



Hydrometallurgical route to recover nickel, cobalt and cadmium from spent Ni–Cd batteries

Aline Fernandes^{a,b}, Julio Carlos Afonso^{a,*}, Achilles Junqueira Bourdot Dutra^b

^a Analytical Chemistry Department, Institute of Chemistry, Federal University of Rio de Janeiro, Av. Athos da Silveira Ramos 149, Room A509, 21941-909 Ilha do Fundão, Rio de Janeiro, Brazil

^b Metallurgical and Materials Engineering Program, Federal University of Rio de Janeiro, Av. Athos da Silveira Ramos 149, Room F204, 21941-909 Ilha do Fundão, Rio de Janeiro, Brazil

H I G H L I G H T S

- ▶ Full metals separation in acidic medium.
- ▶ Cadmium and cobalt recovered by a sequential SX at high free acidity.
- ▶ Detailed study on cobalt extraction using tertiary amines in HCl medium.
- ▶ Nickel recovered as oxalate.
- ▶ Lower generation of final wastes.

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In this work a hydrometallurgical route to recover nickel, cobalt and cadmium after leaching spent Ni–Cd batteries with hydrochloric acid was investigated. Co(II) and Cd(II) were both recovered by solvent extraction. Cd(II) was first extracted (99.7 wt.%) with pure tri-n-butylphosphate (TBP), in the original leachate acidity (5.1 mol L⁻¹), in two stages at 25 °C with an aqueous/organic (A/O) phase ratio = 1 v/v. The Co(II) present in the raffinate (free acidity 4.1 mol L⁻¹) was extracted with Alamine 336 or Alamine 304 (10 vol.% in kerosene) at 25 °C with an A/O ratio = 1 in two stages. 97.5 wt.% of Co(II) was extracted using Alamine 336 while only 90.4 wt.% was extracted in the case of Alamine 304. Ni(II) was isolated from the raffinate as oxalate after addition of ammonium oxalate at pH 2.

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1. Introduction

The recycling of spent batteries is an important issue not only from the viewpoint of treatment of hazardous wastes but also due to the recovery of valuable elements present in such a waste [1]. For instance, 25% of the world produced cobalt [2–4] and about 3% of nickel [4,5] are employed for batteries manufacture. As a result of a continuous technological innovation, the number and variety of portable electronic devices (cell phones, laptops, CD players etc) has been increasing worldwide, thus resulting in an increasing demand for batteries [6]. Another consequence is the generation of increasing amounts of WEEE (waste electrical and electronic equipment) due to fast technological replacement [7,8].

Nickel–cadmium (Ni–Cd) batteries are an example of rechargeable batteries. This technology was proposed by Waldemar Jungner (1869–1924) in 1899. After some technological improvements [9] there was a burst in their consumption in the 1950s followed by another in the 1980s due to the appearance of portable electronic devices [10]. Despite its advantages, cadmium is a very toxic metal (it comprises 15–20 wt.% of the Ni–Cd battery) for humans. Nickel is also a toxic element [11]. In many applications, Ni–Cd batteries have been replaced by Ni–MH and Li-ion systems [12].

Pyro and hydrometallurgical processes are the basic technologies applied to processing spent Ni–Cd batteries. It is advisable to process spent Ni–MH and Ni–Cd batteries separately because the amount (and type) of metals are very different in each case [13]. Cadmium is volatilized at high temperatures, followed by condensation. However, a complex mixture of various materials is also obtained, thus requiring separation and purification steps [14]. Pyrometallurgical processes do not allow a direct recovery of nickel

* Corresponding author. Tel.: +55 21 2562 7555; fax: +55 21 2562 7262.
E-mail address: julio@iq.ufrj.br (J.C. Afonso).

[9,15] and present the risk of toxic gases and fine particles emissions to the environment [16].

Hydrometallurgical routes involve acid leaching followed by a combination of separation techniques. By far the most cited leaching procedures employ sulfuric or hydrochloric acid [17,18]. Solvent extraction (SX) has received much attention due to its advantages such as high selectivity and easy scale up [11,19].

Cd(II) is basically extracted from sulfuric acid medium with organophosphorus extractants [17,20–24]. On the other hand, Cd(II) easily forms chlorocomplexes in chloride medium; therefore, several extractants have been tested: crown ethers, amines (Aliquat 336, TOA, Alamine 336), carboxylic acids (versatic, naphthenic) and organophosphorus extractants (D2EHPA, Cyanex 301, 302 and 923) [15,16,25]. The main focus is to separate Cd(II) from Ni(II) and Zn(II). A limited number of studies employed TBP as extractant [13,26,27]. These studies demonstrate that the increase of free acidity increases Cd(II) extraction (HCl medium). Ni(II) and Co(II) were not significantly extracted. The advantage of extracting metals at high free acidities is avoiding partial or total neutralization of the acid leachate, thus reducing the consumption of chemicals and the generation of highly saline final effluents.

