



# Recovery of rare earths and base metals from spent nickel-metal hydride batteries by sequential sulphuric acid leaching and selective precipitations

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## ABSTRACT

This work describes a hydrometallurgical process to recover rare earth and basemetals from spent NiMH batteries. Laboratory tests were conducted by using NiMH powders obtained in an industrial scale grinding process after a preliminary sieving ( $<500\ \mu\text{m}$ ).

The most important metals present in the initial powder were nickel (29% w/w), manganese (13% w/w), zinc (8% w/w) and rare earths (lanthanum and cerium, 5% w/w); other elements were iron (1% w/w), potassium and cobalt (2.5% w/w).

The results obtained showed that two sequential leaching steps were needed to dissolve almost completely lanthanum and cerium present in the samples. In the leaching experiments three parameters were studied and optimized according to a factorial experiment: sulfuric acid concentration, acid citric concentration and temperature. The average dissolution yields after the second leaching step were 100% for manganese, cobalt, zinc and rare earths and 99% for Ni. A total recovery of RE 99% was obtained after selective precipitation.

Rare earths were recovered by selective precipitation with sodium hydroxide at pH less than 2 after leaching: in these conditions a precipitate composed of lanthanum and cerium sulphates are produced.

A suitable flowsheet to recover RE from NiMH spent batteries with recoveries larger than 99% has been proposed.

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## 1. Introduction

Consumption of NiMH batteries, in recent years, increased proportionally with growing production and sale of electronic devices, digital camera, PC and hybrid cars. In 2010 more than 2 million hybrid cars have been sold and are designing more other hybrids and electronic devices that make use of these batteries.

NiMH spent batteries do not represent a very important problem for environment than other batteries such Ni-Cd, because they do not contain extremely hazardous metals like for example cadmium.

The main parts of these NiMH batteries are constituted by a nickel cathode mainly composed of nickel hydroxide, an anode used as hydrogen storage constituted by alloy based on mischmetal (mainly Ce, La, Nd, Pr) and nickel, cobalt, aluminium and manganese including substituent, a separator between the two electrodes made of non woven polyolefin fibers, and finally an electrolyte solution that is typically KOH.

In any case spent batteries are considered dangerous waste and they must be disposed, in Europe, according to new European Directive n.66 of 2006. An inappropriate waste handling can cause harmful substances to the environment and also the presence of heavy metals should be avoid in filtered and in the slags of incineration plants. In addition to ecological risks, no entry of spent batteries in the recycling process involves a loss of metals such as nickel, manganese, zinc but more important are rare earths.

Nowadays China provides 97% of world demand for RE and the authorities decided to reduce exports from 50,000 tons to 30,000 tons and in July 2010 these have been reduced to 8000 tons for the remainder of 2010 [1]. In this scenario the providing of raw material such as RE in the world is becoming much more important especially for European Union and other West Countries.

Many hydrometallurgical processes have been proposed based on metals recovery by selective precipitation or solvent extraction: some research works have been carried out considering a leaching step and a sequential selective precipitation and very often a liquid–liquid extraction has been considered as the most suitable separation process.

Pietrelli et al. [2] utilized a leaching step with sulfuric acid solutions (2 M) at 20 °C for 2 h. After filtration RE were precipitated

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by the leach liquor adding NaOH until pH <1.5. They showed that about 80% of RE contained in spent NiMH batteries can be recovered.

Bertoul et al. [3] carried out a leaching step with sulfuric acid (2 M) at room temperature; after filtration RE were precipitate adding NaOH until pH <1.6. They showed that about 66% of initial material was leached and that the recovery of rare earths, from leached solutions, was around 98%. Also iron, zinc and manganese were precipitated adding NaOH at pH 5–7 and purified solutions of nickel and cobalt were produced and sent to electrowinning stage contained around 99% and 98% of respectively of Ni and Co.

Pingwei et al. [4], utilized a leaching process with hydrochloric solutions (2 M), at 95 °C for 4 h and RE were precipitated with oxalic acid and calcinated after a solvent extraction step with 25% D2EHPA in kerosene (pH = 2) and stripping RE from organic phase with HCl (2 M). After this step oxalic acid was added for RE precipitation. They, also, recovered nickel and cobalt by solvent extraction with 25% TOA in kerosene, stripping cobalt with HCl (0.01 M) and precipitated Co and Ni as oxalates. Total recovery of RE reached around 98%, total yields of Co and Ni were about 98% and 99.9% respectively.

Pingwei et al. [5] studied an other process that involved leaching with sulfuric acid (2 M) at 95 °C for 4 h. RE were precipitated as oxalates after solvent extraction, from leach solutions, with 25% D2EHPA in kerosene (pH = 2.5) and stripping RE from organic phase with sulfuric acid (1 M).

The process, also, involved recovery of Ni and Co by solvent extraction with 25% Cyanex (pH = 4.1), stripping with 0.5 M sulfuric acid and precipitation of Co and Ni as oxalates. Total recovery of RE reached 94%, for each metals was over 96%.

