

Process Recovery of Nd-Fe-B Permanent Magnets from Hard Disc Drives

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Abstract

The increasing use of rare earths elements (REE) in a number of recent technological innovations led to a rapid increase (>50% in last decade) in 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 centre 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.

This paper shows the results obtained the work done in the frame of the EXTRADE project on the extraction of the Nd-Fe-B permanent magnets from the WEEE deposit, developing units operation of treatment of WEEE intended to retrieve the contents of the magnet type Nd-Fe-B 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.

Keywords: Waste of electric and electronic equipment; Permanent magnets; Rare earth elements; Thermal treatment; Recovery; Vaporization process

Introduction

The developed countries face a persistent concern about the supply of critical metals. These metals, 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 critical metals 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 1983, 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 of treatment, 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 [1].

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,

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Rare earth elements

Rare earths elements are a group of that exhibits special properties (magnetic, electronic, catalytic and optical) and which comprises yttrium, scandium and the 15 lanthanides. Unlike what 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, Tb and Y and not for Nd and Ce.

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.

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.

Application of REEs

The majority of REEs are used in high technology, especially in the manufacture of high performance magnets, in phosphors present in colour 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%).

	World Demand	World supply
	150-170 000 t	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 [1].

End Use	China	USA	Japan and SE Asia	Others	Total	Market Share, %
Permanent Magnets	28000	2000	4500	1500	36000	22
Metal Alloys	20000	2000	2500	1500	26000	16
Catalysts	14500	6500	2500	1500	25000	15
Polishing Powders	19000	3000	2000	1000	25000	15
Phosphors	9000	1000	2000	500	12500	8
Glass Additives	6000	1000	1000	1000	9000	6
Ceramic	4000	2000	2000	1000	9000	6
Other	6500	8000	3500	2000	20000	12
Total Demand	107000	25500	20000	10000	162500	100
Market Share	66%	16%	12%	7%	100%	

Source: IMCOA.

Table 1: Forecast for Global demand of REEs end uses.

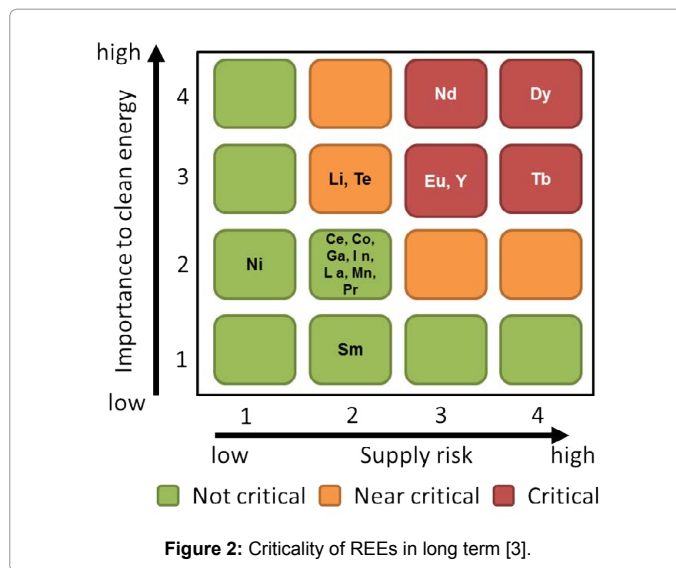


Figure 2: Criticality of REEs in long term [3].

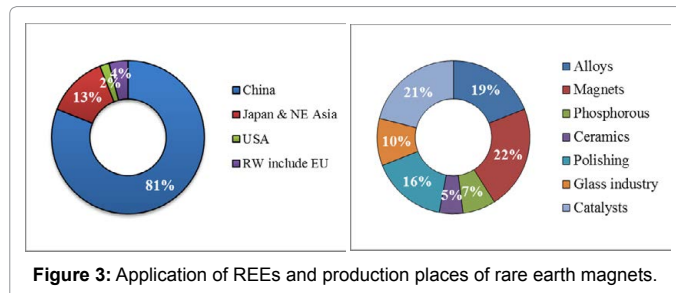


Figure 3: Application of REEs and production places of rare earth magnets.

