

## Characteristics of Nd-Fe-B Permanent Magnets Present in Electronic Components

N Menad\* and A Seron

Unite Dechets et Matieres Premieres (DMP), Waste and Raw Materials Unit, France

### Abstract

The increasing use of rare earths elements (REEs) in a number of recent technological innovations led to a rapid increase (>50% in the last decade) in their applications. Europe is one of the most important regions of consumption of these substances. In this context, Europe in its 'Raw materials' strategy puts the recycling at the center of its concerns to provide a part of securing 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. This paper will present some results obtained from characterization study of permanent magnets (PMs) present in WEEEs. Three components containing PMs are identified: hard disk drives, small electric motors and speakers. The representative sample of these components has been dismantled manually to recover the PMs contained and to quantify their amount. The results show that the weight percentage of the PMs varies from 4 to 6% in the speakers, 2.5 to 2.8% in the hard disks, and between 0.8 and 2% in some electric motors.

The results of the thermal treatment of the Nd-Fe-B PMs of the investigated samples show that the majority of these PMs lose their magnetic property upon reaching Curie temperature (300-400°C) in 15-20 min. Scanning Electronic Microscopy reveals the morphological aspects of the PM which consist in crystals shaped tetrahedral phase Nd<sub>2</sub>Fe<sub>14</sub>B sintered in the presence of the interphase rich in Nd, Dy and Pr. The PM are layer coated with 20 μm thick, consisting of Ni, Zn or metals alloys.

**Keywords:** Electronic equipment; Magnets; Thermal treatment

### Introduction

The increasing use of rare earths elements (REEs) in a number of recent technological innovations led to a rapid increase (more than 50% in the last decade) in their applications. In this context, Europe in its 'Raw materials' strategy puts the recycling at the center of its concerns to provide a part of securing its supplies of REEs. Recycling of these substances, at the industrial scale, remains somewhat developed while it presents numerous advantages over the exploitation of primary resources:

- Europe is one of the most important regions of consumption of these substances. It has, in addition, accumulated during decades of consumer goods that arrived at end of life and are considered as secondary resources which could be extracted from the REEs;
- French and European dependency on resources from foreign countries can be reduced through the recycling of post-consumer waste;
- Treatment of secondary resources for the production of REEs would not cause health and environmental risks induced linked to the presence of processions of radionuclides from primary deposits;
- Production of metal resources through the use of secondary resources is most often done with energy consumption much lower than those observed for the exploitation of primary resources. It also expects that most recycling operations have an environmental benefit.

Thus, in order to increase the efficiency of the use of the REEs and decrease European dependence on these strategic elements, an effort to research and development should be made in all areas of their life cycle whether it is exploitation of ores (mineral processing, extractive metallurgy) or from the equipment at the end of life as the waste of electrical and electronic equipment WEEE.

This paper presents the work done with the project supported by French research agency in the frame of the contract ECO-TS deals with characterisation of permanent magnets present in electronic devices in order to recovery REES contained.

### Rare earth elements

The rare earths market is private, reserved only for professionals and depends on supply and demand. These rare earths have no stock or State regulations instruments such as gold and oil market. Their prices are reported by the main world mines, representing the main stakeholders of rare earths in this case Chinese mines that monopolize the market. The rare earths are sold in different forms (oxide or metal) with 99% purity.

Usually, rare earths elements (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...). Table 1 groups their applications. It can be noted that the applications which consume more than 25% of REEs, are considered as major applications as shown in red color in Table 1. As examples,

**\*Corresponding author:** N Menad, Unite Dechets et Matieres Premieres (DMP), Waste and Raw Materials Unit, BRGM – D3E/DMP 3, Avenue Claude Guillemin - BP 36009, 45060 Orléans Cedex 02, France, Tel: (33) (0) 2 38 64 47 37; E-mail: [n.menad@brgm.fr](mailto:n.menad@brgm.fr)

**Received** December 21, 2016; **Accepted** January 17, 2017; **Published** January 25, 2017

**Citation:** Menad N, Seron A (2017) Characteristics of Nd-Fe-B Permanent Magnets Present in Electronic Components. Int J Waste Resour 7: 263. doi: 10.4172/2252-5211.1000263

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	Catalysts	Magnets	Metallurgy	Glass/polishing	Phosphors	Others
<b>Light</b>						
Lanthanum	50		33	7	2	8
Cerium	23		16	44	2	16
Praseodymium		70	3	2	14	10
Neodymium	2	89	2	1	0	5
Samarium		96			0	4
<b>Heavy</b>						
Europium					80	20
Gadolinium		48	14		17	20
Terbium		22			48	30
Dysprosium		98				2
Holmium					100	
Erbium						4
Tm				96	100	
Yb					100	
Lu					47	53
Yttrium					44	56

Table 1: Global applications of rare earth elements [4].

we can say Samarium, Neodymium, Praseodymium, Gadolinium and Dysprosium which are the most used in the manufacture of permanent magnets

Neodymium is one of the most abundant elements in WEEE. As shown in Figure 1, it is present in high quantity in different electronic devices. (Loudspeakers, HDD, LCDs, Tablets computers, etc...).

