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Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid–liquid extraction with Cyanex 272

Danuza Pereira Mantuano, Germano Dorella,
Renata Cristina Alves Elias, Marcelo Borges Mansur*

Departamento de Engenharia Química, Universidade Federal de Minas Gerais
Rua Espírito Santo, 35, 6° andar, CEP 30160-030 Belo Horizonte, MG, Brazil

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Abstract

A hydrometallurgical route is proposed to recover zinc and manganese from spent alkaline batteries in order to separate base metals such as nickel, copper, aluminium, cadmium, lithium and cobalt which constitute the main metallic species of spent NiCd, NiMH and Li-ion rechargeable batteries. The route comprises the following main steps: (1) sorting batteries by type, (2) battery dismantling to separate the spent battery dust from plastic, iron scrap and paper, (3) leaching of the dust with sulphuric acid and (4) metal separation by a liquid–liquid extraction using Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) as extractant. The metal content of NiCd, NiMH and Li-ion batteries from three distinct manufacturers has been evaluated. A factorial design of experiments was used to investigate the leaching step using operational variables such as temperature, H_2SO_4 concentration, S/L ratio and H_2O_2 concentration. Analysis of metal separation by the liquid–liquid extraction with Cyanex 272 identified a $pH_{1/2}$ 2.5–3.0 for zinc and aluminium, $pH_{1/2}$ 4.0–4.5 for manganese, cadmium, copper and cobalt, $pH_{1/2}$ 6.5 for nickel and $pH_{1/2}$ 8.0 for lithium. These results indicate that batteries must be previously sorted by type and treated separately. In addition, data fitting to an equilibrium model proposed for the reactive test system by the European Federation of Chemical Engineering (EFChE) have indicated that $MR_2(RH)_2$ and MR_2 complexes (where M = Zn, Mn, Co, Cd and Cu) co-exist in the organic phase with Cyanex 272 depending on the loading conditions. The route has been found technically viable to separate the main metallic species of all batteries considered in this study.

Keywords: Leaching; Liquid–liquid extraction; Cyanex 272; NiCd batteries; NiMH batteries; Li-ion batteries

1. Introduction

The increasing public concern about the environment in the last decade has resulted in stricter regulations worldwide particularly those related to the adequate destination of hazardous residues containing heavy metals such as spent portable batteries. It has prompted society to look for technical alternatives in order to treat these types of residues since the consumption of batteries is considerable around the world. In the USA and Europe, for instance, it is estimated to be 8 billion units per year [1]. In Japan, around 6 billion batteries were produced in 2004 while almost 1 billion units are consumed every year in Brazil [2].

According to the directives published in many countries, the adequate destination of spent batteries may involve methods such as landfill disposition, stabilisation, incineration and/or recycling processes. Safe disposal in landfills or stabilisation of battery residues becomes more and more expensive due to the increasing amount of waste produced, and also due to the limited storage capacity of sanitary landfills and/or special waste dumpsites. Incineration of batteries is an expensive method as well and it can even cause mercury, cadmium and dioxin emissions into the environment [1]. Therefore, the recycling of spent batteries appears as the most adequate destination for this type of waste. As pointed out by Conard [3], the recycling of wastes is important since it may contribute to the benefit of future generations and to the preservation of raw materials.

The large amount of portable batteries consumed worldwide is of the primary type such as zinc-carbon and alkaline cells. These batteries represent around 90% of the European market

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* Corresponding author. Tel.: +55 31 3238 1780; fax: +55 31 3238 1789.
E-mail address: mansur@deq.ufmg.br (M.B. Mansur).

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Nomenclature

C	concentration ($\mathrm{mol\,l^{-1}}$)
K_C	equilibrium coefficient defined by Eq. (3) $(\mathrm{mol\,l^{-1}})^{n-m/2}$
K_D	equilibrium coefficient defined by Eq. (1) $(\mathrm{mol\,l^{-1}})^{2-n}$
m	stoichiometric constant for the homogeneous reaction
n	stoichiometric constant for the heterogeneous reaction
V	volume (l)

Subscripts

aq	aqueous phase
BD	dimer-Cyanex 272
CD	organo-metallic complex formed according to Eq. (1)
CM	organo-metallic complex formed according to Eq. (3)
H	hydrogen ion
M	metallic ion
org	organic phase

[1]. However, the consumption of rechargeable batteries has grown substantially in the last few years accompanying their increasing in the mobile phone market. In Brazil, the number of mobiles has increased 21% in 2002, 33% in 2003 and 42% in 2004 [4]. In 2005, one-third of the Brazilian population had a mobile phone (around 80 million phones); in Brasilia, as in Sweden, the number of mobile has surpassed its population. Nowadays, the consumption of rechargeable batteries represents only 8% of the market in Europe [1] but it is tending to increase [5].

In order to promote a general recycling route, the metal composition of batteries must be known. The metal content of zinc-carbon and alkaline batteries consists mainly of manganese, zinc and potassium [2,6] while that of rechargeable batteries depends on the battery type. The batteries commonly used in mobile phones are nickel-cadmium (NiCd), nickel-metal-hydride (NiMH) and lithium-ion (Li-ion). Typical metal composition of these batteries is shown elsewhere [2,5]. Because of the high toxicity of cadmium, NiCd batteries have been progressively replaced by NiMH and Li-ion types in mobile phone applications [5] but NiCd batteries are still used in hospital, industry and military equipments. Cobalt and nickel are found in practically all types of mobile phone batteries. These metals are relatively expensive. Data from London Metal Exchange from January to October 2004 have shown that nickel is about eight times more expensive than aluminium and five times more expensive than copper; the price of cobalt is even higher, around three times that of nickel. Therefore, the recycling of spent rechargeable batteries would seem to benefit not only the environment but also from the economy.

