

# Spent NiMH batteries: Characterization and metal recovery through mechanical processing

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Received 17 January 2006; received in revised form 24 February 2006; accepted 27 February 2006

Available online 18 April 2006

## Abstract

The growing concern about the environment, associated with the continuous increase in the production of electronic equipment, such as computers, cell phones, mobile devices and consequently batteries, has induced research to develop new technologies to recycle the huge numbers of spent batteries generated in the last few years. The amount of spent NiMH batteries will tend to grow continually over the next few years. These batteries have in their chemical composition, valuable metals such as Ni, Co and rare earths. In the first stage of this work a characterization of NiMH batteries was done. Batteries from different brands and models were dissembled and their components were characterized in relation to their chemical composition and main phases. In a second stage of this work, a sample of spent NiMH batteries was milled and the polymeric and metallic fractions were magnetically separated. The results obtained demonstrate that the recycling study, aimed at the recovery of Ni, Co and rare earths, is viable due to the great amount of these metals that are present batteries. It also demonstrates that magnetic separation is a very efficient process to recovery nickel alloys. However the effects of cadmium contamination (originating from fake batteries) will cause the recycling processes to be re-evaluated.

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**Keywords:** Recycling; NiMH batteries; Characterization; Mechanical processing

## 1. Introduction

In the last few years, the production of electronic equipment such as computers, cell phones and consequently batteries, has increased dramatically. Rapid technological development has reduced the useful life of the electronic equipment in each new generation. For instance in 1997 a computer was utilized from 4 to 6 years, on average; for 2006 the expectation is only 2 years. In 1998 there were more than 364 million of personal computers in use around the world, against 222 millions in 1995 and 98 millions in 1990 [1]. Concerning battery consumption, it was estimated that 3 billion batteries are commercialized per year only in the USA, which represents an amount of US

\$2.5 billions. In Europe 5 billion batteries were produced in 2000 [2].

Nowadays another important factor in relation to the amount of spent batteries is that the consumers change their cell phones often before their useful life finishes. It happens due to the continued introduction of new technologies. Each new cell phone generation presents advantages in weight and size reduction, with different accessories as radios, cameras, etc. Thus very large numbers of batteries are discharged before their useful life ends.

In 1992 NiCd batteries were responsible for almost 100% of the world market of portable rechargeable batteries, but in 1999 they represented only 49%. In this same period NiMH batteries, which had an insignificant participation in the market in 1992, already represented around 43% of the world market [3]. The NiCd batteries substitution happened because the NiMH batteries present a better performance, e.g., larger energy density and an absence of memory effect. Another important factor for the substitution of the NiCd batteries is due to Cd toxicity [4].

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The NiMH batteries are considered environmental acceptable and can substitute for the NiCd batteries in many applications. However they present a higher production cost than NiCd batteries [2].

The NiMH operation system is based on the NiCd system, where the Cd electrode is substituted by the MH (metal hydride). The typical examples of MH alloys are  $AB_2$ , that is basically an alloy of  $TiNi_2$ , and  $AB_5$ , that is basically a  $LaNi_5$  alloy [5]. For economic reasons, La is substituted many times by a rare earth alloy [6].

Besides the great number of batteries that are nowadays generated, there is a tendency for an increasing use of batteries every year. An example of this tendency is vehicles powered by electricity, which do not generate atmospheric emissions. The success of implementation of these vehicles will depend on the correct choice of the energy, and NiMH batteries are considered a promising storage alternative [7–9]. In November 2005, the Amberjarc Projects, an UK company, launched a new range of large capacity Prismatic Nickel Metal Hydride cells into the European market. The company also offers these cells in fully integrated battery systems to suit the customers' specifications, particularly for electric vehicles and hybrids [10].

Recently Li-ion batteries, due to their higher energy density, are substituting for NiMH in some applications. This increases even more the amount of disposed NiMH batteries. As the Li-ion batteries present a higher cost, the other types of batteries, especially the NiMH, are still a very attractive alternative.