Lyan et al. [6] utilized a leaching step with sulfuric acid (3 M) at 95 °C for 4 h, obtained 5% RE leaching yields. RE were recovered by alkalization with 1 M of NaOH and filtration, acid dissolution of residue with 1 M of HCl. Recovery other metals required solvent extraction with 20% of P<sub>2</sub>O<sub>4</sub> in kerosene to remove RE, Zn and Fe, scrubbing of Co and Ni with 0.5 M of sulfuric acid and stripping of RE with HCl. After solvent extraction was made at pH 4.5 with 20% Cyanex 272 in kerosene to separate Co from Ni followed by concentration and precipitation of spherical nickel hydroxide. Co was stripped with 1 M of sulfuric acid and concentrated with formation CoSO<sub>4</sub>.

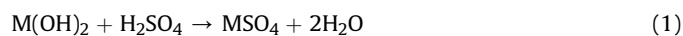
Total recovery of RE reached around 97.8%.

L.E.O.C. Rodrigues et al. [7] utilized two leaching both 8% v/v sulfuric acid and 0% v/v H<sub>2</sub>O<sub>2</sub> at 30 °C for 1 h. The first leaching yields were 80–85% Ni and 95–100% Co, instead the second leaching yields were 87% of RE and 100% of Ni. After leaching and filtration RE were precipitated with NaOH to recover them by leach liquor.

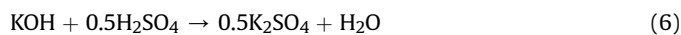
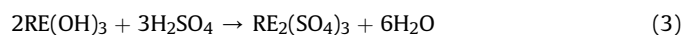
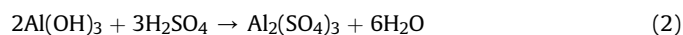
Finally, solvent extraction with 0.5 M D2EHPA (pH = 3) followed by Cyanex 272, >0.6 M (pH = 5.7) could separate cadmium, cobalt and nickel from the leach liquor.

Considering this scenario the present work a possible process for the treatment of the NiMH spent batteries is described consisting in recovery of RE, after two sequential leaching steps and carried out a sequential precipitation with NaOH (5 M).

From the analysis of the cited literature the following chemical reaction can be hypothesized:



Where: M = Ni, Co, Cd, Zn, Mn



Other possible reactions are:



This work approaches the process studied by Rodrigues et al. [7] but it has some differences.

In the cited paper all the initial material was obtained separating plastic and metallic cases by manual procedures. In the present work a powder output of an industrial plant for the physical treatment of spent batteries has been used (spent batteries sorting, shredder and preliminary sieving). Other differences can be found in the leaching conditions and in the final recovery of RE. Aim of the present work was to study the leaching conditions of real black powder obtained by a shredding process of industrial scale. Leaching and selective precipitation has been carried out in order to maximize the separation and recovery of RE and other base metals.

## 2. Experimental

### 2.1. Materials

The black mass of spent batteries was obtained grinding NiMH spent batteries by an industrial shredder and carrying out a preliminary sieving process.

Sulfuric acid (96%) and citric acid (99.5%) were used as leaching reagents and sodium hydroxide (>97%) was used for precipitation.

### 2.2. Experimental procedure

#### 2.2.1. Characterization of NiMH batteries spent powders

Spent NiMH powders (>500 μm; <500 μm) and a sample of powder dried at 105 °C for 24 h, having a size <500 μm, was analyzed by X-ray fluorescence, XRF, (SPECTRO XEPOS).

A quantitative analysis was also carried out by atomic absorption spectrometry, AAS, (VARIAN AA240FS) after chemical attack of the solid samples in order to evaluate percentages of various elements in the powder.

These analyses were made through an acid attack where about 0.5 g of powder was dissolved in 15 ml of aqua regia (6 ml of nitric acid and 9 ml of hydrochloric acid).

At the end of reaction, the solutions were filtered to separate the liquid phase from the solid leaching residue and diluted in 50 ml of distilled water. The different elements were determined by AAS.

#### 2.2.2. Leaching tests

Before carried out leaching tests the powder was washed with distilled water to remove potassium and other soluble products from initial material then a 2<sup>3</sup> full factorial design, with three replications of the central point, was chosen for conducting the leaching tests ('Progettazione e analisi degli esperimenti', Douglas C. Montgomery, Maggio 2005).

The factors investigated were sulfuric acid concentration (low level was 2 M and high level was 4 M), temperature (low level was 40 °C and high level was 80 °C) and citric acid concentration (low level was 0 g l<sup>-1</sup> and high level 30 g l<sup>-1</sup>). Citric acid was used as a suitable reducing agent to promote metal extractions, such as Mn (9). In each tests pulp density of powder was 15%, and the solutions volume was of 50 ml. Table 1 shows the experimental conditions of this full factorial design.

**Table 1**  
Treatments of 2<sup>3</sup> full factorial design.

Test	A, H <sub>2</sub> SO <sub>4</sub> [M]	B, T [°C]	C, citric acid [g l <sup>-1</sup> ]
(1)	2	40	0
a	4	40	0
b	2	80	0
ab	4	80	0
c	2	40	30
ac	4	40	30
bc	2	80	30
abc	4	80	30
I	3	60	15
II	3	60	15
III	3	60	15

The Yate's algorithm was applied to number each test and three replicated central point experiments (I, II, III) were carried out to have an independent estimation of the variance of the experimental error.

