# Process for the recycling of alkaline and zinc–carbon spent batteries

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ABSTRACT

In this paper a recycling process for the recovery of zinc and manganese from spent alkaline and zinc–carbon batteries is proposed. Laboratory tests are performed to obtain a purified pregnant solution from which metallic zinc (purity 99.6%) can be recovered by electrolysis; manganese is recovered as a mixture of oxides by roasting of solid residue coming from the leaching stage. Nearly 99% of zinc and 20% of manganese are extracted after 3 h, at 80 °C with 10% w/v pulp density and 1.5 M sulphuric acid concentration. The leach liquor is purified by a selective precipitation of iron, whereas metallic impurities, such as copper, nickel and cadmium are removed by cementation with zinc powder. The solid residue of leaching is roasted for 30 min at 900 °C, removing graphite completely and obtaining a mixture of $Mn_3O_4$ and $Mn_2O_3$ with 70% grade of Mn. After that a technical-economic assessment is carried out for a recycling plant with a feed capacity of $5000\,t\,y^{-1}$ of only alkaline and zinc–carbon batteries. This analysis shows the economic feasibility of that plant, supposing a battery price surcharge of $0.5\,\text{€}\,kg^{-1}$, with a return on investment of 34.5%, gross margin of 35.8% and around 3 years payback time.

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## 1. Introduction

Disposal of spent batteries represents an environmental problem because of heavy metals that can be dispersed in the environment; as a matter of fact, some types of batteries, like the alkaline and zinc–carbon ones, can be thrown away together with unsorted municipal wastes. Current community legislation is Council Directive 91/157/EEC (and subsequent amending acts of Directives 93/86/EEC and 98/101/EC) on batteries and accumulators containing certain dangerous substances. This Directive only 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, still are landfilled or incinerated, instead of being collected and recycled. Several European Countries have independently developed national collection infrastructures and recycling processes that cover all kinds of portable batteries. Mandatory collection started in Austria in 1991 followed by many other Countries [1], which have arranged a financing system that enables to cover all the costs related to the recycling activities, such as collection, transportation to the plant, process net costs, information campaigns and so on. In 2006 the European Battery Recycling Association's (EBRA) members recycled 30,870 t of portable batteries and accumulators, of which 26,928 t (~87%) were alkaline, zinc–carbon and

zinc–air batteries: compared to 2005, there was an increase of 19% [2]. The best results come from Countries which have introduced collection systems covering all batteries and accumulators, while in Countries that have limited their actions to industrial batteries within the framework of Directive 91/157/EEC the collection rate was very low or even non-existent.

On a resource management level, batteries could be considered as a source of secondary raw materials. Valuable metals such as zinc, manganese and steel can be recovered and put on the market for the manufacture of new batteries or of other products. In Italy only batteries and accumulators covered by Directive 91/157/EEC are subjected to the recycling, while the zinc–carbon and alkaline batteries are simply landfilled because they are not considered as hazardous waste; however, the Italian collection rate of portable batteries is very low if compared with the other European rates: in 2006 around 83 t of Ni–MH, Li-ion and Ni–Cd were recycled [2]. The proposal of 21 November 2003 (COM 2003 – 723 final) for a new directive on each type of batteries and accumulators was enacted by the European Union: the Directive 2006/66/EC of the European Parliament and of the Council of 6 September 2006 on batteries, accumulators and waste batteries was published on the Official Journal of the European Union on 26 September 2006. Directive 91/157/EEC is repealed with effect from 26 September 2008. The Directive 2006/66/EC will be applied to all batteries and accumulators, whereas the ultimate disposal of portable, industrial and automotive batteries and accumulators by incineration or landfilling will be strictly prohibited. Once this new directive will be in force, Member States shall achieve the following minimum

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collection rates: 25% by 26 September 2012; 45% by 26 September 2016 according to the scheme set out in Annex I [3]. Member States shall oblige producers, or third parties acting on their behalf, to finance any net cost arising from public information campaigns on the collection, treatment and recycling of all waste portable batteries and accumulators. Moreover, recycling processes shall achieve the following minimum efficiencies:

- recycling of 65% by average weight of lead-acid batteries and accumulators, including recycling of the lead content to the highest degree that is technically feasible while avoiding excessive costs;
- recycling of 75% by average weight of nickel–cadmium batteries and accumulators, including recycling of the cadmium content to the highest degree that is technically feasible while avoiding excessive costs;
- recycling of 50% by average weight of other waste batteries and accumulators [3].

Several processes for the recycling of batteries were proposed, mainly in Europe, both pyrometallurgical and hydrometallurgical [4]. The most important patented processes that work on industrial scale are Batenus, Recupyl, Batrec and Revabat. Hydrometallurgical processes are generally characterized by different steps of pretreatment followed by leaching and separation of different metals by electrolysis, extraction or precipitation. The Batenus process treats all types of batteries (except for button cells); copper, nickel and cadmium are selectively recovered by ion exchange, whereas zinc and manganese are separated by liquid–liquid extraction and electrodeposited in two cells to obtain metallic zinc and manganese dioxide [5]. In the Recupyl process zinc and manganese are recovered as sulphates [6]. Revabat process treats only zinc–carbon and alkaline batteries; after sorting, batteries are dismantled and treated by sulphuric acid, from which Mn and Zn are recovered as oxides or salts [7]. The Batrec process (pyrometallurgical) recycles every type of battery (except for the Ni–Cd ones). Batteries are pyrolyzed at temperature of 700 °C and mercury is recovered by distillation. Metallic components are reduced and smelted in the induction furnace at 1500 °C: Fe and Mn remain in the melt and form a ferro-manganese alloy, whilst zinc vaporizes and it can be recovered by condensation [8].

