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.

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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

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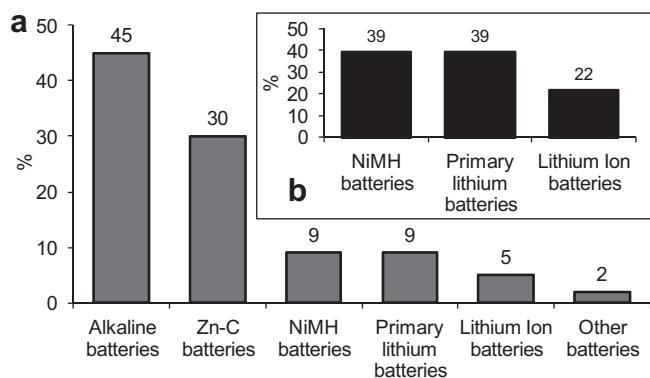
Fig. 1. Statistics of sampling considering all kinds of spent portable batteries (a) and only NiMH, lithium ion and primary lithium batteries (b).

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.

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
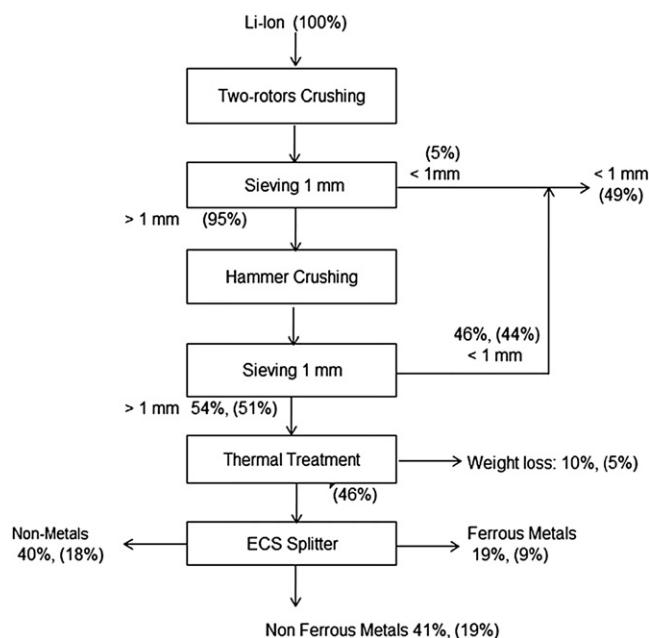
Fig. 2. Mechanical route to treat Li-ion batteries.

Fig. 3. Mechanical route to treat primary lithium batteries.

mixture of HCl 37%$_{w/w}$ and HNO$_3$ 65% $_{w/w}$ with volume ratio 3:1, respectively) at room temperature for 4 h, and then at 130 °C for 2 h after adding 10%$_{v/v}$ of hydrogen peroxide (40%$_{w/v}$). The resulting solutions, after filtration were analysed by ICP-OES to evaluate the metal released in solution and then solid composition.

Once known the metal's concentration in the aqueous phase by ICP-OES analysis, the Cyanex 272 and D2HEPA were dissolved in kerosene in order to have the desired molar ratio extractant/metal. For instance if in the aqueous phase there were 31 g l^{-1} of Mn (0.56 mol l^{-1}) then 1.12, 1.68 and 2.24 mol l^{-1} of D2EHPA were dissolved in kerosene in order to investigate respectively 2, 3 and 4 as molar ratio D2EHPA/Mn. The extracting solutions were partially saponified (65%) by adding a NaOH solution (5 M) under stirring [25,26] and in some tests even adding a phase modifier (TBP, 5 vol.%). 10 ml of solutions were shaken for 5 min with a half volume of extractant, and then with another half volume until reaching an equal volume organic–aqueous (O/A). Volumes were kept constant (O/A = 1) whilst different concentrations of extracting solutions were prepared to investigate the stoichiometric ratio moles of extractant/moles of Me^{n+} (in the range 1–4 as above described). The pH values of the aqueous solutions were adjusted by the addition of NaOH or H$_2$SO$_4$ solutions in the range 2–6 and the two phases were separated by a separating funnel. All experiments were performed at room temperature (25 ± 1 °C).

Aqueous raffinates were analysed by ICP-OES to determine the amount of extracted cobalt, manganese, and nickel.