As shown by Figure 1, the magnets can be found in different electronic devices with different concentrations of Neodymium (Nd). For example: computer contains in average 5.03 mg Nd: 2.4 mg in HDD, 771 mg in CD-ROM and 310 mg in Loudspeakers; Laptop (4.45 mg Nd):1121 mg in HDD, 621 mg in CD-ROM and 626 mg in Loudspeakers; Tablet computer (347 mg Nd); Mobile-phone (46.4 mg Nd); Smartphone (120 mg Nd); Earphones (260 mg Nd) and LCD (3650 mg Nd).

Since the development of powerful magnets (Nd-Fe-B) in 1980, the volume production of Neodymium has increased dramatically. This development permitted to improve significantly the performance of small engines and to reduce the bulk and weight of portable electronic devices. As example, utilisation of miniaturized engines in mobile phones on the basis of small Nd-Fe-B type magnets for their vibration functions. These magnets are also very widely used in the computer HDD where they contribute to the engine, which ensures the positioning of the read/write heads. They allow improve significantly the performance of this storage device and contribute to the reduction of the computer size. If the increase in the prices of rare earths elements has been relatively constant over the last decade, the technological revolution of developed countries made appear of the deficits of supply and the tensions that have resulted in a surge in prices since January 2010.

Despite the fact that the hard disk for computer market is doomed to continue its regression by 2017 (Figure 2), in general, the opportunities have been identified for hard disk drives. According to the literature, an overall increase of 11% by 2016 is expected on the market of hard disks (Figure 3).

China is a larger producer of magnets in the world. In 2010, China and Japan produce about 50 Gg (50 000 t) and more than 10 Gg (10 000 t) of Nd-Fe-B type magnets respectively (Figure 4A). However, the production of magnet in Europe and USA is lower than 14 000 t and 2 000 t, respectively (Figure 4B).

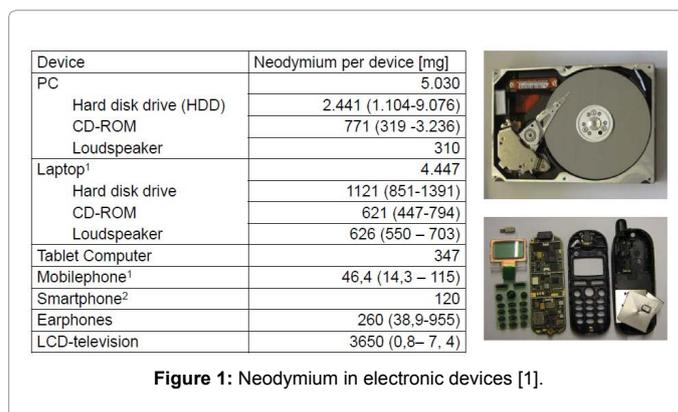


Figure 1: Neodymium in electronic devices [1].

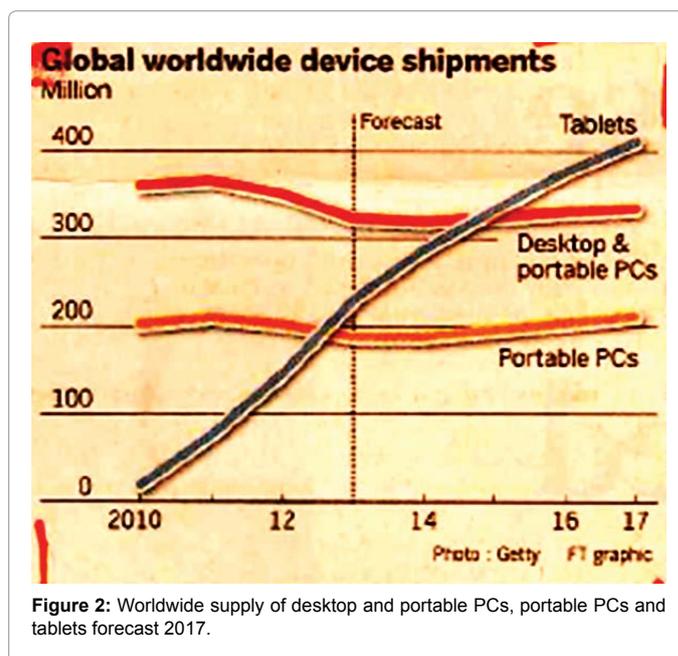


Figure 2: Worldwide supply of desktop and portable PCs, portable PCs and tablets forecast 2017.

