



Hydrometallurgical separation of rare earth elements, cobalt and nickel from spent nickel–metal–hydride batteries

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ABSTRACT

The separation of rare earth elements, cobalt and nickel from NiMH battery residues is evaluated in this paper. Analysis of the internal content of the NiMH batteries shows that nickel is the main metal present in the residue (around 50% in weight), as well as potassium (2.2–10.9%), cobalt (5.1–5.5%), rare earth elements (15.3–29.0%) and cadmium (2.8%). The presence of cadmium reveals that some Ni–Cd batteries are possibly labeled as NiMH ones. The leaching of nickel and cobalt from the NiMH battery powder with sulfuric acid is efficient; operating variables temperature and concentration of H₂O₂ has no significant effect for the conditions studied. A mixture of rare earth elements is separated by precipitation with NaOH. Finally, solvent extraction with D2EHPA (di-2-ethylhexyl phosphoric acid) followed by Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) can separate cadmium, cobalt and nickel from the leach liquor. The effect of the main operating variables of both leaching and solvent extraction steps are discussed aiming to maximize metal separation for recycling purposes.

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1. Introduction

The secondary battery nickel–metal–hydride (NiMH) is commonly used as power source in electronic devices like mobile phones, computers and hybrid electric vehicles (HEV). The main parts of this battery are: a cathode made of nickel coated with nickel hydroxide; an anode made of a hydrogen storage alloy based on mischmetal (mainly cerium, lanthanum, praseodymium and neodymium) and nickel including substituents; a separator between the two electrodes made of fine fibers (usually polyamide, polypropylene fleece or gauze); an electrolyte typically KOH; a metal case; and a sealing plate provided with a self-releasing safety vent. Such structure is similar to that of Ni–Cd batteries. In fact, these two batteries have very similar operating voltage but, in comparison to the Ni–Cd ones, the NiMH batteries do not contain cadmium and they have about twice the energy density of the Ni–Cd batteries.

Because of such advantages, NiMH batteries have constantly substituted the Ni–Cd batteries. For instance, in the market of mobile phones, the use of Ni–Cd batteries decreased from 63.8% to 44.4% during this decade, those of lithium ion batteries increased from 8.4% to 27.3% whereas the use of NiMH batteries were kept practically constant at 28.0% [1]. Also, NiMH batteries currently dominate the HEV market, with lead acid batteries finding appli-

cation in some mild hybrid architectures. The HEV battery market was estimated at \$600 million in 2006 and it is expected to grow to \$2.3 billion by 2015 [2].

As the need for electronic devices grows worldwide, the consumption of batteries is expected to increase in the coming years. Therefore, the continuous development of recycling battery technologies may contribute to economical and environmental aspects as pointed out by several research works with various types of batteries such as Zn–C, alkaline, Ni–Cd, NiMH and Li-ion [1,3–8]. In this context, the present paper aims to investigate the main operating variables of the hydrometallurgical route in order to maximize the separation of the main metals commonly found in the NiMH batteries.

2. Experimental

The experimental work adopted in this study consisted of the following steps: (i) previous treatment, including classification of batteries by type (as suggested by a previous study [5]) followed by dismantling of batteries in order to separate plastic and metallic cases from the internal content of the NiMH batteries; (ii) metal characterization of the internal content of such batteries; (iii) leaching of the internal content of NiMH batteries with sulfuric acid; (iv) precipitation of rare earth elements by pH adjustment, and (v) purification of cobalt and nickel by solvent extraction. All experiments were carried out using gloves, glasses and gas masks. The contact of battery dust with skin, eyes and clothing requires immediate cleaning as suggested by previous studies [9].

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2.1. Previous treatment and metal characterization of the NiMH batteries

NiMH batteries (50% cylindrical and 50% prismatic batteries) from different manufacturers (Nokia, Motorola, Siemens, Ericsson, etc.) were used in this study. Plastic and metallic cases were firstly removed according to the manual procedure depicted elsewhere [9]. The internal content of batteries (including the grids that support the active material) was weighted, dried in a drying oven for 24 h at 60 °C, and weighted again to measure the content of volatile substances. One battery was randomly chosen and it was submitted to qualitative metal characterization by X-ray fluorescence (XRF) using a Philips (model PW 2400) X-Ray Fluorescence Spectrometer, followed by X-ray diffraction (XRD) using a Philips (model PW 1710) X-ray diffractometer, and also by scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS) using a JEOL (model JSM 5410) Microscopy and Noram (model 648C-1SSS) Energy Dispersive Spectrometer in order to identify the main metal species present in the NiMH batteries as well as its morphology and qualitative metal composition. In order to get homogeneous samples for the leaching tests, the dried material was submitted to a knife mill for defragmentation followed by a ball mill for almost 3 h. The material was sieved thus resulting into coarse and fine fractions. The coarse fraction was discarded while homogeneous samples of the fine fraction were obtained using a Quantachome sieving rifler (model SRR-5 with eight collecting plates). Samples of the fine fraction were dissolved in aqua-regia and its metal composition (Ni, Co, Cd, Hg, Pb, Zn, Mn, Al, K and Fe) was analyzed by atomic absorption spectrometry (AAS) using a GBC (model 932 plus) Atomic Absorption Spectrometer and rare earth composition was determined by Energy Disperse X-ray (EDX) using a KeveX (model Sigma X-9050) Spectrometer.