Stripping tests for metal recovery from organic phase were carried out by using 4 M H$_2$SO$_4$ solution, at 25 ± 1 °C (volume ratio organic/aqueous = 1).

3. Results

3.1. Classification and mechanical routes

Results of classification are showed in Fig. 1, where it can be seen that NiMH, primary lithium and lithium ion batteries were found to be in a proportion of around 40–40–20% towards themselves.

Mechanical operations were required since metals in batteries are covered with or encapsulated by plastic or iron shell.
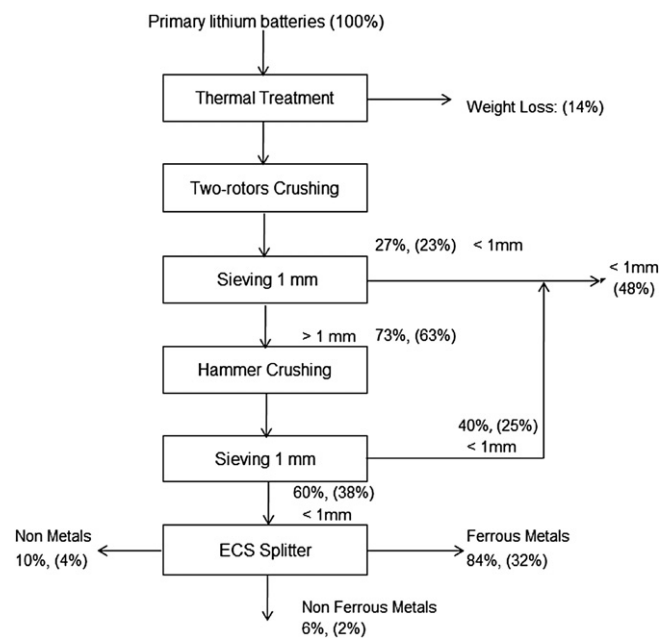
Block diagrams of the developed mechanical routes to treat NiMH, Li-ion and primary lithium batteries are reported in Figs. 2–4, respectively. These flowsheets contain also the mass balances as percentages by weight: in brackets there are percentages referred to the total initial mass of samples (i.e. 49% in brackets meant that fraction was 49% of the total initial weight of batteries sample) whilst the percentages out of brackets can be considered as performances of every single operation (percentages calculated towards to the total mass of samples feeding each operation). Whereas the total percentage in bracket wasn't one hundred the difference must be considered as weight loss. As can be seen the
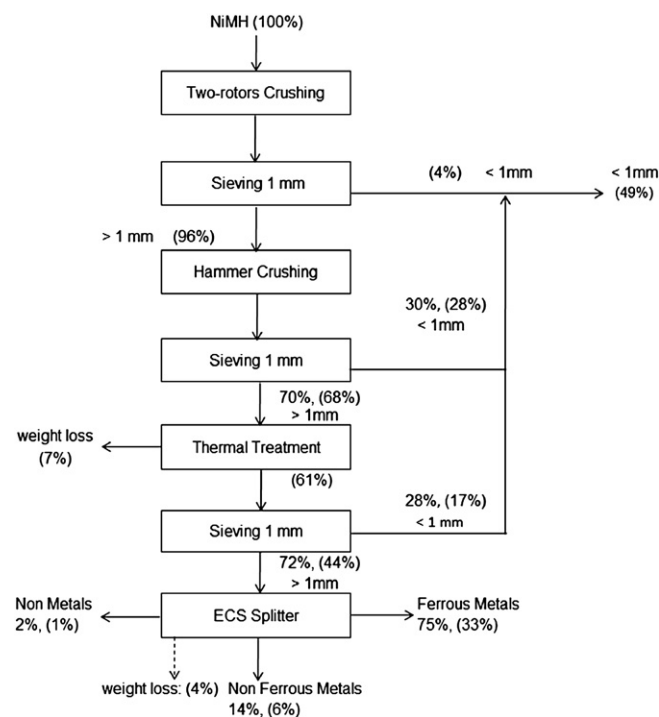

Fig. 4. Mechanical route to treat NiMH batteries.

Table 1
Powder recovered after size reduction operations.

