

Development of a hydrometallurgical route for the recovery of zinc and manganese from spent alkaline batteries

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Abstract

A hydrometallurgical route is proposed in this paper for the selective separation of zinc and manganese from spent alkaline batteries. The recycling route comprises the following steps: (1) *batteries dismantling* to separate the spent batteries dust from other components (iron scraps, plastic and paper), (2) *grinding of the batteries dust* to produce a black homogeneous powder, (3) *leaching of the powder* in two sequential steps, “neutral leaching with water” to separate potassium and produce a KOH solution, followed by an “acidic leaching with sulphuric acid” to remove zinc and manganese from the powder, and (4) *selective precipitation* of zinc and manganese using the KOH solution (pH around 11) produced in the neutral leaching step. For the acidic leaching step, two alternative routes have been investigated (selective leaching of zinc and total leaching) with regard to the following operational variables: temperature, time, sulphuric acid concentration, hydrogen peroxide concentration and solid/liquid ratio. The results obtained in this study have shown that the proposed route is technically simple, versatile and provides efficient separation of zinc and manganese.

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1. Introduction

Spent batteries may represent a serious pollutant in terms of heavy metals content when disposed in an inadequate way. In addition, the worldwide consumption of batteries is significant [1,2] and the cost for safe disposal of this kind of residue is high [3], so the concern on spent batteries destination is not exclusively environmental but economical as well. Table 1 shows the typical metal content of batteries zinc–carbon, alkaline, nickel–cadmium (Ni–Cd), nickel–metal–hydride (NiMH) and lithium. The metal composition differs considerably depending on the battery type, thus some batteries are potentially more hazardous than others as is the case of Ni–Cd batteries, for example [4]. Cadmium, mercury and lead are very toxic metals commonly found in batteries.

According to Table 1, the metal composition of zinc–carbon and alkaline batteries is quite similar. These batteries contain basically manganese, zinc and potassium as main metallic species. As the consumption of zinc–carbon and alkaline batteries is high compared to other batteries (around 90% of the European market [1]), the amount of metals zinc and manganese that can be reused as secondary raw material is expressive.

In the last two decades, several processes have been developed to recycle batteries as a result of new environmental regulations in different countries around the world. These processes are usually grouped as pyro or hydrometallurgical routes. A comparison of these routes is shown elsewhere [1–3,5] including technical information of some industrial plants in current operation for the treatment of batteries. Some industrial plants are designed to treat a particular type of battery as is the case of SNAM-SAVAM and SAB NIFE plants to recycle Ni–Cd batteries, for example.

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Table 1
Typical metal composition of some portable batteries (% w/w) [2,4]

Element	Zinc-carbon ^a	Alkaline ^a	Ni-Cd (AB ₅ type) ^b	NiMH ^b	Li-based ^b
Al			0.019	0.5–2.0	4.6–24
Cd			15–20		
Ce			0.43–5.5		
Co			0.600	2.5–4.3	12–20 ^c
Cr			0.017	0.020–0.080	
Cu					5–10
Fe	0.2–1.0	0.17	29–40	20–25	4.7–25
K		5.5–7.3			
La				1.4–6.6	
Li					1.5 ^d –5.5 ^e
Mn	23–30	26–33	0.083	0.81–3.0	10–15 ^f
Nd				0.96–4.1	
Ni	0.007	0.010	15–20	25–46	12–15 ^g
Pb		0.005			
V					15–20 ^e
Zn	5	12–21	0.060	0.092–1.6	

^a Dry powder only.

^b Include all battery components.

^c Li-ion (Co).

^d Li-ion (Co, Ni, Mn).

^e Li-polymer (V).

^f Li-ion (Mn).

^g Li-ion (Ni).

In this paper, a hydrometallurgical route is proposed to recover zinc and manganese from spent alkaline batteries. The route comprises the steps schematically shown in Fig. 1: *preliminary treatment* (including sorting, dismantling and grinding steps), followed by *leaching* (neutral and acidic) and *precipitation* of zinc and manganese using hydroxides (NaOH, CaO or KOH) as precipitant agent. The route can treat residues from zinc-carbon batteries as well because, as shown in Table 1, metal composition of alkaline and zinc-carbon batteries is similar.

