RECOVERY OF PERMANENT MAGNETS TYPE NDFEB FROM WEEE

N. MENAD*[1], A. SERON[1], M. SAVE[1], Y. MENARD[1], N. MAAT[2], V. JEAN-MARIE LE BRETON[2], V. NACHBAUR[2], A. BIZOUARD[3], M. DELAIN[4], L. WAIGNEIN[5], R. HENNION[5], O. FRANÇOIS[5], & F. VON DER WEID[6]

1. BRGM, 3, avenue Claude-Guillemin, BP 36009 - 45060 Orléans cedex 2 (France)
2. GPM Un. Rouen, ERMMA. Av. de l'Université. 76800 Saint Etienne du Rouvray Cedex (France)
3. Eco-systèmes, Direction Technique, 12, Place de la Défense, 92400 Courbevoie, Paris (France)
4. Cylamen, 101. traverse de l'Escoutaïre, 34830 Clapiers
5. Galloo, 320, wervikstraat ,Menen (Belgium)
6. Selfrag A.G, Biberenzelgli 18CH-3210 Kerzers (Switzerland)
* Corresponding author: n.menad@brgm.fr. Tel: (33) (0) 2 38 64 47 37

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virginie.nachbaur@univ-rouen.fr

Abstract

The increasing use of rare earths elements (REE) in a number of recent technological innovations led to a rapid increase (plus 50% in lastdecade) of their applications. Besides, Europe is one of the most important regions of consumption of these substances. In this context, in its 'Raw materials' strategy, Europe puts the recycling at the center of its concerns to secure its supplies in REEs. Recycling of these substances, on an industrial scale, remains somewhat developed while it presents numerous advantages over the exploitation of primary resources.

Thus, in order to increase the efficiency of the use of the REEs and to decrease European dependence on these strategic elements, research and development efforts must be achieved in all areas of their life cycle whether it concerns exploitation of ores or end-of-life equipment such as the one EXTRADE project targets (Wastes of Electric and Electronic Equipment).

In this context, the project EXTRADE aims to develop new fields of valorization of permanent magnets type NdFeB present in WEEE targeting 3 types of electronic equipment,i) hard disk drives of computers, ii) speakers of audio and video devices and iii) small electric motors present in ICT (information and Communication Technologies).

EXTRADE project proposes to address the extraction of the NdFeB permanent magnetsfrom the WEEE deposit, developing units operation of treatment of WEEE intended to retrieve the contents of the magnet type NdFeB and to develop thermal, physical and physico-chemical treatments for producing new magnets or fractions enriched in alloys of REEs compatible with a recycling in the hydrometallurgical production of REE.

1. INTRODUCTION

The developed countries face a persistent concern about the supply of criticalmetals. Thesemetals, including REEs, are essential to the development of innovative high-tech industries, and particularly those associated with green energy. The recent political crisis caused by China towards Japan putting REEs supply in balance (95% of the world's needs) amplified those concerns. The fundamental issue is to ensure the supply of industries manufacturing for which these chemical compounds made from criticalmetals and alloys are essential, even though their availability shows vulnerabilities at different levels of their supply chain. In this context, the European Union released its report 'Critical raw materials for the EU' that identifies 20 metals described as strategic for the European economy as a whole. At the French level, the roadmap to improve the productivity of resources is marked by the implementation of the Plan of strategic metals and the creation of the COMES(Committee for strategic metals). Among these strategic metals, rare earths contained in permanent magnets of certain WEEE categories are a priority target of growing interest. Since the development of powerful magnets made of neodymium (Nd-Fe-B) in 1980, the volume production of this material has increased dramatically.

The new technologies that use more rare earth elements (REEs) contribute to growing and sustainable demand, at the time, of these substances. Europe is one of the most important regions of REEs consumption through its industries with high added values. She has also accumulated during decades the consumer’s goods that arrived at end of life, and are considered as secondary resources from which REEs can be extracted. The development of a specific sector to recover these permanent magnets contained in the WEEE and recycle rare earths elements contained must therefore become a priority.

The main objective of this work is the implementation of effective techniques oftreatment, recycling and valorization of permanent magnets present in the WEEE.

In Japan, the recycling of REEs from permanent magnets is well developed.It is directed primarily by extractive metallurgy. This problem is relatively recent in Europe. At the scale of the French territory no specific treatment was developed to the point. At present, the current reflections focus on recycling magnets in wind turbines and hybrid or all-electric vehicles as they are the higher magnets -consuming sectors, yet the WEEE have to be considered too as the amount of REEs in the WEEE flow is not negligible.