The recovery of Co(II) via SX appears to be an efficient method to separate it from nickel in acidic leachates [4]. Co(II) forms chlorocomplexes in HCl concentration higher than 2.5 mol L^{-1} , whereas Ni(II) (NiCl^+ in 2.5 mol L^{-1} HCl) only forms chlorocomplexes (NiCl_3^- and NiCl_4^{2-}) in HCl concentration higher than 10 mol L^{-1} [28]. This allows SX of Co(II) by amines in the presence of high Cl^- concentration [29]. These studies basically use synthetic solutions. Free acidity and extractant concentration have remarkable influence on Co(II) extraction [28]. Cobalt extraction using Alamine 336 as extractant increased as free acidity (as HCl) increased [28,30]. However, the amount of co-extracted Ni(II) also increased with increasing acidities [31]. The use of amines as extractants has proven to be a good alternative to separate Co(II) from Ni(II) [28,29] without changing much the original acidity of the leachate. When organophosphorus extractants are employed, the pH must be higher (>2) for an efficient Co(II) extraction [15,16,20,21,32–36]. Extracted Co(II) can be stripped with aqueous inorganic salts (NaCl , Na_2CO_3 , $(\text{NH}_4)_2\text{SO}_4$) [28].

The objective of this research is to investigate a novel hydrometallurgical route to recover cadmium, cobalt and nickel from hydrochloric acid leachates of spent Ni–Cd batteries. Cd(II) and Co(II) will be recovered by a two-step SX procedure, whereas Ni(II) will be isolated via precipitation in acidic medium.

2. Experimental

2.1. Samples and leaching procedure

300 spent batteries ($\sim 1500 \text{ g}$) used in cordless phones (four suppliers) were used in this study. They were dismantled in order to separate the internal components (anode, cathode, electrolyte). These components were leached with concentrated hydrochloric acid (12 mol L^{-1}) in a closed glass reactor equipped with a reflux condenser. The experiments were run at 40°C with a solid/liquid ratio of 150 g L^{-1} . After about 100 min all metallic parts were dissolved, producing a dark-green leachate. The insoluble matter (plastic components) was separated by filtration.

2.2. Solvent extraction (SX) procedures

The extractants employed were: TBP (Aldrich) for cadmium; Alamine 336 and Alamine 304 (Cognis Corporation) for cobalt. They were used without further purification. Deodorized kerosene (Exxon) was used as solvent. All SX experiments were performed at

25°C with an aqueous/organic (A/O) phase ratio = 1 v/v. After shaking for 5 min the system was left motionless for 10 min for phase separation. The experiments were run in triplicate and errors were within always $\pm 5\%$.

2.2.1. Cadmium extraction with TBP

In order to understand the behavior of cadmium extraction with TBP, two different studies were performed: (i) using standard CdCl_2 solutions (8, 12, 17, 20, 25 and $29 \text{ g Cd(II) L}^{-1}$); being the free acidity (as HCl) fixed at 5 mol L^{-1} ; (ii) standard Cd(II) solution (16 g L^{-1}) under different free acidities (pH 5, pH 2 and from 1 to 5 mol L^{-1}). In all experiments pure TBP was used [13]. The experiments with the leachates were performed in their original free acidities or after dilution with water (2 and 4 times). The distribution coefficient, $D_{\text{Cd(II)}}$ (dimensionless), is defined as the ratio of metal concentration in organic phase to the metal concentration in aqueous phase at reaction equilibrium [29].

2.2.2. Cobalt extraction with Alamine 336

As in the case of Cd(II), some initial studies were performed using standard Co(II) (CoCl_2) solutions: (i) the Co(II) concentration was 0.4, 0.8, 1.6, 2.4, 3.2, 4.0 and 5.0 g L^{-1} and free acidity (as HCl) 5 mol L^{-1} . Alamine 336 concentration in kerosene was 10 vol.% (0.23 mol L^{-1}); (ii) the Co(II) concentration was 0.8 g L^{-1} and Alamine 336 concentration was 10 vol.% (0.23 mol L^{-1}) under different free acidities (from 1 to 8 mol L^{-1}); (iii) the Co(II) concentration was 0.8 g L^{-1} and free acidity was 5 mol L^{-1} under different Alamine 336 concentrations (5–20 vol.%) (0.11 – 0.46 mol L^{-1}). The distribution coefficient, $D_{\text{Co(II)}}$ (dimensionless), is defined as the ratio of metal concentration in organic phase to the metal concentration in aqueous phase at reaction equilibrium [29]. The experiments using the leachate and Alamine 304 were performed under the best conditions for Alamine 336.

