



# Hydrometallurgical separation of aluminium, cobalt, copper and lithium from spent Li-ion batteries

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## ABSTRACT

A hydrometallurgical route based on leaching–crystallization steps for the separation of metals Al, Co, Cu and Li from spent Li-ion batteries was evaluated in this paper. Once dismantled for the removal of both plastic and steel cases, the anode (containing mainly Cu) of such batteries was manually separated from the cathode (which contains Al, Co and Li) for the recovery of Cu. The metal content of both anode and cathode was assessed by X-ray diffraction (XRD), X-ray fluorescence (XRF) and atomic absorption analytical methods. The cathode was firstly leached with NaOH for the selective removal of Al, followed by leaching with  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$  for the dissolution of the remaining Co and Li. The operating variables concentration of NaOH and concentration of  $\text{H}_2\text{O}_2$  were found significant for the metal dissolution conditions investigated at basic and acid leaching operations, respectively. On the other hand, the variables temperature and concentration of  $\text{H}_2\text{SO}_4$  showed minor effects at acid leaching step. Reaction schemes were proposed to describe basic and acid leaching operations. The recovery of Co from the acid liquor was carried out by crystallization. This hydrometallurgical route was found to be simple and adequate to separate metals for recycling purposes.

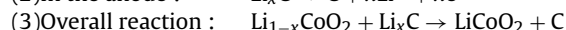
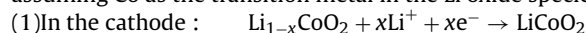
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## 1. Introduction

The Li-ion batteries are comparatively smaller, lighter, have no memory effect and provide much more energy per volume unit than the nickel-cadmium (NiCd) or the nickel-metal hydride (NiMH) batteries [1]. Because of such advantages, Li-ion batteries are mainly used as power source for mobile phones, laptops and electronic devices. In fact, Li-ion batteries lead the global mobile phone market today. And recently, due to the increasing oil prices and strict global environmental regulations, automakers including Nissan, Toyota, Honda, General Motors and Volkswagen announced plans to utilize Li-ion batteries in upcoming electric and hybrid vehicles. As the use of these batteries tends to increase significantly for the next years, the development of new recycling methods as well as the optimization of existing processes to treat spent Li-ion batteries are relevant issues to be addressed in order to obtain sustainability.

In a Li-ion battery, anode and cathode are made of materials into which and from which Li ions can migrate through an electrolyte solution. The anode typically consists of a Cu foil covered by a fine layer of powdered carbon [2], while the cathode is made

of an Al foil covered by a fine layer of a powdered metal oxide like  $\text{LiCoO}_2$  or even  $\text{LiNiO}_2$ ,  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  or  $\text{LiMn}_2\text{O}_4$  [3]. The powdered materials are glued to the respective foils by polymeric binder PVDF (polyvinylidene fluoride) [4], and anode and cathode are rolled up following a cylindrical or a prismatic shape. The electrolyte consists of a Li salt normally  $\text{LiPF}_6$  dissolved in an organic solvent, but other salts like  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$  or  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  can also be used [3]. The following reactions occur in a Li-ion battery discharge process assuming Co as the transition metal in the Li oxide species:



Same reactions but at opposite directions occur during the charge process.

Typical metal composition of Li-ion batteries based on  $\text{LiCoO}_2$  species in the cathode is shown in Table 1, including or not the weight of the steel protective case. These batteries contain mainly Al, Cu, Co and Li. The content of Mn and Ni is low, however such quantities will depend on the transition metal of the Li oxide present in the cathode. Fe is found in the steel case only, while the content of Cd and Zn are typically very low.

Several methods have been proposed to treat spent Li-ion batteries in order to recover their metal content. In industrial scale there are currently two hydrometallurgical-based routes in operation (named Toxco and Sony processes), as well as the INMETCO

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**Table 1**  
Typical metal composition of Li-ion batteries based on LiCoO<sub>2</sub> in the cathode (% wt).

Metal	Excluding steel case [7]	Including steel case [10]
Al	6.5–10.0	4.6–24.0
Cd	0.01–0.03	–
Co	30.8–42.9	12–20
Cu	13	5–10
Fe	0.03–0.10	4.7–25.0
Li	2.45–8.88	1.5–5.5
Mn	<0.01	–
Ni	0.02	–
Zn	≤ 0.01	–

pyrometallurgical-based process which was adapted to treat such type of residue [5,6]. On the other hand, much work at bench scale can be found in the literature using hydrometallurgical methods for metals recovery and the main results are summarized in Table 2.

According to Table 2, Co and Li are easily leached from spent Li-ion batteries using quite dilute acid solutions but reducing agents like hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) are required, otherwise more concentrated acid solutions are necessary to obtain comparative dissolutions. It was verified also that metal separation could be simplified if anode and cathode are leached separately; as Cu exists in the anode only, it can be separated in the dismantling step [3,7]. Acid leaching of cathode involves Al, Co and Li dissolutions, while leaching of cathode with NaOH will dissolve Al selectively. Precip-

itation, solvent extraction (SX) and electrolysis were found as the main separation methods proposed to treat such leach liquors. Precipitation with NH<sub>4</sub>OH, citric acid and ammonium oxalate were evaluated, while SX using cationic commercial extractants such as D2EHPA, PC-88A, Cyanex 272 and Acorga M5640 presented very promising results.

In the present study, the separation of Al, Co and Li from the cathode of spent Li-ion batteries is highlighted using hydrometallurgical operations at bench scale; Cu remains in the anode. The main operation variables affecting the selective leaching of Al with NaOH, and subsequent leaching of Co and Li with H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> were investigated. Further, crystallization was proposed as alternative method to treat the leach liquor aiming to obtain cobalt sulfate (CoSO<sub>4</sub>) as a sub-product of the hydrometallurgical route.

## 2. Experimental

### 2.1. Materials and reagents

Spent Li-ion batteries used in mobile phones of different manufacturers and sizes were collected for this study. The leaching solutions consisted of aqua regia (3:1 HCl:HNO<sub>3</sub> ratio), NaOH and H<sub>2</sub>SO<sub>4</sub> solutions at specified concentrations. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was used as reducing agent in the H<sub>2</sub>SO<sub>4</sub> solutions. All solutions were prepared in distilled water and all reagents were of analytical grade.