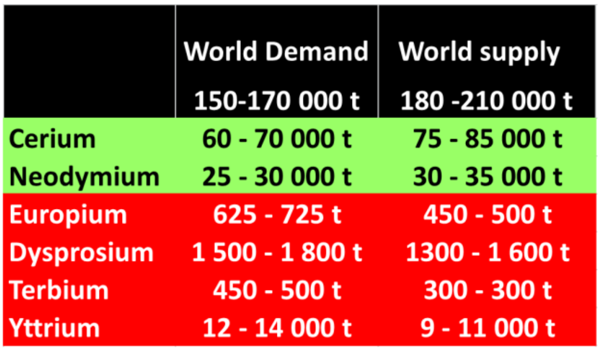
However, the recycling of permanent magnets containing REEs in WEEE is facing many locks. As an example, we can list:

1. the heterogeneity of the WEEE deposit and the difficulty of obtaining representative samples,
2. the dispersion of rare-earth in WEEE deposit,
3. lack of knowledge of rare earths content in small household appliances + IC flow,
4. the magnetic property sought in permanent magnets constitutes a technical lock during recycling operations (these magnets ' stick' in grinding/sorting equipment),
5. the variability of the flow of WEEE (ungraded) input method,
6. the effectiveness of the unit operations of crushing and sorting, comminution/liberation of complex waste matrices,

1.1. Rare earth elements

Rare earths elements are a group of that exhibits special properties (magnetic, electronic, catalytic and optical)and which comprisesyttrium, scandium and the 15 lanthanides.

Unlikewhat is suggested by their name, these metals are quite prevalent in the earth's crust, to the equal of some base metals. Generally they are used in small proportions but their application for mass-market products makes that the world demand quickly increases.It is important to note that all REEs are included in the European list of strategic metals. Worldwide, their demand is slightly higher than their supply (Figure 1). This is true for Eu, Dy, Tband Y and not for Nd and Ce.



	World Demand 150-170 000 t	World supply 180 -210 000 t
Cerium	60 - 70 000 t	75 - 85 000 t
Neodymium	25 - 30 000 t	30 - 35 000 t
Europium	625 - 725 t	450 - 500 t
Dysprosium	1 500 - 1 800 t	1300 - 1 600 t
Terbium	450 - 500 t	300 - 300 t
Yttrium	12 - 14 000 t	9 - 11 000 t

*Figure 1: World demand and supply of rare earth (**Dudley Kingsnorth, /2012**)*

The total demand of REEs for different applications is estimated about 162 500 t representing 66% of market share (Table 1). For permanent magnets (not only in WEEE), the total demand is around 36 000 t representing 22% of market share.

End Use	**China**	**USA**	**Japan & SE Asia**	**Others**	**Total**	**Market Share, %**
Permanent Magnets	28000	2000	4500	1500	36 000	22
Metal Alloys	20000	2000	2500	1500	26 000	16
Catalysts	14500	6500	2500	1500	25 000	15
Polishing Powders	19000	3000	2000	1000	25 000	15
Phosphors	9000	1 000	2000	500	12 500	8
Glass Additives	6000	1000	1000	1000	9 000	6
Ceramic	4000	2 000	2000	1000	9 000	6
Other	6500	8000	3500	2000	20000	12
Total Demand	**107000**	**25500**	**20000**	**10000**	**162 500**	**100**
Market Share	66%	16%	12%	7%	100%	

Table 1: Forecast for Global demand of REEs end uses (**Source: IMCOA**)

Europe has classified all REEs within 20 critical metals and according to US-TMR, the REEs such as Nd, Dy, Eu, Y and Tb will continue to be critical in 5 to 15 years see figure 2.

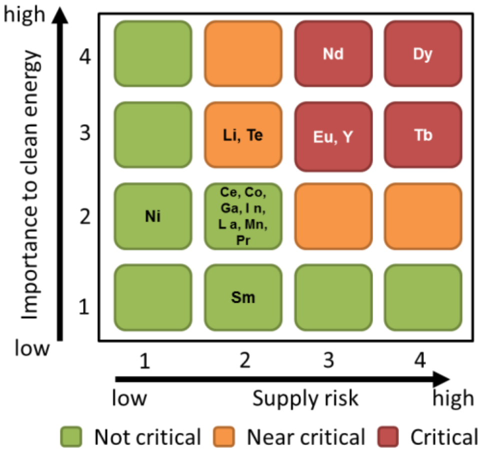


*Figure 2: Criticality of REEs in long term (**Gareth P Hatch, 2013**)*

1.2. Application of REEs

The majority of REEs are used in high technology, especially in the manufacture of high performance magnets, in phosphors present in color televisions or energy saving lamps, catalytic converters, batteries for mobile phones and magnetic alloys. REEs are also used in medical applications (medicines, ophthalmology, NMR, IRM, etc...).