2.3. Nickel precipitation

After the extraction of cadmium and cobalt, the raffinate was partially neutralized with 6 mol L^{-1} NaOH so as to reach a final pH between 0 and 4. 0.3 mol L^{-1} ammonium oxalate was slowly added under stirring (200 rpm) at 60°C . Addition was stopped when the green fine precipitate (NiC_2O_4) was no longer formed. The solution became colorless and was left quiescent for 20 min before filtering the solid. It was washed with 0.01 mol L^{-1} $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (3 mL g^{-1}) and dried at 110°C for 2 h. After weighting the dried precipitate, it was dissolved in 2 mol L^{-1} HNO_3 at 60°C for chemical analysis.

2.4. Analytical methods

Metals concentrations in the leachates, organic and aqueous phases were determined by atomic absorption spectrometry (Shimadzu AA 6800). The following wavelengths were employed: cadmium, 228.8 nm; nickel, 232.2 nm; cobalt, 240.7 nm; iron, 248.3 nm; zinc, 213.9 nm manganese, 279.5 nm. Calibration curves were prepared using standard solutions in 2 mol L^{-1} HCl. The detection and quantification limits for the different metals were determined experimentally, and were found to be, respectively: 0.2 and 0.5 mg L^{-1} (Cd^{2+}); <0.1 and 0.3 mg L^{-1} (Co^{2+}); 0.05 and 0.2 mg L^{-1} (Fe^{3+}); 0.04 and 0.1 mg L^{-1} (Zn^{2+}); 0.1 and 0.4 mg L^{-1} (Mn^{2+} and Ni^{2+}). Free acidity was determined by titration with 0.1 mol L^{-1} NaOH using phenolphthalein as indicator, or by potentiometry using an Ag/AgCl reference electrode and a platinum electrode as indicator. Cl^- ions were determined by ion chromatography (Dionex DX-100).

3. Results and discussion

3.1. Composition of the leachates

Table 1 presents the concentrations of the elements in the leachates. Data agree with literature data [4,37,38], except for iron, which is present in lower amounts.

3.2. SX of cadmium

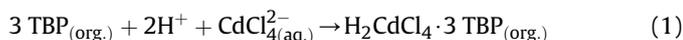
3.2.1. Influence of free acidity and metal concentration

Figs. 1 and 2 present the behavior of Cd(II) extraction with pure TBP as a function of metal concentration and free acidity, respectively. For the experiments with different Cd(II) concentrations, free acidity was fixed at 5 mol L⁻¹, which is similar to the free acidity of the leachates (Table 1).

The amount of extracted cadmium slightly decreased as Cd(II) concentration was increased. Even when [Cd(II)] = 29 g L⁻¹ (0.26 mol L⁻¹), 90 wt.% of the element was extracted in one stage. When [Cd(II)] = 17 g L⁻¹ (0.15 mol L⁻¹), which is similar to the concentration in the leachates (Table 1), 95 wt.% was extracted in one stage.

As shown in Fig. 2, Cd(II) extraction increased with increasing free acidity. This is the same result found in previous studies using TBP [13,20] and Cyanex 923 [39] under high free acidity. Cd(II) easily forms chlorocomplexes (HCl > 0.5 mol L⁻¹ [40]). When pH was 2 or higher, no cadmium was extracted. Fig. 3 presents the graph log D_{Cd(II)} versus log [H⁺]. A linear relationship is observed. The slope (2.174) suggests a relationship 2 mol H⁺ – 1 mol Cd(II). This result is the same as that found in the literature [27], although the experimental conditions are very different: Cd(II) concentration is 14 times higher in our study and TBP concentration is 3.3 times higher.

Using our data and those of a previous study where TBP dissolved in kerosene (25–100 vol.%) was used [13], the relationship TBP – Cd(II) is 3:1 (Fig. 4), which agrees with literature data [17,27], and suggests the following reaction under our experimental conditions:



3.2.2. Cd(II) extraction from Ni–Cd leachates

In the first stage (free acidity 5.1 mol L⁻¹, A/O = 1 v/v, 25 °C), 95 wt.% of Cd(II) was extracted, together with more than 99.9 wt.% of Zn(II) and more than 99.9 wt.% Fe(III). After a second stage, 99.7 wt.% of Cd(II) was extracted (Table 2). The result for one stage is comparable to the one with the standard Cd(II) solution (Fig. 2). The yield found for a one stage process was higher than that found by El Dessouky et al. [27] under a similar free acidity, although it should be considered that metals and TBP concentration in this study are much lower. Taking into account the metals concentration in the leachate (Table 1), only Fe(III) is a significant

Table 1
Elements concentration in Ni–Cd leachates.

