



## Acidic leaching and precipitation of zinc and manganese from spent battery powders using various reductants

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### ABSTRACT

The main objective of this study was to investigate the effects of reductive acidic leaching and further precipitation on the recovery of manganese and zinc from spent alkaline and zinc–carbon battery powders. Ascorbic acid (AA), citric acid (CA) and oxalic acid (OA) were tested as the reductants. Sodium hydroxide and potassium hydroxide were used as precipitating agents. OA with H<sub>2</sub>SO<sub>4</sub> or HCl was not effective on the leaching of zinc due to the formation of zinc oxalate precipitates. However, the other reducing agents (CA and AA) tested under various experimental conditions were effective in the acidic leaching of both zinc and manganese. Leaching yields of both manganese and zinc were higher at leach temperature of 90 °C than those at 30 °C. Leach solutions were purified by the selective precipitation of manganese and zinc using KOH or NaOH. Complete precipitation was obtained for Mn at pH 9–10 and for Zn at pH 7–8. The use of ascorbic acid or citric acid as reductants in acidic leaching appears to be effective in the simultaneous leaching and further recovery of zinc and manganese from spent alkaline and zinc–carbon battery powders.

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### 1. Introduction

The use of spent batteries in a way which may harm the environment and their direct or indirect discharge to the environment are prohibited due to the new stringent environmental regulations in most countries. On account of this, in recent years, numerous studies have been conducted on the recycling of spent alkaline and zinc–carbon batteries. The main metals in zinc–carbon and alkaline batteries are manganese and zinc [1–6]. While the recycling and further reuse of metals from spent batteries are becoming essential due to environmental concerns and new regulations, it is also important that the recycling processes should be environmentally friendly, practical and economically feasible. Detailed information on many pyrometallurgical and hydrometallurgical recovery processes from spent batteries were published [3,5,7,8]. Metals can be leached from their oxides by direct reactions with acid or alkali solutions, or by reactions with either of these solutions in the presence of an oxidizing or reducing agent [9]. After leaching, further separation methods are required to recover metals from leach solutions. Several separation methods can be used such as liquid–liquid extraction [3,10–13], precipitation [4,6,14,15], electro-winning [16–18].

Devi et al. [19] obtained extractions of 99.7% for zinc and 5.0% for manganese using a sodium salt of Cyanex 272 from sulfate solution.

Salgado et al. [3] investigated liquid–liquid extraction tests using 20% (v/v) Cyanex 272 dissolved in Escaid 110 at 50 °C. Their results showed that the method was selective for zinc, leaving manganese in the leach solution. El-Nadi et al. [13] studied CYANEX 301 dissolved in kerosene; the results showed that extracted Zn and Mn were 98% and 7%, respectively. Compared to liquid–liquid extraction, precipitation can be a simpler and cheaper method to separate both metals from leach solutions. Zinc and manganese precipitate at quite distinct pH values, i.e., around 6.5 for Zn(OH)<sub>2</sub> and 10.0 for Mn(OH)<sub>2</sub> in sulfate medium at room temperature [4]. Shin et al. [20] investigated precipitation of Mn, Fe and Zn in leach liquor using 5 M NaOH solution. It was found that incomplete precipitation of metals occurred in the pH range of 5–10, but all three metal ions could be precipitated at a pH value greater than 10. Electrochemical recycling may be another option for the separation of Mn and Zn. The mechanisms of zinc recovery from spent Zn–MnO<sub>2</sub> batteries depend on whether the solution is acidic or alkaline. In acidic solutions, adsorbed hydrogen tends to catalyze the Zn<sup>2+</sup> electro-deposition. In alkaline solutions, hydrogen evolution tends to block zincate electro-deposition [17].

In this study, three different reductants (OA, AA and CA) were compared for their effectiveness in the acidic leaching (sulfuric acid or hydrochloric acid) of manganese and zinc from spent alkaline and zinc–carbon battery powders. After leaching tests, sodium hydroxide or potassium hydroxide solutions were added to leach liquors to evaluate their effectiveness in the precipitation of zinc and manganese with a purpose of their separation from leach liquors. The following reactions were considered for the dissolu-

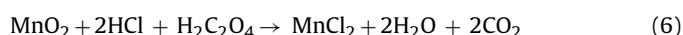
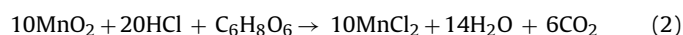
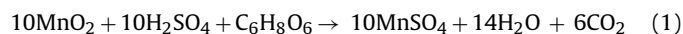
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**Table 1**Factors and investigated levels in leaching tests with H<sub>2</sub>SO<sub>4</sub> and ascorbic acid (leach duration: 3 h).