Leaching tests were performed in 50 ml closed flasks in a thermostatically water batch (DUBNOFF); during each tests 1 ml of leach liquor after centrifugation was taken after 1.5 h and 3 h to measure the various elements and then each sample was diluted 1:10 by a solution of nitric acid (pH ~2) to avoid precipitation of the metals.

At the end of the leaching step the solutions were filtered and the solid residues were recovered and cakes washed and dried at 105 °C for 24 h; these samples were weighted by an analytic balance before and after drying to estimate the water content in the cakes.

Ni, Mn, Co, Zn, Fe and RE extraction yields at 3 h were investigated by ANOVA: Yate's algorithm was used to evaluate the significance of main and interaction effects of the investigated factors. Significance was assessed by F-test with a confidence level of 95% ( $p < 0.05$ ).

### 2.2.3. Recovery of RE after leaching

From the analysis of the experimental leaching tests (which they are presented in Section 3) it is derived that the RE dissolution yields were about 30–35%; so more than half the mass of rare earths remained in the unleached solids.

It was decided to apply a second leaching step to recover RE both from the leaching solutions and from the unleached solids. So in same tests a sequential leaching condition has been applied in several process conditions.

**2.2.3.1. Recovery RE from leached solutions.** NaOH (5 M) was added in the leached solutions to precipitate RE sulfates (precipitation pH is about 1). The initial pH of the solutions were about 0.6 ÷ 0.8 and NaOH (5 M) was added until reaching pH values between 0.7 ÷ 1.6.

The solid precipitates were collected by filtration, washed by water and dried at 100 °C for 24 h: the solid samples were then characterized by XRF analysis.

**Table 2**  
XRF analysis of the original powder, without drying, separated in two size fractions and XRF analysis of the dried and washed powder (<500 μm). n.a. = not available.

Symbol	Element	Powder asis % (>500 μm)	Powder asis % (<500 μm)	Dried powder asis % (<500 μm)	Powder after washing (<500 μm) %
Cl	Chlorine	0.70	0.64	3.59	0.08
K	Potassium	1.76	2.54	5.73	0.54
Mn	Manganese	6.72	14.27	26.20	19.5
Fe	Iron	1.63	1.10	1.74	1.07
Co	Cobalt	1.83	2.6	5.00	3.60
Ni	Nickel	15.68	11.73	22.71	19.17
Cu	Copper	0.15	0.14	0.17	0.06
Zn	Zinc	4.61	5.30	12.24	8.09
La	Lanthanum	1.97	3.65	5.84	5.34
Ce	Cerium	0.94	1.68	2.59	2.36

**2.2.3.2. Recovery RE from unleached solids: second leaching step by sulfuric acid.** To recover RE from the unleached solid residues of the first leaching reactions a second leaching test was usually applied by using sulfuric acid (1 M) at the room temperature for 1 h.

Leaching tests were conducted at low temperature because in this way solubility of the RE sulfates is higher than the first tests of leaching. Then solutions containing RE<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, were filtered and the residue solids were analyzed by XRF. A purification step adding NaOH has been then carried out on leach liquor to obtain solid RE sulfates.

## 3. Results and discussion

### 3.1. Characterization of batteries powder

Table 2 shows the results of XRF of the original powder with different particle size (>500 μm and <500 μm) and it shows the results of XRF analysis of the dried and washed powder (<500 μm). The sample <500 μm showed a moisture content of around 3% w/w determined by weight loss after drying at 105 °C. From the analysis of these data it was possible to observe that nickel, manganese and zinc were found as predominant metals in the analyzed powder (6.72–26.20% Mn, 4.61–12.24% Ni, 11.73–22.71% Ni). Lanthanum and cerium were also found significant (1.97–5.84% La and 0.94–2.59% Ce). Other rare earths (Pr and Nd) are contained in the NiMH cells but in this work La and Ce were considered as rare earths references.

From the XRF analysis it was observed that the maximum values of metal concentrations were for dried and washed powder (<500 μm). The present of potassium was important (5.73% K for dried powder, <500 μm) and this element was removed by washing with distilled water (0.54% K for washed powder, <500 μm).

These tests also showed that aluminum was present in the powder (<500 μm) with an amount equal to about 3.3%. Results of quantitative analysis by AAS indicated a metal content of about 29%, 13% and 8% of Ni, Mn and Zn, respectively. It was observed that the amount of Mn was higher than the classical composition of NiMH batteries (Mn in treated powder was 10 times higher than traditional composition). This difference of composition could be caused by contamination of other types of cells like alkaline and zinc carbon spent batteries that were not well separated during the manual separation of NiMH spent batteries from other cells before grinding. Other elements should be present in the initial powder, particularly Na and Li, due to the presence of other types of batteries. The electrolyte of alkaline cells is always composed of KOH, NaOH and LiOH mix solution but in this work Na and Li were not analysed due to limitations of the measuring instrument.

Washing step was able to remove KOH and chlorine compounds with efficiency of about 91% for K and 98% for chlorine compounds.

This step can be useful to eliminate any soluble compounds and elements before the leaching step.