As shown by figure 3, 81% of rare earth elements are produced in China, 13% in Japan and north east of Asia, 2% in USA, and 4% in the rest of world including Europe. These REEs are used in permanent magnets (22%), as alloys (19%), as catalysts (21%), in glass industry (10%), in polishing (16%), in ceramics (5%) and in phosphorous (7%).

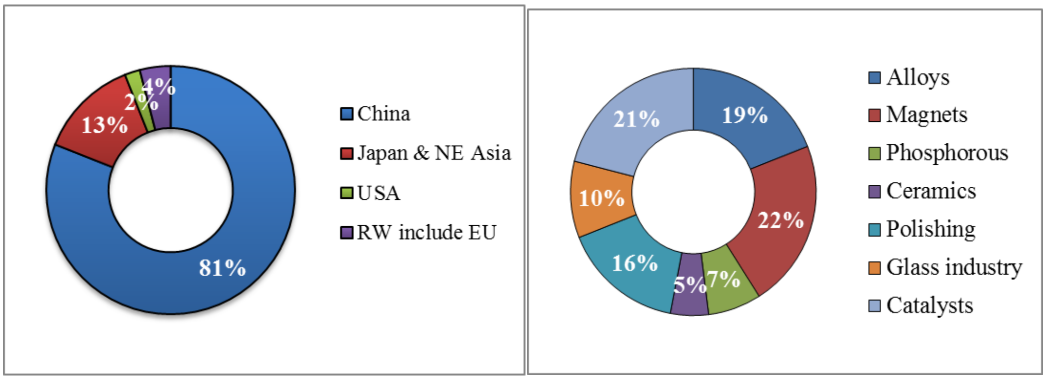


Figure 3: Application of REEs and production places of rare earth magnets

1.3. Extrade process [2]

The extraction of REEs from permanent magnets is well documented in the literature. There is a large enough set of publications and patents regarding the extraction of rare earth from permanent magnetsscraps, and their recycling.However, there are few studies regarding the recyclingof the magnets from the small household appliances ‘stream. The only studies so far are mostly Japanese, with the development of a machine to separate and collect NdFeB type magnets from hard disks drives and compressors. This new machine can process up to 100 HDD per hour.

The Extrade process shown in Figure 4 is focusing on the improvement of the classical treatment process of WEEE. After depollution of WEEE, the components containing magnets would beisolated,thermally treated to demagnetize them and fragmentedto release the magnets, then sorted regarding there technologies (in order to isolated theNdFeB magnets),. The magnets would berecovered by a separator X, and after cleaning, the recovered magnets would bemicronized. The powders obtained would bepurified for the production of new magnets or for the extraction of the rare earths contained.

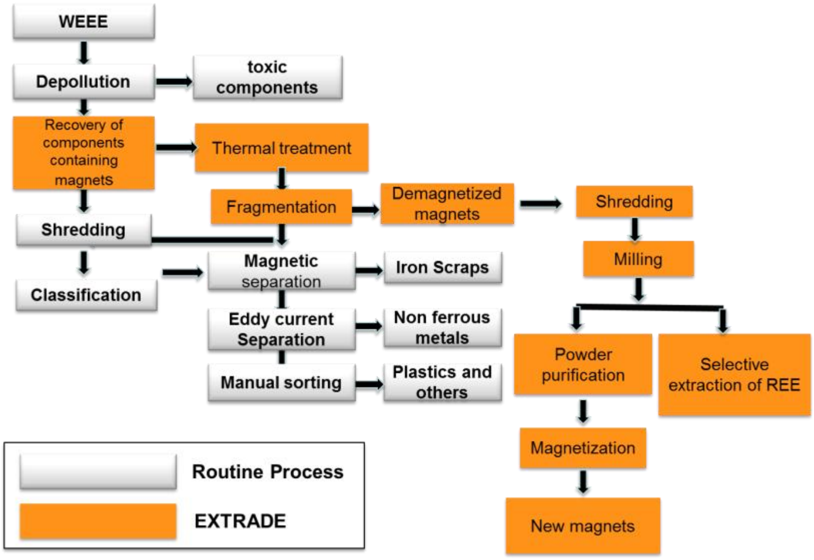


Figure 4: Extrade process to be developed

The project includes the following steps:

1. Thermal treatment (demagnetization)
2. Electrical (high-voltage electric pulses) and Mechanical treatment to recover magnets from the computer system unit
3. **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
4. **Route 2** – extraction of REE using innovative hydrometallurgical techniques
    - *Weak & cheap acid selective dissolution*
    - *Selective recovery of REE using sorbents*

2. MATERIALS AND METHODS

2.1. Materials

The EXTRADE project aims to develop new fields of development of permanent rare earth type magnets present in the WEEE, targeting 3 types of electronic devices: i) hard drives of computers, ii) loudspeakers of audio and video materials and iii) the small electric motors present in ICT (information and Communication Technologies) and small electronic appliances see figure 5.

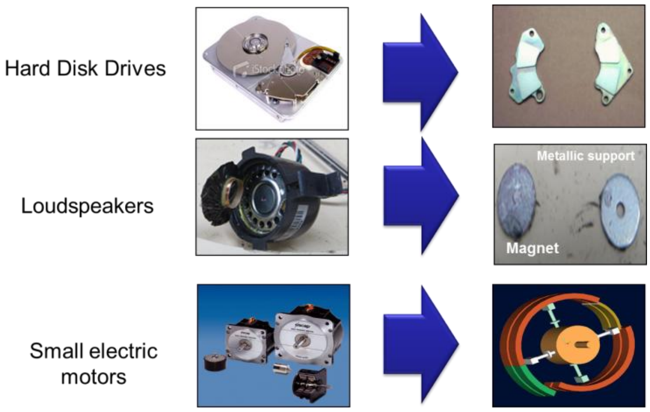


Figure 5: Electronic devices containing REEs

2.2. Methods

Several possibilities were explored to extract the NdFeB type magnetsfrom the three targeted samples of the Extrade project. The first one deals with the recovery of magnet from WEEE stream by manual or mechanical dismantling. After identifyingthe NdFeB type magnets in different collected electronic devices of WEEE, the materials were subjected to liberate the magnets manually by using different tools. The main objective of this action is to minimize the time and thus the labor cost to remove the magnets from the three project's targets. Concerning the mechanical dismantling, different shredders were used on the investigated demagnetized samples. The objective is to choose the most available equipment which can liberate the magnets.

The sortedNdFeB type magnets were crushed and a physical separation technique was used in order to remove the metal coating (figure 6). The objective of this operation wasto produce a powder rich in rare earth elements (Nd, Dy and Pr), which can be treated by hydrometallurgical techniques to recover REEs selectively.

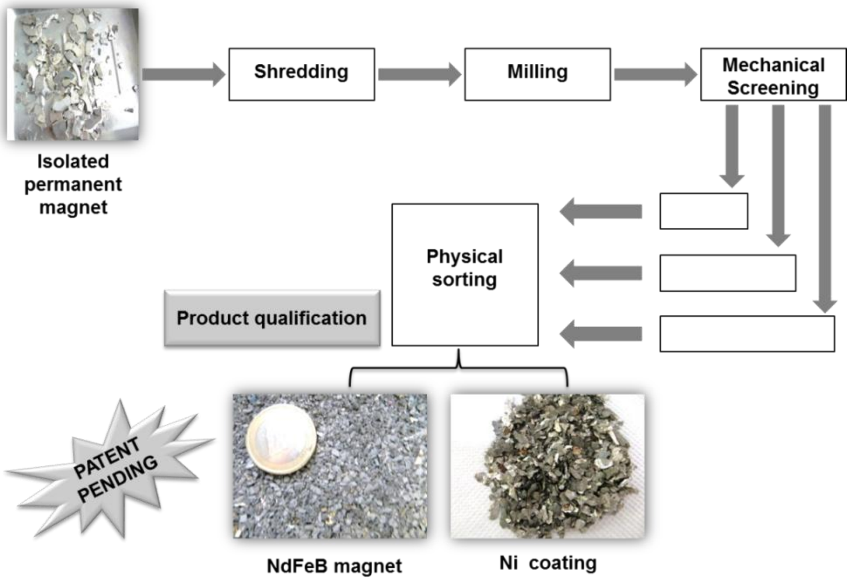


Figure 6: Physical process of purification of magnet powder

The NdFeB powder was dissolved by a new simple method and the REEs were selectively recovered by several tested sorbents. All products generated form the cited methods were characterized by XRD, SEMand chemical analyses.