## 2. Experimental

The aim of the present work is to recover zinc and manganese from spent alkaline and zinc–carbon batteries by means of a selective leaching, proposing a whole recycling process. Tests with different sulphuric acid concentrations were performed to optimize the experimental conditions. Zinc oxide is quantitatively dissolved by sulphuric acid, and the chemical reaction can be described as follows:

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \tag{1}$$

Unfortunately, there is dissolution of manganese oxides such as $Mn_2O_3$ and $Mn_3O_4$, as shown by reactions (2) and (3):

$$Mn_2O_3 + H_2SO_4 \rightarrow MnO_2 + MnSO_4 + H_2O \tag{2}$$

$$Mn_3O_4 + 2H_2SO_4 \rightarrow MnO_2 + 2MnSO_4 + 2H_2O \tag{3}$$

Thus, these dissolutions are partial because $MnO_2$ is insoluble [9–11]. Besides other metals like Fe, Cd, Ni, Cu, Cr are dissolved in the leach liquor, so purification tests were carried out to precipitate them obtaining a purified solution suitable for the electrolysis of zinc: in fact, in an industrial plant, accumulation of those metals in exhausted solution recycled into the leaching reactor reduces the purity of zinc deposited on the cathode [12–14]. Those metals more electropositive than zinc are contained in the battery casing alloys, or they could come from battery of other types (mistakes during the sorting process). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a solid residue to establish the optimal temperature for roasting experiments. Solid residue coming from the best leaching test was calcined at 900 °C at different times to remove graphite and to obtain a mixture of manganese oxides that can be used as pigments in ceramic and paint industry or as raw material for the production of other manganese compounds. Finally a flow-sheet of an industrial plant for zinc and manganese recovery from spent alkaline and zinc–carbon batteries is proposed: the whole process was simulated by using Super-Pro Designer software by Intelligen Inc., USA, developing a profitability analysis as well.

## 3. Materials and methods

### 3.1. Battery dismantling

A representative sample of spent alkaline and zinc–carbon batteries of different size from several manufacturers were manually dismantled to recover the internal paste. The resulting black paste was mixed and dried for 24 h at 105 °C. That paste represented about 55% of the total battery weight, and it was composed by pieces of different size up to 2 cm. Dismantling products such as plastic and paper films, ferrous and non-ferrous scraps were separated. Paste was ground for 30 min by a ball mill (Retsch PM100) and then sieved at 1000 μm; the powder obtained in this manner was washed with distilled water in a jacketed stirred reactor tank at 60 °C with 10% w/v pulp density. The purpose of this washing was the removal of potassium hydroxide and other water-soluble compounds, like chlorides. That temperature was chosen to increase the solubility of KOH. Removal of KOH reduces 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 in the pilot-scale unit [11]. Washed powder was dried for 24 h at 105 °C, recovered and weighted. All the leaching tests shown in this paper were carried out with the washed powder.

### 3.2. Characterization of battery powder

Original and washed powders were analyzed by X-ray fluorescence (XRF) (Spectro Xepos) and X-ray diffraction (XRD) (Philips X-Pert).

A quantitative analysis was also carried out by atomic absorption spectroscopy (AAS) (spectrometer SpectrAA 200, Varian) in order to evaluate the accurate content of manganese, zinc and iron. Iron was measured because it represents the major contaminant of the leach liquor in zinc electrowinning, so it must be precipitated by an alkaline reagent (Ullmann's [12]). Quantitative analysis was performed in a 250 mL closed flask: 1 g of washed powder was dissolved in 20 mL of aqua regia (HCl:HNO₃ = 3:1) in a digestion bomb. Concentrated hydrochloric and nitric acids of analytical grade were used (Merck).

### 3.3. Leaching tests

Leaching tests were carried out at 80 °C and 10% w/v pulp density by means of four sulphuric acid solutions with different concentration: 0.5, 1, 1.5, 2 M. Each test was replicated twice. Preliminary tests at room temperature and 50 °C with 1–1.5 M sulphuric acid solution and 10% w/v pulp density showed that zinc and iron extraction is not acceptable for the aim of the present study. An other test with 20% w/v pulp density and 2 M sulphuric acid concentration led to a

quantitative dissolution of Zn, but the final pH was higher than 5, so the solid residue, consisting of manganese and graphite, was contaminated by iron. Whereas on the one hand a pregnant solution with low contamination is required, on the other hand iron cannot be left in the solid residue, because it contaminates manganese oxides recovered after roasting.

