

Recovery of zinc and manganese from alkaline and zinc-carbon spent batteries

I. De Michelis^{a,*}, F. Ferella^a, E. Karakaya^b, F. Beolchini^c, F. Vegliò^a

^a Department of Chemistry, Chemical Engineering and Materials, University of L'Aquila, Monteluco di Roio, 67040 L'Aquila, Italy

^b Department of Environmental Engineering, Suleyman Demirel University, 32260 Isparta, Turkey

^c Department of Marine Sciences, Polytechnic University of Marche, Via Breccia Bianche, 60131 Ancona, Italy

Received 23 October 2006; received in revised form 13 March 2007; accepted 29 April 2007

Available online 31 May 2007

Abstract

This paper concerns the recovery of zinc and manganese from alkaline and zinc-carbon spent batteries. The metals were dissolved by a reductive-acid leaching with sulphuric acid in the presence of oxalic acid as reductant. Leaching tests were realised according to a full factorial design, then simple regression equations for Mn, Zn and Fe extraction were determined from the experimental data as a function of pulp density, sulphuric acid concentration, temperature and oxalic acid concentration. The main effects and interactions were investigated by the analysis of variance (ANOVA). This analysis evidenced the best operating conditions of the reductive acid leaching: 70% of manganese and 100% of zinc were extracted after 5 h, at 80 °C with 20% of pulp density, 1.8 M sulphuric acid concentration and 59.4 g L⁻¹ of oxalic acid. Both manganese and zinc extraction yields higher than 96% were obtained by using two sequential leaching steps.

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Keywords: Manganese; Zinc; Oxalic acid; Battery; Recycling; Leaching

1. Introduction

Disposal of spent batteries represents an increasing environmental problem in terms of heavy metals content when these devices are disposed off in inadequate way. The total weight of portable batteries sold in the East and West Europe in 2003 was about 164,000 tonnes, of which 50,197 tonnes and 99,138 tonnes were zinc-carbon and alkaline batteries, respectively (30.5% and 60.3% of the total annual sales) [1]. Current community legislation on batteries is Council Directive 91/157/EEC that covers batteries and accumulators containing more than 0.0005% mercury, more than 0.025% cadmium and more than 0.4% lead (percentages by weight). Many batteries and accumulators, like alkaline and zinc-carbon ones, still are landfilled or incinerated, instead of being collected and recycled. Several European Countries have developed national collection infrastructures and recycling processes that cover all kinds of portable batteries. These countries have arranged a financing system that enables to

cover all the costs related to the recycling activities by applying a surcharge on the battery price. In the majority of these countries this surcharge depends on the battery format (either AAA, AA, C, D or 9V), but in the others the financing scheme provides a fee per kilogram of batteries collected not dependent on battery type. The 15 members of the European Battery Recycling Association's (EBRA) recycled in 2004 about 23,900 tonnes of portable batteries and accumulators, of which 20,400 tonnes (~85%) were alkaline, zinc-carbon and zinc-air batteries [2]. As concerns Italian scenario, only batteries and accumulators covered by Directive 91/157/EEC are subjected to the recycling, while the zinc-carbon and alkaline batteries are landfilled because they are not considered as dangerous waste; however, the Italian collection rate of portable batteries is very low if compared with the other European rates.

On a resource management level, batteries could be considered as secondary raw materials. Valuable metals such as zinc and manganese can be recovered. Additionally, a range of substances such as various acids, salts and plastics, which are also contained in the batteries, can be separated and moved from municipal waste to specific installations equipped to deal with waste batteries. The use of recycled metals in battery produc-

* Corresponding author. Tel.: +39 0862 434223; fax: +39 0862 434203.
E-mail address: ida.demi@ing.univaq.it (I. De Michelis).

tion instead of virgin metals would have a positive environmental impact through reduced energy use and reduced pollution related to the mining of the virgin source. As an example, the use of recycled cadmium and nickel requires respectively, 46% and 75% less primary energy compared to the extraction and refining of virgin metal. As concerns the zinc used in batteries manufacturing, the energy needed for recycling and the one needed for extraction from primary resources are in the ratio 1:4 [3]. This aspect may be particularly significant considering that the primary production of metals is the source of approximately 10% of global CO₂ emissions [3]. Furthermore, the production of secondary raw zinc is very important, considering that in 2005 there was a world shortage of 432,000 tonnes of zinc concentrates: zinc price reached record values around 4000 US\$ tonne⁻¹ [4].

The purpose of the proposal of 21 November 2003 for a Directive of the European Parliament (COM/2003/723 final) is to reduce the quantity of spent batteries and accumulators and to set European targets for collection and recycling. The proposal will be applied to all batteries and accumulators, unlike the current legislation that will be cancelled. The ultimate disposal of industrial and automotive batteries and accumulators by incineration or landfilling will be prohibited.