Extrade process

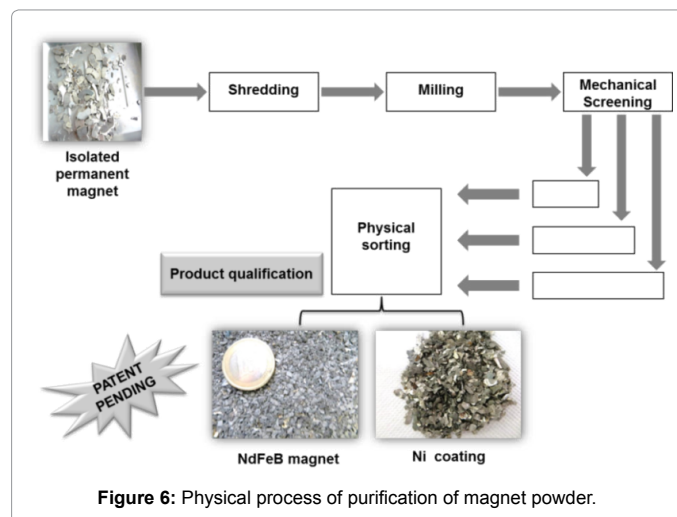
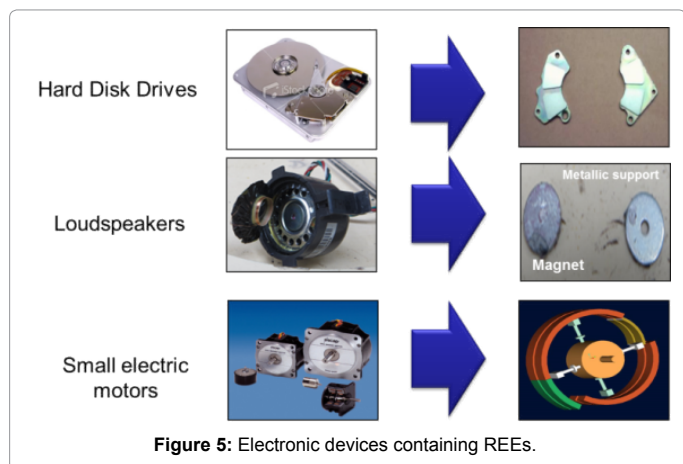
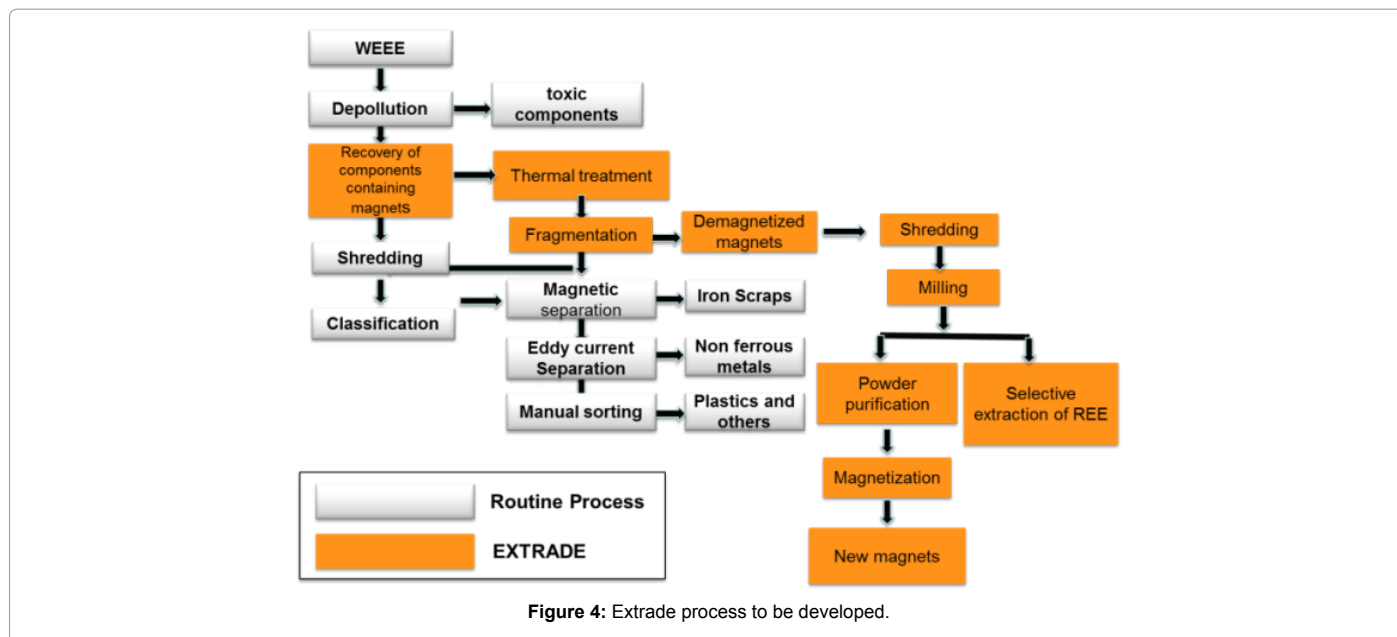
The extraction of REEs from permanent magnets is well documented in the literature. There is a large enough set of publications and patents regarding the extraction of rare earth from permanent magnets scraps, and their recycling. However, there are few studies regarding the recycling of the magnets from the small household appliances ‘stream’. The only studies so far are mostly Japanese, with the development of a machine to separate and collect Nd-Fe-B type magnets from hard disks drives and compressors. This new machine can process up to 100 HDD per hour [2].