Test no.	A (pulp density) (%) <sup>a</sup>	B (ascorbic acid) (%) <sup>b</sup>	C (H <sub>2</sub> SO <sub>4</sub> ) (%) <sup>b</sup>	D (temperature) (°C)
1	10	-30	-30	45
2	20	-30	-30	45
3	10	30	-30	45
4	20	30	-30	45
5	10	-30	30	45
6	20	-30	30	45
7	10	30	30	45
8	20	30	30	45
9	10	-30	-30	75
10	20	-30	-30	75
11	10	30	-30	75
12	20	30	-30	75
13	10	-30	30	75
14	20	-30	30	75
15	10	30	30	75
16	20	30	30	75
17	15	0	0	60
18	15	0	0	60
19	15	0	0	60
20	15	0	0	60
21	5	0	0	60
22	25	0	0	60
23	15	-60	0	60
24	15	60	0	60
25	15	0	-60	60
26	15	0	60	60
27	15	0	0	30
28	15	0	0	90

<sup>a</sup> Percent pulp density: powder mass (g)/acid solution volume (mL) × 100.<sup>b</sup> Percent ascorbic acid and sulfuric acid dosages with respect to their stoichiometric requirement. (-) indicates less than stoichiometric requirement, (+) indicates more than stoichiometric requirement.

tion of manganese oxides from battery powders with AA (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>), CA (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) and OA (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) in sulfuric acid or hydrochloric acid media. The required stoichiometric dosages of H<sub>2</sub>SO<sub>4</sub>, HCl and reducing agents were calculated based on these reactions. Such approach was also applied for zinc oxides in the battery powders.



## 2. Materials and methods

### 2.1. Battery dismantling and powder preparation

Spent alkaline and zinc-carbon batteries were manually dismantled. Dismantling products such as plastic films, ferrous scraps and paper pieces were discarded. The powders, which were about 40–64% of the total weight of dismantled batteries, were dried for 24 h at 105 °C. The powder samples (mixture of spent alkaline and zinc-carbon batteries) were crushed using a jaw crusher (Fritsch) and then ground using a ball mill (Fritsch) for particle size reduction. The powder samples were manually sieved to obtain particles less than size 425 μm. This fraction was then washed with distilled and deionized water (DDW) at 1/5 solid/liquid ratio by mixing at 200 rpm, at 80 °C, for 1 h. The aim of the washing (neutral leaching) was to remove salts including potassium and chloride from powders. Neutral leaching was conducted in a 1-L batch-reactor equipped with a water jacket. The washed powder was dried up to 24–32 h at 105 °C until moisture was removed and constant weight

was achieved. The dried powder was kept in a vacuum desiccator. All leaching tests were carried out with the same batch of this washed and dried powder fraction. Original (unwashed) and washed zinc-carbon, alkaline, mixed (50% zinc-carbon, 50% alkaline) battery powders were analyzed by X-ray fluorescence (XRF) (Spectro Xepos). Further details on battery dismantling, powder treatment and characterization are presented in our previous publication [21].

**Table 2**

Leaching results with different reducing agents (10% pulp density, 45 °C, leach duration: 3 h).

Test no.	Dosage <sup>a</sup>		MnEY <sup>e</sup> (%)	ZnEY <sup>f</sup> (%)
	Acids	Reducing agents		
1	+30% H <sub>2</sub> SO <sub>4</sub>	-30% OA <sup>b</sup>	64.0	101.0
2	+30% HCl	-30% OA	64.3	91.9
3	Stoich. H <sub>2</sub> SO <sub>4</sub>	Stoich. OA	81.9	90.4
4	+30% H <sub>2</sub> SO <sub>4</sub>	-30% CA <sup>c</sup>	65.4	98.8
5	+60% H <sub>2</sub> SO <sub>4</sub>	Stoich. CA	71.4	100.3
6	+60% HCl	Stoich. CA	75.6	89.6
7	+30% HCl	+30% CA	73.7	89.1
8	Stoich. HCl	Stoich. CA	75.2	103.4
9	+60% H <sub>2</sub> SO <sub>4</sub>	Stoich. AA <sup>d</sup>	59.6	104.6
10	+30% H <sub>2</sub> SO <sub>4</sub>	+30% AA	66.5	99.8
11	Stoich. H <sub>2</sub> SO <sub>4</sub>	Stoich. AA	56.7	103.0
12	+30% HCl	+30% AA	70.8	88.1
13	Stoich. HCl	Stoich. AA	68.6	89.2

<sup>a</sup> Reductant and inorganic acid dosages with respect to their stoichiometric requirements (as percentage). (-) indicates less than stoichiometric requirement, (+) indicates more than stoichiometric requirement.<sup>b</sup> Oxalic acid.<sup>c</sup> Citric acid.<sup>d</sup> Ascorbic acid.<sup>e</sup> Manganese extraction yield.<sup>f</sup> Zinc extraction yield.