Thus, the recycling of the metal present in the NiMH batteries should be studied, avoiding the disposal of tons of dangerous waste [11]. This fact, associated to the economical value of metals such as nickel, cobalt and rare earths, requires that efficient recycling processes are found. Therefore, the recycling of this kind of waste, besides bringing profit in environmental terms, can also bring benefits in economical terms.

This work consisted of two stages. The purpose of the first stage was to characterize NiMH batteries, aiming to quantify the metals content, the possible contaminants as well as to estimate the variation in the chemical composition that a group composed of different batteries from different brands and models can present. In a previous work the characterization was accomplished using a batch composed of just one model of battery [12]. The use of different brands and models of batteries will give results closer to that found in real situations.

The second stage consisted of the application of different mechanical processing techniques (e.g., grinding and magnetic separation), aiming to evaluate the efficiency of the separation of different materials that comprise NiMH batteries. The data obtained in this work are important to evaluate the most efficient technique for the recovery of valuable metals present in this type of battery.

## 2. Experimental

### 2.1. Battery characterization

To quantify the different materials present in the NiMH batteries, five cell phone batteries from different brands and models

were selected. They were manually opened and their different components were separated, classified and weighted.

The cells present inside the batteries were opened with the aid of tools such as saws and pliers and their components were also classified and weighted. The qualitative and semi-quantitative chemical analyses of several metallic components and paste were accomplished by X-ray fluorescence (XRF). The paste had its crystalline phases identified by X-ray diffraction in the interval of  $5^\circ < 2\theta < 80^\circ$ . In the positive electrodes of the prismatic batteries, the paste was inside a highly porous metallic screen. In this case it was not possible to separate the screen from the paste. So the paste was crushed together with the screen and the resulting powder was then characterized.

### 2.2. Mechanical processing

Fig. 1 shows the different steps used in the mechanical processing where 50 NiMH batteries were utilized. These batteries were the same brand and model of battery 3 utilized in the characterization step, despite some small model variation being observed. The following sequence of operations were performed: hammer milling; a first magnetic separation to release the metallic fraction (accumulators) from the polymeric fraction; knife milling of the accumulators to separate the metallic cases and screen from paste and separators; a second magnetic separation of the Ni-containing parts of the accumulators; finally, a last magnetic separation to release the strong magnetic material (metallic cases and screen) from weak magnetic material (powder, containing the material from positive and negative electrodes).

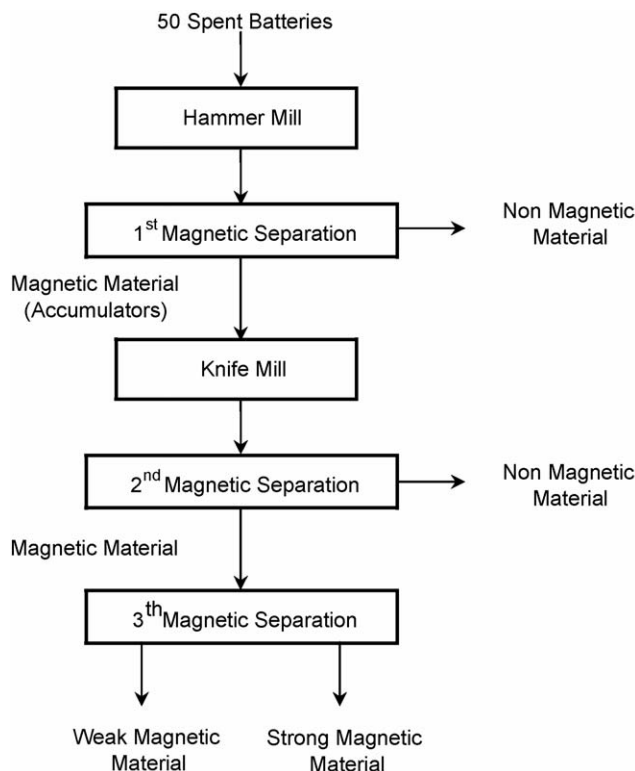


Fig. 1. Flow chart to the Ni alloys recovery by mechanical processing.

