

# RECOVERY OF RARE EARTHS FROM E-WASTE RESIDUES BY AN INTEGRATED APPROACH

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## Abstract

The objective of this work is the recovery of rare-earth elements (REEs) and magnesium (Mg) from several waste streams to produce new REE-Mg alloys of high performance and low cost. The selection procedure of the waste residues, the characterisation results and the general description of the recovery processes are presented; TOPSIS and LCA methodology, which were used as tools for the identification of the best process routes, are introduced as well.

## Introduction

This paper describes the first outcomes from the research activities performed within the EU REMAGHIC project, which is focused on the recovery of rare-earth elements and magnesium from secondary sources to produce new REE-Mg alloys with improved mechanical properties, reduced weight and low cost, which can find application in several industrial sectors, such as the automotive, aeronautic and biomedical industries.<sup>1,2</sup> The aim is to reduce the European dependency of critical raw materials (REEs and Mg) from non-European countries and to partially mitigate the “Balance Problem”, that is defined as the balance between the demand by the economic markets and REEs in ores.<sup>3,4</sup> The Balance Problem implicates that the REE industry has to find new applications for REEs that are available in excess, or to search for substitutions for REEs that have limited availability and that are high in demand.

The first task of the project was the selection of the potential sources of REEs. Several parameters were taken into account, such as the REEs concentration and the relevance from the balance perspective. Afterwards the residues were characterised by different techniques in order to gather information about their composition. For each waste stream, combinations of several processes, namely pyrometallurgical, hydrometallurgical and iono/solvometallurgical processes, have been applied. The results collected during the experimental activity represent the input data for the TOPSIS and the LCA methodology, which can be regarded as useful tools for the selection of the best process routes from both technical and environmental point of view.

## **Results and discussion**

### **Residues selection**

A preliminary study was performed to identify the most promising REE-containing waste residues. Among several waste streams, which include waste electrical and electronic equipment (WEEE or e-waste) and industrial by-products, three materials were selected: lamp phosphors (1), cathode-ray tubes (CRT) phosphors (2) and nickel metal hydride (NiMH) batteries (3). The choice was supported by a decision matrix, which took into account several factors. First of all, REEs concentration was considered, which is very high both in lamp phosphors and in NiMH batteries.<sup>5-8</sup> Moreover, the number of REEs contained in these residues is limited, so that the recovery process is facilitated. Furthermore, in contrast to REE ores and industrial by-products (such as red mud and phosphogypsum), there are no radioactivity issues related to e-waste. Another important parameter considered in the selection process was the Balance Problem perspective. Recycling of fluorescent lamps, CRTs and NiMH batteries will generate a supply of lanthanum, europium, terbium, yttrium, cerium and gadolinium. Most of these REEs can be used in other applications whilst lanthanum, cerium and especially yttrium can find new uses in the magnesium alloys, thus contributing to partially mitigate the Balance Problem.<sup>3,4</sup>

### **Characterisation**

The selected waste streams were characterised by ICP-OES, SEM/EDS and XRD in order to gather information about their chemical and mineralogical composition. The elemental composition of the lamp phosphors and the identified mineralogical phases are reported in Table 1 and 2, respectively:

**Table 1:** Lamp phosphors – elemental composition (wt%)

Si	Ca	Y	La	Ce	Eu	Tb	Gd
18.9	7.1	6.3	0.9	0.7	0.4	0.3	0.1

**Table 2:** Lamp phosphors – mineralogical composition (wt%)

Compound	Concentration
Yttrium europium oxide	9.0
Lanthanum cerium. terbium phosphate	3.0
Magnesium cerium terbium aluminium oxide	1.5
Magnesium cerium gadolinium aluminium oxide	0.3
Glass	60.0
Fluorapatite	13.0
Barium silicate	3.0
Calcite	3.0
Strontium magnesium phosphate	0.6

As shown in Table 1, the fluorescent powder represents an interesting source of yttrium (6 wt%), which is present as oxide in the red phosphor YOX ( $Y_2O_3:Eu^{3+}$ ).<sup>3-9</sup> Yttrium can find new applications in the Mg alloys and its recovery from the selected waste stream was the main purpose of the investigated technologies. An added value is, however, represented by the presence of terbium (0.3 wt%), which has a high economic value. Terbium (together with lanthanum and cerium) is present in the phosphate ( $LaPO_4:Ce^{3+}, Tb^{3+}$ , LAP) and aluminate ( $(Ce,Tb)MgAl_{11}O_{19}$ , CAT) phosphors and its recovery is very challenging due to the fact that these compounds are much more resistant towards attack from acids.<sup>4</sup> Table 3 shows the concentration of the main elements present in the CRT phosphors, while the mineralogical phases are reported in Table 4.

