



# Product recovery from Li-ion battery wastes coming from an industrial pre-treatment plant: Lab scale tests and process simulations

Giuseppe Granata, Emanuela Moscardini, Francesca Pagnanelli\*, Franco Trabucco, Luigi Toro

Department of Chemistry, Sapienza University of Rome, P.le A. Moro 5, Rome I-00185, Italy

## ARTICLE INFO

### Article history:

Received 30 September 2011  
Received in revised form 17 January 2012  
Accepted 18 January 2012  
Available online 2 February 2012

### Keywords:

Lithium ion batteries  
Metal recovery  
Leaching  
Solvent extraction  
Process simulation

## ABSTRACT

In this paper two hydrometallurgical processes were analyzed for recovery of lithium and cobalt from lithium ion batteries. The effect of adding a secondary purification step by solvent extraction was evaluated in terms of product purity and economical feasibility of the process. Process routes were made of the following steps: mechanical pretreatment, leaching, primary (and secondary) purification, product recovery. Electrode material used in leaching experiments was produced in a large scale pre-treatment plant for waste recycling. Leaching tests were performed both using chloridric acid and sulphuric acid plus glucose. In optimized conditions quantitative extraction of Co and Li were obtained for both tested systems. Iron, aluminum and copper were removed by precipitation as hydroxides, while Ni can be separated only using solvent extraction. Process simulations showed that, for the same input flow rate of batteries, the addition of solvent extraction improves the economical feasibility of the process for lithium ion battery recovery.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Lithium ion batteries (LIB) are widely used as electrochemical power sources in modern electronic equipments, mainly because of their high energy density, high cell voltage, long storage life, low self discharge rate and wide temperature range of use [1].

European Guideline 66/2006 declared the necessity of reducing pollutant effects related to the wastes of end of life batteries and accumulators. Mandatory collection rates and target material recovery were then established: 25% and 45% collection rates within 2012 and 2016, respectively, and 50% material recovery for LIB [2].

New hydrometallurgical processes should be then developed in order to satisfy such targets.

Literature survey showed that research has been mainly focused on the optimization of operating conditions for leaching operation. Most works reported experimental results of acid-reductive leaching where  $H_2O_2$  is generally used as reducing agent along with sulphuric acid [3–6]. Otherwise organic reducing agents can be used such as citric acid [7] and oxalic acid [8]. Some works also compared different leaching mixtures: Zhang et al.

[9] investigated three acids (nitric, sulphuric and chloridric) and evaluated the effect of acid concentration, temperature, leaching time and solid-to-liquid ratio. They found that hydrochloric acid gave the best performance in agreement with experimental results reported by Contestabile et al. [10]. Nitric acid was also tested in leaching experiments using LIB electrode powder [11].

Few works were published addressing the complete process route to recover Co and/or Mn products [5,12] or to regenerate lithium cobalt oxide [13,14].

All the works cited above used powder samples obtained by manual dismantling of batteries or laboratory scale mechanical dismantling. This can seriously affect the scalability of process outputs obtained in these studies for two main reasons. First the sequence and type of mechanical pre-treatments used for large scale dismantling can completely alter the composition of the input material of leaching section. In particular considering the internal structure of LIB (made up of thin layers of electrode material within alternate sheets of Al and Cu), the manual dismantling and the selective recovery of electrode material gives a solid sample completely different from that obtained from real battery grinding. Then hand-made separation of electrode material gives an input material which is not representative of ground material from large scale plants. In addition treatment of few units of batteries means that feed heterogeneity is completely neglected. On the other side process development and feasibility

\* Corresponding author. Tel.: +39 0649913333; fax: +39 06490631.  
E-mail address: [francesca.pagnanelli@uniroma1.it](mailto:francesca.pagnanelli@uniroma1.it) (F. Pagnanelli).

analysis required that input material come from large scale treatment to be representative of real wastes that will be treated in plant scale.

Another general observation about literature papers reported above is the complete lack of economic analysis for the proposed process.

Then two main limits emerged from the state of the art of literature:

- use of LIB powders coming from few samples of manually or lab-scale dismantled batteries, focus on leaching section rather than on the whole process feasibility.

The aim of this work is overcoming these limits by addressing the process economics of different routes to recover Co and Li products from LIBs using a real waste fraction coming from a large scale pre-treatment plant.

Innovative aspects are then:

- LIB powder which is representative of what would be treated in large scale facilitating the scale-up of the process, economical feasibility of different process options to recover lithium and cobalt products from LIB wastes. In particular, the effect of adding a secondary purification step by solvent extraction was estimated in terms of product purity and process economic feasibility.
- use of glucose as reducing agent: this carbohydrate (potentially coming from waste of food factories) have been already used for Mn(IV)oxides leaching [15], but never tested for cobalt reductive leaching.

## 2. Materials and methods

### 2.1. Materials

The input material used in leaching experiments was kindly provided by S.E.Val. s.r.l., an Italian medium enterprise working in the recycling of wastes of electric and electronic equipments, batteries and accumulators. LIBs were treated in a large scale mechanical route of pre-treatment ( $5000 \text{ t y}^{-1}$ ), which was made up of a combination of crushing, milling, sieving, and physical separations such as eddy current separator, magnetic, pneumatic and densimetric splitter.

All chemicals ( $\text{H}_2\text{SO}_4$ , NaOH,  $\text{Na}_2\text{CO}_3$ , di-2-ethylhexylphosphoric acid, D2EHPA) were analytical grade reagents (Sigma–Aldrich). The extractant Cyanex 272 was supplied by Cytec USA Incorporation and was used without further purification.

Low boiling point kerosene ( $180\text{--}270^\circ\text{C}$ ) was used as diluent.