## 2.2. Acidic leaching tests

A 2<sup>4</sup> factorial design with replicated central point tests was chosen for conducting the leaching tests where the factors were pulp density, reducing agent (AA, CA or OA) dosage, acid (H<sub>2</sub>SO<sub>4</sub> or HCl) dosage, and temperature. The factors and investigated levels are shown in Table 1 as an example for ascorbic acid and H<sub>2</sub>SO<sub>4</sub>. Other leaching tests were carried out similarly. Tests were numbered in conformity with the Yates algorithm [22]. Acidic leaching tests were conducted in 250-mL high-density polyethylene flasks (solution volume 100 mL) located in a water bath (ST402, Nuve) under constant stirring (200 rpm) for 3 h. Required quantities of acid (H<sub>2</sub>SO<sub>4</sub> or HCl) and reducing agent to be dosed to the flasks were calculated according to the 2<sup>4</sup> full factorial design. During these leach tests, 1.5 mL of leach liquor sample was withdrawn from flasks after 1, 3 and 5 h to determine the concentrations of Mn and Zn. Before the analysis for Mn and Zn, such liquor samples were centrifuged at 10,000 rpm for 5 min (MiniSpin Plus, Eppendorf). Each sample was diluted by 1:10 using nitric acid solution (pH ~2) to avoid the precipitation of metals and then samples were kept at 4 °C in the fridge until analysis. Zn and Mn concentrations were determined by inductively coupled plasma (ICP-OES) (DV2100, PerkinElmer). Our previous results [21] showed that a leach duration of 3 h was sufficient for the leaching equilibrium to be reached for both Zn and Mn. Thus, a 3 h of leaching was employed in all tests.

Percent coefficient of variations for the triplicate measurements of Zn and Mn concentrations were less than ±5%. The pH of the leach solutions was monitored using a digital pH meter (6250, Jenco). In addition to the factorial design tests, further acidic leaching tests were carried out at a temperature of 45 °C, pulp density of 10%, and leaching duration of 3 h (Table 2). Inorganic acid and reductant dosages were chosen according to the best leaching conditions (tests no. 5, 6, 28 for OA; tests no. 14, 26, 28 for CA; and

tests no. 8, 16, 26, 28 for AA) achieved as shown in Tables 3 and 4. A 98% sulfuric acid (Merck) and a 37% hydrochloric acid solution (Merck) were used as the stock solutions for all experiments. The used OA (Merck), AA (Carlo Erba), and CA (Merck) were obtained in high purity (>99%) powder forms. DDW was used for stock solution preparations and dilutions.

## 2.3. Precipitation tests

After the leaching step, precipitation experiments were carried out. These experiments were conducted on the filtered leach solutions as shown in Table 2. A solution of 2 M KOH (Merck) or 2 M NaOH (Merck) was added very slowly to the leach solution to raise the pH up to 11. The pH of the solution was monitored during precipitation. Samples were withdrawn at specified pH values (3, 6–11) and filtered (0.45 μm cellulose acetate filter papers). The metal concentrations in the filtered solutions were determined by ICP-OES (DV2100, PerkinElmer). The solid precipitates remained on the filter papers after filtration were dried in the oven (FN 500, Nuve) at 105 °C for 24 h, which was found to be sufficient duration to achieve constant weight. The dried solid residues were then analyzed by X-ray diffraction (XRD) (Philips, X'Pert PRO MPD) to investigate their mineralogical composition.

## 3. Results and discussion

### 3.1. Leaching experiments

Acidic leaching experiments using various reductants were carried out to determine the most effective leaching conditions in terms of simultaneous manganese and zinc extractions. Our previous results showed that simultaneous high extractions for Mn and Zn from spent battery powders may not be possible when OA is used as a reducing agent, mainly due to the formation of zinc