Several processes for the recycling of batteries have been proposed, mainly in Europe, and the pyrometallurgical processes are the most used. As for secondary raw material exploitation, there are different patented processes in the literature for manganese and zinc recovery from exhausted cells (BATENUS; BATREC; ZINCEX; RECUPYL) [5]. Pyrometallurgical and hydrometallurgical processes can be used with different energy consumption and environmental impact that generally favour the application of the second ones. A comparison of these processes is shown elsewhere [2,6,7], including technical information about some industrial plants for the treatment of batteries; the majority of these plants treats a particular type of battery, as in the case of SNAM-SAVAM and SAB-NIFE designed to recycle NiCd batteries [8]. Hydrometallurgical processes are generally characterised by different steps of pretreatment followed by leaching and metal separation. The main differences among the patents lay just in the methods used to recover metals from leach liquor. Concerning the selective recycling of alkaline batteries, Veloso et al. [9] proposed a process in which the metals are leached by H₂SO₄ and H₂O₂, then manganese and zinc are precipitated selectively by KOH. De Souza and Tenorio [10] described another process for the recovery of zinc and manganese by an acid leaching; metallic zinc and manganese dioxide are further recovered by simultaneous electrowinning. Salgado et al. [8] investigated the separation of zinc and manganese by liquid–liquid extraction, after a leaching step with H₂SO₄. Toro et al. [11] also developed a patented process for the recycling of all cell components and the production of new cells (named as “green cells” for the zero-waste approach adopted) where the metals are leached in acid environment in the presence of carbohydrates as reducing agents.

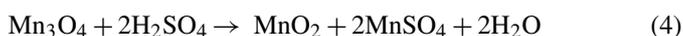
The aim of the present work is to recover zinc and manganese from spent batteries by means of sulphuric acid leaching in the presence of oxalic acid as reducing agent. Oxalic acid was chosen considering both its high efficiency in the reduc-

tive dissolution of Mn (IV) and its cheap availability since it can be produced by the fermentation of waste carbohydrates (molasses). Furthermore, the extraction of manganese from MnO₂ using oxalic acid is a known process [12,13].

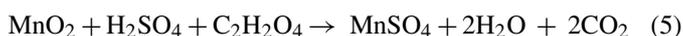
Tests with sulphuric acid and oxalic acid were designed according to a full factorial design (four factors, two levels) [14]. Zinc and manganese (II) oxides can be quantitatively dissolved by sulphuric acid, and the chemical reactions can be described as follows:



On the other hand, dissolution of manganese oxides such as Mn₂O₃, Mn₃O₄ is partial because the produced MnO₂ is insoluble, as shown by the following reactions:



Therefore a reducing agent is necessary to leach all manganese contained in the powder [8]. The reaction between manganese dioxide and oxalic acid in sulphuric acid solution is the following:



The aim of experimental tests of the present work was to maximize the extraction yields of zinc and manganese from battery paste. After single stage leaching treatments, further experiments were carried out to establish the best operating conditions of two sequential leachings (countercurrent leaching), in order to obtain the maximum extraction yields for both manganese and zinc. Additional tests were performed to evaluate the precipitation rate of Mn and Zn oxalates by synthetic solutions. Iron concentration was also determined in solution because iron is the major contaminant of the liquor leach during the electrowinning of Zn and MnO₂: in fact, the recycling of the electrolytic solution in the industrial process would lead to the growth of its concentration, so a purification step is needed.

2. Materials and methods

2.1. Battery dismantling and powder pre-treatments

Spent alkaline and zinc-carbon batteries size C and D from several manufacturers were manually dismantled. The black paste was a mixture of the cathodic (manganese oxides and graphite) and the anodic (zinc oxides and electrolytic solution) materials. Dismantling products such as plastic films, ferrous scraps and paper pieces were separated. The paste, which was about 57% of the battery total weight, was dried for 24 h at 130 °C. Sample showed a weight loss of 6% after drying, so the moisture was easily determined by weight difference. The paste was subsequently ground for 30 min by a ball mill, and then it was sieved by hand using a 500 μm standard sieve. The powder obtained was washed with distilled water in a jacketed stirred reactor tank (volume 1 L) at 60 °C (solid to liquid ratio

Table 1
Semi-quantitative analysis of the original and washed powder

Element	Original powder (%, w/w)	Washed powder (%, w/w)
Mn	33.59	35.59
Zn	15.46	18.58
Fe	0.50	0.49
Cr	0.19	0.20
Al	0.36	0.19
K	3.26	0.36
Cl	3.38	0.13
Ti	0.27	0.26
Si	0.49	0.42

1:5). After a contact time of 1 h, the solution pH was 10.2 due to dissolution of potassium hydroxide in water. The purpose of this washing was the removal of both potassium hydroxide and ammonium chloride in order to reduce the consumption of sulphuric acid in the subsequent leaching step. Furthermore, KOH solution may also contribute to the precipitation of iron in the purification step, avoiding the treatment of a wastewater flow. Chlorides represent one of the most damaging contaminant in the electrowinning of metallic zinc [13].

Washed powder was dried for 24 h at 105 °C, recovered and weighted: the weight loss was 5.8%. All the experimental tests showed in this paper were carried out with the washed powder.

2.2. Powder characterization

Original and washed powders were analyzed by X-ray fluorescence (XRF) (Spectro Xepos) and X-ray diffraction (XRD) (Philips X-Pert). XRF data are shown in Table 1.

X-ray diffraction analyses (not reported here) showed the presence of ZnO, MnOOH, MnO₂, Mn₂O₃, Mn₃O₄, KOH, NH₄Cl, Fe₂O₃, and graphite in the original powder, and of the same compounds except KOH and NH₄Cl in the washed powder.

Small amounts of potassium peroxide (KO₂) were also found in the washed powder, probably due to the oxidation of KOH by air oxygen during the pre-treatment procedure [15].