2.2. Leaching tests with sulfuric acid

The leaching experiments were carried out by taking a given volume of H₂SO₄ solution in a 1 L covered glass reactor immersed in a water bath maintained at controlled temperature. As soon as the temperature of the solution reached the desired value, weighted amounts (8 g) of sample was added and pulp was mechanically mixed at 510 rpm. All tests lasted 1 h in accordance to previous studies [5]. The following variables were evaluated: H₂SO₄ concentration (2, 4, 6, 8 and 10% (v/v)), H₂O₂ concentration (0, 1, 3, 5 and 7% (v/v)), temperature (30, 40, 50, 60 and 70 °C) and solid/liquid ratio (1/10, 1/20, 1/30, 1/40 and 1/50 g mL⁻¹). In these tests, the effect of each operational variable was investigated by keeping the remaining variables at their intermediate level. After leaching, the pulp was vacuum filtered and a sample of the aqueous solution was submitted to AAS analysis for Cd, Co and Ni. All tests were carried out in duplicate.

2.3. Precipitation tests

The aqueous solution used in the subsequent tests was obtained by leaching the NiMH powder in the following conditions: two stages, [H₂SO₄]=8% (v/v), [H₂O₂]=0% (v/v), T=30 °C, S/L ratio = 1/10 g mL⁻¹ and t = 1 h. The solutions were mixed and vacuum filtered to remove solids in suspension. As the pH of the leach solution was near zero, NaOH was added to raise the pH to 2.5. Consequently, the formation of a dense and white precipitate was verified. The solution was vacuum filtered again and the solid phase was dried and stored. The precipitation still lasted for some days but at a very slow rate; then, the solution was vacuum filtered for the third time. Samples of the final solution were analyzed by AAS for Cd, Co and Ni while samples of the precipitate were submitted to EDX analysis.

2.4. Solvent extraction tests

Suitable volumes of the aqueous (leach liquor) and organic phases were contacted in a glass reactor for 5 min (initial experiments showed that equilibrium was reached within 1 min), the phases were separated and the metal concentration in the aqueous phase (raffinate) was estimated by AAS. The pH adjustment in the aqueous phase was performed by the addition of dilute NaOH or H₂SO₄ solutions. The organic phases consisted of extractants D2EHPA (di-2-ethylhexil phosphoric acid) or Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) dissolved in aliphatic kerosene Exxsol D-80; no modifier was added. The following operating variables were investigated in the extraction step: pH of the aqueous solution (2.5–8.0), D2EHPA concentration (0.02–0.50 M), Cyanex 272 concentration (0.3–0.7 M) and aqueous/organic (A/O) ratio (1/5 to 5/1). The metal loaded organic phases were stripped out by contacting it with aqueous phases at changing H₂SO₄ concentrations (0.25–2 M); the aqueous solutions were suitably analyzed by AAS. All experiments were carried out at room temperature (25 ± 1 °C).

3. Results and discussion

3.1. Previous treatment and metal characterization of the NiMH batteries

After manual dismantling of the NiMH batteries for the separation of both plastic and metallic cases, the internal content of batteries was weighted before and after drying at 60 °C for 24 h. The obtained weight difference (4.2%) is quite similar to that verified at previous study (5.8%) for NiMH batteries [5], so nearby 5% of weight is associated to volatile species.

Regarding to the chemical composition, X-ray fluorescence analysis indicated the predominance of nickel species in the internal content of NiMH batteries, as well as small amounts of cobalt, zinc and manganese. The presence of rare earth elements cerium, lanthanum, praseodymium and neodymium was also identified. Such result was confirmed by X-ray diffraction analysis as shown in Fig. 1. Nickel was found predominantly as NiOOH, Ni(OH)₂ and NiO species, the first two species are related to the charge–discharge process of NiMH batteries while the last one is due to the Ni oxidation with air after dismantling operation. The presence of rare earth elements of lanthanum group was identified predominantly as hydroxides La(OH)₃ but La₂O₃ due to corrosion of alloys LaNi₅ according to the following reactions was also found, thus corroborating previous investigations [10,11].