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 be isolated, thermally treated to demagnetize them and fragmented to release the magnets, then sorted regarding there technologies (in order to isolated the Nd-Fe-B magnets). The magnets would be recovered by a separator X, and after cleaning, the recovered magnets would be micronized. The powders obtained would be purified for the production of new magnets or for the extraction of the rare earths contained.

Materials and Methods

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.



Methods

Several possibilities were explored to extract the Nd-Fe-B type magnets from 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 identifying the Nd-Fe-B 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 sorted Nd-Fe-B 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 was to produce a powder rich in rare earth elements (Nd, Dy and Pr), which can be treated by hydrometallurgical techniques to recover REEs selectively.

The Nd-Fe-B powder was dissolved by a new simple method and the REEs were selectively recovered by several tested sorbents. All

products generated from the cited methods were characterized by XRD, SEM and chemical analyses.

The valorisation of Nd-Fe-B type magnets of HDD requires being able 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.

The equipment set-up for the tests was using a 2L closed vessel and a standard electrode (8 mm). The objective was to investigate

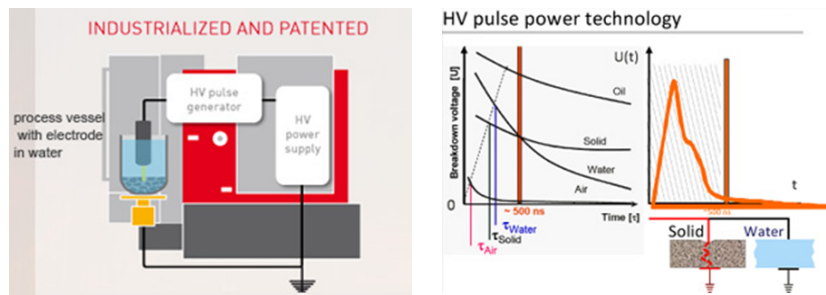


Figure 7: Physical and electrical requirements for the Selfrag process.

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.

the selective liberation of the three targets of the Extrade project. Six samples were processed using appropriate conditions.

Results

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.

Characterization of the magnets was performed according to method described (Menad N and Seron A). Figure 8 shows the morphological aspects of the investigated sample of magnet obtained by scanning electron microscopy (SEM). Figure 9 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 Nd₂Fe₁₄B phase tetrahedral shape and rich rare earth oxides (Nd, Dy and Pr) at interphase (see EDS in Figure 8).

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, ThermoGravimetry Analysis (TGA) was carried out on the investigated samples. About 15 g 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.

