Artigo

SEPARATION OF ZINC FROM MANGANESE BY SOLVENT EXTRACTION FROM ACIDIC LEACHATES OF SPENT ZINC-MnO₂ DRY CELLS USING NEUTRAL ORGANOPHOSPHORUS EXTRACTANTS

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This paper describes a route for recovering manganese and zinc from spent zinc-MnO₂ dry cells via acid leaching using sulfuric or hydrochloric acids as leachants. Hydrogen peroxide was added as reductant. Experiments were run at 25-40 °C for 1-3 h. Under the best optimal conditions, over 97.5 wt.% of zinc and manganese were leached by both acids. Zn(II) was best extracted at high free acidity (≥ 1 mol L^{-1}) with tributylphosphate (TBP) or trialkylphosphine oxides (Cyanex 923) diluted in n-heptane. Cyanex 923 was a better extractant than TBP, and the extraction was better performed in hydrochloric leachates. Mn(II) was more co-extracted from hydrochloric leachates and when Cyanex 923 was the extractant, but was easily scrubbed with dilute leachant (~1-2 mol L^{-1}). Zn(II) striping was possible using 5 mol L^{-1} HCl or H₂SO₄. Manganese was precipitated as oxalate (MnC₂O₄.2H₂O), free of leached contaminants. High-purity sodium salts of the anions of the leachants were recovered after slow evaporation of the final solution.

Keywords: Zinc-MnO₂ dry cells; acid leaching; zinc extraction; neutral organophosphorus extractants; manganese oxalate; sodium salts.

INTRODUCTION

Zinc-MnO₂ dry cells (alkaline and Leclanché ones) are non-rechargeable (primary cells) and therefore designed to be fully discharged.[1-3] Their demand is steadily increasing due to the popularity of small electronic devices where small quantities of power are required.[4] These batteries are easy to manufacture and safe to carry.[5] Zinc-MnO₂ dry cells are the most widely used portable chemical source of electricity.[1,2,6]

Over the last decades, the development of electronic technologies using a battery as a source of energy has led to an increase in the amount of spent batteries reaching landfill sites or incinerators.[6,7] Disposal of spent zinc-MnO₂ batteries has become an environmental challenge.[2,8] Ideally, all batteries should be collected and recycled.[3] For countries where an established flux of collection, transport and recycling of batteries is not implemented the huge majority of spent batteries are still disposed in landfill sites.[6] They constitute an important source of metal pollution in landfill leachates.[8-13] Safe disposal of spent batteries in landfills becomes increasingly expensive due to the high amounts of waste as well as the limited sanitary landfill storage capacity. Collection schemes for each type of battery are more difficult to implement due to difficulties in identification by the consumer of the various types of batteries. On the other hand, the incineration of batteries is restricted by environmental legislation because it can release metals such as mercury and cadmium and toxic gases to the atmosphere;[3,10] also, recyclable materials are lost.[10]

Spent zinc-MnO₂ dry cells have been regarded as a secondary source of zinc and manganese.[14-17] Due to the rising demand and limited supply from natural sources, manganese and zinc have been listed among the strategic metals by many countries.[18,19] It is estimated that more than 200,000 t of portable batteries go on the market annually in the United States, but only approximately 27,000 t of spent batteries are recycled per year.[3,6] The recovery of metals from zinc-MnO₂ batteries is based on pyrometallurgical or hydrometallurgical processes. Pyrometallurgical processes are the most used in the European Union.[3,18] Examples of such processes are BATREC, SNAM-SAVAN, and INMETCO. They consist basically of selective volatilization of metals at high temperatures followed by condensation. However, pyrometallurgical routes have negative effects on the environment because of emissions[3] (thus requiring a gas purification system[5]), secondary waste streams, energy consumption and hazardous work environments.[1,7]

The hydrometallurgical option is more versatile considering the final metal species produced and the lower energy consumption.[3,17,20,21] Many processes to recover metals from spent batteries have been intensively studied at the laboratory scale and proved to be very promising.[6] The first step is usually a physical treatment step, which includes crushing and magnetic separation. The electroactive components (anode, cathode and electrolyte) account for 50% of total weight.[5] Hydrometallurgical processes are usually based on the dissolution of metal phases (essentially Zn and Mn oxides) in aqueous alkali or acidic media.[3,22] Sulfuric acid is by far the most used leachant, followed by hydrochloric acid[10,17,23-30] Since Mn(IV) is insoluble in acidic and alkaline media, reduction of tetravalent manganese is an important issue in acid leaching step. A reductant (such as hydrogen peroxide, sulfur dioxide, oxalic acid, carbohydrates etc.) is necessary to bring all manganese to 2+ state, which is soluble and stable in acidic medium.[31,32] However, concentrated solutions, high temperatures and long reaction times are usually required, which are great disadvantages of these processes.[3,10,12,22]

Leached Zn(II) can be separated from Mn(II) has been performed using chemical precipitation,[33,34] solvent extraction[10,23-29,35] or electrowinning.[21,34] Chemical precipitation is a simple and cheap method,[5,33,36,37] although toxic reactants such as sulfide and oxalate ions are frequently used. Solvent extraction (SX) is one of the most popular methods used for separation of metal ions from industrial and waste solutions, which are frequently required in hydrometallurgical processing. SX techniques have become essential

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to the hydrometallurgical processes due to the growing demand for high purity metals and the need to process low-grade ores with great complexity.[35] Organophosphorus and organothiophosphorus extractants have been extensively studied for the separation and recovery of many metals by solvent extraction.[38]