**Table 3:** CRT phosphors – elemental composition (wt%)

Zn	S	Y	Si	Al	Pb	Eu
30.6	16.5	15.5	7.2	2.0	1.7	1.0

**Table 4:** CRT phosphors – mineralogical composition (wt%)

Compound	Concentration
Yttrium europium oxysulphide	23
Zinc sulphide	46
Glass	25
Aluminium	1.5

The analysis of CRT phosphors showed yttrium concentrations of about 15 wt% (together with 1 wt% of europium). The red phosphor ( $Y_2O_2S:Eu^{3+}$ ) is the only one containing REEs, whilst the blue and green phosphors are based on zinc sulphide (the green phosphor is ZnS:Cu and the blue phosphor is ZnS:Ag).<sup>4</sup> Finally, the characterisation of the NiMH batteries is reported in Tables 5-6. As shown in Table 5, NiMH batteries represent an interesting source of lanthanum and cerium, which can be used as mischmetal in the Mg alloys.

**Table 5:** NiMH batteries electrode powder – elemental composition (wt%)

Ni	La	Ce	Co	Zn	Fe	Mn
56.9	12.3	4.0	5.2	1.1	0.5	0.4

**Table 6:** NiMH batteries electrode powder – mineralogical composition (wt%)

Compounds	Concentration
LaNi <sub>5</sub> (hydrogen storage alloy based on mischmetal -mainly lanthanum, cerium and neodymium- and nickel incl. cobalt, aluminium and manganese)	45
Metallic nickel	15
Nickel hydroxide	35
Others (electrolyte, Co, Zn, graphite, etc.)	5

### Recovery routes

REE recovery from the selected waste residues was performed by an integrated approach which combined different techniques, namely pyrometallurgical, hydrometallurgical and iono/solvometallurgical processes. REE recovery from the lamp phosphor waste was performed by a leaching step with  $H_2SO_4$  followed by precipitation with oxalic acid in the HydroWEEE process.<sup>10,11</sup> The recovered product is a mixed REE oxalate that was further treated by calcination giving a mixed REE oxide. Y/Eu separation from this oxide was then investigated by leaching and solvent extraction with a phosphonium ionic liquid. Tb, La and Ce recovery from the lamp phosphors residue was enhanced by applying a pyro-treatment before leaching (roasting in the presence of  $Na_2CO_3$ ). The obtained leachate was then subjected to a solvent extraction step with di-(2-ethylhexyl)phosphoric acid (D2EHPA) followed by oxalate precipitation and calcination. An alternative approach is the leaching of the Tb-rich residue with organic solvents (the so-called solvometallurgical leaching), where metal recovery is performed using non-aqueous solutions.<sup>12</sup> Regarding the CRT phosphors, a thermal pre-treatment was investigated to convert the ZnS to ZnO, thus avoiding  $H_2S$  release during the leaching step. ZnO was then selectively removed from the roasted phosphors by leaching with acetic acid, giving access to the REE content. Y and Eu recovery from the residue was then studied by leaching with methanesulfonic acid, followed by precipitation with oxalic acid. A pyrometallurgical treatment was investigated for the recovery of lanthanum and cerium from NiMH

batteries. This pre-treatment allowed obtaining a metal phase rich in nickel and other minor metallic compounds, whilst the REEs are concentrated in the slag phase as oxides. After leaching with mineral acids, REEs are recovered by solvent extraction with ionic liquids. The recovery process is based on the “split-ion extraction”, which allows the extraction of rare-earth ions from concentrated chloride solutions to an organic phase consisting of nitrate ionic liquids (Aliquat 336 NO<sub>3</sub>).<sup>13</sup> La and Ce recovery from NiMH batteries was also investigated by direct leaching of the black electrode powder with hydrochloric acid; REE recovery from the leachate was finally performed by split-anion extraction.

