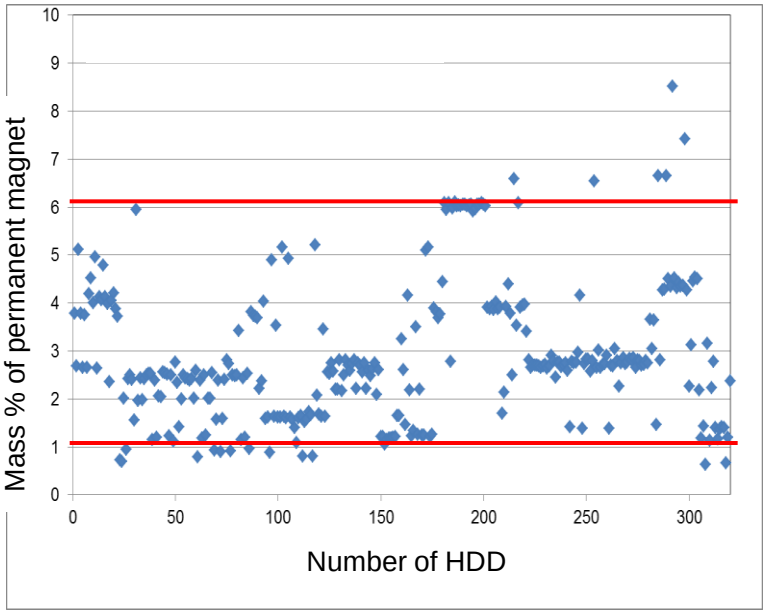
Manual sorting of HDD

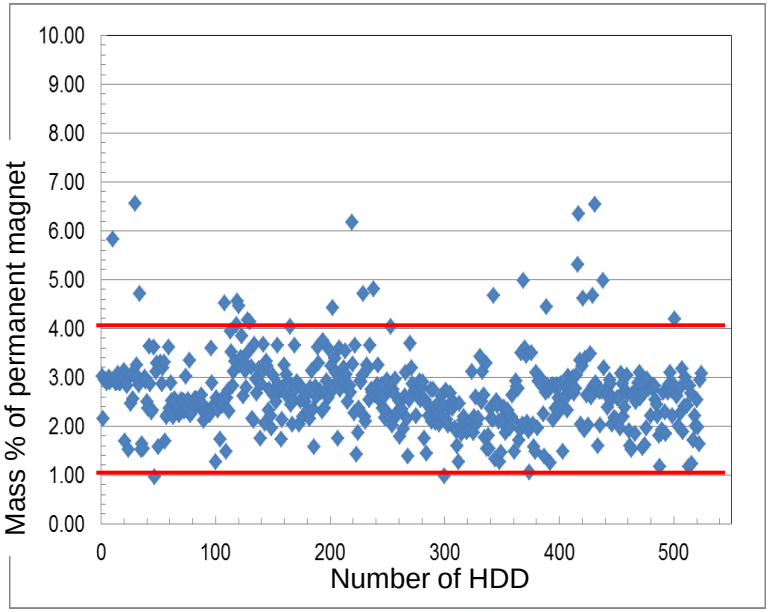
Loudspeaker shredding



Characterization

HDD characterization





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Recycling process units

- **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
- **2 patents in progress + 2 Soleau envelopes**

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ENVIREE (Started March 2015)

ENVIronmentally friendly and efficient methods for extraction of Rare Earth Elements from secondary sources

Contact point : Yannick MENARD
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Context, objectives & topics

- **Tailings and other by-products from previous mining activities can hold significant amount of critical metals including REE**
- **ENVIREE project is aimed at completing the picture of effective REE supply within Europe by addressing exploitation of specific secondary sources (mining and industrial waste)**
- **Topics**
  - Identification/characterization/sampling of most suitable 2nd resources
  - Mineral processing
    - Enhanced comminution
    - centrifugal concentration, multi-gravity separations, magnetic sep, column flotation
  - Bio-Hydro-metallurgy
    - Bioleaching, selective oxidative leaching, use of strong halide solutions
    - New technologies for recovery of REE and better utilization of natural resources
    - Separation of REE using ionic liquids
    - Selective recovery using membrane contactors (grafted polymers, inorganic resins…)

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Consortium – 11 partners, 8 countries

Partner	Country	Contact person
CHALMERS	SE	Christian Ekberg (coordinator)
CEA	FR	Stéphane Bourg
BRGM	FR	Yannick Menard
AGH	PL	Katarzyna Grzesik
SAVONA PROJECT	PL	Slawomir Duda
AICU	RO	Catalin-Gabriel Borcia
IST-ID	PT	Maria Isabel Flausino de Paiva
EDM	PT	Mario Jorge Ferreira Guedes
CGS	ZA	Hendrik Coetzee
PIPAS	NO	Dag Oistein Eriksen
KIT	DE	Andreas Geist

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