Many SX methods for separating and preconcentrating Mn(II) have been reported using D2EHPA (di-(2-ethylhexyl)phosphoric acid), TBP (tributylphosphate), TOA (trioctylamine) or TOPO (trioctylphosphine oxide).[39,40] However, the existing methods suffer from several drawbacks, such as long extraction time, multiple extraction stages, the need of masking agents and co-extraction of commonly associated ions, such as Zn(II) and Fe(III).[40] On the other hand, the extraction of Zn(II) from sulfate/chloride leachates or galvanizing liquors has been proposed as a route to zinc concentration and separation from impurities (such as Fe(III), Co(II), Cu(II) and Mn(II)). Both neutral and cation exchanger extractants such as TBP, D2EHPA, carboxylic acids, amines, Cyanex 923 (trialkylphosphine oxides) and Cyanex 302 (bis(2,4,4-trimethylpentyl)monothiophosphinic acid) have been tested in acidic medium.[41-45] In general, Zn(II) is preferably extracted over Mn(II) in sulfuric acid medium, but the extraction curves may be close to each other according to the experimental conditions.[24,26,27,35]

Growing attention is being paid to the development of new synergistic effects to improve the extractability and selectivity of divalent transition metal ions, enhance the stability and the solubility of the extracted complexes in the organic phase, eliminate emulsification and the formation of a third phase, and increase the extraction reaction rate.[41,42] The mixtures presenting synergistic effects on Zn(II) extraction from other divalent metal ions usually contain a neutral (or solvating) organophosphorus extractant.[42] Extractants of this class coordinate to certain neutral metal complexes by replacing waters of hydration, thereby causing the resulting organo-metal complex to become aqueous insoluble, but organic soluble. Neutral extractants have an atom capable of donating electron density to a metal in the formation of an adduct.[41] Few data have been presented regarding the behavior of these extractants alone in the SX of Zn(II).

The aim of this study was to carry out a complete investigation involving leaching of manganese and zinc from spent zinc-MnO$_2$ dry cells under mild experimental conditions on lab-scale using the most common acid leachants (sulfuric and hydrochloric acids). Experimental studies were carried out to assess the main factors that affect leaching efficiency. Zn(II) and Mn(II) were separated by a combination of SX and precipitation techniques. The final solution was processed to recover the sodium salt of the anion of the leachant.

EXPERIMENTAL

Materials

Spent AA zinc-MnO$_2$ dry cells (alkaline and Leclanché) were employed in this study. The AA format is the most current size employed in Brazil. Their expiration date was between March-July 2014. Alkaline and Leclanché dry cells were processed together. Twenty samples of each were manually dismantled (using gloves, glasses and dust masks). The active components (anode, cathode and electrolyte) were separated from other components such as plastic and paper films, ferrous and non-ferrous scraps and carbon rods. Samples were not calcined in order to recover carbon as insoluble matter. They were fed into a milling machine for size reduction (100% < 1 mm, 30 min). This mass was dried at 40 ºC for 24 h. The main elements present (wt.%) are manganese (29.0), zinc (23.0) and carbon (9.0). The full average composition of the solid after milling and drying the active components was presented in our previous work.[45]

HCl (37 wt.%, ~12 mol L^{-1}), H$_2$SO$_4$ (49 wt.%, 9 mol L^{-1} and 98 wt.%, 18 mol L^{-1}), H$_2$O$_2$ (30 wt.%, ~10 mol L^{-1}), NaOH (6 mol L^{-1}) and Na$_2$C$_2$O$_4$ were of analytical grade and used as received.

The extractants TBP (Sigma-Aldrich) and Cyanex 923 (Cytec) were used without further purification. n-Heptane (Sigma-Aldrich) was used as diluent.

Leaching procedure

The experiments were run in triplicate and carried out in closed glass reactors under stirring (200 rotations per minute) for 1-3 h in a fume hood. Equal volumes of aqueous H$_2$O$_2$ and HCl or H$_2$SO$_4$ were combined. The solid/liquid ratio was set at 100 g L^{-1} (~16.7 g mol^{-1} HCl or 22 g mol^{-1} H$_2$SO$_4$; 20 g mol^{-1} H$_2$O$_2$). Initial temperature was 25 ºC. After adding the dried mass, temperature increased by 10-15 ºC after ~1 h. Temperature decreased to 28-30 ºC at the end of the experiment. Handling of acids, H$_2$O$_2$ and leachants was performed using appropriate personal protective equipment.

The following equations describe the possible reactions of zinc metal and manganese/zinc oxides with values of ΔG^0 at 25 ºC:[46]

$$Mn_2O_3 + H_2O_2 + 4\ HCl \rightarrow 2\ MnCl_2 + 3\ H_2O + O_2$$
$$\Delta G^0 = -55.1\ kJ \quad (1)$$
$$Mn_2O_3 + H_2O_2 + 2\ H_2SO_4 \rightarrow 2\ MnSO_4 + 3\ H_2O + O_2$$
$$\Delta G^0 = -152.5\ kJ \quad (2)$$
$$MnO_2 + H_2O_2 + 2\ HCl \rightarrow MnCl_2 + 2\ H_2O + O_2$$
$$\Delta G^0 = -53.9\ kJ \quad (3)$$
$$MnO_2 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + 2\ H_2O + O_2$$
$$\Delta G^0 = -103.2\ kJ \quad (4)$$
$$MnO + 2\ HCl \rightarrow MnCl_2 + H_2O \qquad \Delta G^0 = -52.2\ kJ \quad (5)$$
$$MnO + H_2SO_4 \rightarrow MnSO_4 + H_2O \qquad \Delta G^0 = -232.5\ kJ \quad (6)$$
$$ZnO + 2\ HCl \rightarrow ZnCl_2 + H_2O \qquad \Delta G^0 = -23.5\ kJ \quad (7)$$
$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \qquad \Delta G^0 = -211.2\ kJ \quad (8)$$
$$Zn + 2\ HCl \rightarrow ZnCl_2 + H_2 \qquad \Delta G^0 = -147.1\ kJ \quad (9)$$
$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \qquad \Delta G^0 = -147.1\ kJ \quad (10)$$
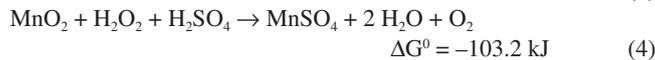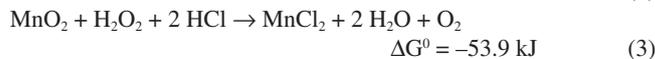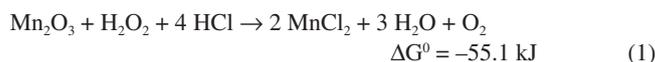
All calculated values of ΔG^0 are negative. It follows that the reactions occur with high probability in the direction of product formation under the temperature range used, as described earlier.