**Table 2**  
Summary of operational conditions for the metal recovery from Li-ion batteries.

Reference	Leaching step				Liquor treatment step		
	Leaching agents	T (°C)	S/L ratio (g mL <sup>-1</sup> )	Main leaching results	Methods	Reagents	Main liquor treatment results
[11]	H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub>	75	1:20	Co (95%) and Li (100%) at the presence of H <sub>2</sub> O <sub>2</sub> (15% (v/v)). Granulometry effect was found significant for Co only	–	–	–
[18]	H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub>	75	1:10	Co (93%) and Li (94%) with 2 M H <sub>2</sub> SO <sub>4</sub> and H <sub>2</sub> O <sub>2</sub> (5%)	–	–	–
[7]	H <sub>2</sub> SO <sub>4</sub>	80	1:30	Low recovery of Co (30%). Acid concentration and temperature were found significant	SX	Cyanex 272	Co/Li separation at pH 5. Co/Al and Co/Cu separations were found difficult
[8]	H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub>	65	1:30	Co (75%) and Li (100%) at the presence of H <sub>2</sub> O <sub>2</sub> (1% (v/v))	Precipitation and SX	NH <sub>4</sub> OH and Cyanex 272	Al (80%), Co (8%) and Li (13%) were precipitated at pH 5. A stripping solution Co (63 g L <sup>-1</sup> ) and Li (0.4 g L <sup>-1</sup> ) was obtained
[12,19]	HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>	75	1:100	Co (95%) and Li (95%) with H <sub>2</sub> O <sub>2</sub> (1,7% (v/v))	Precipitation	Citric acid	Pure LiCoO <sub>2</sub> was obtained
[4]	HCl	80	–	<i>n</i> -methylpyrrolidone solubilized PVDF aiming to separate powdered materials from Al and Cu foils	–	–	–
[1]	HCl, NH <sub>2</sub> OH.HCl and H <sub>2</sub> SO <sub>3</sub>	80	1:100	Co (> 90%) and Li (> 90%) with concentrated NH <sub>2</sub> OH.HCl and HCl. H <sub>2</sub> SO <sub>3</sub> showed low metal recoveries	SX	D2EHPA and PC-88A	PC-88A was found more selective: Co (> 99.9%) and Li (12.6%) extracted with 0.9 M PC-88A
[9]	NaOH and H <sub>2</sub> SO <sub>4</sub>	25 and 70	1:10 and 1:5	NaOH leached Al (98%) selectively. Co (> 90%), Li (> 90%) and Cu (< 10%) were leached with H <sub>2</sub> SO <sub>4</sub>	Precipitation and SX	ammonium oxalate, Acorga M5640, Cyanex 272	Co (90%) precipitated with 0.5% impurities. Cu (97%) and Co (97%) extracted with Acorga and Cyanex 272, respectively
[13]	–	–	–	–	SX and electrolysis	Cyanex 272	Full extraction of Co (100%). Electrolysis solution containing Co (< 1 ppm) and Ni (< 100 ppm) was obtained

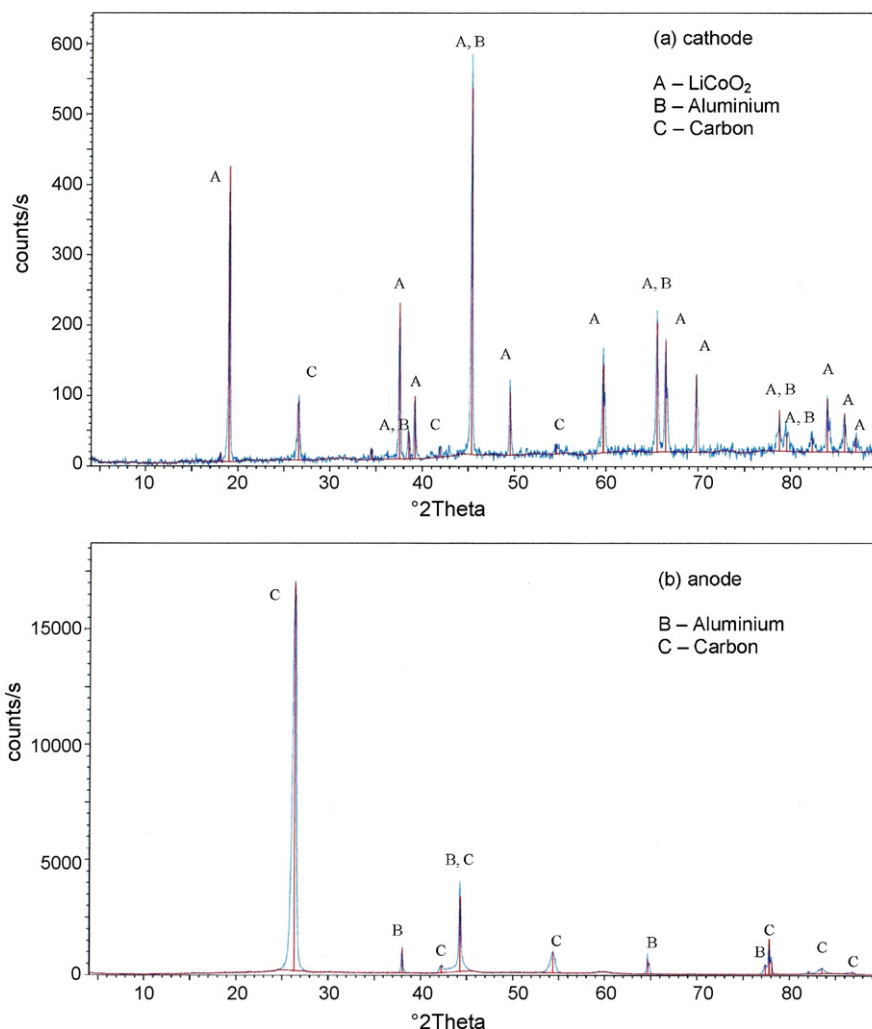


Fig. 1. XRD patterns of the powdered material that covers the metallic foils of Li-ion batteries: (a) cathode, and (b) anode.

## 2.2. Dismantling, anode/cathode separation and metal characterization

The Li-ion batteries were dismantled using a manual procedure described elsewhere [7,8] to remove both plastic and steel cases that cover the batteries. Once dismantled, anode and cathode were manually uncurled and separated, then dried for 24 h at 60 °C. Anode and cathode foils were cut into very small parts using a scissors and homogeneous samples (weighting 5 g each and stored in individual plastic bags) were collected using a Quantachome sieving rifler, model SRR-5 with eight collecting plates.