Data of washed powder (Table 1) show significant amount of Zn and Mn, which represents about 54% of the total mass of the sample, in agreement with literature data [10,11]. The presence of Cl and K is due to the electrolytes, i.e. ammonium chloride and potassium hydroxide. Other trace elements are present, while graphite is not detectable by XRF. Metals are contained both in the outer casing and in the anode rod structure. It should be noted the potassium and chlorine reduction of about 83% and 96%, respectively, after washing.

A quantitative analysis was also carried out by atomic absorption spectrometry (AAS) (spectrometer SpectrAA 200, Varian) in order to evaluate the accurate percentages of manganese, zinc and iron. Quantitative analysis was performed in a 250 mL closed flask as follows: 10 g of washed powder were dissolved in 100 mL of 3 M H₂SO₄ solution. 1.3 g of glucose were then added, when the solution reached 90 °C. Temperature was controlled by a heater equipped with magnetic stirrer (200 rpm). Concentrated sulphuric acid and glucose of analytical grade were used (Merck). The reaction mixture was filtered after 5 h to separate undissolved material from pregnant solution, which was diluted 1:10 by a solution of nitric acid (pH ~2) to avoid precipitation of metals. At the end of reaction time pH was measured by a digital pH-meter (Mettler Toledo MP 220). The filtered residue was recovered and weighted by an analytical balance (Mettler PE 600) after drying for 24 h at 105 °C. This quantitative analysis was repeated at room temperature using a different reductant (1 M H₂O₂ solution instead of glucose) in 100 mL of 3 M H₂SO₄ solution with a solid to liquid ratio 1:10 and 200 rpm magnetic stirring. Manganese, zinc and iron were determined by atomic absorption spectrometry.

Results of the quantitative analyses showed that washed powder was composed by 40.8% Mn, 25.2% Zn and 0.45% Fe.

Table 2
Experimental conditions of 2⁴ full factorial design

N	Treatment	A (pulp density)	B (oxalic acid)	C (sulphuric acid)	D (temperature)	A (g L ⁻¹)	B (g L ⁻¹)	C (M)	D (°C)
1	(1)	–	–	–	–	100	29.7	0.9	40
2	a	+	–	–	–	200	59.4	1.8	40
3	b	–	+	–	–	100	89.0	0.9	40
4	ab	+	+	–	–	200	178.0	1.8	40
5	c	–	–	+	–	100	29.7	1.4	40
6	ac	+	–	+	–	200	59.4	2.7	40
7	bc	–	+	+	–	100	89.0	1.4	40
8	abc	+	+	+	–	200	178.0	2.7	40
9	d	–	–	–	+	100	29.7	0.9	80
10	ad	+	–	–	+	200	59.4	1.8	80
11	bd	–	+	–	+	100	89.0	0.9	80
12	abd	+	+	–	+	200	178.0	1.8	80
13	cd	–	–	+	+	100	29.7	1.4	80
14	acd	+	–	+	+	200	59.4	2.7	80
15	bcd	–	+	+	+	100	89.0	1.4	80
16	abcd	+	+	+	+	200	178.0	2.7	80
17	0	0	0	0	0	150	89.0	1.7	60
18	0	0	0	0	0	150	89.0	1.7	60
19	0	0	0	0	0	150	89.0	1.7	60

Table 3
Results of the leaching tests after a reaction time of 1 h, 3 h and 5 h (see Table 2 for the treatments operating conditions)

N	Treatment	Manganese extraction (g L^{-1})			Zinc extraction (g L^{-1})			Iron extraction (g L^{-1})			Final pH	Weight loss (%)
		1 h	3 h	5 h	1 h	3 h	5 h	1 h	3 h	5 h		
1	(1)	22.3	22.0	25.1	20.3	20.5	21.9	0.09	0.09	0.09	2.31	73.2
2	a	51.3	45.1	49.2	40.3	44.2	48.6	0.20	0.20	0.19	2.09	76.5
3	b	30.4	28.3	31.2	0.9	1.6	1.5	0.16	0.18	0.19	1.68	19.4
4	ab	62.9	58.0	65.3	2.4	2.9	2.2	0.36	0.39	0.40	1.51	14.3
5	c	26.8	22.8	25.3	23.4	23.0	24.9	0.13	0.13	0.14	1.48	74.4
6	ac	49.3	44.9	51.4	48.8	43.1	44.0	0.26	0.30	0.30	1.24	74.4
7	bc	33.7	30.4	33.7	1.6	1.7	1.7	0.18	0.19	0.20	1.60	27.0
8	abc	67.3	60.7	66.4	3.9	3.2	3.1	0.38	0.41	0.43	0.73	22.9
9	d	26.9	28.1	28.2	21.8	25.7	24.0	0.09	0.05	0.03	2.05	76.3
10	ad	54.2	59.1	57.0	43.7	48.9	50.5	0.17	0.14	0.13	1.64	68.9
11	bd	27.5	25.8	29.4	1.6	0.9	0.9	0.30	0.34	0.39	1.07	13.8
12	abd	53.8	58.1	56.8	1.8	1.3	1.1	0.71	0.87	0.87	0.88	5.5
13	cd	26.8	28.7	28.0	23.3	24.9	24.4	0.17	0.24	0.29	0.99	74.2
14	acd	58.7	60.6	59.3	45.4	48.0	48.9	0.47	0.65	0.71	0.79	68.3
15	bcd	30.3	31.2	32.3	2.2	1.3	1.3	0.39	0.45	0.46	0.89	40.6
16	abcd	55.0	57.3	59.9	3.0	2.0	2.2	0.63	0.75	0.79	0.73	49.2
17	0	52.9	55.8	55.8	18.2	17.3	17.1	0.30	0.31	0.37	1.12	51.7
18	0	52.9	57.2	55.1	19.3	17.4	17.0	0.28	0.34	0.33	1.13	52.2
19	0	54.5	53.2	53.0	16.8	15.3	16.8	0.31	0.36	0.39	1.02	58.3