The solid residue was separated from the leachate by filtration under vacuum. It was washed with water until pH 5.5. The washings were added to the leachate. The washed solid was dried at 150 ºC for 3 h, cooled down in a desiccator and weighed. The dried solids were then placed in ceramic crucibles and went through an oxidation step in air (600 °C, 3 h) in a furnace in order to eliminate carbon and other volatile components present. The gaseous effluent of the furnace was passed through distilled water at 25 ºC. The roasted mass was cooled down in the furnace and weighed.

Procedure for solvent extraction (SX)

All SX experiments were performed at 25 ºC. The aqueous/organic (A/O) phase ratio was set at 1 v/v. The extractant concentration varied from 3 to 16 vol.%. Free acidity of the leachate changed from its original value to 10^{-4} mol L^{-1} (pH 4) by adding 6 mol L^{-1} NaOH or increased up to 6 mol L^{-1} by adding 12 mol L^{-1} HCl or 18 mol L^{-1} H$_2$SO$_4$. The system was shaken for 10 min after which it was left to stand for phase separation. The experiments were carried out in triplicate. The distribution ratio, $D_{M(II)}$, (M = Zn, Mn) is defined as the ratio of metal ion concentration in organic phase to the metal ion concentration in aqueous phase at reaction equilibrium.

The best conditions to remove Mn(II) and Zn(II) from the organic phase were also investigated. The organic solutions were contacted

with aqueous solutions of acid leachants. The experimental conditions were similar to those of the extraction process.

Precipitation of Mn(II)

pH of the raffinate was set at 4 by adding 6 mol L^{-1} NaOH. 1 mol L^{-1} $Na_2C_2O_4$ (sodium oxalate) was added dropwise to the raffinate under stirring (200 rpm) at 25 °C.[36] A pink precipitate was formed:

$$Mn^{2+} + C_2O_4^{2-} \rightarrow MnC_2O_4\downarrow \qquad (K_{sp} = 5 \times 10^{-6}) \qquad (11)$$

If pH is below 4, Mn(II) is not completely precipitated as oxalate.[36] The precipitate was filtered and washed with 0.01 mol L^{-1} sodium oxalate (5 mL g^{-1}) and water (2 mL g^{-1}), dried at 150 °C for 3 h and weighed.

Recovery of sodium salts

The final solution contains basically Na^+ and H_3O^+ ions and the anion of the leachant (SO_4^{2-} or Cl^-). 6 mol L^{-1} NaOH was carefully added to adjust the pH to the equilibrium pH of the saturated solution of Na_2SO_4 or NaCl (7.0).[47,48] A small amount of a gelatinous precipitate (containing Al, Fe, Si, Cr and Pb)[45] was formed and separated by filtration. The treated solution was then slowly evaporated at 60-70 °C (without stirring). A white crystalline solid was obtained. The solids were weighed and kept in tightly closed containers.

Analytical methods

The solids, after milling and drying the active components, the insoluble matter isolated after leaching, the ash isolated after calcining the insoluble matter and the solids obtained during the separation procedure were weighed in an analytical balance (Scientech SA 120) and analyzed by x-ray fluorescence (Shimadzu XRF 800HS). Crystalline phases in the solid samples were identified by X-ray powder diffraction (XRPD, Shimadzu model XRD 6000) by continuous scanning method at 20 mA and 40 kV, using Cu Kα as the radiation source. Metal ion concentrations in the leachates were determined by atomic absorption spectrometry (Perkin Elmer AAS 3300). The acidity of the leachates was determined by titration with 0.1 mol L^{-1} NaOH using phenolphthalein as indicator, or by potentiometry using an Ag/AgCl/KCl 3 mol L^{-1} reference electrode and a platinum electrode as indicator.

RESULTS AND DISCUSSION

Leaching results

The reproducibility of leaching was determined to be about ± 4%. Manganese and zinc were leached with high yields (> 97 wt.%, Table 2) after 2 h (HCl) or 3 h (H_2SO_4). These results are comparable to the best ones reported in the literature[18] using strong acids. Leaching with both acids was somewhat longer than the average time reported in the literature,[4,20,21] but temperature was higher in such studies (40-90 °C) than in the present work and carbon was not eliminated. There was no difference on zinc leaching by both acids, but manganese was somewhat better leached by HCl when compared to H_2SO_4 at a given leaching time. Probably, some HCl (like H_2O_2) reduced Mn(III) and Mn(IV) to Mn(II):[47-49]

$$Mn_2O_3 + 6\ HCl \rightarrow 2\ MnCl_2 + 3\ H_2O + Cl_2 \quad (\Delta E^o = + 0.10\ V)\ (12)$$
$$MnO_2 + 4\ HCl \rightarrow MnCl_2 + 2\ H_2O + Cl_2 \quad\quad (\Delta E^o = + 0.15\ V)\ (13)$$
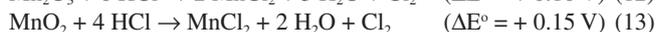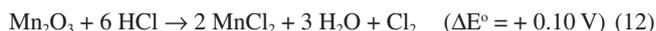
Iron and aluminum were especially leached by HCl probably due to formation of complexes[47,48] such as $[AlCl_4]^-$ and $[FeCl_4]^-$. Calcium, barium and lead were not found in H_2SO_4 leachates because their sulfates are insoluble or very sparingly soluble in water.[47-49] HCl leached these elements with high yields: $CaCl_2$ and $BaCl_2$ are soluble in water and Pb(II) is easily complexed by Cl^- ions ($K_{form}\ PbCl_4^{2-} = 3 \times 10^8$).[47,49]