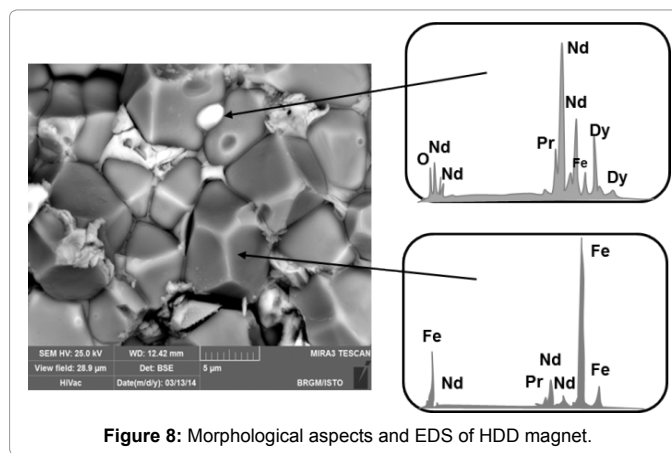


Figure 8: Morphological aspects and EDS of HDD magnet.

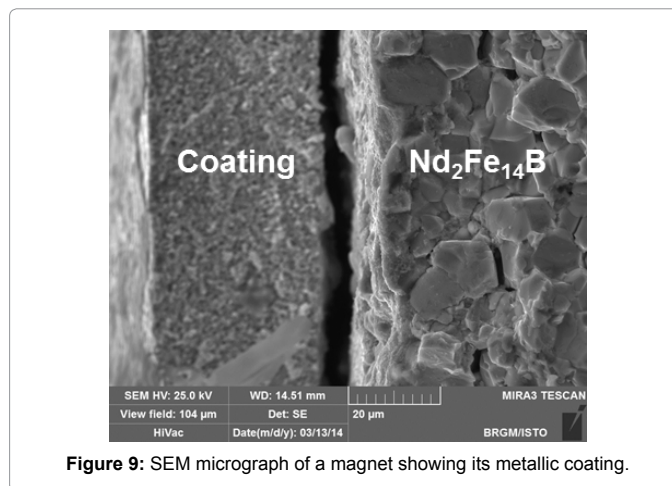


Figure 9: SEM micrograph of a magnet showing its metallic coating.

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. The last one is attributed to the Curie temperature of the rare earth type magnets at which they lose their magnetic properties. Then, to demagnetize the Nd-Fe-B and ferrites type magnets, it must be heated, respectively, at the temperatures around 300°C and 500°C.

Recovery of magnet from electronic components

Manual dismantling

Strictly manual disassembly: Different tools of market were used

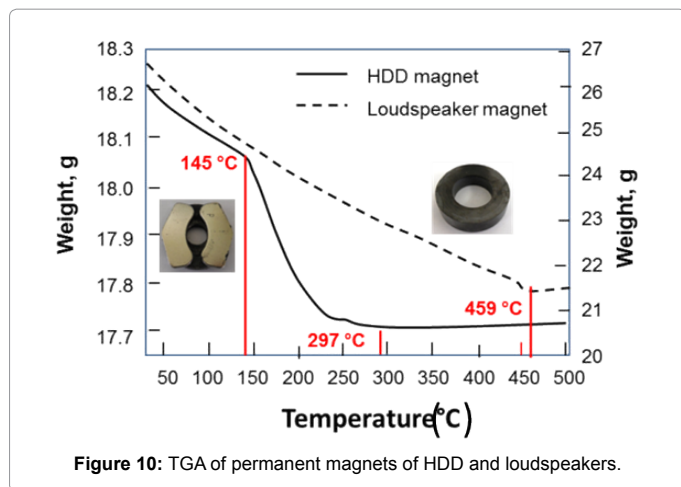


Figure 10: TGA of permanent magnets of HDD and loudspeakers.

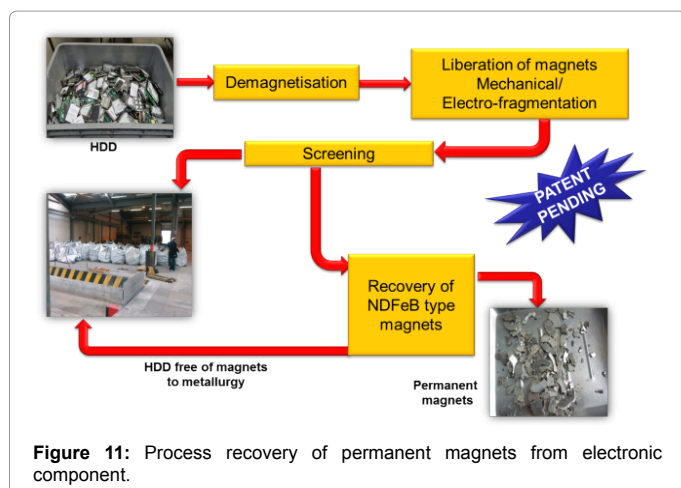


Figure 11: Process recovery of permanent magnets from electronic component.

