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Simultaneous recycling of nickel metal hydride, lithium ion and primary lithium batteries: Accomplishment of European Guidelines by optimizing mechanical pre-treatment and solvent extraction operations

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ABSTRACT

In this paper the recycling of nickel metal hydride (NiMH), lithium ion (Li-ion) and primary lithium batteries was examined. Three mechanical routes of treatment were developed for each type recovering mainly three fractions: ferrous metals, non-ferrous metals and electrodic powders. The above mentioned types of spent batteries were also treated together by a unique mechanical route, obtaining in this way a powder enriched in cobalt, nickel and manganese which can be further extractable by chemical leaching. Experimental tests of solvent extraction were performed on synthetic leach liquors simulating a feed mixture of spent devices with weight composition 40% NiMH, 40% primary lithium, and 20% Li-ion (as determined by manual sorting of 3 tons of end of life batteries collected in Northern Italy). Under these conditions nickel and cobalt can be easily separated by using Cyanex 272 (stoichiometric ratio Cyanex/Co = 4, pH 5–6), but in presence of manganese Cyanex 272 loses its selectivity towards cobalt. Thus manganese must be preliminarily removed by using D2EHPA (stoichiometric ratio D2EHPA/Mn = 2, pH 4). Mechanical treatments and hydrometallurgical section to recover metals from electrodic powder are unavoidable operations in order to recover at least 50% of batteries as weight according to European Guideline 2006/66/EC.

1. Introduction

Both technological innovation and market expansion lead to a dramatic increase in the production of electric and electronic equipments as well as household batteries necessary for their usage. In particular end of life household batteries become a source of possible contamination because, once in landfill, their components (mercury, lead, copper, zinc, cadmium, manganese, nickel and cobalt etc.), can be leached following up natural infiltration processes [1].

According to the European Guideline, 2006/66/EC [2] which aims to minimize the environmental impact of both productive process and end of life batteries, in the next years several goals must be achieved about collection and recycling. In particular 25% of spent batteries must be collected by September 2012 and 45% by September 2016. Moreover the guideline established that recycling processes of batteries must ensure to achieve at least a 50% of recycling by average weight.

Research activities were focused on the development of economically and environmentally sound processes for battery recycling [3], also considering that they contain considerable amounts of valuable materials and then possible economical benefits for investors in this field. Economical benefits are related to the possibility of both selling all recovered products and earning public money just by the activity of collecting and recycling [4].

In the current literature there are many works concerning the hydrometallurgical treatment of batteries and accumulators. Most of them focused on the treatment of a single-type of devices such as Li-ion [5–7] and NiMH accumulators [8–11]. Important reviews summarizing the technologic advances about battery recycling have been also published [12,13].

In addition only few researchers focused on the recycling of primary lithium batteries [14] and this could be due to the more hazardous and less valuable substances such as Li and Mn, contained in this kind of devices [15].

Many authors mainly focused on leaching investigations and they found up the required operating conditions to dissolve all metals from the electrodic powders. Anyway most works were performed by preliminary manual dismantling of few samples in laboratory scale, without considering the upstream operations of

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dismantling [16–23] and their effects on the composition of the powders sent to leaching. Manual dismantling and reduced number of batteries used can then seriously affect the results obtained in this study due to the lack of representativity of samples used for leaching. Moreover the investigation concerning only one type of battery implies that a manual or automatic sorting of collected batteries should be performed in large plants but this step can be very expensive if deeply performed for each kind of battery.

Ruffino et al. [24] developed a pre-treatment route to treat more kinds of batteries working on battery samples of the order of 400 kg which can be considered as representative of real wastes. They proposed a mechanical route to treat spent batteries but they didn't focus on the real possibility to further recover metals from obtained fractions.

In this scenario the aims of this work are:

- To develop mechanical routes for the treatment of NiMH, Li-ion and primary lithium batteries evaluating also the technical feasibility of a unique pre-treatment route for a mixture of these batteries in order to obtain a fine fraction enriched in valuable metals (Co, Ni, Mn).
- To optimize the chemical separation of metals extracted from this fine fraction as a function of the feed composition. By this way we can predict the optimal chemical route to recover metals depending on the feed composition of battery wastes.