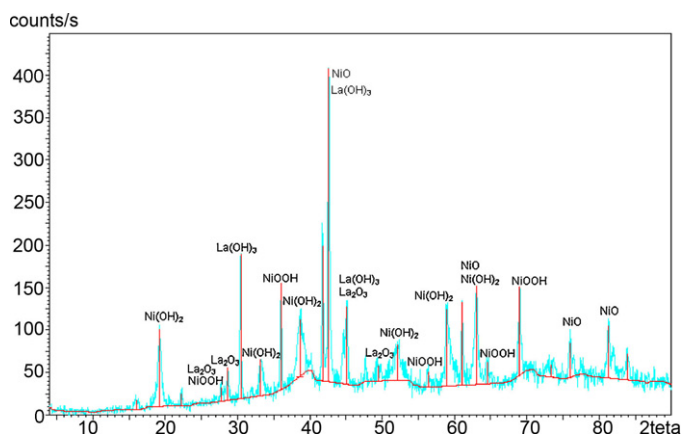
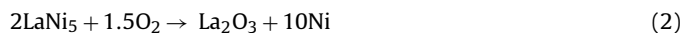
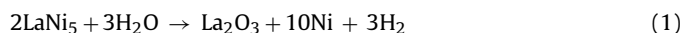


Fig. 1. X-ray diffraction analysis of the internal content of NiMH batteries.

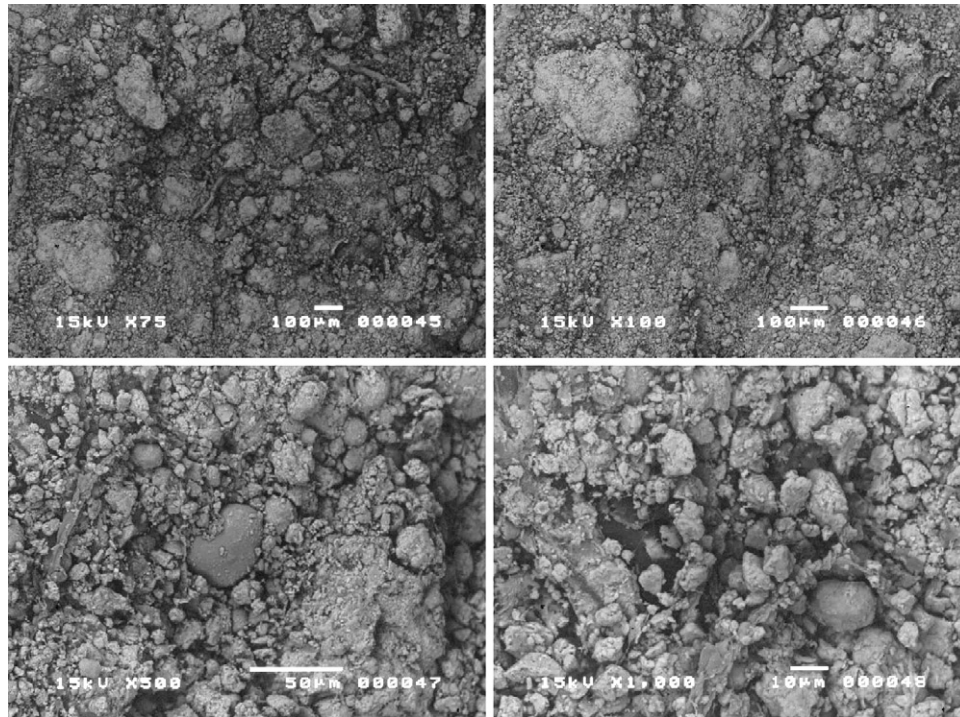


Fig. 2. Scanning electronic microscopy pictures of the internal content of NiMH batteries at different resolutions (75 \times , 100 \times , 500 \times and 1000 \times).

Scanning electronic microscopic analysis of the powder of NiMH batteries shown in Fig. 2 revealed that the powder is quite homogeneous regarding to both color and shape of particles.

The metal composition of NiMH batteries including and excluding the metallic cases is shown in Table 1. In the first column, a semi-qualitative metal content of a randomly chosen battery determined by SEM-EDS analysis is presented; the second column shows the composition of the powder from several batteries after mill operations which was determined by AAS and EDX. Typical compositions including the metal case are also shown in the same table for the sake of comparison. When metal cases are removed, the content of iron is significantly reduced and the composition of remaining metals is increased. Nickel was found as the predominant metal species in the analyzed battery, nearby 50% in weight of the internal

content of NiMH batteries. The presence of potassium, cobalt and rare earth elements was also found significant (2.2–10.9%, 5.1–5.5% and 15.3–29.0%, respectively), thus revealing the studied batteries are AB₅ type. Curiously cadmium was found in the powder of NiMH batteries at significant amount (2.8%). As Ni–Cd and NiMH batteries are quite similar in their structures, it seems that Ni–Cd batteries were labeled as NiMH as evidenced also by other study [10]. Therefore, cadmium must be removed from the dust and treatment processes for NiMH batteries must consider the presence of cadmium in the residue.

NiMH batteries are normally classified into AB₂ and AB₅ types depending on how metals A and B are combined in the hydrogen-absorbing alloys that constitute the anode of the battery. Such alloys can absorb hydrogen atoms equivalent to about a thousand

Table 1
Metal composition of NiMH batteries (% weight).

