

Short Communication

Recovery of zinc and manganese from spent batteries

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Abstract

The necessity of recycling spent batteries in order to recover metals and to protect the environment is emphasized. Some experiments have been made to develop a hydrometallurgical process for metal recovery in alkaline manganese batteries. The components are easily separated: zinc can be electroplated and manganese(II) can be oxidized to dioxide; Mn(IV) is solubilized in acidic hydrogen peroxide and reprecipitated by bases.

Introduction

We have previously summarized in a review with 36 references [1] the research, mainly published as patents, on the recycling of spent alkaline manganese batteries for recovery of components, especially zinc and manganese, with economical and environmental benefits. Scientific literature proposes two solutions, pyrometallurgical or hydrometallurgical.

There has been a recent renewal in these research activities, perhaps coinciding with the starting of two plants for the treatment of batteries in Switzerland with pyrometallurgical Sumitomo–Batrec process and mixed pyro- and hydrometallurgical Recytec process [2–6].

In a previous work [7], a general flow sheet for the separation and the recovery of various components by a hydrometallurgical method was suggested, based on analytical results concerning the composition of zinc–manganese batteries; in addition, a thermal treatment was considered for mercury.

The present work proposes to develop a completely hydrometallurgical separation process, which includes the recovery of mercury, usually recovered by pyrometallurgical way, for batteries on a laboratory scale.

Experimental

Analysis

Approximately 15 kg of spent batteries from a municipal collection in Tuscany (Italy) in 1992 were dismantled, producing 9.5 kg of black powder and 5.5 kg of plastic

TABLE 1

Percentage composition of the powder from dismantled 15 kg spent batteries, dried and leached with several acid solutions^a

Mn total (%)	24.2
Zn (%)	19.4
Graphite, paper and plastic (%)	22.1
Hg (ppm)	820
Cd (ppm)	848
Ni (ppm)	526
Fe (ppm)	2445

^aTrace amounts of lead, copper and barium were also present.

and iron cases. The powder had a strong smell of ammonia due to the reaction between the ammonium chloride contained in zinc-carbon and potassium hydroxide of the alkaline manganese batteries.

The composition of the coarse materials was: graphite (5%), plastic (11%), iron (included batteries not completely dismantled) (68%), zinc (15%), and copper (1%).

Iron cases were more plentiful than zinc cases, showing, in the material examined, a large predominance of alkaline manganese batteries. This mixture can be treated by flotation and magnetic separation for the recovery of the components.

Some samples of black powder were dried at 105 °C in order to determine the humidity (in %) after dismantling. The mean value was 11.2% by weight of the initial powder.

A sample of dry powder was leached with several acid solutions in order to obtain a complete solubilization of the metals. The sample was analysed by atomic absorption spectrophotometry and the results referring to the dry powder are given in Table 1.

The quantity of manganese dioxide present was determined by volumetric analysis: Mn(II) and Mn(III) were determined by sulfuric acid dissolution: Mn(II) and Mn(III) (12.8%), and Mn(IV) (11.4%) (MnO₂ 18.0%).

The dry black powder was suspended in distilled water for the determination of soluble salts. These proved to be 7 wt.%, of which 3.4% were chlorides. There were trace amounts of carbonates and hydroxides and a substantial quantity of potassium.

Process on powder

The recovery of zinc and manganese from spent batteries is given in Fig. 1.

Leaching

A portion of initial black powder was suspended in water (ratio volume of water/weight of powder = 5 l/kg) for 1 h at room temperature to separate soluble salts. Afterwards the solid residue was leached with 32% sulfuric acid, the ratio between the volume of acid solution and the weight of powder = 5 l/kg. The reaction took place in a stirred reactor for 2 h at 50 °C.

The resulting slurry could be easily separated, yielding a brown-black paste containing Mn(IV), graphite, paper and plastic and a pink-violet solution with the other metals; the pH was 0.9.

This solution contained Mn(II) and Mn(III), 12.8 kg from 100 kg of dry powder; the total Zn and Fe contents (19.4 kg and 0.24 kg from 100 kg, respectively); 75%