### 2.2. Granulometric analysis and acid digestion

The input material was vibro-sieved 3 times for 10 min using 6 sieves with different cut-off: 2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.2 mm, 0.125 mm. After sieving samples of each fraction (2 g) were digested using 40 mL of aqua regia (a mixture of HCl 36%, w/w and  $\text{HNO}_3$  65%, w/w formulated with 3:1 volume ratio, respectively) for 5 h, filtered and analyzed by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Varian Vista-MPX Simultaneous CCD) in order to determine concentration in solid of each metal ( $x_0$ ). For each digestion three replicates were performed and average values reported.

### 2.3. Leaching

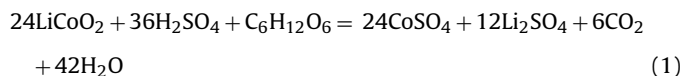
Leaching experiments were carried out in 0.5 L Pyrex jacket reactors provided of impeller stirrer, vapor condenser and thermometer. Heating was provided by an external thermostatic

apparatus.  $\text{H}_2\text{SO}_4$  solutions were put inside the reactors at the desired temperature. Then the desired weight of solid input material ( $m_0$ ) and the reducing agent (if present) were added under stirring for three hours. Experimental conditions (temperature, amount of acid expressed as g of acid per gram of solid, reducing agent concentration expressed as % stoichiometric excess) used in all leaching tests were listed in Tables 1 and 2.

Aliquots of concentrated acids (HCl 36%, w/w and  $\text{H}_2\text{SO}_4$  96%, w/w) were used in order to have the specified values of gram of acid/gram of treated solid as detailed in Tables 1 and 2.

As an example for the first condition of Table 2 after weighting a solid sample of 2 g the desired final ratio g acid/g solid was 2, then 4 g of  $\text{H}_2\text{SO}_4$  were used corresponding to 4.2 g of  $\text{H}_2\text{SO}_4$  96% (w/w) concentrated solution. This amount of acid was then diluted to 20 mL with distilled water in order to have the desired solid–liquid ratio ( $100 \text{ g L}^{-1}$ ).

Stoichiometric concentration of glucose was calculated according to reaction (1)



During leaching time, leach liquor samples (2 mL) were periodically drawn, filtered and analyzed by ICP-OES.

At the end of each experiment, residual solids were separated by filtration, washed with water, dried in a oven, weighted ( $m_f$ ) and digested as reported in Section 2.2 to determine the residual concentration of each metal in solid phase ( $x_f$ ).

Extractive yields for each metal were determined as

$$\text{extractive yield (\%)} = \frac{x_0 m_0 - x_f m_f}{x_0 m_0} \times 100 \quad (2)$$

where  $x_0$  is the metal concentration ( $\text{g g}^{-1}$ ) in the solid before leaching,  $m_0$  is the weight (g) of solid used for leaching,  $x_f$  is the metal concentration in solid residue after leaching, and  $m_f$  is the weight of solid residue after leaching.

Treatments were arranged according to two factorial designs [16] for the preliminary optimization of the operating conditions using HCl (Table 1) and  $\text{H}_2\text{SO}_4$  plus glucose (Table 2) at fixed solid liquid ratio ( $s/l = 100 \text{ g L}^{-1}$ ). A third set of experimental tests was performed using  $2 \text{ g}_{\text{H}_2\text{SO}_4} \text{ g}_{\text{powder}}^{-1}$  with 50% of stoichiometric excess of glucose at  $90^\circ\text{C}$  in order to investigate the effect of solid–liquid ratio by increasing the solid concentration from  $100 \text{ g L}^{-1}$  to  $135 \text{ g L}^{-1}$ , and finally to  $200 \text{ g L}^{-1}$ .

### 2.4. Primary purification: precipitation

Iron, aluminum and copper were removed by leach liquor by adding sodium hydroxide pellets up to pH 5.0 under stirring at room temperature. After 2 h stirring suspensions were filtered and solutions analyzed by ICP-OES.

### 2.5. Solvent extraction

Cyanex 272 and D2EHPA (extractants) were dissolved in kerosene (diluent) until reaching the same molar concentration of cobalt in the leach liquor (0.84 M) and then partially saponified (65%) by adding a NaOH solution (5 M) under stirring [17,18]. 10 mL of purified leach liquor ( $50 \text{ g L}^{-1}$  of Co,  $10 \text{ g L}^{-1}$  of Li,  $5 \text{ g L}^{-1}$  of Ni,  $1.5 \text{ g L}^{-1}$  of Mn) were shaken for 5 min with the organic phase. The volume of aqueous phase was kept constant for all experiments, while the volume of the organic phase was varied from 10 to 60 mL. Then the ratio between organic phase volume and aqueous phase volume, O/A, changed from 1 to 6. Considering that the molar concentration of the extractant in the organic phase is the same of Co in aqueous phase, working with variable O/A ratios means working

**Table 1**Metal extraction yields (%) after 3 h using HCl in a full factorial design replicated two times (A: temperature; B: HCl concentration; s/l ratio = 100 g L<sup>-1</sup>).

T (°C)	[HCl] (g g <sub>powder</sub> <sup>-1</sup> )	Treatments	Al	Co	Cu	Fe	Li	Mn	Ni
30	1.5	1	99	98	100	100	88	72	100
			98	95	98	100	97	100	99
90	1.5	a	100	100	100	58	99	100	100
			100	98	98	79	99	100	100
30	2.0	b	99	58	99	100	88	93	100
			98	48	98	91	76	61	99
90	2.0	ab	100	98	100	100	95	96	100
			99	98	99	100	98	100	100

under different stoichiometric conditions ( $O/A = \text{mol}_{\text{SLV}} \text{mol}_{\text{Co}}^{-1}$ , where  $\text{mol}_{\text{SLV}}$  are the mol of extractant in organic phase). After shaking the two phases were separated by a separating funnel. pH values of leach liquors were adjusted by the addition of NaOH or H<sub>2</sub>SO<sub>4</sub> solution in the range 1–6. All experiments were performed at room temperature ( $25 \pm 1$  °C) in duplicates.