Metals	Concentration
Cd	16.10 ± 0.09 g L ⁻¹ (1.4 × 10 ⁻¹ mol L ⁻¹)
Co	0.85 ± 0.05 g L ⁻¹ (1.0 × 10 ⁻² mol L ⁻¹)
Ni	20.80 ± 1.00 g L ⁻¹ (3.5 × 10 ⁻¹ mol L ⁻¹)
Zn	0.02 ± 0.005 g L ⁻¹ (3.0 × 10 ⁻⁴ mol L ⁻¹)
Mn	0.02 ± 0.004 g L ⁻¹ (3.0 × 10 ⁻³ mol L ⁻¹)
Fe	2.71 ± 0.06 g L ⁻¹ (8.0 × 10 ⁻² mol L ⁻¹)
Free acidity	5.1 ± 0.1 mol L ⁻¹

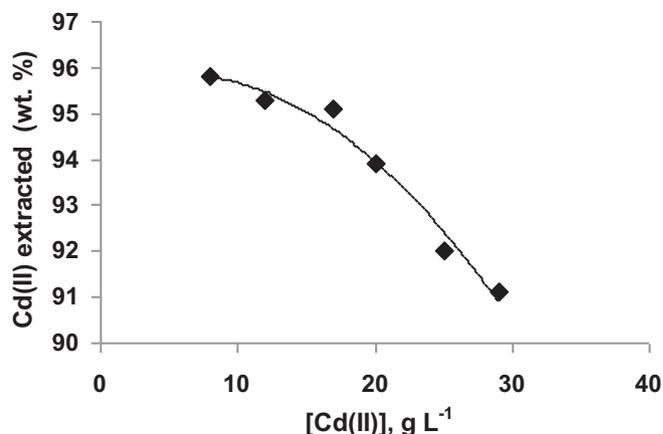


Fig. 1. Influence of the Cd(II) concentration on the SX of the element with pure TBP (free acidity (HCl) 5 mol L⁻¹). A/O phase ratio = 1, v/v, 25 °C.

contaminant in the organic phase loaded with Cd(II). As in the literature [27], Fe(III) and the tiny amounts of Zn(II) were removed by washing the organic phase with distilled water at 25 °C (A/O = 1, v/v) in one stage.

Cd(II) stripping was tested with water and HCl/H₂SO₄. The best results were obtained with 0.5 mol L⁻¹ H₂SO₄ (A/O = 1, v/v, 25 °C) in four stages (more than 99.5 wt.% of the element was removed from the organic phase). This procedure requires further studies in order to find a better stripping procedure.

3.3. SX of cobalt

3.3.1. Influence of free acidity, metal concentration and extractant concentration

Fig. 5 shows that Co(II) extraction increased with the increase of extractant concentration. This result agrees with literature data using the amine employed in this study [30]. The maximum extractant concentration is 20 vol.% (0.28 mol L⁻¹). The formation of a third phase (precipitation of the Co(II) salt) and a remarkable viscosity increase took place above this concentration. Alamine 336 concentration above 10 vol.% did not present significant advantage results. For this reason the amine concentration was fixed at 10 vol.%.

The graph log D_{Co} versus log [Alamine 336] (Fig. 6) shows that the slope is 0.7398, thus suggesting a relationship 1 mol Alamine

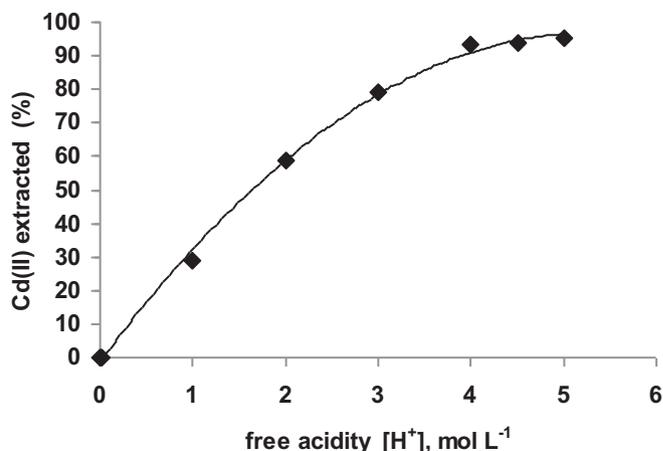


Fig. 2. Influence of the free acidity (as HCl) on Cd(II) extraction ([Cd(II)] = 16 g L⁻¹) with pure TBP. A/O phase ratio = 1, v/v, 25 °C.