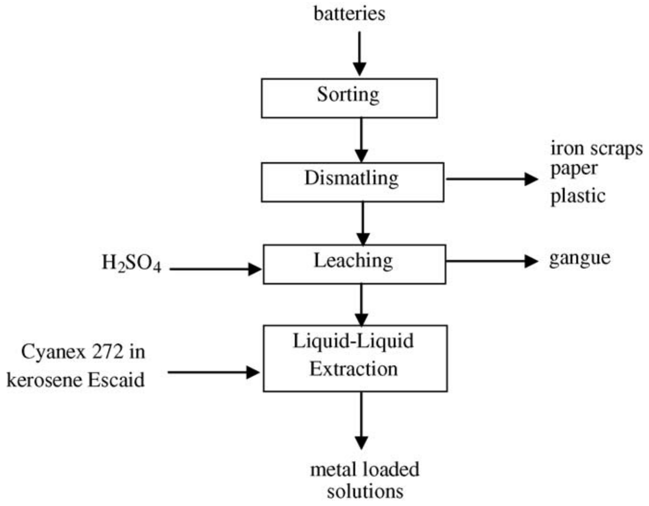

Fig. 1. Scheme of the hydrometallurgical route evaluated in this paper to treat NiCd, NiMH and Li-ion batteries.

Recycling processes of waste materials must be as simple and as cheap as possible. An overview of the current processes including pyrometallurgical and hydrometallurgical routes for the recycling of portable batteries is shown elsewhere [1,2,7]. In this paper, a hydrometallurgical route developed to recover zinc and manganese from alkaline and zinc-carbon batteries [2] is extended in order to separate base metals from NiCd, NiMH and Li-ion portable batteries. The route comprises the main steps schematically shown in Fig. 1: preliminary treatment of batteries, followed by leaching with sulphuric acid and metal purification/separation by liquid–liquid extraction with Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) as extractant.

The preliminary treatment of batteries consists of sorting and dismantling. The collected batteries are firstly sorted by type (i.e., by chemical composition) in order to make leaching and liquid–liquid extraction operations more efficient [1,8]. In the dismantling step, the spent battery dust is separated from plastic, iron scraps and paper residues which can be recycled. The dust is leached by an acidic solution in order to transfer the metals of interest from the dust to the aqueous liquor. Table 1 summarises the best operational conditions found by several authors for the leaching of portable batteries including different acidic media such as sulphuric, hydrochloride and nitric. No study has been found in the literature using sulphuric acid as leaching agent for NiMH and Li-ion batteries.

NiCd, NiMH and Li-ion batteries contain nickel and/or cobalt in a relatively high grade, so liquid–liquid extraction is an attractive method to separate these metals. The following industrial battery-recycling processes use liquid–liquid extraction as the separation method:

- *TNO*: This route has been developed for the recycling of NiCd batteries. Nickel and cadmium are leached in 6N HCl solution at 90 °C with a solid/liquid ratio of 10/1. Cadmium is selectively extracted from the liquor by liquid–liquid extraction using 75% of tributilphosphate (TBP) dissolved in kerosene

Table 1
Summary of the best operational conditions for the leaching of spent portable batteries

Type of battery	Reference	Leaching agent	Temperature (°C)	Time (h)	S/L ratio (g ml^{-1})	Reduction agent	Results
Alkaline	[9]	6.0 mol l^{-1} H_2SO_4	50	2	1/5	H_2O_2	53% Mn, 75% Ni, Cd, Hg and 100% Zn, Fe
	[10]	0.13 mol l^{-1} H_2SO_4	50	2	1/50	H_2O_2	Around 100% Zn and 30% Mn
	[11]	0.9 mol l^{-1} H_2SO_4	50	0.5	1/10	No agent	72.8% Zn from anode after thermal treatment
	[2]	0.19 mol l^{-1} H_2SO_4	87 ± 2	2	1/10	No agent	Around 100% Zn and 40% Mn
	[6]	Water	25	0.33	1/5	No agent	99% K
		0.56 mol l^{-1} H_2SO_4	40	0.33	1/30	2% (v/v) H_2O_2	100% Zn and Mn
NiCd	[12]	4.0 mol l^{-1} HCl	60	2	1/15–1/45	No agent	–
	[13]	2.5 mol l^{-1} H_2SO_4	95	4	1/20	No agent	Around 100% Ni, Cd, Co
NiMH	[14]	3.0 mol l^{-1} HCl	95	3	1/9	No agent	96% Ni, >99% rare earths and 100% Co
Li-ion	[15]	4.0 mol l^{-1} HCl	80	1	1/10	No agent	Around 100% Li, Co
	[16]	2.0 mol l^{-1} HNO_3	80	2	–	No agent	Around 100% Li
	[17]	1.0 mol l^{-1} HNO_3	75	1	1/50	1.7% (v/v) H_2O_2	Around 85% Li, Co

Shellsol R, stripped out using a diluted HCl solution and recovered from this solution by electrolysis.

- *Batenus*: This process can treat any type of battery, except button cells that contain high levels of mercury. After leaching with sulphuric acid, the zinc present in the liquor is separated by liquid–liquid extraction while copper, nickel and cadmium are selectively separated by ion exchange. The stripping of the organic phase with sulphuric acid yields a pure zinc sulphate solution from which zinc metal is generated electronically [18].
- *Zincex*: This route has been developed for the recycling of alkaline batteries. Zinc is extracted from a sulphuric leach liquor using di-2-ethylhexyl phosphoric acid (D2EHPA) as extractant dissolved in kerosene Escaid 100 and stripped out in a H_2SO_4 solution. A high quality of the loaded zinc electrolyte is suitable to produce zinc metal SHG or a highly pure zinc sulphate solution by evaporation [19].

The treatment of NiCd batteries using a liquid–liquid extraction as the separation method has been investigated using D2EHPA and Cyanex 272 as extractants [20]. Equilibrium tests carried out in an aqueous sulphuric solution containing 1.0 g l^{-1} of metal with an organic solution containing 1.0 mol l^{-1} of extractant at aqueous/organic (A/O) volumetric ratio of unity have shown that the metals were extracted according to the following sequence for both extractants investigated: $Cd^{2+} > Co^{2+} > Ni^{2+}$. D2EHPA was found to be more selective for cadmium whereas Cyanex 272 was found to be more selective for nickel. In addition, practically constant separation factors for D2EHPA have been obtained at $1.5 \leq pH \leq 3.0$ ($\beta_{Cd/Co} = 45$ and $\beta_{Cd/Ni} = 110$), so the authors proposed removal of cadmium from the chloride leach liquor with D2EHPA and sent the raffinate for Co–Ni separation with Cyanex 272.

