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# Leaching of electrodic powders from lithium ion batteries: Optimization of operating conditions and effect of physical pretreatment for waste fraction retrieval

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ABSTRACT

Experimental results of leaching tests using waste fractions obtained by mechanical pretreatment of lithium ion batteries (LIB) were reported. Two physical pretreatments were performed at pilot scale in order to recover electrodic powders: the first including crushing, milling, and sieving and the second granulation, and sieving. Recovery yield of electrodic powder was significantly influenced by the type of pretreatment. About 50% of initial LIB wastes was recovered by the first treatment (as electrodic powder with size <0.5 mm, Sample 1), while only 37% of powder with size <1 mm (Sample 2) can be recovered by the second treatment. Chemical digestion put in evidence the heterogeneity of recovered powders denoting different amounts of Co, Mn, and Ni. Leaching tests of both powders were performed in order to determine optimized conditions for metal extraction. Solid/liquid ratios and sulfuric acid concentrations were changed according to factorial designs at constant temperature (80 °C). Optimized conditions for quantitative extraction (>99%) of Co and Li from Sample 1 are 1/10 g/mL as solid/liquid ratio and +50% stoichiometric excess of acid (1.1 M). Using the same solid/liquid ratio, +100% acid excess (1.2 M) is necessary to extract 96% of Co and 86% of Li from Sample 2. Best conditions for leaching of Sample 2 using glucose are +200% acid excess (1.7 M) and 0.05 M glucose concentration. Optimized conditions found in this work are among the most effective reported in the literature in term of Co extraction and reagent consumption.



## 1. Introduction

Lithium Ion Batteries (LIB) are the most used rechargeable energy sources in portable devices (Larcher and Tarascon, 2015). The great diffusion of these devices is accompanied by the generation of big amounts of end of life wastes, potentially harmful for the environment due to the presence of metals such as Co, Ni, Mn, Al and Cu (Xu et al., 2008). Recent regulations imposed the collection and recycling of LIB with minimum target of mass recovery (50%) to be accomplished by the development of innovative processes (Bossche, 2006). By this way, release of polluting metals in the environment is avoided along with the loss of material resources, which can be reused in other productive processes. In fact, exploitation of end of life LIB is extremely interesting due to the composition of the cathodic materials, mainly $LiCoO_2$ pasted onto aluminum foils, but also mixed oxides such as $LiNi_xMn_yCo_zO_2$ (Zeng et al., 2014; Chen et al., 2015).

Hydrometallurgical processes represent a competitive technological alternative to recycle LIB (Wang et al., 2014). These processes are performed to recover valuable metal from the electrodic powder that is separated by physical pretreatment of batteries (Zeng et al., 2014) including crushing, sieving and eddy current separation. This approach offers the possibility to recover all the materials and metals in the batteries with limited energy consumption in comparison with alternative battery recycling processes, such as pyrometallurgical processes (Wang et al., 2014). On the other hand, hydrometallurgical processes can be very complex in both physical pretreatment and chemical section, due to the complexity of internal structure of input materials and heterogeneity of electrodic powder composition.

Hydrometallurgical processes have been mainly investigated at laboratory scale. Most often, few samples of one type of LIB are manually dismantled, the cathodic powder recovered and fed to the leaching section (Chen et al., 2011; Jha et al., 2013; Shuva and Kurni, 2013). In few cases, automated processes have been reported as pretreatment step of hydrometallurgical process (Granata et al., 2012a; Gratz et al., 2014; Pagnanelli et al., 2016).

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Some recent papers started investigating the effect of different mechanical pretreatments on waste fraction composition (Wang et al., 2016; Zhang et al., 2013; Zhang et al., 2014a).

Acid reducing conditions are necessary to reduce Co(III) to Co(II) and bring it in solution during leaching. This is why sulfuric acid alone is not able to completely dissolve $LiCoO_2$ and hydrogen peroxide is generally added (Dorella and Mansur, 2007; Meshram et al., 2015) to enable the following reaction:

$$2LiCoO_2 + 3H_2SO_4 + H_2O_2 \leftrightarrow 2CoSO_4 + Li_2SO_4 + 4H_2O + O_2 \qquad (1)$$

The use of other mineral acids (such as nitric acid and hydrogen chloride) was also investigated (Shuva and Kurni, 2013), and organics, such as ascorbic acid (Li et al., 2012), citric acid (Li et al., 2010a), and glucose (Pagnanelli et al., 2014) were proposed as green alternatives.