**Table 3**  
Acidic leaching test results with H<sub>2</sub>SO<sub>4</sub> (leach duration: 3 h).

Test no. <sup>a</sup>	H <sub>2</sub> SO <sub>4</sub> + OA		H <sub>2</sub> SO <sub>4</sub> + CA		H <sub>2</sub> SO <sub>4</sub> + AA	
	MnEY <sup>b</sup> (%) R <sup>2</sup> : 0.76	ZnEY <sup>c</sup> (%) R <sup>2</sup> : 0.78	MnEY (%) R <sup>2</sup> : 0.97	ZnEY (%) R <sup>2</sup> : 0.62	MnEY (%) R <sup>2</sup> : 0.94	ZnEY (%) R <sup>2</sup> : 0.76
1	77.5	85.4	54.2	113.2	41.7	100.89
2	68.4	70.8	56.0	113.6	50.5	113.5
3	67.2	7.1	55.9	106.6	60.3	106.4
4	68.9	9.0	65.2	119.3	59.3	108.8
5	91.2	112.5	60.8	111.3	45.4	101.7
6	82.0	104.5	74.2	112.4	51.8	111.2
7	80.3	8.0	84.1	121.5	65.8	108.2
8	80.5	8.0	89.5	110.9	64.5	93.8
9	35.3	28.1	49.2	113.9	67.3	115.9
10	45.8	27.0	51.8	107.9	56.2	100.9
11	50.1	5.8	58.1	112.9	68.6	115.5
12	61.5	7.7	62.1	113.6	73.4	118.9
13	80.8	101.7	69.6	117.8	68.9	121.9
14	82.9	97.3	83.2	120.4	72.2	110.8
15	77.8	9.5	87.6	112.2	88.5	118.3
16	69.8	8.2	113.8	121.7	93.4	123.7
17	77.8	32.3	75.8	107.5	79.8	132.6
18	76.6	31.3	76.3	111.3	76.4	120.1
19	76.9	31.5	75.7	109.2	78.9	114.0
20	76.2	32.3	76.9	109.1	80.1	121.4
21	71.4	11.3	59.9	108.8	72.2	112.7
22	81.3	25.1	73.9	100.6	78.4	109.3
23	25.9	53.0	52.7	111.9	51.5	121.4
24	49.2	3.7	86.9	105.5	84.6	111.1
25	36.4	7.3	31.5	93.5	39.4	69.0
26	98.5	32.8	89.4	101.1	92.0	130.0
27	58.2	24.9	46.1	106.3	51.8	106.2
28	92.4	91.9	84.1	118.1	97.0	128.8

<sup>a</sup> Same test numbers as indicated in Table 1.

<sup>b</sup> Manganese extraction yield.

<sup>c</sup> Zinc extraction yield.

**Table 4**  
Acidic leaching test results with HCl (Leach duration: 3 h).

Test no. <sup>a</sup>	HCl + OA		HCl + CA		HCl + AA	
	MnEY <sup>b</sup> (%) R <sup>2</sup> : 0.88	ZnEY <sup>c</sup> (%) R <sup>2</sup> : 0.95	MnEY (%) R <sup>2</sup> : 0.86	ZnEY (%) R <sup>2</sup> : 0.81	MnEY (%) R <sup>2</sup> : 0.84	ZnEY (%) R <sup>2</sup> : 0.72
1	66.1	50.4	61.4	101.1	61.3	99.6
2	69.1	58.4	59.5	105.6	66.7	108.8
3	63.8	8.4	67.1	98.1	67.9	106.7
4	65.7	10.5	65.8	114.4	68.2	102.6
5	84.0	86.9	67.2	96.7	78.3	109.7
6	85.6	95.0	75.3	104.3	98.8	103.9
7	79.9	15.2	91.9	100.1	82.2	97.5
8	68.7	14.4	98.1	106.7	101.6	108.6
9	66.7	37.2	66.3	108.6	72.4	109.9
10	57.6	52.0	68.3	109.3	71.6	103.5
11	66.3	3.2	70.1	102.6	74.4	100.9
12	52.1	7.2	66.4	102.1	71.8	98.5
13	80.8	88.6	76.6	105.0	85.5	92.8
14	79.3	95.2	83.9	103.7	97.8	96.5
15	74.2	4.8	103.8	111.8	109.1	106.5
16	81.5	5.5	100.5	106.7	102.7	104.3
17	82.9	43.8	91.3	103.2	98.7	103.7
18	81.8	45.2	89.8	103.2	100.8	102.8
19	82.8	49.9	89.4	102.8	98.8	104.5
20	83.8	49.0	90.8	102.6	98.0	103.4
21	88.7	16.2	84.1	101.5	100.4	94.3
22	64.0	58.2	33.5	67.1	98.7	100.0
23	55.2	92.4	35.3	106.4	88.7	107.2
24	55.8	4.9	97.9	102.0	99.4	96.8
25	48.4	7.0	98.1	109.7	63.0	99.8
26	91.0	57.5	102.8	116.6	99.5	104.6
27	81.4	48.6	40.2	101.4	90.0	112.1
28	92.9	57.6	113.2	120.8	105.8	109.3

<sup>a</sup> Same test numbers as indicated in Table 1.

<sup>b</sup> Manganese extraction yield.

<sup>c</sup> Zinc extraction yield.

oxalate precipitates during reductive leaching [21]. Tables 3 and 4 show the Mn and Zn extraction yields obtained by H<sub>2</sub>SO<sub>4</sub> and HCl leaching, respectively. The impacts of the tested organic acids as reductants on the extraction yields are shown. The regression coefficients (*R*<sup>2</sup>) obtained from ANOVA (analysis of variance) method are also indicated in these tables. These results showed that HCl exhibited better performance than H<sub>2</sub>SO<sub>4</sub> in terms of Mn and Zn leaching yields. Among the tested reducing agents, both ascorbic acid and citric acid appeared to be effective on the leaching of Zn and Mn.