Raffinates (aqueous phase after extraction) were analyzed by ICP-OES to determine the amount of extracted Co<sup>2+</sup>, Li<sup>+</sup>, Ni<sup>2+</sup>, and Mn<sup>2+</sup>.

Stripping tests for metal recovery from organic phase were carried out using 4 M H<sub>2</sub>SO<sub>4</sub> solution at  $25 \pm 1$  °C with the same volume of organic phase and aqueous phase ( $O/A = 1$ ).

### 2.6. Cobalt recovery

Cobalt was recovered as carbonate from solutions coming both from primary purification (NaOH precipitation) and secondary purification (stripping solution after solvent extraction). A saturated Na<sub>2</sub>CO<sub>3</sub> solution was added to purified leach liquors under stirring in order to have a final pH of 9–10. After 2 h under stirring at room temperature, suspensions were filtered and analyzed by ICP-OES. Solid precipitates were washed with water to remove soluble salt (as Na<sub>2</sub>SO<sub>4</sub>) and then dried at 60 °C for 24 h. In order to evaluate the purity of obtained products, cobalt carbonate samples were dissolved in water and solutions analyzed by ICP-OES.

### 2.7. Lithium recovery

Lithium was recovered as carbonate from raffinates. A saturated Na<sub>2</sub>CO<sub>3</sub> solution was added to raffinates under stirring up to pH 8. After 2 h under stirring, suspensions were filtered and analyzed by ICP-OES. Solid precipitates (mainly Ni, Mn, and Cu carbonates) were removed by filtration and the residual solution was evaporated leaving different amounts of residual water (tested degree of evaporation: 70, 80, 90%). Lithium carbonate was separated by filtration,

washed in hot water (90 °C) and dried. Lithium carbonate samples were dissolved in water and solutions analyzed by ICP-OES.

## 3. Results and discussion

### 3.1. Input material composition and metal distribution in the different fractions

The input material used in leaching experiments contains Co ( $250 \pm 30 \text{ mg g}^{-1}$ ), Cu ( $60 \pm 20 \text{ mg g}^{-1}$ ), Al ( $50 \pm 20 \text{ mg g}^{-1}$ ), Li ( $35 \pm 5 \text{ mg g}^{-1}$ ), Mn ( $15 \pm 3 \text{ mg g}^{-1}$ ), and Ni ( $3 \pm 1 \text{ mg g}^{-1}$ ). Considering this composition and in particular the amount of cobalt (lithium can be also contained in the electrolyte), it can be evaluated that LiCoO<sub>2</sub> is 50% (w/w) of the input material.

Granulometric distribution shows that 42% of mass weight has a diameter ( $d$ ) which is  $< 0.125 \text{ mm}$ , 8% has  $0.125 < d < 0.200 \text{ mm}$ , 5% has  $0.200 < d < 0.250 \text{ mm}$ , 10% has  $0.250 < d < 0.500 \text{ mm}$ , 4% has  $0.500 < d < 1 \text{ mm}$ , 12% has  $1 < d < 2 \text{ mm}$ , and 19% has  $d > 2 \text{ mm}$ . According to the charts showed in Fig. 1, all metals are mainly contained in the fractions with  $d < 1 \text{ mm}$  (82% of Li, 81% of Co, 88% of Mn, 62% of Ni) with the exception of copper and aluminum, which are concentrated in the fraction with  $d > 1 \text{ mm}$  (67% of Al, 79% of Cu).

### 3.2. Leaching

Metal extraction yields obtained using HCl are reported in Table 1: temperature (changing from 30 to 90 °C) and acid amount (changing from 1.5 to 2.0 g of acid per gram of electrodic powder) exhibit significant effects (95% significance level) [16] only for Al, Co and Fe as evidenced in Fig. 2.

In particular analysis of variance shows:

- positive effect of temperature (A factor) on Al and Co extraction;
- negative effect of acid concentration (B factor) on Co extraction;

**Table 2**Metal extraction yields (%) after 3 h using H<sub>2</sub>SO<sub>4</sub> in a full factorial design replicated two times (A: temperature; B: H<sub>2</sub>SO<sub>4</sub> concentration; C: stoichiometric excess of reducing agent; s/l ratio = 100 g L<sup>-1</sup>).

T (°C)	[H <sub>2</sub> SO <sub>4</sub> ] (g g <sub>powder</sub> <sup>-1</sup> )	[glu] (% exc)	Treatments	Al	Co	Cu	Fe	Li	Mn	Ni
30	2.0	50	1	75	48	38	70	77	67	97
				70	51	51	75	77	62	97
90	2.0	50	a	99	97	98	89	98	100	100
				98	98	99	90	99	100	100
30	2.5	50	b	89	82	79	85	90	87	98
				72	64	55	39	77	67	96
90	2.5	50	ab	99	98	97	31	98	100	100
				99	97	97	28	98	100	99
30	2.0	100	c	74	64	54	64	79	73	96
				75	61	59	72	77	71	96
90	2.0	100	ac	97	94	87	84	98	100	100
				98	96	89	85	98	100	100
30	2.5	100	bc	98	97	97	90	98	100	99
				99	93	98	88	98	100	100
90	2.5	100	abc	64	33	28	43	67	64	95
				70	51	54	27	77	73	97