D2EHPA has been applied also to recover metals from leach liquors of NiMH batteries [14]. The following metal extraction sequence with pH from chloride aqueous solutions using 25% (v/v) of D2EHPA dissolved in kerosene has been obtained: $Zn^{2+} > Mn^{2+} > Cu^{2+} > Cd^{2+} \sim Co^{2+} > Ni^{2+}$. The $pH_{1/2}$ of metals Zn^{2+}, Mn^{2+}, Fe^{3+} and Al^{3+} is below 3.0 while for Co^{2+} and Ni^{2+} their $pH_{1/2}$ values are 4.08 and 4.52, respectively. According to these results, cobalt and nickel are extracted together with D2EHPA and separated from each other in a further purification step. Experiments carried out in two counter-current stages at a A/O volumetric ratio of 1/3 resulted in extraction levels of 87.5% of zinc, 99.6% of manganese and aluminium, 100% of iron and rare earths, 13% of cobalt and nil nickel. According to the authors, the extraction of zinc with D2EHPA was incomplete due to the formation of non-extractable acquo-complexes of zinc and chloride ions.

The liquid–liquid extraction separation method has been applied to recover cobalt and lithium from chloride leach liquors of Li-ion batteries using 0.29 mol l^{-1} of D2EHPA or 0.30 mol l^{-1} of PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) as extractants [15]. Both reagents have shown a quite similar behaviour with pH in the extraction step. Cobalt extraction increased with pH and it was fully extracted at $pH \geq 6.5$. The extraction of lithium started only at $pH > 5.5$ and it increased very slowly with pH (around 18% at pH 7.0). Large separation factor values $\beta_{Co/Li}$ have been obtained for the operational conditions studied (710 and 88,000 for D2EHPA and PC-88A, respectively), so PC-88A is more selective than D2EHPA to separate cobalt from lithium. Once loaded with cobalt, the organic phase has been washed with an aqueous chloride solution of $CoCl_2$ in order to remove traces of co-extracted lithium. Then, the cobalt was stripped out from the washed extract solution by 2.0 mol l^{-1} of H_2SO_4 at an A/O ratio of 1/5. The stripping solution containing 108 g l^{-1} of cobalt was submitted to a crystallisation step resulting in salts of $CoSO_4 \cdot 6H_2O$ with 99.99 wt.% purity. Around 80% of the lithium that remained in the raffinate has been recovered as $LiCO_4$ 99.30 wt.% purity by precipitation with $NaCO_4$ solution at 100 °C.

In the present work, the use of a liquid–liquid extraction technique for the separation of base metals present in the leach liquors from NiCd, NiMH and Li-ion batteries is highlighted. Cyanex 272 has been chosen as extractant because it is a very efficient reagent to separate cobalt and nickel from both sulphate and chloride media [21]. The leaching step has been investigated using a factorial analysis design. In the liquid–liquid extraction study, the separation level of several metals according to their equilibrium pH has been assessed and stoichiometric reactions have been proposed based on the model valid to the test system $ZnSO_4$/D2EHPA by the European Federation of Chemical Engineering (EFChE) [22] in order to simulate the metal separation process with Cyanex 272.

2. Experimental

2.1. Materials and reagents

Spent NiCd, NiMH and Li-ion batteries from three different manufacturers (namely A, B and C) were used in this study. The leaching solutions consisted of aqua regia and sulphuric acid solutions at specified concentrations in distilled water.

The extractant Cyanex 272 was kindly supplied by Cytec Canada and it was used as received (without any further purification, average content of active reagent equal to 85 wt.% purity). The commercial kerosene Escaid 110 was used as diluent (mainly aliphatic, aromatics content of 0.1%, w/w). The aqueous solutions used in the liquid–liquid extraction tests were prepared by dissolving sulphate salts of the respective metals Zn, Mn, Ni, Cu, Al, Cd, Li and Co in distilled water. All salts and acids were of analytical grade. No modifier was used in these experiments because no problem concerning to phase disengagement or third phase formation was observed.

2.2. Dismantling step and metal characterisation of batteries

Batteries were dismantled manually to separate the spent dust from plastic, paper and iron scraps. The battery dust was dried in a drying oven for 24 h at 60 °C in order to determine the content of volatile substances. The dried dust of NiCd and NiMH batteries was submitted to a grinding step using a ball mill for 30 min to provide a fine powder that was screened in sequential sieves with openings ranging from 10 to 500 μm. A distinct procedure has been adopted for the Li-ion batteries because these cells are made of two thin electrode films, one made of metallic copper and other of aluminium; both films are covered by the active material of the Li-ion battery, thus containing lithium and cobalt as a fine powder of $LiCoO_2$ aggregated with a polymeric binder [23] and rolled up in cylindrical or prismatic shape. So, in order to get homogeneous samples of Li-ion batteries for the leaching step, both copper and aluminium dried films were cut into small pieces using scissors. All tests were carried out using homogeneous samples of NiCd and NiMH powders (collected using a Quantachome siewing rifler, model SRR-5 with eight collecting plates) and Li-ion small pieces films.

Samples of NiCd, NiMH and Li-ion batteries were submitted to fluorescence for qualitative analysis of metal content. The quantitative analysis was determined by atomic absorption spectrophotometry (GBC 932 plus model) after dissolving samples in aqua regia of batteries from three distinct manufacturers.

All steps in the experimental procedure were carried out using glasses, gloves and gas masks for safe operation.

2.3. Leaching step

Leaching tests were carried out in a 1000 ml covered reactor made of glass immersed in a controlled temperature bath under constant stirring for 1 h. Factorial design and analysis of experiments using the software Minitab were done to determine the main effects and interactions for the leaching process of NiCd, NiMH and Li-ion batteries in sulphuric acid solutions. The main responses under investigation were the percentages of leached metals nickel, cobalt and manganese for NiMH batteries, nickel, cadmium and cobalt for NiCd batteries, and aluminium, copper, cobalt and lithium for Li-ion batteries. In the case of NiMH, 27 tests were carried out including a triplicate test for the average. The following variables and levels were studied at 50 °C: sulphuric acid concentration (2, 5 and 8%, v/v), solid/liquid ratio (1/10, 1/30 and 1/50 g powder per ml of solution) and H_2O_2 concentration (0, 2 and 4%, v/v). The last variable has been analysed because reduction agents such as H_2O_2 may affect the manganese leaching rate as verified in alkaline battery studies [10]. In the case of NiCd and Li-ion batteries, 2^3 tests were done in triplicate and the following variables (and levels) were studied: sulphuric acid concentration (4 and 8%, v/v), temperature (50 and 80 °C) and solid/liquid ratio (1/10 and 1/50 g ml^{-1} for NiCd batteries; 1/30 and 1/50 g ml^{-1} for Li-ion batteries). After each leaching test, the pulp was filtered and the filtrate submitted to atomic absorption spectrophotometry analysis.