Input devices	Double crushing by two-blade rotors crusher [%]	Double crushing by two-blade rotors and hammer crushing [%]
Primary lithium batteries	37	48
Li-ion batteries	21	49
NiMH batteries	28	49

core of all developed mechanical routes included two operations of crushing and two operations of sieving (1 mm). Hence taking as reference factor the amount of recovered electrodic powder, the performances of a double crushing by a two-blade rotor crusher were compared with those of a crushing by a two-blade rotor crusher followed by a hammer crushing. Results of this investigation (listed in Table 1 as percentage of total mass of samples), showed that hammer crushing was able to maximize the recovery of electrodic powders.

The metal compositions of all characterized powders recovered by mechanical operations are listed in Table 2. It must be observed that NiMH electrodic powder contained also 3.1 ± 0.5% of Ce 6.5 ± 0.7% of La and 4.5 ± 0.5% of Nd.

Developed mechanical routes allowed to recover as valuable fractions (ferrous metals, non-ferrous metals and non-metals) around 40% of NiMH batteries, 46% of Li-ion batteries and 38% of primary lithium batteries. Electrodic powders as they are cannot be considered as a recycled fraction because there is no direct destination for this kind of product, which must be further valorised by hydrometallurgical treatments. Moreover according to the obtained results a hydrometallurgical treatment of electrodic powders obtained by mechanical operations must be carried out in order to reach the target of 50% recycling fixed by European Guideline 66/2006 by recovering the most significant components as valuable products.
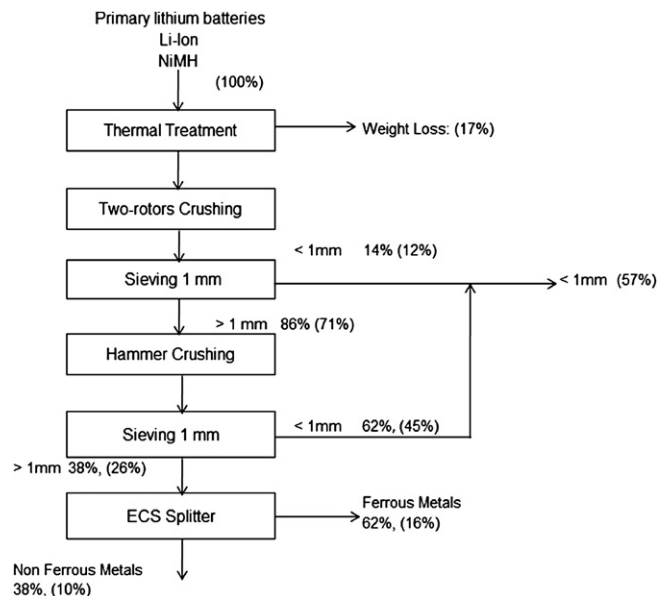
Since the core of developed mechanical routes is similar in terms of types of operations, the technical feasibility of a unique mechanical route was investigated by using as input stream a mixture of NiMH, Li-ion and primary lithium batteries having the same composition found in the sampling in real scale (Fig. 1b). This unique route is showed in Fig. 5 with all mass balances. By this choice several advantages were observed. For instances treating all battery types together there was a dilution of the explosive power of primary lithium and also the concurrent combustion of lighter fractions like papers and the dielectric materials which can cause problems during the ECS separation. In spite of these advantages, it wasn't possible to recover plastic fractions by ECS because they were burnt during the preliminary thermal treatment.

3.2. Composition of leach liquors

Synthetic leach liquors were formulated considering the chemical composition of the electrodic powders determined by acid digestion. The hypotheses for their formulations were complete dissolution of metals contained in electrodic powders according to


Fig. 5. Mechanical route to treat a mixture of NiMH–Li-ion–primary lithium batteries.

literature results [8,10,27] and solid–liquid ratio 1:5 for leaching operation. It was also assumed that Fe and Al can be removed at pH 4–5 [28,29]. We did not focus on rare earths because their separation was already well investigated and easily achievable by a precipitation at pH 1.0–2.5 [30,31], hence as an intermediate step between leaching and Fe–Al removal. Then several Mn–Co–Ni bearing solutions were formulated corresponding to different input mixtures of batteries. For instance, considering a mixture of 40% NiMH, 40% primary lithium, and 20% Li-ion batteries a quantitative dissolution of their electrodic powders with S/L ratio 1:5 will result in a solution containing 12 g l^{-1} of Co, 31 g l^{-1} of Mn and 15 g l^{-1} of Ni (Mn relative concentration = 53%).

