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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 D2EHPA (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 LiCoO₂ pasted onto aluminum foils and mixed oxides such as LiNi_x-Mn_yCo_zO₂ (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

(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_3 .

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_3 . 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).

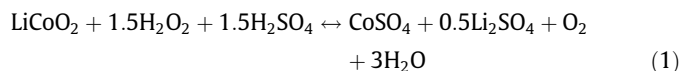
The two fractions lower than 1 mm were mixed and used for characterization and leaching tests.

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 $\geq 65\%$ (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[®] 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):



For all the experiments, sulfuric acid $\geq 96\text{--}98\%$ (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.

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