2.3. Leaching tests with sulphuric acid–oxalic acid

In the present work, a 2^4 factorial design with replicated central point was chosen for conducting the leaching tests where factors (levels in parentheses) were: pulp density (10% and 20%, w/v), oxalic acid concentration (0.5 stoichiometric ratio, 1.5 stoichiometric ratio), sulphuric acid concentration (stoichiometric ratio, 1.5 stoichiometric ratio) and temperature (40 and 80 °C) [12,14]. Stoichiometric ratios for sulphuric and oxalic acid were calculated according to reactions (1) and (5). These levels were chosen to investigate a wide response surface area by ANOVA [14].

Leaching tests were performed in 250 mL closed flasks submerged in a thermostatically controlled water bath equipped with a mechanical stirrer (Dubnoff, ISCO). For each test the solution mixture was freshly prepared by dissolving the required amount of analytical grade oxalic acid (Carlo Erba) and washed battery powder in 100 mL of H_2SO_4 solution, according to the experimental plan. The experimental conditions of each performed treatment are given in Table 2.

During each test, 1 mL of leach liquor was withdrawn after 1 h, 3 h and 5 h to measure the concentration of Mn, Zn and Fe by AAS. Each sample was diluted 1:10 by a solution of nitric acid to avoid precipitation of metals and stored at 5 °C. After 5 h, when reactions were stopped, pH was measured and the mixtures were filtered, washed and put in the oven at 105 °C. After 24 h solid residues were recovered and weighted to evaluate the weight loss.

Tests were numbered in conformity with the Yates' algorithm [14]. Values shown in Table 2 were calculated by using reactions (1) and (5), considering all zinc as ZnO and all manganese as MnO_2 . Three central points experiments were carried out to have a good valuation of the experimental error variance and to test the adequacy of the models [14].

2.4. Precipitation tests

Precipitation tests were performed to evaluate the precipitation rate of both zinc and manganese due to the high concentration of oxalic acid in solution. In fact, in some leaching tests a high Mn concentration was observed together with very low weight loss and zinc concentration: this might be due to the fact that Mn and Zn precipitate as oxalates after dissolution by oxalic acid and sulphuric acid. Precipitation tests were carried out by dissolving $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck) in five 1 M H_2SO_4 solutions in order to have about 30 g L^{-1} of Mn and 30 g L^{-1} of Zn. 5 g L^{-1} , 10 g L^{-1} , 35 g L^{-1} , 50 g L^{-1} and 100 g L^{-1} of oxalic acid were added in 250 mL closed flasks, immersed in a water bath at 40 °C under mechanical stirring. For each flask 1 mL of leach liquor was withdrawn at 1 h and 3 h; after 5 h reactions were stopped. pH values were measured and the weight of solid residues were determined after filtration and 24 h evaporation at 105 °C. Mn and Zn were measured by AAS. Concentration of Mn and Zn in the original solution was 31.1 g L^{-1} and 27.8 g L^{-1} , respectively, measured by AAS.

2.5. Countercurrent leaching tests

ANOVA analysis demonstrated that it is not possible to reach the maximum simultaneous extraction yield both of manganese and zinc because of their different optimum leaching conditions: for this reason two additional tests were carried out to simulate a double step leaching. First leaching (named I) was performed by a 1.1 M H_2SO_4 solution and 20% pulp density at 80 °C, without oxalic acid; the second one (named II) by a 2 M H_2SO_4 solution, 10% pulp density, 66.8 g L^{-1} oxalic acid at 80 °C.

These conditions were chosen taking into account the results of 2^4 full factorial design and the scheme of a countercurrent leaching: in this case it is possible to obtain the best extraction

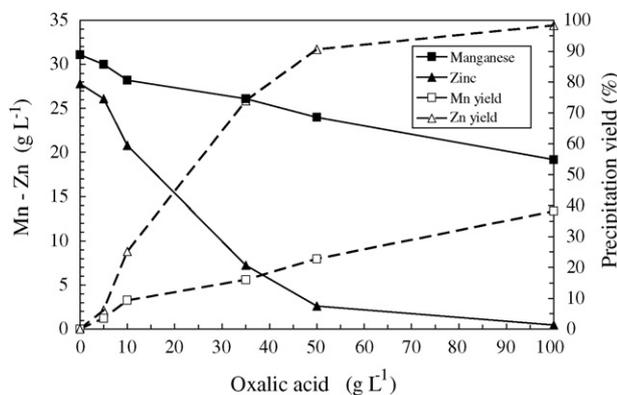


Fig. 1. Results of precipitation tests: temperature 40 °C, H₂SO₄ concentration 1 M; time 5 h; stirring 200 rpm.

yields of manganese and zinc together to a pre-neutralization of leach liquor, saving alkaline reagent needed to the iron precipitation. In the leaching II a large excess of sulphuric acid was chosen because this solution is recycled back to the reactor of leaching I (see Fig. 5): the resulting sulphuric acid concentration in the first stage should be enough for dissolving all zinc. Besides acid excess is needed to enhance the kinetics during the extraction of insoluble manganese.