Metal	NiMH ^a (SEM-EDS, this work)	NiMH powder ^a (AAS/EDX, this work)	NiMH ^b (AB ₂) [3]	NiMH ^b (AB ₅) [3,5,8,11]
Al	1.1	0.6	0.5–1.0	0.5–2.0
Cd	n.d.	2.8		0.04–0.22
Ce	3.4	6.1		0.4–5.5
Co	5.1	5.5	1.0–3.0	2.5–4.3
Cr			0–1.6	0.02–0.08
Cu				0.02
Fe	0.9	0.3	23–25	20–25
Hg		0.0072		–
K	10.9	2.2		2.4–3.1
La	11.5	5.4		1.4–6.6
Mn	1.4	2.4		0.8–3.0
Nd	10.9	3.0		1.0–4.1
Ni	52.8	49.8	34–39	25–46
Pb	n.d.	0.0033		–
Pr	3.2	0.8		0.3–1.3
Si				
Ti	1.4		2.2–3.9	
V			2.2–4.7	
Zn	2.8	1.0		0.1–1.6
Zr			3.9–8.7	

^a Excluding metallic case.

^b Including metallic case.

Table 2
Summary of the main effects of sulfuric leaching of NiMH battery powder for cobalt, nickel and cadmium ($t = 1$ h).

Operating variable	Co	Ni	Cd
Temperature (from 30 to 70 °C)	No effect, leaching around 95%	No effect, leaching around 82%	No effect, leaching around 84%
H ₂ SO ₄ concentration (from 2% to 10% (v/v))	No effect, leaching around 95–100%	Leaching increased from 72% to 97%, stabilizing at 8% (v/v) H ₂ SO ₄	No effect, leaching around 80%
H ₂ O ₂ concentration (from 0% to 7% (v/v))	No effect, leaching around 93–100%	No effect, leaching around 75–85%	Leaching increased from 62% to 80%, stabilizing at 1% (v/v) H ₂ O ₂
S/L ratio (from 1/10 to 1/50 g mL ⁻¹)	No effect, leaching around 93–100%	Leaching increased from 60 to 83%, stabilizing at S/L = 1/20 g mL ⁻¹	Leaching slightly decreased from 85% to 75%

times of their own volume, generating metal hydrides and also releasing the hydrogen that was absorbed. During this process, the combination of metal A whose hydrides generate heat exothermically with metal B whose hydrides generate heat endothermically to produce the suitable binding energy allows that hydrogen can be absorbed and released at or around normal temperature and pressure levels. As a result, the alloy reduces the gaseous oxygen given off from the cathode during overcharge by sufficiently increasing the capacity of the anode, thus keeping constant the internal pressure of the battery so it is possible to seal it [12]. In the AB₂ type alloys, the metal A is normally zircon or titanium while metal B is nickel, cobalt, vanadium, aluminium, chromium or iron. In the AB₅ type alloys, the metal A is a mixture of rare earth elements from the lanthanum group (total amount around 8–10%, consisting of 50–55% of cerium, 18–28% of lanthanum, 12–18% of neodymium, 4–6% of praseodymium) or manganese while metal B is nickel, cobalt or aluminium [13].

3.2. Leaching tests with sulfuric acid

The leaching of nickel, cobalt and cadmium from the NiMH battery powder with sulfuric acid was found to be quite efficient for the operational conditions investigated. In fact, such metals were easily leached in one single stage resulting in a deep green aqueous solution due to the presence of nickel which represents around 50% of the leached material. The main effects of the studied operating variables are summarized in Table 2.

No significant effect was verified for the studied range of temperature; cobalt, nickel and cadmium were leached around 95%, 82% and 84%, respectively, in one single step ([H₂SO₄] = 6% (v/v), [H₂O₂] = 3% (v/v), S/L ratio = 1/30 g mL⁻¹, $t = 1$ h). Similar behavior was obtained for the leaching of NiMH batteries with HCl 2 M for 2 h at same temperature range [14]. So, NiMH battery residue can be efficiently treated at room temperature [13].

The increase on the concentration of H₂SO₄ influenced the leaching of nickel only (it increased from 72% to 97%, stabilizing at 8% (v/v) of H₂SO₄) while that of cobalt and cadmium were found practically unaffected (around 95–100% and 80%, respectively) for the studied conditions ($T = 50$ °C, [H₂O₂] = 3% (v/v), S/L ratio = 1/30 g mL⁻¹, $t = 1$ h). As nickel is the predominant metal in the residue, the higher is the amount of reagent the higher is the dissolution of nickel; same behavior was obtained elsewhere [14].