The preliminary treatment of batteries consists of the following sequential steps: sorting, dismantling and grinding. In the sorting step, zinc-carbon and alkaline batteries are separated from other types of batteries. Sorting processes are associated with different manual separation steps or with different equipment designed to achieve this goal as recently revised by Bernardes et al. [6]. In the dismantling step, the spent batteries dust consisting of a mixture of graphite and metallic oxides is separated from iron scraps, paper and plastic. The metallic scraps, for instance, could be recycled by a pyrometallurgical treatment. Finally, in the grinding step, the spent batteries dust is grinded using ball mills to reduce its particle size in order to improve the efficiency of the leaching step. Particle size, irrespective of other process variables affecting leaching operations, imposes the major constrain on extraction rate. However, grinding processes are usually expensive because they exhibit a high energy demand, so economic limits of grinding must be experimentally determined for particular ores and conditions. According to Mantuano [7], similar leaching rates of nickel with sulphuric acid were obtained using grinded and not-grinded NiMH battery dusts. Contrary to natural ores, spent battery powders seem to be

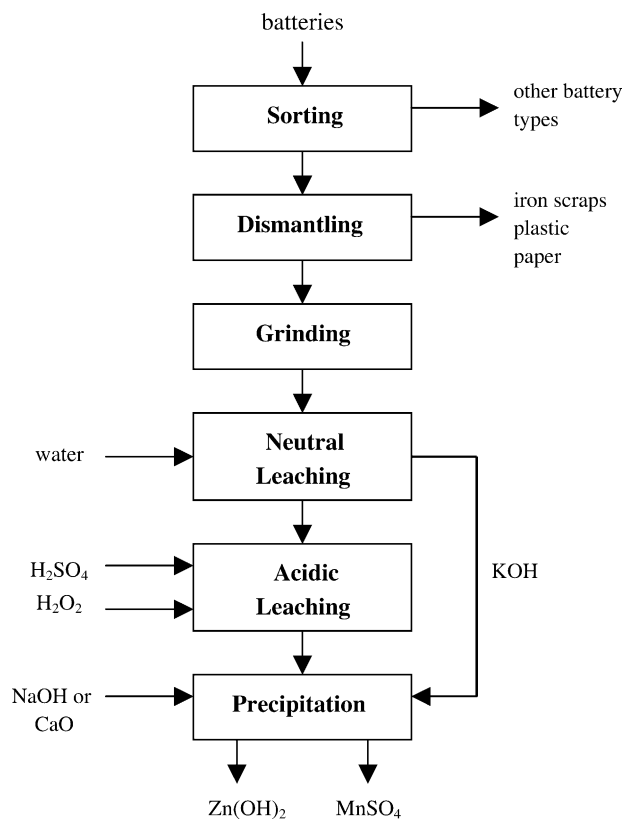
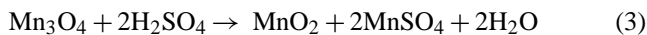
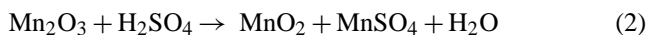
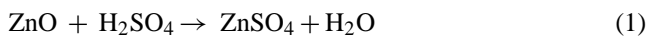


Fig. 1. Hydrometallurgical route proposed for the treatment of spent zinc-carbon and alkaline batteries.

more reactive due to the high concentration of metallic oxides which are easily accessible to the leach solution.

The leaching step is conducted with aqueous solutions in which there is a solubility of the metallic species in the spent battery powder being leached sufficient to obtain an acceptable concentration in solution. Fluorescence and X-ray analysis of spent alkaline battery powders have shown that potassium, zinc and manganese are predominantly present as KO_2 (potassium superoxide), ZnO , Mn_2O_3 and Mn_3O_4 species [2]. From these oxides, only KO_2 is soluble in water. The potassium superoxide found in this kind of powder results from the oxidation of the electrolyte solution of KOH with air during the preliminary treatment step. Oxides of zinc and manganese are insoluble in water, so the separation of potassium from zinc and manganese can be achieved by washing the powder with water (hereafter called neutral leaching), thus resulting in a KOH solution that can be evaporated to give pure KOH salt or used as precipitant solution in the selective precipitation step. After removal of potassium, the dissolution of zinc and manganese oxides can be achieved by leaching the washed powder using sulphuric acid solutions (hereafter called acidic leaching). The removal of potassium from the powder may also contribute to reduce the consumption of sulphuric acid in the acidic leaching step. The following reactions are considered for the dissolution of zinc and manganese oxides [2]:



Zinc oxide can be fully dissolved by sulphuric acid solutions according to Eq. (1). On the other hand, the dissolution of Mn_2O_3 and Mn_3O_4 oxides is partial because MnO_2 produced is insoluble [see Eqs. (2) and (3)]. For instance, the leaching of alkaline battery powders with 1.0% (v/v) H_2SO_4 at 90 °C for 2 h has resulted on the dissolution of only 43% of total manganese originally present in the powder [3]. A similar result (dissolution of 40% of manganese and 100% of zinc oxides) was obtained using 0.7% (v/v) H_2SO_4 at 70 °C and 3 h [8]. Therefore, to leach 100% of the manganese present in the powder, the use of hydrogen peroxide (H_2O_2) as reduction agent is a plausible alternative [2,9] as can be observed by the following reaction:



