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# Cobalt products from real waste fractions of end of life lithium ion batteries



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#### ABSTRACT

An innovative process was optimized to recover Co from portable Lithium Ion Batteries (LIB). Pilot scale physical pretreatment was performed to recover electrodic powder from LIB. Co was extracted from electrodic powder by a hydrometallurgical process including the following main stages: leaching (by acid reducing conditions), primary purification (by precipitation of metal impurities), solvent extraction with D2EPHA (for removal of metal impurities), solvent extraction with Cyanex 272 (for separation of cobalt from nickel), cobalt recovery (by precipitation of cobalt carbonate). Tests were separately performed to identify the optimal operating conditions for precipitation (pH 3.8 or 4.8), solvent extraction with D2EHPA (pH 3.8; Mn/D2EHPA = 4; 10% TBP; two sequential extractive steps) and solvent extraction with Cyanex 272 (pH 3.8; Cyanex/Cobalt = 4, 10% TBP, one extractive step). The sequence of optimized process stages was finally performed to obtain cobalt carbonate. Products with different degree of purity were obtained depending on the performed purification steps (precipitation with or without solvent extraction). 95% purity was achieved by implementation of the process including the solvent extraction stages with D2EHPA and Cyanex 272 and final washing for sodium removal.

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#### 1. Introduction

Lithium Ion Batteries (LIBs) represent the emerging energy storage technology in the manufacture of portable electronic devices (Zhang et al., 2014). This market expansion will directly turn into huge amounts of end of life LIBs to be collected and treated (Wanger, 2011). European Guideline 66/2006 established mandatory material recovery yield for LIBs larger than 50% (Bossche, 2006). Exploitation of end of life LIBs is extremely interesting due to the composition of the cathodic materials. These include LiCoO<sub>2</sub> pasted onto aluminum foils and mixed oxides such as LiNi $_x$ -Mn $_y$ Co $_z$ O<sub>2</sub> (Zeng et al., 2014).

Two different classes of processes can be distinguished to recovery material from end of life LIBs: pyrometallurgical and hydrometallurgical processes.

Pyrometallurgical processes include direct melting of battery scraps and allow recovering high value metals (such as Co and Ni in the case of LIB). At industrial scale, the common practice is feeding LIB scraps to existing plants as, for example, metallurgical plants including cobalt and nickel extraction sections, which are however not specifically designed and constructed for LIB recycling

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(Georgi-Maschler et al., 2012). This approach is quite attractive at large industrial scale because it does not require tailoring the implemented process to the characteristics of the treated waste. However, pyrometallurgical plants are characterized by negative environmental impact mainly owing to elevated energy consumption and large pollutant emissions. In addition, pyrometallurgical processes do not allow recovering low value metals (Li, Mn, Ni, Fe, Al) and non metallic materials (plastic and electrolytes).

Hydrometallurgical processes are implemented following the recovery of battery electrodic powder and include the extraction of metals by leaching of electrodic powder, refining and recovery of metals. This kind of processes allows in principle the recovery of each component present inside the batteries (both metals and non metals). Recovery of electrodic powder is achieved by mechanical pre-treatment including crushing and sieving. The parameters of mechanical pre-treatment (e.g. type of crushing) can significantly influence the composition and the particle size distribution of recovered electrodic powder. This can in turn determine large variations in the purities and yields of metal products recovered by the downstream hydrometallurgical process. Despite the practical relevance of these arguments, research studies investigating the hydrometallurgical treatment of LIBs have frequently neglected the influence of mechanical pre-treatment and almost exclusively considered the application of electrodic powder

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recovered through manual dismantling of batteries with specific attention to leaching operation (Sun and Qiu, 2012; Swain et al., 2007; Ferreira et al., 2009), even performed with environmental friendly reagents (Li et al., 2010, 2012; Pagnanelli et al., 2014). Manual dismantling may however generate powder with size distribution and composition significantly different from those attained through industrial crushing and sieving. This can lead to the development of hydrometallurgical processes, which might hardly be reproduced at industrial scale. Following the latter idea, few works investigated the mechanical pre-treatment of batteries at a scale, which can simulate the conditions imposed by industrial application.

Shin et al. (2005) proposed a two-step crushing followed by leaching of cobalt and lithium from electrodic powder without product recovery. Gratz et al. (2014) used hammer mill crushing followed by leaching and recovery of a mixture of nickel, manganese and cobalt as hydroxides. Zhang et al. (2014) performed the mechanical crushing of spent LIBs by a rotating impact crusher without any treatment of derived powder.

Jha et al. (2013) after manual dismantling performed a crushing of both electrodic materials and Al and Cu layers: this ground mixture was then used just for leaching tests.

Granata et al. (2012) identified a sequence of pilot scale mechanical operations enabling the treatment of different types of batteries (LIB, NiMeH and Li primary batteries) without treatment of obtained powders.

Further studies have mainly focused on the optimization of the stages composing hydrometallurgical process. In this framework, solvent extraction (SX) tests were performed to selectively separate Co from leach liquor (Mantuano et al., 2006; Chen and Zhou, 2014; Chen et al., 2015). However, results achieved by these latter tests might be quite misleading since they have been obtained by application of manually dismantled materials. In fact, when mechanical treatment is performed even fine fractions, mainly made up of electrodic materials, presented significant concentration of metals such as Cu, Al, and Mn (Zhang et al., 2014; Vassura et al., 2009).