The leaching test results indicated that OA dosages more than 30% of the stoichiometric requirement (Test No. 3, 4, 7, 8, 11, 12, 15, 16, 24, and 25) yielded very low Zn extractions. Zinc was leached only around 3–15% by both H<sub>2</sub>SO<sub>4</sub> and HCl when excessive OA was dosed (Tables 3 and 4). This finding is consistent with other studies published in literature [6,21]. On the other hand, results for CA and AA showed that significant amounts of zinc and manganese were extracted (Tables 3 and 4). About 87–100% of manganese and almost 100% of zinc were leached after 3 h by both H<sub>2</sub>SO<sub>4</sub> and HCl acids (Test No: 15. Inorganic acids: +30%, reductants (AA or CA): +30%, temperature: 75 °C, pulp density: 10%). Similarly, De Michelis et al. [23] indicated that almost complete manganese and zinc extractions were achievable with the following conditions; leach duration: 5 h, sulfuric acid: stoichiometric requirement, temperature: 80 °C, CA: +50%, pulp density: 10%. Extraction yields higher than 100% are mainly due to inherent variability in leach tests and powder characterization, and analytical measurement errors. As indicated previously, percent coefficient of variations for the triplicate measurements of Zn and Mn concentrations were generally less than ±5%. However, although the used battery powder obtained from various types of spent alkaline and zinc–carbon batteries was sieved and mixed thoroughly, this powder batch may not be completely homogenous in terms of its Mn and Zn contents. It should be noted that a small amount of powder was taken from

this batch and transferred to each leach flask. Therefore, extraction yields were presented in percentages to compensate for the variability in initial metal contents of the powders transferred to each leach flask.

Overall, it was found that the zinc precipitation problem observed for OA did not occur for CA and AA. Both inorganic acids were effective for the solubilization of zinc oxides in the battery powder. These acids were also effective for the solubilization of all types of manganese oxides (i.e., MnO, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>) present in the powder when CA or AA was used to reduce MnO<sub>2</sub>. MnO<sub>2</sub> is an insoluble by-product formed from the reactions among Mn<sub>2</sub>O<sub>3</sub> and strong acids, or Mn<sub>3</sub>O<sub>4</sub> and strong acids. While both CA and AA were effective for almost complete leaching of Mn under acidic conditions, they also did not form zinc precipitates, a problem which was observed for OA (as zinc oxalate precipitates).

In terms of the impact of leach temperature, it was found that the extraction yields of both manganese and zinc were higher at a temperature of 90 °C (Test 28) compared to those at 30 °C (Test 27). While about 58% MnEY and 25% ZnEY were achieved at 30 °C with OA, MnEY and ZnEY were both increased to about 92% at 90 °C. The positive impact of increasing temperature was also observed for leaching of Mn and Zn with other reducing agents. Although both inorganic acids were effective for the leaching of Zn and Mn, HCl provided about 11% less Zn extraction and about 12% more Mn extraction compared to H<sub>2</sub>SO<sub>4</sub> when the other variables were constant (Tests 11 and 13 in Table 2). Similarly, El-Nadi et al. [13] found that while H<sub>2</sub>SO<sub>4</sub> was relatively more efficient for the leaching of Zn, HCl provided slightly higher extraction of Mn.

ANOVA analyses of the tests carried out with OA were presented in our previous publication [21]. Thus, only ANOVA analysis of citric acid and ascorbic acid tests are presented in this paper. Fig. 1 shows the main and interaction effects on the ZnEY (A) and MnEY