The aqueous solution obtained in the acidic leaching step is sent to a purification step to separate zinc and manganese. Several separation methods can be used such as liquid–liquid extraction [3,10,11], precipitation [12], electrowinning [13,14], etc. The precipitation method has been chosen in the present work. Compared to liquid–liquid extraction, for example, precipitation seems to be a simpler and cheaper method to separate both metals. Zinc and manganese precipitate at quite distinct pH values, i.e., around 6.5

for $\text{Zn}(\text{OH})_2$ and 10.0 for $\text{Mn}(\text{OH})_2$ in sulphate medium at room temperature [15]. The species $\text{Zn}(\text{OH})_2$ dissolves again at pH values higher than 10.5. On the other hand, it should be pointed out that selective separations by precipitation may fail due to co-precipitation effects if very concentrated metal solutions are used.

In this paper, the leaching (neutral and acidic) and precipitation steps have been investigated in order to optimise the selective separation of metals manganese and zinc from spent zinc–carbon and alkaline batteries.

2. Methodology

2.1. Preliminary treatment of alkaline batteries

The following procedure was adopted to obtain a homogeneous powder to be used in the tests. Firstly, all batteries were dismantled using the cryogenic method described elsewhere [3]. Only discharged alkaline batteries (size D) from the same manufacturer were used in this study. After the separation of iron scraps, plastic and paper, the remaining material, the so-called spent batteries dust (around 50% in weight of the original battery) was dried for 24 h and grinded for 3 h using a ball mill, resulting thus in a fine black powder. In this study, all tests were carried out using homogeneous samples of this powder. The samples were collected using a Quantachrome sieving rifler (model SRR-5 with 8 collecting plates).

2.2. Characterisation of the powder

The black powder was characterised in terms of its metal content, humidity and particle size distribution. Firstly, the qualitative metal content was obtained by X-ray fluorescence method. Then, a sample of the black powder was dissolved in aqua regia and its metal composition quantitatively determined by atomic absorption spectrophotometry (GBC 932 plus model). Afterwards, four 10.0 g samples of the powder were dried for 24 h at 60 °C, and their humidity content obtained by weight difference. Finally, the powder was screened to determine its particle size distribution using a standard vibration system (opening sieves from 0.037 to 0.420 mm) and an air sieving system (opening sieves from 0.010 to 0.075 mm).

2.3. Leaching

The leaching of the black powder was carried out in two sequential steps: neutral and acidic leaching. All tests were carried out in a 1 L covered glass reactor immersed in a controlled-temperature bath under constant stirring. The reactor was provided with mechanical stirring using a marine-type impeller made of glass. The pH of the aqueous solution was monitored using a digital pH meter (Digimed model DM20).

In neutral leaching, potassium superoxide was dissolved in distilled water at room temperature and separated from zinc and manganese. All experiments were done using 50 g of dried powder. Two operating variables were evaluated: solid/liquid ratio (1/20, 1/10, 1/5, 1/2 and 1/1 g mL⁻¹) and number of contacting stages (1 and 2). At the end of each experiment, the suspension was filtered by vacuum and the solid residue containing graphite and not dissolved metals remained on the paper. The solid was dried and weighed. The filtration pulp was not washed in order to avoid the dissolution of the potassium which remained inside the pores of the wet powder. A sample of the resulting basic solution (pH around 11) was withdrawn and analysed by atomic absorption.

Two alternative routes were investigated for the acidic leaching step: (1) zinc selective leaching and (2) total zinc and manganese leaching from the washed powder. The powder used in these tests was previously washed with distilled water to remove all potassium. Preliminary experiments carried out at 10, 20, 30, 60 and 120 min have pointed out no significant variation in metal concentrations with time, so all subsequent tests lasted 20 min. In the selective acidic leaching, the following operating variables were studied: temperature (40, 55 and 70 °C), concentration of H₂SO₄ (0.2, 0.4 and 0.6% v/v and solid/liquid ratio (1/10, 1/30 and 1/50 g mL⁻¹). For total acidic leaching, the operational variables investigated were temperature (40, 55 and 70 °C; tests at room temperature were also done for comparison), concentration of H₂SO₄ (1, 3 and 5% v/v), concentration of H₂O₂ (0, 2 and 4% v/v) and solid/liquid ratio (1/10, 1/30 and 1/50 g mL⁻¹). In these tests, the effect of each operational variable was investigated by keeping the remaining variables at their intermediate level. At the end of each test, the pulp was filtered and a sample of the solution submitted to atomic absorption analysis of zinc and manganese. The leached solid was discarded. All tests were done in triplicate.