In the present work, electrodic powder was recovered from LIBs by mechanical treatment in a pilot unit granulator, which can effectively reproduce the conditions imposed by industrial application. Recovered electrodic powder was successively processed by a sequence of hydrometallurgical stages allowing for recovery of high purity CoCO<sub>3</sub>.

Important novelty of the study is the application of electrodic powder derived by pilot scale mechanical pretreatment. This ensures the achievement of final products with chemical characteristics (content of metal impurities), which are representative of what can be expected at large industrial scale.

In addition, these real waste fractions have been treated for the first time according to a novel flexible process including purification by solvent extraction and final product recovery as CoCO<sub>3</sub>. This is a significant original aspect of the work because none of the other research starting from mechanically dismantled LIB (Shin et al., 2005; Gratz et al., 2014; Jha et al., 2013; Granata et al., 2012), investigated all the process steps necessary for producing commercial grade products.

#### 2. Materials and methods

#### 2.1. Sample retrieval and pretreatment

A sample of 50 kg of portable LIBs was pretreated by using a granulator machine (FS Forrec). Sieving of grinded samples was performed over a time interval of 10 min by a vibrating sieve including three different mesh clothes (cut-off: 2, 1, and 0.5 mm).

The two fractions lower than 1 mm were mixed and used for characterization and leaching tests.

#### 2.2. Chemical characterization of the electrodic powders

Metal content in the sieved fractions of electrodic powder was determined by microwave assisted digestion (Milestone Ethos 900 Microwave Labstation) with aqua regia (prepared by mixing hydrochloric acid 36% (Sigma–Aldrich) with nitric acid  $\geqslant$ 65% (Sigma–Aldrich), both of chemical grade, with ratio 3:1), solid to liquid (S/L) ratio 1:20, over a time interval of 30 min at 200 °C and 1000 W. Analytical determination of metals in solution was performed by Atomic Absorption Spectrophotometer (AAS) (contrAA  $^{\circ}$  300 – Analytik Jena AG). Characterizations were performed in triplicates.

# 2.3. Preliminary tests of purification by precipitation and solvent extraction

Leaching of the electrodic powder produced by pilot scale mechanical pre-treatment of LIBs was performed to extract metals. Leaching was performed by using sulfuric acid and hydrogen peroxide (as reducing agent):

$$\begin{aligned} \text{LiCoO}_2 + 1.5\text{H}_2\text{O}_2 + 1.5\text{H}_2\text{SO}_4 &\leftrightarrow \text{CoSO}_4 + 0.5\text{Li}_2\text{SO}_4 + \text{O}_2 \\ &\quad + 3\text{H}_2\text{O} \end{aligned} \tag{1}$$

For all the experiments, sulfuric acid  $\geqslant$  96–98% (Sigma–Aldrich) and hydrogen peroxide 34.5–36.5% (Sigma–Aldrich) of chemical grade were used. Leaching was performed by using S/L = 1:10, 15%v/v of the  $H_2O_2$  solution, and +100% acid excess in jacketed glass reactors at 80 °C under magnetic stirring using cylindrical magnets (length 5 cm, diameter 0.9 cm) at 800 rpm. Acid excess was computed as the relative (percent) difference between the employed amount of acid and the stoichiometric one required to leach, in accordance with reaction (1), the entire Co powder fraction (Table 1).

Leach liquor samples generated by filtration of leaching suspension were employed to perform preliminary purification tests (including precipitation and solvent extraction). In preliminary precipitation tests, leach liquor with composition reported in Table 1 was treated with 5 M NaOH to induce the precipitation of Cu, Fe, Ni, Mn and Al. Precipitation tests were performed at pH 3.8, 4.0, 4.5, 4.8, 5.0 and 5.2 (final equilibrium values reached after 3 h magnetic stirring at 800 rpm and room temperature). At the end of each test, a solid liquid separation was carried out by centrifugation, and residual metals in solution were determined by AAS. Solvent extraction was performed with the leach liquor purified by precipitation at pH 3.8. Composition of the purified leach liquor is reported in Table 1.

Di-2-ethylhexylphosphoric acid (D2EHPA) (Sigma–Aldrich analytical grade reagent) was dissolved in low boiling kerosene to ensure the prescribed ratio (2, 3 and 4) between D2EHPA and Mn present in purified leach liquor (Table 1). Then, D2EHPA was partially saponified (65%) by adding NaOH (5 M) under stirring. Different amounts (5%, 10% and 15%) of tributyl phosphate (TBP) (98% Sigma–Aldrich) were added to the obtained organic phase as phase modifier. 10 mL samples of purified leach liquor were mixed to the organic phase with volume ratio O/A = 1:1 and shaken over a time interval of 10 min. After shaking, organic and aqueous phases were separated through a separating funnel. Raffinate (aqueous phase after solvent extraction) was analyzed by AAS to determine the amount of extracted metals. When performing successive solvent extractions, raffinate obtained by the first solvent extraction was further treated by fresh organic solution.

**Table 1**Chemical characterization of electrodic powder recovered after treatment of LIB wastes by granulator and sieving (<1 mm); leach liquor composition obtained by leaching of sieved powder using S/L = 1/10 and +100% acid excess; purified leach liquor after precipitation at pH 3.8 by sodium hydroxide addition (ND: not detectable, <0.1 mg/L).

