Recovery of zinc and manganese from spent alkaline batteries by liquid–liquid extraction with Cyanex 272

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Abstract

A hydrometallurgical route based on the liquid–liquid extraction technique using Cyanex 272 as extractant is investigated for the selective separation of metal values, in particular, zinc and manganese from spent alkaline batteries. The recycling route consists of following steps: (1) cryogenic dismantling of the spent batteries, (2) pre-treatment of the internal material consisting of drying, grinding and screening steps in order to produce a dry homogeneous powder, (3) leaching of the powder with sulphuric acid and (4) metal separation by liquid–liquid extraction. Bench scale experiments have shown that zinc and manganese are easily separated ($\Delta pH_{1/2} \approx 2.0$) using 20% (v/v) Cyanex 272 dissolved in Escaid 110 at 50 °C. Therefore, the proposed route can treat residues from both zinc–carbon and alkaline batteries because metal composition of these batteries is quite similar. The metal content of other batteries such as Ni–Cd and nickel-metal hydride (NiMH) has been also determined in order to include them in future investigations.
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1. Introduction

In recent years, there has been observed a growing interest concerning the recycling of spent batteries such as zinc–carbon, alkaline, nickel–cadmium (Ni–Cd), nickel–metal hydride (NiMH), button and automotive batteries, mainly for environmental reasons. Spent batteries represent a serious pollutant in terms of heavy metals content when discarded in an inappropriate way. The cost for safe disposal of this hazardous material is quite high due to the amount of waste produced and the limited storage capacity of landfills and/or waste dumpsites. In developing countries like Brazil, for example almost 1 billion batteries units (6 units per capita) are consumed nowadays; of these, 25–30% are alkaline battery type [1] and 2% are automotive batteries. The recycling of these automotive batteries, for instance, could represent savings around 150,000 t per year of lead [2]. Considering the battery consumption per capita is even higher in industrial countries, metal recovery from spent

batteries is convenient also for economic reasons since large amounts of solid waste can be reused as secondary raw material.

Several methods to recover metal values from spent batteries are found in the literature but industrial routes are generally based on pyrometallurgical and/or hydrometallurgical operations. The RECYTEC process, for example involves a combination of both operations to recycle mercury from lamps and batteries at high operational costs [3].

The pyrometallurgical method consists basically of selective volatilisation of metals at elevated temperatures followed by condensation. The processes in current use are BATREC [4], SNAM-SAVAN [5], SAB-NIFE [6] and INMETCO [7]. Except the BATREC process, the remaining ones are commonly used to recover cadmium from Ni–Cd batteries by volatilisation at temperatures around 900 °C. Highly pure cadmium (99.95%) is obtained but most valuable metals such as cobalt and nickel are not usually recovered. On the other hand, the BATREC process recycles zinc and mercury from zinc–carbon and alkaline batteries at 1500 °C. Highly pure zinc is obtained when no Ni–Cd batteries are treated because zinc and cadmium are not selectively volatilised in the furnace, so a previous

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Nomenclature

C_i	concentration of specie i (mol/m^3)
%E	percent of metal extracted
K	equilibrium constant
Me	metal
n, p	stoichiometric constants defined in Eq. (1)
R^2	fitting coefficient
RH	extractant molecule of Cyanex 272 defined in Eq. (1)
V	phase volume (m^3)

Greeks letter

$\beta_{i/j}$	selectivity factor between species i and j

Subscripts

aq	aqueous phase
A	metal
B	extractant
C	metal complex
H	protons
org	organic phase

Superscript

0	initial value or feed

classification step is necessary. In general terms, pyrometallurgical routes do not require battery dismantling however, operations are very energy consuming and some emissions of dust and gases are expected.

Hydrometallurgical routes are commonly found more economical and efficient than pyrometallurgical ones. Metal separation routes based on hydrometallurgical operations are characterised by lower energy consumption, higher metal selectivity and no air pollution, as there are no particles produced. However, some pre-treatment steps are required in order to improve metal dissolution rates in the aqueous phase like battery classification, dismantling, magnetic separation and leaching. The following processes are found in commercial use: BATENUS [8], Modified ZINCEX [9] and RECUPYL [10]. These processes differ basically in the metal separation method used to treat the obtained leach liquor. The BATENUS process can treat any type of battery, except button cells that contain high mercury levels. 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 an ion exchange technique and manganese is precipitated. The Modified ZINCEX process uses liquid–liquid extraction to produce a high quality zinc electrolyte solution suitable for producing zinc metal SHG or zinc sulphate by evaporation. Zinc extraction from the leached liquor (pH 2) is performed with D2EHPA (di-2-ethylhexyl phosphoric acid) as extractant, leaving manganese in the raffinate while other metals such as copper, cadmium, nickel and mercury are cemented. The liquid–liquid extraction technique has been