### **Life Cycle Assessment and TOPSIS methodology**

Life Cycle Assessment (LCA) and TOPSIS methodology (Technique for Order of Preference by Similarity to Ideal Solution) were employed for the evaluation of the most promising routes for further upscaling activities. LCA studies allowed the assessment of the environmental performance of the different process combinations developed within the project. The balance between the resources needed and the emissions to the environment of these new technologies was investigated based on the Life Cycle Assessment, a tool standardised by the ISO 14040/14044 norm. The TOPSIS methodology was then applied as decision making method to support the selection. This choice was based on its main advantages, *e.g.*, it is easier to implement and consider different criteria with different units, and different weighting, which is the case of REMAGHIC project. The criteria were defined according to seven Key Performance Indicators (KPI): (1) TRL (Technology Readiness Level) [1-9], (2) Process efficiency [%]; (3) Waste generation [kg]; (4) Toxicity [Comparative Toxic Unit (CTUe)], (5) Global Warming Potential (GWP) [CO<sub>2</sub>e]; (6) Material cost [€]; (7) Income [€].

### **Conclusions**

Yttrium, lanthanum and cerium recovery from a selection of three waste residues was investigated by a combination of different techniques within the REMAGHIC project (pyro-, hydro- and iono/solvometallurgical processes). The recovered rare-earths can find new applications in REE-Mg alloys, thus offering a unique opportunity to partially mitigate the Balance Problem.

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## References

1. <http://www.remaghic-project.eu/>
2. L. Yurramendi, F. Forte, C. Del Río, R. Lagioia, T. Müller, S. Sgarioto and K. Binnemans, "Recovery of rare earths from e-waste residues for production of high-performance REE-Mg alloys", *2<sup>nd</sup> Conference on European Rare Earth Resources (ERES 2017)*, Santorini, Greece, 28-31 May 2017.
3. K. Binnemans, P. T. Jones, K. Van Acker, B. Blanpain, B. Mishra and D. Apelian, "Rare-earth economics: the balance problem", *JOM*, **65** (7) 846-848 (2013).
4. K. Binnemans and P. T. Jones, "Rare Earths and the Balance Problem", *J Sustain Metall*, **1** (1), 29-38 (2015).
5. K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton and M. Buchert, "Recycling of rare earths: a critical review", *J Clean Prod*, **51** 1-22 (2013).
6. C. Tunsu, M. Petranikova, M. Gergorić, C. Ekberg and T. Retegan, "Reclaiming rare earth elements from end-of-life products: A review of the perspectives for urban mining using hydrometallurgical unit operations", *Hydrometallurgy*, **156** 239-258 (2015).
7. K. Binnemans and P. T. Jones, "Perspectives for the recovery of rare earths from end-of-life fluorescent lamps", *J Rare Earths*, **32** (3) 195-200 (2014).
8. Y. Wu, X. Yin, Q. Zhang, W. Wang and X. Mu, "The recycling of rare earths from waste tricolor phosphors in fluorescent lamps: A review of processes and technologies", *Resour Conserv Recycl*, **88** 21-31 (2014).
9. D. Dupont and K. Binnemans, "Rare-earth recycling using a functionalized ionic liquid for the selective dissolution and revalorization of Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> from lamp phosphor waste", *Green Chem*, **17** 856-868 (2015).
10. V. Innocenzi, I. De Michelis, F. Ferella and F. Vegliò, "Recovery of yttrium from cathode ray tubes and lamps' fluorescent powders: experimental results and economic simulation", *Waste Manage*, **33** 2390-2396 (2013).
11. V. Innocenzi, I. Michelis, F. Ferella, F. Beolchini, B. Kopacek and F. Vegliò, "Recovery of yttrium from fluorescent powder of cathode ray tube, CRT: Zn removal by sulphide precipitation", *Waste Manage*, **33** (11) 2364-2371 (2013).
12. K. Binnemans and P.T. Jones, "Solvometallurgy: An Emerging Branch of Extractive Metallurgy", *J Sustain Metall*, **3** (3) 570-600 (2017).
13. K. Larsson and K. Binnemans, "Selective extraction of metals using ionic liquids for nickel metal hydride battery recycling", *Green Chem*, **16** 4595-4603 (2014).