Few base metals and RE could remain in the washing water after this step and waste water can be easily treated by coagulation (or Fenton process), process to reduce COD (Chemical Oxygen Demand) in solution. An advantage of this step is to ensure a  $\text{Cl}^-$  remove that can be useful if leach solution should be sent to electrowinning (EW) process and in any case can improve the purity of the final product. Finally this step can guarantee the presence of only  $\text{Na}_2\text{SO}_4$  in the final solution obtained during a necessary neutralization of leach liquor obtained after the leach step. In this manner  $\text{Na}_2\text{SO}_4$  could be recovered and commercialized.

### 3.2. Leaching test results

#### 3.2.1. ANOVA

The sample <500  $\mu\text{m}$  was used for leaching tests according to the experimental plan shown in Table 2. The % extraction yields after 3 h of leaching are shown in Table 3.

The average extraction yields were about 88% for zinc, 33% for cerium and lanthanum, 93% for manganese, 90% for nickel and about 69% for aluminum. The results were elaborated by ANOVA analysis to evaluate the significance of the investigated factors. The statistical analysis showed that no significant effects were found to be important for leaching extraction yields with the exception of the negative interaction AB for cerium (sulfuric acid concentration and temperature) significant at 96% and for Mn dissolution (B – Temperature) with a positive effect. For aluminum three factors were found relevant: A- sulfuric acid concentration, B - Temperature and C citric acid concentration, all with negative effect and significance respectively 96%, 98% and 97%. In conclusion, the dissolution of the metals of interest were not significantly influenced, except for aluminum, by the change of the process conditions selected in the experimental plan whereas it was confirmed that the solubility of cerium sulfates decreases increasing the level of temperature. As reported in previous works [8,9] Mn dissolution is positively influenced by temperature in sulfuric acid leaching in presence or not of reducing agents (i.e. sucrose,  $\text{H}_2\text{O}_2$ ).

The results obtained from ANOVA permitted to highlight that the most suitable conditions for leaching process were: 2 M of sulfuric acid, temperature 80 °C, absence of citric acid and 3 h of leaching time reaction. In this condition the yields were about >94% for nickel and zinc, 65% for aluminum, 100% for manganese and 35% for lanthanum and cerium.

**Table 3**  
% Extraction in the leaching tests.

Test	% Extraction						
	Element						
	Ni	Mn	Zn	La	Ce	Al	Co
(1)	100.31	86.56	86.00	49.25	47.06	77.20	99.59
a	91.34	94.18	89.12	0.00	1.67	75.76	99.40
b	93.34	102.25	93.74	18.24	19.68	65.94	99.46
ab	100.82	106.47	96.03	35.61	35.95	63.20	98.06
c	76.76	84.06	84.03	37.22	34.44	68.20	95.35
ac	91.74	94.40	87.43	22.49	24.13	65.97	99.36
bc	94.94	102.79	94.60	42.08	42.94	67.62	99.39
abc	96.31	101.87	93.56	37.88	38.73	46.04	97.62
I	82.93	82.58	78.44	45.85	46.51	76.03	97.97
II	78.07	82.31	78.22	31.96	32.54	75.11	99.57
III	82.13	86.91	83.66	33.46	32.54	79.13	99.47
Average	89.89	93.31	87.71	32.19	32.38	69.11	98.66

### 3.3. Recovery of RE

#### 3.3.1. Recovery from leached solutions: precipitation test

As indicated from the literature analysis a precipitation step has been suggested to recover the RE from leached solutions.

Several precipitation tests were carried out and three kind of leach liquor solutions were taken into consideration for selective precipitation tests. The main leaching conditions are shown in Table 4.

The results of previous leaching tests showed that the sulfuric acid concentration was not significant for metal dissolution yields in the range of investigated conditions; for this reason to produce leach liquors for precipitation tests sulfuric acid 3 M was selected for leaching tests.

Test I and test III were carried out at the same conditions but at different temperature of filtration. In the first experiment the leach liquor was cooled and then the filtration was carried out at room temperature. In the test III the filtration of undissolved solid was performed at the leaching temperature, immediately after the end of the leaching step. The aim of these experiments was to produce leach liquors for precipitation tests in different process conditions and to study the influence of filtration temperature on RE dissolution yields.

Table 4 summarizes the metal extraction yields: Mn, Zn and Ni leaching yields were quite large (>95%). These values confirmed that the solubility of these metal oxides are high enough at room temperature and generally increase with rising temperature. RE dissolution yields were lower than 50% and the maximum values of solubilization were at low temperature (test II) confirming that the solubility of rare earths sulfates reduces with rising temperature [6]. This trend was also demonstrated by test III in which the dissolution yields were zero when filtration of the leach solution was realized at the same leach temperature (83 °C). In the test III RE were not present in the leach liquors and La and Ce remains in the solid residue. The results shown that when the filtration step after leaching is carried out with the slurry at the same leaching temperature (~83 °C) the almost total amount of RE remain in the solid residues. So this process conditions could be considered useful in order to selectively separate RE from the other base metals. Precipitation tests were performed only on test I and II which RE dissolution were obtained. After leaching and filtration leach liquor were kept at room temperature and pH increased adding step by step NaOH 5 M. Adding NaOH step by step a precipitation of RE sulfates take place starting from pH = 0.7 with the formation of a white solid. Precipitation take place in a range of pH from 0.7 to 2.0. The solid precipitates were collected by filtration, washed by water and dried at 100 °C for 24 h: the solid samples were then characterized by XRF analysis. Table 5 shows the XRF analysis of these residues.