The valorisation of NdFeB type magnets of HDD requires beingable to isolate the magnets and therefore to selectively fragment the HDD structure that preserve the integrity of these magnets. One of the technologies identified to achieve this fragmentation is the electro-fragmentation equipment developed by SELFRAG(Figure 7 left). It involves applying high voltage electric pulses (Figure 7 right), (few kV per cm), through complex multi-phased or multi-constituents matrices, immersed in a dielectric liquid (water preferably). The spread of these impulses in the water and in the solid is materialized by electric arcs that propagate preferentially at the interfaces between mineral phases of ores or components of waste and which lead to a smart, selective crushing of HDD and so, to the release of permanent magnets contained.

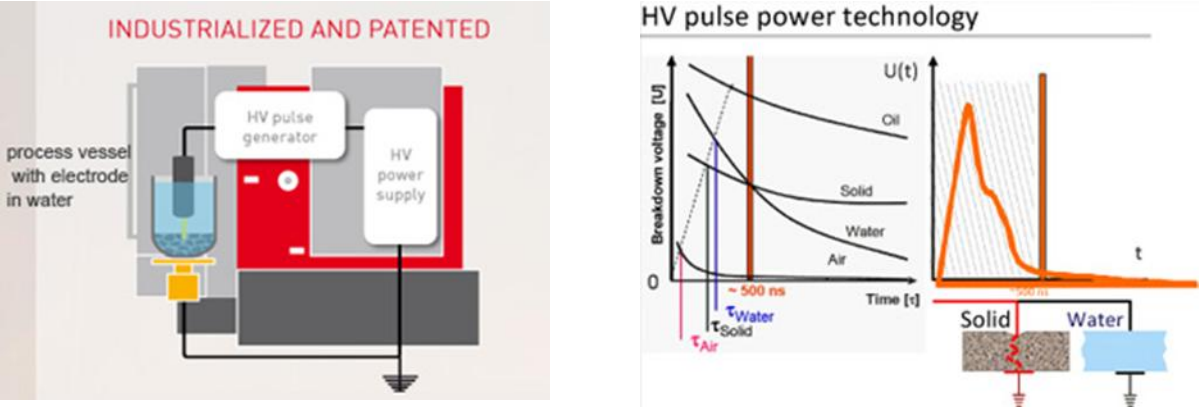


Figure 7 - Physical and electrical requirements for the Selfrag process

The equipment set-up for the tests was using a 2 L closed vessel and a standard electrode (8 mm). The objective was to investigate the selective liberation of the three targets of the Extrade project. Six samples were processed using appropriate conditions.

3. RESULTS

3.1. Characteristics of permanent magnets

The three representative samples were dismantled for characterisation. The first action deals with determination of Wt% of magnets in the investigated electronic devices. The results are shown in Table 2. It can be seen that, central unit computer HDD, loudspeakers, laptop and electric motors contain respectively, 2.5 - 2.8 wt%, 4 - 6 wt %, 22 - 26 wt % or 0.8 - 2 wt % of magnets.

Sources	Weight % of magnet
Computer loudspeakers	4 – 6
HDD from central unit computer	2.5 - 2,8
HDD from Laptop	2 - 3
Small electric motors (A)	22 – 26
Small electric motors (B)	0.8 – 2

Table 2: Weight percent of magnets in different electronic components

Characterization of the magnets was performed according to method described (**N. Menad and A. Seron, 2016)**. Figure 8 show the morphological aspects of the investigated sample of magnet obtained by scanning electron microscopy (SEM). Figure9 shows that the Ni or Zn protective coating of magnet consists of a layer of approximately 20 µm thick. The texture of these magnets consists of sintered crystals of $Nd_2Fe_{14}B$ phase tetrahedral shape and rich rare earth oxides (Nd, Dy and Pr) at interphase (see EDS in figure 8).