3. Results and discussion

3.1. Precipitation tests

Precipitation tests were carried out with synthetic solutions of manganese and zinc sulphate, to evaluate if manganese and zinc precipitate as oxalates during battery powder leaching experiments. The experimental conditions were fixed as follows: temperature 40 °C, sulphuric acid 1 M, time of treatment 5 h; oxalic acid ranging from 0 g L⁻¹ to 100 g L⁻¹. These conditions were chosen in order to simulate the battery powder leaching, described further. Fig. 1 shows the results of precipitation tests,

in terms of manganese and zinc concentration (and precipitation yield) at the end of the treatment as a function of oxalic acid concentration.

It can be observed in Fig. 1 that as expected both manganese and zinc precipitation increase with oxalic acid concentration. In particular, when oxalic acid is 100 g L⁻¹, a complete precipitation (98%) is achieved together with a partial precipitation (38%) of manganese. This difference is probably associated to a different solubility of the two oxalates: the solubility product (K_{sp} at 25 °C) of MnC₂O₄ is 1.70×10^{-7} , while it is 1.38×10^{-9} for ZnC₂O₄ [16]. According to K_{sp} values, it is clear that manganese oxalate is more soluble than zinc oxalate and precipitation phenomena might take place also during battery powder leaching.

3.2. Leaching tests: factorial experiments with sulphuric acid–oxalic acid

The experimental results of the full factorial design at different leaching times are shown in Table 3, where the final pH and the weight loss of samples are also reported.

It is possible to observe that when the oxalic acid concentration was 1.5 fold the stoichiometric ratio (all treatments with the b letter in Table 3) there is a high Mn concentration but very low weight loss and zinc concentration. This aspect might be due to a partial precipitation of Zn and a little quantity of Mn as oxalates. Two leaching solid residues were analyzed by XRF. Residue of test ab (17.15 g, original weight 20 g) showed 5.6% Mn and 16.4% Zn; in the residue of test b (8.1 g, original weight 10 g) Mn and Zn were 5.5% and 19.7%, respectively. The precipitation tests previously reported confirmed these data. Mn, Zn and Fe extraction yields after 5 h reaction are shown in Fig. 2. Results of central point tests are reported as average values of the three-replicated experiments (tests 17–19 in Table 3).

Fig. 2 shows that the highest extraction yield for manganese was reached in test 0 (arithmetic mean 89.2%), with stoichio-

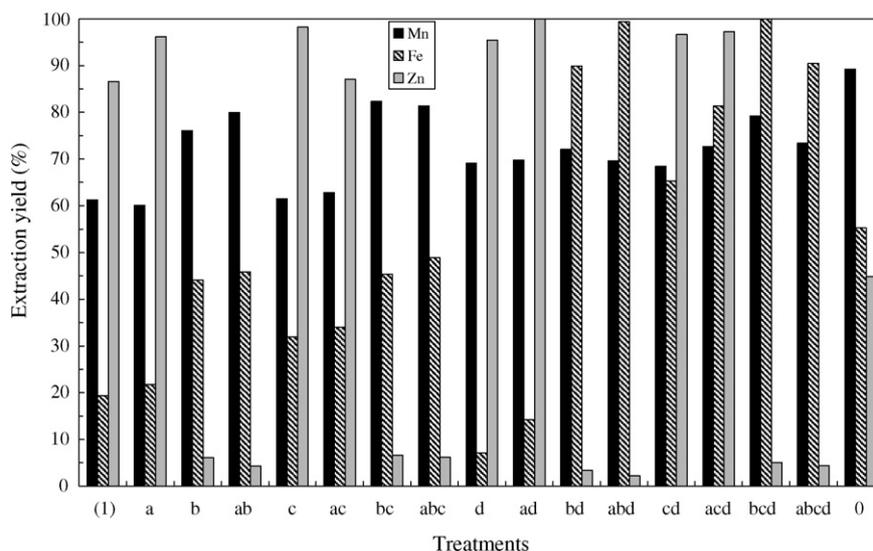


Fig. 2. Mn, Zn and Fe extraction yields after 5 h (see Table 2 for the treatments operating conditions).

metric concentration of oxalic acid and a 1.25 stoichiometric ratio of sulphuric acid: in this case precipitation of manganese oxalate was supposed not to occur. Comparing tests with the same oxalic acid, sulphuric acid and temperature values (*B*, *C*, *D* factors) manganese concentration of a 20% pulp density test is about double with respect to the corresponding 10% pulp density test: this aspect suggests that the pulp density is not significant for the extraction process in the investigated range, because manganese concentration is directly proportional to pulp density, as expected. As concerns temperature effect, manganese dissolution yield increases with temperature: manganese concentration at 80 °C is always higher than the corresponding value at 40 °C, for each couple of tests at fixed values of pulp density, oxalic acid and sulphuric acid (*A*, *B*, *C* factors, tests (1)–d, a–ad, c–cd, ac–acd). This is not true when the oxalic acid is 1.5 fold the stoichiometric ratio (treatments b–bd, ab–abd, bc–bcd, abc–abcd in Fig. 2), probably because at 80 °C the precipitation rate of manganese oxalate is higher than the one at 40 °C. The oxalic acid concentration showed a positive effect on manganese dissolution due to the improving of the dissolution rate of reaction (5) (treatments (1)–b, a–ab, c–bc, ac–abc, ...). On the other hand, sulphuric acid concentration did not influence manganese dissolution when its concentration is either equal or higher than the stoichiometric ratio (treatments (1)–c, a–ac, ...).