2.4. Liquid–liquid extraction step

Liquid–liquid extraction experiments were carried out with suitable volumes of aqueous sulphate solutions containing 0.1 mol l^{-1} of metals found in the batteries (Zn, Mn, Ni, Cu, Al, Cd, Li and Co) with an organic phase consisting of 0.3 mol l^{-1} Cyanex 272 (monomeric base) dissolved in Escaid 110. The experiments were carried out at 50 °C in a cylindrical glass reactor of 400 ml provided with a glass impeller, a thermometer and a pH electrode (Digimed DM 20). Both phases were mechanically stirred for 20 min (time enough to reach equilibrium as verified in preliminary tests for all metals studied). The pH was controlled by addition of small quantities of NH_4OH (1, 3, 6 and 12 mol l^{-1}) and H_2SO_4 (12 mol l^{-1}) solutions. After phase separation, the metal concentration in the aqueous phase was analyzed by atomic absorption and the concentrations in the organic phase were determined by mass balance. Experiments were carried out to determine: (1) the $pH_{1/2}$ of various metals at constant A/O volume ratios of unity and (2) equilibrium isotherms at changing A/O ratios (5/1, 3/1, 2/1, 1.5/1, 1/1, 1/1.5, 1/3, 1/5). Data were fitted to the equilibrium model proposed for the reactive test system $ZnSO_4$/D2EHPA by the EFChE which is valid over a wide concentration range of extraction and stripping conditions [22].

3. Results and discussion

3.1. Dismantling and characterisation of batteries

NiCd, NiMH and Li-ion batteries from manufacturers A, B and C were dismantled and the following components were found (in wt.%): spent dust 47 ± 7, iron scraps 24 ± 3, plastic cases 23 ± 8 and paper 3 ± 2. These results indicate that around 50 wt.% of the spent battery residue constitutes the feed to be treated by the hydrometallurgy route evaluated in this paper. The small fraction of paper obtained was contaminated with dust so it should be treated together with dust or incinerated, while plastic cases and iron scraps may be washed and submitted for recycling.

The content of volatile substances in the spent dust of NiCd, NiMH and Li-ion batteries was determined to be 6.7, 5.8 and 4.0 wt.%, respectively. These figures are quite similar to 6.0 wt.% found for alkaline batteries [6].

The particle size distribution of the NiCd and NiMH battery powders has been assessed using sieves in a series from 10 to 500 μm. Both powder sources were found very fine (Sauter mean diameter of 16 and 30 μm, respectively, as calculated by the sigmoidal model), so leaching is expected to be fast. However, the powder was found too polydisperse according to Geldart's parameter [24] ($GD \gg 0.17$ for both powders), so the powder is heterogeneous and the calculated mean diameters are not representative of the population.

Table 2 shows the average metal content of dried samples of NiCd, NiMH and Li-ion batteries for manufacturers A, B and C, including the interval of 95% of confidence level in order to show their variability. It can be observed that the metal composition differs according to the battery type but not significantly between manufacturers. This result reveals that batteries must be sorted by type, independent of manufacturer.

Metals found in more significant quantities for each type of battery are shown in Table 2. Such metal composition indicates that NiMH(AB_5) and Li-ion(Co) types were used in this study [5]. The metals nickel, cobalt and cadmium were found at relatively higher grades compared to the other metals analyzed. The first two metals are valuable while cadmium is toxic, so the separation of these metals from batteries is both economic and environmentally positive [25].

3.2. Acid leaching step

The leaching step was investigated using a factorial design of experiments in order to qualitatively determine the main effects and interactions of the leaching process of NiCd, NiMH and Li-ion batteries in sulphuric acid solutions. A summary of main effects for each metal considered in the study is shown in Table 3.

In the case of NiMH batteries, metals were preferentially leached according to the following sequence for the operational conditions investigated: nickel ≫ cobalt ≈ manganese. It has been found that variables "concentration of sulphuric acid" and "S/L ratio" are statistically significant for the leaching of cobalt, manganese and nickel (95% of confidence level). In fact, these variables are closely related to the quantity of leaching agent in the aqueous phase, so the more the amount of acid in the leach solution the higher is the metal leaching rate as shown in Fig. 2 for the leaching of nickel at different S/L ratios. No significant effect from the statistical point of view has been identified for the variable "concentration of H_2O_2" as shown in Fig. 3 for the leaching of manganese. Therefore, no interaction of a third order has been found to be significant. The use of H_2O_2 was found unnecessary to leaching NiMH batteries for the operational range investigated.

In the case of NiCd batteries, metals were preferentially leached according to nickel ≈ cadmium > cobalt for the operational conditions investigated. The leaching rate of metals was mainly influenced by the variables: "concentration of sulphuric acid" and "temperature", and no third order interaction was found to be significant.