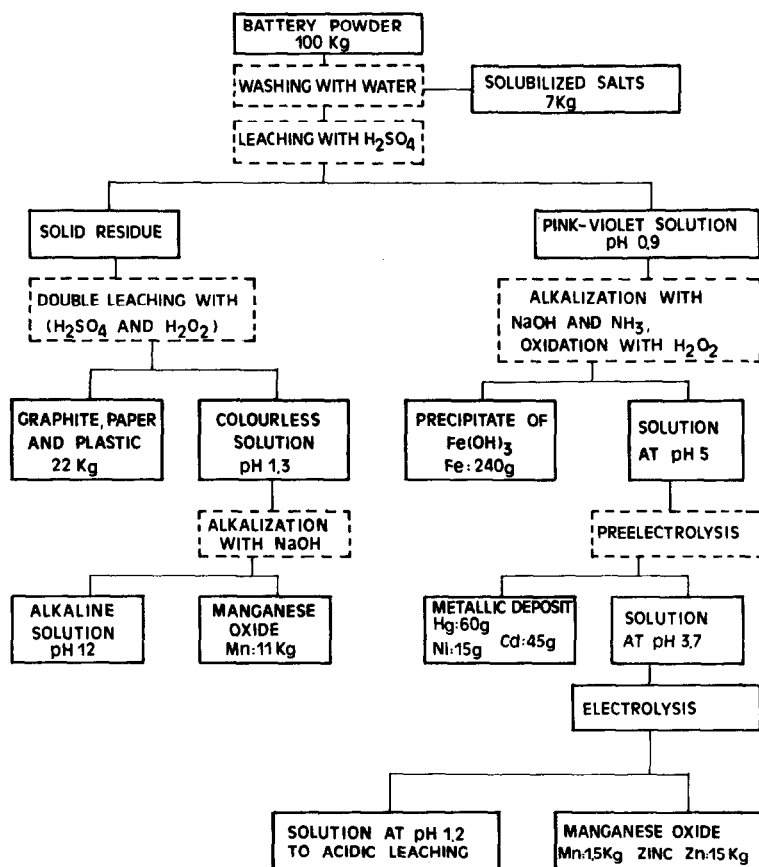


Fig. 1. Schematic presentation of the recovery of zinc and manganese from spent batteries.

of the heavy metals, that is 64 g of Cd; 62 g of Hg, and 40 g of Ni, always referring to 100 kg of initial dry powder.

Following this, the pH of this solution was raised to 3.7 by 50% NaOH and then to pH 5.0 by 32% ammonia and, thereupon heated at 60 °C: a small quantity of H₂O₂ was added, iron hydroxide was precipitated.

Pre-electrolysis for recovery of minor heavy metals

Subsequently, the solution was electrolyzed to remove Hg, Ni and Cd. The cathode was a commercial steel net and the anode a platinum net, both had a surface area of 6 cm². A constant potential of -900 mV versus saturated calomel electrode (SCE) was used: the distance between the electrodes was 35 mm, the temperature was 50 °C and the solution was magnetically stirred. The cell voltage remained practically constant at 2.5 V, the total current was 20 mA. 96% of Hg, 71% of Cd and 37% of Ni was removed by electroplating from the solution, the final pH of the solution was 3.7.

Electrolysis for recovery of zinc and MnO₂

The resulting solution was then electrolyzed a second time in the same reactor, using a lead anode (6 cm² in surface area). The temperature was 50 °C and the run was performed at a constant current of 300 mA for 8.5 h. 78% of zinc in solution was recovered (current yield 82%), while 11% of manganese was deposited on the anode as an oxide having a titre of 70% in MnO₂. In a typical experiment, the change in concentration of zinc and manganese in solution was from an initial concentration of 16.5 and 10.8 g/l to a final concentration of 3.7 and 9.6 g/l, respectively.

The solution had a pH of 1.2, it could be recycled, with further acidification, for further leaching of the initial powder.

Treatment of the residue of acidic leaching

The black residue was 40.1 wt.% of the initial dry powder and contained, in addition to graphite, paper and plastic (22.1 wt.%) Mn(IV) equivalent to 11.4% of initial dry powder. This mixture was in part solubilized by heating with 35% H₂O₂ and concentrated sulfuric acid, by means of double leaching. 6 ml of H₂O₂ and 12 ml of H₂SO₄ were used at suitable concentrations, per gram of dry powder. Manganese dioxide was completely dissolved, allowing the separation of graphite, plastic and cellulose. The pH of the solution was then slowly raised to 12, by stirring at 40 °C, using 50% NaOH, obtaining again a manganese oxide free from graphite.

The titre was 70% in MnO₂. All the dissolved manganese was precipitated again. The residue of graphite, paper and cellulose was totally burnt, yielding 2 wt.% of the ash content.

Conclusions

The process described is completely hydrometallurgical, includes mercury recovery; the 100 °C temperature is never exceeded. This process was applied to a typical mix of a municipal collection, where alkaline manganese batteries largely predominate. The results are as follows:

- The dismantling method allows an almost complete separation of iron from electrode powder
- Leaching is performed at moderate temperature and acidity, giving immediate separation of graphite, paper, plastic and half of the manganese content; afterwards, the remaining manganese could be recovered as MnO₂ by a chemical method
- Pre-electrolysis almost completely removes mercury and, to a great extent, cadmium
- Electrolysis gives a good recovery of zinc and recovers a part of the manganese
- Electrolysis regenerates sulfuric acid which can be reused in acidic leaching

References

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