3.3. Solvent extraction

Solvent extraction procedure has been studied in order to evaluate the possibility to separate cobalt, nickel and manganese in three different streams.

Metal extraction takes place according to the following reaction [32]

$$M_{Aq}^{2+} + A_{Org}^{-} + 2(HA)_{2Org} \leftrightarrow MA_2 \cdot 3HA_{Org} + H_{Aq}^{+} \qquad (1)$$
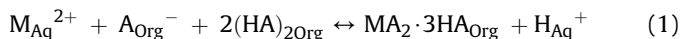
where $A_{Org}^{-} + 2(HA)_{2Org}$ represents the solvent saponified by the reaction:

$$Na_{Aq}^{+} + 1/2(HA)_{2Org} \rightarrow NaA_{Org} + H_{Aq}^{+} \qquad (2)$$
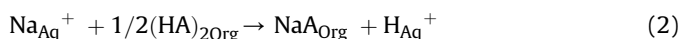
The efficiency of single metal extraction was evaluated by extractive yield and selectivity.

Extractive yield (EY) towards a specific metal (Me) was calculated as:

Table 2
Composition of powders (<1 mm) resulting from mechanical treatments of batteries.

	Al [%]	Co [%]	Cu [%]	Fe [%]	Li [%]	Mn [%]	Ni [%]
Li-ion batteries	5 ± 2	25 ± 3	0.2 ± 0.1	3.5 ± 0.5	3.5 ± 0.5	1.5 ± 0.3	6 ± 2
Primary lithium batteries	0.8 ± 0.2	<0.01	0.08 ± 0.04	3.0 ± 0.5	5.5 ± 0.5	37 ± 1	0.12 ± 0.01
NiMH batteries	0.15 ± 0.01	1.5 ± 0.07	0.5 ± 0.2	1 ± 0.2	<0.01	3.8 ± 0.2	22 ± 3

$$EY\left(\%\right) \;=\; [Me]_{org}/[Me]_{tot} \times 100 \tag{3}$$

where:

[Me]$_{tot}$ is the total concentration of metal determined in the aqueous solution before the extraction,

[Me]$_{org}$ is the extracted metal determined as the difference between [Me]$_{tot}$ and concentration on the aqueous phase after extraction.

Extractive selectivity of metal (Me1) against a competitor (Me2) was evaluated by factor β calculated as:

$$\beta \;=\; D_{Me1}/D_{Me2} \tag{4}$$

where D is a distribution coefficient for a specific metal calculated as:

$$D \;=\; [Me]_{org}/[Me]_{Aq} \tag{5}$$

There are several works in the literature which describe the possibility to separate Ni and Co using Cyanex 272 [33,34] even from nickel metal hydride batteries [35,36] Nevertheless the efficiency of solvent extraction required to be checked for a specific leach liquor in a specific range of concentration of the metal of interest.

Pseudo-isotherms were preliminarily determined to estimate the behaviour of the extractant towards single metal. These results (not reported here) showed that for pH ranging from 5 to 6 and [Cyanex 272]/Co $=$ 3–4 a quantitative extraction of Co was obtained.

Co–Ni separation was then investigated using bimetal solutions with a constant Co concentration (20 g l^{-1} of cobalt) and increasing nickel concentration (from 10 to 300% of cobalt corresponding to 2, 10, 20 and 60 g l^{-1} of nickel).

As can be seen in Fig. 6, by increasing nickel concentration the extractive yields were almost constant and even with high concentrations of nickel ([Ni]/[Co] $=$ 3), cobalt could be quantitatively extracted by Cyanex 272. Separating factors towards cobalt in general decreased when increasing Ni concentration except for the lowest [Ni]/[Co] ratio. Actually this can be easily explained because, even if only a small amount of nickel was extracted, since its concentration was low, the resulting extractive yield was high and hence the separating factor was low too. Anyway selectivity towards cobalt was very high even when nickel was 3 times more concentrated than

cobalt and the resulting solution, after stripping, had a [Ni]/[Co] ratio $=$ 0.35. Hence a second extractive step determined a further enrichment of the extract as cobalt because of a behaviour exactly like [Ni]/[Co] $=$ 0.5 as in Fig. 6. After two extractive steps by Cyanex 272 we achieved an aqueous solution containing 95% of cobalt and 5% of nickel from an initial one which had 25% of cobalt and 75% of nickel meaning that cobalt–nickel separation is easy performable in a wide range of Ni/Co stoichiometric ratio.