In the case of Li-ion batteries, metals were leached according to the following sequence for the operational conditions investigated: aluminium > lithium > cobalt ≫ copper. The leaching of cobalt was influenced by all variables studied but it was found relatively low for economical purposes (around 30%). It may be

Table 2
Average metal composition of NiCd, NiMH and Li-ion batteries determined for three different manufacturers (A, B and C) (wt.%)

	NiCd				NiMH				Li-ion			
	A	B	C	Average (wt.%)	A	B	C	Average (wt.%)	A	B	C	Average (wt.%)
Al	0.01	0.02	0.03	0.02 ± 0.01	0.81	0.94	0.85	0.9 ± 0.1	10.0	6.5	6.6	8 ± 3
Cd	39.4	35.3	28.4	34 ± 8	0.01	n.d.	n.d.	<0.01	0.03	0.01	0.03	0.02 ± 0.02
Co	2.08	2.56	1.43	2.0 ± 0.8	5.64	6.16	6.64	6.1 ± 0.7	42.9	30.8	34.2	36 ± 9
Cu	0.03	–	–	0.03	0.02	–	–	0.02	13	–	–	13
Fe	0.01	0.03	0.04	0.03 ± 0.02	0.09	0.06	0.15	0.10 ± 0.07	0.03	0.06	0.10	0.06 ± 0.05
Li	0.05	0.07	0.04	0.05 ± 0.02	0.05	0.07	0.10	0.07 ± 0.04	8.88	2.48	2.45	5 ± 6
Mn	n.d.	0.01	n.d.	<0.01	1.11	1.37	2.62	2 ± 1	n.d.	n.d.	0.01	<0.01
Ni	14.3	19.8	33.3	22 ± 14	46.8	52.8	47.9	49 ± 5	0.02	0.02	0.02	0.02
Pb	n.d.	n.d.	n.d.	n.d.	0.08	n.d.	n.d.	0.03 ± 0.07	n.d.	n.d.	n.d.	n.d.
Zn	0.90	0.01	0.03	0.3 ± 0.8	1.56	0.01	1.13	1 ± 1	0.01	n.d.	n.d.	≤0.01

n.d.: not detected.

Table 3
Main statistical effects verified for the leaching of NiCd, NiMH and Li-ion batteries

Battery	Leached metal	Significant effects from the statistical point of view		
		Variables	Second order interaction	Third order interaction
NiMH	Cobalt Manganese Nickel	Conc. of acid S/L ratio Conc. of acid S/L ratio Conc. of acid S/L ratio	Conc. of acid and S/L ratio No interaction No interaction	No interaction No interaction No interaction
NiCd	Cadmium	Conc. of acid Temperature	Conc. of acid and S/L ratio Conc. of acid and temperature	No interaction
	Cobalt	Conc. of acid	Conc. of acid and S/L ratio	No interaction
	Nickel	Conc. of acid S/L ratio Temperature	Conc. of acid and temperature	No interaction
Li-ion	Aluminium	Conc. of acid Temperature	Conc. of acid and temperature	No interaction
	Cobalt	Temperature	Conc. of acid and temperature S/L ratio and temperature	Yes
	Copper	Conc. of acid	No interaction	No interaction
	Lithium	Conc. of acid S/L ratio Temperature	Conc. of acid and temperature	No interaction

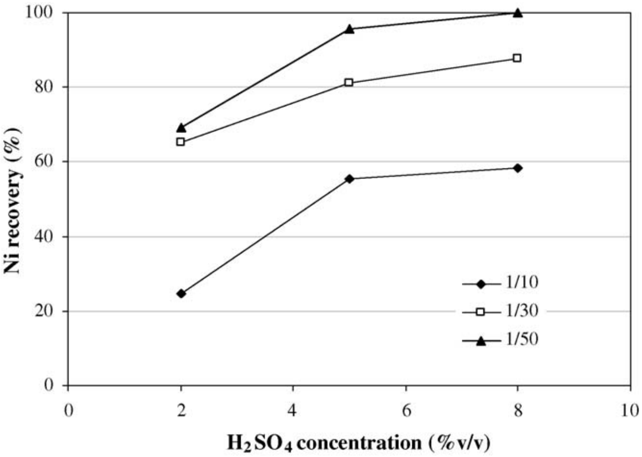

Fig. 2. Effect of H_2SO_4 concentration and S/L ratio on the leaching of nickel from NiHM battery dust ($H_2O_2 = 4\%$, v/v, $t = 1$ h, $T = 50$ °C).

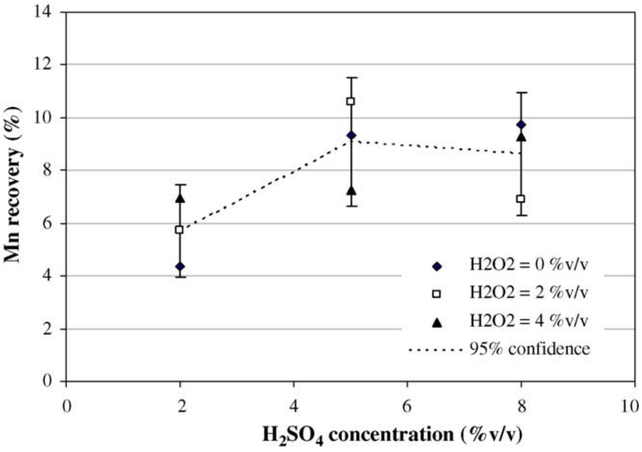

Fig. 3. Effect of H_2SO_4 and H_2O_2 concentrations on the leaching of manganese from NiHM battery dust (S/L = 1/10 g ml^{-1}, $t = 1$ h, $T = 50$ °C).

because the chemical bond between cobalt and oxygen in the $LiCoO_2$ and CoO_2 species is extremely strong, so acid leaching of these species is quite difficult. In this case, the addition of H_2O_2 may improve the leaching rate of cobalt since the evolved oxygen from the decomposition of hydrogen peroxide may convert Co(III) to Co(II) [26].

3.3. Liquid–liquid extraction step

The influence of pH on the extraction of several metallic species from a sulphuric solution using Cyanex 272 as extractant is shown in Fig. 4. The results indicate that the metals are extracted according to the following sequence: $Zn^{2+} > Al^{3+} > (Cu^{2+} \approx Mn^{2+} \approx Co^{2+} \approx Cd^{2+}) > Ni^{2+} > Li^{+}$. The $pH_{1/2}$ values obtained are 2.5–3.0 for zinc and aluminium, 4.0–4.5 for copper, manganese, cobalt and cadmium, 6.3 for nickel and 8.0 for lithium. Taking into consideration the metal composition of batteries shown in Table 2, the $pH_{1/2}$ values obtained in this study point out that batteries must be leached by