2.4. Precipitation

Precipitation experiments were carried out at room temperature in a 1 L covered glass reactor immersed in a controlled-temperature bath under constant stirring and monitoring the pH of the solution. In these tests, a basic solution of KOH and/or NaOH was added very slowly to the liquor obtained in the acidic leaching step in order to raise the pH of the aqueous solution to a given value. The KOH solution obtained in the neutral leaching step was evaluated as precipitant agent. Samples were withdrawn at specified pH values (from 6 to 11) and filtered in a membrane. The metal content in the aqueous phases was determined by atomic absorption.

2.5. Health precautions

All experiments were carried out using gloves, glasses and gas masks. The contact of spent batteries dust with skin, eyes and clothing requires immediate cleaning as suggested by

Salgado et al. [3]. Ingestion, inhalation and persistent skin irritation require medical attention.

3. Results and discussion

3.1. Characterisation of the powder

3.1.1. Metal content

The qualitative analysis of metal content by X-ray fluorescence method has indicated that manganese and zinc are the predominant metals in the black powder of alkaline batteries, followed by potassium which has been identified with an intermediate intensity peak. These metals are present in the powder in the form of oxides [2]. Other species were detected as traces such as Fe, Ti, Ca, Na, Si, Al, F and S.

Table 2 compares the quantitative metal content of the dried powder determined in this work and that found by Salgado et al. [3]. The same powder has been used in both works. Values shown in Table 2 confirm the X-ray fluorescence results. In fact, manganese, zinc and potassium correspond to approximately 58% (w/w) of the sample. The content of zinc and manganese determined by Salgado et al. [3] and in this work deviated around 17%. A significant difference has been found for potassium (60%), but analysis of neutral leaching results point out the value obtained in the present work (4.53% w/w) is more realistic (see Section 3.2.1). The metal content shown in Table 2 is quite close to those of Table 1. All other metals (below 0.4% w/w) were found as traces as previously pointed out by the X-ray fluorescence analysis. However, a considerable difference in the content of mercury was found in both works (650% deviation).

3.1.2. Humidity

All samples have shown a weight loss of 0.6 g after drying for 24 h, so the humidity of alkaline batteries powder was determined as 6.0% (w/w).

3.1.3. Particle size distribution analysis

The particle size distribution of powder was determined firstly using a standard vibration system with sieves disposed in a Tyler series from 35# to 400# (0.420–0.037 mm, respectively). It has been found that almost 40% (w/w) of powder has particle sizes smaller than 0.037 mm, thus

Table 2
Metal composition of dry black powder of alkaline battery

Metal	Content (% w/w) (this work)	Content (% w/w) [3]
Zn	17.05	19.56
Mn	36.53	31.10
K	4.53	7.25
Na	0.13	0.10
Hg	<0.002	0.015
Fe	0.07	0.174
Pb	–	0.005
Ni + Cd + Co	–	0.03
Others	41.69	41.77

Table 3
Dissolution of potassium in two stages at changing solid/liquid ratios

Number of stages	Solid/liquid ratio (g mL ⁻¹)	Conc. of K (g L ⁻¹)	Mass of K (g)	% K leached
1	1/20	2.19	2.190	96.6
	1/10	4.46	2.230	98.4
	1/5	8.97	2.243	99.0
	1/2	18.55	1.855	81.9
	1/1	36.53	1.827	80.6
2	1/20	0.13	0.114	101.7
	1/10	0.23	0.128	104.1
	1/5	0.86	0.187	107.3
	1/2	2.75	0.241	92.5
	1/1	9.38	0.422	99.2

indicating the powder is very fine. To better characterise its particle size, the powder was analysed again but using an air sieving system with opening sieves from 0.010 to 0.075 mm. It has been found that 4.7% (w/w) of powder particles were still smaller than 0.010 mm. The experimental findings were fitted to the following distribution models [16] in order to get an estimative of the mean Sauter diameter of the powder: Gates–Gaudin–Schuman (GGS), Rosin–Rammler–Bennet (RRB), log-normal e-sigmoidal. The best fit was found by the sigmoidal model and the Sauter mean diameter of powder was estimated to be around 11 μm . This value indicates that leaching of metals will proceed rapidly, within 6 min based on typical values of common ores [17], so no grinding step seems necessary to treat this kind of residue.

3.2. Leaching

3.2.1. Neutral leaching

In these experiments, 50 g of black dried powder were contacted with different volumes of distilled water. Preliminary tests at solid/liquid ratio of 1/20 g mL⁻¹ have shown that dissolution of potassium in water is practically instantaneous. A fast increase in the solution pH to values around 11–12 was observed in the first 30 s and the value stabilised afterwards. Therefore, in order to warrant the system to reach equilibrium, all tests were carried out for 5 min. It was verified also that practically 100% of potassium was dissolved in one single stage at a solid/liquid ratio of 1/20 g mL⁻¹. Taking into consideration the solubility of potassium in water (97 parts/100 mL of water [16]), it was decided to carry out the neutral leaching tests in two sequential stages varying the solid/liquid ratio.