In order to characterize the metal content of the Li-ion batteries, dried samples of powdered materials that cover anode and cathode foils were submitted to X-ray fluorescence (XRF spectrometer, Philips model PW 2400) and X-ray diffraction (XRD diffractometer,

Philips model PW 1710) for qualitative analysis. The quantitative metal content for Co, Li, Al, Cu, Pb, Hg and Cd was assessed by atomic absorption spectrometry (AA spectrometer, GBC 932 plus model) after dissolving samples (anode and cathode, including metallic foils) in the following solutions for 6 h at 70 °C: aqua regia, H<sub>2</sub>SO<sub>4</sub> 40% (v/v), and H<sub>2</sub>SO<sub>4</sub> 40% (v/v) + H<sub>2</sub>O<sub>2</sub> 15% (v/v).

## 2.3. Metal leaching of the cathode of Li-ion batteries with NaOH and H<sub>2</sub>SO<sub>4</sub>

The leaching of cathodes from Li-ion batteries was investigated in two steps: firstly with NaOH aiming to leach Al in a selective way, then with H<sub>2</sub>SO<sub>4</sub> in order to leach Co and Li. All tests were carried out using a glass reactor that was immersed in a controlled temperature bath ( $\pm 1$  °C sensitivity). The reactor was covered to reduce the loss of water by evaporation and the solutions were stirred mechanically at 300 rpm using a glass impeller marine type. After leaching, the pulp was filtered and a sample of the aqueous phase was withdrawn for metal determination by AA spectrophotometry.

In the leaching tests with NaOH, the following operational variables and levels were investigated: temperature (30–70 °C) and concentration of NaOH (1% to 15% (w/w), or 0.25–3.75 mol L<sup>-1</sup>). Leaching time was defined in exploratory tests (up to 300 min) carried out at fixed temperature (50 °C) and concentration of NaOH (10% (w/w)). The solid/liquid ratio was kept constant at 1:10 g mL<sup>-1</sup>

Table 3  
Metal composition of anode and cathode of Li-ion batteries.

Material	Composition (% (w/w))						
	Co	Al	Cu	Li	Hg	Pb	Cd
Cathode <sup>a</sup>	43.3	10.2	0.7	5.0	1.3	<0.005	0.010
Anode <sup>b</sup>	0.047	0.054	40.7	0.5	<0.15	<0.005	<0.001

<sup>a</sup> Dissolution with H<sub>2</sub>SO<sub>4</sub> 40% + H<sub>2</sub>O<sub>2</sub> 10% solution.

<sup>b</sup> Dissolution with aqua regia.

[9] and tests were done in duplicate. At the end of each test, a sample of the aqueous phase was withdrawn for analysis. The solid phase from all tests was collected, leached twice with NaOH (10%, w/w NaOH, solid/liquid ratio of 1:30 g mL<sup>-1</sup>) to remove remanent Al, then it was thoroughly washed with distilled water and dried; homogeneous samples weighting 5.0 g was obtained using a Quantachome sieving rifler. One sample of this solid phase was dissolved in aqua regia for metal determination of Al, Co and Li by AA.

In the leaching tests with H<sub>2</sub>SO<sub>4</sub>, the following operational variables and levels were studied: temperature (40–80 °C), concentration of H<sub>2</sub>O<sub>2</sub> (0–2% (v/v), or 0–0.64 mol L<sup>-1</sup>) and concentration of H<sub>2</sub>SO<sub>4</sub> (4–8% (v/v), or 0.75–1.50 mol L<sup>-1</sup>). All tests were carried out in duplicate at constant time of 60 min and solid/liquid ratio of 1:30 g mL<sup>-1</sup> [8]. At the end of each test, a sample of the aqueous phase was withdrawn for analysis and the remaining solution was collected for the crystallization study.

#### 2.4. Crystallization tests

In the crystallization tests, four beckers containing 100 mL of the liquor produced in the acid leaching step was placed in an oven at 60°C aiming to evaporate 80%, 85%, 90% and 95% of the total volume of water, respectively. At the end of each test, the remaining solution was filtered. The pink solid phase thus evidencing the formation of CoSO<sub>4</sub> was washed with acetone, filtered, and 1.0 g was solubilized again in aqua regia and submitted for metal determination by AA. A sample of the pink crystal was analyzed by XRD as well.

### 3. Results

#### 3.1. Characterization of Li-ion batteries

The main elements identified in the XRF analysis of the cathodic powder material were Co and O (high intensity peaks) thus evidencing the predominance of LiCoO<sub>2</sub> in the cathode, followed by P and F (intermediate intensity peaks) which constitutes the electrolyte LiPF<sub>6</sub>, and traces of Al, Sn, Fe, Cl, Na and Ni. Li was not found by XRF, but the crystalline phase LiCoO<sub>2</sub> was clearly identified by the XRD analysis as shown in the Fig. 1a thus corroborating previous studies [1,3,5,7–14]. On the regard of the XRF analysis of the anodic material, Cu was the main element identified (high intensity peak), followed by P, Al, O and Co (intermediate intensity peaks, the last three possibly due to some contamination during the dismantling step), and traces of Fe, Mg and Na. Carbon was the main phase identified by XRD analysis of the anode powdered material (Fig. 1b). The identification of peaks of carbon in the cathode, and peaks of Al in the anode as shown by Fig. 1a and b, respectively, is also devoted to some contamination (i.e., piece of anode in the separated cathode material and vice-versa) during the dismantling step.

The metal composition of anode and cathode of Li-ion batteries is shown in Table 3. According to these results, Co (43.3%) is the main element in the cathode, followed by Al (10.2%) and Li (5.0%), while Cu is the predominant metal element in the anode (40.7%). The presence of Cu in the cathode as well as the presence of Co and Al in the anode can be assumed negligible (<1%) and probably due to contamination during the dismantling step as previously commented. Finally, in order to ascertain how hazardous spent Li-ion batteries might be to the environment if safe disposal is not attempted, the content of Hg, Pb and Cd in both anode and cathode were determined. As verified in Table 3, the content of Hg in the cathode was found to be high (1.3%). This value drops to nearly 0.2% if the weight of the whole battery is considered in the calculation (anode, cathode, plastics and metallic shell) but it is still very high