	Co	Li	Fe	Cu	Ni	Mn	Al
Electrodic powder (g/kg)	227 ± 5	36.7 ± 0.6	20 ± 1	$12.4 \pm 0.2$	61 ± 1	58 ± 3	10.6 ± 0.7
Leach liquor (g/L)	$21.8 \pm 0.4$	$3.2 \pm 0.1$	$0.030 \pm 0.02$	$1.2 \pm 0.1$	$2.7 \pm 0.1$	$4.6 \pm 0.3$	1.1 ± 0.1
Purified leach liquor (g/L)	$20.0 \pm 0.1$	$2.8 \pm 0.2$	ND	$1.0 \pm 0.1$	$2.4 \pm 0.2$	$3.9 \pm 0.2$	$0.9 \pm 0.1$

Extraction with Cyanex 272 (supplied by Cytec USA Incorporation and used without further purification) was performed by using 10 ml samples of leach liquor separated after precipitation at pH 4. Cyanex was dissolved in kerosene using Cyanex/Co = 4 M ratio, 10% TBP, O/A = 1 and one extractive step.

All experimental tests of SX were performed in duplicate.

#### 2.4. Process in micro-pilot scale

After preliminary optimization of any operation, the entire hydrometallurgical process was analyzed by consecutively carrying on the entire sequence of operations up to the recovery of CoCO<sub>3</sub>. Six sequences of operations were tested corresponding to different combinations of leaching, precipitation and solvent extraction (Table 2). Each of these complete sequences will be referred to as "process". Investigated processes can be divided in two types: the first type using only precipitation by pH variation for purification (Processes I, II, and III of Table 2) schematized in Fig. 1A, and the second type including also a refining section using SX (Processes IV, V and VI) detailed in Fig. 1B.

Leaching tests were performed by using 200 g of electrodic powder, different solid/liquid ratios and sulfuric acid excess, while  $\rm H_2O_2$  amount was kept constant (15%v/v). Purification was performed by precipitation at pH 3.8 and 4.8. These latter pH values were achieved by controlled addition of NaOH.

Solvent extraction was performed by using only D2EHPA (D2EHPA/Mn = 4 M ratio; O/A = 1; 10% TBP; two sequential extractive steps) (Process IV) or by adding a further step with Cyanex 272 for Co extraction (pH 4; Cyanex/Co = 4, 10% TBP, one extractive step) (Process V). In the latter case, after extraction with Cyanex, Co ions were stripped from the organic phase by using  $H_2SO_4$  (3 M solution with O/A = 1:1.5).

Co recovery was performed after adjusting pH to 3 by addition of NaOH when necessary (Processes V and VI). Na $_2$ CO $_3$  (Sigma–Aldrich analytical grade reagent) was added till reaching pH 9. After 0.5 h of magnetic stirring (800 rpm) at room temperature, solid–liquid separation was performed by filtration. The solid was then dried in an oven at 110 °C for 24 h.

All the processes were replicated two times and average values reported in graphs.

For Process VI, the obtained solid sample was further refined by washing with water at pH 6 (three sequential washings with 1/10 *S/L* ratio) and drying in an oven at 90 °C for 1 h.

Produced samples of  $CoCO_3$  were digested by  $H_2SO_4$  (3 M with S/L = 1:20) and the content of Co and other metal impurities was

 $\begin{tabular}{lll} \textbf{Table 2} \\ \textbf{Operating conditions adopted for the different processes performed for $CoCO_3$ production.} \end{tabular}$ 

Process	S/L (g/L)	H <sub>2</sub> SO <sub>4</sub> excess (%)	Purification and refining steps
I II III IV V	1:5 1:5 1:10 1:10 1:10 1:10	+50 +100 +100 +100 +100 +100	pH 3.8 pH 4.8 pH 3.8 pH 3.8 + SX (2 * D2EHPA) pH 3.8 + SX (2 * D2EHPA + Cyanex) pH 3.8 + SX (2 * D2EHPA + Cyanex) + washing

determined by AAS. All characterizations were performed three times and mean values and standard deviations are reported in Table 3.

X Ray diffraction (Rigaku D-max X Ray diffractometer equipped with Cu k $\alpha$  radiation source) was performed on CoCO $_3$  sample obtained by Process VI. As reference for peak assignment also a "synthetic" sample was produced starting from a solution of CoSO $_4$  with initial Co concentration equal to the one in the refined leach liquor after SX with D2EHPA and Cyanex (Table 1). This solution was added with Na $_2$ CO $_3$  (up to pH 9) and recovered CoCO $_3$  was used for XRD characterization.

#### 3. Experimental results

# 3.1. Characterization of pretreated samples

Physical pre-treatment of LIB samples resulted in a mixture of electrodic powder, aluminum and copper foils, plastic, paper and alloys. Electrodic powder was separated from this mixture by sieving. Different sieves were used to ensure the effective separation of the different fractions constituting the crushed solid. Fig. 2 displays the particle size distribution of crushed LIBs. The weight percent covered by any of the four fractions which were obtained by application of three considered sieves is reported. Based on the size distribution reported in Fig. 1A, two coarse fractions (>2 and 1–2 mm) and two fine fractions (0.5–1 and <0.5 mm) are distinguished.

The two coarse fractions (>2 and 1–2 mm) include fragments of external casing and internal layers and are characterized by the presence of black powder residues. These fractions are mainly made of plastics, papers, copper, aluminum and steel. Mechanical separation units exploiting differences between density and shape can be implemented to separate the coarse fractions into non metals (plastics and papers) and metals (copper and aluminum). Separation units exploiting differences between magnetic properties can successively be adopted to separate the metal fraction (copper and aluminum) into ferrous and non ferrous metals (Granata et al., 2012).