used also by Zhang et al. [11] to separate nickel and rare earths from NiMH rechargeable batteries and by Nogueira and Delmas [12] to separate nickel, cadmium and cobalt from Ni–Cd batteries. The RECUPYL process, on the other hand, uses a selective electrowinning method to separate metals present in the leach liquor. The electrowinning separation method has been used also by Bartolozzi et al. [13] to recover cadmium from Ni–Cd batteries and Ferracin et al. [2] to recover lead from exhausted lead–acid batteries. Recently, Pietrelli et al. [14] have proposed a precipitation method with NaOH to separate rare earths from NiMH batteries.

A hydrometallurgical route based on the liquid–liquid extraction technique using Cyanex 272 (di-2,4,4 trimethyl-pentyl phosphinic acid) as extractant is proposed in this paper to separate zinc and manganese from spent alkaline batteries. The reagent Cyanex 272 has been extensively proved to extract cobalt and nickel in a very selective way [15], however its performance in other metallic systems has not been investigated so far. Previous studies have shown that Cyanex 272 selectively extracts zinc and manganese (Cytec catalogue). Devi et al. [16] have obtained extractions of 99.7% for zinc and 5.0% for manganese using a sodium salt of Cyanex 272. The determination of the metal content from discharged zinc–carbon, Ni–Cd and NiMH batteries is presented in this paper as well.

2. Experimental

2.1. Materials

Discharged zinc–carbon, alkaline, Ni–Cd and NiMH batteries typically consumed in Brazil, from different manufacturers, were used in this study. The leaching solutions consisted of aqua regia (3:1 HCl:HNO$_3$ ratio) and sulphuric acid solutions at specified concentrations.

The extractant Cyanex 272 (85 wt.% purity) was kindly supplied by Cytec Canada and used as received without any further purification. The diluent was kerosene Escaid 110 from Exxon (aromatics content 0.1% w/w). No phase modifier to enhance phase disengagement separation was necessary. All other reagents were of analytical grade. The aqueous solutions used in the liquid–liquid extraction experiments were prepared by dissolution of the respective metal sulphates in distilled water or by leaching battery powders with sulphuric acid.

2.2. Dismantling and metal characterisation of batteries

The cryogenic method has been found suitable to dismantle all batteries investigated in this study. Firstly, each battery was individually immersed in liquid nitrogen for 4 min and then fragmented by impact using a hammer. The internal parts were separated into plastics, papers, iron scraps and spent batteries dust; this later consisted of a

mixture of graphite and metallic oxides. The metal content of this mixture was determined quantitatively by atomic absorption after dissolving it in aqua regia for 2 h, 1:20 ratio (g sample per ml solution) at room temperature. Other dismantling methods such as manual and impact with a hammer at room temperature were also evaluated. Based on the metal characterisation results, the alkaline batteries were chosen to continue this study. Other batteries might be incorporated in future work.

2.3. Pre-treatment and batch leaching tests with alkaline batteries

Alkaline batteries were dismantled under cryogenic conditions. Then, the spent dust was dried in a drying oven for 2 h. The dry material was submitted to a grinding step to provide a fine powder in order to improve the leaching efficiency with sulphuric acid; firstly using a roll mill and then a ball mill for 3 h for further size reduction. Small pieces of paper and plastic were removed in a preliminary screening step, then the powder was screened in two sequential sieves with openings of 0.354 and 0.149 mm (−42# +100# mesh Tyler), respectively. Samples of dry powder were submitted to X-ray diffraction and fluorescence methods for qualitative analysis. The quantitative metal content was determined by atomic absorption spectrometry after dissolving the powder in aqua regia.

Leaching tests were carried out in a 1 l covered reactor made of glass immersed in a bath controlled temperature ($87 \pm 2\,^\circ$C) under constant stirring for 2 h. A 2^2 factorial design was proposed to investigate the combined effect of the variables: sulphuric acid concentration (0.5 and 1.0% v/v) and solid:liquid ratio (1:10 and 1:50 g of weight sample per ml of leaching solution volume). After each leaching test, the suspension was filtered and the solid residue containing graphite and not dissolved metals remained on the paper. The filtrate was submitted to atomic absorption spectrometry analysis.