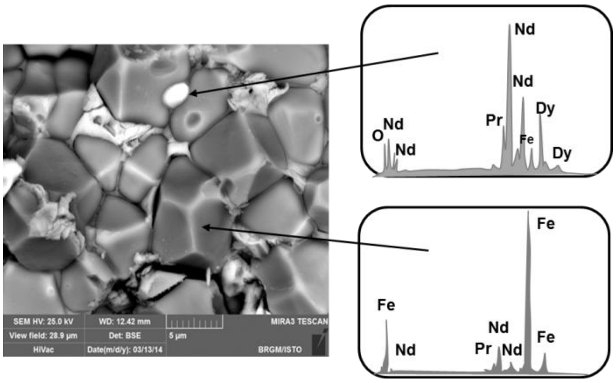


Figure 8: Morphological aspects and EDS of HDD magnet

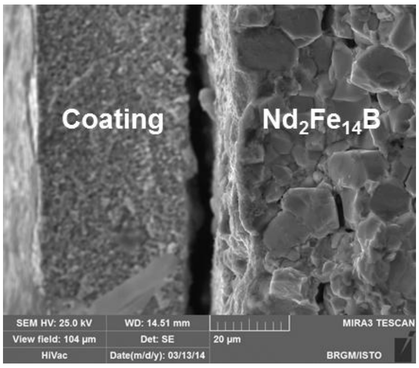


Figure 9: Photo SEM of magnet coating

3.2. Thermal treatment (demagnetization)

Permanent magnets have several physical properties, including the Curie temperature and maximum operating temperature which differ from a type of magnet to another. The Curie temperature (T_c) is the temperature above which a magnetic body loses irreversibly its magnetization. When heating a magnetic material above this temperature, the order of the magnetic fields disappears to a paramagnetic disordered state. The maximum operating temperature (T_{max}) is the temperature at which the magnet loses its magnetic property but remains usable after cooling. It is important to underline that T_{max} is a function of the size of the magnets.

To determine those parameters, TGA was carried out on the investigated samples. About 15g of the investigated samples (whole magnets) are heated in nitrogen atmosphere until 500°C with temperature rate of 2°C min^{-1}in a specific way in order to determine physical properties, particular Curie temperature at which the magnets lose their magnetic properties.The results are shown in Figure 10. It can be seen that the effect for loudspeakers permanent magnet is at 459°C, this can be attributed to the Curie temperature of ferrite magnets. However, for HDD, two effects are observed. The first one is started at 145°C, which is attributed to their maximum operating temperature, and the second one at 297°C. Thelast one is attributed to the Curie temperature of the rare earth type magnets at which they lose their magnetic properties. Then, to demagnetize the NdFeB and ferrites type magnets, it must be heated, respectively, at the temperatures around 300°C and 500°C.

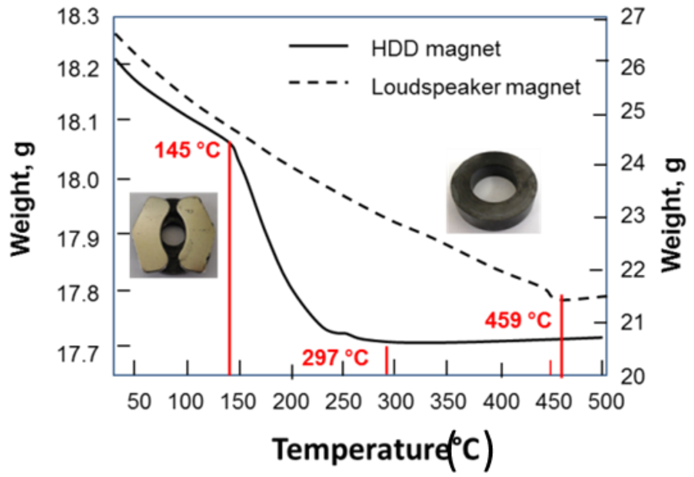


Figure 10: TGA of permanent magnets of HDD and loudspeakers

3.3. Recovery of magnet from electronic components

3.3.1. Manual dismantling

Strictly manual disassembly

Different tools of market were used to perform this task. By investing in learning optimized movements, repeatability and durability, it is possible to minimize the time of this action, which is incompressible due to the number of screws and change of tools. A significant time remainsnecessary to extract the magnets from their support.

Semi-mechanized disassembly

To save time by avoiding total manual disassembly to get near-identical own fractions, hacksaw and stand drill were tested. The results show that the drill gives the same disassembly time than manual process, however it offers two significant advantages. It requires less effort and it allows delivering strong screws, while the hacksaw provided no benefit.

3.3.2. Mechanical dismantling

Different shredders that can be found in mineral processing were tested. The objective was to liberate the magnets contained in the three investigated samples of electronic devices. From several shredders tested, only one allowed to liberate around 98% of magnets. The results will be patented. As shown in figure 11, the products generated are classified in different fractions, and the fractionenrichedin magnets was subjected to physical separation to recover selectively all magnets.