Concerning zinc extraction, Fig. 2 shows that the highest extraction yield was obtained in treatment ad (100%), at 80 °C, 20% pulp density, stoichiometric concentration of sulphuric acid and 0.5 fold the stoichiometric ratio of oxalic acid. Furthermore eight treatments (b, ab, bc, abc, bd, abd, bcd, abcd in Fig. 2) were characterized by very low zinc concentration in solution, probably due to the precipitation of zinc oxalate. Oxalic acid is not needed for the extraction of zinc, because ZnO is readily soluble in sulphuric acid solution and this precipitation might be avoided by using a reducing agent that forms no complex with zinc, as for example hydrogen peroxide [9]. In the other tests the increasing of pulp density from 10% to 20% leads to a double concentration as in the case of manganese. The dissolution rate improves with the increasing of temperature, while there are good extraction yields with all the sulphuric acid concentrations (when oxalic acid is not in stoichiometric excess).

Fig. 2 shows that the highest iron extraction yields was obtained in test bcd (100%) at 80 °C, 10% pulp density, 1.4 M H₂SO₄ solution, the lowest one in tests (1), a, d, ad. Probably this is due to the precipitation of iron, for example as jarosite: the final pH values confirm this hypothesis.

3.3. ANOVA analysis

The experimental results at 5 h reaction time were analyzed by ANOVA, according to the Yates' algorithm [14]. Their significance was determined by *F*-test method at 95% confidence level [14]. The main effects and interactions are showed in Fig. 3. Effects with a statistical significance lower than 95% have not been reported.

As reported in Fig. 3, the significant effects for Mn extraction yield are three: oxalic acid (factor *B*) has a strong positive effect

(+11%) on dissolution of insoluble manganese, sulphuric acid concentration (factor *C*) as expected has a positive effect (3%), and finally the interaction of oxalic acid and temperature (*BD*) has a negative effect on Mn extraction yield (−7.5%) calculated from experimental data of manganese concentration in solution. This last aspect indicates that when temperature increased from 40 °C to 80 °C, the positive effect of oxalic acid decreased. This is probably associated to an increase in the precipitation kinetics of manganese oxalate, favoured by high temperature: the dissolved manganese precipitated as manganese oxalate as soon as it was leached from the battery powder. As regards Zn extraction yield, Fig. 3 shows that there are several significant interactions. The most important factor seems to be oxalic acid concentration (factor *B*), which has a strong negative effect (−90%) probably due to the precipitation of zinc oxalate as soon as zinc was leached, as previously reported in the case of manganese. Sulphuric acid concentration (factor *C*) has a light positive effect (+1%) in the investigated range because any stoichiometric excess resulted to be enough to leach all zinc. Temperature (factor *D*) has a light positive effect on zinc extraction yield, due to both the higher solubility of zinc oxalate and to the higher kinetics of reaction. Pulp density (factor *A*) did not show any effect neither on manganese nor on zinc extraction yields, in the investigated range of operating conditions.

Concerning iron dissolution, Fig. 3 shows that the main factors for iron extraction yield are sulphuric acid concentration (factor *C*) that, as expected, has a positive effect (+19%), oxalic acid (factor *B*) with a +36% and temperature (factor *D*) with a +32% positive effect associated to the increase in the process kinetics. The effect of oxalic acid may be due to its reducing action: in fact the reduction of iron (III) to iron (II) might favour the leaching action of sulphuric acid.

The ANOVA results have been used to derive simple empirical equations in order to predict manganese, zinc and iron extraction yields in a wide range of operating conditions that were not directly experimentally tested:

$$Y_{Mn} = 0.712 + 0.055 X_2 + 0.015 X_3 - 0.037 X_2 X_4 \quad (6)$$

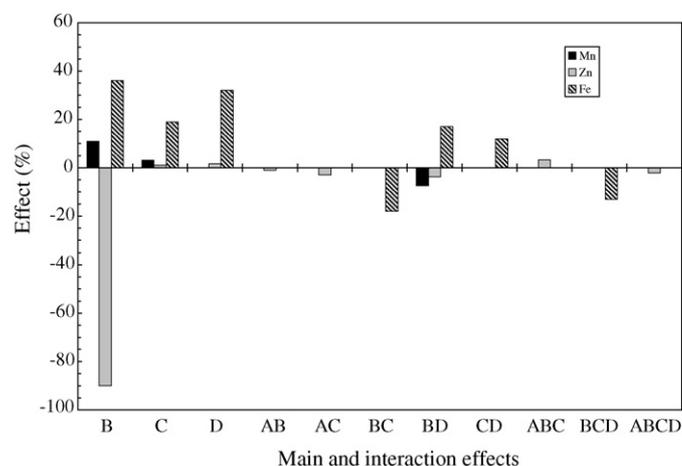


Fig. 3. Effects of the most significant factors and of their interactions on Mn, Zn and Fe extraction yields after 5 h (*A*: pulp density; *B*: oxalic acid; *C*: sulphuric acid; *D*: temperature).