2.4. Batch liquid–liquid extraction tests with alkaline batteries

Extraction and scrubbing batch tests were carried out by contacting suitable volumes of aqueous and organic phases in a 150 ml cylindrical jacketed glass reactor provided with magnetic agitation for 15 min. This time was found sufficient to reach chemical equilibrium as verified in preliminary tests. Experiments were performed at $50 \pm 1\,^\circ$C and the pH was constantly adjusted to the appropriate pH value through the addition of NH$_4$OH (1, 3 or 6 mol/l) or H$_2$SO$_4$ 97% solutions. Neither a third phase nor a significant change in volume of phases was observed in all tests. After phase separation, the metal content in the aqueous phase was determined by atomic absorption spectrometry. Experiments using synthetic aqueous solutions (25 g/l ZnSO$_4$ or MnSO$_4$) were carried out to determine the pH$_{1/2}$ values and equilibrium isotherms at changing aqueous/organic volume ratios (A/O) for zinc and manganese with Cyanex 272. Experiments using leached solutions from alkaline battery powder were carried out to investigate the metal separation levels.

2.5. Analysis

The alkaline battery powder was qualitatively analysed by X-ray diffraction and fluorescence methods. The concentration of zinc, manganese, nickel, cadmium, cobalt, iron, lithium, lead, potassium, sodium, aluminium and mercury in the aqueous phase were determined by atomic absorption spectrometry (CG AA 7000SBC model). The metal concentration in the organic phase was found by mass balance.

2.6. Health precautions

All steps of the experimental procedure must be carried out using gloves, glasses and gas masks for safe operation. The contents of an open battery can cause serious chemical burns of mouth, oesophagus and gastrointestinal tract if swallowed. Furthermore, inhalation causes respiratory irritation and contact with skin can cause irritation and/or chemical burns. Eye contact requires immediate flushing with water for at least 15 min, lifting upper and lower lids until no evidence of the chemical remains. If any contact with clothing occur remove contaminated clothing and wash skin with soap and water. Ingestion, inhalation and persistent skin irritation require medical attention.

3. Results and discussion

3.1. Dismantling and metal characterisation of batteries

The following dismantling procedures have been investigated in this study: manual, impact with a hammer at room temperature and cryogenic method. All procedures were found suitable to dismantle zinc–carbon batteries at the laboratory level. However, the first two methods have shown some problems regarding safe laboratory operation due to gas release followed by occasional combustion (Ni–Cd and NiMH batteries) and ejection of liquid electrolyte (alkaline battery) when the internal content of these sealed batteries were exposed to the atmospheric. On the other hand, no operational problem has been identified using the cryogenic dismantling method, so this method is recommended for laboratory work.

The spent battery dust obtained by cryogenic dismantling of individual batteries was dissolved in aqua regia for metal content characterisation. The quantitative metal composition of each battery found in this study is summarised in Table 1.

Zinc–carbon and alkaline batteries from two distinct manufacturers were investigated for comparison. Similar metal compositions have been found for the zinc–carbon

Table 1
Metal content of different batteries in the aqueous phase after dissolution with aqua regia (% of the sample weight)

Battery type	Sample weight (g)	Volume (ml)	Zn (%)	Mn (%)	Ni (%)	Cd (%)	Fe (%)	Co (%)	Li (%)	K (%)	Na (%)	Pb (%)	Al (%)	Hg (%)
Zinc–carbon 1	7.0	131	4.92	23.58	0.007	0.0004	0.98	–	–	–	–	–	–	–
Zinc–carbon 2	7.4	153	5.05	29.04	0.006	0.0002	0.18	–	–	–	–	–	–	–
Alkaline 1	14.3	145	12.19	32.35	0.013	0.0130	0.17	–	–	5.5	1.35	0.005	–	0.009
Alkaline 2	17.5	315	20.56	26.60	0.008	0.0007	0.15	–	–	7.3	0.10	0.005	–	0.012
NiMH	21.1	465	0.01	1.09	41.6	0.0020	9.13	2.04	0.006	3.08	0.22	–	0.49	–
Ni–Cd	14.7	325	0.02	0.08	22.7	24.52	12.58	0.24	0.007	3.66	0.05	–	–	–