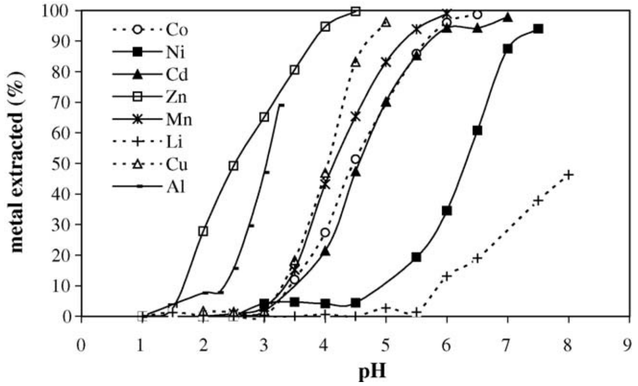

Fig. 4. Extraction equilibria of several metals with Cyanex 272 (initial metal concentration = 0.1 mol l^{-1}, 0.3 mol l^{-1} Cyanex 272, A/O = 1, $T = 50$ °C).

type because copper, manganese, cobalt and cadmium are not easily separated using Cyanex 272. Different treatment routes depending on the type of battery have to be considered, so a very flexible plant design is necessary to treat alkaline, zinc-carbon, NiCd, NiMH and Li-ion batteries.

For NiCd batteries, the results shown in Fig. 4 indicate that Cyanex 272 can efficiently separate cadmium from nickel that is present in a major proportion in this type of battery (see Table 2). An additional scrubbing step may wash co-extracted cobalt from cadmium but it seems to be more appropriate to use a selective extractant to separate these metals if cobalt recovery is desirable; for example, cobalt can be easily separated from cadmium using D2EHPA as extractant [13]. However, if cobalt recovery is not advantageous, it is necessary to minimise its concentration in the leach liquor.

For NiMH batteries, zinc and aluminium are in practice extracted together, the same occurs with the metals cobalt and manganese, while nickel remains in the aqueous solution. Since zinc, aluminium and manganese are present in very small quantities (Table 2), the recovery of nickel and cobalt seems to be more attractive. In addition, the leaching of manganese with sulphuric acid was low for the operational conditions investigated in this study.

For Li-ion batteries, aluminium, copper/cobalt and lithium can be separated as shown in Fig. 4. Leaching of copper and aluminium films must be avoided in order to obtain a more efficient separation so it can be done according to the following three-step process: (1) washing of batteries to remove the active material (lithium and cobalt) from the metallic films (aluminium and copper), (2) filtration of active material which is submitted to leaching with sulphuric acid solutions and, finally, (3) separation of lithium and cobalt by liquid–liquid extraction with Cyanex 272.

Extraction isotherms for cadmium, cobalt, copper, manganese and zinc were obtained experimentally in order to find the stoichiometric reaction of these metals with Cyanex 272. For all metals considered, plots of equilibrium concentration in the organic phase versus equilibrium concentration in the aqueous phase have shown a typical behaviour as shown in Fig. 5 for the isotherm of cobalt. According to the McCabe-Thiele method, this behaviour indicates that metal extraction can be achieved using a minimum number of theoretical extraction stages [27].

Experimental data were fitted to an equilibrium model assuming two stepwise reactions [22], the first one occurring at the liquid–liquid interface:

$$\mathrm{M}^{2+} + n(\mathrm{RH})_2 \Leftrightarrow \mathrm{MR}_2(\mathrm{RH})_{2(n-1)} + 2\mathrm{H}^+ \qquad (1)$$

$$K_\mathrm{D} = \frac{C_\mathrm{CD}C_\mathrm{H}^2}{C_\mathrm{M}C_\mathrm{BD}^n} \qquad (2)$$

and the second reaction in the bulk of the organic phase thus considering that the complex $\mathrm{MR}_2(\mathrm{RH})_{2(n-1)}$ formed at the interface breaks down as its concentration increases according to:

$$\mathrm{MR}_2(\mathrm{RH})_{2(n-1)} \Leftrightarrow \mathrm{MR}_2(\mathrm{RH})_{m-2} + \left(n - \frac{m}{2}\right)(\mathrm{RH})_2 \qquad (3)$$

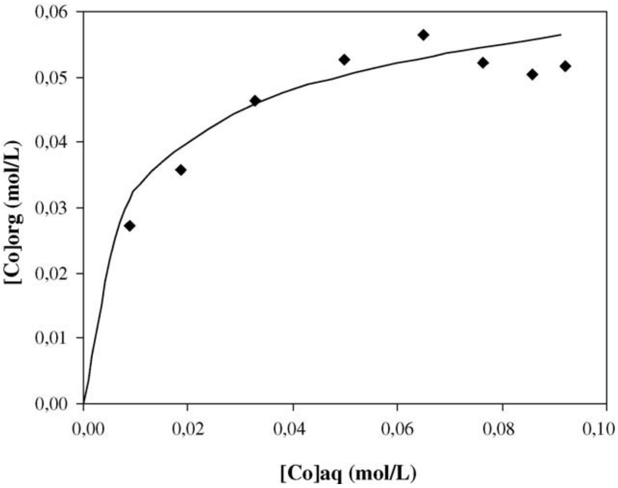

Fig. 5. Equilibrium isotherm of cobalt with Cyanex 272 (0.1 mol l^{-1} Co, 0.3 mol l^{-1} Cyanex 272, $T = 50\,^\circ\mathrm{C}$, pH 4.5).

$$K_\mathrm{C} = \frac{C_\mathrm{CM}C_\mathrm{BD}^{n-m/2}}{C_\mathrm{CD}} \qquad (4)$$

The stoichiometric constants (n and m) and equilibrium coefficients (K_D and K_C) were found for each metal by data fitting using a numerical procedure [22]. The equilibrium model including mass balances of metal and extractant was solved using the Newton-Raphson method while the estimates of parameters n, m, K_C and K_D were obtained by the Hooke-Jeaves optimisation method. It was verified that both stoichiometric constants converged to a value of 2 for all metals considered in this study. The equilibrium coefficients K_D and K_C shown in Table 4 were obtained by fixing $n = m = 2$, including 95% confidence levels for the error. The respective mass balances of metal and Cyanex 272 are given as:

$$C_\mathrm{CM} + C_\mathrm{CD} = C_\mathrm{CM}^0 + C_\mathrm{CD}^0 + (C_\mathrm{M}^0 - C_\mathrm{M})\frac{V_\mathrm{aq}}{V_\mathrm{org}} \qquad (5)$$

$$C_\mathrm{BD} = C_\mathrm{BD}^0 - 2(C_\mathrm{M}^0 - C_\mathrm{M})\frac{V_\mathrm{aq}}{V_\mathrm{org}} - (C_\mathrm{CM}^0 - C_\mathrm{CM}) \qquad (6)$$

Information on the equilibrium constants is helpful for guiding plant design procedures in order to calculate the number of theoretical stages for a given separation level or even to simulate best operational conditions for scrubbing and stripping steps, for example. For this attempt Eqs. (2), (4)–(6) has to be solved numerically.