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 remains necessary 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.

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 fraction enriched in magnets was subjected to physical separation to recover selectively all magnets.

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 casing 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).

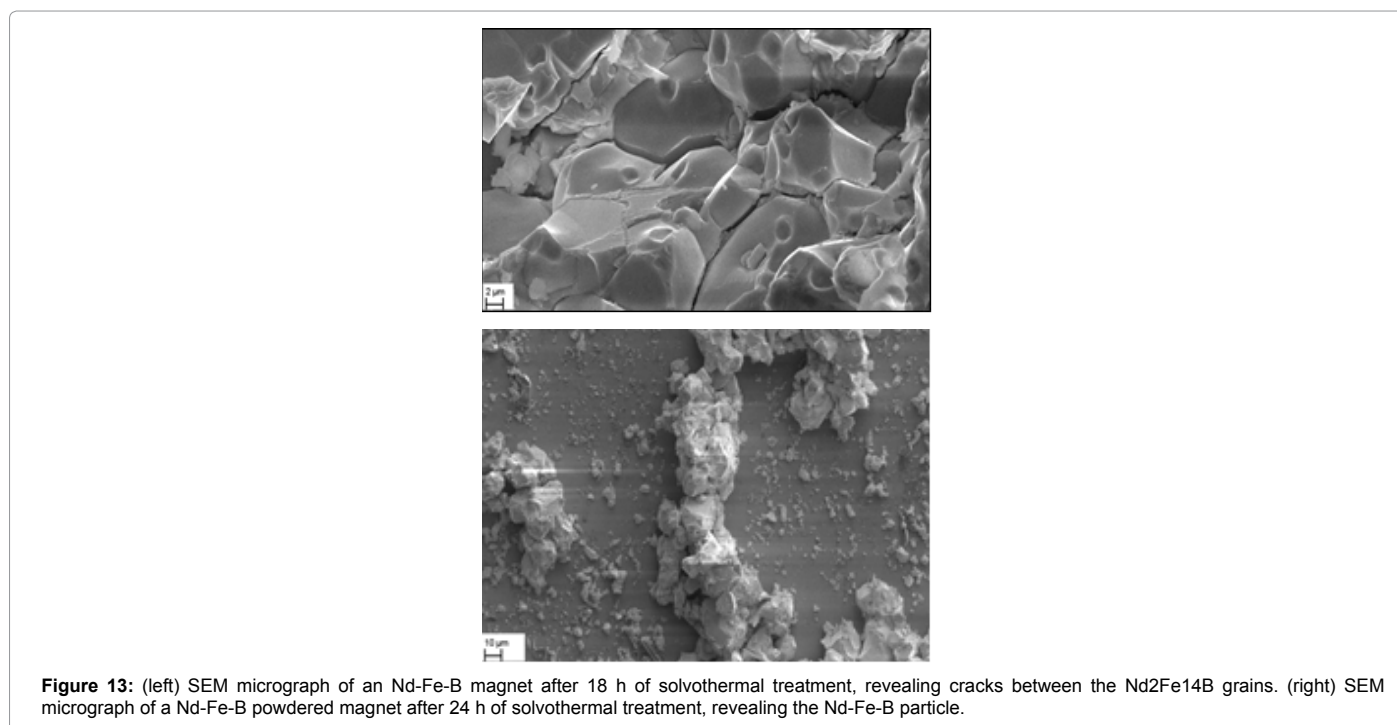
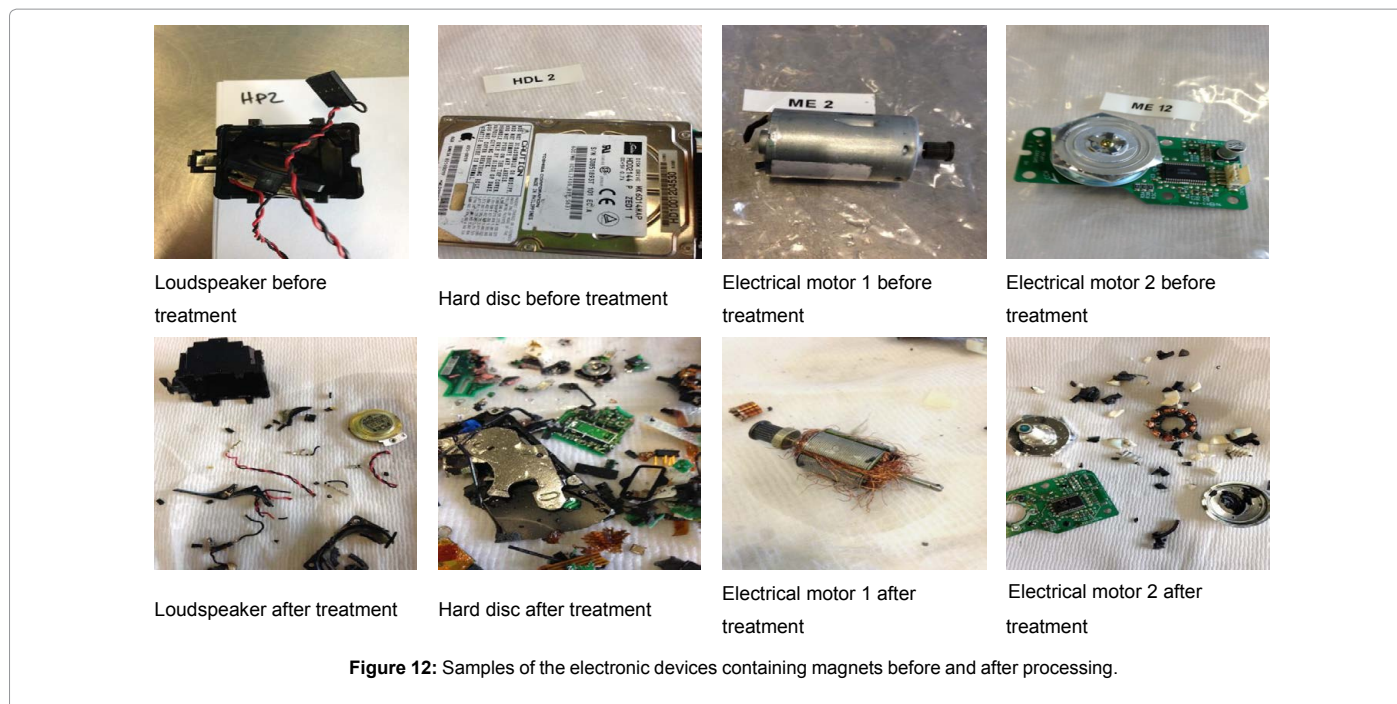
Chemical treatment: solvo-thermal process: We have investigated rare earth permanent magnets recycling with a solvo-thermal process. The investigated samples are Nd-Fe-B permanent magnets coated with electrolytic nickel. We managed to perform magnet hydrogenation in tetralin (a hydrogen-donor solvent), which is a new and environmentally friendly approach for recycling rare earth permanent magnets. A specific catalyst has been prepared, which is constituted of active charcoal with a very low percentage of sulfur has been synthesized, and a solvo-thermal treatment for recycling Nd-Fe-B magnets has been set up. One gram of activated charcoal has been heated under vacuum at 700°C for one hour. 0.01g of Na₂S₂O₅ is dissolved in 5 mL of distilled water. The solution has been deposited on the activated charcoal, and evaporated under vacuum for one hour. The reaction takes place in a Teflon lined bomb. The permanent magnet has been put into the reactor, and 15 mL of tetralin have been added. The volume of the reactor is 25 mL. The solution has been deoxygenated with an Argon flow for 15 minutes. During the experiment, the reactor has been closed and heated at 225°C for various times up to 24 hours. The temperature has been chosen to be slightly higher than the evaporation point. At the end of the reaction the reactor has been cooled in ambient air and the remaining powder has been washed several times with absolute ethanol and finally dried under vacuum.