According to the results shown in Table 3, potassium was practically extracted in one single contact at solid/liquid ratio of 1/20, 1/10 and 1/5 g mL⁻¹, and in two contacts at solid/liquid ratios of 1/2 and 1/1 g mL⁻¹. The adherence of potassium in more concentrated pulps may explain the results. The smaller the solid/liquid ratio, the higher the concentration of potassium in the aqueous phase. It is possible to concentrate it even more if liquors are reused or contacted with powder in a countercurrent scheme. In some tests in the second stage, the computed potassium extraction exceeded

100%. This is possibly due to the potassium present in the liquid phase that remained in the pores of the filtered wet pulp after the first stage (no pulp washing was done during filtration); this filtered pulp was dried and fed to the second stage.

Regardless of the solid/liquid ratio investigated in this study, the mean total mass of potassium extracted in two stages was 2.3 ± 0.2 g, which corresponds to $4.6 \pm 0.4\%$ (w/w) of the black powder. This result confirms that the potassium content in the black powder is 4.53% (w/w), as found in the present work (see Table 2).

Analysis of the KOH aqueous solutions produced in the neutral leaching step revealed no zinc or manganese in solution, so these metals remained in the solid matrix.

3.2.2. Acidic leaching

3.2.2.1. *Selective acidic leaching.* In these experiments, dilute sulphuric acid solutions were used in order to maximise zinc extraction and minimise manganese extraction. Fig. 2 shows the effect of the concentration of sulphuric acid on the leaching of zinc and manganese, including the corresponding 95% confidence intervals. As expected, the leaching of both metals has increased with the increase in the concentration of acid. This effect seems to be more significant for

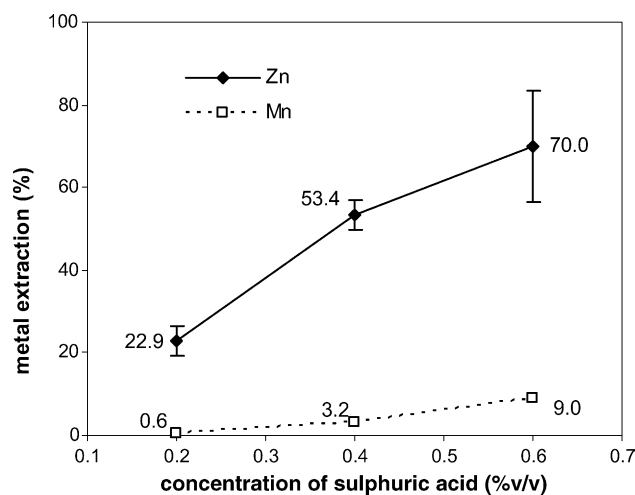


Fig. 2. Influence of the concentration of sulphuric acid on the leaching of zinc and manganese ($T = 55^\circ\text{C}$, solid/liquid ratio = 1/30).

the extraction of manganese, so more selective conditions for zinc requires the use of more dilute acid solutions. However, since the mass of zinc extracted in the inferior level of acid concentration is low (around 23% w/w at 0.2% v/v H_2SO_4), the separation of zinc and manganese must be carried out in a staged scheme.

Fig. 3 shows the influence of temperature on the leaching of zinc and manganese at the intermediate levels of concentration of sulphuric acid and solid/liquid ratio investigated in this study. It has been found the increase of temperature from 40 to 55 °C has no effect on the leaching of zinc and manganese. However, the extraction of zinc increases significantly at temperature levels greater than 55 °C. This behaviour is an indicative that leaching of zinc is controlled by the extraction kinetics [18]. At 70 °C, all zinc was leached from the powder and only 4.5% of manganese was extracted. Similar behaviour has been found by Souza et al. [2].

Fig. 4 shows the influence of solid/liquid ratio on the leaching of zinc and manganese. The extraction of both metals increases when smaller solid/liquid ratios are used. However, the leaching of zinc seems statistically similar at solid/liquid ratios 1/30 and 1/50 g mL^{-1} . The most selective condition for zinc extraction was found using the smallest solid/liquid ratio (1/10 g mL^{-1}), but various stages are required to leach all zinc because the mass of metal leached is small for these operating conditions.