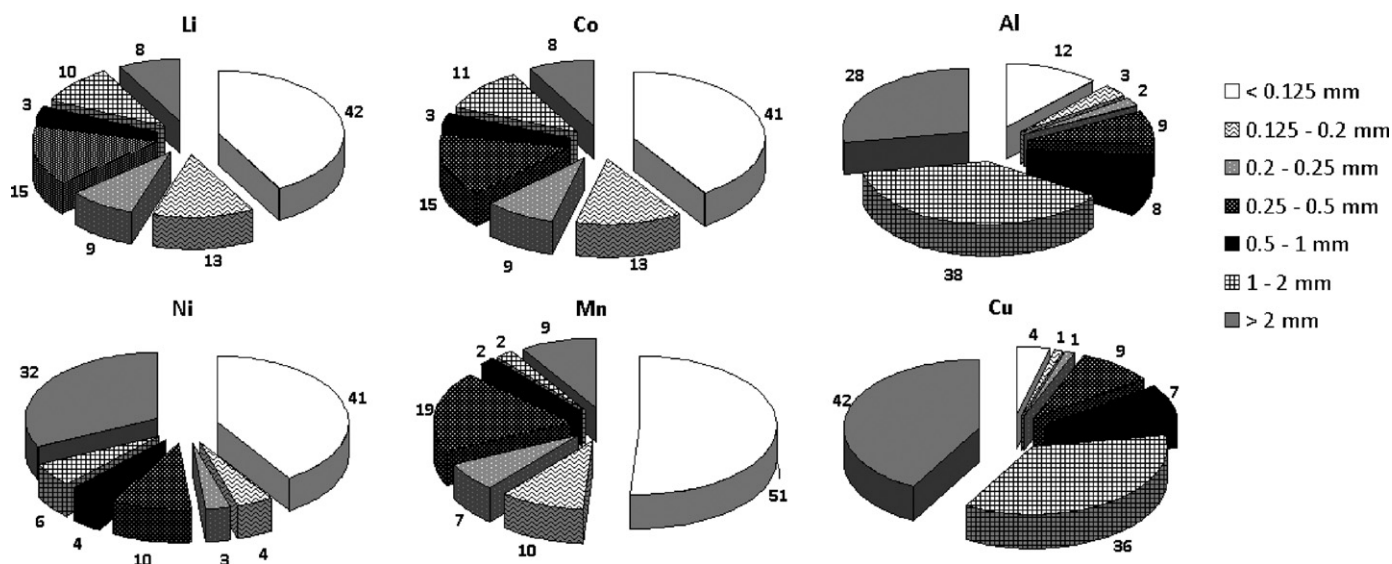


Fig. 1. Distribution of all investigated metals.

- positive effect of the interaction temperature-acid concentration (AB) on Co and Fe yields.

A series of hypotheses can be made to explain such experimental findings:

- temperature plays a crucial role in chemical reactions also occurring in leaching processes: the effect of this factor is much larger for chemical reactions with high activation energy and then a plausible conclusion could be that Al and Co compounds that undergo to dissolution present activation energy larger than other extracted metals. This characteristic could be exploited to enrich leach liquor in the target metal Co
- inhibition of Co extraction could be due to the high concentrations of acid used in these tests (4 M for  $1.5 \text{ g g}^{-1}$  and 5.5 M for  $2 \text{ g g}^{-1}$ ): in these conditions water can be the limiting reactant both for acid dissociation and for extracted metal solvation. This is in

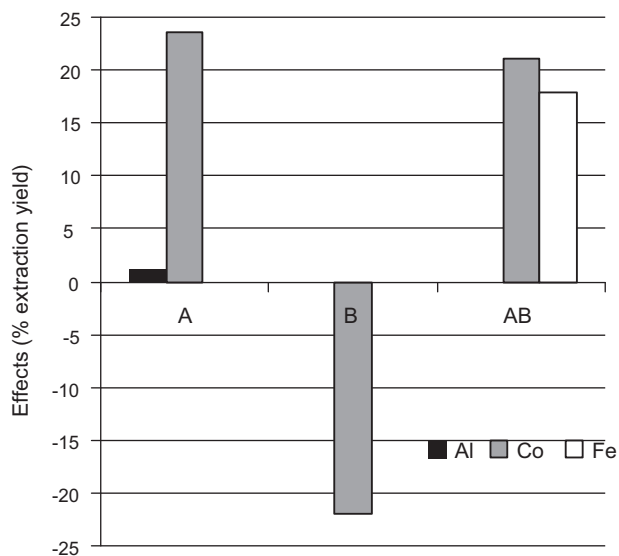


Fig. 2. Estimates of significant effect on metal extraction yield (%) for acid leaching with HCl: (A) temperature; (B) HCl concentration (Solid-liquid ratio  $100 \text{ g L}^{-1}$ ).

agreement with the fact that this effect is significant only for the most concentrated metal

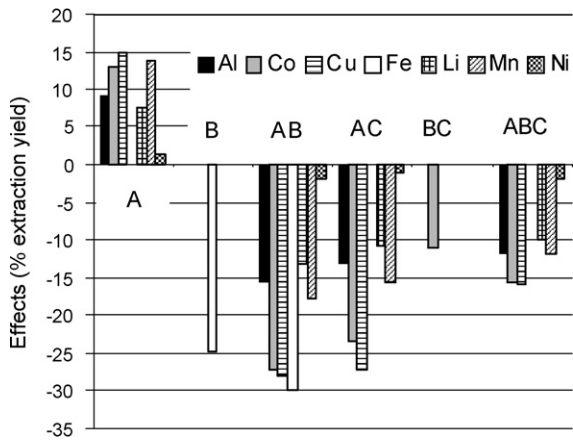
- positive interaction observed for Co and Fe means that factor A and B do not act independently on the variables yield of Co and yield of Fe. Then the effect of a factor is larger when also the other factor is taken at the highest level. Phenomenological interpretation of this could be that since temperature was found to be the limiting factor the effect of acid concentration become significant only at the high level of temperature, just requiring activation at high temperature. This observation could be exploited to reduce iron extraction.