After 12 h, we observed that the coating has been completely removed from the magnet. The coating pieces can be separated from the magnetic powder by sieving. After 18h, both Nd-rich phase and Nd₂Fe₁₄B have been hydrogenated, resulting into the formation of cracks at the surface of the magnet, and to the loosening of some Nd₂Fe₁₄B grains from the magnet (Figure 13).

Permanent magnets can thus be processed directly after dismantling the electronic products (Figure 14). This recycled powder can thus be compacted by sintering to make other magnets.

It is also possible to reuse the bulk magnetic material by only removing the metallic coating. This can be achieved by stopping the solvothermal process after the removing of the metallic coating. This allows avoiding a manual stripping (Figures 15 and 16) [3,4].

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 Fe²⁺ and Fe³⁺. The results are reported in Figure 17. It shows the evolution of the dissolution rate of magnet as function of the time. From this figure, it can be concluded that all metals are dissolved in 7 hours except nickel which is stable



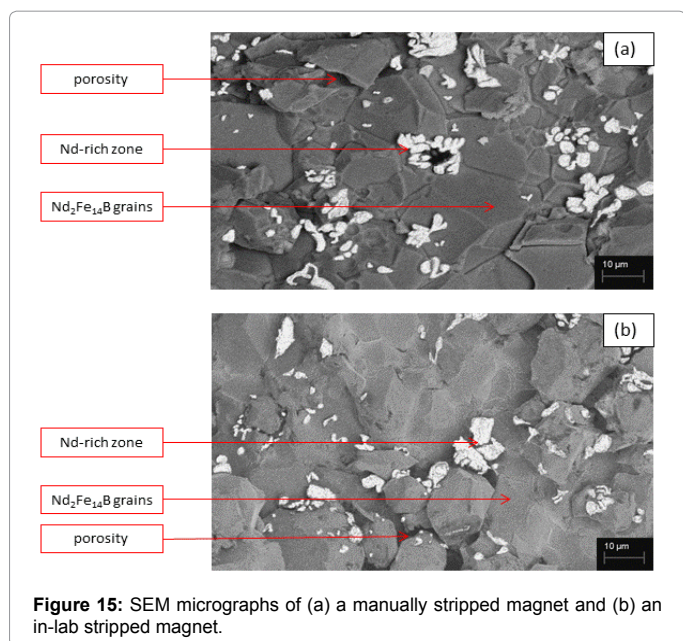


Figure 15: SEM micrographs of (a) a manually stripped magnet and (b) an in-lab stripped magnet.

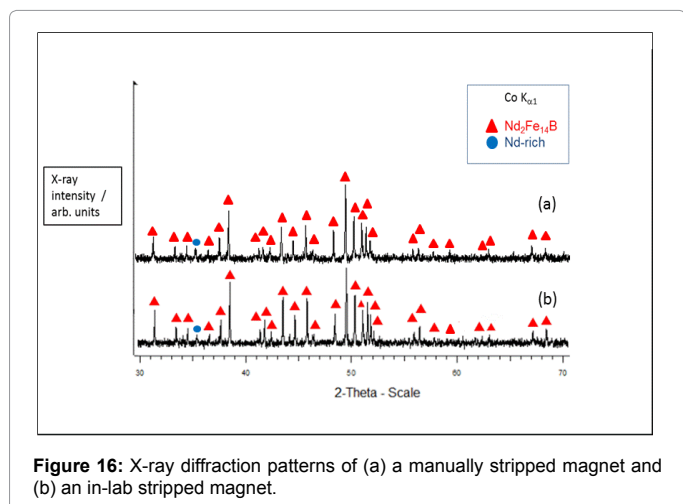


Figure 16: X-ray diffraction patterns of (a) a manually stripped magnet and (b) an in-lab stripped magnet.