A step forward in the application of hydrometallurgical processes imposes recognizing that manual extraction of cathodic powders from LIB is not sustainable on large industrial scale. Therefore, the interaction between physical pretreatment and chemical section cannot be neglected anymore. These batteries present an internal structure characterized by layers of aluminum and copper covered by $LiCoO_2$ and graphite, respectively. Mechanical operations must be performed in a way that electrodic powder is separated from Al and Cu layers, and other materials composing the external case (Huang et al., 2011; Granata et al., 2012a; Granata et al., 2012b). Nevertheless, as a result of any mechanical treatment for opening batteries and retrieving electrodic powder, metal impurities will be included in the electrodic powder as fragments of the internal layers (Al and Cu) and of external case (Fe) (Zhang et al., 2014b; Gratz et al., 2014; Pagnanelli et al., 2016). Process development cannot neglect the presence of such metal impurities for the optimization of leaching, but also purification and recovery of metal products.

Based on this analysis, it emerges the central importance of optimizing leaching section working with electrodic materials recovered from automatic physical pretreatment.

In the present work, electrodic powders were recovered from LIB by two different mechanical pretreatments in pilot scale. Recovered powders were used for leaching tests in order to evaluate best conditions for metal extraction and to determine the composition of real leach liquors. Leaching was performed under reducing acid conditions obtained by using hydrogen peroxide or glucose as reducing agent and sulfuric acid.

Main novelties of the work include:

- The application of real waste fractions obtained by two different pilot scale physical pretreatments.
- The assessment of glucose efficacy in leaching even with such heterogeneous real waste fractions.
- The assessment of the efficacy of leaching conditions used in this work (both using conventional and innovative reducing agents) compared with literature data.

The application of waste fractions emerging from two different pilot scale mechanical pretreatments is a step forward in process development taking in consideration that majority of works concerning LIB treatment is affected by the original sin of using manually dismantled cathodic powders. Using real waste fractions allows optimizing leaching conditions also taking in consideration reagent consumption due to impurity dissolution. The efficacy of standard leaching system ($H_2SO_4$ plus $H_2O_2$) was evaluated taking in consideration waste fractions with different purities, thus denoting the effect of powder characteristics on leaching results. In addition, representative composition of leach liquors is obtained, which can guide further steps in process optimization. In fact, representativeness of initial powders treated in leaching tests could give further insight in determining possible downstream strategies for leach liquor purification and product recovery.

As for the use of glucose in leaching of real waste fractions, this is a fundamental preliminary test for evaluating if low cost reducing agents can be used effectively even with high heterogeneous fractions without losing their properties. In fact, glucose can be taken as representative of carbohydrate-rich wastes (such as lactose from whey) which can be used as alternative to expensive hydrogen peroxide. To our knowledge this is the first time that glucose is used for heterogeneous matrix such those treated in this work. The results are not obvious in principle taking in consideration the complex network of glucose oxidation reactions occurring simultaneously even when working with pure $LiCoO_2$ material (Pagnanelli et al., 2014).

As for the comparison between leaching data obtained in this work and literature results, a quantitative analysis was performed evaluating the extractive efficiency as a function of the acid and reducing type and dosage, per mol of Co in the electrodic powder used in each specific work. Generally papers reporting tables with operating conditions and % extractive yields can be found in the literature (Meshram et al., 2015), giving only a qualitative idea of the efficacy of the different conditions. In this work, for the first time we evaluated the efficacy of acid and reducing agents accounting for the different operating conditions used in each work (solid to liquid ratio, powder composition, chemicals concentration). In this way, we can quantitatively compare the different conditions used that proving the real efficacy of a leaching conditions with respect to others.

## 2. Waste battery management and strategies

The extended application of portable electronic devices has progressively increased over the past decade the demand for rechargeable batteries. Producers and importers reported having placed on the market in the EU area, plus Switzerland, close to 71,000 tons of rechargeable batteries in 2013, out of which 40,000 tons were LIB (Perchards SAGIS EPR Report, 2014). These batteries contain harmful elements and compounds including, for example, heavy metals and flammable organic compounds. On the other hand, LIB include valuable materials that can be reintroduced to the production/manufacturing chain. The potential release of harmful elements to the environment and the interest towards the recovery and reuse of valuable material fractions have motivated the application of regulations imposing the collection and recycle of batteries. The EU Directive 2006/66/EC fixed that mandatory collection rates equal to 25% and 45% should be achieved by 2012 and 2016, respectively, and that 65%, 75% and 50% (by weight) recycling efficiencies should be achieved by processing of lead, nickel-cadmium and others batteries (including lithium ion ones), respectively.

Two main approaches can be implemented to treat end of life LIB: pyrometallurgical and hydrometallurgical processes. Pyrometallurgical processes include the treatment at high temperature of metal-bearing fractions for the recovery of heavy metals such as Co and Ni. These processes are highly energy demanding, characterized by toxic gas emission, and do not allow for the integral recovery of battery materials, plastic, paper, and metals such as Li, Al, Fe and Mn (Georgi-Maschler et al., 2012).

Hydrometallurgical processes can be performed to recover valuable metals from the electrodic powder that is produced by physical pretreatment of LIB. Particularly, physical pretreatment, including crushing, sieving and eddy current separation, allows separating the following battery fractions: plastic, paper, ferrous and non-ferrous metals, electrodic powder (Zeng et al., 2014).