In test I AAS results of liquors after precipitation and filtration showed that the white precipitate was 89% La and Ce sulfates. The

**Table 4**

Metal extraction yield after 3 h of leaching ( $\text{H}_2\text{SO}_4$  3 M, 15% pulp density). E.Y. = extraction yield of the dissolved elements. n.a. = not available.

	Test I	Test II	Test III
T	83 °C	30 °C	83 °C
Filtration	Filtration after cooling	Filtration after cooling	Filtration without cooling
Element	% E.Y.	% E.Y.	E.Y.
Al	71	76	n.a.
Zn	99	97	94
Mn	98	99	93
Ni	95	91	99
La	33	45	0
Ce	32	44	0

**Table 5**  
XRF analysis of an RE precipitate obtained in test I and test II respectively (pH <1.6).

Symbol	Element	Test I%	Test II%
S	Sulfur	29.48	33.24
Al	Aluminum	2.93	3.48
Mn	Manganese	2.16	2.22
Fe	Iron	0.28	0.29
Co	Cobalt	0.11	0.12
Ni	Nickel	<0.02	<0.02
Cu	Copper	<0.001	<0.001
Zn	Zinc	0.01	<0.01
La	Lanthanum	14.91	15.62
Ce	Cerium	6.74	6.85

major impurities are Mn and Al respectively with about 2.16% and 2.93% as shown by XRF analysis. In test II the solid precipitate was 91% La and Ce sulfates with about 3.48% Al and 2.22% Mn. These results give good indication about the feasibility to recovery RE sulfates with acceptable purity levels.

The leach liquors after RE precipitation were collected after removal of the RE precipitates by filtration in order to carry out a further selective precipitation steps evaluating if other base metals could be selectively removed from the leach liquor. Precipitation of base metals was carried out adding further NaOH investigating larger pH levels: after reaching a pH value the suspension was filtered, the solid recovered and further NaOH was added to reach the next pH level repeating this procedures three times (approximately pH 2, 5, 7 have been investigated respectively).

Fig. 1 shows the results of these precipitation tests in which Mn, Zn and Ni were monitored in solution by AAS.

From the analysis of these experimental results it was possible to observe that

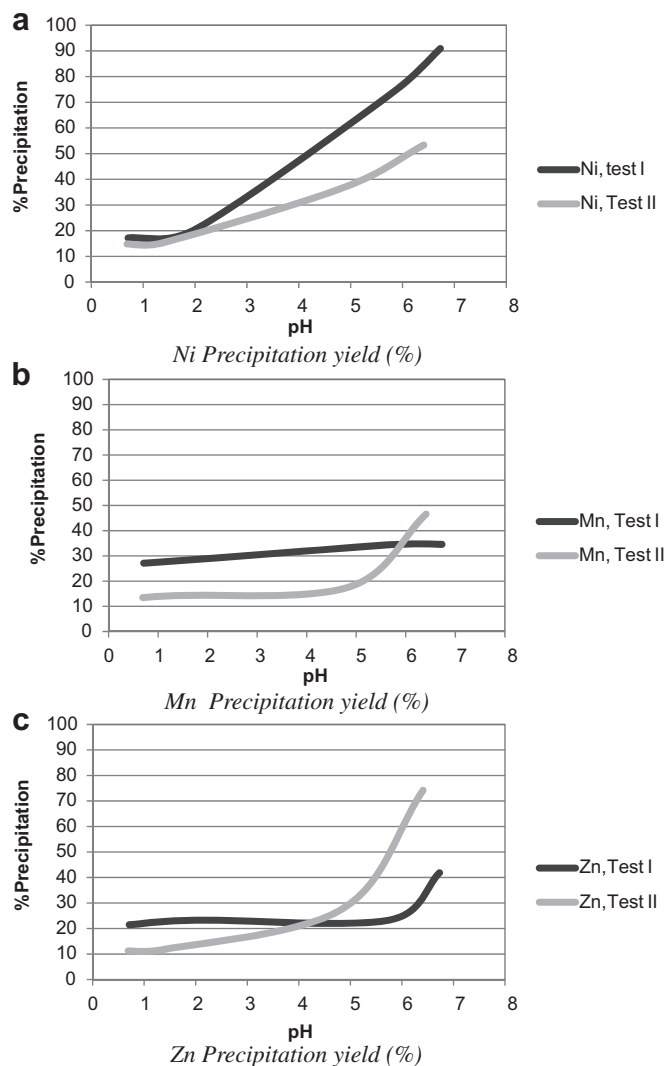
- Filtration of the solid after leachy at large temperature should be cooled if it is necessary to maximize the solubilization of RE reducing their amount in the leach solid residues.
- The contrary, leachy at large temperature (ie. 80–90 °C) and filtration at the same temperature could be used to retain RE in the solid residues maximizing the solubilization of the other base metals.
- RE can be selectively recovered from the leach liquor in the pH range 0.7–1.6 adding NaOH to the leach liquor. Recoveries and purities were estimated as about 95% and 89–91% respectively.
- From the solution obtained after RE removal it is possible to collect some rich fraction (with Ni, Mn, Zn and Mn) by selective precipitation but in order to obtain larger purities and base metal separations a liquid–liquid process seems necessary.