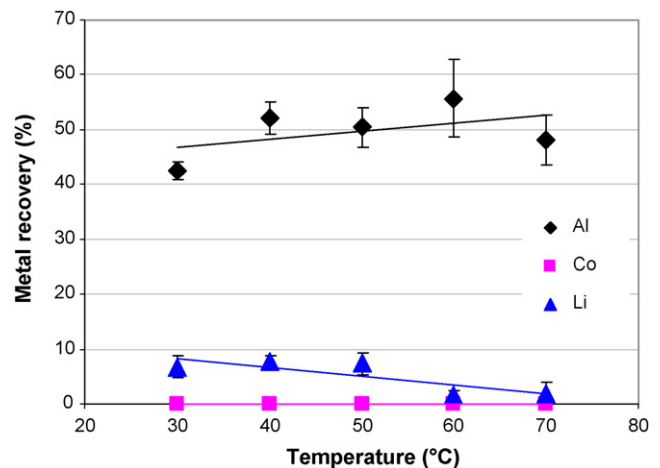


Fig. 2. Leaching of Al, Co and Li from the cathodes of Li-ion battery with NaOH ([NaOH] = 10% (w/w), solid/liquid ratio = 1:10 g mL<sup>-1</sup>,  $t = 1$  h).

for environmental standards, so Li-ion batteries must be sent to recycling. According to the Brazilian standards, the following limits are considered for safe disposal of batteries [15]: 0.01% Hg, 0.2% Pb and 0.015% Cd.

Therefore, based on the characterization results, the hydrometallurgical route to treat Li-ion batteries aiming to separate their metal content will consist of the following operating steps: (1) dismantling of Li-ion batteries for the removal of both plastic and metallic cases that can be sent for appropriate recycling, (2) separation of Cu (and C) by manual separation of anode and cathode, (3) separation of Al by leaching the cathode with NaOH, (4) separation of Co and Li by leaching the undissolved cathode material with H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub>, and finally (5) recovery of Co by crystallization. The last three steps are highlighted as follows.

#### 3.2. Metal leaching of the cathode of Li-ion batteries with NaOH

Exploratory transient tests were carried out in order to obtain the most adequate time to leach the cathodes of Li-ion batteries with NaOH. Leaching of Al was found very fast at the first 40 min, reaching a plateau after 60 min for the operation conditions tested, so all remaining tests were carried out at constant time of 1 h. A similar result (and behavior) was obtained in a previous investigation using H<sub>2</sub>SO<sub>4</sub> as leaching agent [8].

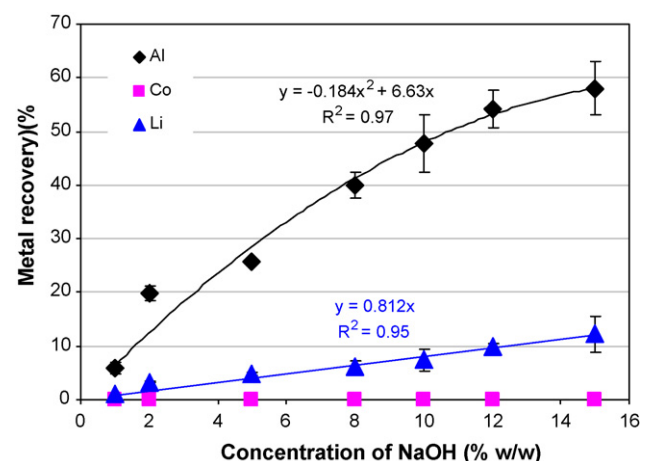


Fig. 3. Effect of the concentration of NaOH on the leaching of Al, Co and Li from the cathode of Li-ion batteries ( $T = 50$  °C, solid/liquid ratio = 1:10 g mL<sup>-1</sup> and  $t = 1$  h).

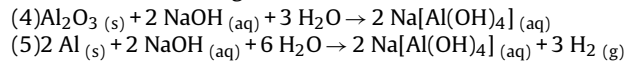
As shown by Fig. 2, the effect of temperature on the leaching of Al, Co and Li was found not significant from the statistical point of view, for the temperature range investigated in this study; Co leaching was negligible, Li extraction below 10% and Al recoveries oscillated between 40% and 60%. Despite of quite large variations verified mainly for the curves for Al and Li, the leaching of cathodes with NaOH was found an interesting step to be included in a treatment route for Li-ion batteries because it is very selective for Al over Co. Leaching of Al oscillated around 40–60% thus indicating that temperature is not statistically significant for the conditions studied, while the leaching behavior observed for Li is probably due to some non-homogeneity character verified in the samples of the solid phase. In fact, cathodes were cut using a scissors and then quartered as an attempt to obtain homogeneous samples. However, as Li ions transfer from the anode to cathode (and vice-versa) and batteries with different charge loadings were used in the study, the content of Li in the samples could be different in the samples used.

The effect of the concentration of NaOH on the leaching of Al, Co and Li from the cathode of Li-ion batteries is shown in Fig. 3. As verified in this figure, no Co was leached for the concentration range investigated. On the contrary, the leaching of Al and Li increased significantly; Al was extracted from 5% to 58% while Li was leached from 1% to 12% when the concentration of NaOH was raised from 1% to 15% (w/w). However, a white precipitate was verified in the filtrate solutions after a few hours when the concentration of NaOH was higher than 10% (w/w); XRD analysis of the solid revealed the formation of  $\text{LiAl}_2(\text{OH})_7 \cdot x(\text{H}_2\text{O})$  species.

The dissolution of Co by NaOH solutions was found to be practically zero for the operating conditions investigated in this study.

As can be seen in the Eh-pH diagrams shown in Fig. 4a and b, the  $\text{LiCoO}_2$  phase is thermodynamically stable at alkaline conditions while stable aqueous phases of Co do not exist in the investigated systems – the solid compounds  $\text{Co}_3\text{O}_4$  and  $\text{Co}(\text{OH})_2$  are stable at alkaline conditions. Therefore, as evidenced in the leaching tests, the presence of Co into the leaching liquor is not expected. On the other hand, a low dissolution of Li was observed experimentally and it can possibly be related to the dissolution of  $\text{LiCoO}_2$  to some extent thus forming the  $\text{Co}(\text{OH})_2$  or  $\text{Co}_3\text{O}_4$  solid phases. In addition, the presence of Li into the solution could also be related to the dissolution of the electrolyte  $\text{LiPF}_6$  which is a possible contaminant of the cathode. As can be seen in the Eh-pH diagrams shown in Fig. 4c and d, Li aqueous phases  $\text{Li}^+$  and  $\text{Li}(\text{OH})$  are thermodynamically stable in alkaline solutions. Thus, as evidenced in the leaching tests, the presence of Li in the leaching liquor is expected. All diagrams were made using the HSC Chemistry software and values for the Gibbs energy ( $\Delta G$ ) of species  $\text{LiCoO}_2$  were obtained from the literature [16].