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 prepared by dissolving 10 g of washed battery powder in 100 mL of $H_2SO_4$ solution of the required concentration. 1 mL of leach liquor was withdrawn after 1, 2 and 3 h to measure the concentration of Mn, Zn and Fe by AAS. After 3 h the pH (pH-meter Mettler Toledo MP 220) was measured and suspensions were filtered, whereas filter cakes were washed by distilled water and dried at 105 °C for 24 h for the determination of weight loss.

### 3.4. Purification tests

The accumulation of impurities in the recirculated solution makes chemical treatment and purification of the electrolyte indispensable for all electrowinning processes. Iron can disturb zinc electrowinning seriously by electrochemical short-circuiting [15]. The maximum iron concentration cannot be precisely specified, but it should not exceed 20–30 mg L$^{-1}$ [12].

A purification test was carried out to remove iron from leach liquor of test No. 3 (1.5 M $H_2SO_4$). This test was repeated three times. Iron was precipitated as ferric hydroxide by using 2 M solution of KOH. This test was carried out at room temperature adding KOH under stirring in 100 mL of leach liquor, until pH 4.8 was reached.

After half hour, the precipitate was filtered by vacuum pump (Millipore) and the solution was stored for the measurement of Zn, Mn and Fe by AAS.

Once iron was removed, the leach liquor was treated to remove other metals such as Cu, Ni, and Cd. The content of copper and nickel cannot be higher than 0.6 and 1.4 mg L$^{-1}$, respectively, otherwise they promote the discharge of hydrogen due to the decrease of $H_2$ over-voltage, resulting in a lower current utilization. Cadmium concentration should be lower than 24 mg L$^{-1}$, because it can be co-deposited impairing the quality of the metallic zinc. The optimum pH is within the range 4.8–5.2 [13]. One cementation test, repeated twice, was carried out by adding 400 mg L$^{-1}$ of Cu, Ni and Cd as sulphates in 100 mL of leach liquor coming from the iron precipitation stage; these metals were added because of the low concentration in the leach liquor: in fact, percentage of metals such as Cu, Cr, Ni or Cd is rather low in the battery powder (see Table 1); in an industrial plant, where the exhausted electrolytic solution is recir-

culated, a cementation stage is required because of the increase of the concentration of those metals.

Concentration of 400 mg L$^{-1}$ was chosen according to the values coming from a preliminary simulation, at the equilibrium operation, of the whole process by Super-Pro Designer software. pH was adjusted to 4.8 by KOH, and 2.3 g L$^{-1}$ fine zinc powder were added (111% of the stoichiometric amount) under vigorous stirring at 90 °C; 0.01 g L$^{-1}$ of K–Sb tartrate ($KSbC_4H_2O_6$) were also added as activator; copper sulphate, another catalyst, is already present in solution [12,13]. After 90 min the sludge was removed and the solution stored for the determination of Cu, Ni and Cd by AAS.

### 3.5. Roasting tests

Solid residue coming from test No. 3 was characterized by XRD and XRF. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using a Netzsch-STA 409 apparatus, with a heating rate of 10 °C min$^{-1}$ in air flow from room temperature to 1000 °C. Once the optimal roasting temperature was fixed, four tests were carried out at different times – 0.5, 1, 2, 4 h – to set the right time for the removal of graphite. At the end, every roasted sample was analyzed by XRD and XRF to investigate the chemical and mineralogical composition of the powder obtained.

## 4. Results and discussion

### 4.1. Pre-treatment of the battery powder

Moisture of original sample was 6.5%, calculated by weight difference after drying at 105 °C. XRF of original and washed powder is reported in Table 1.

AAS analysis highlighted that no Zn, Mn and Fe were leached by washing water. Data of washed powder show significant amount of Zn and Mn, which represent more than 50% of the total mass of the powder. The presence of Cl and K is due to ammonium chloride and potassium hydroxide that are the electrolytes of zinc–carbon and alkaline batteries, respectively. After washing there is a reduction of about 98% Cl and 96% K. Iron is the most important contaminant, whereas graphite is not detectable by XRF. XRD analyses are shown in Fig. 1(a) and (b).

Spectra are characterized by high background noise and, moreover, the structure of those compounds is not crystalline. The most probable compounds identified by spectra were ZnO, $MnO_2$, $Mn_2O_3$, $Mn_3O_4$, KOH and a zinc–chlorine compound in the original powder, and the same phases except for K and Cl complexes in the washed powder [16]. $Zn(OH)_2$ and MnOOH, discharge products of Zn–C batteries, were not found, probably due to overlapping of other compound's spectra. Results of AAS analysis showed that washed powder was composed by 41.2% Mn, 13.4% Zn and 0.95% Fe by weight.

### 4.2. Leaching tests

The extraction of all three elements increases with sulphuric acid concentration, as expected, so the greatest yield for zinc and iron is achieved within 3 h. Extraction yields, calculated with respect to the content of metals in washed powder (measured by AAS) are given in Table 2.