### 3.3.2. Recovery of RE from unleached solid residues: sequential second leaching by $H_2SO_4$

The results of leaching tests showed that 35–45% of RE contained in NiMH spent batteries were leached and that it is possible to retain a larger amount of RE in the leach solid residue enhancing the temperature during the filtration step carried out after leachy. For these reasons series of experiments including two leaching reaction in series were carried out to try to dissolve all RE in a first and second step of leachy. One representation test was reported in this work when the leaching conditions of leaching are indicated in the follow:

First leaching. 3 M sulfuric acid concentration, 80 °C, 15% pulp density, 3 h;

Second leaching. 1 M sulfuric acid concentration, room temperature, 15% pulp density, 1 h.



**Fig. 1.** Precipitation yields of Ni (a), Mn (b) and Zn (c) In the Test I and Test II.

The conditions for the first step were chosen to the same reasons listed in the previous paragraph for the preparation of solutions for RE precipitation tests. The residue solid of the first leaching was sequentially leached again in the conditions described for the second leaching step. In this treatment 1 M sulfuric acid concentration was selected because considering that most of base metals were already dissolved in the previous leaching step. One hour the reaction has been sufficient to complete powder dissolution and dissolve RE. Room temperature was chosen because RE sulfates solubility is more greater at low temperature as shown in the previous tests.

Metals leaching yields were determined by AAS analysis from leach liquors and by XRF from solid residues of both leaching steps.

Table 6 shows the results of XRF and AAS data for these series of tests.

Weight loss percentage of the sample (leached powder) was for the first leaching 80%, while for the second leaching was about 83%; so total leached mass percentage was 96.67% only 3% of the powder was not leached (mainly carbon fraction and residual Ni).

From the analysis of Table 6 it is possible to observe that the first leaching was enough to dissolve the most of elements in the powder except for RE. The leach liquor was very concentrated of Ni ( $\sim 39 \text{ g l}^{-1}$ ), Mn ( $\sim 19 \text{ g l}^{-1}$ ), Zn ( $\sim 10 \text{ g l}^{-1}$ ) and other metals in smaller quantities were Co ( $\sim 4 \text{ g l}^{-1}$ ), Al ( $3.80 \text{ g l}^{-1}$ ), La ( $\sim 2 \text{ g l}^{-1}$ ) and Ce ( $\sim 0.8 \text{ g l}^{-1}$ ).

**Table 6**AAS<sup>a</sup> and XRF<sup>b</sup> analysis after the first leaching step and the second leaching step (E.Y. = extraction yield of the dissolved elements).

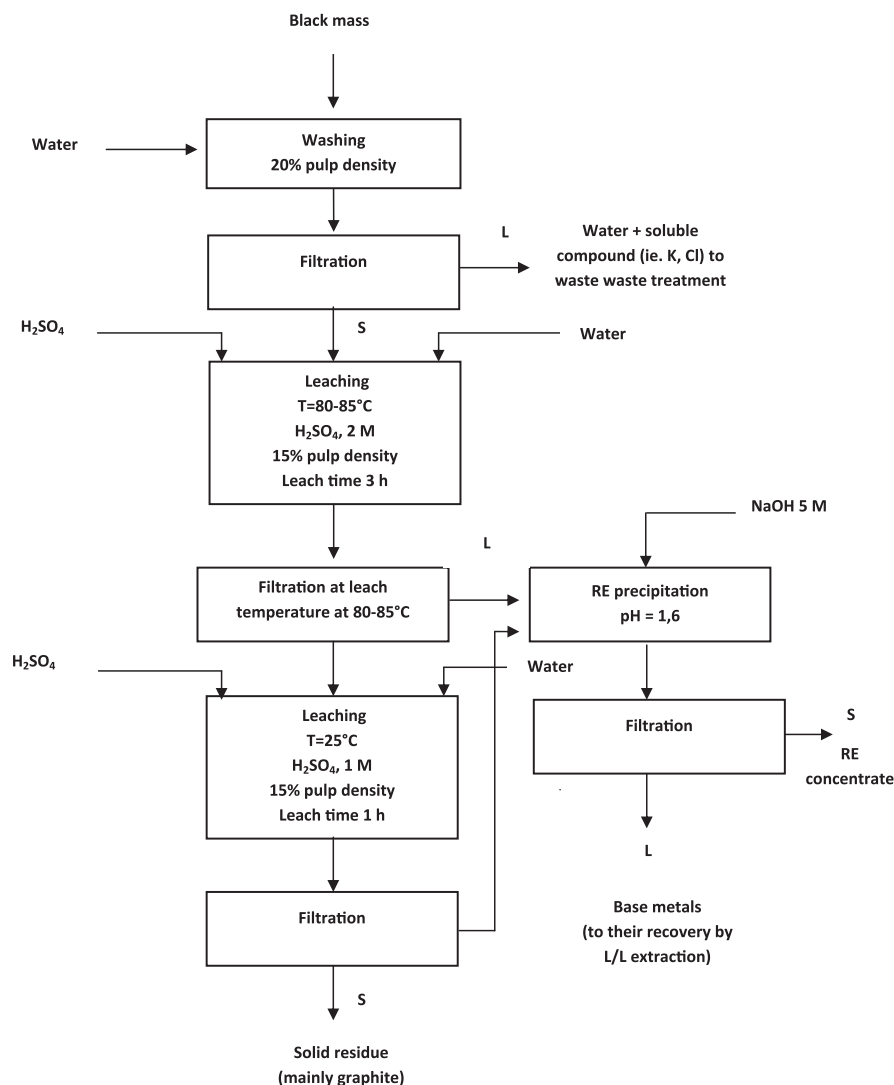
Spent batteries		First leaching			Second leaching		
Symbol	Solid initial %	Solid leach residue I (%)	Concentration of leach liquor (g l <sup>-1</sup> )	E.Y. (%)	Solid leach residue II (%)	Concentration of leach liquors (g l <sup>-1</sup> )	E.Y. (%)
Mn <sup>a</sup>	13.90	5.17	19.30	92.61	0.04	7.60	98.61
Al <sup>b</sup>	3.29	3.46	3.80	79.11	1.729	4.72	91.61
Fe <sup>b</sup>	1.10	0.29	1.56	94.55	0.13	0.39	92.48
Co <sup>b</sup>	2.60	0.12	3.86	99.09	0.14	0.13	75.84
Ni <sup>a</sup>	29.16	15.91	39.00	89.45	10.48	21.08	88.95
Zn <sup>a</sup>	8.18	6.07	10.46	85.25	0.05	9.04	99.85
La <sup>b</sup>	3.65	12.23	1.84	33.58	0.36	18.11	99.51
Ce <sup>b</sup>	1.68	5.69	0.82	32.54	0.17	8.50	99.99