The leaching of Al with NaOH from the cathode foil of Li-ion batteries might involve the dissolution of two species [17]:  $\text{Al}(\text{OH})_3$  from the protective layer surrounding of surface foil and metallic Al. Both reactions are given as follows:



According to these reactions and as verified experimentally (Fig. 3), the leaching of Al increases with the increase on the concentration of NaOH. Such behavior is also verified in the Eh-pH diagrams for the Al–Na–H<sub>2</sub>O system (see Fig. 5). In fact, the stability region for soluble species  $\text{Na}[\text{Al}(\text{OH})_4]$  in the aqueous phase increases significantly when the concentration of NaOH is raised

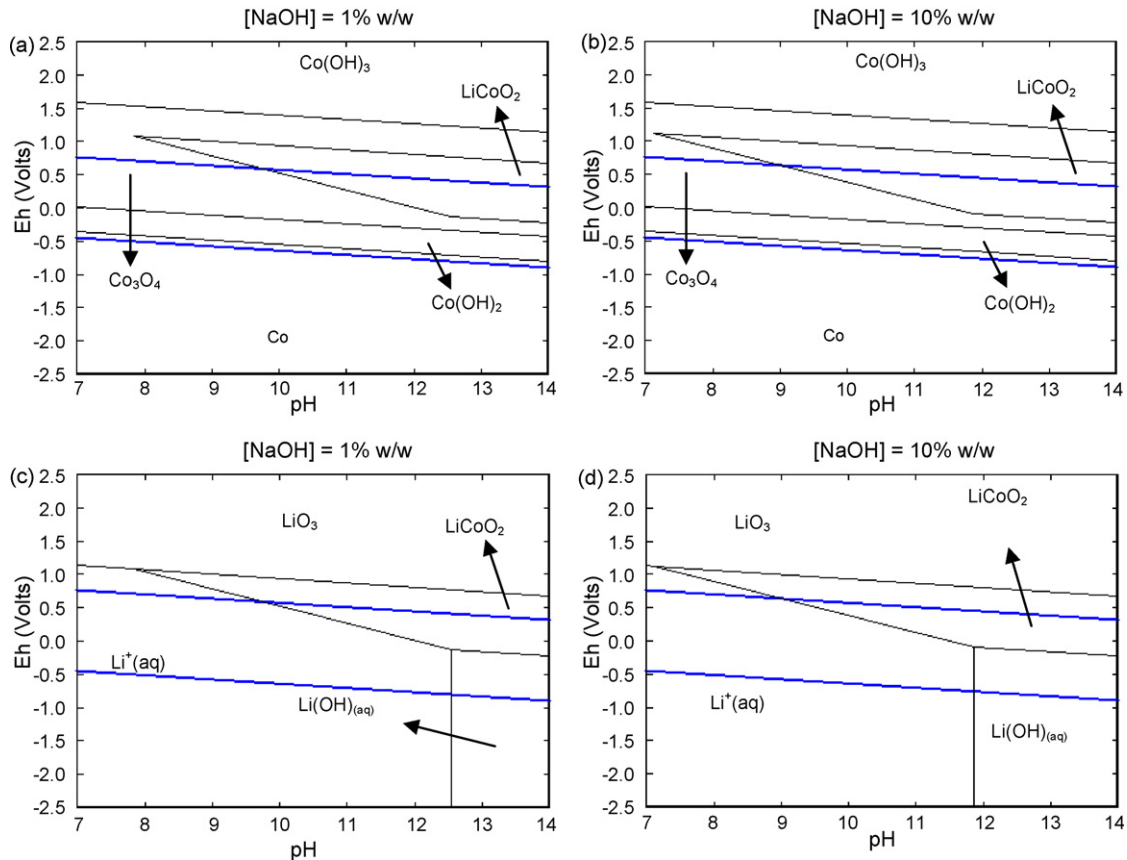


Fig. 4. Eh-pH diagram of Co–Li–H<sub>2</sub>O system at 50 °C: (a) Co species, [NaOH] = 1% (w/w), (b) Co species, [NaOH] = 10% (w/w), (c) Li species, [NaOH] = 1% (w/w), (d) Li species, [NaOH] = 10% (w/w).