3.2.2.2. *Total acidic leaching.* In these experiments, concentrate sulphuric acid solutions in the presence of peroxide of hydrogen were used in order to maximise zinc and manganese extractions. Fig. 5 shows the effect of the sulphuric acid concentration on the leaching of these metals. As expected, the extraction of both metals increased in more concentrated sulphuric acid solutions. According to Fig. 5, zinc and manganese were fully extracted from the powder with

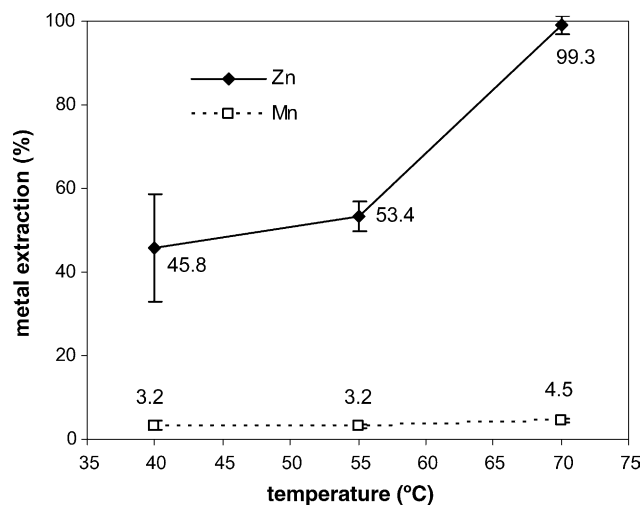


Fig. 3. Influence of the temperature on the leaching of zinc and manganese ($[\text{H}_2\text{SO}_4] = 0.4\%$ v/v, solid/liquid ratio = 1/30).

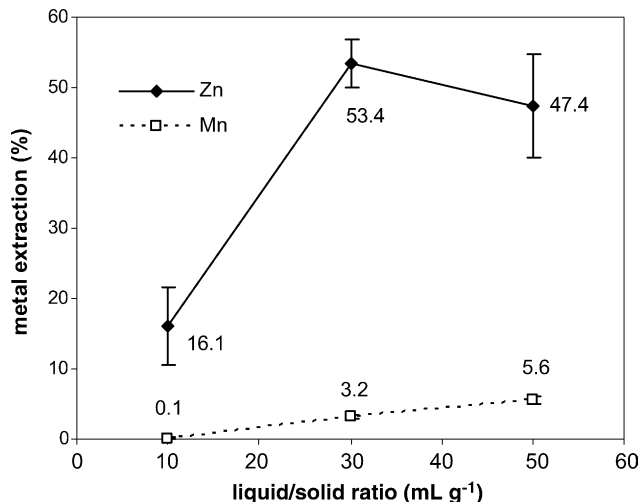


Fig. 4. Influence of the solid/liquid ratio on the leaching of zinc and manganese ($T = 55\text{ }^\circ\text{C}$, $[\text{H}_2\text{SO}_4] = 0.4\%$ v/v).

3% (v/v) of sulphuric acid in one single contact, so more concentrated solutions are not economical.

The effect of temperature on the total leaching of zinc and manganese is shown in Fig. 6, including 95% confidence intervals. Zinc was totally extracted in the investigated temperature range. This was attributed to the high concentration of sulphuric acid used in these experiments. On the other hand, the extraction of manganese is low at room temperature (around 50%) but it increases significantly (almost 100%) at temperatures higher than 40 °C.

The effect of the solid/liquid ratio on the leaching of zinc and manganese was found statistically similar for both metals under the operational conditions studied as shown in Fig. 7. Around 50% of zinc and manganese were leached at solid/liquid ratio of 1/10 and these metals were fully extracted at ratios greater than 1/30. However, a more concentrated solution in zinc and manganese was obtained at ratio of 1/10.

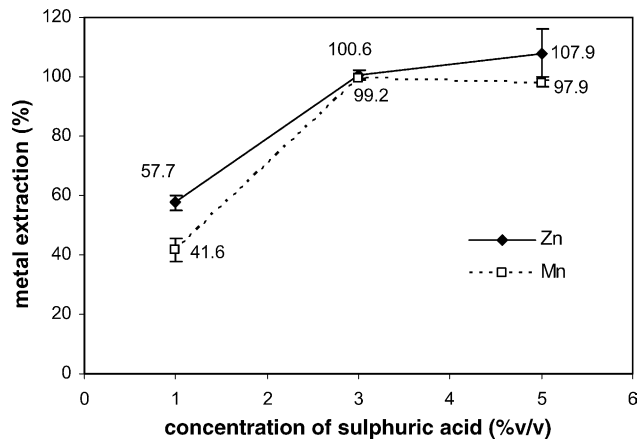


Fig. 5. Influence of the concentration of sulphuric acid on the leaching of zinc and manganese ($T = 55\text{ }^\circ\text{C}$, solid/liquid ratio = 1/30, $[\text{H}_2\text{O}_2] = 2\%$ v/v).