It is possible to see that the best test is No. 4, corresponding to the greatest $H_2SO_4$ concentration, with 100% extraction yield both for Zn and Fe. Nevertheless, recovery of Zn and Fe is almost quantitative in test No. 3, but $H_2SO_4$ concentration is lower. Considering the subsequent purification step, pregnant solution No. 3 has a higher

**Table 1**
XRF analysis of original and washed powder

| Element | Original powder % (w/w) | Washed powder % (w/w) |
|---|---|---|
| Mn | 37.45 | 39.77 |
| Zn | 9.86 | 11.32 |
| Fe | 1.04 | 1.22 |
| Cr | 0.12 | 0.16 |
| Al | 0.49 | 0.58 |
| K | 3.57 | 0.13 |
| Cl | 4.38 | 0.10 |
| Ca | 0.13 | 0.14 |
| Si | 0.91 | 0.90 |
| S | 0.18 | 0.16 |
| Ni | 0.03 | 0.04 |
| Cu | 0.02 | 0.02 |
| Cd | 0.01 | 0.02 |
| Graphite and other | 41.81 | 45.44 |

**Table 2**
Zn, Mn and Fe extraction yields: temperature 80 °C; pulp density 10% w/v; stirring 300 rpm

| No. | $H_2SO_4$ conc. (M) | Zinc extraction yield (%) | | | Manganese extraction yield (%) | | | Iron extraction yield (%) | | | Final pH | Weight loss (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 h | 2 h | 3 h | 1 h | 2 h | 3 h | 1 h | 2 h | 3 h | | |
| 1 | 0.5 | 69.2 | 80.3 | 82.5 | 11.3 | 12.9 | 13.7 | 18.7 | 20.2 | 23.7 | 1.20 | 31.8 |
| 2 | 1 | 70.3 | 82.9 | 88.8 | 12.3 | 15.7 | 17.1 | 36.3 | 55.6 | 80.0 | 0.95 | 37.1 |
| 3 | 1.5 | 71.3 | 88.4 | 98.8 | 14.2 | 17.9 | 19.3 | 43.4 | 70.4 | 99.5 | 0.88 | 42.7 |
| 4 | 2 | 79.7 | 91.5 | 99.7 | 19.0 | 23.0 | 25.2 | 53.5 | 81.2 | 100 | 0.75 | 44.3 |

final pH, and this means a smaller consumption of KOH. A titration test confirmed a saving of about 30% of KOH to achieve pH 4.8 between pregnant solutions No. 3 and No. 4.

For this reason, test No. 3 was chosen as the better one, and its solid residue was analyzed by XRF and XRD (Fig. 1(c)): its spectrum shows that $MnO_2$ and graphite are the main phases. Composition by weight of that solid, once dried, was: 50.4% Mn, 0.3% Zn, 0.02% Fe, 2.1% as sum of Al, Si, K, Ca, Ti and Cr concentrations.

### 4.3. Purification tests

Results of iron precipitation showed that iron was quantitatively removed with a precipitation yield higher than 99% (3.5 mg L$^{-1}$ as final concentration). The increase of volume of the solution was 106%. At the same time 9% Zn and 5% Mn co-precipitation occurred, in spite of the greater solubility with respect to Fe(OH)$_3$: that should be due to the adsorption of Mn and Zn onto iron hydroxide particles [12].

The purification of the solution by cementation showed a removal higher than 99.8% for each metal; the final concentrations were 0.98 mg L$^{-1}$ Ni, 0.45 mg L$^{-1}$ Cu and 0.73 mg L$^{-1}$ Cd.

### 4.4. Roasting tests

TGA and DTA of the solid black residue of leaching test No. 3 are shown in Fig. 2.

TG curve exhibits a weight loss with an approximately linear behaviour up to 420 °C (−4% of the original weight); after that the rate of weight loss increases up to 600 °C (−17%) and afterward it is less leaning, reaching a constant weight at 900 °C (−26%). This curve exhibits three well-defined behaviours, that correspond to three regimes of graphite oxidation: up to 400 °C, the oxidation is very slow and it is not significant; in 400–600 °C range, the oxidation is controlled by chemical reaction, whereas in 600–800 °C range the oxidation kinetics is driven by in-pore diffusion [17]. At the same time DTA shows one endothermic peak at about 130 °C, due to dehydration (1% weight loss), another endothermic peak at 510 °C and one exothermic peak at 570 °C, due to the oxidation of $Mn_3O_4$ to $Mn_2O_3$ [18]. After 570 °C, DTA curve shows several peaks, both endothermic and exothermic, small in magnitude; this may be related to processes like decomposition and phase transition of other compounds contained in small amounts.