Table 4
Stoichiometric constants and equilibrium coefficients for the extraction reaction of main metals present in batteries with Cyanex 272 ($T = 50\,^\circ\mathrm{C}$)

Metal	n	m	K_D	K_C (mol l^{-1})
Cadmium	2	2	$(2.6 \pm 0.2) \times 10^{-7}$	$(1.6 \pm 0.1) \times 10^{-2}$
Cobalt	2	2	$(6.3 \pm 0.3) \times 10^{-7}$	$(8.1 \pm 0.2) \times 10^{-3}$
Copper	2	2	$(8 \pm 1) \times 10^{-7}$	$(1.3 \pm 0.3) \times 10^{-1}$
Manganese	2	2	$(1.6 \pm 0.1) \times 10^{-6}$	$(1.4 \pm 0.1) \times 10^{-2}$
Zinc	2	2	$(6.88 \pm 0.01) \times 10^{-3}$	$(6.19 \pm 0.01) \times 10^{-3}$

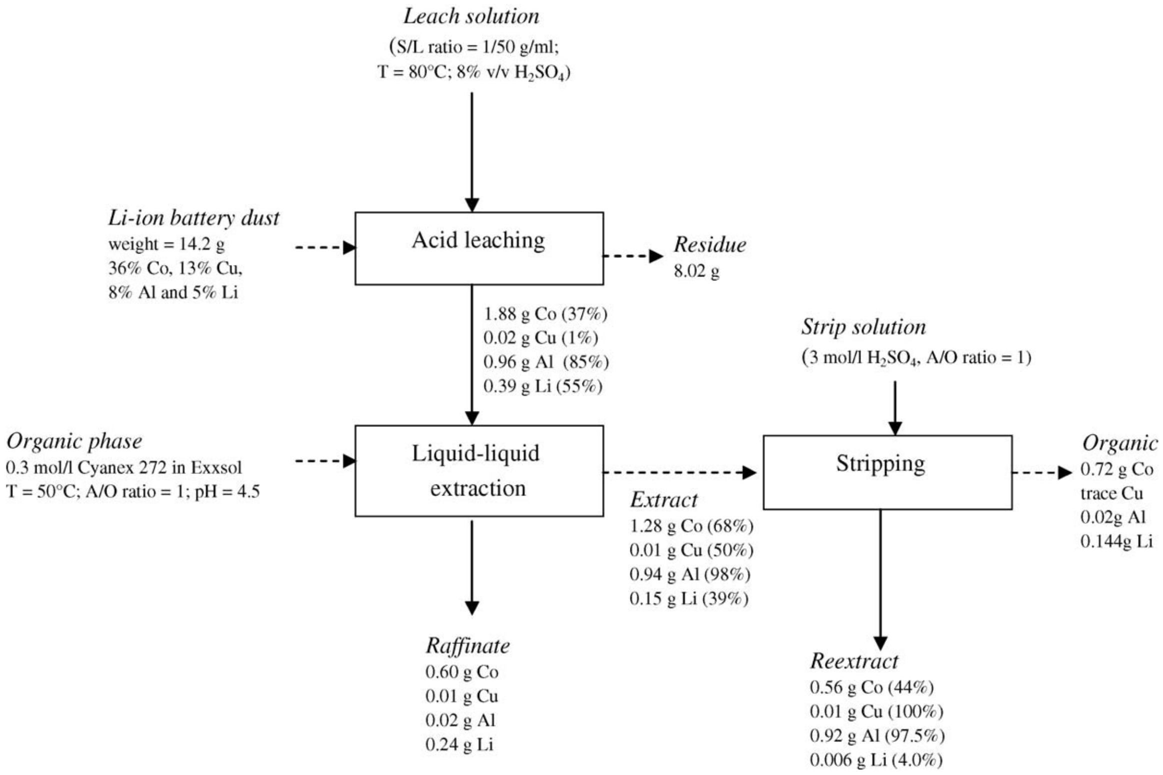

Fig. 6. Illustrative application of hydrometallurgical route to treat Li-ion batteries.

3.4. Application of the route to separate cobalt from Li-ion batteries

The hydrometallurgical route has been applied in this section to illustrate its technical viability to separate cobalt from Li-ion batteries, so the operational conditions shown here are not optimised. In addition, leaching and extraction tests were carried out in one single stage, so results schematically shown in Fig. 6 can be considerably improved.

In the leaching step, 37% of cobalt was removed from the battery dust in one leach stage. Cobalt leaching efficiency may improve considerably if H_2O_2 is used as the reductive agent. Metals were removed according to the same sequence shown in Section 3.2, so aluminium was preferentially leached while copper remained in the solid phase.

Metal separation by liquid–liquid extraction with Cyanex 272 must be carried out in two sequential steps: firstly to extract aluminium at pH 2.5–3.0 and secondly to remove cobalt at pH 4.5 thus leaving lithium in solution. As shown in Fig. 6, only one experiment was performed at pH 4.5 so aluminium was in practice fully extracted. Cobalt extraction was 68% in one single stage; the calculated value using the equilibrium constants shown in Table 4 resulted in 74% assuming no other metals in solution (i.e., more extractant available to react with cobalt). A scrubbing step to remove lithium and aluminium is recommended to improve cobalt purity in the organic phase prior to the stripping step that should be carried out in multiple stages.