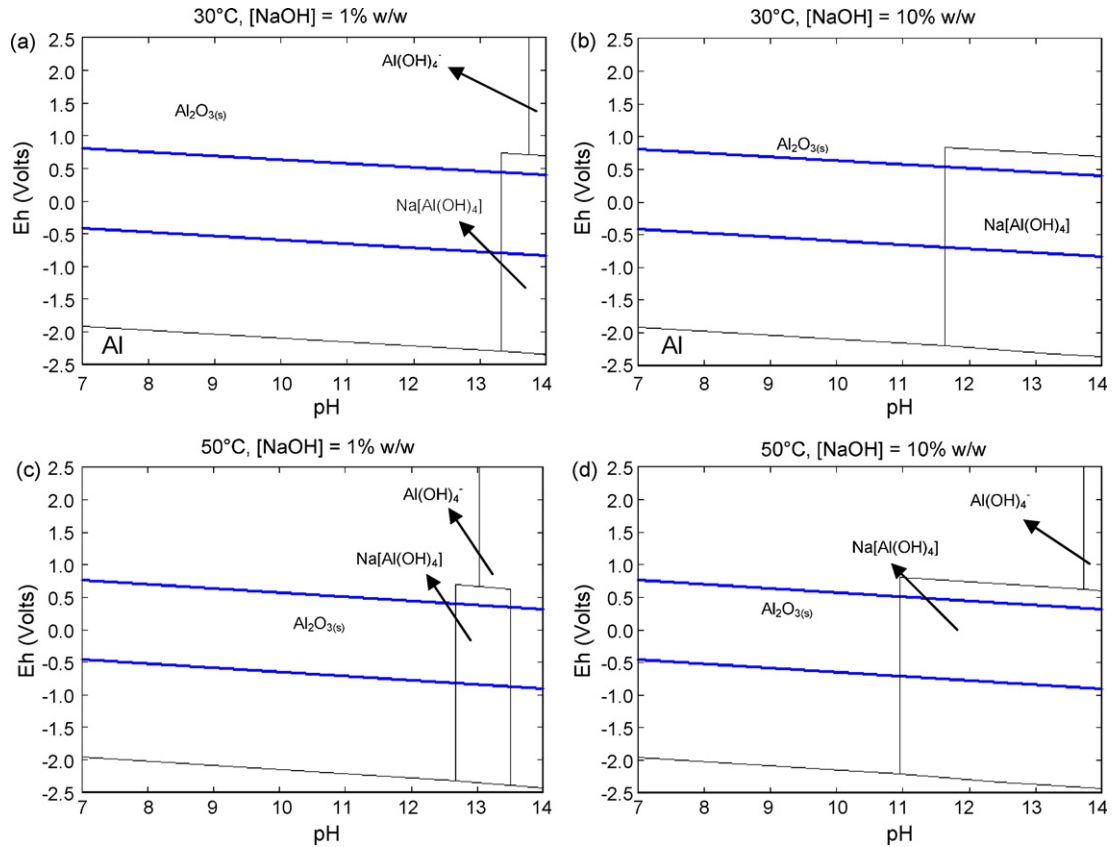


Fig. 5. Eh-pH diagram of Al-Na-H<sub>2</sub>O system at changing temperature and concentration of NaOH.

from 1%–10% (w/w), for both temperature levels investigated. In addition, the effect of temperature was found to be less significant than that of the concentration of NaOH, thus corroborating the experimental evidence (Fig. 2).

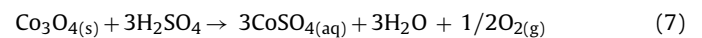
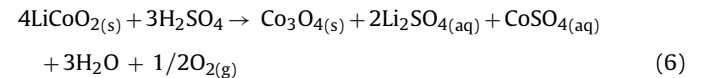
### 3.3. Metal leaching of the cathode of Li-ion batteries with H<sub>2</sub>SO<sub>4</sub>

Before leach the cathodes of Li-ion batteries with H<sub>2</sub>SO<sub>4</sub>, this material was first leached with NaOH aiming to diminish the Al content. For this attempt, the cathodes were contacted twice with a leaching solution containing [NaOH] = 10% (w/w), solid/liquid ratio of 1:30 g mL<sup>-1</sup> and  $T = 30^\circ\text{C}$ , followed by throughout washing with distilled water for the removal of remanent NaOH. The leached cathodes were dried and quartered. Samples of cathode before and after this procedure were dissolved in aqua regia and analyzed by AA. The content of Al, Co and Li dropped from 10.2%, 43.2% and 5.0% (w/w) to 2.1%, 42.5% and 4.8% (w/w), respectively, thus indicating a selective leaching of nearly 80% of Al. Therefore, for practical operations, a higher removal of Al will involve a higher number of contact stages.

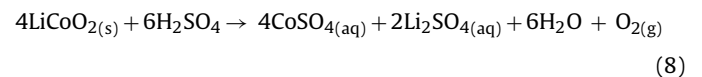
The effect of temperature and concentration of H<sub>2</sub>SO<sub>4</sub> on the leaching of metals Al, Co and Li from the cathodes of Li-ion batteries are shown in Fig. 6a and b, respectively. For the operating range investigated, both variables were found to be not significant from the statistical point of view. Metal leaching was relatively high for all metals considered (around  $90 \pm 10\%$ ). On the contrary, the effect of the concentration of H<sub>2</sub>O<sub>2</sub> was found to be significant mainly for Co whose recovery was doubled from  $40 \pm 1\%$  at the absence of H<sub>2</sub>O<sub>2</sub> to  $85 \pm 2\%$  when the concentration of H<sub>2</sub>O<sub>2</sub> was raised to 0.5% (v/v) as it can be viewed by Fig. 7. The leaching of Li was also affected

positively, thus pointing out that the solubilization of LiCoO<sub>2</sub> is favored at the presence of H<sub>2</sub>O<sub>2</sub>. The effect of the concentration of H<sub>2</sub>O<sub>2</sub> on the Al leaching was not conclusive, but it seems not to be affected. Comparing the leaching results for Co and Li obtained in this work with those shown in Table 1, it can be concluded that high leaching of Co can be achieved at low temperatures, low acid concentrations and low solid/liquid ratio but solely at the presence of a reductive agents like H<sub>2</sub>O<sub>2</sub>. In terms of an industrial plant to treat Li-ion batteries, such result implies in lower operation costs.

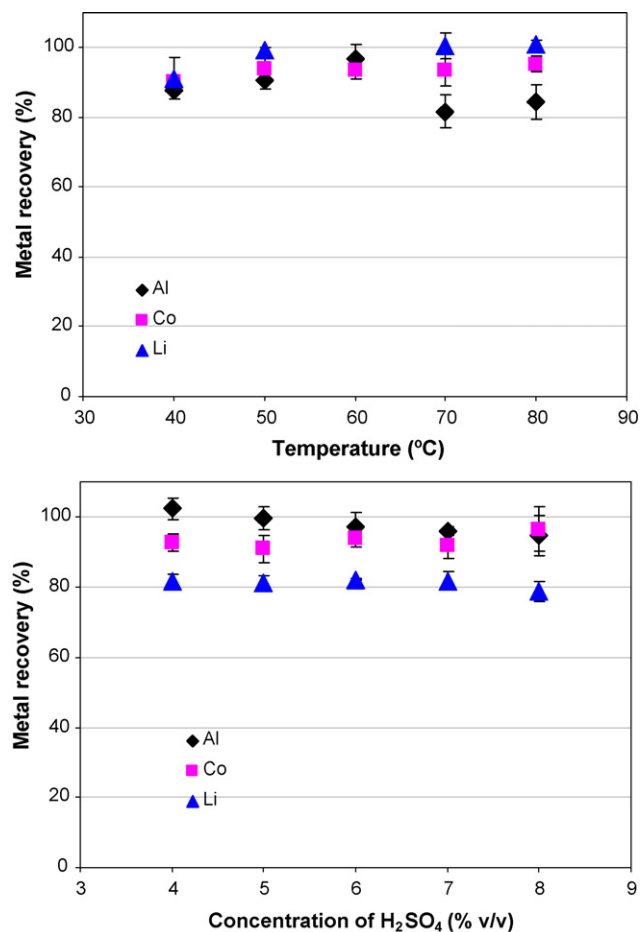
The effect of H<sub>2</sub>O<sub>2</sub> is possibly related to some change in the leaching kinetics of LiCoO<sub>2</sub>. In fact, the solubilization of LiCoO<sub>2</sub> involves the reduction of Co<sup>3+</sup> in the solid species to Co<sup>2+</sup> in the aqueous phase. At the absence of H<sub>2</sub>O<sub>2</sub> in the leaching solution, LiCoO<sub>2</sub> seems to leach forming Co<sub>3</sub>O<sub>4</sub> that remains in the solid phase, thus requiring an excess of H<sub>2</sub>SO<sub>4</sub> to be converted into soluble CoSO<sub>4</sub> according to the sequential reaction scheme:



which result in the following global reaction proposed elsewhere [18]:

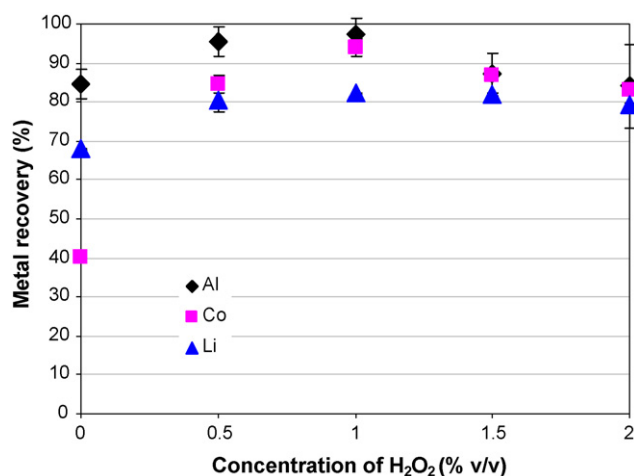


Such reaction scheme may explain why nearly 40% of Co and 68% of Li was leached in the experiment carried out at the absence

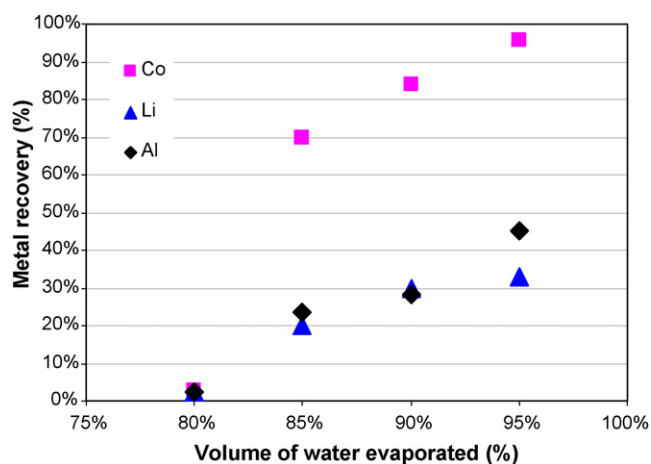


**Fig. 6.** Effect of (a) temperature ( $[\text{H}_2\text{SO}_4]=6\%$  (v/v)) and (b) concentration of  $\text{H}_2\text{SO}_4$  ( $T=60^\circ\text{C}$ ) on the leaching of Al, Co and Li from cathodes of Li-ion batteries ( $[\text{H}_2\text{O}_2]=1\%$  (v/v), solid/liquid ratio = 1:30  $\text{g mL}^{-1}$  and  $t=1$  h).

of  $\text{H}_2\text{O}_2$  as shown in Fig. 7. In fact, as leaching of Li was little affected by the increase on the concentration of  $\text{H}_2\text{O}_2$ , it seems that Eq. (6) is probably prevailing at the operating conditions investigated while the reaction given by Eq. (7) is not too rapid. According to speciation calculations, soluble  $\text{Co}(\text{SO}_4)_4$  was expected at pH near zero at

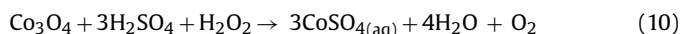
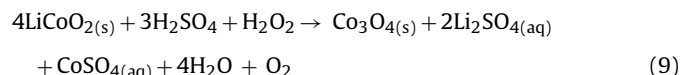


**Fig. 7.** Effect of the concentration of  $\text{H}_2\text{O}_2$  on the leaching of Al, Co and Li from the cathodes of Li-ion batteries ( $[\text{H}_2\text{SO}_4]=6\%$  (v/v),  $T=60^\circ\text{C}$ , solid/liquid ratio = 1:30  $\text{g mL}^{-1}$ ,  $t=1$  h).

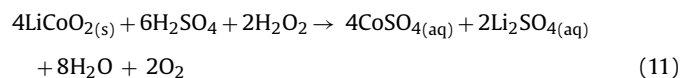


**Fig. 8.** Recovery of Al, Co and Li versus the volume of water evaporated (initial liquor composition:  $[\text{Al}]=0.6\text{ g L}^{-1}$ ,  $[\text{Co}]=11.3\text{ g L}^{-1}$  and  $[\text{Li}]=1.2\text{ g L}^{-1}$ ).

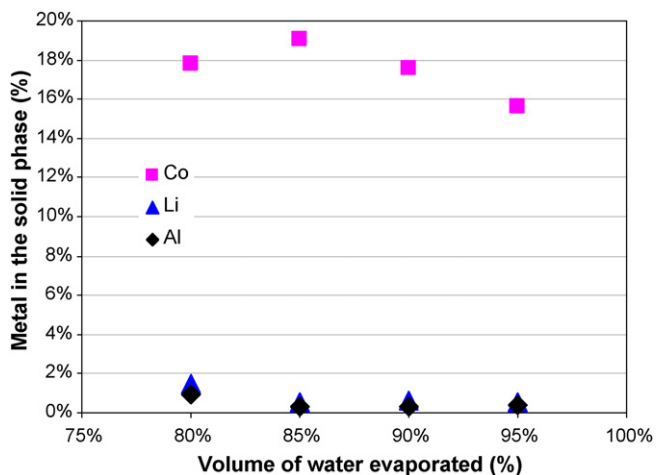
equilibrium conditions ( $t \rightarrow \infty$ ) but it was verified only partially, so it might be occurred due to the low kinetics as evidenced experimentally by Nan et al. [9] and equilibrium seems not to be reached in 1 h leaching. When 1% (v/v) of  $\text{H}_2\text{O}_2$  was added, the leaching of Co raised to 94% and that of Li changed to 82% at the same time, so the reaction kinetics seems to be much faster at the presence of the reductive agent  $\text{H}_2\text{O}_2$  as investigated in this study. Therefore, equilibrium is reached in 1 h, as verified elsewhere [8,9] and the following reaction scheme is proposed to the leaching of  $\text{LiCoO}_2$  at the presence of  $\text{H}_2\text{O}_2$ :



thus resulting in the following global reaction as proposed elsewhere [18]:



Finally, it can be concluded the concentration of  $\text{H}_2\text{O}_2$  was the most significant variable in the leaching of  $\text{LiCoO}_2$  with  $\text{H}_2\text{SO}_4$  from



**Fig. 9.** Metal composition of solid phase versus the volume of water evaporated (initial liquor composition:  $[\text{Al}]=0.6\text{ g L}^{-1}$ ,  $[\text{Co}]=11.3\text{ g L}^{-1}$  and  $[\text{Li}]=1.2\text{ g L}^{-1}$ ).