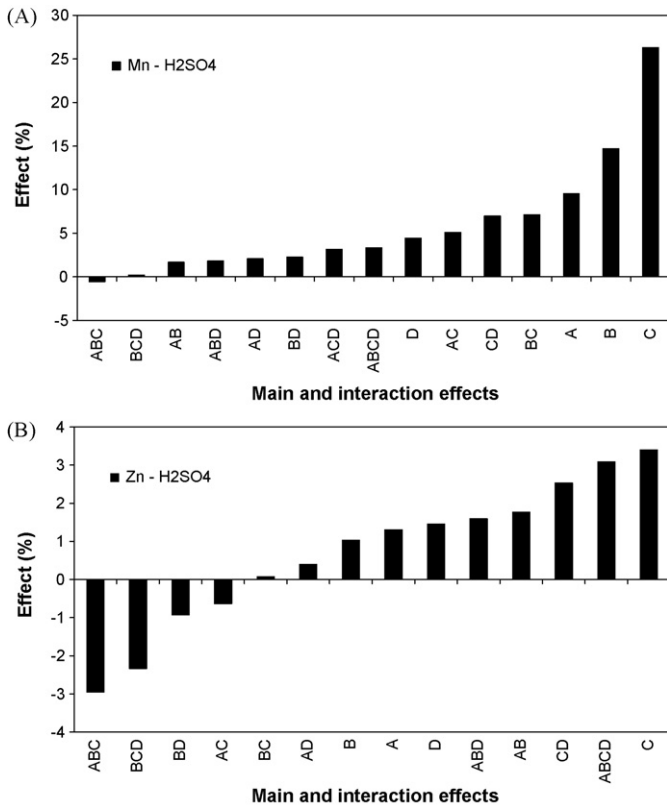


Fig. 1. Main and interaction effects on the MnEY (A) and ZnEY (B) values obtained by H<sub>2</sub>SO<sub>4</sub> leaching with citric acid.

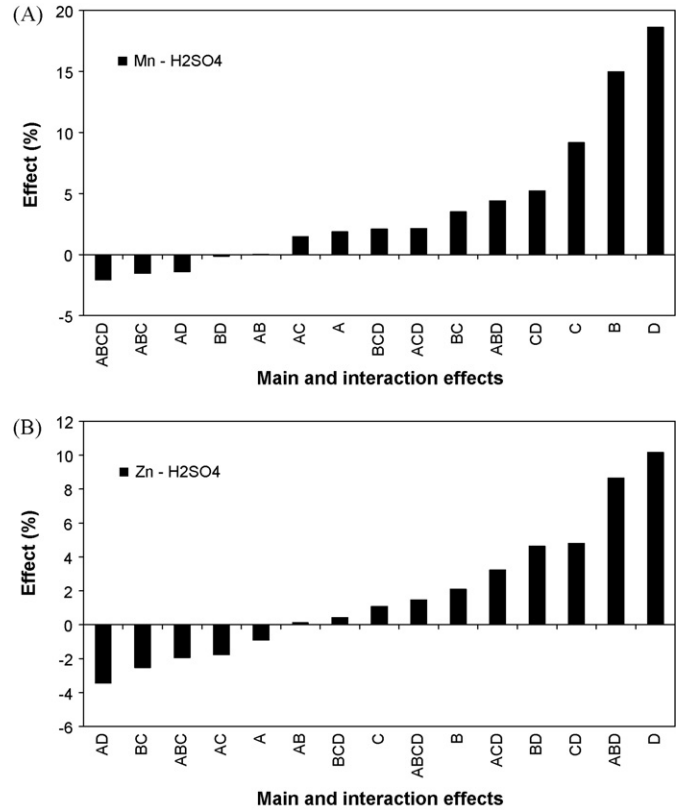


Fig. 2. Main and interaction effects on the MnEY (A) and ZnEY (B) values obtained by H<sub>2</sub>SO<sub>4</sub> leaching with ascorbic acid.

(B) values obtained by H<sub>2</sub>SO<sub>4</sub> leaching with citric acid. The percentage of pulp density (A) had little effect in the investigated range. Therefore, it may be suggested that acidic leaching may be carried out with 20% pulp density in full-scale applications to prevent the excessive usage of water. Citric acid concentration (B) had positive effect on the dissolution of both manganese (+15%) and zinc (+1%). These results indicated that citric acid can be used as an effective reducing agent. H<sub>2</sub>SO<sub>4</sub> concentration (factor C) had positive effects both for MnEY and ZnEY in the investigated conditions. The main effect of temperature (factor D) did not significantly influence MnEY and ZnEY. The interaction effect of all variables was not statistically significant in the investigated conditions. Fig. 2 shows the main and interaction effects on the ZnEY (A) and MnEY (B) values obtained by H<sub>2</sub>SO<sub>4</sub> and ascorbic acid. As shown in Fig. 2, the most significant main and interaction effect on ZnEY was the temperature (factor D) (10%). Pulp density, ascorbic acid and temperature factors (ABD) had also positive effect (9%) on the dissolution of zinc. Ascorbic acid did not cause Zn precipitant. In terms of MnEY, no significant interactions were found. The most important main effect for MnEY was temperature (factor D), which had a positive effect (+18%) due to the higher reaction kinetics at higher temperatures. Ascorbic acid (factor B) had also positive effect (15%) on MnEY in the investigated range.