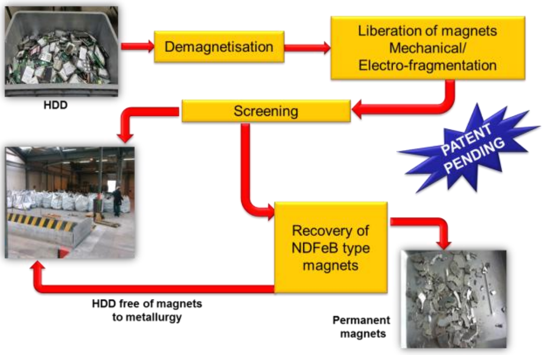


Figure 11: Process recovery of permanent magnets from electronic component.

3.3.3. Electrical (high-voltage electric pulses)treatment

The results obtained from electro fragmentation tests show:

1. After only 10 pulses the hard disc itself began to “swell” and surface components started to become liberated. After 40 pulses, internal components started to be liberated and by 80 pulses, the entire drive was separated into distinct components (casing, hard drive, motor, etc.). With 120 pulses, there was liberation and size reduction of the all parts, except for the metal casing.

2. Regarding the small electrical motor 1, the magnet was immediately fragmented upon the application of 10 pulses and the internal coils were separated from casting after 50 pulses and by adding the energy the tightly wound copper wires began to liberate.

3. Only 10 pulses were needed to liberate the electrical motor 2 from the board along with the internal components of the motor, and any additional energy was used to fragment said components further as well as remove those still attached to the circuit board (Figure 12)

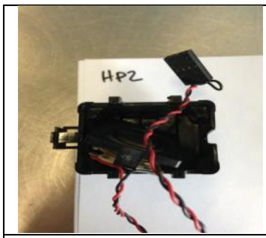
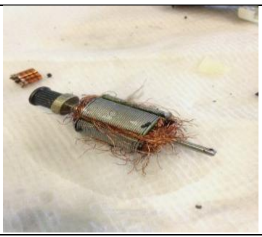
 	 	 	
Loudspeaker before treatment	Hard disc before treatment	Electrical motor 1 before treatment	Electrical motor 2 before treatment
			
Loudspeaker after treatment	Hard disc after treatment	Electrical motor 1 after treatment	Electrical motor 2 after treatment

Figure 12: Samples of the electronic devices containing magnets before and after processing

3.3.4. *Chemical treatment: solvo-thermal decrepitation ???? Rouen*

3.3.5. *Press-molding in magnetic field / sintering / magnetization ???? Rouen*

3.3.6. *Extraction of REE using innovative hydrometallurgical techniques*

The dissolution of the magnet powder was carried out by using a weak acid. The solution obtained contained Nd, Dy, Pr and high content of iron present in the form of Fe^{2+} and Fe^{3+}. The results are reported in Figure 13. It shows the evolution of the dissolution rate of magnet as function of the time. From this figure, it can be concludedthat all metals are dissolved in 7 hours exceptnickel which is stable and can thus be recovered in the solid phase after filtration of the solution. It is important to note that this result is under processing of patent.

The precipitation tests of the solution containing ion metals by NaOH were performed at different pH. The results are given in Figure 14 showing the evolution of the precipitation rates of Nd, Dy and Fe as function of pH. From this figure, it can be seen that at pH lower than 4, about 80% of iron is precipitated in the form of Fe^{+3}, while Fe^{+2} will be totally precipitated at pH = 10 with Nd and Dy. As the precipitation of those elements contained in the solution is notselective, several tests were carried out on the useof different biomaterials to selectively extractthe ion metals contained.