### 3. Results and discussion

#### 3.1. Batteries characterization

##### 3.1.1. Characterization through manual opening

In the batteries characterization the components were manually separated and classified as: accumulators, polymers and metals (electronic circuits and contacts). The average results showed that the accumulators represent 81.5%, polymers 17.3% and metals 1.2% of the total weight. Among the five kinds of selected batteries, three presented prismatic accumulators denominated batteries 1–3; two presented cylindrical accumulators, denominated batteries 4 and 5. A similar procedure was used in a previous work however the sample that was previously characterized was basically composed of just one type of battery with cylindrical accumulators [12].

The prismatic accumulators consist of an external case containing the positive and negative electrodes as well as the separators. The negative electrode of the prismatic accumulators (batteries 1–3) consists of a plate symmetrically perforated and covered by a dark paste. The positive electrode of the prismatic accumulators is a very fine metallic screen impregnated also by a dark paste. The cylindrical accumulators (batteries 4 and 5) are comprised of three coiled layers in the form of a bobbin. The first layer consists of a plate symmetrically perforated and covered with a dark paste (the negative electrode). The second layer comprises a separator and the third layer consists of a dark paste (the positive electrode).

Table 1 shows the results obtained in the accumulators characterization. These results indicate that the electrodes are responsible for more than 50 wt.% of the accumulators for all batteries and for batteries 4 and 5, they represent around 70 wt.% of them.

For all batteries it was possible to separate the perforated plates from the paste in the negative electrodes and the results are presented separately. The paste that constitutes the positive electrode of the batteries with cylindrical accumulators was also easily removed from the separator. As to the positive electrodes of the batteries with prismatic accumulators, these being a very fine metallic screen impregnated by the dark paste, it was not possible to accomplish the separation of the components. That is why the results are presented combined. It was also observed that the number of accumulators varies from five accumulators to the batteries 1, 3 and 5, to four for the battery 2 and to three for the battery 4.

##### 3.1.2. Characterization of the metal composition

Aiming at the characterization of the chemical composition of several metallic components present in the batteries, qualitative and semi-quantitative analyses were done by X-ray fluorescence. Fig. 2 presents the results obtained from the external case characterization. It shows that these cases are constituted basically of a Ni–Fe alloy. The chemical analysis also demonstrated that, besides Ni and Fe, other chemical elements are present, mainly in the cases of the batteries 1 and 3. They are possibly related to the presence of substances from the electrolyte, glues and other contaminants, that adhered to the case surface, since the external cases did not suffer any treatment before the charac-

Table 1  
Main components present in the accumulators

Material	Weight (g)	wt. %
Accumulators from battery 1		
External case	32.63	37.00
Polymers	2.78	3.16
Metallic contacts	0.42	0.48
Negative electrodes		
Perforeted plates	4.75	5.38
Paste	22.15	25.11
Positive electrodes		
Paste and metallic screen	20.90	23.70
Accumulators from battery 2		
External case	26.70	38.55
Polymers	1.69	2.44
Metallic contacts	0.72	1.05
Negative electrodes		
Perforeted plates	2.27	3.28
Paste	18.82	27.17
Positive electrodes		
Paste and metallic screen	18.26	26.36
Accumulators from battery 3		
External case	24.28	29.19
Polymers	5.37	6.46
Metallic contacts	2.20	2.65
Negative electrodes		
Perforeted plates	3.92	4.71
Paste	21.16	25.44
Positive electrodes		
Paste and metallic screen	25.57	30.74
Accumulators from battery 4		
External case	11.04	19.82
Polymers	4.83	8.66
Metallic contacts	0.00	0.00
Negative electrodes		
Perforeted plates	3.64	6.53
Paste	16.30	29.27
Positive electrodes		
Paste	18.28	32.82
Accumulators from battery 5		
External case	28.30	20.44
Polymers	12.42	8.97
Metallic contacts	0.00	0.00
Negative electrodes		
Perforeted plates	20.06	14.49
Paste	20.26	14.63
Positive electrodes		
Paste	55.23	39.89

terization. By the analysis of these results it is possible to infer the chemical composition of the external case and the amount of contaminants, which is an important factor in the definition of a recycling process.