### 3.2. Precipitation experiments

After the leaching experiments, precipitation experiments were carried out in the filtered leach solutions at different pH values. Fig. 3 shows the zinc and manganese precipitation yields as a function of solution pH adjusted with NaOH. As would be expected, both manganese and zinc precipitation yields increased with increasing pH. It was found that at a pH value of 8 almost complete zinc precipi-

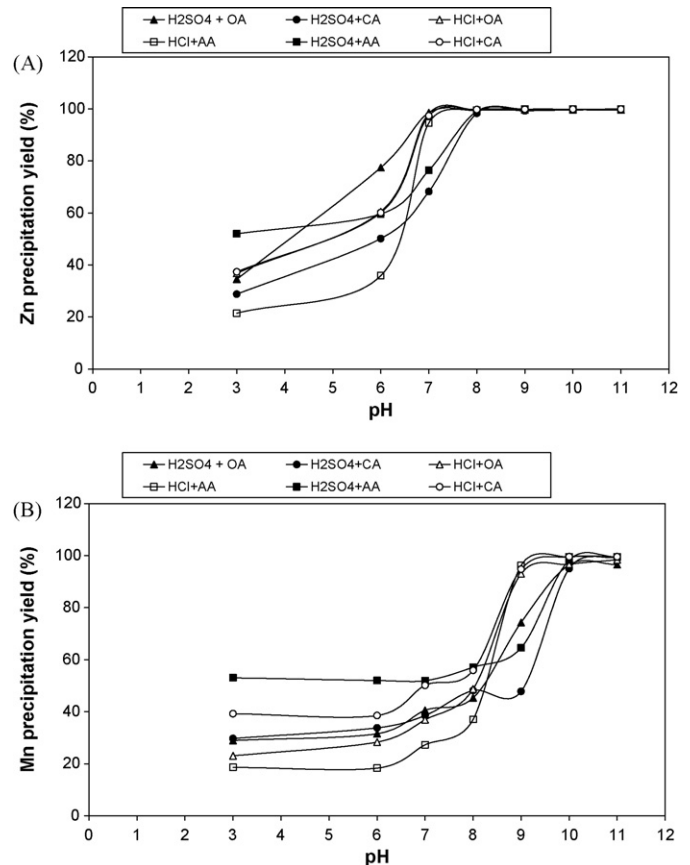


Fig. 3. Precipitation of zinc (A) and manganese (B) at different solution pH values adjusted with NaOH.



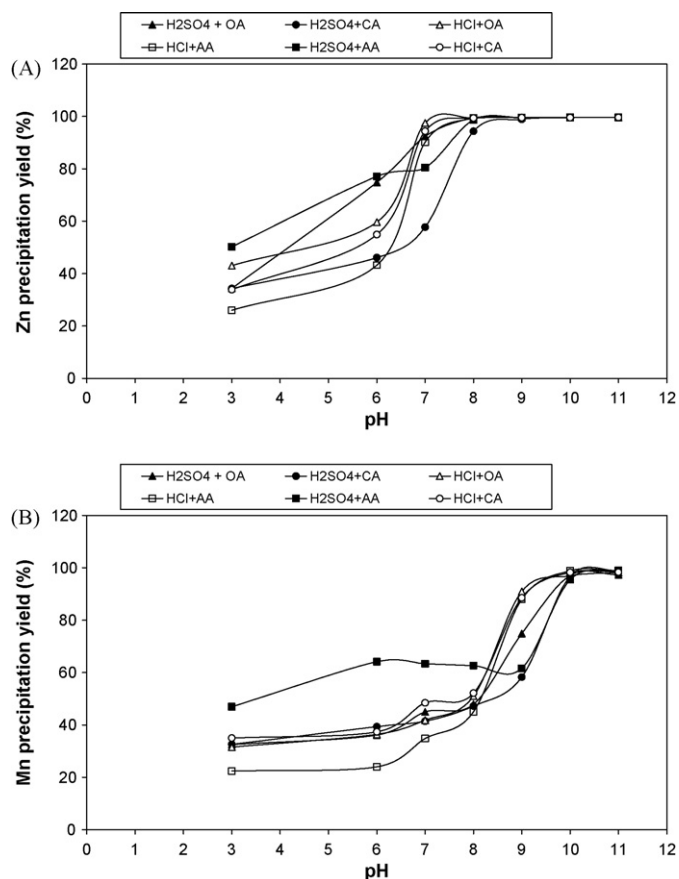


Fig. 4. Precipitation of zinc (A) and manganese (B) at different solution pH values adjusted with KOH.

itation occurred for all the leach solutions (i.e., different inorganic acids and reductants). For the complete manganese precipitation, a pH value of about 10 was required. Similarly, Veloso et al. [4] found that all zinc could be selectively separated from manganese at pH 8. These results overall indicated that Mn and Zn can be separated through hydroxide precipitations by adjusting solution pH values. It was predicted that  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  could be readily separated from  $\text{Mn}^{2+}$  by hydroxide precipitation while separation of  $\text{Zn}^{2+}$  from  $\text{Mn}^{2+}$  was possible; but that of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  from  $\text{Mn}^{2+}$  was difficult by a hydroxide precipitation method [24].