Table 2 presents the concentration of leached species after adding the washing waters. All solutions were pale pink, which is typical of $Mn^{2+}_{(aq.)}$.[47,48] Iron and aluminum were present in very low amounts. Other elements found (< 0.1 mg L^{-1}) were nickel, copper and chromium. The concentrations shown in Table 2 vary according to the amount of water used to wash the insoluble matter (H_2SO_4, 80 mL g^{-1} dried electroactive components; HCl, 60 mL g^{-1}). The average pH was 0.5 (HCl) and 0.9 (H_2SO_4). Mn^{2+} ions were the stable aqueous species over a broad redox potential (E_h) range.[31,32]

Analysis of the insoluble matter after leaching

The amount of insoluble matter (Table 3) was lower after experiments with HCl. This result is due to the leaching of Mn, Pb, Fe, Al, Ca and Ba by this acid (Table 2). After calcination, the mass loss was essentially the same (82-94 mg g^{-1}), in agreement with the carbon content of the electroactive components (~9 wt.%).[45]

The pH of the aqueous solution of the gaseous effluent

Table 1. Leached elements* (wt.%) after 1-3 h

Leachant	Time (h)	Zn	Mn	Ba + Ca	Pb	Fe	Al
H_2SO_4 + H_2O_2	1	99.5	92.4	negligible	negligible	26.0	74.1
	2	99.8	96.3	negligible	negligible	34.1	77.1
	3	> 99.9	97.3	negligible	negligible	35.9	78.0
HCl + H_2O_2	1	> 99.9	98.0	97.1	93.6	90.1	97.8
	2	> 99.9	> 99.9	99.5	> 99.9	93.8	99.5

* After adding the washings to the leachate.

Table 2. Average metal ions concentration* after leaching for 3 h

Leachant	Mn(II) (g L^{-1})	Zn(II) (g L^{-1})	Fe(III) (mg L^{-1})	Al(III) (mg L^{-1})	Pb(II) (mg L^{-1})	Ba(II) + Ca(II) (mg L^{-1})
H_2SO_4 + H_2O_2	3.3	2.6	4.0	5.1	negligible	< 0.1
HCl + H_2O_2	6.5	5.0	20.0	12.2	0.6	16.1

*After adding the washings to the leachate.

Table 3. Mass of insoluble matter after leaching before and after calcining (600 ℃, 3 h) (Base: 1 g of dried original mass)

Leachant	Time (h)	Before calcining (mg)	After calcining (mg)	Difference (mg)
$H_2SO_4 + H_2O_2$	1	142	56	86
	2	147	57	90
	3	109	25	84
$HCl + H_2O_2$	1	95	9	86
	2	92	10	82

Table 4. Main components (wt.%) of the insoluble matter after calcination at 600 ℃ for 3 h

Leachant	Time (h)	ZnO	MnO	SiO_2	PbO	Fe_2O_3	Al_2O_3	BaO + CaO
$H_2SO_4 + H_2O_2$	1	1.7	69.9	22.6	0.2	0.8	1.9	2.6
	2	1.6	49.6	45.8	0.1	0.6	0.6	1.6
	3	1.4	48.6	44.9	0.1	0.6	0.4	3.8
$HCl + H_2O_2$	1	3.0	4.0	89.5	< 0.1	2.2	0.2	0.8
	2	2.8	3.4	92.5	< 0.1	0.2	< 0.1	0.8

produced during calcination was acid (6.2). After adding acetic acid (elimination of CO_2) no precipitate or turbidity (AgCl or $BaSO_4$) was found after adding $AgNO_3$ or $Ba(NO_3)_2$ to the corresponding solutions from the experiments with HCl and H_2SO_4. The acidity comes from $CO_{2(aq.)}$.

The chemical composition of the insoluble matter after calcination is presented in Table 4. Manganese is the most abundant element after experiments with H_2SO_4. Silicon is by far the main element present after experiments with HCl. The high amounts of alkali-earth metals and the presence of lead in the insoluble matter after experiments with H_2SO_4 correlate with the insolubility of $CaSO_4$, $BaSO_4$ and $PbSO_4$ in water.[47-49]

The diffractogram of the insoluble matter after leaching with $HCl + H_2O_2$ corresponds to an amorphous material (Figure 1A). The one after leaching with $H_2SO_4 + H_2O_2$ shows the presence of Mn_2O_3 (Figure 1B). Mn_3O_4 is the expected phase when manganese oxides are heated in air at about 500 ℃,[50] but tends to be slowly oxidized to Mn_2O_3 above 560 ℃.[34]
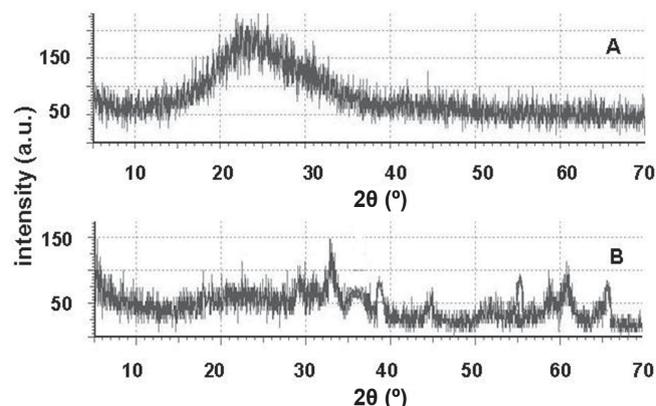
Figure 1. *XRPD patterns of the insoluble residue in water after leaching with $HCl + H_2O_2$ (A) and $H_2SO_4 + H_2O_2$ (B) followed by calcination at 600 ℃ for 3 h*

SX of Zn(II)