<sup>a</sup> AAS analysis.<sup>b</sup> XRF analysis.

The second leaching was efficient enough to dissolve RE present in the solid residue of the first leachy step. Concentration of Ni (~21 g l<sup>-1</sup>), La (~18 g l<sup>-1</sup>), Ce (~8.5 g l<sup>-1</sup>) and Mn (~7.6 g l<sup>-1</sup>) were observed in the leach liquor of second step.

From the analysis of leaching steps in series it was possible to observe that:

- two leaching reactions in series could be sufficient to dissolve RE present in NiMH spent batteries
- selected conditions for the second leaching appear to be suitable since it gives good extraction yields
- if liquors obtained from two leach steps would be mixed the total solution should have the following composition: ~17 g

**Fig. 2.** Block diagram suggested for the recovery of rare earths from NiMH spent batteries.

**Table 7**  
Metal composition of NiMH batteries (%).

Element	NiMH powder <sup>a</sup> (<500 μm; AAS/XRF, this work)	NiMH powder <sup>b</sup> (AAS/EDX)
Al	3.29	0.6
Cd	0.089	2.8
Co	2.60	5.5
Cr	0.37	–
Cu	0.14	–
Fe	1.09	0.3
K	2.54	2.2
Mn	13.90	2.4
Ni	29.16	49.8
Pb	0.012	0.0033
Ti	0.046	–
Zn	8.18	1.0
La	3.65	5.4
Ce	1.68	6.1

<sup>a</sup> Powder used in this work that it from the grinding section of a treatment plant of spent batteries.

<sup>b</sup> Rodrigues et al. (2010) [7].

1<sup>-1</sup> Mn, ~36 g l<sup>-1</sup> Ni, ~10 g l<sup>-1</sup> Zn, ~4.6 g l<sup>-1</sup> La, ~2.1 g l<sup>-1</sup> Ce, 3.7 g l<sup>-1</sup> Al and ~3.2 g l<sup>-1</sup> Co.

- the precipitation test could be used to recover RE sulfates from total leach liquor.

#### 4. Process analysis

The experimental results obtained suggest a possible flow sheet to recover La and Ce from the NiMH spent batteries, that involve two leaching with sulfuric acid and obtain a rich solution of nickel, zinc and manganese.

Fig. 2 shows the block diagram proposed to recover rare earths from NiMH spent batteries.

Literature mentions another research work (Rodrigues et al. [7]) on the treatment of NiMH spent batteries including a second leaching in series to dissolve rare earths present in the powder of the NiMH spent batteries. The main differences of this work and that one reported by Rodrigues et al. [7] are:

- the initial materials of the present work has been obtained from an industrial scale production site in which NiMH spent batteries have been selected, crushed and sieved. In the cited work the black mass has been obtained by dismantling of batteries in order to separate plastic and metallic cases from the internal content of such batteries then the material was dried and submitted to a knife mill for defragmentation followed by a ball mill [7]. The different composition in two works can be obtained in Table 7.
- Different leachy conditions have been proposed in this work.