The precipitation curves of zinc and manganese obtained with KOH additions are shown in Fig. 4. Similar to the results obtained with NaOH, both manganese and zinc precipitation yields increased with increasing pH, as would be expected. The zinc precipitation yields increased from about 40–75% to complete precipitation with increasing solution pH from 6 to 8. Manganese precipitation yields increased from about 40–60% to complete precipitation with increasing solution pH from 8 to 10.

Fig. 5a shows the X-ray diffraction spectrum of the solid precipitates remained on the filter papers after filtration (precipitation at pH 7 with NaOH). At this pH, the main precipitate form was zinc hydroxides and incomplete precipitation was observed. Mn precipitates were not found. On the other hand, at a pH of 9, both zinc oxides and manganese oxides were found in the solid precipitates remained on the filter paper (Fig. 5b), indicating that the extent of precipitation increased with increasing pH from 7 to 9. This result is consistent with the higher precipitation yields found for Mn and Zn at pH of 9.

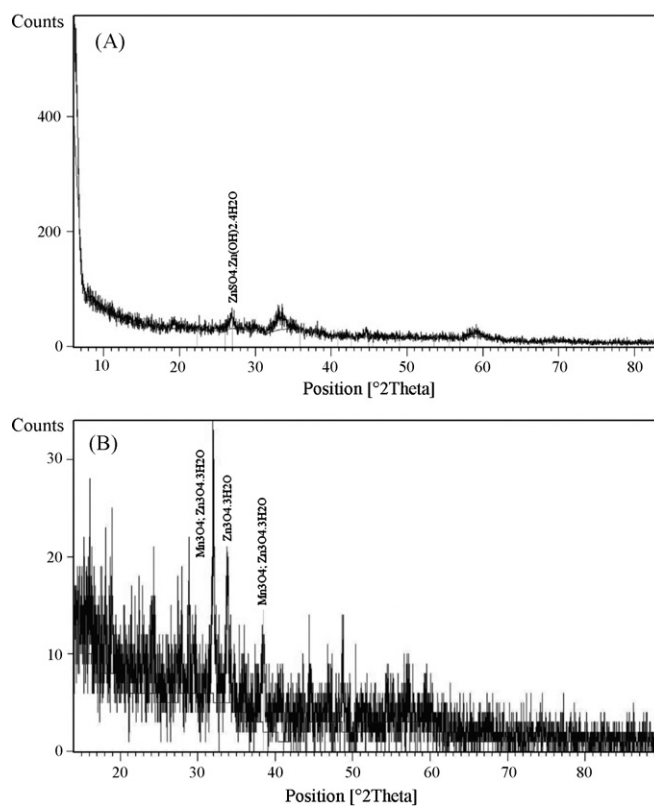


Fig. 5. XRD patterns of the solid precipitates remained on the filter papers after filtration (A: precipitation at pH 7 with NaOH, B: precipitation at pH 9 with KOH).

#### 4. Conclusions

Three different reductants (OA, AA and CA) were compared for their effectiveness in the acidic leaching (sulfuric acid or hydrochloric acid) of manganese and zinc from spent alkaline and zinc–carbon battery powders. OA with  $\text{H}_2\text{SO}_4$  or HCl was not effective on the leaching of zinc due to the formation of zinc oxalate precipitates, which significantly decreased the extraction yields of Zn. On the other hand, by the use of AA or CA as the reductants, about 87–100% of manganese and almost 100% of zinc were leached after 3 h by both  $\text{H}_2\text{SO}_4$  and HCl acids. While both CA and AA were effective for almost complete leaching of Mn under acidic conditions, they also did not form zinc precipitates. It was found that the extraction yields of both manganese and zinc were higher at a temperature of  $90^\circ\text{C}$  compared to those at  $30^\circ\text{C}$ .

Both manganese and zinc precipitation yields increased with increasing solution pH. Complete precipitation of Zn and Mn occurred at pH of about 8 and 10, respectively, indicating that Mn and Zn can be separated through precipitations by adjusting solution pH values. The use of ascorbic acid or citric acid as reductants in acidic leaching appears to be effective in the simultaneous leaching and further recovery of zinc and manganese from spent alkaline and zinc–carbon battery powders. As a next step, the leached zinc and manganese can be selectively precipitated from leach solutions by adjusting the pH. Although this combined approach appears to be technically effective for spent alkaline and zinc–carbon battery powders, cost issues should also be evaluated especially due to the use of various chemicals including an inorganic acid, organic acid and a base. In terms of unit price, citric acid and sulfuric acid are cheaper than the other tested inorganic acid and reducing agents. However, economical evaluations should be made prior to each specific full-scale application.

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