Influence of extractant concentration

In these experiments, the pH of the leachate was not modified. The reproducibility was determined to be within ±5%. Phase separation was quickly achieved (~10 min) as found is some

earlier studies.[27] Zn(II) extraction increased with the increase of the extractant concentration regardless of the leachant (Figures 2 and 3). This result is in agreement with literature data for both extractants.[27,28,42,51-53] High extraction yields (95-97 wt.%) were possible using a high Cyanex 923 concentration (16 vol.%), as found in the literature in H_2SO_4 medium at pH ~0.5.[52] TBP was less performant than Cyanex 923 whatever the leachant. SX of Zn(II) was practically not affected by the nature of the leachant for each extractant tested. The traces of Fe(III) found in the leachates (Table 2) were also extracted by both extractants. Fe(III) is more strongly extracted than Zn(II) under the same conditions by both extractants in both acidic media.[43,44,52]
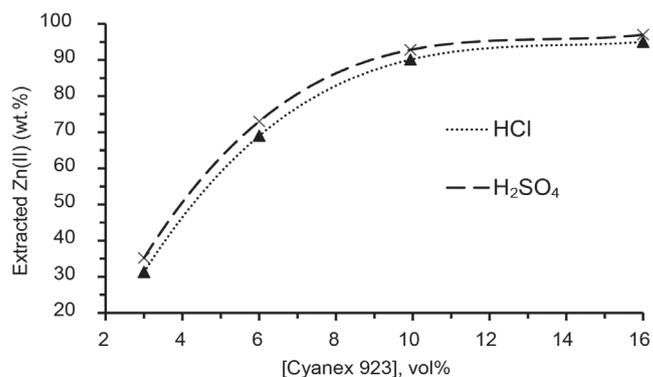
Figure 2. *Influence of Cyanex 923 concentration on Zn(II) extraction in the pH of the leachates (one stage, A/O = 1 v/v, 25 ℃)*
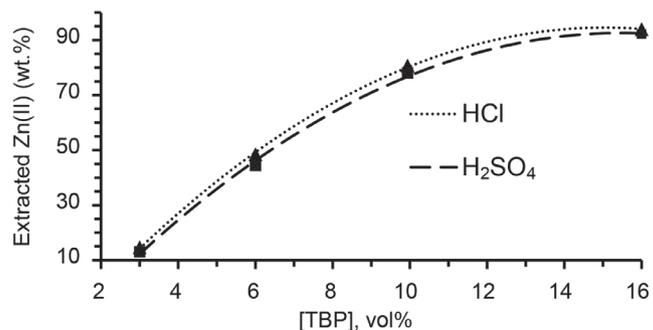
Figure 3. *Influence of TBP concentration on Zn(II) extraction in the pH of the leachates (one stage, A/O = 1 v/v, 25 ℃)*

The graphs log D (distribution ratio) as a function of log [extractant] (Figures 4 and 5) show that the slope is close to 2 for both leachants and extractants. SX of Zn(II) with TBP or Cyanex 923 has particularly been performed at high HCl concentration.[27,28,41,42,50-52] The general extraction reaction is well established in sulfuric and hydrochloric media:[41-44,52,53]

$$Zn^{2+}_{(aq.)} + 2\ extractant_{(org.)} + (2 + n)\ X^-_{(aq.)} +$$
$$n\ H_3O^+ \rightleftharpoons H_nZnX_{(2+n)}.2(extractant)_{(org.)} + n\ H_2O$$
$$(X = Cl^-, \tfrac{1}{2}\ SO_4^{2-};\ extractant = TBP\ or\ Cyanex\ 923) \qquad (14)$$
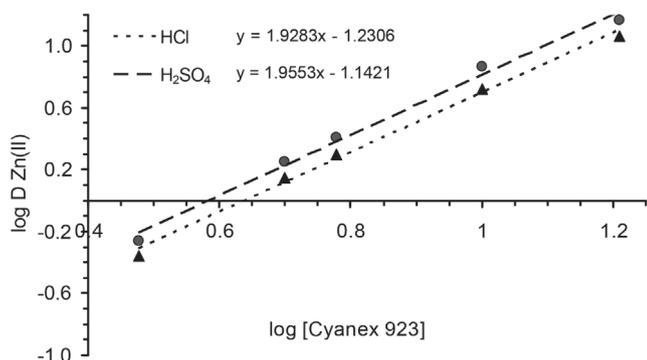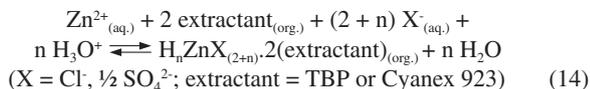
Figure 4. *Graph of log D as a function of log [Cyanex 923] for Zn(II) extraction in the pH of the leachates (one stage, A/O = 1 v/v, 25 ºC)*
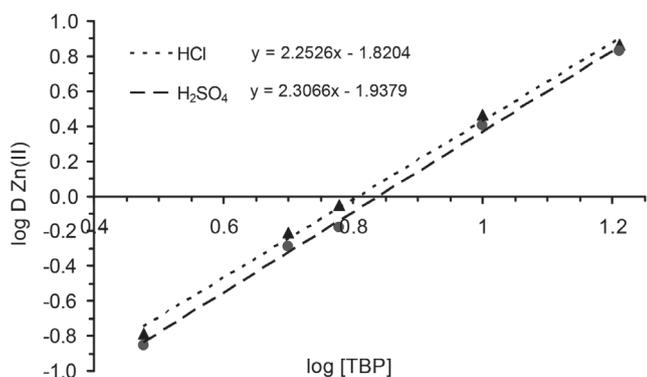
Figure 5. *Graph of log D as a function of log [TBP] for Zn(II) extraction in the pH of the leachates (one stage, A/O = 1 v/v, 25 ºC)*

The value of n depends on the concentration of the anion of the acid leachant and the free acidity. The dominant mechanism appears to involve extraction of the $ZnX_2.2extractant$ complex (n = 0) at the pH of the leachants (0.5-0.9).[43] As free acidity increases, a change in the extraction mechanism takes place. Both $HZnX_3.2extractant$ (n = 1) and $H_2ZnX_4.2extractant$ (n = 2) complexes are formed and extracted in the free acidity range 2-5 mol L^{-1}.[52,53]

Typical pH$_{0.5}$ values (equilibrium pH at which 50% metal extraction occurs) for Zn(II) are between 0.8-1.3.[23,25,28,29] Furthermore, Zn(II) concentration in the leachates (Table 2) was lower than in most literature studies (usually above 10 g L^{-1}).