Thus, temperature of 900 °C was chosen as optimal value to roast samples at 0.5, 1, 2 and 4 h, optimizing the residence time. XRD spectra are shown in Fig. 3. All the samples obtained by the thermal treatment became brown in colour.
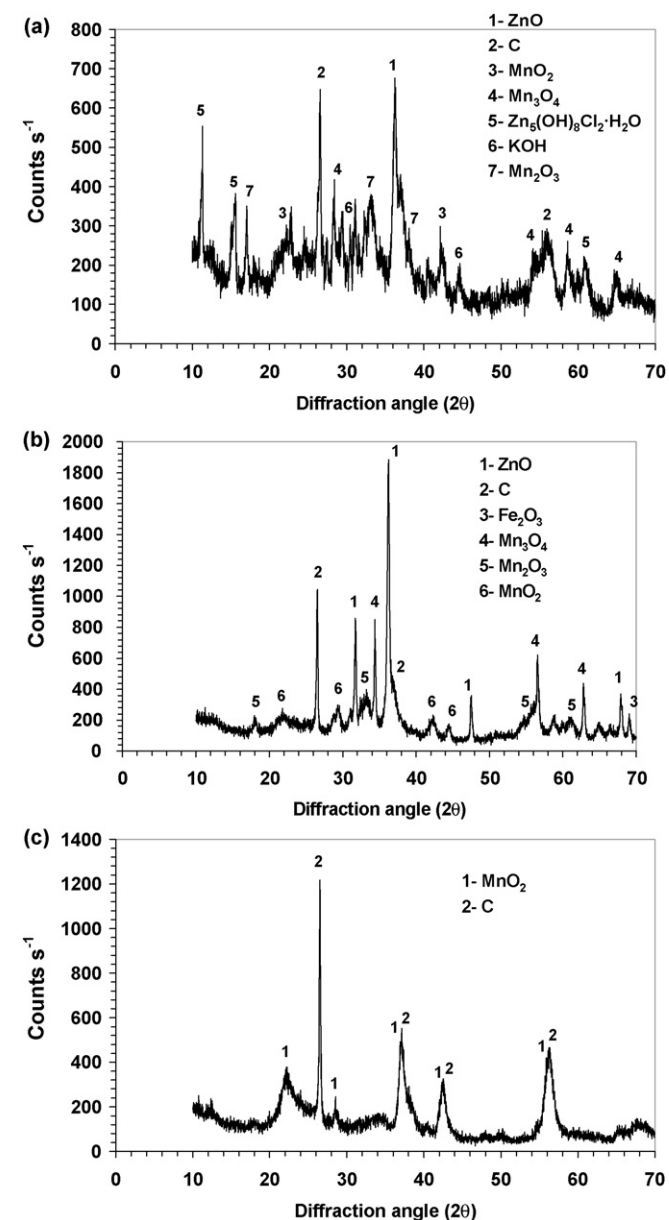


**Fig. 1.** XRD patterns: (a) original powder; (b) washed powder; (c) solid residue of test No. 3.
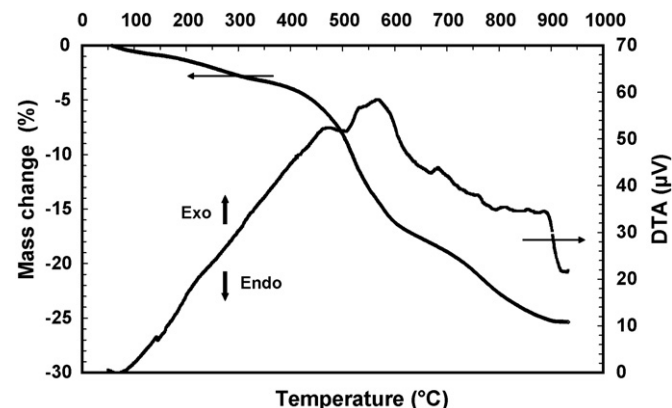


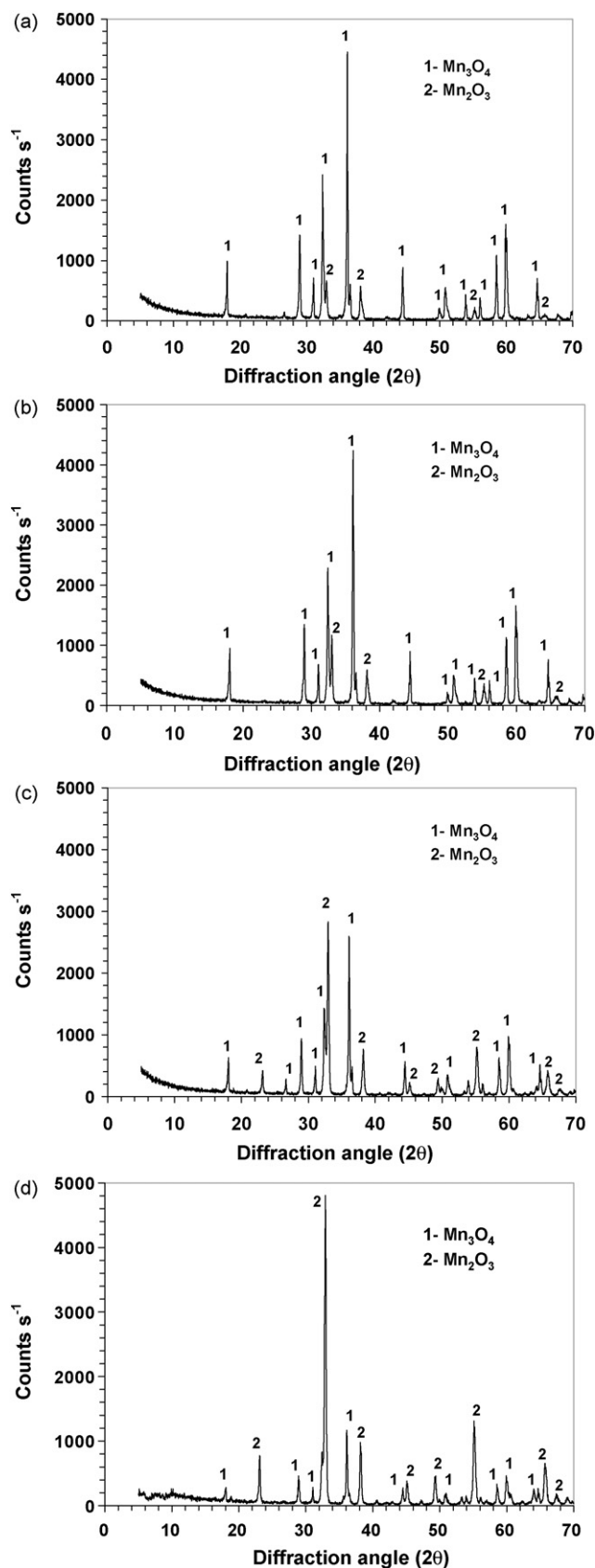**Fig. 2.** TGA and DTA of solid residue coming from leaching test No. 3.