Primary lithium, Li-ion and NiMH batteries were treated based on the assumption of preliminary removal of the predominant alkaline and zinc–carbon batteries (i.e. by using an X-ray sorting machine set up for zinc recognition). Moreover button cells, lead acid and industrial NiCd accumulators could be easily separated because of their different sizes/shapes. By this work primary lithium, Li-ion and NiMH batteries were treated by the same mechanical route and different fractions (ferrous metals, non-ferrous metals, electrodic powders) were obtained and characterized. Based on the compositions of fine fractions, synthetic leach liquors were formulated to simulate real solutions coming from the leaching of different mixtures of pretreated batteries. Therefore solvent extraction operations were optimized to separate Ni, Co and Mn from these solutions.

Novelty aspects:

- All mechanical routes developed in a medium scale in order to obtain waste fractions which are representative of large-scale situation.
- A unique pre-treatment route for spent primary lithium, Li-ion, and NiMH batteriestreatment of primary lithium batteries which haven't been investigated yet.
- Determination of the correlation between purification scheme and upstream feed composition.

Mass balances obtained by this work will better explain which fractions need to be recovered in order to accomplish the European Guideline as minimum recycling of batteries.

2. Experimental

2.1. Material

Around 100 tons of portable batteries were collected by S.E.Val. s.r.l. between March 2009 and March 2010. In the same period a total amount of 3 tons of batteries was classified in three times, (1 ton for each time) in order to find the input composition and its variability in a year. Results of classification are reported in Fig. 1. Once composition was determined, 50 kg of each kind of devices were thoroughly mixed by the ring and cone method and quartered three times in order to get representative subsamples. NiMH, Li-ion and primary lithium batteries used in this work were drawn from these samples.

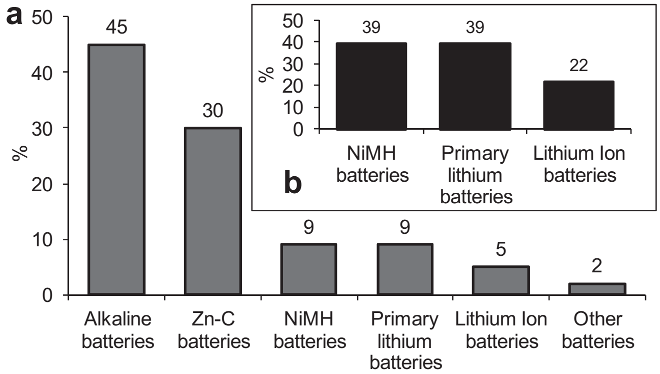

Fig. 1. Statistics of sampling considering all kinds of spent portable batteries (a) and only NiMH, lithium ion and primary lithium batteries (b).

All metal salts ($CoSO_4\cdot 7H_2O$, $NiSO_4\cdot 6H_2O$, $MnSO_4$) and other chemicals such as HCl (37%), HNO_3 (65%), H_2O_2 ($40\%_{w/v}$), H_2SO_4 (96%), NaOH and bis-2-ethylhexylphosporic acid (D2EHPA) used for the experiments were bought by Sigma–Aldrich as reagent grades. The extractant bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) was supplied by Cytec USA corporation and it was used without further purification. Low boiling point kerosene (180–270 °C) was used as diluents. All reagents were used without further purification.

Analysis for metal determinations was performed by an Inductively Coupled Plasma Optical Emission Spectrometer (Varian Vista-MPX Simultaneous CCD).

2.2. Mechanical treatment tests

All thermal treatments reported in this work were performed at 300 °C for 2 h in a silite resistance furnace. Since the oxidation of metallic lithium in presence of air is a sharp reaction able to produce dangerous explosions, thermal treatments of primary lithium batteries were carried out using a steel vessel ($V = 0.1\ m^3$) as container and a nitrogen atmosphere ($15\ l\ min^{-1}$) in order to contain all possible explosions due to the oxidation of residual metallic lithium.

Crushing operations were carried out in a two blade rotors crusher (Castulik DR120/360 9.2 kW_9/5, made in Slovak Republic) without any controlling sieve and in a hammer crusher (Strojnè Zamocnictvo TP ŠK 600 7.5 kW, made in Slovak Republic) using a 5 mm sieve. A sieving operation (1 mm) allowed the separation of fine powders (electrodic powders) from larger fractions mainly containing pieces of metals. The powders (<1 mm) were used for chemical tests whilst the larger fractions were sent to further separating operations. Therefore ferrous metals, non-ferrous metals and non-metals were separated by an Eddy Current Separator with a mobile splitter (EPA SKR-240 N, made in Czech Republic). All initial, intermediate and final fractions were weighed in order to evaluate the performances of all operations and the eventual weight loss.

2.3. Laboratory tests

The electrodic powders (<1 mm) obtained by mechanical treatments were characterized by acid digestions with aqua regia (a