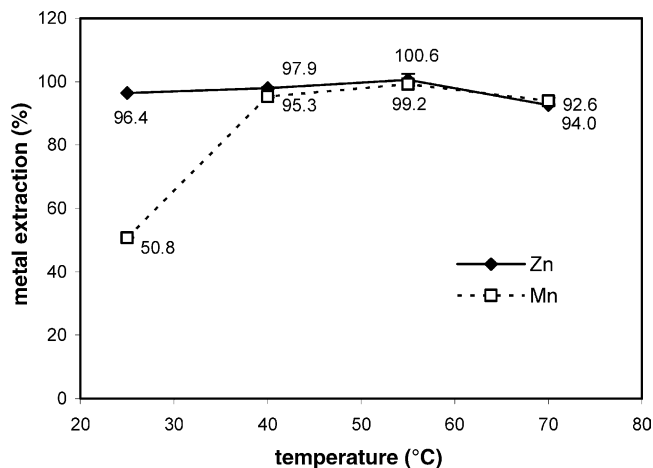


Fig. 6. Influence of the temperature on the leaching of zinc and manganese ($[\text{H}_2\text{SO}_4] = 3\%$ v/v, solid/liquid ratio = 1/30, $[\text{H}_2\text{O}_2] = 2\%$ v/v).

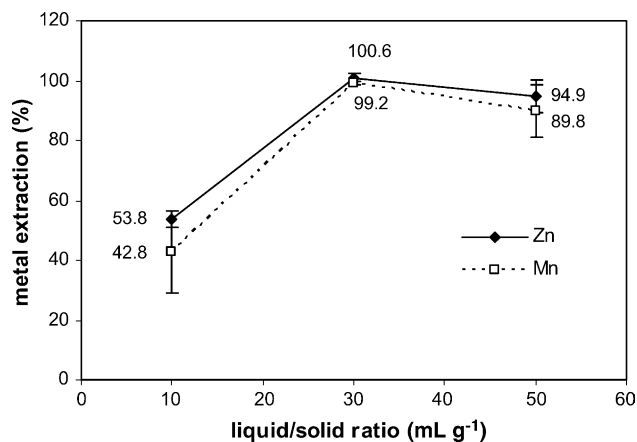


Fig. 7. Influence of the solid/liquid ratio on the leaching of zinc and manganese ($T = 55^\circ\text{C}$, $[\text{H}_2\text{SO}_4] = 3\%$ v/v, $[\text{H}_2\text{O}_2] = 2\%$ v/v).

The effect of H_2O_2 on the leaching of zinc and manganese from alkaline battery powder is shown in Fig. 8. As expected, H_2O_2 has shown no effect on the leaching of zinc and 100% of zinc was extracted at the operational conditions investigated.

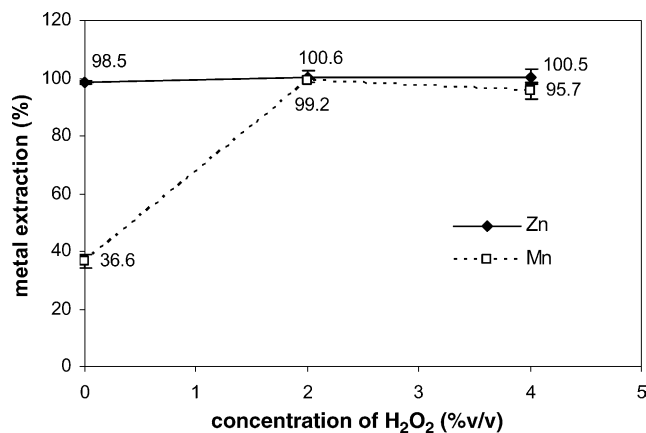


Fig. 8. Influence of the concentration of H_2O_2 on the leaching of zinc and manganese ($T = 55^\circ\text{C}$, $[\text{H}_2\text{SO}_4] = 3\%$ v/v, solid/liquid ratio = 1/30).

Contrariwise, only about 40% of manganese was leached at the absence of hydrogen peroxide, corroborating other studies found in the literature [3,8]. This result indicates that 60% of manganese originally found in the powder as Mn_2O_3 and Mn_3O_4 was converted into insoluble MnO_2 as shown by Eqs. (2) and (3). Therefore, according to Eq. (4), the presence of H_2O_2 as reduction agent to leach MnO_2 is necessary to extract all manganese from the powder.