**Fig. 3.** XRD patterns of roasted samples at different time: (a) 0.5 h; (b) 1 h; (c) 2 h; (d) 4 h.

Residual manganese in the leaching solid residue is in the form of $Mn^{4+}$ as indicated by reactions (2) and (3) after digestion with sulphuric acid [19]; after roasting, XRD showed that Mn is present as $Mn_2O_3$ and $Mn_3O_4$; the latter, hausmannite, is a spinel with $Mn^{2+}$ cations in the tetrahedral sites and $Mn^{3+}$ cations in the octahedral sites [18]. This means that $Mn^{4+}$ is reduced by graphite which oxidizes to carbon dioxide, as indicated by the following reaction:

$$10MnO_2 + 3C \rightarrow 2Mn_2O_3 + 2Mn_3O_4 + 3CO_2 \tag{4}$$
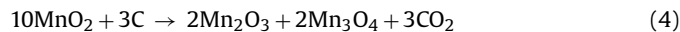
At the same time, as mentioned above, a certain amount of graphite is directly oxidized by oxygen:

$$C + O_2 \rightarrow CO_2 \tag{5}$$

Kinetics of the previous reaction increases with temperature, but it becomes considerable for more than 400 °C [17]; this is the main reaction which drives the behaviour of TGA curve. According to the XRD patterns, $Mn_3O_4$ phase decreases with time, whereas $Mn_2O_3$ increases: it should be assumed that Mn is oxidized by oxygen contained in the air:

$$4Mn_3O_4 + O_2 \rightarrow 6Mn_2O_3 \tag{6}$$

That oxidation is very slow, because after 4 h hausmannite is still present (see Fig. 3(d)). However, oxidation of hausmannite starts at about 560 °C and leads to the stable $Mn_2O_3$ phase. The reverse process, which corresponds to the reduction of Mn(III), occurs at 950 °C [18], even though in this case the reduction seems to start at 900 °C, when an endothermic peak appears. The sample obtained after 0.5 h roasting time exhibited 70.1% Mn content, 0.43% Zn, 0.28% Fe and 3.8% as sum of Al, Si, K, Ca, Ti and Cr concentrations. The higher the roasting time, the higher the content of $Mn_2O_3$, but, once graphite is completely burned, the grade of manganese does not change. For this reason 30 min seem to be the right time for the treatment of the solid residue, that can be used in ceramic and paint industry as well as for the production of other manganese compounds ($\gamma$-$MnO_2$, $MnSO_4$, $MnCO_3$).

## 5. Process analysis

A preliminary design and an economic assessment of a recycling plant were carried out using results obtained by experimental tests. The plant was designed to work in continuous operation mode (7920 h y$^{-1}$), with a capacity of 5000 t y$^{-1}$ of alkaline and Zn–C batteries. That plant capacity was chosen taking into account the amount of batteries annually collected in Italy. The collection rate is still low, but it is going to increase in the next years due to the new Directive 2006/66/EC. Flow-sheet of the recycling plant with the annual mass balance is shown in Fig. 4.

Mass balance indicated in Fig. 4 concerns the equilibrium operation, that means after the first cycle when spent solution coming from zinc electrowinning is recycled into the leaching reactor and reagents only are made up.