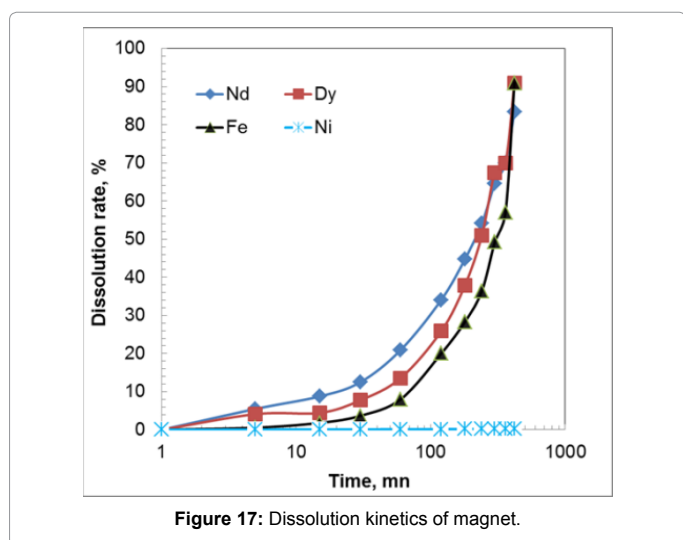


Figure 17: Dissolution kinetics of magnet.

and can thus be recovered in the solid phase after filtration of the solution. The dissolution rate is consistent with the literature [5-7]. 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 18 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 not selective, several tests were carried out on the use of different biomaterials to selectively extract the ion metals contained.

The test results of sorption of rare earths on solutions (Figure 19) clearly show that some biomaterials allow a specific extraction of dissolved iron and consequently enrichment in REEs of the 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 to their separation before their recovery.

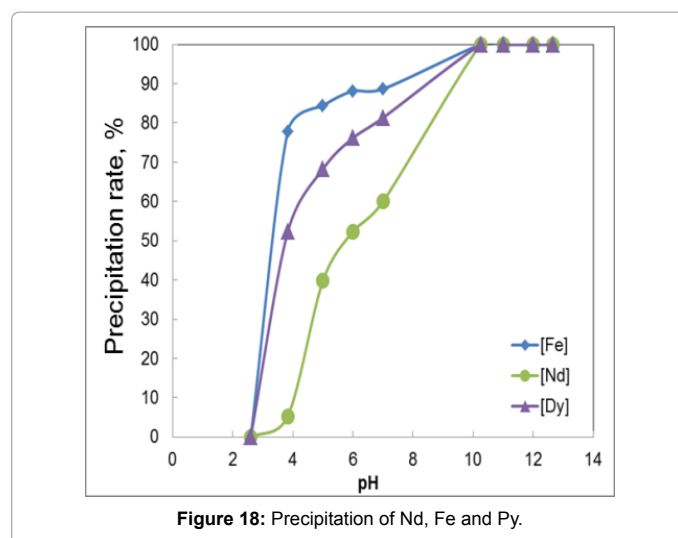


Figure 18: Precipitation of Nd, Fe and Py.

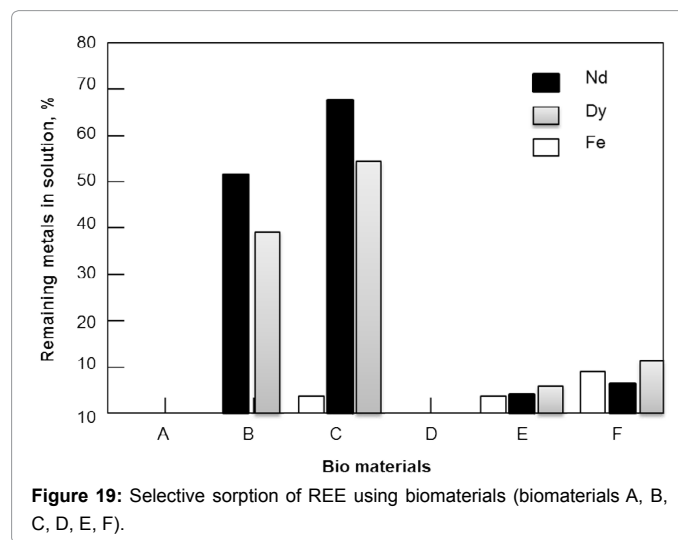


Figure 19: Selective sorption of REE using biomaterials (biomaterials A, B, C, D, E, F).

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 are 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 Nd-Fe-B 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” 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) are precipitated; the remaining 20% are in the dissolved 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 these biomaterials tested for their selective adsorption capacity of REEs, two have given encouraging results.

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