$$Y_{Zn} = 0.497 - 0.449 X_2 + 0.005 X_3 + 0.008 X_4 - 0.005 X_1 X_2 - 0.014 X_1 X_3 - 0.019 X_2 X_4 + 0.017 X_1 X_2 X_3 - 0.011 X_1 X_2 X_3 X_4 \quad (7)$$

$$Y_{Fe} = 0.529 + 0.181 X_2 + 0.097 X_3 + 0.160 X_4 - 0.090 X_2 X_3 + 0.084 X_2 X_4 + 0.061 X_3 X_4 - 0.065 X_2 X_3 X_4 \quad (8)$$

where factors and interactions with a <95% significance do not have been considered and X_1 X_2 X_3 X_4 are the dimensionless coded factors corresponding to the four tested factors. The relations between coded and actual values are the following:

$$X_1 = \frac{A - 15}{5} \quad (9)$$

$$X_2 = \frac{B - 1}{0.5} \quad (10)$$

$$X_3 = \frac{C - 1.25}{0.25} \quad (11)$$

$$X_4 = \frac{D - 60}{20} \quad (12)$$

where A is the pulp density (%), B the oxalic acid concentration (expressed as stoichiometric ratio multiples: e.g., 1 for stoichiometric ratio, 1.5 for 50% stoichiometric excess), C the sulphuric acid concentration (expressed as stoichiometric ratio multiples) and D is the temperature (°C). The comparison between the experimental extraction yields at 5 h and the estimated ones by using the above equations is shown in the scatter diagram of Fig. 4. It can be observed that there is a good agreement between predicted and experimental metals extraction yields, as a confirmation that this empirical equations are suitable to predict the leaching behaviour in the range of the studied experimental conditions for process optimization purposes.

3.4. Countercurrent leaching tests

The full factorial design previously described demonstrates that it is not possible to reach the best extraction yields of both manganese and zinc at the same time with a single leaching step, due to precipitation phenomena. In fact, oxalic acid in a stoichiometric ratio is necessary for a good extraction yield of manganese (~90%—see treatments 17–19 in Table 2), but at the same time it favours zinc precipitation: zinc extraction yield is

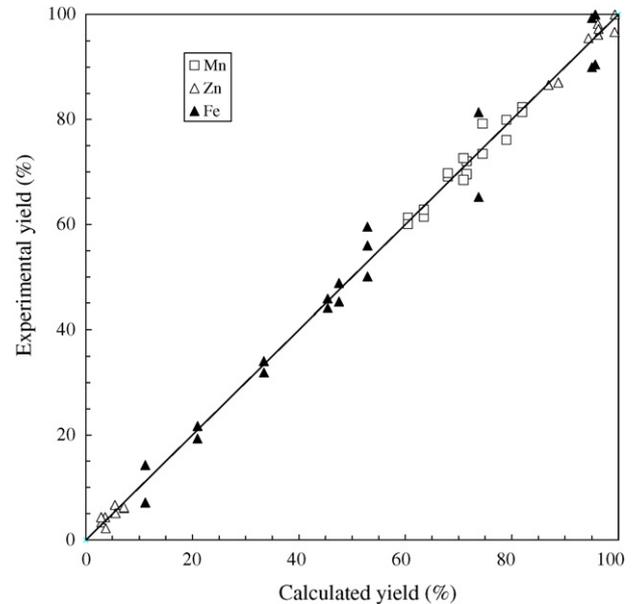


Fig. 4. Scatter diagram of the experimental extraction yields at 5 h (Fig. 2) vs. calculated extraction yields by Eqs. (6)–(8).

not satisfactory. These results suggest to replace a single stage leaching section with a countercurrent leaching with two different steps: one acid leaching for dissolution of zinc followed by one reductive-acid leaching for the recovery of insoluble manganese oxides.

The countercurrent leaching might allow a saving of KOH, in the precipitation reactor, with respect to a single reductive-acid leaching. In fact, the strong acid solution coming from the second reactor is neutralized by fresh battery powder in the first reactor, as shown in Fig. 5.

The investigated experimental conditions and the results are reported in Table 4. The experimental conditions were chosen taking into account the results of the previously described 2⁴ full factorial design. Each test was replicated twice. In the leaching I step, a 20% pulp density was chosen in order to reduce the volume of the leach liquor, with a 1.5 fold the stoichiometric ratio of sulphuric acid with respect to the zinc percentage in the battery powder. In the leaching II step, a 10% pulp density was fixed in order to avoid the precipitation of manganese oxalate. Considering previous results, the reaction time was fixed at 3 h for leaching I, while it was 5 h for leaching II.