No significant effect was identified for the operating variable concentration of H₂O₂ for the leaching of nickel and cobalt (leaching around 93–100% and 75–85%, respectively, at $T = 50$ °C, [H₂SO₄] = 6% (v/v), S/L ratio = 1/30 g mL⁻¹, $t = 1$ h) thus corroborating previous investigation [5,13]. However, according to Rabah et al. [7], the addition of H₂O₂ improved the level of solubility of both Ni and Co, and also enhanced the leaching process in a shorter time. On the other hand, the presence of H₂O₂ increased the leaching of cadmium (it changed from 62% to 80%, stabilizing at 1% (v/v) H₂O₂); such behavior is probably due to the leaching of metallic cadmium which is formed in the charge–discharge process of Ni–Cd batteries.

The effect of S/L ratio affected positively the leaching of nickel only (it increased from 60% to 83%, stabilizing at S/L = 1/20 g mL⁻¹) while that of cobalt was practically unaffected for the conditions studied ($T = 50$ °C, [H₂SO₄] = 6% (v/v), [H₂O₂] = 3% (v/v), $t = 1$ h). The higher is the S/L ratio the higher is the amount of reagent, so it maybe affected the leaching of nickel. Curiously, a slight decrease on the leaching of cadmium was observed; actually it seems to be not affected by the conditions range studied in this work and the slight decrease is probably due to some fluctuation on the chemical analysis.

Based on the operating conditions investigated in this study, around 80–85% of nickel and 95–100% of cobalt can be leached from the NiMH powder in one single stage. Similar results were obtained elsewhere [5,13]. Leaching reactions with H₂SO₄ are presented by Pietrelli et al. [13,15].

3.3. Precipitation tests

In order to produce the leaching liquor for the subsequent study, the powder of NiMH batteries was leached according to the conditions schematically shown in Fig. 3. Around 88% of powder was dissolved in two stages, so a considerable reduction on the amount of residue was achieved. The obtained leach liquor was a deep green acid solution (pH 0.03–0.05) containing 28.5 g L⁻¹ of nickel, 4.7 g L⁻¹ of cobalt and 2.4 g L⁻¹ of cadmium corresponding to respective leaching of 64.5%, 96.4% and 95.7%. In fact, higher leaching of nickel could be achieved if a third stage was considered or if a lower S/L ratio was used. The total leaching of rare earth elements (La + Ce + Pr + Nd) was 87.3%.

As the pH of the leach solution was near zero, it was raised to pH 2.5 by addition of NaOH in order to precipitate the rare earth elements and also obtain a suitable solution for the subsequent solvent extraction tests. The solution was filtrated and 26 g of a dense white precipitate was obtained thus corresponding to 50% removal of rare earth elements. The separation of rare earth elements of the lanthanum group was investigated elsewhere by solvent extraction with D2EHPA [14] and PC-88A [16] at pH < 2.

3.4. Solvent extraction tests

Preliminary solvent extraction tests with the filtered solution at changing pH values resulted in quite viscous organic phases at pH > 6, thus making phase disengagement a difficult operation. In order to avoid such problem, the aqueous solution was diluted two times so the liquor used in the solvent extraction tests at changing pH values contained 13–14 g L⁻¹ of nickel, 2 g L⁻¹ of cobalt and 1 g L⁻¹ of cadmium. The subsequent tests were carried out with the undiluted liquor.

The effect of pH on the extraction of cadmium, cobalt and nickel with cationic extractants D2EHPA and Cyanex 272 is shown in Fig. 4. As expected, metal extraction increases with the increase of pH because such metals exist in the aqueous phase as cation species. According to the curves shown in Fig. 4, it can be seen that Cyanex 272 generally needs higher pH values than D2EHPA to extract the same metal ions amount because phosphinic acids derivatives are