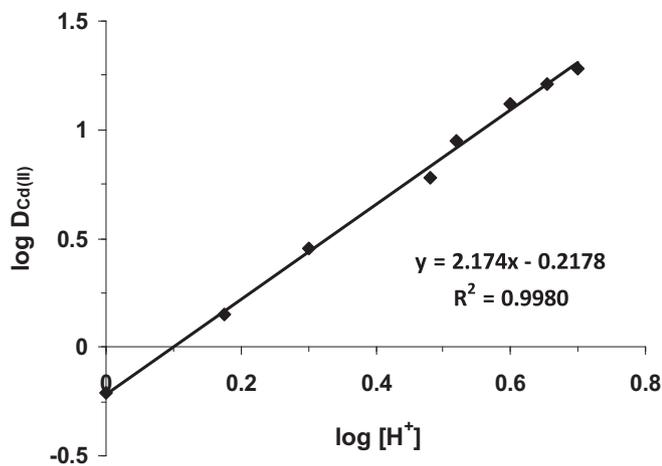
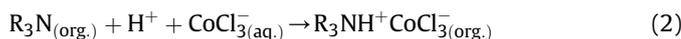


Fig. 3. $\log D_{\text{Cd(II)}}$ versus $\log [\text{H}^+]$.

336–1 mol Co(II) and the following reaction under our experimental conditions:



As shown in Fig. 7, Co(II) extraction with Alamine 336 increased at higher acidities, as expected from previous literature data [28,30,31]. The best extraction results were found for a free acidity in the range of 5–8 mol L⁻¹. The extraction of Co(II) is due to the rapid formation of anionic species (CoCl₃⁻, CoCl₄²⁻) with increasing free acidity [28,39]. At low free acidities (<2.5 mol L⁻¹) Co(II) was not significantly extracted, since the cationic species (Co²⁺, CoCl⁺) should predominate in this acidity range in chloride medium [39,41].

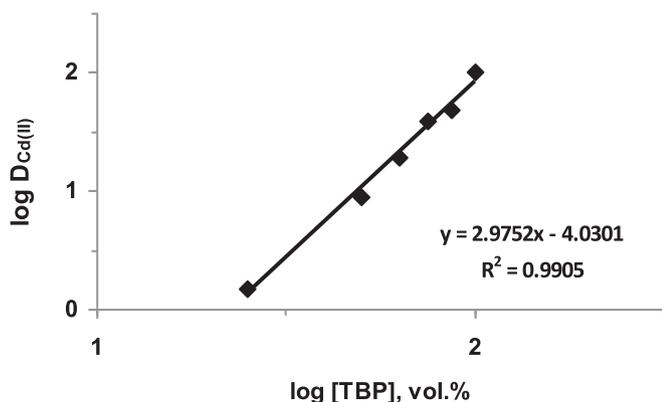


Fig. 4. $\log D_{\text{Cd(II)}}$ versus $\log [\text{TBP}]$.

Table 2

Cd(II) extraction data from Ni–Cd leachates with pure TBP (two stages, A/O = 1 v/v, 25 °C).

Metal	[M] _{initial} (g L ⁻¹)	[M] _{1st stage} (g L ⁻¹)	[M] _{2nd stage} (g L ⁻¹)	Total (%)
Cd	16.1 ± 0.09	0.77 ± 0.07	0.05 ± 0.03	99.7
Fe	2.71 ± 0.06	*	*	100
Zn	0.02 ± 0.005	*	*	100
Co	0.85 ± 0.05	0.85 ± 0.07	0.85 ± 0.04	0
Ni	20.80 ± 1.00	20.80 ± 0.12	20.80 ± 0.11	0
Mn	0.02 ± 0.004	0.02 ± 0.005	0.02 ± 0.005	0
Free acidity	5.10 mol L ⁻¹	4.70 mol L ⁻¹	4.10 mol L ⁻¹	–

*Not detected.

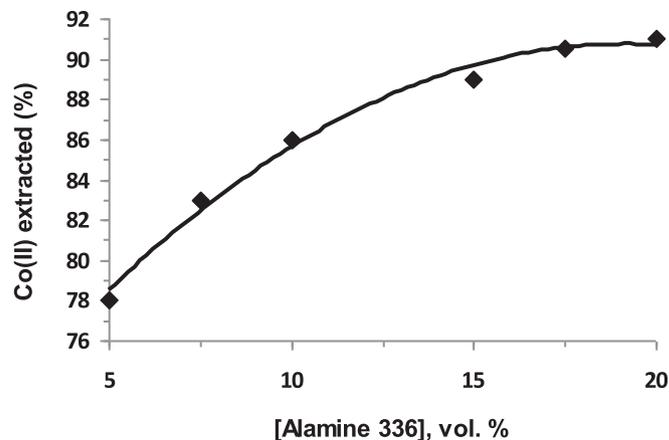
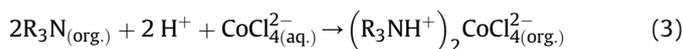


Fig. 5. Influence of Alamine 336 concentration on Co(II) extraction. [Co(II)] = 0.8 g L⁻¹, free acidity (HCl) 5 mol L⁻¹, one stage, A/O = 1 v/v.