The two fine fractions (<0.5 mm and 0.5–1 mm) were mainly constituted of black powder and accounted for about 37% by weight of the processed LIBs. The two fine fractions were mixed and the metal content of the resulting solid mixture was determined. Mineralization results (Table 1) evidenced the presence of both Co and Li as characteristic components of LIB cathodes. Co is the predominant metal (22.7%) in the powder. Additional metals including Mn, Ni, Fe, Al, and Cu are however found along with Co and exhibit relevant concentration values. According to the typical structure of LIB, the presence of Al and Cu can be related to the presence of internal layer fragments generated during grinding, while detected Mn and Ni concentrations can probably be imputed to the current trend of including mixed oxides (LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub>) as cathodic materials to reduce battery production costs.

### 3.2. Preliminary tests of precipitation and solvent extraction

The proposed hydrometallurgical process was developed to recover cobalt from electrodic powder. To maximize the purity of recovered cobalt, stages were integrated into the process allowing

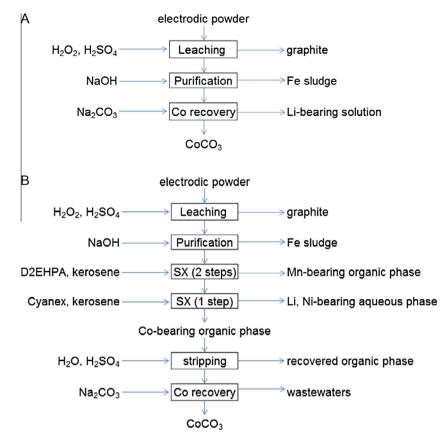
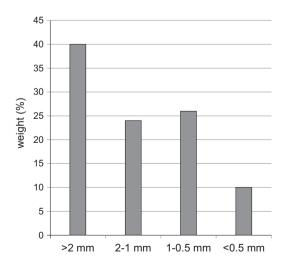


Fig. 1. Block diagram of the process routes including only refining by NaOH precipitation (A) corresponding to Processes I, II and III (Table 2), and process route including double SX procedure corresponding to Process V (Table 2).

**Table 3**Chemical composition (mg/g) of the final products of CoCO<sub>3</sub> obtained at the end of the different operations detailed in Table 2.

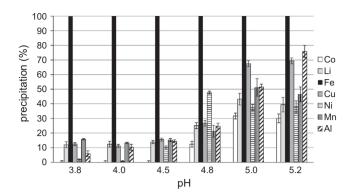
Process	Co	Li	Cu	Ni	Mn	Al	Na
I	180 ± 20	12.1 ± 0.2	$9.4 \pm 0.4$	45 ± 1	35 ± 1	$8.4 \pm 0.1$	270 ± 40
II	$180 \pm 10$	5 ± 1	4 ± 1	$65 \pm 3$	$50 \pm 2$	5 ± 1	$300 \pm 10$
III	$220 \pm 50$	$7.5 \pm 0.7$	8 ± 1	$25 \pm 8$	$39 \pm 8$	8 ± 2	$230 \pm 20$
IV	189 ± 2	10 ± 1	$1.7 \pm 0.5$	31 ± 3	5 ± 1	$0.3 \pm 0.1$	$230 \pm 20$
V	162 ± 3	$0.5 \pm 0.4$	2 ± 1	5 ± 3	6 ± 2	0.2 + 0.1	480 + 60
VI	470 ± 10	$0.4 \pm 0.1$	4 ± 1	13 ± 1	18 ± 8	$0.3 \pm 0.1$	$20 \pm 9$



**Fig. 2.** Particle size distribution as  $\%_{w/w}$  of the grinded material: size fractions <0.5 mm and 0.5–1.0 mm were joined and used for hydrometallurgical recovery of Co

for the preliminary separation of metal impurities. Different degrees of purification can be achieved depending on the nature and number of implemented separation stages. In the present study, the sequence of precipitation (induced by controlled pH increase) and of two different SX stages (with D2EPHA and Cyanex) was implemented (Processes V and VI in Table 2). Further, the effect of reducing the number of purification stages was analyzed. For this purpose, two additional solutions were tested which include only precipitation (Processes I–III), and the sequence of precipitation and SX with D2EPHA (Processes IV–VI) respectively. For each implemented process, CoCO<sub>3</sub> was recovered following purification by precipitation (induced by the addition of Na<sub>2</sub>CO<sub>3</sub>) and filtration. Performances of implemented solutions were compared in terms of purities of the recovered CoCO<sub>3</sub>.

The influence of pH on precipitation of metal impurities induced by the addition of NaOH is described in Fig. 3. Reported data evidence that the overall amount of metals precipitated in the form of hydroxides increases with pH. This result can be explained by observing that an increase in the concentration of OH<sup>-</sup> shifts the equilibrium toward the formation of precipitated solid hydroxide. Further, Fig. 3 shows that different metals are



**Fig. 3.** Metal precipitation (%) after raising the pH of leach liquors at different levels.

precipitated to different extent depending on relative concentration and hydroxide solubility. Particularly, it can be observed that pH increase determined the simultaneous precipitation of both target metal (Co) and metal impurities. Co losses are not significant below pH 4.5. Increasing pH over this latter value induces however the precipitation of a large Co fraction (up to 30% at pH 5). Iron is completely removed at any pH falling within the range 3.8–5.2 due to the very low solubility of iron hydroxides (Fe concentration in solution was always below the analytical low detection limit of the instrument, i.e. <0.1 mg/L). The other metals (Li, Cu, Ni, Mn, Al) presented slight abatement (about 10%) up to pH 4.5. Larger removal can be obtained by increasing pH over this value leading to about 30–50% removal for Li, Ni and Mn, and 70% for Cu and Al.