Fig. 3 presents the results obtained by the characterization of the perforated plates from the negative electrode. It can be observed that these plates are also basically a Ni–Fe alloy. The presence of different elements such as Ce, La, Mn, S, etc., was observed and denominated as “others”. The presence of these

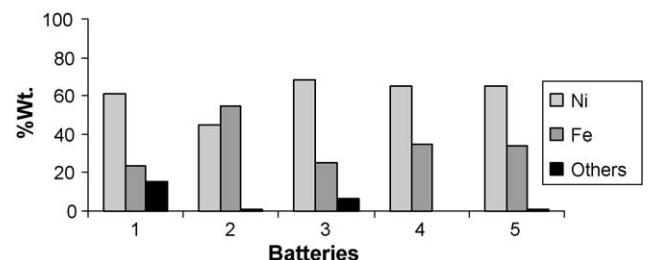


Fig. 2. Main constituents of the accumulators external cases.

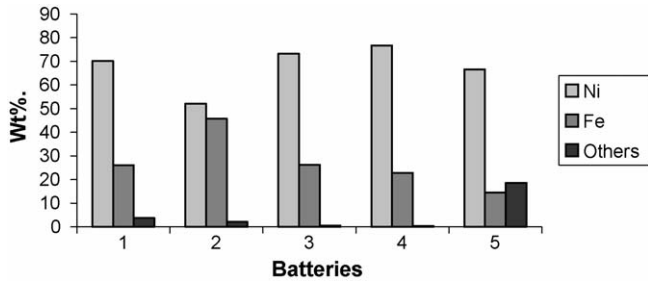


Fig. 3. Main constituents of the perforated plates from the negative electrodes.

elements is related to the contamination of the plates by the electrolyte and the paste that covered the plates, because the plates also did not suffer any other treatment.

The qualitative and semi-quantitative results obtained by the characterization of the pastes from negative electrodes, as well as those obtained for the paste and screen from positive electrodes, are presented in Table 2. The chemical analyses of the negative electrodes of batteries 1–4 show a high concentration of rare earths, Ni and Co, metals that compose the AB<sub>5</sub> alloy. In this alloy A represents La, Mn [13] or a rare earth alloy and B represents Ni, Co and Al [14]. In the negative electrodes, the absence of Ni was observed in batteries 1 and 3. In battery 2 a high concentration of La was observed and an absence of Ce and Nd. In this battery the concentration of Pr was higher than in the other batteries and the Mn concentration was lower than in the other batteries. Related to the positive electrodes from batteries 1 to 4, the main constituents were Ni, Co and Zn.

The most surprising result was observed for battery 5. Despite this battery being labeled a NiMH battery, the chemical characterization showed that in reality this battery was NiCd. Table 2 shows the high concentration of Cd and Ni in battery 5. This fact complicates the recycling of NiMH batteries because is not possible to characterize all batteries before sending them to the recycling process. Therefore an efficient recycling process should foresee the possible presence of NiCd batteries together with the NiMH ones, even if only batteries labeled as NiMH are selected.