Influence of free acidity of the leachate on Zn(II) and Mn(II) extraction

The extractant concentration was fixed at 6 vol.%. Zn(II) and Mn(II) were not extracted at pH above 3 whatever the leachant (Figures 6 and 7). SX of Mn(II) using TBP was found to be very low (0–2%) at pH 2.5 whatever its concentration in sulfuric leachates.[38]

Zn(II) extraction increased as free acidity of the leachant increased from 10^{-4} mol L^{-1} (pH 4) to 1 mol L^{-1} (pH 0), thus agreeing

with literature data.[53] Cyanex 923 was a better extractant than TBP in this free acidity range. More than 99.5 wt.% was extracted in both acidic media with Cyanex 923 at free acidity 1 mol L^{-1}. The increase of free acidity notably reduced the concentration of the extractant required to extract Zn(II) with high yield in a single stage. Free acidity levels above 1 mol L^{-1} did not change SX of Zn(II) in HCl medium but decreased it in H$_2$SO$_4$ one (Figure 6). The best TBP performance was found at very high free acidities (> 5 mol L^{-1}, Figure 7). SX of Zn(II) was slightly more effective from HCl leachates, especially at free acidities above 1 mol L^{-1}. Co-extraction of Mn(II) increased as free acidity increased, particularly above 2 mol L^{-1} (HCl > H$_2$SO$_4$ and Cyanex 923 > TBP).

These results follow the same trend found in our previous studies using D2EHPA, a cation exchanger:[45] a preferential extraction of Zn(II) over Mn(II) was observed under our experimental conditions.
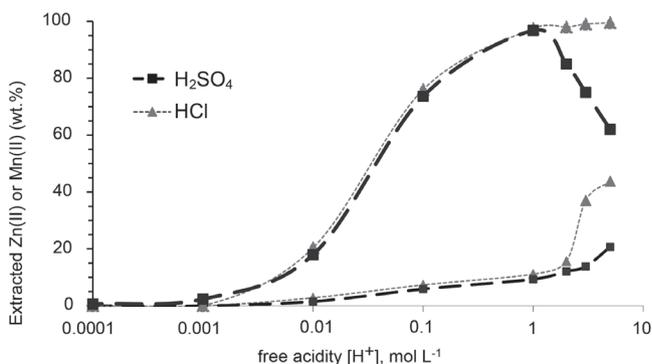
Figure 6. *Effect of free acidity on Zn(II) and Mn(II) extractions with 6 vol.% Cyanex 923 (one stage, A/O = 1 v/v, 25 ºC)*
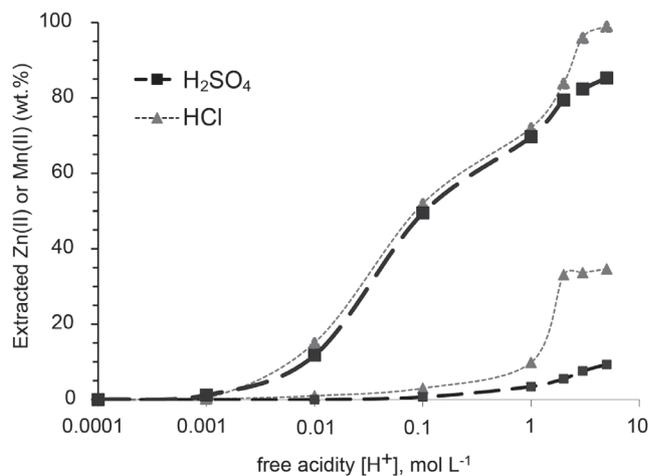
Figure 7. *Effect of free acidity on Zn(II) and Mn(II) extractions with 6 vol.% TBP (one stage, A/O = 1 v/v, 25 ºC)*

Although no additional studies were preformed, it is known that the extraction of metal ions by these neutral extractants may be enhanced in the presence of anion complexes of metal ions.[27,28,52,54] HCl (> 4 mol L^{-1}) is a ligand for Mn(II), forming [MnCl$_4$]$^{2-}$ complexes; [ZnCl$_4$]$^{2-}$ ions are much easier to form.[42,49] Sulfate anions also form complexes with Zn^{2+} and Mn^{2+}, but are less stable. [47-49]

Removal of Mn(II) and Zn(II) from the organic phase

Mn(II) was easily scrubbed (> 99.5 wt.%, Table 5) in one stage using a dilute leachant (2 mol L^{-1}). A similar result has already been reported in the literature.[24] Zn(II) was not removed. The aqueous solution was added to the raffinate.

Zn(II) stripping from the organic phase (Table 5) required a higher

acid concentration.[9,10,24,25,29,53] 3 mol L^{-1} H$_2$SO$_4$ or HCl began to strip it. More than 99.5 wt.% was stripped in one stage using 5 mol L^{-1} H$_2$SO$_4$ or HCl. Concentration should not surpass 8 mol L^{-1} to avoid emulsification.