Alkaline and Zn–C batteries are manually sorted from other types of batteries. Nearly 631 kg h$^{-1}$ of batteries are crushed by a hammer or Hazemag mill in the dismantling section. The black powder is separated by a vibrating screen from the coarse fraction composed by iron scraps, plastic and paper films. The size of the screen is 1 mm. 347 kg h$^{-1}$ of black powder (fine fraction) are sent to the leaching section, whereas the coarse fraction (284 kg h$^{-1}$) is treated to recover marketable secondary raw materials; in fact, a representative sample of alkaline and Zn–C batteries of different shape contains about 45% by weight of coarse fraction [20]. Magnetic scraps are separated by magnetic separation, and then non-ferrous materials are recovered by using an Eddy-current separator. Remaining plastic and paper are landfilled or incinerated
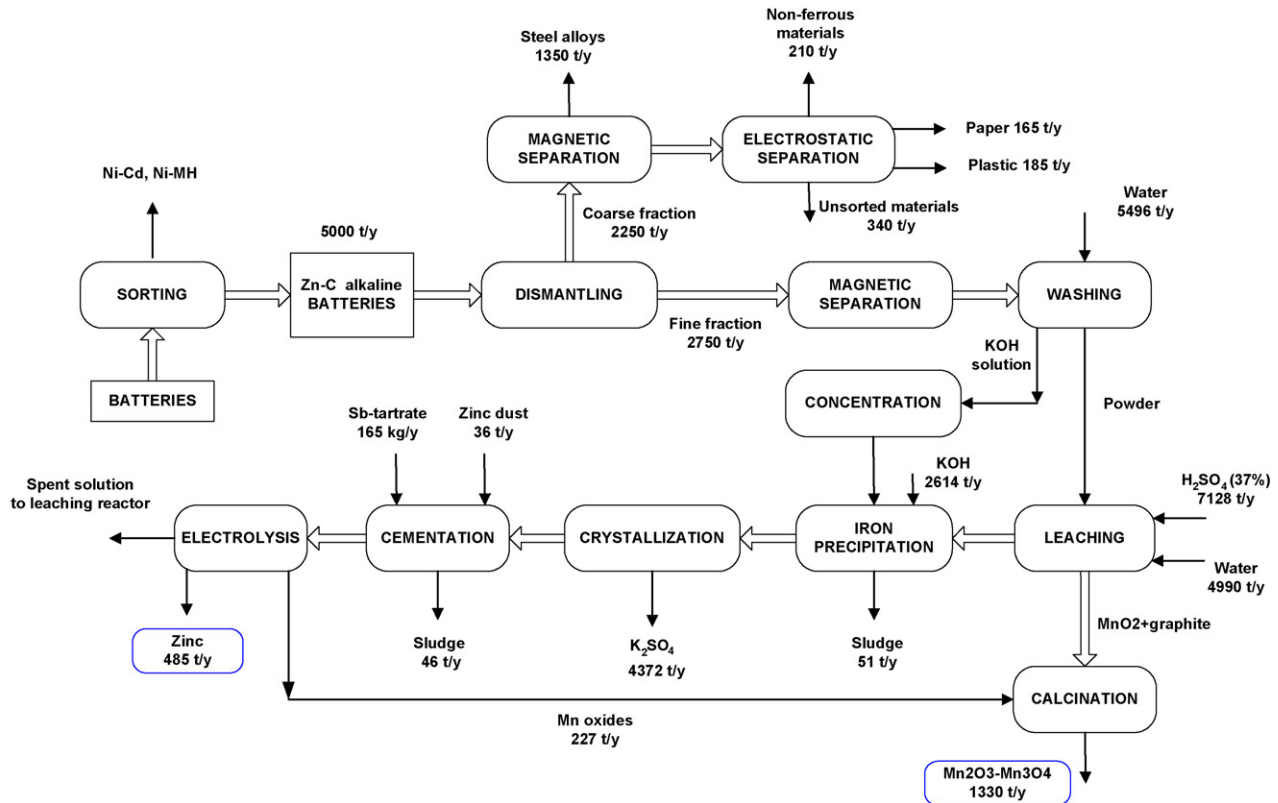
**Fig. 4.** Flow-sheet of the recycling process.

as RDF (Refuse Derived Fuel). Unsorted materials are left after the separation stage.

Current value of steel and iron for secondary fusion is very high as well as value of non-ferrous materials: the latter depends on chemical composition. Thus, it was assumed a selling price of $250 \in t^{-1}$ for both of them [20].

Metallic scraps can be recycled by a pyrometallurgical process for steel and ferro-alloy production. Battery powder is sent to a water washing for the removal of KOH. Resulting solution is concentrated by evaporation: this washing allows to save $H_2SO_4$ during the leaching, and about 5% KOH in the subsequent neutralization stage. Energy and water recovery is also possible in this stage. After leaching stage, neutralization of pregnant solution is required to remove iron as ferric hydroxide at pH 4.8. Neutralization leads to the formation of a large amount of $K_2SO_4$, which must be crystallized because its concentration is close to the maximum solubility. $K_2SO_4$ with a degree of pureness of at least 96% can be sold as raw material to avoid landfilling cost ($150 \in t^{-1}$ for hazardous materials): this is an essential requisite for the economic feasibility of the recycling process. The resulting $K_2SO_4$ dissolved into solution is needed during the electrowinning, because that salt increases the conductivity of electrolyte. Before electrowinning, cementation is carried out as indicated in subsection 3.4.