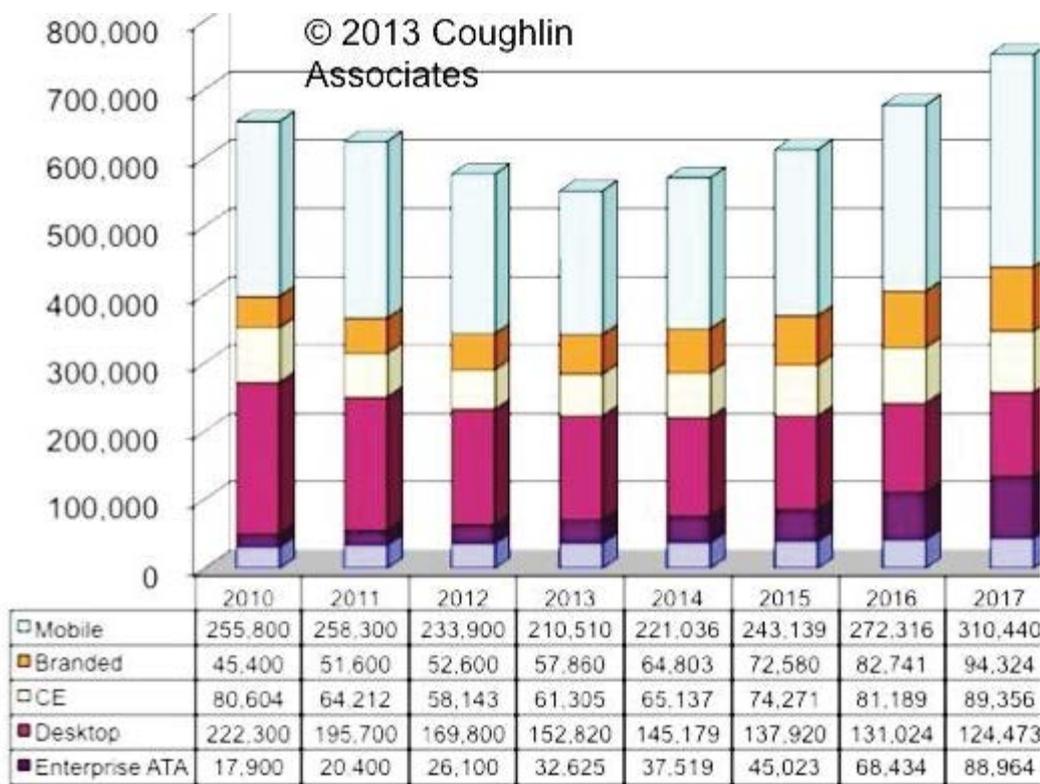


Figure 3: Evolution of the global market of hard disks - forecasts 2017 [2].

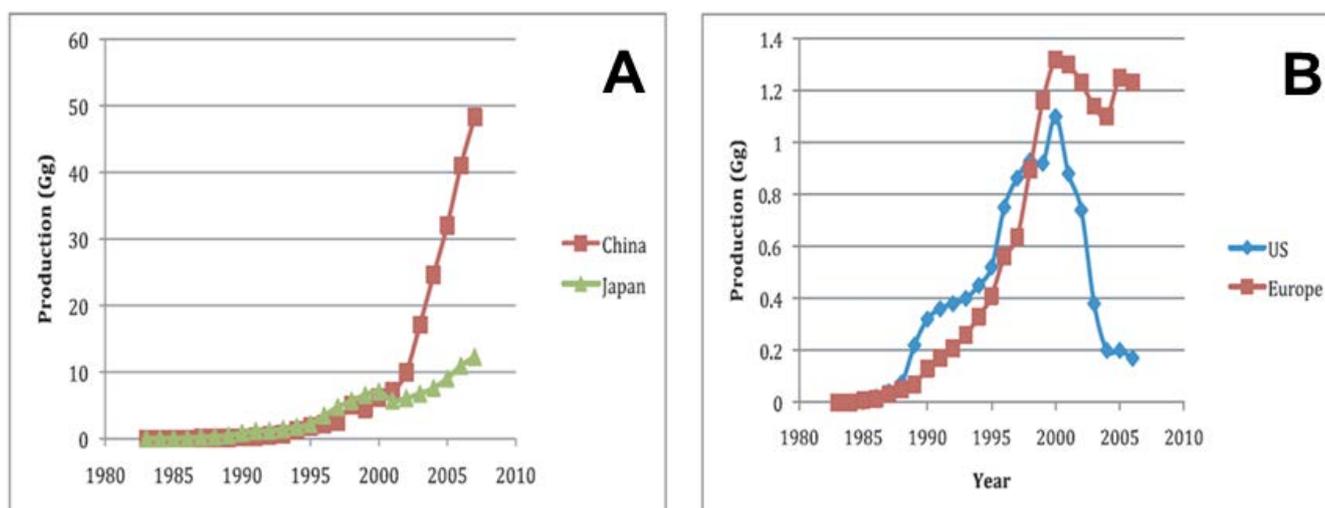
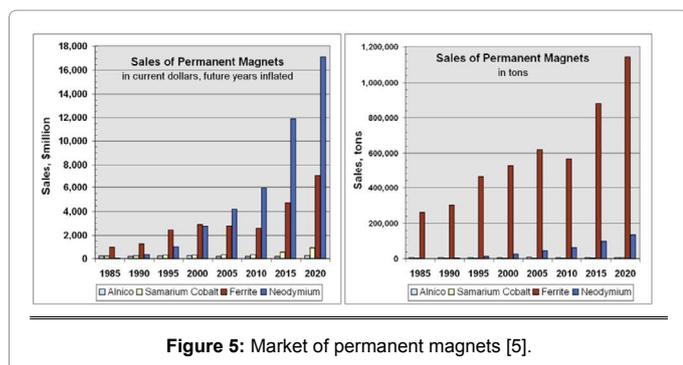


Figure 4: Production of NdFeB magnets in China and Japan (A), USA and Europe (B) [3].