After this evaluation, a synthetic leach liquor was prepared including also manganese. This operation was made as explained in Section 3.2 in order to simulate a solution coming from the leaching of a powder obtained by mechanical treatment of a primary feeding containing 40% of NiMH, 40% of primary lithium batteries and 20% of Li-ion. The obtained results showed that in presence of 31 g l^{-1} of manganese the extractant Cyanex 272 lost completely its selectivity towards cobalt since a large amount of manganese was extracted. Hence another attempt to remove manganese was made reducing its concentration to the value it would have if the input stream didn't contain the primary lithium batteries, most important source of manganese. As can be seen in Fig. 7, even reducing manganese concentration to 6, 4 and 3 g l^{-1}, corresponding respectively to an input stream NiMH–Li-ion 50–50%, 40–60% and 25–75%, a selective separation of cobalt by Cyanex 272 wasn't feasible.

These results clearly showed the impossibility of selectively extract cobalt in presence of manganese and then the necessity of removing manganese before cobalt extraction. Manganese separation was performed by using bis-2 ethylhexylphosporic acid (D2EHPA) as extractant [37]. The effect of the stoichiometry D2EHPA/Mn was investigated by modifying the extractant concentration from 1.12 to 2.24 M. The equilibrium pH has been investigated first on a solution containing only manganese (results not reported here) and then using multimetallic solutions. As can be seen in Fig. 8a–c, manganese extractive yield increased for increasing pH. This result was due to the degree of deprotonation of active sites on D2EHPA molecules which increases for increasing pH. The best selectivity was obtained at pH 4 (Fig. 9). By increasing the stoichiometric ratio D2EHPA/Mn from 2 to 3 and 4 the extractive yields increased for all metals but also a decrease of extractive selectivity towards manganese was observed.

It should also be noticed that D2EHPA granted a high selectivity towards manganese even with respect to nickel meaning that these operating conditions could be adopted also for Mn–Ni separation.