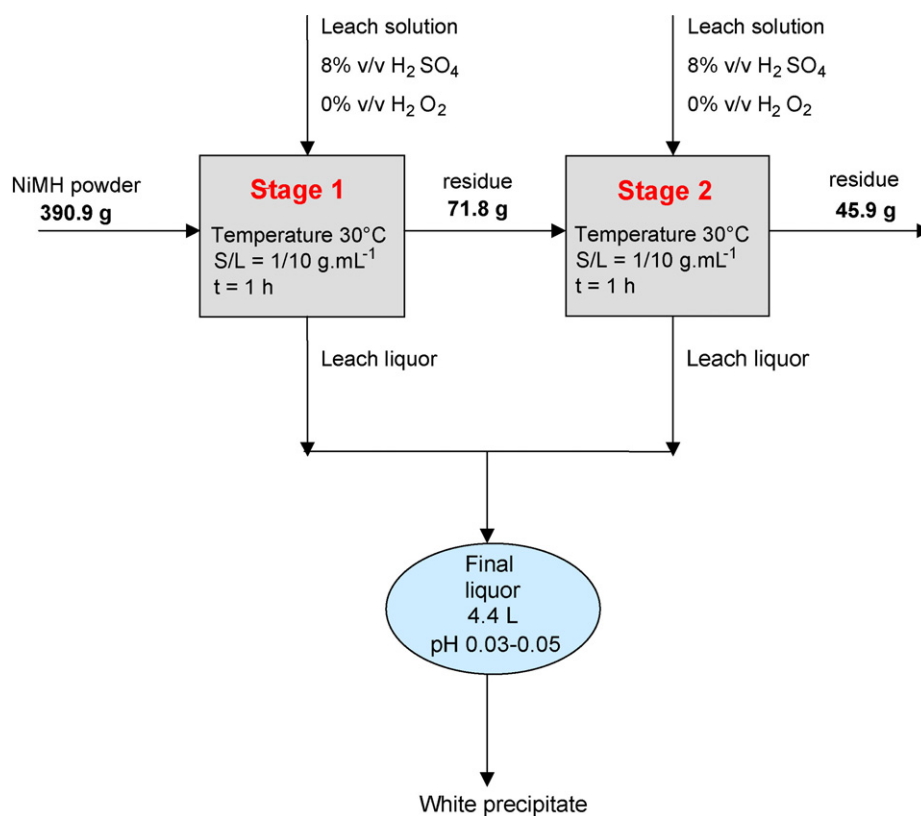


Fig. 3. Operating conditions used in the leaching step of the NiMH batteries powder.

weaker acids than phosphoric ones [17]. In fact, the $\text{pH}_{1/2}$ of cadmium, cobalt and nickel is 2.7, 4.3 and 6.2 for D2EHPA and 5.0, 4.8 and 7.1 for Cyanex 272, respectively; in terms of $\Delta\text{pH}_{1/2}$ for Co–Cd, Ni–Cd and Ni–Co, it is 1.6, 3.5 and 1.9 for D2EHPA and 0.2, 2.1 and 2.3 for Cyanex 272. Therefore, D2EHPA is an efficient reagent to separate cadmium from cobalt and nickel, while Cyanex 272 can separate cobalt and cadmium from nickel [18,19]. The respective selectivity factors $\beta_{\text{Cd/Co}}$, $\beta_{\text{Cd/Ni}}$ and $\beta_{\text{Co/Ni}}$ calculated based on the curves shown in Fig. 4 are 46, 84 and 2 for D2EHPA at pH 3.4 and 0.4, 382 and 950 for Cyanex 272 at pH 5.8.

In order to remove cadmium in a selective way, the undiluted liquor ($[\text{Ni}] = 25.8 \text{ g L}^{-1}$, $[\text{Co}] = 3.7 \text{ g L}^{-1}$ and $[\text{Cd}] = 2.1 \text{ g L}^{-1}$) was contacted with organic phases containing D2EHPA dissolved in Exxsol D-80 at different concentrations. For these tests, the pH of

the liquor was slightly changed around the optimum value obtained with the diluted liquor, so tests were carried out at pH ranging from 3.0 to 4.2. As expected, the increase on the concentration of D2EHPA resulted in higher metal extractions. In addition, as the pH was chosen to favor the cadmium removal instead of cobalt and nickel, cadmium was preferentially extracted as verified in Fig. 5; the extraction of nickel was below 5% for such operating conditions. It can be seen that pH and concentration of extractant are key variables on the extraction of metals with cationic extractants [20]. Based on the results shown in Fig. 5, the selective removal of cadmium over cobalt is maximized at $[\text{D2EHPA}] = 0.5$ and pH 3.0 ($\beta_{\text{Cd/Co}} \approx 350$).

Fig. 6 shows metal extraction from the undiluted liquor ($[\text{Ni}] = 24.5 \text{ g L}^{-1}$, $[\text{Co}] = 4.4 \text{ g L}^{-1}$ and $[\text{Cd}] = 1.9 \text{ g L}^{-1}$) at changing

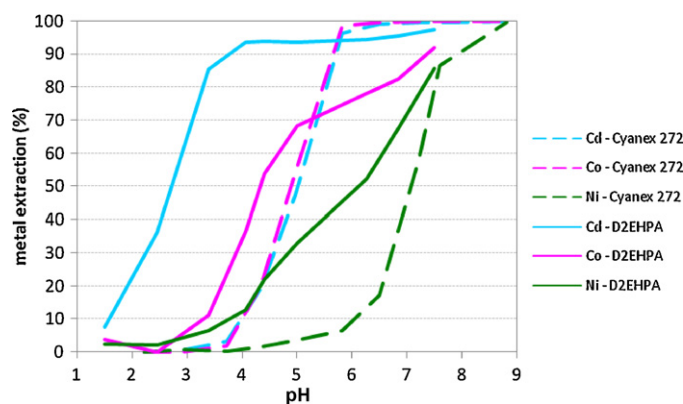


Fig. 4. Effect of pH on the extraction of nickel, cobalt and cadmium using D2EHPA (continuous line) and Cyanex 272 (dashed line) as extractants diluted in Exxsol-D80 ($[\text{Ni}] = 13\text{--}14 \text{ g L}^{-1}$, $[\text{Co}] = 2 \text{ g L}^{-1}$ and $[\text{Cd}] = 1 \text{ g L}^{-1}$, $[\text{extractant}] = 0.5 \text{ M}$, $T = 25^\circ\text{C}$, A/O ratio = 1).