Table 5. Mn(II) scrubbing and Zn(II) stripping from the loaded organic phase

Acidic solution	Scrubbed Mn(II) (wt.%)	Stripped Zn(II) (wt.%)
H$_2$SO$_4$ 1 mol L^{-1}	99.5	< 0.1
H$_2$SO$_4$ 2 mol L^{-1}	> 99.5	< 0.1
H$_2$SO$_4$ 3 mol L^{-1}	-	10
H$_2$SO$_4$ 4 mol L^{-1}	-	90
H$_2$SO$_4$ 5 mol L^{-1}	-	> 99.5
HCl 1 mol L^{-1}	> 99.5	< 0.1
HCl 2 mol L^{-1}	> 99.5	< 0.1
HCl 3 mol L^{-1}	-	15
HCl 4 mol L^{-1}	-	94
HCl 5 mol L^{-1}	-	> 99.5

What is the choice: a cation or a neutral extractant?

The sulfuric leachates examined in this work were also subjected to SX of Zn(II) using D2EHPA, a cation exchanger.[45] The performance of Cyanex 923 (this work) at pH 0 (free acidity 1 mol L^{-1}) and of D2EHPA (pH 2)[45] at the same concentration (6 vol.% in n-heptane) is comparable. Their market price is very close.[55] The key to answer the above question is the pH of the leachate. The original pH of the sulfuric leachates is ~0.9. The difference between Cyanex 923 and D2EHPA is the optimum pH for Zn(II) extraction. The use of Cyanex 923 required an additional amount of H$_2$SO$_4$ to change pH of the leachate from 0.9 to 0. This means an additional consumption of NaOH$_{(aq.)}$ to adjust pH for Mn(II) precipitation (~4) and an additional production of sodium sulfate. When D2EHPA was the extractant, SX of Zn(II) only required some NaOH$_{(aq.)}$ to adjust pH from 0.9 to 2 before adding more NaOH$_{(aq.)}$ to precipitate Mn(II).[45] Therefore, less sodium sulfate is produced. It appears that Cyanex 923 is suitable as extractant for Zn(II) from leachates with high free acidities ($\geq$ 1 mol L^{-1}), whereas D2EHPA is more appropriate when pH of the leachates is 1 or above.

Mn(II) precipitation

Manganese oxalate comprises over 99 wt.% of the solid precipitated at pH ~4. The impurities (Zn(II), Fe(III), Al(III), Cr(III), Pb(II)) were not significantly precipitated at this pH in contrast to precipitation of manganese as MnO$_2$ (pH 9).[45] Their concentrations are too low to allow precipitation of their corresponding oxalates.[47,49] The diffractogram shows that the pink solid containing manganese is MnC$_2$O$_4$.2 H$_2$O.

The choice of oxalate as precipitant for manganese(II)[36] instead of hydroxide ions[45] allowed a lower consumption of NaOH$_{(aq.)}$ because pH was adjusted to 4 instead of 9. This fact also reduced the consumption of H$_2$SO$_{4(aq.)}$ as neutralization of the final solution was directly performed by simply adding NaOH$_{(aq.)}$.

Recovery of the sodium salt of the anion of the leachant

The diffractograms contain peaks corresponding to a single anhydrous salt. XRF data show the absence of zinc, manganese and other metals found in the leachates (they were precipitated prior to the evaporation step). This is of special importance for the recovery of high purity salts (NaCl and Na$_2$SO$_4$). After drying the solids at 150 °C for 3 h, the mass loss was lower than 2 wt.%, thus confirming that all salts were anhydrous.

It is possible to identify three sources of Cl$^-$ and SO$_4^{2-}$ anions: the leachant used for processing the active components and the solutions employed to scrub Mn(II) and to strip Zn(II) from the organic phase. Na$^+$ comes from sodium oxalate used to precipitate manganese(II) oxalate and the aqueous NaOH used to adjust pH for Mn(II) precipitation and also recovery of sodium salts. It is expected that each anion will be recovered as its sodium salt. Taking into account the solid/liquid ratio (100 g L^{-1}) and the amount of water used to wash the insoluble matter after leaching, recovery of sodium sulfate and sodium chloride is very close to the theoretical amount based on all sources of sodium ions and the anion of the leachant (Table 6).

Table 6. Average recovery of the sodium salts of the anions of the leachants (Base: 1 kg of electroactive components)

Acid leachant	Salt	Expected mass (kg)	Recovered mass (kg)	%
H$_2$SO$_4$	Na$_2$SO$_4$	33.50	33.27	99.3
HCl	NaCl	10.82	10.71	99.0

Rough economic analysis

No detailed study on economics was performed, but some insight can be obtained based on the market value of the reactants, energy, water and products. The present average prices (for the same purity grade) in Brazil for bulk quantities are:[55] 49 wt.% (9 mol L^{-1}) H$_2$SO$_4$, US\$ 10 L^{-1}; 98 wt.% (18 mol L^{-1}) H$_2$SO$_4$, US\$ 15 L^{-1}; 12 mol L^{-1} HCl, US\$ 38 L^{-1}; 30 wt.% (~10 mol L^{-1}) H$_2$O$_2$, US\$ 350 L^{-1}; Cyanex 923, US\$ 500 L^{-1}; n-heptane, US\$ 103 L^{-1}; 6 mol L^{-1} NaOH, US\$ 50 L^{-1}; sodium oxalate 99 wt.%, US\$ 90 kg^{-1}; water, US\$ 5 m^{-3} (including taxes); energy, US\$ 0.30 kWh^{-1} (including taxes); Na$_2$SO$_4$ (> 99.5 wt.%), US\$ 160 kg^{-1}; NaCl (> 99.5 wt.%), US\$ 75 kg^{-1}; ZnO (99.5 wt.%), US\$ 100 kg^{-1}; MnC$_2$O$_4$.2H$_2$O (99 wt.%), US\$ 200 kg^{-1}. Carbon was not included in this study because of its very low price (~US\$ 0.10 kg^{-1}) and the low amount recovered (Table 3). Table 7 presents the estimated costs and the market value of the products obtained in this study (base: 1 kg active components, 6 vol.% Cyanex 923 as extractant (at free acidity 1 mol L^{-1}), three uses of the extractant solution, Mn(II) scrubbing with 2 mol L^{-1} H$_2$SO$_4$ or HCl and Zn(II) stripping with 5 mol L^{-1} H$_2$SO$_4$ or HCl).