Preliminary tests showed that it is possible to obtain metallic zinc with a minimum purity of 99.6%; the best operating conditions are as follows: $Zn^{2+}$ 20 g L$^{-1}$, $Mn^{2+}$ 7 g L$^{-1}$, $K_2SO_4$ 15 g L$^{-1}$, current density 120 A m$^{-2}$; cell voltage 3.8 V; pH 4.8; time 2 h; temperature 40 °C; platinum mesh as cathode and a spiral of platinum wire as anode. Current efficiency was 72.4% with an electric energy requirement of 4.3 kWh kg$^{-1}$ [21]. At the same time, during the deposition of zinc, a black sludge precipitated on the anode side. XRD showed that the sludge is a mixture of $MnO_2$ and other manganese oxides, which can be dried and sent to the kiln for calcination (0.5 h at

900 °C) together with the solid residue of leaching stage. Without this co-deposition, manganese should have chemically been precipitated to regulate the balance of Mn ions. The electrowinning is able to remove about 98% of zinc and 13% of manganese from solution. However, this work is still in progress to optimize every parameter. Only 96% of spent solution is recycled back, whereas the remaining 4% is treated as liquid effluent to keep the equilibrium of all compounds, whose concentration could increase too much after few cycles (treatment cost $200 \in t^{-1}$).

The economic evaluation of the recycling plant was carried out assuming a price surcharge equal to $0.5 \in kg^{-1}$ of batteries treated. It should be noted that the price surcharge hereafter indicated covers the recycling costs, so it is only a percentage of the total battery price surcharge that consumers will pay: the rest will be used to finance public information campaigns, collection and transportation costs. Without financing scheme, as provided by new Directive 2006/66/EC, the recycling of batteries is not economically feasible.

Other important hypotheses were: project lifetime 10 years; depreciation period 9 years; inflation rate 3%; income taxes 40%. The main economic indexes of the investment are given in Table 3.

Total capital investment comprises total plant direct cost (equipment purchase cost, installation, process piping, instrumentation, electricals and auxiliary facilities), total plant indirect cost (engineering and construction), contractor's fee and contingency. Every item was calculated as a fixed percentage of the equipment purchase cost [22]. The return on investment (ROI) is quite high: it could be possible to earn $34.5 \in y^{-1}$ per $100 \in$ invested in that project, with around 3 years payback time. Gross profit is $2,008,000 \in y^{-1}$, whereas the net profit, taking into account income taxes and depreciation, is $1,679,000 \in y^{-1}$. Expenses weighing upon the annual operating costs are the following: raw materials 39.6%, labour-dependent 7.2%, facility-dependent (depreciation of investment, insurance, etc.) 20.7%, laboratory and quality control 0.4%,

**Table 3**
Summary of the economic evaluation report

| Item | |
|---|---|
| Processing rate | $5000\,t\,y^{-1}$ |
| Price surcharge | $0.50\,€\,kg^{-1}$ |
| Total capital investment | $4,863,000\,€$ |
| Operating cost | $3,597,000\,€\,y^{-1}$ |
| Unit processing cost | $0.72\,€\,kg^{-1*}$ |
| Total revenues | $5,605,000\,€\,y^{-1}$ |
| Gross margin | 35.8% |
| R.O.I | 34.5% |
| Payback time | 2.9 years |
| I.R.R. (after taxes) | 33.5% |
| N.P.V. (at 7% interest) | $4,598,000\,€$ |

* kg of batteries treated.

waste treatment and disposal 6.5%, utilities (electricity, steam, etc.) 25.3%, other 0.3%. A quick look at simulation results reveals that in this project the largest cost is associated with raw materials, which is mainly caused by KOH (55% of raw materials expense), water (14.7%) and $H_2SO_4$ (25%). Other large items are facility-dependent cost and utilities, which account for about 21% and 25%, respectively.

Total revenues amount as follows: batteries (price surcharge) 44.6%, magnetic and non-ferrous scraps 7.1%, zinc 26%, manganese oxides 8.3%, potassium sulphate 14%. As we can see, the majority of revenues come from money that consumers will pay for batteries. The percentage of the total price surcharge for recycling could be reduced, but it must not be lower than $0.3\,€\,kg^{-1}$, otherwise one or more economic indexes become negative and the investment is not profitable.

## 6. Conclusions

In this paper some leaching tests were carried out to recover Mn and Zn from spent alkaline and zinc–carbon batteries. These tests showed that Zn is completely dissolved within 3 h with 1.5 M sulphuric acid concentration, 10% w/v pulp density at 80 °C. Pregnant solution was purified by precipitation of iron as ferric hydroxide by means of KOH. After that, neutralized solution was purified by zinc powder to remove metals more electropositive than zinc, such as nickel, cadmium and copper. Zinc was recovered by electrowinning, obtaining a metallic deposit with 99.6% zinc grade: the current efficiency was 72.4% and the electric energy requirement was $4.3\,kWh\,kg^{-1}$. After 2 h about 98% of zinc contained into solution was removed, together with 13% of manganese which is deposited on the anode side as a mixture of oxides. The solid residue

of leaching was roasted at 900 °C to remove graphite, and 30 min were chosen as optimum treatment time obtaining a mixture of $Mn_2O_3$ and $Mn_3O_4$.

The whole process, consisting of several simple unit operations, was simulated using data obtained by experimental tests; as initial hypothesis, it was assumed a price surcharge of $0.5\,€\,kg^{-1}$ of batteries as financing system, otherwise recycling of batteries is not economically feasible. On the contrary, the technical feasibility of the recycling process was fully demonstrated.

Further zinc electrowinning tests are required to optimize every cell parameter, and some heat and water recoveries should be studied to reduce the consumption of energy and raw materials, improving the economic balance of that plant.

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