In 2012, the global demand of REEs for the manufacturing of permanent magnets is estimated around 25 500 t, approximately 21% of the worldwide demand which is about 120, 000t [4]. The demand for the magnets is very rapid increases (>150%) from 2000 to 2007 before decreasing to about 1/3 during the financial crisis between 2008 and 2009. The permanent magnets represent a very important market for REEs with a rapid increase in 2014. About 27 Ktons of rare earth oxides (REOs) have been consumed for the production of magnets representing 22% of total consumption.

As shown in light blue bar in the charts (Figure 5) the sales of neodymium-iron-boron (Neo) magnets are increasing exponentially. Sales of all permanent magnets were about \$8 billion in 2005 and NeO alone will be sold over \$17 billion in 2020 [5].

The NdFeB type magnets are the most commercialized in 2015. China is the country that consumes most REOs for magnet manufacturing. According to Roskill, the global application of NdFeB magnets is expected to increase on average about 9% per year by 2020:



6-8% per year by 2016 with acceleration from 2016 [6]. Demand will be driven by three sectors:

1. ICT: hard drives, mobile phone, DVD, etc. that contain low amounts of NdFeB magnets but are produced by mass (14 000t of magnets would have sold in 2012);
2. Electric motors (between 60 g and 350 g of NdFeB magnets by engine) in Asia primarily and hybrid and electric cars (approximately 2 kg of magnets per vehicle);
3. Wind turbines: current wind turbines use close to 600 kg of magnets per MW (direct drive), which corresponds to 155 Kg of neodymium and praseodymium Kg 27.5 per MW. The new generation of wind turbines will require much less reported power (165-250 kg of magnet/MW). However, the power of wind turbines to increase the size of the magnets will continue to grow and consequently the demand for rare earths. Some authors announce the figures of 2.3 tons of neodymium and 400 Kg of praseodymium by wind for 10 to 15 MW of power [7].

The majority of the rare earth type magnet is manufactured in China (80%), 17% in the Japan and 3% in Europe. According to Contantinides [8], the change in the use of the magnet predicts a necessary increase of dysprosium by 80% between 2010 and 2015, while the requirement for neodymium will increase much less to approximately 54%.

## Material and Methods

Three samples of hard disks drive (HDD), electric motors and loudspeakers were characterised in this work. More attention is given to HDD. After collection, the electronic devices containing magnets were subjected to sampling shown in Figure 6. The working of specimen samples that can be defined as samples made without special precautions for HDD, the loudspeakers and electronic motors in the small electronic appliances were collected from various industrial plants. The characterisation of these specimens allowed us to define the minimum masses to be taken to ensure the representativeness of the samples and analyses. As noted, the magnets in these electronic products are very heterogeneous. One tonne of each product containing these magnets is required to perform the tests at the laboratory and pilot scales.

## Results

The representative samples of electronic components collected from industrial plant were sampled again for characterisation. As shown in Figure 7, the bag containing Laptop HDD contains about 70% of Laptop HDD and 30% computer HDD. However, the bag containing computer HDD consists of 98% of computer HDD and 2% others non-identified components.



Two samples from hard drives of computers and laptop (Figure 7) representing about 500 HDD were dismantled manually to recover the contained magnets. These magnets are then heated up to 300°C between 15 and 20 min to demagnetize them. Each HDD is referenced by brand name, the year and the memory content volume. The samples are dismantled manually and all parts are weighted and the weight percent of the magnets contained each HDD is calculated. Furthermore, the recovered permanent magnets are characterised by Scanning Electron Microscopy (SEM) and chemical analyses.

A hundreds of loudspeakers and a few tens of small electric motors were collected from representative professional equipment (Figure 8). The characterization procedure performed is the same as that used for HDD. To determine the temperature at which the magnet loses its magnetic properties, the test of TG/DTA was carried out on the permanent magnet recovered from electronic devices. X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were carried out on the investigated samples of permanent magnets. SEM analysis permits to identify the morphology aspects and to determine the chemical composition contained of permanent magnets.

## Discussion

The results obtained from characterisation of computer HDD show that magnet represents about 3 Wt%, aluminium 80 Wt%, PCB 7 Wt%, plastics 1 Wt%, iron 8 Wt% and 1 Wt% others (ceramics, etc...) (Figure 9).

After dismantling of components containing rare earth type permanent magnets, the total fraction of electronic components containing permanent magnets was determined by weighing of all components and the only magnets were taking into account for the determination of an average concentration of magnet in each type of components. It can be seen from Figure 10, for central unit, the Wt% of magnet is varied from 1 Wt% to 6 Wt% in average 3 Wt%. However, for laptop, the Wt% of magnet is varied from 1 to 4 Wt% in average 2.5 Wt%. Table 2 gives the weight percentages of magnets contained in other electronic components such as loudspeakers (4-6 Wt%) and electric motors (22-26 Wt% or 0.8-2 Wt%).