With the exception of for iron, which invariably undergoes complete precipitation, all metals reach larger precipitation as the pH is increased.

Experimental findings were compared with theoretical speciation. The latter was predicted by the application of a software (Puigdomenech, 2010) allowing for modeling metal equilibrium in solution (reported in Fig. 1A of supplemental material). These simulations confirmed that, with the composition of tested leach liquors, Fe can be completely precipitated as Fe<sub>2</sub>O<sub>3</sub>. For Cu, a good agreement was observed between theoretical and experimental findings: simulation predicted 50% precipitation of Cu (as Cu<sub>3</sub>SO<sub>4</sub>(-OH)<sub>4</sub>) at pH 5 while 68% was determined experimentally. A underestimation was found for Al: 52% experimentally precipitated at pH 5 versus 100% theoretical removal as AlOHSO<sub>4</sub>.

Theoretical speciation predicts that Co, Li, Mn and Ni cannot precipitate in the form of hydroxides with the specific composition of the tested leach liquor. In particular, the software predicts that Co and Ni should start precipitating at pH 6, while Mn and Li should precipitate above pH 8 and pH 12 respectively.

Observed precipitation could be then explained by considering that inside real reactors local gradients of concentration can expose metal to larger concentration of OH<sup>-</sup> which results in the formation of precipitates even with equilibrium pH lower than the predicted one. In addition, co-precipitation-adsorption effects can also occur: precipitating metals (Fe, Cu, Al) can work as promoters and centers of aggregation and adsorption of other metals such as Co, Ni, Mn and Li which would thus be transferred to solid phase.

Two antagonist factors must be balanced in precipitation section: minimizing Co loss and maximizing removal of metal impurities. In accordance with reported data, successive tests at micro-pilot scale were performed with two pH levels (3.8 and 4.8) to evaluate the effect of pH on the final purity of Co carbonate.

Li, Ni, Mn, Al and Cu are only partially removed from leach liquor after precipitation. This made necessary to include an additional step allowing for selective removal of these metals. For this purpose, further purification of the post-precipitation leach liquor was performed by SX with Bis(2-ethylhexyl)hydrogenphosphate

(D2EHPA). This extracting agent was previously demonstrated to ensure separation of manganese from cobalt (Granata et al., 2012).

SX operations including the addition of an extractant operate according to the following mechanism (Granata et al., 2012):

$$M_{Aq}^{2+} + A_{Org}^{-} + 2(HA)_{2Org.} \rightarrow MA_2 \cdot 3HA_{Org.} + H_{Aq}^{+} \eqno(2)$$

where  $A_{\rm Org}^{} + 2({\rm HA})_{\rm 2Org}$  represents the extractant saponified by the following reaction:

$$Na_{Aq}^{+} + 1/2(HA)_{20rg.} \rightarrow NaA_{0rg.} + H_{Aq}^{+} \tag{3} \label{eq:3}$$

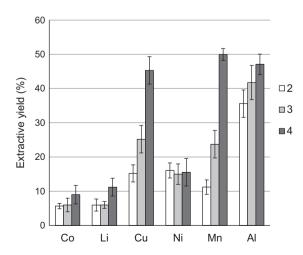
Accordingly, different factors can affect residual concentration of metal in aqueous phase such as the pH of extraction and the amount of available extractant. Previous tests on synthetic solutions (not shown here) denoted that optimum pH for Mn extraction was 4.

Extraction tests were conducted at D2EHPA/Mn molar ratio values 2, 3 and 4 (Fig. 4). The largest D2EHPA/Mn molar ratio improved the removal of any impurity and did not significantly influence Co removal. This effect can be explained by considering the higher affinity of D2EHPA for Mn, and the equilibrium of the reaction between the extractant and the metal in solution (Eq. (2)). Therefore, larger extractant concentrations increase the amount of bound extracted metals because of the displacement of equilibrium.

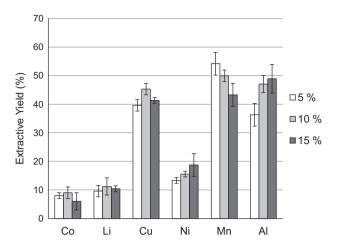
Molar ratio equal to 4 was chosen for further tests to maximize the amount of Mn and other metal impurities transferred to organic phase while preventing significant Co losses.

The influence of three TBP concentrations on extraction was also evaluated (Fig. 5). TBP is a modifier whose addition to the organic phase prevents the formation of third phase during SX tests. The effect of modifier concentration on kinetic and equilibrium of metal extraction cannot be predicted and have to be assessed by dedicated tests.

Negligible variation of Co, Li and Cu removal was found at any considered TBP concentration. Larger removal of Ni and Al was in contrast found as TBP concentration was increased. Further, Mn extraction yield was found to decrease with TBP concentration. Since target metals to be removed by the considered SX are Mn, Cu and Al (as explained below, separation of Co from Ni requires an additional different SX step), the optimum level of TBP chosen for process tests was 10%. With this TBP concentration, intermediate extraction yields were obtained for both Mn and Al.



**Fig. 4.** Extractive yields in solvent extraction: effect of different D2EHPA/Mn molar ratios (2, 3 and 4) with 10% TBP after a single extractive step.



**Fig. 5.** Extractive yields in solvent extraction: effect of different TBP concentrations (5%, 10% and 15%) with D2EHPA/Mn = 4 after a single extractive step.

Sequential extractive steps were performed (Fig. 6) evidencing that a second extractive step increased metal extraction. A third step did not improve purification and increased Co loss.