The graph $\log D_{\text{Co}}$ versus $\log [\text{H}^+]$ (Fig. 6) shows different behaviors according to the free acidity. In very high acidities (5.2–8 mol L⁻¹, Fig. 8a) the slope is close to 2, suggesting the following reaction:



When the free acidity is in the range of 4–5 mol L⁻¹ (Fig. 8b) the slope is 1.2515. This result agrees with the proposed reaction for cobalt extraction as a function of Alamine concentration (Fig. 6, Eq. (1)), since the free acidity was set at 5 mol L⁻¹. This behavior can be explained by the change of cobalt species distribution formed under different free acidities [39,41].

As for Cd(II) (Fig. 1), the increase of Co(II) concentration decreased the extraction yield (Fig. 9). This behavior has already been observed in the literature [30,31] and can be attributed to saturation of the solvent [41].

3.3.2. Behavior of Ni(II)

Ni(II) extraction with Alamine 336 was also studied using standard NiCl₂ solutions (12, 24, 36 and 38 g L⁻¹ Ni(II)) in order to determine its behavior under the best conditions for Co(II) extraction. Data of Fig. 10 show that some Ni(II) was extracted (3.8 wt.% at 48 g L⁻¹). When Ni(II) concentration was below 24 g L⁻¹, there was no significant extraction. This result is very different from previous literature data [31] under comparable conditions, where 60 wt.% of the element was extracted from

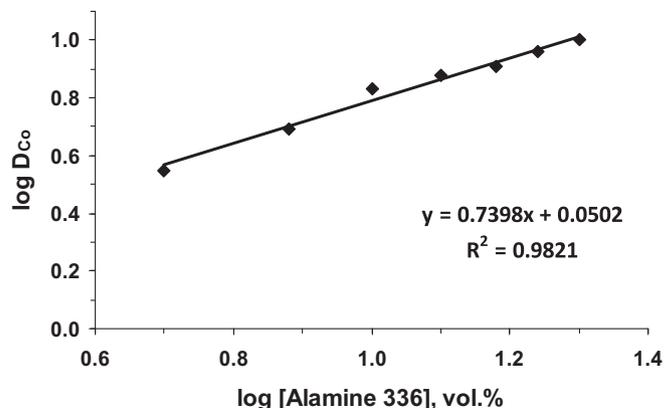


Fig. 6. $\log D_{\text{Co(II)}}$ versus $\log [\text{Alamine 336}]$ (free acidity 5 mol L⁻¹). Data from this work and reference [13].

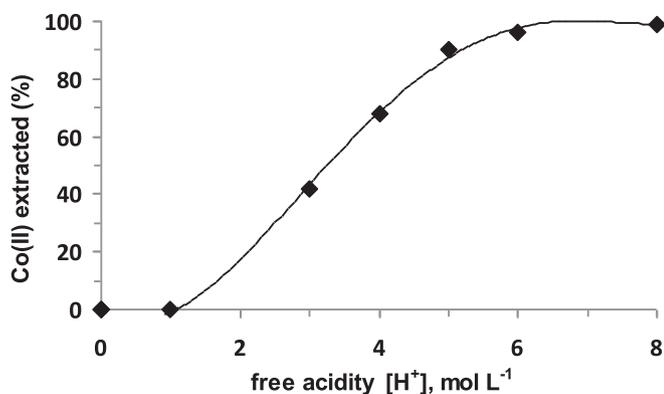


Fig. 7. Influence of the free acidity on Co(II) extraction with Alamine 336 (10 vol.% in kerosene). [Co(II)] = 0.8 g L⁻¹, one stage, A/O = 1 v/v, 25 °C.

a solution containing 3 g L⁻¹. Therefore, Alamine 336 is much more selective for Co(II) than for Ni(II) under our experimental conditions. This is the expected result due to the predominance of NiCl⁺ and NiCl₂ species in the acidity range used in this work [28,39–41].

3.3.3. Extraction of Co(II) from Ni–Cd leachates

In one stage, 87 wt.% of Co(II) and only ~1 wt.% of Ni(II) were extracted (Table 3). This result is comparable to the experiments

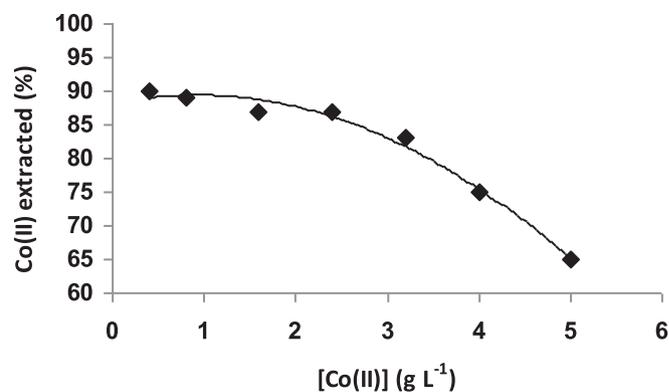


Fig. 9. Influence of Co(II) concentration on its extraction with Alamine 336 (10 vol.% in kerosene). Free acidity (HCl) 5 mol L⁻¹, one stage, A/O = 1 v/v, 25 °C.