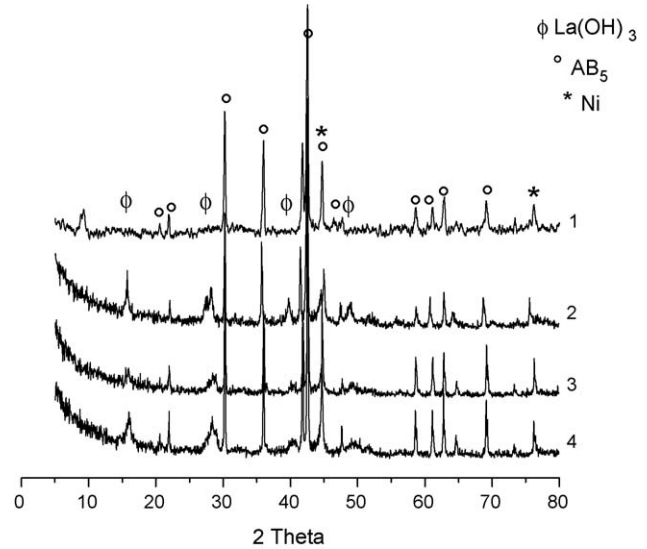


Fig. 4. X-ray diffraction pattern obtained from the negative electrode.

### 3.1.3. Characterization by X-ray diffraction

The X-ray diffraction analyses of the paste from the negative electrode and of the paste mixed with the metallic screen from the positive electrode are shown in Figs. 4 and 5, respectively. The phases observed are very similar for the different batteries. The analysis revealed that the main phase of the negative electrode has a hexagonal structure type CaCu<sub>5</sub> [15,16], being this phase related to the AB<sub>5</sub> alloy. Ni and La(OH)<sub>3</sub> were also observed. For the positive electrode, the presence of Ni(OH)<sub>2</sub> was observed followed by Ni and NiO. The X-ray diffraction test for the electrodes of the battery 5 was not accomplished because this was a NiCd battery.

### 3.2. Mechanical processing

The initial weight of the 50 batteries was 6040.40 g. This material was firstly processed in a hammer mill and then was sent to the first magnetic separation step. This separation resulted in

Table 2  
Chemical analysis of the electrodes (wt.%)

Metals	Negative electrodes					Positive electrodes				
	Battery 1	Battery 2	Battery 3	Battery 4	Battery 5	Battery 1	Battery 2	Battery 3	Battery 4	Battery 5
Ce	24.14	ND	25.04	23.06	ND	ND	ND	0.80	ND	ND
La	16.02	48.67	21.38	20.33	ND	ND	ND	0.84	0.78	ND
Nd	10.57	ND	9.36	9.09	ND	ND	ND	ND	ND	ND
Pr	1.63	4.35	1.14	0.96	ND	ND	ND	ND	ND	ND
Ni	ND	10.75	ND	10.60	34.80	31.28	29.31	32.96	32.56	29.07
Co	25.58	22.67	21.76	20.31	1.56	38.29	34.09	27.38	26.20	13.41
Mn	15.55	2.40	16.23	11.05	0.20	2.91	0.96	1.60	3.12	ND
K	4.58	6.90	2.32	2.14	ND	7.70	11.47	12.45	15.27	3.15
Fe	0.28	3.21	1.14	1.25	1.50	0.73	0.90	0.61	0.57	0.90
Zn	1.16	0.27	1.23	0.66	ND	18.40	21.45	22.30	19.60	0.18
Others	0.47	0.74	0.34	0.53	1.15	0.53	1.66	0.85	1.74	0.28
Cd	ND	ND	ND	ND	60.80	ND	ND	ND	ND	52.75
Total	99.98	99.96	99.94	99.98	100.01	99.84	99.84	99.79	99.84	99.74

ND, not detected.

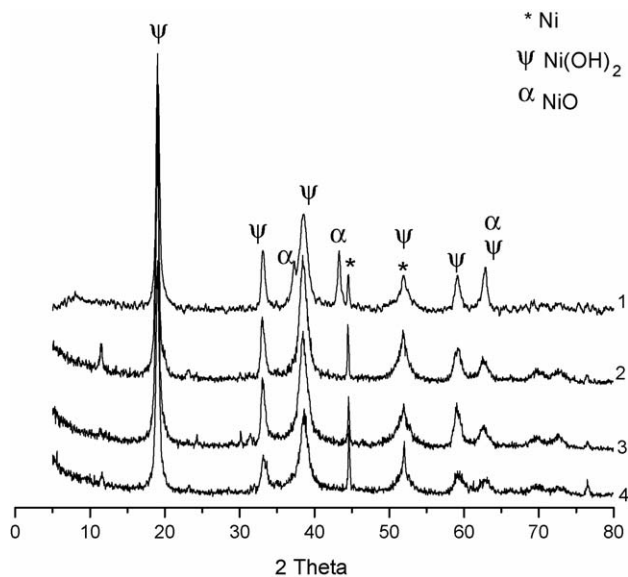


Fig. 5. X-ray diffraction pattern obtained from the positive electrode.