The results obtained from TGA are shown in Figure 11. This figure shows the thermal behaviour of permanent magnets of HDD and loudspeakers in the temperature range of 50 to 500°C. 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

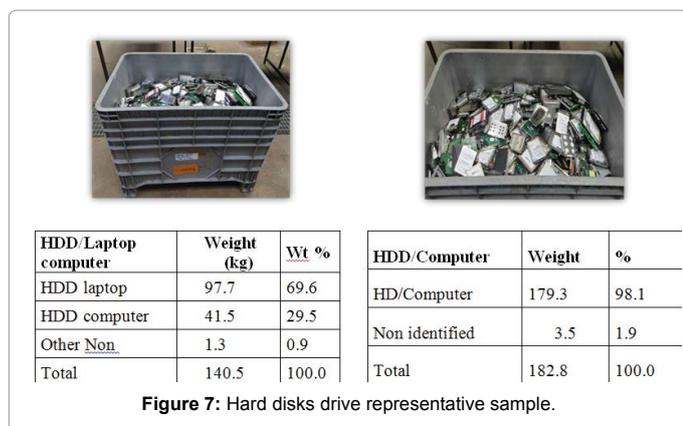


Figure 7: Hard disks drive representative sample.

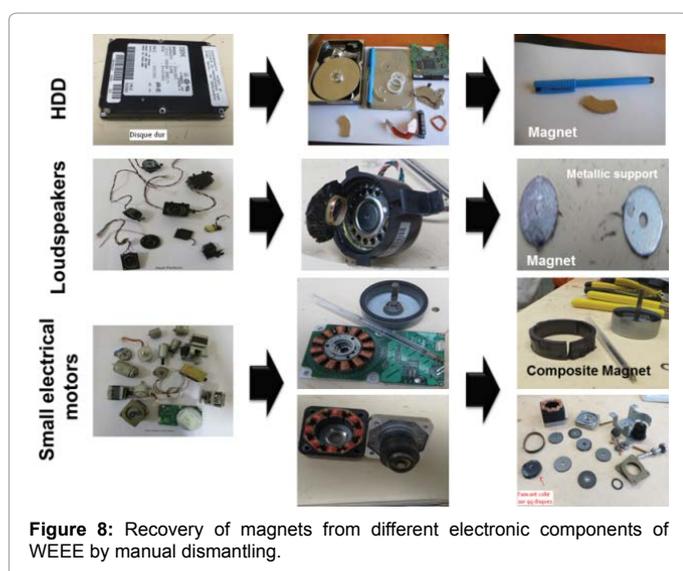


Figure 8: Recovery of magnets from different electronic components of WEEE by manual dismantling.

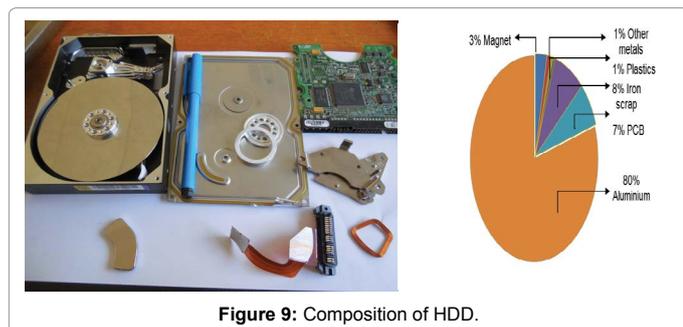


Figure 9: Composition of HDD.

second one at 297°C. This last temperature 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.

The collected samples of loudspeakers and electronic motors are heterogeneous in point of view of type of magnets contained. To select those interested samples, X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were carried. Figure 12 shows the XRD patterns of loudspeakers and electric motors. From this figure, it can be seen that not all permanent magnets present in the collected samples of electronic devices contain NdFeB type magnet.

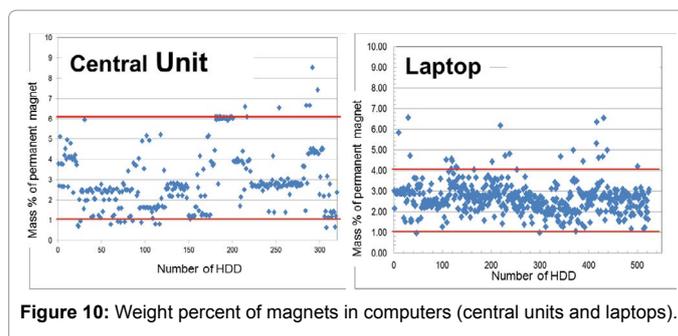


Figure 10: Weight percent of magnets in computers (central units and laptops).