batteries but the zinc content in alkaline battery 2 is almost 70% higher than alkaline 1. Average values shown in Table 1 corroborate Bartolozzi et al. [13] and Bueno et al. [1], thus indicating that a separation process adequate to recover alkaline batteries can also efficiently treat zinc–carbon cells because the same metals are present in both battery types. Alkaline batteries were chosen in this work because sales trends indicate an increasing consumption of alkaline instead of zinc–carbon batteries [17]. Alkaline batteries are predominantly consumed in industrial countries in comparison to zinc–carbon batteries. The results shown in Table 1 indicate also that metal content of more toxic species such as cadmium, lead and mercury in these batteries are low, thus obeying the Brazilian government regulation [18].

In contrast to zinc–carbon and alkaline batteries, Ni–Cd batteries contain basically nickel, cadmium and iron while NiHM batteries contain nickel, iron and cobalt as predominant metals. These batteries might be investigated in a future study in order to evaluate the separation method based on the liquid–liquid technique using Cyanex 272 proposed in this paper.

3.2. Pre-treatment and batch leaching tests with alkaline batteries

The dust from 57 alkaline batteries (AA size) obtained by cryogenic dismantling was dried for 2 h in order to determine the water content of the solid waste (11.5% by weight of the initial material). The dry solid was then sent to mills, resulting in 4.21 kg of dry powder (efficiency 95%). Table 2

shows the metal content of the dry powder determined by atomic absorption spectrometry after dissolving the powder in aqua regia. The predominance of species manganese, zinc and potassium in the alkaline battery powder was confirmed by qualitative analysis from X-ray diffraction and fluorescence spectrums.

Leaching results with sulphuric acid are shown schematically in Table 2. The figures reveal that manganese and potassium are leached with zinc while iron is not significantly dissolved by the aqueous solution. The extraction of zinc increases in more concentrated sulphuric acid solutions and higher solid:liquid ratios; practically all zinc was leached with 1 wt.% H_2SO_4 solution while manganese was only dissolved to around 40%. According to Bueno et al. [1], alkaline battery powder has compounds other than ZnO which probably can cause a decrease in the active contact surface with the solvent, so dissolution of zinc at lower sulphuric acid concentrations and low solid:liquid ratio is quite difficult. The same behaviour has been observed with other metals present in the powder, thus tests could possibly be carried out at a lower temperature and shorter leaching time as reported by Vatistas et al. [19] and Bueno et al. [1]. According to the results shown in Table 2, experimental conditions investigated in this study resulted in very similar extraction extends for both zinc and manganese. Therefore, we chose to leach alkaline batteries in 0.5% (v/v) H_2SO_4 and a 1:10 solid:liquid ratio because the highest leaching Zn/Mn ratio = 1.57 has been found for these conditions. Furthermore, a more concentrated solution can be achieved at a lower solid:liquid ratio and the

Table 2
Leaching results from dry alkaline battery powder

Metals	Powder composition (wt.%)	H_2SO_4 0.5% (v/v)		H_2SO_4 1.0% (v/v)	
		1:10 (wt.%)	1:50 (wt.%)	1:10 (wt.%)	1:50 (wt.%)
Zn	19.56	17.0 (86.9)	17.9 (91.5)	19.5 (99.7)	19.8 (100)
Mn	31.10	10.8 (34.7)	13.6 (43.7)	13.5 (43.4)	13.6 (43.7)
K	7.25	6.1 (84.1)	6.3 (86.9)	8.3 (100)	6.4 (88.3)
Hg	0.015	0.002 (13.3)	0.021 (100)	0.002 (13.3)	0.019 (100)
Fe	0.174	0.0007 (0.4)	0.0065 (3.7)	0.004 (2.3)	0.009 (5.2)
Pb	0.005	0.001 (20)	0.005 (100)	0.002 (40)	0.01 (100)
Ni + Cd + Co	0.03	0.0016 (5.3)	0.0051 (17.0)	0.002 (6.7)	0.007 (23.3)

Values in parentheses indicate % metal extracted from the dry powder.

consumption of sulphuric acid is much lower, so this condition seems to be more economical for practical purposes. The extraction of mercury and lead is also lower under these conditions.