Considering the extraction of target metals (Li and Co), Li extraction is not significantly affected in the range of operating conditions considered here, while Co extraction yield is maximized working at the high level of temperature and the low level of acid.

According to these findings acid concentration could be used at the lower level in order to save reagents and minimize Fe extraction, which is an impurity. In these preliminary optimized conditions ( $90^\circ\text{C}$ ,  $1.5 \text{ g HCl per g of solid}$ ) acid leaching using HCl is able to extract quantitatively Co, Li, Ni, Mn, Al and Cu (see Table 1).

Preliminary tests (not reported here) using only  $\text{H}_2\text{SO}_4$  to leach the input material show that the acid without reducing agents does not extract quantitatively both Co and Li: at  $90^\circ\text{C}$  extraction yields were lower than 50% and 80% for Co and Li, respectively). In presence of a reducing agent Co(III) is reduced to Co(II) and extraction yields arrive to values higher than 90%. Based on these results a factorial design is arranged for  $\text{H}_2\text{SO}_4$  considering the effect of three factors (A: temperature; B: acid concentration; C: glucose stoichiometric excess) (see Table 2 for the complete list of treatments of this factorial design).

Extraction yields in acid-reducing conditions ( $\text{H}_2\text{SO}_4$  plus glucose) are listed in Table 2, while the estimates of significant effects (95% significance level) are reported in Fig. 3. Analysis of variance shows that only temperature (factor A) has a positive effect on all metals (except Fe), while the other factors and their interactions negatively affect metal extractions. For this system acid concentration does not affect negatively Co yield probably because of the lower concentration of acid used ( $2\text{--}2.5 \text{ M}$ ). The lack of significance for glucose effect means that even the lowest investigated concentration is sufficient to extract all target metals requiring a reducing agent.



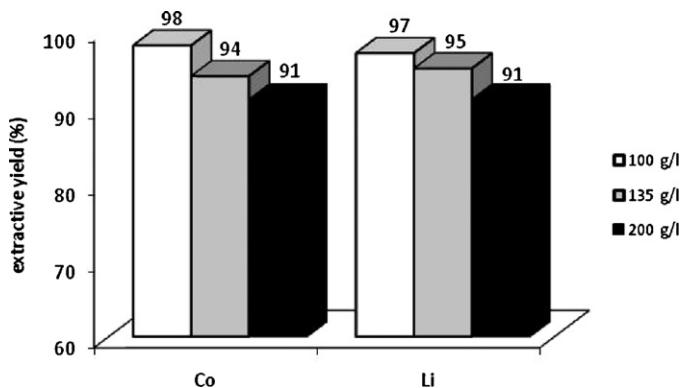
**Fig. 3.** Estimates of significant effect on metal extraction yield (%) for acid reducing leaching with  $\text{H}_2\text{SO}_4$ : (A) temperature; (B)  $\text{H}_2\text{SO}_4$  concentration; (C) reducing agent concentration (Solid–liquid ratio  $100 \text{ g L}^{-1}$ ).

As for the other significant interactions of second and third order it quite hard giving a phenomenological interpretation which would requires further investigation and is beyond the purposes of the work (preliminary optimisation of the operating conditions of leaching process for process analysis).

According to these data, preliminary optimized conditions for acid-reducing leaching are  $90^\circ\text{C}$ ,  $2 \text{ g}$  of  $\text{H}_2\text{SO}_4$  for each gram of solid and 50% of stoichiometric excess of reducing agent. These data confirm the efficiency of carbohydrates as reducing agent in leaching processes, as already verified for the leaching of electrodic powder from alkaline and Zn–C batteries [15].

The effect of solid–liquid ratio (solid concentration) is evaluated performing leaching experiments with sulphuric acid ( $90^\circ\text{C}$ ,  $2 \text{ g}$  of  $\text{H}_2\text{SO}_4$  for each gram of solid and 50% of stoichiometric excess of reducing agent) varying the weight of treated solid. Experimental results reported in Fig. 4 show that increasing the solid concentration from  $100$  to  $200 \text{ g L}^{-1}$  determines a 10% decrease of both cobalt and lithium extractive yields. An explanation of this finding could be that increasing the solid concentration in leaching reactor, stirring can get worsen and then transport phenomena occurring during leaching (species transport in bulk liquid and at the solid–liquid interface) resulted slower. This determines a deceleration of leaching process and then a decrease of the extraction yield at fixed time.

Anyway operating in large scale plants this decrease could be negligible compared with the reduction of leaching reactor volume obtainable by increasing the solid–liquid ratio.



**Fig. 4.** Effect of solid–liquid ratio (leaching conditions:  $90^\circ\text{C}$ ,  $2 \text{ g}$  of  $\text{H}_2\text{SO}_4$  for each gram of solid and 50% of stoichiometric excess of reducing agent).