Sources	Weight % of magnet in average
Computer loudspeakers	4–6
HDD from central unit computer	2,5-2,8
HDD from Laptop	02-Mar
Small electric motors (A)	22–26
Small electric motors (B)	0,8–2

Table 2: Weight percent of magnet in different electronic components.

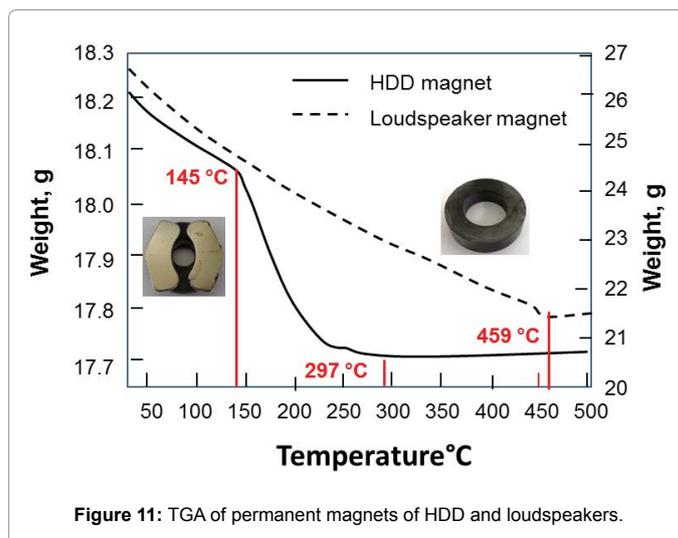


Figure 11: TGA of permanent magnets of HDD and loudspeakers.

To understand the morphology, the texture and the composition of the Nd-Fe-B magnets covered by this study, a characterization by Scanning Electronic Microscopy (SEM) was conducted. The texture of these magnets consists of sintered crystals of Nd<sub>2</sub>Fe<sub>14</sub>B phase tetrahedral shape and a rich rare earth (Nd, Dy, Pr) as shown by EDS analysis in Figure 13.

Figure 14 shows the Ni or Zn protective coating of magnet consisting in a layer of approximately 20 μm thick. The morphology aspect of the magnet under coating observed from a polished section that characterized by the small size of tetrahedral grains. Some of them are filled with a mixture of rare earths and other almost nonexistent because of a sintering performance (Figure 13). The analysis conducted by EDS (Energy Dispersive Spectroscopy) on the magnet constituents is similar to that obtained theoretically by calculation from the formula Nd<sub>2</sub>Fe<sub>14</sub>B (Table 3) The analysis performed on tetrahedral grains confirms their composition of Fe, Nd and Pr and the composition of inter-granular phase which is rich in rare earth (Nd, Pr, Dy).