According to these results, SX was performed at micro-pilot scale with D2EHPA/Mn molar ratio equal to 4, 10% TBP and two extractive steps.

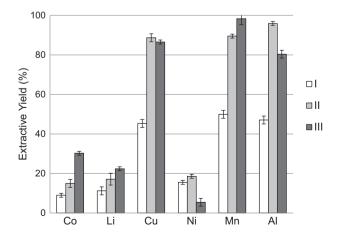
After this treatment, about 90% of Cu, Mn and Al were removed, while less than 20% of Ni removal was achieved. To separate Co from Ni, an additional SX step was performed by using Cyanex 272, which can selectively extract Co while leaving Ni in aqueous phase. Preliminary tests performed with leach liquors recovered from precipitation at pH 3.8 evidenced 99.9% extraction and dissolution in the organic phase of Co, Cu, Mn and Al. Together with these latter elements, about 10% of Li and Ni were also extracted and transferred to the organic phase.

In micro-pilot tests, Processes V and VI included Cyanex extraction performed after two extractive steps of D2EHPA.

#### 3.3. Micro-pilot scale tests

Six different processes were tested including part or the whole sequence of operations discussed in the previous sections: leaching, precipitation (and solvent extraction), Co recovery as carbonate. The sequence of operations performed in any process is described in Table 2.

Metal extraction by leaching is a multistep process governed by the interplay of different chemical and physical mechanisms



**Fig. 6.** Extractive yields in solvent extraction: effect of the number of sequential extractive steps (I: one; II: two; III: three) with 10% TBP and D2EHPA/Mn = 4.

including chemical dissolution reactions, transport of reactants between solid and liquid bulk, modification of the structural properties of the solid particles (particle size distribution and porosity). Reported experimental yields evidenced two main parameters: the concentration of acid, which directly affects the kinetics of chemical reaction (Eq. (1)), and the S/L ratio which determines the relevance of transport phenomena. The latter mechanism can be elucidated by noting that increasing the S/L ratio while maintaining the stirring rate and reactant concentrations unchanged, transport phenomena within the liquid bulk can become rate limiting owing to the increased amount of solid in the suspension.

Data reported in Fig. 7 evidenced that the influence of acid concentration and S/L on the experimental yield at 3 h is qualitatively the same for any metal. Increasing the acid excess from +50% (Process I) to +100% (Process II) determined the increase of metal extraction. In the case of Co, the yield increased from 65% to 89%. Unfortunately the same effect was observed also for the other metals, and thus increased impurity amounts are associated to increased extraction yields of Co.

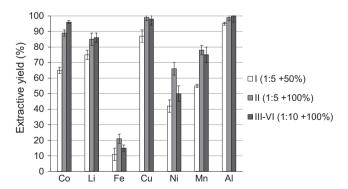
It can be observed that decreasing the S/L ratio (at constant acid excess +100%) from 1:5 to 1:10 determined an improvement of Co extraction for the same leaching time (3 h). In particular, Co extraction varied from 89% (Process II) to 96% (Processes III–VI). No significant variation in the extraction yield of Li, Cu, Mn and Al was induced by the considered modification of the S/L ratio. A reduction in the extraction yield of Fe and Ni was in contrast found as the S/L ratio was decreased. No clear explanation has been found yet for this finding. Based on reported experimental results of leaching tests, a S/L ratio and an acid excess equal to 1:10 and +100% respectively were selected to maximize Co recovery.

Purification by precipitation was performed at two pH values (3.8 and 4.8) by employing solutions resulting from leaching performed with 1:5 and 1:10 *S/L* ratios (Fig. 8).

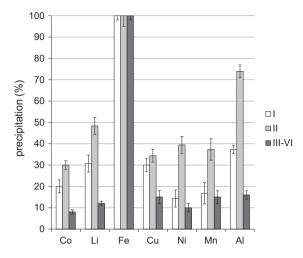
Precipitations performed at the same pH (3.8) with leach liquors obtained by leaching tests performed with different S/L ratios (Process I with S/L 1:5 and Process III with S/L 1:10) led to different removal of metals. In particular, increasing the S/L ratio during leaching determined an increased precipitation of all metals. This caused significant loss of Co (20%) probably due to coprecipitation effect.

As precipitation pH was increased from 3.8 to 4.8 (Process I versus II), significantly larger precipitation yields were observed for all metals: 30% as average removal at pH 4.8 versus 20% average removal at pH 3.8. Further comparison of product purity obtained by Process I and Process II revealed eventual benefits due to increased removal of metal impurity with particular attention to the final purity of CoCO<sub>3</sub>.

Leach liquors treated according to different purification schemes were finally added by Na<sub>2</sub>CO<sub>3</sub> to obtain CoCO<sub>3</sub>. The



**Fig. 7.** Extractive yields (%) after 3 h leaching using different operating conditions as detailed in Table 2: I process (1:5 S/L, +50% acid excess); II process (1:5 S/L, +100% acid excess); III–VI processes (1:10 S/L, +100% acid excess).



**Fig. 8.** Precipitation yields for the different metals using leach liquors and precipitation conditions detailed in Table 2: I process (1:5 S/L, +50% acid excess, pH 3.8); II process (1:5 S/L, +100% acid excess, pH 4.8); III–VI processes (1:10 S/L, +100% acid excess, pH 3.8).

chemical composition of these products is reported in Table 3. As a general finding, Fe is not detectable in any of the produced carbonate: considering the low detection limit of AAS (<0.1 mg/L) and the specific *S/L* ratio used for characterization (Section 2.4) this means that Fe concentration in solid is lower than 0.002 mg/g.