3.3. Batch liquid–liquid extraction tests with alkaline batteries

The extraction of zinc and manganese by Cyanex 272 from sulphate solution as a function of the equilibrium pH at 50 °C is shown in Fig. 1. It was observed that negligible manganese co-extraction took place at pH < 2, so zinc can be extracted from the mixed electrolyte solution with little or no manganese contamination. Similar behaviour was exhibited by extractant D2EHPA [20]. The difference in $pH_{1/2}$ values for zinc and manganese (defined as the pH at which 50% of metal in solution is extracted) has been chosen to identify the separation degree between these metals. The greater the $\Delta pH_{1/2}$ value, the higher the selectivity of the extractant, so that a better separation efficiency is obtained. For the system under study, $\Delta pH_{1/2} = pH_{1/2,Mn} - pH_{1/2,Zn} = 3.75 - 1.78 \approx 2.0$, i.e. zinc extraction can be carried out 2 pH units lower than manganese, indicating a relatively good separation level between these metals in a short number of equilibrium stages. Cyanex 272 can extract zinc quantitatively at $2.0 < pH < 2.6$ whereas manganese extraction is not significant. On the other hand, the extraction of manganese is high at pH > 4.5, so isotherms of zinc and manganese using 20% (v/v) Cyanex 272 in Escaid 110 at 50 °C are determined at pH 2.5 and 4.5, respectively. The equilibrium data presented in Table 3 have been used to propose a simplified extraction mechanism valid for both metals at specific conditions investigated in this study assuming metal extraction as described by the following expression:

$$Me^{2+} + n(RH)_p \Leftrightarrow MeR_{np}H_{np-2} + 2H^+ \tag{1}$$

where

$$K = \frac{C_C C_H^2}{C_A C_B^n} \tag{2}$$

Eq. (1) is valid to describe metallic extraction systems with acidic extractants, as is the case of Cyanex 272 and D2EHPA. Combining Eq. (2) with respective mass balances of metal and extractant in the organic phase, the following expression has been derived:

$$\frac{\%E}{100} = K \frac{C_A(C_B^0 - nC_C)^n}{C_A^0 C_H^2 (V_{aq}/V_{org})} \tag{3}$$

The model assumes both phases are non-miscible and the reaction between metal Me^{2+} and extractant $(RH)_p$ occurs at the liquid–liquid interface. Equilibrium data shown in Table 3 have been converted to mol/m^3 units and then fitted to Eq. (3) using the Hooke–Jeaves and Quasi–Newton optimisation methods in order to estimate parameters C_B^0 and n [21,22]. The parameter n determines the metal extraction mechanism (Eq. (1)) whereas parameter C_B^0 determines if Cyanex 272 exists as a monomer or in a polymerised form. Because data have been obtained using 20% (v/v) Cyanex 272 (85 wt.% purity, molar weight 290 g/mol), $C_B^0 = 540 \, mol/m^3$ if Cyanex 272 molecules exist as a monomer or $C_B^0 = 270 \, mol/m^3$ as a dimer in the diluent Escaid 110. Fitting results for zinc ($C_B^0 = 252.8 \, mol/m^3$, $n = 1.92$ with $R^2 = 0.994$) and manganese ($C_B^0 = 293.5 \, mol/m^3$, $n = 2$ with $R^2 = 0.919$) indicates that Cyanex 272 occurs predominantly as a dimer when dissolved in Escaid 110 ($p = 2$). The same behaviour is exhibited by D2EHPA in aliphatic diluents [23], so the following mechanisms are proposed for zinc and manganese under the experimental conditions investigated in this work:

$$Zn^{2+} + 2(RH)_2 \Leftrightarrow ZnR_2(RH)_2 + 2H^+ \tag{4}$$

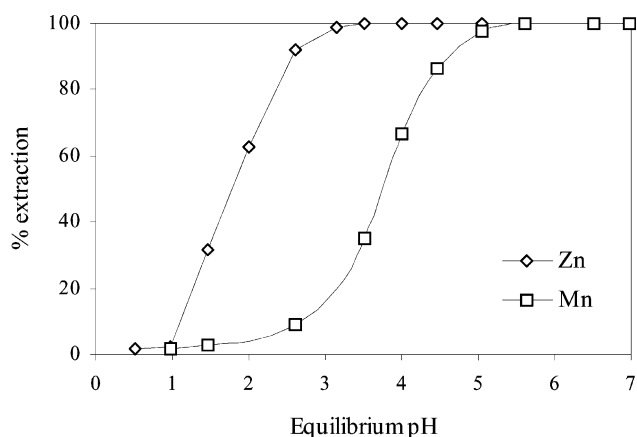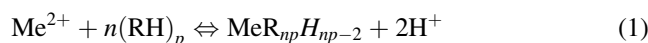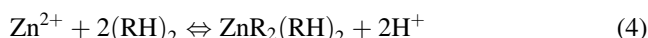$$Mn^{2+} + 2(RH)_2 \Leftrightarrow MnR_2(RH)_2 + 2H^+ \tag{5}$$