### 3.3. Primary purification: chemical precipitation

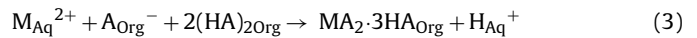
Leach liquor composition obtained in optimized conditions using acid-reducing leaching ( $90^\circ\text{C}$ ,  $2 \text{ g}$  of  $\text{H}_2\text{SO}_4$  for each gram of solid, and 50% of stoichiometric excess of reducing agent) is:  $50 \text{ g L}^{-1}$  of Co,  $10 \text{ g L}^{-1}$  of Li,  $7 \text{ g L}^{-1}$  of Al,  $5 \text{ g L}^{-1}$  of Ni,  $2 \text{ g L}^{-1}$  of Fe,  $3 \text{ g L}^{-1}$  of Cu,  $1.5 \text{ g L}^{-1}$  of Mn. Primary purification (precipitation at pH 5 for NaOH addition) determines the removal of metal impurities and, in particular, complete removal of iron and aluminum, and 60% removal of copper.

Precipitation was performed at this pH as an optimum condition between impurity removal and target metal loss. Increasing pH at 6.5 would have result in significant loss of target metals, while pH 5 is a compromise to eliminate impurities and save Co and Li.

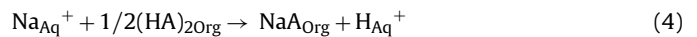
### 3.4. Secondary purification: solvent extraction

Solvent extraction is performed testing the selectivity of two extractants, D2EHPA and CYANEX 272, on leach liquors after primary purification. Solvent extraction operation aims to separate cobalt from nickel in order to recover high purity cobalt products.

Metal extraction occurs according to the following mechanism [19]:



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



The efficiency of metal extraction was evaluated by the distribution coefficient of metal in aqueous and organic phase

$$D_{\text{Co}} = \frac{[\text{Co}]_{\text{org}}}{[\text{Co}]_{\text{aq}}} \quad (5)$$

$$D_{\text{Ni}} = \frac{[\text{Ni}]_{\text{org}}}{[\text{Ni}]_{\text{aq}}} \quad (6)$$

where metal concentration in organic phase is determined by a mass balance considering the residual concentration in aqueous phase.

An index of the extraction selectivity ( $\beta$ ) can be then evaluated considering Ni as the main competitor of Co during solvent extraction

$$\beta = \frac{D_{\text{Co}}}{D_{\text{Ni}}} \quad (7)$$

Experimental results show that for both extractants (D2EHPA and CYANEX 272) the minimum stoichiometric ratio (moles of extractant per moles of cobalt) which is necessary to extract quantitatively cobalt was 4 (Fig. 5a and b). Increasing D2EHPA amount above this value, all the investigated metals are extracted simultaneously, while increasing CYANEX 272 nickel starts to be significantly extracted only after cobalt extraction is complete. This result denotes the higher selectivity of CYANEX 272 for Co with respect to D2EHPA, as confirmed by the trend of the selectivity coefficient reported in Fig. 6a.

As for the effect of pH (fixing the stoichiometric ratio at 4 and then working at  $O/A=4$ ) optimal pH value to have a quantitative extraction of cobalt was 6 for both extractants (Fig. 7a and b). Further increase of pH determines Co and Ni precipitation. Analyzing the selectivity coefficient versus pH (Fig. 6b) it is evident that CYANEX 272 is significantly better than D2EHPA for Co–Ni separation.

Stripping tests are performed to re-extract cobalt in aqueous phase. Experimental results show that cobalt can be quantitatively

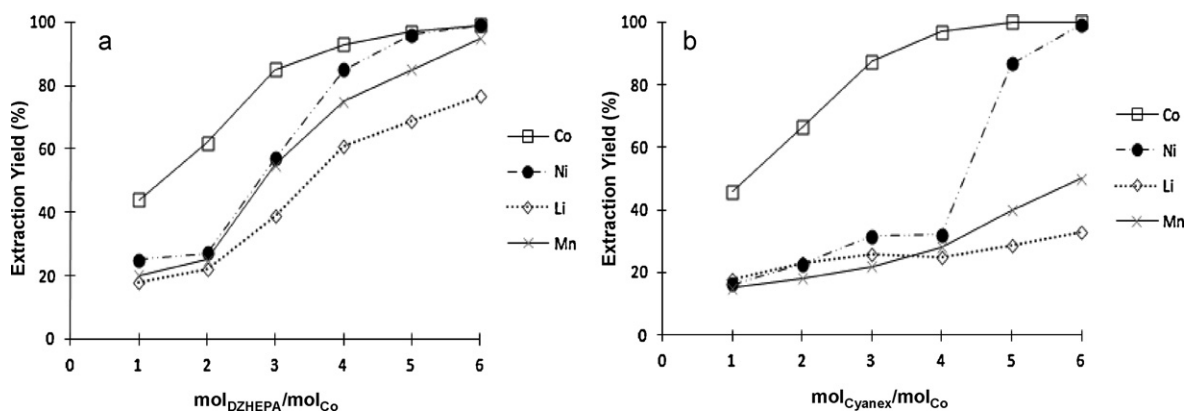


Fig. 5. Effect of stoichiometry on the extraction with D2EHPA (a) and Cyanex 272 (b) at pH 5.5.