The increase of precipitation pH from 3.8 to 4.8 (Process I and Process II) did not alter the final Co purity. Accordingly, performing precipitation at pH 3.8 seems to be the best option to simultaneously reduce Co loss and reagent consumption.

The addition of SX by D2EHPA (Process IV) allowed reducing by one order of magnitude metal impurities such as Cu, Mn and Al, while it could not enforce satisfactory Ni removal.

The addition of a further SX step with Cyanex (Process V) allowed reducing the concentration of Ni. However, SX stages determined an increase of Na content due to the use of saponified extracting agents, which released Na to aqueous phase (Eqs. (2) and (3)). Final refining stage (Process VI) including a pH controlled washing allowed for the removal of Na and thus significantly increased the final Co purity. In particular, by assuming that Co is present as CoCO<sub>3</sub>, a final purity of 95% is found.

CoCO<sub>3</sub> samples obtained according to Process VI (after purification by D2EHPA, Cyanex, and final washing at pH 6) were characterized by XRD diffraction to confirm the nature of the final product (Fig. 2A in supplemental material). Produced sample of CoCO<sub>3</sub> starting from purified leach liquor presents XRD diagnostic peaks of both CoCO<sub>3</sub> (sphaerocobaltite) and Na<sub>2</sub>SO<sub>4</sub> (thenardite) Cong and Yu, 2009; Xu and Zeng, 2003. XRD spectrum of CoCO<sub>3</sub> obtained starting from a solution of CoSO<sub>4</sub> confirmed such assignment presenting the same peaks found in the product obtained from purified leach liquor. Main difference between "real" and "synthetic" products is the absence of the peaks at 2theta equal to 19.61° and 34.51° in the synthetic product. These peaks are probably due to metal impurities (such as Li, Al and Cu) still present in the purified leach liquor and then also present in the final carbonate solid (Tables 1 and 3).

# 4. Conclusions

A hydrometallurgical process was implemented for the first time to recover cobalt from electrodic powder obtained by pilot scale pretreatment of portable LIBs. Preliminary characterization evidenced the heterogeneity of the recovered electrodic powder, containing not only Co and Li, but also significant amount of Ni, Mn, Cu, Al and Fe. This composition is determined by mechanical operations (Fe, Al and Cu) and by the heterogeneity of cathodic materials (Ni and Mn).

Both these latter factors have been neglected by most of the studies about LIB treatment by using electrodic powder manually extracted from few selected samples of batteries. Nevertheless, large scale applications require using mechanical pretreatment and necessitate treating all present and future types of Li batteries with variable composition.

Accordingly, the development of a flexible purification section becomes fundamental to ensure successful implementation of the process at industrial scale.

In this work, operating conditions were optimized for leach liquor purification by precipitation and SX.

Precipitation by pH increase at 3.8 allowed for the effective removal of iron, while only partial removal of other metals was obtained. Increasing pH determined the abatement of metal impurities, but simultaneously the loss of Co.

SX can be a valid alternative for selective metal separation. Two different SX stages were necessary because a single extractant allowing simultaneously separating Co from Ni and Mn is not currently available. Therefore, a first SX stage was adopted to separate Mn from Co, and then a second stage to separate Co from Ni.

Commercial grade CoCO<sub>3</sub> was obtained as main target of the hydrometallurgical process here proposed after the two considered SX stages and final refining for Na removal.

Reported results demonstrate that SX operation optimized in this work is fundamental to ensure process flexibility and, particularly, to produce high purity Co even in presence of unwanted metals such as Mn and Ni.

Further tests are currently carried on to optimize the recovery of other metals such as Li, Mn and Ni. More specifically, Mn can be recovered after stripping of the organic phases generated through SX with D2EHPA (see block diagrams in Fig. 1B) by using a chemical route for dioxide production (Pagnanelli et al., 2007). Ni and Li can be recovered from the aqueous phase generated by SX with Cyanex. A process route including the selective precipitation of Ni(OH)<sub>2</sub>, followed by Na<sub>2</sub>SO<sub>4</sub> crystallization and Li<sub>2</sub>CO<sub>3</sub> precipitation is currently being validated.

The recovery of these additional metals is of fundamental importance because of the tendency of LIB manufacturers to replace Co with less valuable metals, and of the emerging field of application of Li batteries for electric vehicles.

The inclusion of SX section giving high purity products (47% of Co content) can be advantageous from the economy standpoint if a minimum amount of treated batteries is reached. In a previous work (Granata et al., 2012), we addressed the economic advantage resulting from increasing the final purity of the Co products by introducing the SX with Cyanex after precipitation. Main conclusion emerging from previous process simulations was that the inclusion of SX section, giving high purity products, is economically advantageous if at least 250 ton/y of batteries are treated in the plant. For lower potentiality, the capital investment necessary for including SX section and the associated operating costs are not balanced by the increased revenues due to sale of high purity CoCO<sub>3</sub>.

Further economic and also environmental analyses are now in course using the experimental results obtained in the present paper.

In conclusion, hydrometallurgical processes can be easily adapted to changes in LIB technology (for instance by the inclusion of SX operations) and potentially allow for the recycling of all elements and components in LIB. This is a fundamental advantage with respect to pyrometallurgical processes enabling process feasibility for future applications in large scale (Wang et al., 2014).

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2015.11.003.