Fig. 1. Extent of zinc and manganese extraction by Cyanex 272 (20% v/v in Escaid 110) at 50 °C. Initial feed solution: 5.24 g/l Zn or 6.69 g/l Mn; A/O = 1.

Table 3
Equilibrium data for zinc and manganese extractions with 20% (v/v) Cyanex 272 at 50 °C

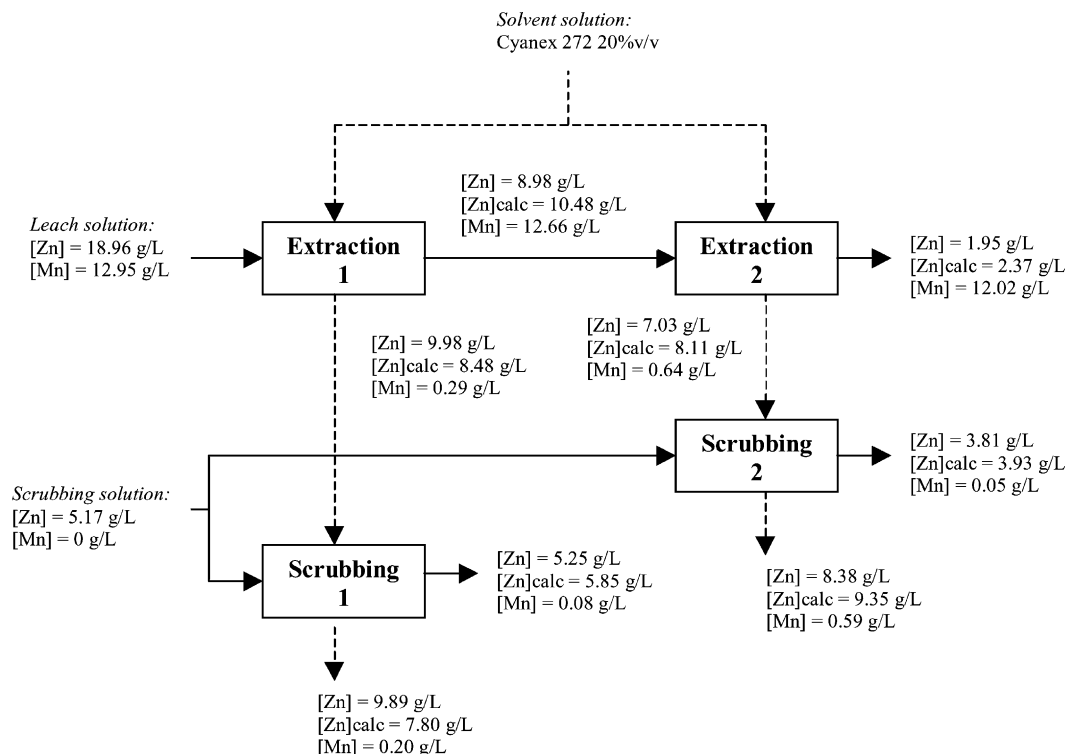| A/O ratio	Zinc (g/l)		Manganese (g/l)	
	Aqueous phase	Organic phase	Aqueous phase	Organic phase
10:1	4.750	4.900	5.539	5.792
7.5:1	4.640	4.500	5.918	5.792
5:1	4.235	5.025	5.423	6.353
3:1	3.680	4.680	4.703	5.973
2:1	3.043	4.394	3.256	6.870
1:1	1.731	3.509	0.715	5.979
1:2	0.282	2.479	0.187	3.251
1:2.5	0.296	1.978	–	–
1:3	0.217	1.674	0.132	2.184
1:5	0.103	1.027	0.066	1.326
1:7.5	0.133	0.681	–	–
1:10	–	–	0.033	0.666

Solvent solution:
Cyanex 272 20%v/v

Fig. 2. Batch crosscurrent contact scheme. All stages were operated with A/O = 1 at 50 °C (continuous lines are aqueous phases while dashed lines are organic phases).