with standard Co(II) and Ni(II) solutions (Sections 3.3.1 and 3.3.2). After a second stage, 97.5 wt.% of Co(II) and 2.9 wt.% of Ni(II) were extracted. These results are better than those reported in the literature [28] using comparable experimental conditions, where Ni(II) was much more co-extracted. The overall cobalt recovery is comparable to data for element recovery from spent NiCd and Ni–MH battery leachates using organophosphorus extractants [15,16,32,33], but without changing the free acidity of the leachate.

3.3.4. Extraction of Co(II) using Alamine 304

The experiments performed with this amine were run with the best experimental conditions achieved for Alamine 336. After a two-stage SX, 90.4 wt.% of Co(II) and 23.1 wt.% of Ni(II) were extracted from the raffinate (Table 4). These results indicate that Alamine 304 is much less selective for Co(II) than Alamine 336 because a considerable amount of Ni(II) was co-extracted.

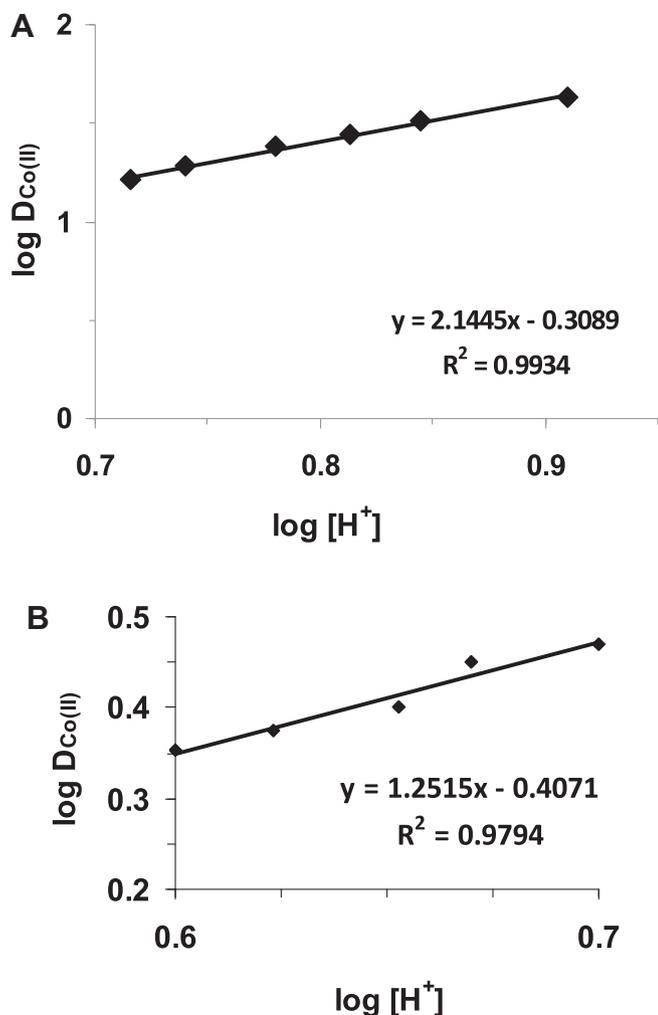


Fig. 8. log $D_{Co(II)}$ versus log $[H^+]$.

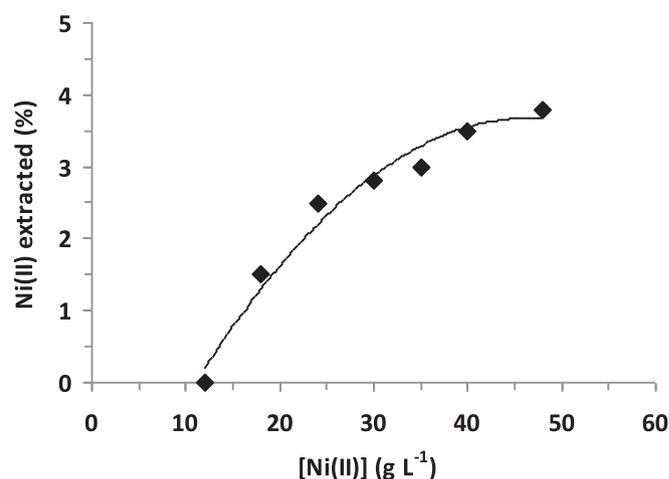


Fig. 10. Extraction of Ni(II) with Alamine 336 (10 vol.% in kerosene). Free acidity (HCl) 5 mol L⁻¹, one stage, A/O = 1 v/v, 25 °C.