#### References

- Bossche, P.V.D., 2006. January the Current Legislative Development in the EU Waste Policy: Challenge or Opportunities for Metal Industry. Cobalt Development Institute, Guildford, UK.
- Chen, X., Zhou, T., 2014. Hydrometallurgical process for the recovery of metal values from spent lithium-ion batteries in citric acid media. Waste Manage. Res. 32, 1083–1093.
- Chen, X., Chen, Y., Zhou, T., Liu, D., Hu, H., Fan, S., 2015. Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries. Waste Manage. 38, 349–356.
- Cong, H.P., Yu, S.H., 2009. Shape control of cobalt carbonate particles by hydrothermal process in a mixed solvent: an efficient precursor to nanoporous cobalt oxide architectures and their sensing properties. Cryst. Growth Des. 9 (1), 210–217.
- Ferreira, A.D., Prados, L.M.Z., Majuste, D., Mansur, M.B., 2009. Hydrometallurgical separation of aluminium, cobalt, copper and lithium from spent Li-ion batteries. J. Power Sources 187, 238–246.
- Georgi-Maschler, T., Friedrich, B., Weyhe, R., Heegn, H., Rutz, M., 2012. Development of a recycling process for Li-ion batteries. J. Power Sources 207, 173–182.
- Granata, G., Pagnanelli, F., Moscardini, E., Takacova, Z., Havlik, T., Toro, L., 2012. 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. J. Power Sources 212, 205–211.
- Granata, G., Moscardini, E., Pagnanelli, F., Trabucco, F., Toro, L., 2012. Product recovery from lithium ion battery wastes coming from an industrial pretreatment plant: lab scale tests and process simulations. J. Power Sources 206, 393–401.
- Gratz, E., Sa, Q., Apelian, D., Wang, Y., 2014. A closed loop process for recycling spent lithium ion batteries. J. Power Sources 262, 255–262.

- Jha, M.K., Kumari, A., Jha, A.K., Kumar, V., Hait, J., Pandey, B.D., 2013. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. Waste Manage. 33, 1890–1897.
- Li, L., Ge, J., Chen, R., Wu, F., Chen, S., Zhang, X., 2010. Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries. Waste Manage. 30, 2615–2621.
- batteries. Waste Manage. 30, 2615–2621. Li, L., Lu, J., Ren, Y., Zhang, X.X., Chen, R., Wu, F., Amine, K., 2012. Ascorbic-acid-assisted recovery of cobalt and lithium from spent Li-ion batteries. J. Power Sources 218, 21–27.
- Mantuano, D.P., Dorella, G., Alves Elias, R.C., Mansur, M.B., 2006. Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid-liquid extraction with Cyanex 272. J. Power Sources 159, 1510-1518.
- Pagnanelli, F., Sambenedetto, C., Furlani, G., Vegliò, F., Toro, L., 2007. Preparation and characterisation of chemical manganese dioxide: effect of the operating conditions. J. Power Sources 166, 567–577.
- Pagnanelli, F., Moscardini, E., Granata, G., Cerbelli, G., Agosta, L., Fieramosca, A., Toro, L., 2014. Acid reducing leaching of cathodic powder from spent lithium ion batteries: glucose oxidative pathways and particle area evolution. J. Ind. Eng. 20, 3201–3207.
- Puigdomenech, I., 2010. MEDUSA: Make Equilibrium Diagrams Using Sophisticated Algorithms. <a href="https://sites.google.com/site/chemdiagr/">https://sites.google.com/site/chemdiagr/</a>.
- Shin, S.M., Kim, N.H., Sohn, J.S., Yang, D.H., Kim, Y.H., 2005. Development of a metal recovery process from Li-ion battery wastes. Hydrometallurgy 79, 172–181.
- Sun, L., Qiu, K., 2012. Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries. Waste Manage. 32, 1575–1582
- Swain, B., Jeong, J., Lee, J.C., Lee, G.H., Sohn, J.S., 2007. Hydrometallurgical process for recovery of cobalt from waste cathodic active material generated during manufacturing of lithium ion batteries. J. Power Sources 167, 536–544.
- Vassura, I., Morselli, L., Bernardi, E., Passarini, F., 2009. Chemical characterisation of spent rechargeable batteries. Waste Manage. 29, 2332–2335.
- Wang, X., Gaustad, G., Babbitt, C.W., Bailey, C., Ganter, M.J., Landi, B.J., 2014. Economic and environmental characterization of an evolving Li-ion battery waste stream. J. Environ. Manage. 135, 126–134.
- Wanger, T.C., 2011. The lithium future-resources, recycling, and the environment. Conserv. Lett. 4, 202–206.
- Xu, R., Zeng, H.C., 2003. Dimensional control of cobalt-hydroxide-carbonate nanorods and their thermal conversion to one-dimensional arrays of Co<sub>3</sub>O<sub>4</sub> nanoparticles. J. Phys. Chem. B 107, 12643–12649.
- Zeng, X., Li, J., Singh, N., 2014. Recycling of spent lithium-ion battery: a critical review. Crit. Rev. Environ. Sci. Technol. 44, 1129–1165.
- Zhang, T., He, Y., Wang, F., Li, H., Duan, C., Wu, C., 2014. Surface analysis of cobaltenriched crushed products of spent lithium-ion batteries by X-ray photoelectron spectroscopy. Sep. Purific. Technol. 138, 21–27.
- Zhang, T., He, Y., Wang, F., Ge, L., Zhu, X., Li, H., 2014. Chemical and process mineralogical characterizations of spent lithium-ion batteries: an approach by multi-analytical techniques. Waste Manage. 34, 1051–1058.