According to Eqs. (4)–(5), both metal complexes have similar molecular structures. Keeping constant the parameters $C_B^0 = 270$ mol/m^3 and $n = 2$ as previously indicated gives the following equilibrium constants for zinc and manganese, $K_{Zn} = 0.0728$ at pH 2.5 and $K_{Mn} = 39.472$ at pH 4.5, respectively. Further investigation is necessary to confirm this mechanism for all operational conditions, however the model might describe the zinc/manganese separation by liquid–liquid extraction using the leach liquor from alkaline batteries with some accuracy. To confirm this, a two-stage crosscurrent batch simulation was conducted including two scrubbing stages as shown schematically in Fig. 2. The liquor containing zinc and manganese has been obtained by leaching alkaline battery powder with 0.5% (v/v) H$_2$SO$_4$ at a 1:10 solid:liquid ratio for 2 h at 87 °C. Experimental and calculated concentrations for zinc in both phases are presented in Fig. 2 and an approximate composition is theoretically predicted using the model (deviation 17.4%). The model was not used to predict the manganese concentration because the parameter K_{Mn} was evaluated at pH 4.5 only, so further experimental work is required for a complete theoretical description.

The results shown in Fig. 2 indicate the proposed liquid–liquid extraction process with Cyanex 272 selectively separates zinc and manganese. In the first stage, 52.6% of zinc and 2.2% of manganese were extracted ($\beta_{Zn/Mn} = 47.7$) whereas 78.3 and 5.1% of zinc and manganese, respectively, were extracted in the second stage ($\beta_{Zn/Mn} = 67.7$), so almost 90% of zinc and 7.2% of manganese were extracted.

Manganese co-extracted was not scrubbed efficiently because the scrubbing feed phase was not concentrated enough in zinc. The proposed model might be useful to predict more appropriate zinc concentrations for scrubbing. In commercial operations, the contaminated scrubbed solutions can be fed back into the extraction stages. The stripping of the metal loaded organic phase was not investigated in this study. Better separation results are expected if a countercurrent operation is used.

4. Conclusions

The metal content of different spent batteries in commercial use in Brazil such as zinc–carbon, alkaline, Ni–Cd and NiMH have been determined quantitatively in order to propose a selective separation method based on the liquid–liquid extraction technique using Cyanex 272 as extractant. The following steps have been investigated experimentally in this paper: (1) different battery dismantling procedures, (2) sulphuric acid leaching and (3) metal separation by liquid-liquid extraction. Step 1 was carried out for zinc–carbon, alkaline, Ni–Cd and NiMH batteries. Steps 2 and 3 were performed using spent dust from alkaline batteries only; other battery types will be incorporated in a future work.

For laboratory purposes, the cryogenic method was found adequate for any type of battery investigated, thus avoiding gas release or ejection of liquids when sealed batteries were

dismantled by manual and/or impact methods at room temperature. All methods were found suitable to dismantle zinc–carbon batteries.

Leaching tests with alkaline battery powder have shown that manganese and potassium are leached with zinc while iron is not dissolved by the aqueous phase. Practically all zinc and 40% manganese initially present in the dry powder from alkaline batteries were leached with 1 wt.% H_2SO_4 solution. However, a more concentrated solution with a higher Zn/Mn ratio was obtained using 0.05% (v/v) H_2SO_4 and 1:10 solid:liquid ratio.

Bench scale experiments have shown that zinc and manganese are easily separated ($\Delta pH_{1/2} \approx 2.0$) using 20% (v/v) Cyanex 272 dissolved in Escaid 110 at 50 °C. Batch cross-current liquid–liquid extraction tests using a leaching solution containing 18.96 g/l Zn and 12.95 g/l Mn at pH 2.5 have shown that the method is selective for zinc, leaving manganese in the raffinate. The proposed route can treat residues from both zinc–carbon and alkaline batteries because the metal composition of these batteries is quite similar.

The mechanism for zinc and manganese extraction with Cyanex 272 at 50 °C has been found by fitting equilibrium data to a simple model valid at specific pH values investigated in this study. The model has been used to simulate a two-stage crosscurrent batch operation and predictions are quite satisfactory (within 17.4% deviation).

Acknowledgements

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