Table 3

Co(II) and Ni(II) extraction data from Ni–Cd leachates with Alamine 336 (10 vol.% in kerosene, two stages, A/O = 1 v/v, 25 °C).

Metal	[M] _{initial} (g L ⁻¹)	[M] _{1st stage} (g L ⁻¹)	[M] _{2nd stage} (g L ⁻¹)	Total (%)
Co	0.85 ± 0.04	0.11 ± 0.02	0.02 ± 0.005	97.5
Ni	20.80 ± 0.11	20.62 ± 0.04	20.20 ± 0.09	2.9
Mn	0.02 ± 0.005	0.02 ± 0.006	0.02 ± 0.004	0
Free acidity	4.10 mol L ⁻¹	4.10 mol L ⁻¹	4.00 mol L ⁻¹	–

*Not detected.

Table 4

Co(II) extraction from Ni–Cd leachates^a with Alamine 304 (10 vol.% in kerosene, two stages, A/O = 1 v/v, 25 °C).

Metal	[M] _{initial} (g L ⁻¹)	[M] _{1st stage} (g L ⁻¹)	[M] _{2nd stage} (g L ⁻¹)	Total (%)
Co	0.85 ± 0.04	0.22 ± 0.01	0.08 ± 0.005	90.4
Ni	20.80 ± 0.11	17.21 ± 0.51	16.02 ± 0.70	23.1
Mn	0.02 ± 0.005	0.02 ± 0.005	0.02 ± 0.004	0
Free acidity	4.10 mol L ⁻¹	4.00 mol L ⁻¹	3.80 mol L ⁻¹	–

^a After Cd, Zn and Fe removal with TBP (data on Table 2).

3.4. Nickel recovery

Nickel oxalate (NiC₂O₄) only begun to precipitate at pH 0.5. 99 wt.% of Ni(II) was precipitated at pH 2. This result was not modified at higher pH. Among the interfering elements (Table 5), Fe(III) and Zn(II) were previously extracted with TBP, whereas Mn(II) did not co-precipitate (<0.01 wt.% of the NiC₂O₄ precipitate). The only interfering element is the non-extracted Co(II) by Alamine 336 but it comprises only 0.16 wt.% of the solid (as CoC₂O₄). Cl⁻ ions were not detected.

Table 5

Chemical analysis (wt.%) of NiC₂O₄ after filtration and drying.

Cations	Amount	Anions	Amount
Ni ²⁺	99.93 ± 0.05	C ₂ O ₄ ²⁻	>99.95
Co ²⁺	0.07 ± 0.01	Cl ⁻	Not detected
Mn ²⁺	<0.01		
Cd ²⁺ , Zn ²⁺ and Fe ³⁺	Not detected		

4. Conclusions

The internal components of spent Ni–Cd batteries were leached with 12 mol L⁻¹ HCl (40 °C, 100 min). Cd(II) was extracted from the leachate with pure TBP (free acidity 5.1 mol L⁻¹, A/O = 1 v/v, 25 °C). In one stage, 95 wt.% of the element was extracted, and after two stages, 99.7 wt.% of Cd(II) was removed from the aqueous phase. Zn(II) and Fe(III) were also extracted but were easily stripped after washing the organic phase with water. Cd(II) stripping was performed with 0.5 mol L⁻¹ H₂SO₄ (A/O = 1 v/v) in four stages. This step requires further studies in order to improve it. Cd(II) extraction follows the relationships 1 mol H⁺ – 1 mol Cd(II) and 3 mol TBP – 1 ml Cd(II).

Co(II) was successfully extracted from the raffinate with Alamine 336 (10 vol.% in kerosene) at 25 °C, under free acidity 4.1 mol L⁻¹ and A/O ratio = 1 v/v. In two stages, 97.5 wt.% of the element was extracted and only 2.9 wt.% of Ni(II) was co-extracted. Alamine 304 was less efficient (90.4 wt.% after two stages) whereas Ni(II) co-extraction was much higher (23.1 wt.%). Co(II) extraction follows the relationship 1 mol Alamine 336–1 mol Co²⁺. The optimum extraction zone was in the free acidity range of 5–8 mol L⁻¹. Tertiary amines appear to be good extractants for Co(II) in high free acidity. Ni(II) was successfully precipitated as oxalate (>99 wt.%) at pH 2. The non-extracted Co(II) is its only significant contaminant.

The complete separation of metals in high acidity prevents the use of reagents normally used for partial/total neutralization of the leachate, and reduces the volume (and salinity) of the wastewater generated in the separation processes.

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