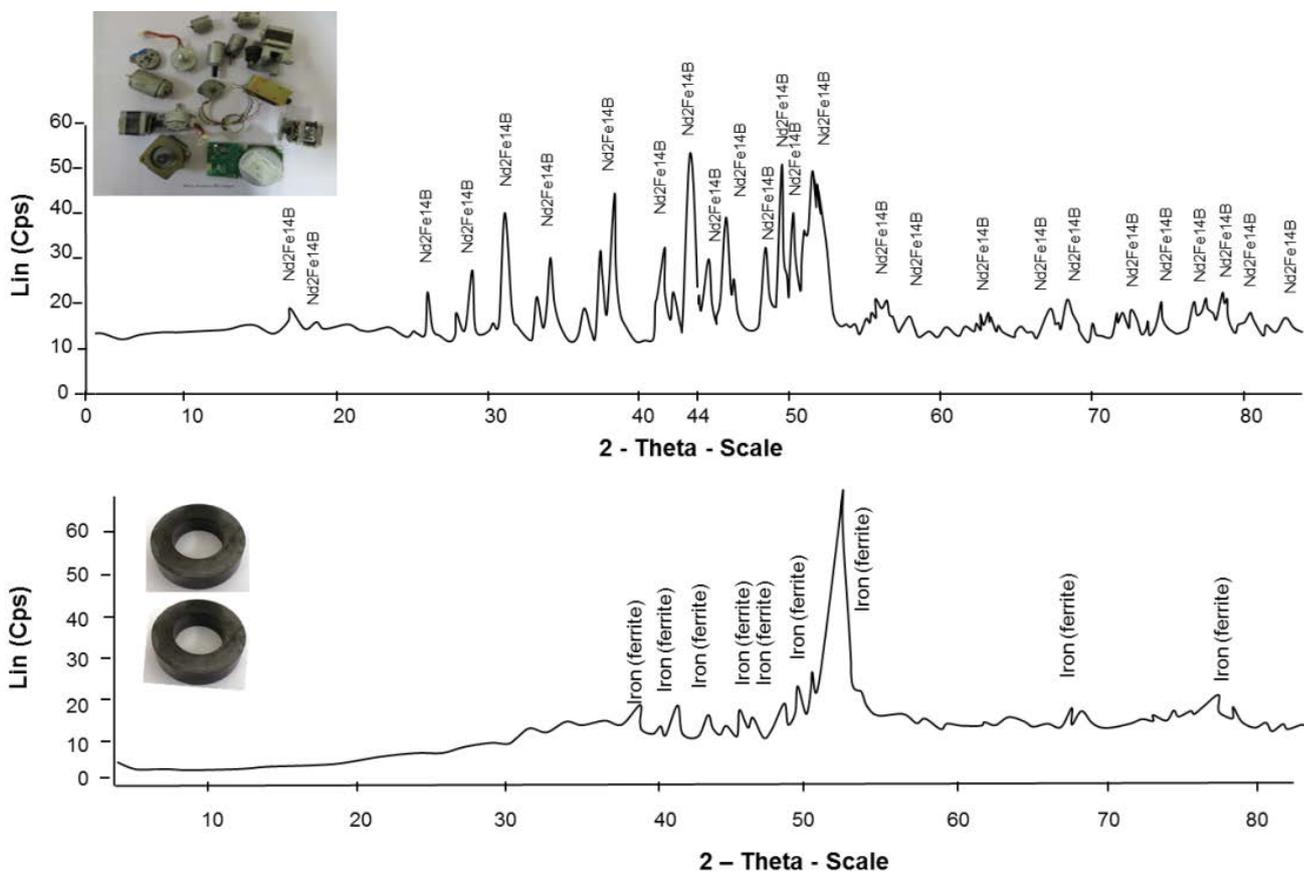


Figure 12: XRD patterns of loudspeaker and small electric motor magnets.

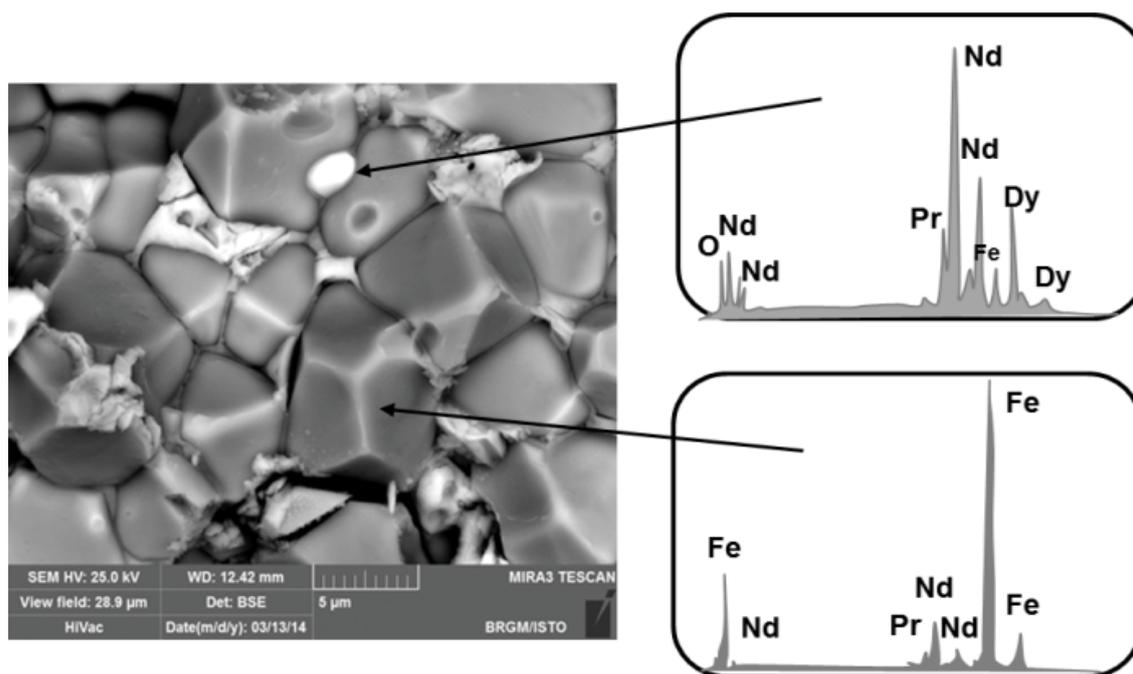


Figure 13: Morphological aspects and EDS of HDD magnet.

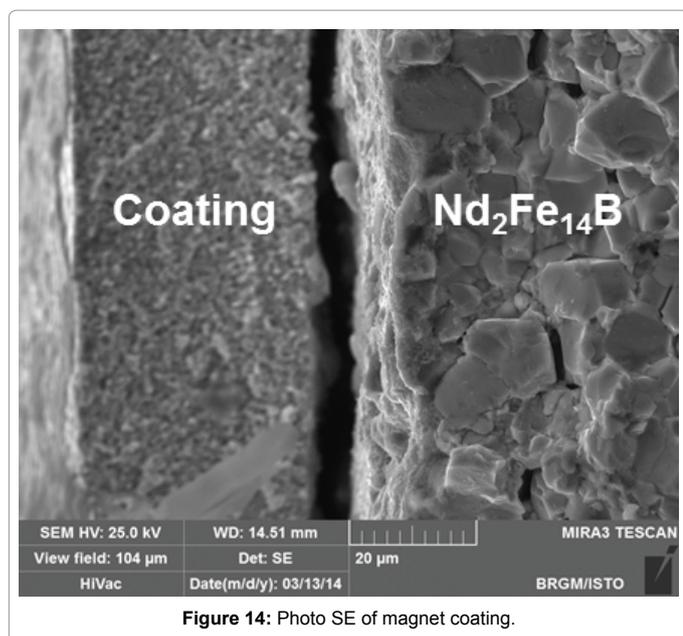


Figure 14: Photo SE of magnet coating.