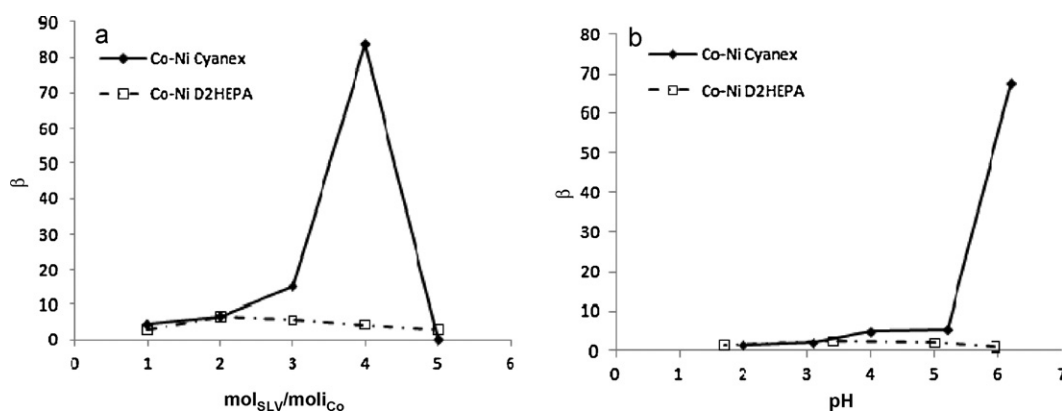


Fig. 6. Selectivity index for Ni–Co separation versus stoichiometry (a) and versus pH (b).

re-extracted by using 4 M  $\text{H}_2\text{SO}_4$  solution ( $O/A=1$ ) (these conditions were chosen in order to maximise Co recovery: other results not reported here showed that using lower acid concentration (2 M) the stripped Co was only 70%).

### 3.5. Cobalt recovery

Cobalt is recovered as carbonate (98% yield) from both solutions (primary and secondary purification). Co carbonate recovered after secondary purification has a cobalt content of about 47% (w/w), while carbonate recovered after primary purification had 36–37% (w/w) Co content. These data show that only performing solvent

extraction it is possible to have a product satisfying the commercial standard required for this chemical (45–47%, w/w of Co content).

### 3.6. Lithium recovery

Lithium is recovered as carbonate with a yield of 80% and with a purity higher than 98% by evaporation of 80% of water volume.

Evaporation degree was chosen in order to maximise Li recovery and purity. In fact during  $\text{Li}_2\text{CO}_3$  crystallisation also  $\text{Na}_2\text{SO}_4$  (formed during precipitation steps) crystallised too. Hot washing just aims to remove  $\text{Na}_2\text{SO}_4$  but during this operation also small amounts of Li were lost for mass effect. Surpassing 80% determined no significant positive effect on Li recovery but a

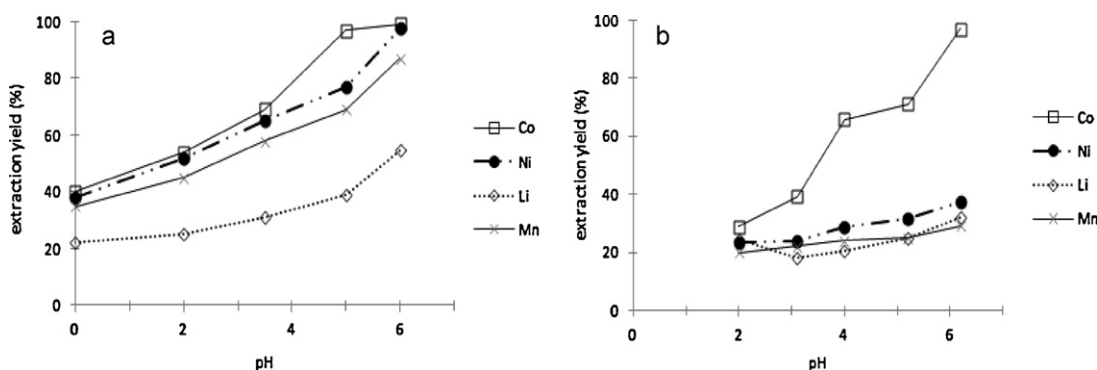


Fig. 7. Solvent extraction: effect of pH on the extraction with D2EHPA (a) and Cyanex 272 (b) (stoichiometric ratio =  $4 \text{ mol}_{\text{SLV}} \text{ mol}_{\text{Co}}^{-1}$ ).