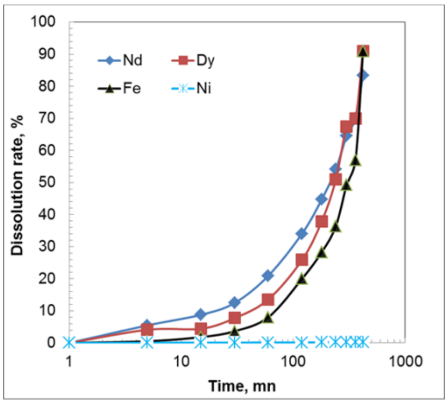


Figure 13: Dissolution kinetics of magnet

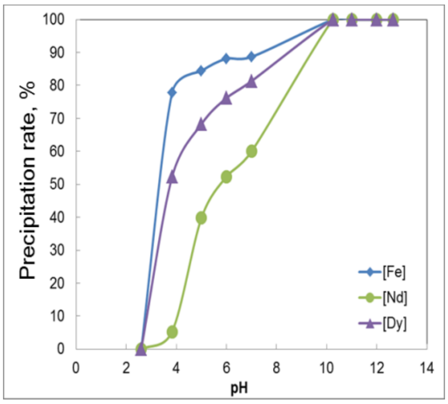


Figure 14: Precipitation of Nd, Fe and Py

The test results of sorption of rare earths on solutions (Figure 15) clearly show that some biomaterials allow a specific extractionof dissolved iron and consequently enrichment in REEs ofthe solution.Such a process seems to be able to lead to a quantitative separation of iron and rare-earth elements. Other Experiments are under way to optimize the conditions for implementation. The process subjected to patenting procedure will lead to the protection of a process from the preparation of constituent elements solution of the magnets up totheir separation before their recovery.

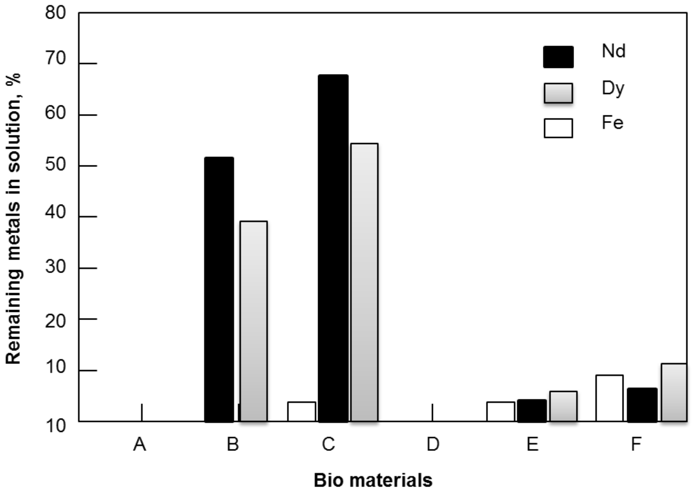


Figure 15: Selective sorption of REE using biomaterials (biomaterials A, B, C, D, E, F)

4. CONCLUSIONS

From the characterization of the small household flow, the magnets present in hard drives, small electric motors and speakers, represent around 98% of the magnet deposit collectable in the small electronic appliances flow. The rest of the magnets in this stream is disseminated in other equipment such as fixed or mobile phones, internet boxes which cannot be easily sorted regarding the current processing treatment chain.

The best way to reduce the time of manual disassembly of the electronic devices containing NdFeB type magnets is to recover the magnets still stuck on the stainless steel carrier at the stage of downstream valorization.

The results of the thermal treatments show that the majority of the magnets present in the three investigated electronic devices lose their magnetic properties in reaching the Curie temperature (300-400 ° C) in 15-20 minutes.

Pilot-scale trials on mechanical dismantling of hard drives to recover the magnets give encouraging results. More than 87% of magnets were released without pulverizing them. An innovative physical separation technique will be tested on the class-20 mm to extract contained magnets.

Fragmentation of the investigated samples of the electronic devices containing magnets in the SELFRAG process is easily achieved. For material completely encased in metal, the liberation is difficult, but not impossible. The initial energy required to “break in to” to casing and loosen it may be high, but once liberation is initiated, it tends to propagate rapidly. Any exposed components are quickly broken down, especially liberating plastic from metal

Physical and chemical techniques are developed to extract the magnet coating. A mass balance of the developed process will be performed.Dissolution test results with weak acid show that magnet-alloys are dissolved in 7 hours while the coating of Ni or zinc is not attacked.

The precipitation study of cations of the solutions obtained from dissolution of magnets with NaOH shows that at pH 3, approximately 80% of Fe (III) areprecipitated; the remaining 20%are in thedissolved iron (II)form. The co-precipitation of iron (II) with REEs starts at pH > 3.Consequently, 6 biomaterials have been tested to extract iron and enrich the solution in REES. From thesebiomaterials tested for theirselective adsorption capacity of REEs, two have given encouraging results.

REFERENCES

[1] Dudley Kingsnorth, The Global Rare Earths Industry: A Delicate Balancing Act, Deutsche Rohstoffagentur, Berlin, 16thApril 2012

[2] Extrade Project, http://extrade.brgm.fr/

[3] Gareth P Hatch, the Rare-Earth Supply-Chain Challenge: Light at the End of the Tunnel. Magnetics 2013, February 7-8, 2013, Rosen Plaza Hotel, Orlando, Florida, USA.

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