1174.00 g of non magnetic material (polymers and circuits) and 4624.00 g of magnetic material (accumulators). The accumulators, obtained in the first stage of magnetic separation, were sent to a knife mill. After milling, the material was subjected to a second magnetic step, where 4234.00 g of magnetic material and 97 g of non magnetic material were obtained. The separators comprise this non magnetic material. The separators are made of fabric. Then the obtained magnetic material was submitted to a third step of magnetic separation. In this step it was possible to separate the strongly magnetic material (external case and screen), constituting Ni alloys, from the weakly magnetic material, made up of the powders that form the positive and negative electrodes. In the weak magnetic material the presence of frayed separator was also observed. This happened because some powder was attached to the fabric that constitutes the separators.

The weight of the strongly magnetic material obtained was 1848.79 g, what is equivalent to 30.60% of the initial weight. The weight of the weak magnetic material (powder plus fabric fibers) obtained was 2385.21 g, equivalent to 39.43% of the initial weight. In the different steps of the mechanical processing a loss of 534.4 g took place, which represents almost 9% of the initial weight. In agreement with previous work, the strongly magnetic material is suitable for charging in electric furnaces without any kind of melting or briquetting process [12].

A separation based on particle size difference between the powder and the Ni alloy parts was also accomplished, but it was less effective, since the fabric fibers had a tendency of blocking the sieves, making the process very slow and difficult to handle. An effective separation of the strongly magnetic material was obtained through the variation of the distances between the magnet and the magnetic material. With small distances, both materials, the strongly and the weakly magnetic, were attracted to the magnet, but after a certain distance only the strongly magnetic material was attracted. After this procedure was repeated for two or three times, the separation of all strongly magnetic

material was obtained practically free of powder or of some fabric fiber originating from the separators.

#### 4. Conclusions

The results showed that nickel is present in a great amount in all the metallic parts of the batteries, except for the negative electrodes of batteries 1 and 3. Besides nickel, it was observed that cobalt is also present in appreciable amounts in both electrodes. In the negative electrodes it was observed that rare earth metals are present in large amounts, more than 50 wt.%. The large amount of nickel, cobalt and rare earths present in the batteries and the economic value associated with these metals demonstrates that the development of a recycling process is valuable. However, in the characterization step, the presence of NiCd batteries was identified in a lot where all the selected batteries were labeled as NiMH. This cautions that an efficient recycling process should be prepared to receive a fraction of NiCd batteries. In the case of using a pyrometallurgical recycling process, this should contain a step for the recovery of Cd from the gaseous emissions, assuring that Cd will not be emitted into the environment. The results also demonstrated that the batteries selected for the characterization were of the AB<sub>5</sub> type, because Ti was not found. This element is one of the most important elements present in batteries of the type AB<sub>2</sub>.

Despite of material loss (smaller of 10% of the initial weight), the mechanical processing was shown to be very efficient for the separation of the different materials present in the batteries (polymeric, circuits and metals). This loss happened because in each experimental stage a small amount of material was retained in the equipment. In a process where all equipment will be continually fed by batteries this loss should be drastically reduced. Through mechanical processing it was also possible to separate strongly magnetic material (metallic cases and screen) from weakly magnetic one (powder). The strongly magnetic material was a Ni–Fe alloy. This material could be used, without any previous treatment, as the raw material for secondary ferrous-alloy production. The weakly magnetic material could be send without further purification to the next separation stages.

#### Acknowledgements

The authors wish to thank Capes, CNPq and Fapergs for the financial support to this work.

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