The revenue of the process decreased following the order H$_2$SO$_4$ >> HCl. The process using H$_2$SO$_4$ (the cheapest acid) presented a favorable revenue. However, the high water consumption during washing of the insoluble residue increased the costs for Zn(II) extraction, Zn(II) stripping and Mn(II) precipitation, thus reducing its overall revenue. The process using HCl appears not to be viable: although its estimated cost is about 10% lower, the market value of NaCl is very low.

The contribution of recovered ZnO and MnC$_2$O$_4$.2 H$_2$O to the revenue was very low although manganese(II) oxalate presents a higher market value than MnO$_2$[45,55] of the same purity grade. Although the contribution of carbon to the revenue was nil, its elimination via controlled burning (before leaching) would impact costs due to high energy consumption.[18,34] On the other hand, if impurities were brought into the sodium salts, their market value would decrease by a factor of 10-15, making all processes not economically viable. At present, considering other costs (labor, equipment etc.), it is likely

Table 7. Rough economic analysis of the processes described in this work (Base: 1 kg of active components of spent zinc-MnO_2 dry cells)

Item	H_2SO_4	HCl
Acid	5 L (US$ 50)	5 L (US$ 190)
H_2O_2	5 L (US$ 1750)	5 L (US$ 1750)
Energy consumption[*1]	10 kWh^{-1} (US$ 3)	10 kWh^{-1} (US$ 3)
Adjust free acidity at 1 mol L^{-1}	0.850 L (US$ 12.75)	0,640 L (US$ 57.60)
Washing insoluble matter	8.0 L (US$ 0.04)	4.0 L (US$ 0.02)
n-heptane	17.77 L (US$ 610.30)	13.72 L (US$ 437.17)
Cyanex 923	1.13 L (US$ 565.95)	0.88 L (US$ 391.07)
Mn(II) scrubbing[*2]	18.9 L (US$ 43.95)	14.6 L (US$ 33.95)
Zn(II) stripping[*3]	18.9 L (US$ 111.36)	14.6 L (US$ 86.03)
6 mol L^{-1} NaOH[*4]	6.3 L (US$ 314.33)	4.9 L (US$243.33)
1 mol L^{-1} $Na_2C_2O_4$[*5]	5.3 L (US$ 63.60)	5.3 L (US$ 63.60)
6 mol L^{-1} NaOH[*6]	0.001 L (US$ 0.05)	0.001 L (US$ 0.05)
Washing $MnC_2O_4.H_2O$	2.5 L (US$ 0.013)	2.5 L (US$ 0.013)
Energy consumption[*7]	50 kWh^{-1} (US$ 15)	40 kWh^{-1} (US$ 12.0)
Total estimated costs	**US$ 3,540.34**	**US$ 3,267.83**
ZnO	260 g (US$ 26)	260 g (US$ 26)
$MnC_2O_4.2 H_2O$	440 g (US$ 88)	450 g (US$ 90)
Sodium salts[*8]	31.27 kg (US$ 5,040)	9.02 kg (US$ 676.50)
Total value products	**US$ 5,154.00**	**US$ 792.50**

[*1] Stirring/heating; [*2] 9 mol L^{-1} H_2SO_4 + water to prepare a 2 mol L^{-1} solution; [*3] 9 mol L^{-1} H_2SO_4 + water to prepare a 5 mol L^{-1} solution; [*4] Adjust pH to precipitate Mn(II); [*5] Mn(II) precipitation; [*6] Adjust pH to neutralize the final aqueous solution; [*7] Evaporation; [*8] See Table 6

that the revenue will partially come from money (price surcharge) that consumers will pay for recycling batteries.[34]

CONCLUSIONS

Over 97 wt.% of zinc and manganese were leached from the electroactive components of spent zinc-MnO_2 dry cells under mild experimental conditions in the presence of a strong acid and a reductant. Leaching of zinc was comparable for both acids but Mn(II) was somewhat more leached in the presence of HCl. Precipitation and complexation reactions influenced leaching of minor elements present in the electroactive components. The insoluble matter corresponded to carbon and non-leached elements.

More than 99.5 wt.% of Zn(II) was extracted by Cyanex 923 in one stage (6 vol.%, A/O = 1 v/v, 25 °C) at free acidity ≥ 1 mol L^{-1} from hydrochloric leachates. SX of Zn(II) with this extractant from sulfuric leachates presented a maximum (99.5 wt.%) at free acidity 1 mol L^{-1}. TBP was only effective at very high free acidities (≥ 5 mol L^{-1}), and Zn(II) extraction was best performed from hydrochloric leachates. The effect of free acidity and extractant concentration was the opposite: the lower the acidity the higher the extractant concentration to achieve a comparable Zn(II) extraction. Mn(II) co-extraction increased as free acidity increased, particularly from hydrochloric leachates and when Cyanex 923 was the extractant. However, organic loaded Mn(II) was easily scrubbed with 2 mol L^{-1} leachant. Zn(II) stripping required a higher concentration (5 mol L^{-1}). High purity crystalline manganese(II) oxalate and sodium salts of the anions of the leachants were obtained

after careful pH adjustment of the raffinate followed by addition of sodium oxalate (Mn) and slow evaporation of the final solution. Recovery of these salts reduced the amount of final wastes.

SUPPLEMENTARY MATERIAL

Figure 1S presents the general scheme for the recovery of zinc and manganese from spent zinc-MnO_2 dry cells after acid leaching in the presence of a reductant. Figure 2S presents the diffractogram of the pink solid obtained after precipitation of Mn(II) by oxalate ions. Figure 3S shows the diffractograms of the sodium salts recovered after evaporation of the final neutralized solution. They are available for download at http://quimicanova.sbq.org.br in pdf format with free access.

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