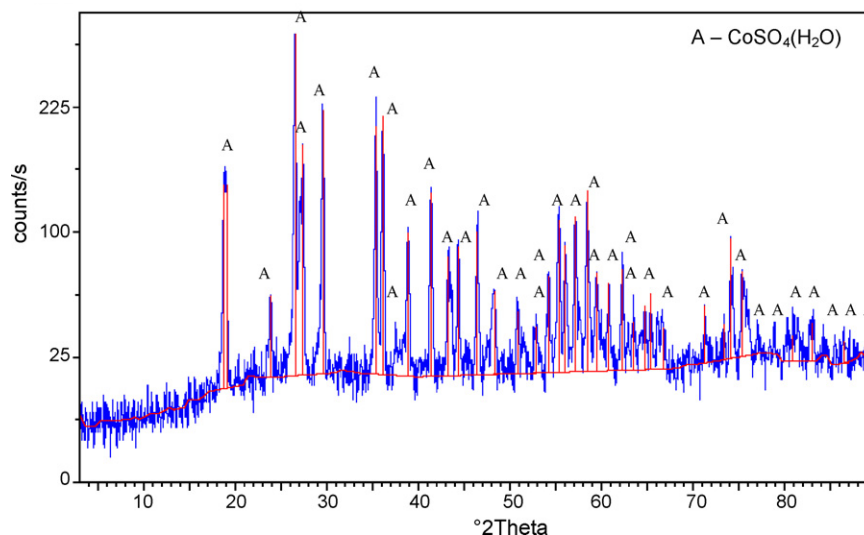


Fig. 10. X-ray patterns of the salt obtained after crystallization (initial liquor composition:  $[Al] = 0.6 \text{ g L}^{-1}$ ,  $[Co] = 11.3 \text{ g L}^{-1}$  and  $[Li] = 1.2 \text{ g L}^{-1}$ ).

Li-ion batteries, for the operating conditions studied. The best operating conditions were  $T = 40^\circ\text{C}$ ,  $[H_2SO_4] = 4\%$  (v/v) and  $[H_2O_2] = 1\%$  (v/v). Recoveries of Co and Li of 97% and 100%, respectively, were obtained experimentally. A high recovery of Al was also obtained, so this metal must be fully removed in the alkaline leaching with NaOH. In this study, an acid leach liquor containing  $0.6 \text{ g L}^{-1}$  Al,  $11.3 \text{ g L}^{-1}$  Co and  $1.2 \text{ g L}^{-1}$  Li was obtained which was treated by crystallization to obtain purified  $CoSO_4$  salt.

#### 3.4. Crystallization tests

The sulfuric acid liquor was submitted to crystallization by means of water evaporation at different rates (from 80% to 95%) in order to obtain crystals of  $CoSO_4$  to be recycled. Fig. 8 shows the percentage of metal that crystallized while Fig. 9 shows the metal content on the salt for different evaporating rates. The amount of solid produced at 80% of evaporation was too small (nearly 3% of Co was recovered) despite of the high grade of Co in the solid phase (around 18%). At 90% of evaporation, 70% of Co was crystallized and the metal grade was maximum (19%). Higher evaporation rates of water result into higher crystallization rates of metals but at the expense of higher contamination of Al and Li in the solid phase. Therefore, 85% of evaporation of water was found the most adequate condition from the operational point of view. In this condition, Al and Li grades in the solid were lower than 0.4% and 0.6%, respectively.

The solid phase was then analyzed by XRD. The main patterns shown in Fig. 10 indicate the predominance of  $CoSO_4 \cdot H_2O$  in the form of deeply pink crystals, thus corresponding to 55.8% (w/w) of the formed solid. Metals Al and Li were not identified but their presence is relatively low as identified quantitatively, probably in the form of hydrated sulfates. A more complete study on the crystallization step need to be carried out aiming to control mainly the supersaturation level of the solution with relation to  $CoSO_4$  and consequently the purity of this final product but the method showed to be feasible for practical operation.

#### 4. Conclusions

The use of rechargeable and long lasting Li-ion batteries can make a positive impact towards the reduction of battery wastes and pollution if compared to other commercial batteries. In fact,

Li-ion batteries can be recharged several times but one day they will become a residue to be recycled. So, in this paper, a hydrometallurgical route to separate the metal content of Li-ion batteries was investigated. The main conclusions are drawn as follows:

Al and  $LiCoO_2$  are the main phases identified in the cathode of Li-ion batteries while Cu is the predominant metallic element in the anode, so manual separation of anode and cathode after battery dismantling is advantageous to separate Cu from the material to be treated by leaching.

Leaching of cathodes with NaOH was found very selective for the separation of Al, thus leaving all Co and majority of Li in the solid phase. The recovery of Al (and Li) increased with the concentration of NaOH (1–15% (w/w)) and it was found practically unaffected by the temperature range investigated (30–70°C). Eh-pH diagrams were used to explain such behavior. The operation seems adequate to be carried out in stages, using maximum 10% (w/w) of NaOH to avoid the formation of precipitates.

In the leaching of  $LiCoO_2$  with  $H_2SO_4$ , the use of a reductive agent like  $H_2O_2$  was found essential to accelerate the dissolution process and reduce the consumption of acid. The effect of operating variables temperature and concentration of  $H_2SO_4$  were found not significant at the presence of  $H_2O_2$  and 97% Co was leached in one single stage.

Crystallization was found adequate to produce a purified monohydrated  $CoSO_4 \cdot H_2O$  for recycling. The purity grade of the deep pink crystal salt obtained by crystallization will depend on the volume of water evaporated from the acid liquor. In the present study, the best result was found for 85% of water evaporation.

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