According to these results a selective separation of manganese from cobalt and nickel can be achieved by a multi-step extraction procedures in which each single step gives a low extractive yield
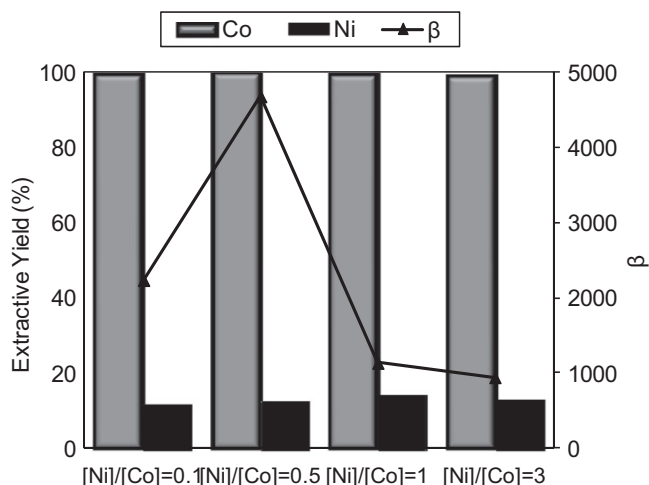
Fig. 6. Cobalt separation with Cyanex 272. Extractive yields and separating factors.
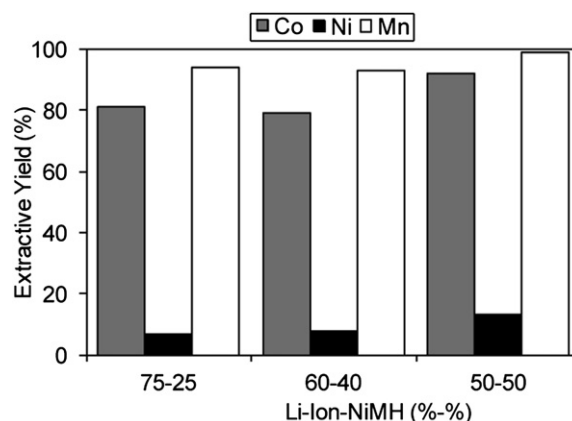
Fig. 7. Cobalt separation in presence of manganese (no primary lithium batteries).
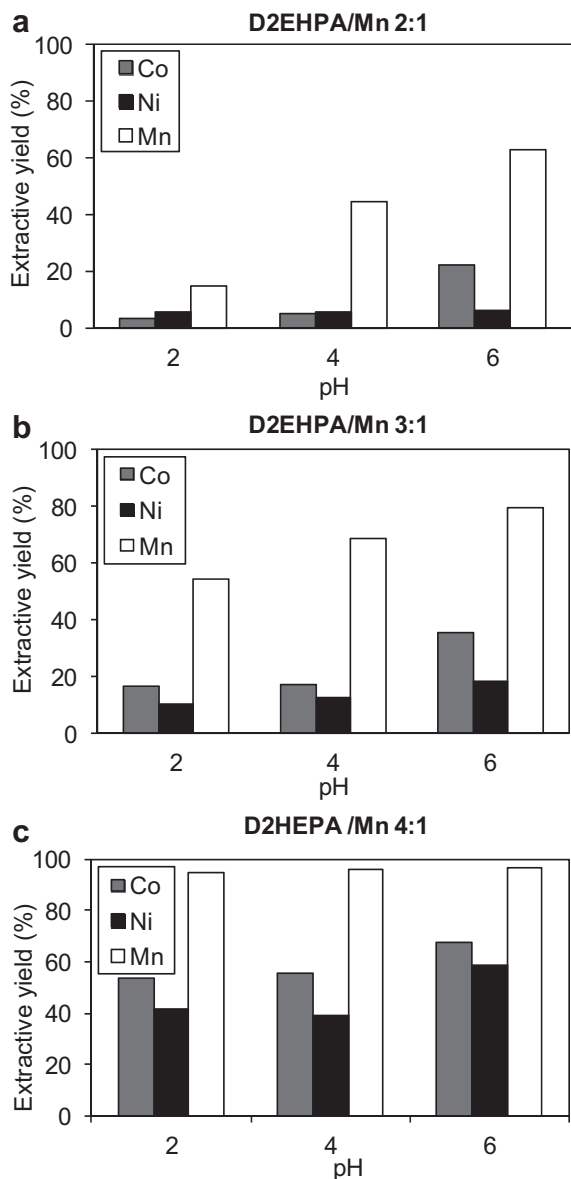
Fig. 8. Extractive yields at different pH values and stoichiometric ratios D2EHPA/Mn, 2:1 (a), 3:1 (b) and 4:1 (c).
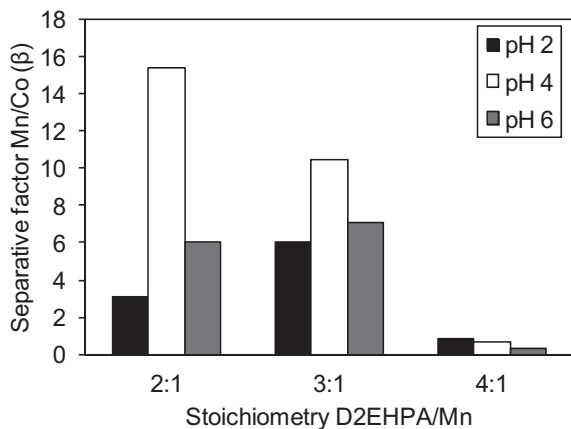

Fig. 9. Separating factors Mn/Co at different pH values and stoichiometric ratios D2EHPA/Mn.
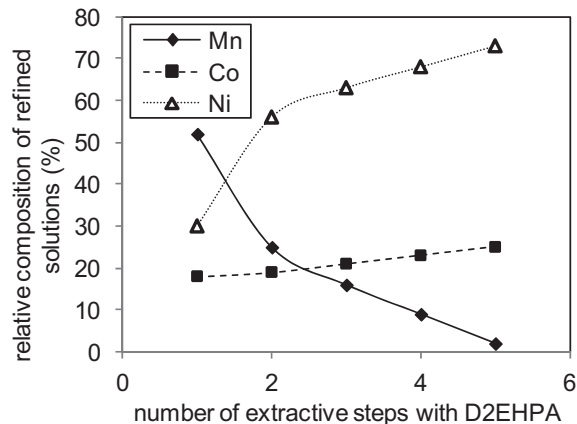

Fig. 10. Relative composition of refined solutions after each extractive step with D2EHPA/Mn 2:1.

with a high selectivity for manganese, but the quantitative recovery of manganese is ensured by the execution of more extractive steps. Therefore a multi-step extraction on the same solution was carried out using 2 mol of D2EHPA for mole of manganese at pH 4. Results of this experiment are reported in Fig. 10: Mn concentration decreased during the extractive procedures whilst Co and Ni content increased. In fact, by following an extractive behaviour as in Fig. 8a there was a progressive relative enrichment in Ni and Co because the extractive yields towards them were much lower than the one towards manganese.