The elementary maps made by EDS on a polished section of a HDD magnet are presented in Figure 15. These maps indicate, as expected, the presence of two phases which are respectively the predominant  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy (red phase, 91%) and REEs enriched (inter-granular phase (blue phase, 9%). The oxygen is predominantly present in the inter-granular areas in association with Pr and Dy. Nd and Fe are predominantly present in tetrahedral phase grain Nd-Fe-B.

The permanent magnets that we are looking for contained Nd-Fe-B doped with Dy and Pr, and the chemical composition is shown in Table 3.

### Conclusion

1. Identification has been done on deposits of the Nd-Fe-B magnets present in WEEE, and focusing on hard drives, small electric motors and speakers, we take into account 98% of the magnet field receivable in the small electronic appliances feed. The rest of the present magnets in this stream are disseminated in other equipment such as phones fixed, mobile, internet boxes...more difficult to recover.
2. Two sampling campaigns were conducted on two different sites of industrial plant to collect a representative sample of hard drives and loudspeakers.
3. The characterization study shows that the weight percent of magnets varies in the three investigated targets: 4-6% in the loudspeakers, 2.5-2.8% in the hard disks of station unit of computers, 2-3% in the laptops, and between 0.8 and 2% in small electric motors.
4. Scanning electron microscopy (SEM) shows that the magnets containing rare earth elements present in WEEE consist of Nd-Fe-B alloy in a tetrahedral form with an inter-granular space rich in REEs (Nd, Dy and Pr). About 20 µm thick coating layer consisting of Ni, Zn or an alloy of Cu/Ni is detected at the surface of the magnets.
5. According to the XRD, the permanent magnets present in WEEE contain not only REEs, but also ferrites.
6. The Curie point temperature at which the magnets lose their magnetic properties was determined by TGA for different

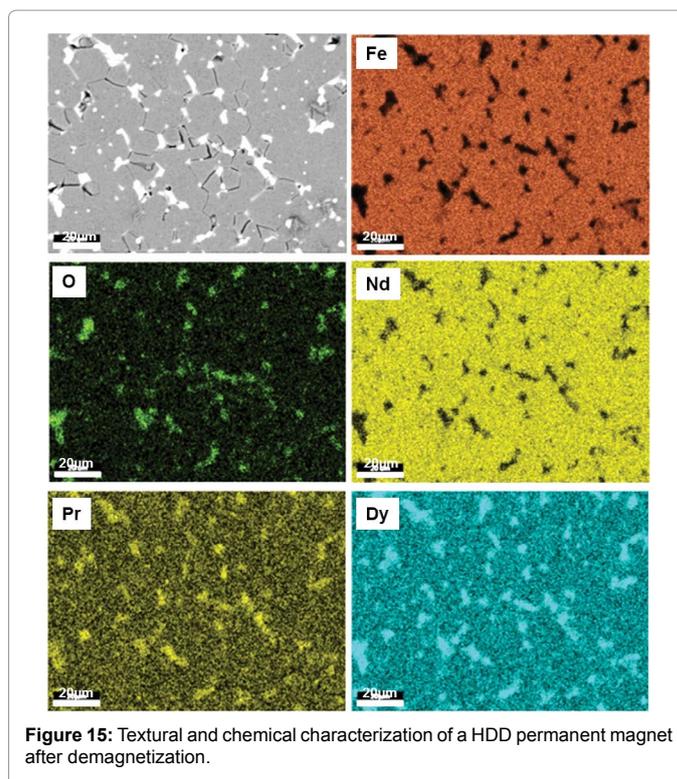


Figure 15: Textural and chemical characterization of a HDD permanent magnet after demagnetization.

$\text{Nd}_2\text{Fe}_{14}\text{B}$ magnet	Fe	Nd	Dy	Pr	Ni	B	Total
Analysed (EDS)	64.4	24.1	1.4	4.0	1.0	1.1	96.0
Calculated	72.0	27.0	ND	ND	ND	1.0	98.0

Table 3: Chemical composition of magnet from computer hard disks, %.

investigated samples of magnets. The results show that the working temperature of Nd-Fe-B type magnet is around 150°C while Curie point is about 300°C. However the ferrite magnets lose its magnet property at about 500°C.

### Acknowledgement

This work presented herein was performed in the frame of contract N° ANR-13-ECOTS-0006-01. The authors gratefully acknowledge the financial support of the French National Research Agency which has made this collaboration possible, Team 2 and other partners of the research project for samples and discussions: Galloo, GPM Rouen, Eco-systèmes, Selfrac and Cyclamen. The authors also thank the reviewers for their constructive comments.

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