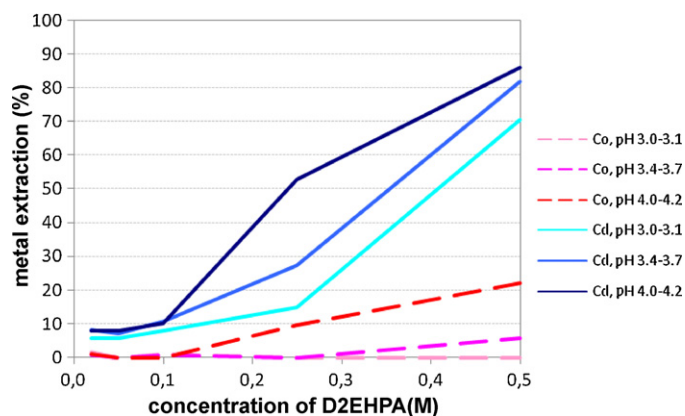


Fig. 5. Effect of the concentration of D2EHPA on the selective extraction of cadmium at changing pH values around the optimum value ($[\text{Ni}] = 25.8 \text{ g L}^{-1}$, $[\text{Co}] = 3.7 \text{ g L}^{-1}$, $[\text{Cd}] = 2.1 \text{ g L}^{-1}$, $T = 25^\circ\text{C}$, A/O ratio = 1).

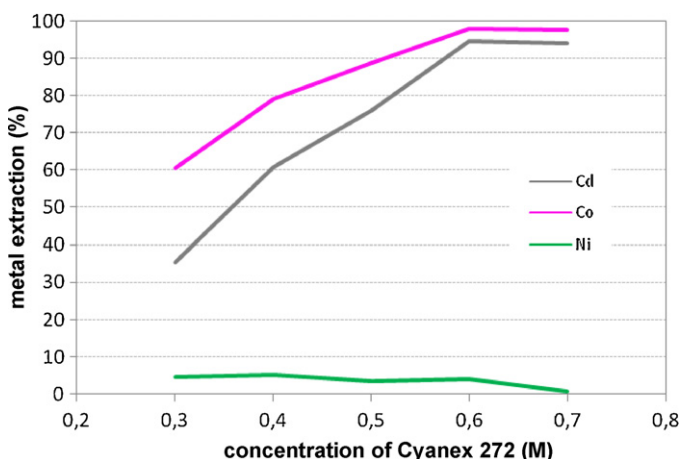


Fig. 6. Effect of the concentration of Cyanex 272 on the selective extraction of cobalt over nickel at changing pH values around the optimum value ($[\text{Ni}] = 24.5 \text{ g L}^{-1}$, $[\text{Co}] = 4.4 \text{ g L}^{-1}$, $[\text{Cd}] = 1.9 \text{ g L}^{-1}$, $T = 25^\circ \text{C}$, A/O ratio = 1, $\text{pH} \approx 5.8$).

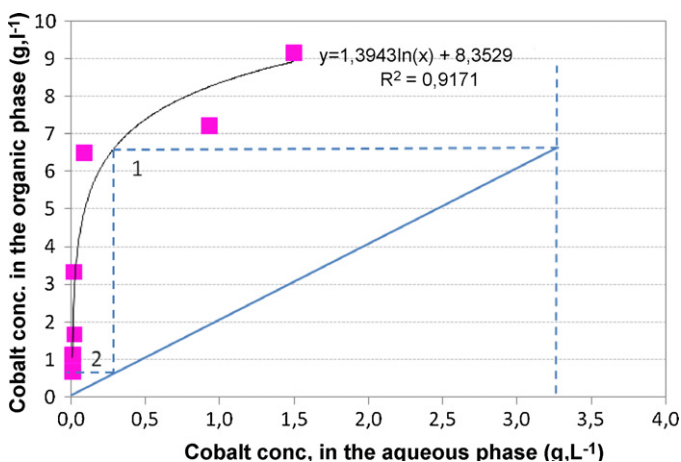


Fig. 7. Extraction isotherm of cobalt with Cyanex 272 ($[\text{Ni}] = 24.1 \text{ g L}^{-1}$, $[\text{Co}] = 3.3 \text{ g L}^{-1}$, $[\text{Cd}] = 0.7 \text{ g L}^{-1}$, $[\text{Cyanex 272}] = 0.6 \text{ M}$, $T = 25^\circ \text{C}$, $\text{pH} 5.7$).

concentrations of Cyanex 272 ($\text{pH} \approx 5.8$). Again, the higher is the concentration of extractant the higher is the metal extraction; such effect was not significant for nickel extraction because conditions were chosen to minimize its extraction. In terms of selectivity factors, calculated $\beta_{\text{Co/Ni}}$ was found to be higher than 1000 for concentrations of Cyanex 272 higher than 0.6 M, so the best con-