4. Conclusions

The problem caused by spent mobile phone batteries is widely known to have environmental repercussions. A hydrometallurgical plant consisting of sorting, dismantling, sulphuric acid leaching and metal separation by liquid–liquid extraction with Cyanex 272 was found to be technically viable to treat such residue. The metal composition of NiCd, NiMH and Li-ion batteries has been assessed. It has been pointed out that the metals nickel and cobalt are economically attractive enough to be recovered from spent mobile batteries because of their price and grade. Cyanex 272 can separate cadmium from nickel ($\Delta pH_{1/2} \approx 2$) of the NiCd batteries, nickel from others metals ($\Delta pH_{1/2} \approx 2$) present in NiMH batteries and cobalt from lithium ($\Delta pH_{1/2} \approx 3$) in Li-ion batteries. The battery treatment plant has to be flexible enough in order to accommodate different types of batteries. Isotherms of the metals zinc, manganese, cobalt, cadmium and copper have been assessed at changing loading conditions in order to estimate the stoichiometric reaction constants and equilibrium coefficients.

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References

[1] A.M. Bernardes, D.C.R. Espinosa, J.A.S. Tenório, Recycling of batteries: a review of current processes and technologies, J. Power Sources 130 (2004) 291–298.

[2] A.L. Salgado, A.M.O. Veloso, D.D. Pereira, G.S. Gontijo, A. Salum, M.B. Mansur, Recovery of zinc and manganese from spent alkaline batteries by liquid–liquid extraction with Cyanex 272, J. Power Sources 115 (2003) 367–373.

[3] B.R. Conard, The role of hydrometallurgy in achieving sustainable development, Hydrometallurgy 30 (1992) 1–28.

[4] ANATEL, Agência Nacional de Telecomunicações, www.anatel.gov.br.

[5] C.J. Rydh, B. Svärd, Impact on global metals flows arising from the use of portable rechargeable batteries, Sci. Total Environ. 302 (2003) 167–184.

[6] L.R.S. Veloso, L.E.O.C. Rodrigues, D.A. Ferreira, F.S. Magalhães, M.B. Mansur, Development of a hydrometallurgical route for the recovery of zinc and manganese from spent alkaline batteries, J. Power Sources 152 (2005) 295–302.

[7] D.C.R. Espinosa, A.M. Bernardes, J.A.S. Tenório, An overview on the current processes for the recycling of batteries, J. Power Sources 135 (2004) 311–319.

[8] A.M. Bernardes, D.C.R. Espinosa, J.A.S. Tenório, Collection and recycling of portable batteries: a worldwide overview compared to the Brazilian situation, J. Power Sources 124 (2003) 586–592.

[9] M. Bartolozzi, G. Braccini, P.F. Marconi, S. Bonvini, Recovery of zinc and manganese from spent batteries, J. Power Sources 48 (1994) 389–392.

[10] C.C.B.M. Souza, D.C. Oliveira, J.A.S. Tenorio, Characterization of used alkaline batteries powder and analysis of zinc recovery by acid leaching, J. Power Sources 103 (2001) 120–126.

[11] N. Vatistas, M. Bartolozzi, S. Arras, The dismantling of the spent alkaline zinc manganese dioxide batteries and the recovery of the zinc from the anodic material, J. Power Sources 101 (2001) 182–187.

[12] C.-C. Yang, Recovery of heavy metals from spent Ni-Cd batteries by a potentiostatic electrodeposition technique, J. Power Sources 115 (2003) 352–359.

[13] C.A. Nogueira, F. Margarido, Leaching behaviour of electrode materials of spent nickel-cadmium batteries in sulphuric acid media, Hydrometallurgy 72 (2004) 111–118.

[14] P. Zhang, T. Yokoyama, O. Itabashi, Y. Wakui, T.M. Suzuki, K. Inoue, Hydrometallurgical process for recovery of metal values from spent nickel-metal hydride secondary batteries, Hydrometallurgy 50 (1998) 61–75.

[15] P. Zhang, T. Yokoyama, O. Itabashi, T.M. Suzuki, K. Inoue, Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries, Hydrometallurgy 47 (1998) 259–271.

[16] S. Castillo, F. Ansart, C. Laberty-Robert, J. Portal, Advances in the recovering of spent lithium battery compounds, J. Power Sources 112 (2002) 247–254.

[17] C.K. Lee, K.I. Rhee, Preparation of $LiCoO_2$ from spent lithium-ion batteries, J. Power Sources 109 (2002) 17–21.

[18] S. Frohlich, D. Sewing, The Batenus process for recycling mixed battery waste, J. Power Sources 57 (1995) 27–30.

[19] D. Martín, M.A. Garcia, G. Diaz, J. Falgueras, A new zinc solvent extraction application: spent domestic batteries treatment plant, in: Proceedings of the International Solvent Extraction Conference, vol. 1, Barcelona, Spain, 2001, pp. 201–206.

[20] C.A. Nogueira, F. Delmas, New flowsheet for the recovery of cadmium, cobalt and nickel from spent Ni-Cd batteries by solvent extraction, Hydrometallurgy 52 (1999) 267–287.

[21] B.K. Tait, Cobalt-nickel separation: the extraction of cobalt(II) and nickel(II) by Cyanex 301, Cyanex 302 and Cyanex 272, Hydrometallurgy 32 (1993) 365–372.

[22] M.B. Mansur, M.J. Slater, E.C. Biscaia Jr., Equilibrium analysis of the reactive liquid–liquid test system $ZnSO_4$/D2EHPA/*n*-heptane, Hydrometallurgy 63 (2002) 117–126.

[23] M. Constantible, S. Panero, B. Scrosati, A laboratory-scale lithium-ion battery recycling process, J. Power Sources 92 (2001) 65–69.

[24] D. Geldart, Gas Fluidization Technology, John Wiley & Sons, New York, 1986.

[25] D.P. Mantuano, Desenvolvimento de uma rota processual hidrometalúrgica para a recuperação de metais provenientes de baterias de celular descarregadas, M.Sc. Thesis, UFMG, Belo Horizonte, Brazil, 2005.

[26] C.K. Lee, K.-I. Rhee, Preparation of $LiCoO_2$ from spent lithium-ion batteries, J. Power Sources 109 (2002) 17–21.

[27] G.M. Ritcey, A.W. Ashbrook, Solvent Extraction—Principles and Applications to Process Metallurgy Part I, Elsevier, 1984.