The graph in Fig. 10 could be used to estimate the number of required extractive steps to separate manganese when its relative concentration in a ternary mixture Mn–Co–Ni is known.

Therefore, in the investigated range of metal concentrations corresponding to different upstream mixtures of spent batteries, it could be also possible to predict the number of extractive steps necessary for manganese removal.

4. Conclusions

A mechanical route of pre-treatment for end of life NiMH, Li-ion and primary lithium batteries has been developed showing the possibility of using a unique process route for a mixture of these three kinds of batteries. Then the possibility of avoiding a preliminary sorting of NiMH, Li-ion and primary lithium batteries has been showed by feeding the mechanical section with a mixture of these spent devices.

Mass balances for these processes performed on representative amounts of wastes showed that the weight% of fractions obtained by mechanical pre-treatment (ferrous metals, non-ferrous metals and non-metals) cannot accomplish 50% of recycling as fixed by European Guideline 66/2006.

Then the fine powders mainly containing electrodic materials (and then metals) should be further treated by hydrometallurgical operations in order to recover metal compounds.

After metal extraction by leaching, solvent extraction is a necessary step in order to separate Ni, Co and Mn.

A solvent extraction procedure has been developed to preliminarily and selectively remove manganese from the leach liquor using D2EHPA at pH 4 in a stoichiometric ratio D2EHPA/Mn = 2. By a multi-step extraction it was possible to quantitatively remove manganese enriching the aqueous solution in cobalt and nickel.

Once manganese has been removed, cobalt can be selectively separated from nickel for a wide range of nickel concentration using Cyanex 272 in a stoichiometric ratio 4:1 at pH 5.5. If necessary

a multi-step extraction can be easily carried out in order to better separate the cobalt.

According to these results a plant equipped with a pre-treatment operations as in Fig. 5 and with a hydrometallurgical section can be used to treat each kind of spent battery alone and/or their mixtures. The hydrometallurgical route must include: a leaching section to extract metals from the fine powder produced by physical pre-treatments; a precipitating section for iron and aluminium removal; a solvent extraction section for metals separation; a product recovery section (i.e. recovery of Mn, Co and Ni by precipitation or by electro winning [38−40] from their aqueous sources after extractions and recovery of lithium as carbonate by crystallization−precipitation after nickel recovery [28]).

This kind of plant can be used to treat the following feed categories:

a) primary lithium batteries alone containing only manganese (in this case solvent extraction can be by-passed).
b) Li-ion batteries alone containing only cobalt and nickel, which would be separable in a wide range of Ni/Co ratios by solvent extraction with Cyanex 272.
c) NiMH alone containing Ni, Co and Mn: in this case manganese relative concentration in solution after leaching and precipitations would be lower 20% (included in the investigated range as in Fig. 10). Thus Mn can be separated by solvent extraction using D2HEPA and then Co and Ni can be separated by solvent extraction using Cyanex 272.
d) mixtures of Li-ion and NiMH accumulators because Li-ion batteries do not contain manganese and hence Mn relative concentration would be even lower than by feeding only NiMH (included in the investigated range as in Fig. 10) and then, as in the case before, two solvent extraction operations will guarantee for Mn removal and then for Co removal.
e) a mixture of spent devices composed by 20% Li-ion 40% NiMH and 40% primary lithium batteries (as found in industrial scale sampling): in this case the relative concentration of manganese would be around 50%, as the starting condition of Fig. 10.

Whereas the mechanical section was fed with a percentage as primary lithium batteries higher than 40% a further investigation would be required because manganese concentration would be out of the investigated range.

After separation by solvent extraction all metals can be recovered as valuable products in the desired form. Only in this way, even considering the fractions recovered by mechanical operations, it would be possible to achieve the 50% of recycling as fixed by European Guidelines.

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