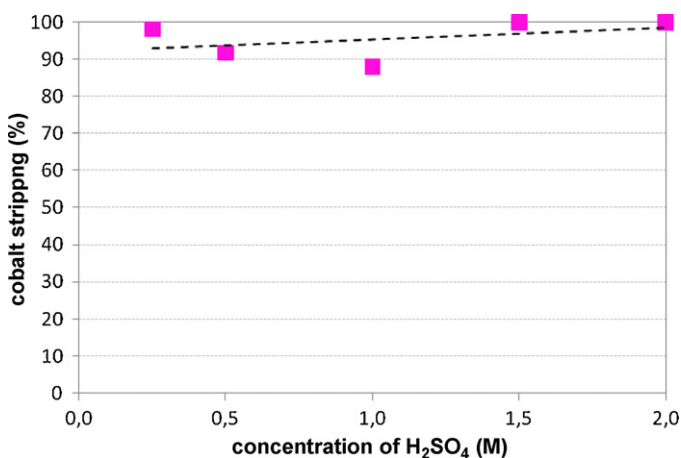


Fig. 8. Stripping of cobalt at changing H_2SO_4 concentrations (A/O ratio = 1, $T = 25^\circ \text{C}$).

dition for the separation of cobalt over nickel may occur at $\text{pH} 5.7$ with $[\text{Cyanex 272}] = 0.6\text{--}0.7 \text{ M}$. According to the isotherm shown in Fig. 7, at least two theoretical stages operated in counter-current are necessary for the removal of cobalt from the NiMH leach liquor ($[\text{Ni}] = 24.1 \text{ g L}^{-1}$, $[\text{Co}] = 3.3 \text{ g L}^{-1}$ and $[\text{Cd}] = 0.7 \text{ g L}^{-1}$, $\text{pH} 5.7$, after previous removal of cadmium with D2EHPA). As shown in Fig. 8, nearly 100% of cobalt was stripped out from the loaded organic phase ($[\text{Cyanex 272}] = 0.6$, A/O ratio = 2, $\text{pH} 5.8$, two stages, $[\text{Co}] = 2 \text{ g L}^{-1}$) at varying concentrations of H_2SO_4 ($T = 25^\circ \text{C}$ and A/O ratio = 1). The concentration of cobalt in the stripping solution was 4 g L^{-1} but more concentrated solutions can be obtained at changing A/O ratios as shown by previous study [21]. Once purified, the aqueous solutions could be directly submitted to crystallization or electrowinning operations for metal recovery.

4. Conclusions

NiMH batteries (AB_5 type) were treated using a hydrometallurgical route consisting of classification, dismantling, sulfuric acid leaching, precipitation and solvent extraction steps, aiming to recover its main metal values (rare earth elements, cobalt and nickel) for recycling purposes. The following conclusions can be drawn:

- After dismantling operation for the removal of plastic and metallic cases, the internal content of NiMH batteries was comminuted and submitted to several analysis including XRD, XRF, SEM-EDS, AAS and EDX. Nickel was found as major metal component, around 50% in weight, predominantly as Ni, NiO, $\text{Ni}(\text{OH})_2$ and NiOOH species. The presence of potassium (2.2–10.9%), cobalt (5.1–5.5%) and rare earth elements (15.3–29.0%) was also found significant. Cadmium was found in the powder of NiMH batteries at significant amount (2.8%) thus revealing that Ni–Cd batteries were labeled as NiMH, so treatment processes for NiMH batteries must consider the removal of cadmium from the residue.
- Leaching with sulfuric acid was considered efficient for the dissolution of metal content of NiMH battery powder. Cobalt, nickel and cadmium were easily leached from the powder; around 80–85% of nickel and 95–100% of cobalt was leached from the NiMH powder in one single stage. No significant effect has been identified for the operating variables concentration of H_2O_2 and temperature. The full extraction of nickel and rare earth elements will require staged operation (nearly 87% of rare earth elements (La + Ce + Pr + Nd) was leached in two stage operation).
- A mixture of rare earth elements can be separated from the acid leach liquor by precipitation with NaOH. In this study, a dense white precipitate was obtained thus corresponding to 50% removal of rare earth elements.
- Solvent extraction with D2EHPA and Cyanex 272 was found adequate to separate cadmium, cobalt and nickel from the leach liquor. In terms of selectivity factors, the removal of cadmium over cobalt is maximized at $[\text{D2EHPA}] = 0.5$ and $\text{pH} 3.0$ ($\beta_{\text{Cd/Co}} \approx 350$) while cobalt/nickel separation factors higher than 1000 were calculated at $[\text{Cyanex 272}] > 0.6 \text{ M}$, so the best condition for the separation of cobalt over nickel may occur at $\text{pH} 5.7$ with $[\text{Cyanex 272}] = 0.6\text{--}0.7 \text{ M}$. No modifier agent was necessary in the organic phase. Counter-current staged operations at given controlled pH and room temperature are suggested for scale operations.

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