**Table 8**  
Main differences of two works.

Research	Leaching		% Leaching	Concentration of leach solution	% RE precipitation
	Conditions				
	First leaching	Second leaching			
Work <sup>a</sup>	80 °C 15% pulp density 2 M H <sub>2</sub> SO <sub>4</sub> 3 h	25 °C 15% pulp density 1 M H <sub>2</sub> SO <sub>4</sub> 1 h	100% for Mn, Co and Zn 99% for Ni and RE	36 g l <sup>-1</sup> Ni, 17 g l <sup>-1</sup> Mn, 10 g l <sup>-1</sup> Zn, 4.6 g l <sup>-1</sup> La, 2.1 g l <sup>-1</sup> Ce	pH = 1.6 Recovery about 99% of total RE contained in the initial material
Work <sup>b</sup>	30 °C S/L = 1/10 gml <sup>-1</sup> 8% v/v H <sub>2</sub> SO <sub>4</sub> 1 h	30 °C S/L = 1/10 gml <sup>-1</sup> 8% v/v H <sub>2</sub> SO <sub>4</sub> 1 h	100% for Ni 87% for RE	28.5 g l <sup>-1</sup> Ni, 4.7 g l <sup>-1</sup> Co, 2.4 g l <sup>-1</sup> Cd	pH = 2.5 Recovery about 50% of removal of RE elements

<sup>a</sup> This work.

<sup>b</sup> Rodrigues et al. (2010) [7].

Table 8 summarizes the main difference of two works.

In any case it is possible to conclude that two sequential leachy is a suitable strategy to recovery large amount of RE from NiMH spent batteries. In previous mentioned research the authors suggested a treatment that included two leaching in series with sulfuric acid (8% v/v) at 30 °C, S/L = 1/10 for 1 h. The total leaching yields were about 100% for Ni and 87% for RE and concentrations of leach liquor were 28.5 g l<sup>-1</sup> Ni, 4.7 g l<sup>-1</sup> Co and 2.4 g l<sup>-1</sup> of Cd.

After the second leaching and filtration RE were precipitated adding NaOH (pH < 2) and the recovered (%) of leached rare earths was about 50%.

Our work suggests a process that involves washing of material, the first leaching of the powder with sulfuric acid 2 M at high temperature (for example 80°C/90 °C), 15% w/v of solid for 3 h and then second leaching of solid residue with sulfuric acid 1 M at room temperature for 1 h.

In these conditions total extraction yields were about 100% for Mn, Co, Zn and 99% for Ni, Al and RE. From the results obtained by XRF analysis around 99% of total mass of La and Ce content in the powder are dissolved and total recovered by adding NaOH (5 M) to pH of precipitation of RE (pH < 2).

#### 5. Conclusions

NiMH spent batteries obtained in an industrial scale grinding process (<500 μm) were used for experimental tests to recover RE from this powder.

The aim of this work was to study the recoveries of lanthanum and cerium (RE in the powder) and to investigate if selective precipitation was efficient to separate the other leached metals like nickel, manganese and zinc. These elements were the major component of initial material.

The experimental data suggested a possible flowsheet that it describes a possible process to treat NiMH spent batteries.

Summarizing the following conclusions can be drawn:

- XRF and AAS analysis of initial industrial NiMH spent batteries powder showed that nickel, manganese and zinc were the major metals (29% w/w Ni, 13% w/w Mn, 8% w/w Zn). Very important elements were lanthanum and cerium (rare earths) content to about 5% w/w, cobalt and potassium were 2.5% w/w.
- Washing of powder seems important to remove KOH and other soluble elements.
- The statistical analysis showed that no significant effects were found to be important for leaching extraction yields with the exception of the negative interaction AB for cerium (sulfuric acid concentration and temperature) significant at 96%, for Mn dissolution (B – Temperature) with a positive effect and for aluminum three single factors were found relevant, A (sulfuric

acid concentration), B (temperature) and C (citric acid concentration) all with negative effect and significance respectively of 96%, 98% and 97%.

- In conclusion, the dissolution of the metals of most interest were not influenced by the process conditions selected in the experimental plan whereas it was confirmed that the solubility of cerium sulfates decreases increasing the level of temperature.
- Two leaching in series with sulfuric acid solutions, at different conditions, were efficient to dissolve metals and for Ni, Co, Zn, Mn, La and Ce the % leaching were about 100% for each element.
- The filtration of unleached residue should be carry out at room temperature after a cooling step because the solubility of RE sulfates decreases with the increase of temperature.
- Leach liquors after the two leaching steps have about 17 g l<sup>-1</sup> of Mn, 36 g l<sup>-1</sup> of Ni, 10 g l<sup>-1</sup> of Zn, 4.6 g l<sup>-1</sup> of La, 2.1 g l<sup>-1</sup> of Ce, 3.7 g l<sup>-1</sup> Al and 3.2 g l<sup>-1</sup> of Co.
- RE sulfates can be separate from leach solution by precipitation with NaOH. In this work the % recovery of La and Ce was about 99%.

The precipitate of RE sulfates was white solid and analysis showed that about 64% w/w was lanthanum sulfate and 28% w/w was cerium sulfate. The major impurities consisted of manganese and aluminum (about in the range 2–3.5% each other) and other metals like nickel and zinc.

Precipitation is not efficient to recover selectively the other metals content in leach liquor, so another process should be studied. In our next research the solvent extraction will be considered to separate manganese and zinc from leach solutions.

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