Results reported in Table 4 show that all the zinc present in the battery powder is dissolved in the leaching I step, together with a 21% of total manganese: this soluble manganese can be extracted without a reductant, as indicated in reactions (3) and

Table 4
Results of experimental tests for the simulation of a countercurrent leaching

Leaching	A, pulp density (g L ⁻¹)	B, oxalic acid (g L ⁻¹)	C, sulphuric acid (M)	D, temperature (°C)	Manganese extraction		Zinc extraction		Iron extraction		Final pH	Weight loss (%)
					g L ⁻¹	%	g L ⁻¹	%	g L ⁻¹	%		
I	200	–	1.1	80	17.2	21.3	49.9	99.0	0	–	5.30	34.5
II	100	66.8	2.0	80	47.8	96.5	0	–	0.43	97.7	1.24	48.6

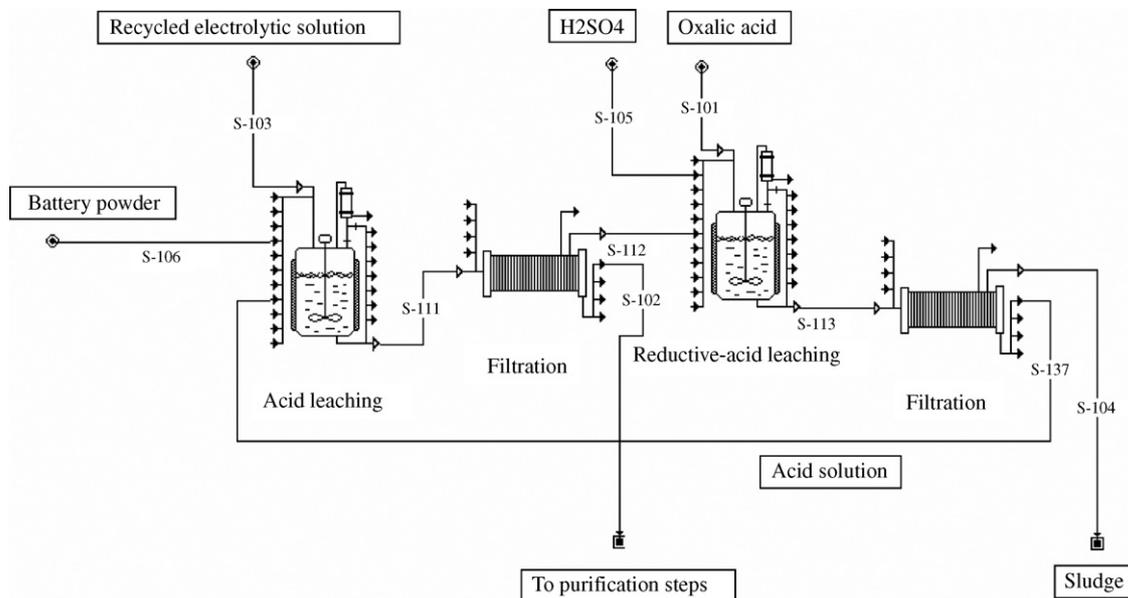


Fig. 5. Scheme of countercurrent leaching.

(4). Concerning iron, it was not found in the liquor leach: in fact considering that the final pH was 5.30, the dissolved iron is precipitated (neutralization of H_2SO_4 by fresh battery powder). Table 4 also shows that more than 96% of total manganese was extracted by a stoichiometric concentration of oxalic acid in leaching II. The resulting sulphuric acid concentration in the exhausted solution of leaching II was about 1.2 M, so that one chosen for leaching I (1 M) was enough for dissolving all zinc. Moreover the countercurrent scheme permitted a saving of KOH higher than 50% with respect to a single leaching, in the iron precipitation step.

4. Conclusions

In this paper a reductive-acid leaching was studied for the recovery of zinc and manganese from alkaline and zinc-carbon spent batteries. Leaching tests were developed according to a 2^4 full factorial design and the effect of oxalic acid concentration, temperature, pulp density and sulphuric acid concentration were analyzed in order to achieve the best extraction yields of both manganese and zinc. The experimental results showed that the maximum extraction yields of zinc and manganese cannot be reached simultaneously: in fact, the high oxalic acid concentration needed to dissolve manganese oxides causes the precipitation of zinc oxalate. Precipitation tests by using synthetic solutions confirmed these data. In any case, 70% of manganese and 100% of zinc were extracted after 5 h, at 80°C with a 20% of pulp density, 1.8 M sulphuric acid concentration and 59.4 g L^{-1} of oxalic acid. The main and interaction effects of each factor were evaluated by ANOVA, and empirical models able to predict manganese, zinc and iron extraction yields have been found which can be used for process optimisation, in the investigated range of operating conditions.

Considering that the best simultaneous Mn and Zn extraction yields were not reached by a single reductive-acid leaching, a

countercurrent leaching was proposed to obtain the maximum extraction yields of both elements. Results showed that 99% of zinc and 96% of manganese can be extracted: besides this process solution permits a reduction of more than 50% of KOH in the iron precipitation step.

Further work will be aimed at the investigation of the purification section (precipitation of iron and cementation) and electrowinning, in order to achieve reliable process parameters for the design and the simulation of a pilot-scale plant for the recycling of spent alkaline and zinc-carbon batteries.

Acknowledgements

Authors are very grateful to Ms. Fabiola Ferrante and Mr. Marcello Centofanti for their helpful collaboration during the AAS and XRF analyses.

This work was carried out with the financial support of the Italian Ministry of Education, University and Research (MIUR – Project PRIN 2005). Moreover this work has been carried out in cooperation with the Department of Environmental Engineering of the Suleyman Demirel University (Turkey) in the ambit of a Socrates-Erasmus project.

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