3.3. Precipitation

The precipitation of zinc and manganese was investigated using two different aqueous liquors obtained at the best operational conditions found in the study of the acidic leaching step (Section 3.2.2). The liquor from the selective acidic leaching step contains predominantly zinc ($[\text{Zn}] = 1.48 \text{ g L}^{-1}$, $[\text{Mn}] = 2.65 \text{ ppm}$, pH 6.1) and it was obtained by leaching the washed powder at following operational conditions: $[\text{H}_2\text{SO}_4] = 0.2\%$ (v/v), $T = 70^\circ\text{C}$ and solid/liquid ratio = 1/10 g mL^{-1} . The liquor from the total acidic leaching step is more concentrated in zinc and manganese ($[\text{Zn}] = 5.66 \text{ g L}^{-1}$, $[\text{Mn}] = 11.56 \text{ g L}^{-1}$, pH 0.8) and was obtained by leaching the washed powder at following operational conditions: $[\text{H}_2\text{SO}_4] = 3\%$ (v/v), $T = 40^\circ\text{C}$, $[\text{H}_2\text{O}_2] = 1\%$ (v/v) and solid/liquid ratio = 1/30 g L^{-1} . Tests were carried out in one single stage.

The precipitation curves of zinc and manganese with KOH are shown in Fig. 9. A shift to the right was observed in the curves of both metals as more concentrated metal solutions were used. The shift affects zinc more significantly than manganese, so it is more difficult to separate these metals from concentrated solutions. In addition, a higher volume of precipitant agent is required to raise the pH from 0.8 to 9.0. In our tests, an additional very concentrated solution of KOH (105.4 g L^{-1}) was added to the system. On the other hand, no extra potassium was added to treat the aqueous liquor obtained in the selective acid leaching. In this case, the route seems to be more economical because all KOH required to

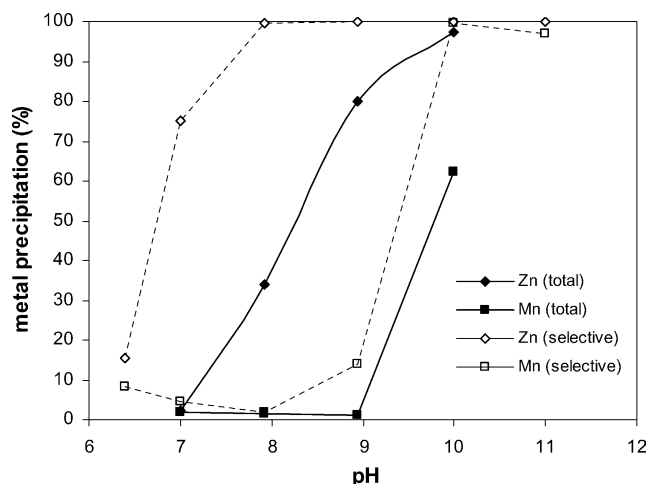


Fig. 9. Precipitation of zinc and manganese with KOH.

separate zinc and manganese was produced on the neutral leaching step. In our experiments, neutral leaching was carried out at solid/liquid ratio of $1/20 \text{ g mL}^{-1}$, so about 160 mL of KOH solution was necessary to raise the pH from 6 to 9; the volume of KOH solution to precipitate zinc can be reduced to a quarter if neutral leaching is carried out at solid/liquid ratio of $1/5 \text{ g mL}^{-1}$.

According to Fig. 9, zinc and manganese can be separated by precipitation in both cases, but it is easier to separate them from dilute metal solutions. In this case, all zinc can be selectively separated from manganese at pH 8. On the other hand, around 80% of zinc can be selectively separated from manganese at pH 9. This operation, however, requires a strict control of pH to be done successfully because zinc and manganese curves are very close.

4. Conclusions

A hydrometallurgical route to separate zinc and manganese from spent alkaline batteries has been proposed in this work. The results have shown the route is technically viable to treat this kind of residue.

The black powder obtained after dismantling (around 50% w/w of the original battery) was characterised in terms of its metal composition, humidity (6% w/w) and particle size. Zinc, manganese and potassium were found as the main metallic constituents of the powder and they were considered as oxides according to the literature [2]. The powder is very thin so a grinding step seems unnecessary.

Potassium can be fully removed from the powder by washing it with water at room temperature in one single stage at solid/liquid ratio of $1/5 \text{ g mL}^{-1}$ (neutral leaching).

Zinc and manganese were leached by sulphuric acid solutions (acidic leaching). Selective and total metal separation operations were studied. Zinc selective leaching requires staged operation scheme using dilute sulphuric acid solutions (0.2% v/v), relatively high temperatures (70°C) and small solid/liquid ratios ($1/10 \text{ g L}^{-1}$). On the other hand, total zinc and manganese leaching can be achieved in one single contact at concentrate sulphuric acid solutions (up to 3% v/v), relatively low temperatures (around 40°C), presence of H_2O_2 (up to 1% v/v) and larger solid/liquid ratios (around $1/30 \text{ g L}^{-1}$).

Selective precipitation of zinc using the KOH solution produced on the neutral leaching step as precipitant agent was studied to separate zinc and manganese from the liquors produced on the acidic leaching step. The results point out the method can treat dilute and concentrate liquors.

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