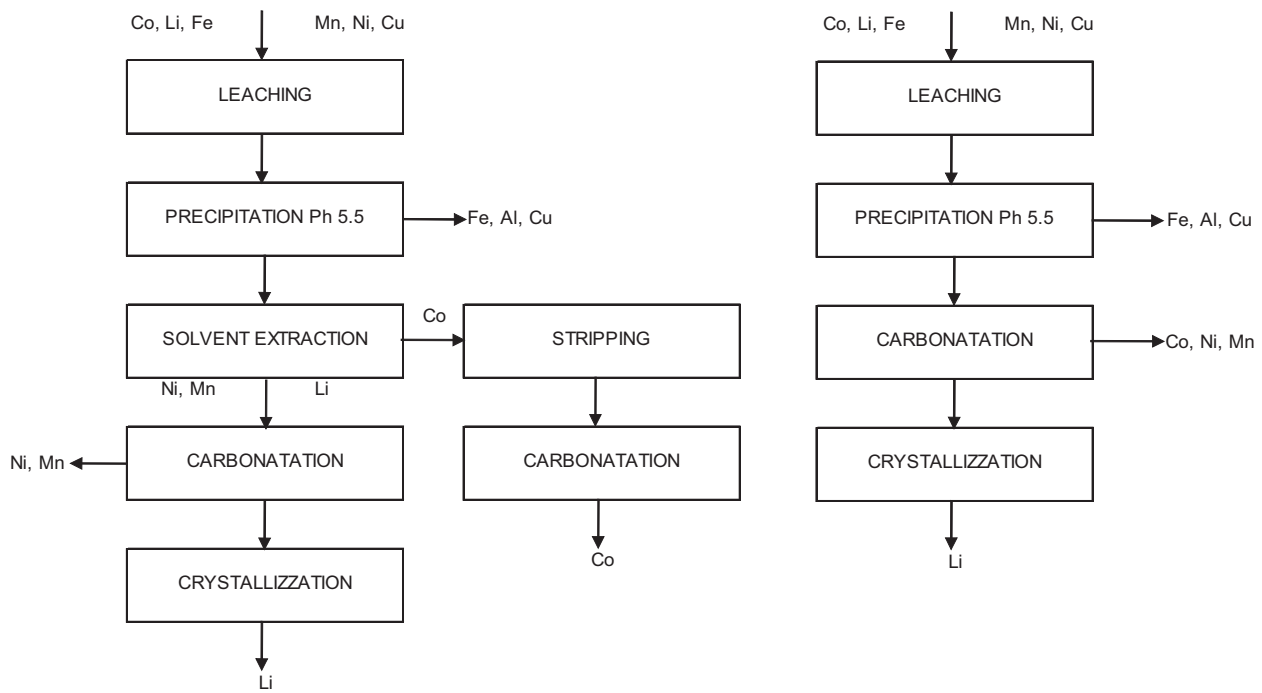


Fig. 8. Simulated flowcharts.

decrease of its purity due to further formation of  $\text{Na}_2\text{SO}_4$  which is difficult to remove by washing without significant loss of Li.

### 3.7. Process simulations

Process simulations consisted in mass and energy balances for the two process routes reported in Fig. 8 which differ for the presence or not of secondary purification by solvent extraction. Simulation were performed by a dedicated software (Super Pro Design) using as input data the lab-scale results obtained for leaching, purification (only primary or both primary and secondary) and recovery operations as detailed before. In particular yields of operation (leaching, purifications, product recovery), consumption of chemicals, energy requirements, and operation scheduling are estimated for each units according to experimental data reported above. Other economic parameters (cost of materials, utilities, waste treatment, process potentiality, equipment characteristics) are fixed as reported in Table 3. Cost of raw materials is taken from sellers, while the selling prices of high purity products ( $\text{CoCO}_3$

and  $\text{Li}_2\text{CO}_3$ ) are taken from the international market of chemicals (Table 3). Costs of the mechanical pre-treatment section are not included in simulations and then they should be used only for comparison among the two different process routes considered here (with and without solvent extraction).

Once all input parameters have been chosen, mass and energy balances are obtained for the two process options along with other technical (equipment size and chemical and energy consumption) and economical outputs such as

- total capital investment,
- operating costs,
- total revenues
- gross margin (%) =  $(\text{total revenues} - \text{operating cost}) / \text{total revenues} \times 100$
- payback time (the time necessary to balance the investment by the total revenues)

Simulations are performed considering

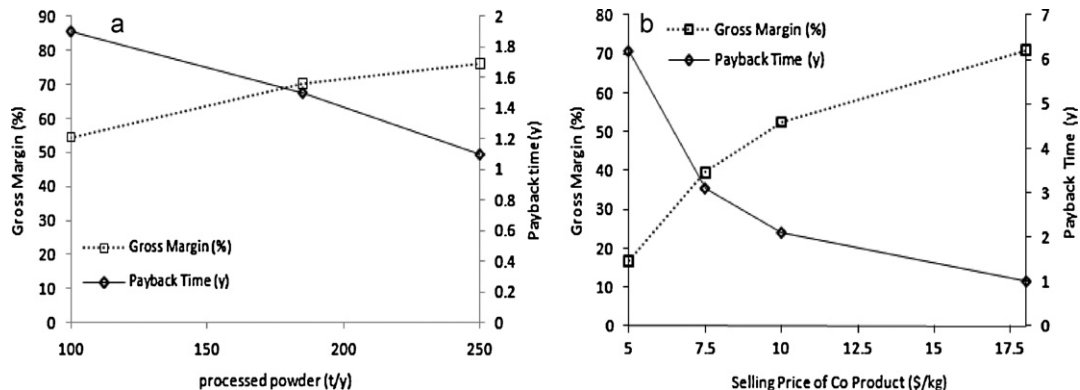


Fig. 9. Main economical results for the process analysis with solvent extraction (a) and without solvent extraction (b) for several sell prices of  $\text{CoCO}_3$  (input flowrate:  $250\text{t y}^{-1}$ ).

**Table 3**  
Main inputs and outputs of process simulations.

	Amount purchased or sold (t $y^{-1}$ )	Costs for process with solvent extraction (\$)	Costs for process without solvent extraction (\$)
Processed powder	100–250	500 t $^{-1}$	500 t $^{-1}$
Cobalt carbonate selling price	110–560	45,000 t $^{-1}$	5000–18,000 t $^{-1}$
Lithium carbonate selling price	18–50	5000 t $^{-1}$	5000 t $^{-1}$
Solvent purchasing price	1.5–3.2	35,000 t $^{-1}$	–
Sulphuric acid purchasing price	180–500	70 t $^{-1}$	70 t $^{-1}$
Sodium carbonate purchasing price	100–275	50 t $^{-1}$	50 t $^{-1}$
Water	265–675	20 t $^{-1}$	20 t $^{-1}$
Electricity		0.20 kWh $^{-1}$	0.20 kWh $^{-1}$
Wastewater treatment		50 t $^{-1}$	50 t $^{-1}$
Solid waste and sludge disposal	40–120	100 t $^{-1}$	100 t $^{-1}$
Total operating cost		1,542,000–2,127,000 y $^{-1}$	1,301,000–1,550,000 y $^{-1}$
Total equipments		2,300,000–4,000,000	1,500,000–2,300,000
Total capital investment		2,500,000–4,500,000	1,500,000–2,500,000

**Table 4**  
Process simulations for the option without solvent extraction.

Processed powder (t y $^{-1}$ )	CoCO $_3$ selling price (\$ kg $^{-1}$ )	Total capital investment (\$)	Operating costs (\$ y $^{-1}$ )	Total revenues (\$ y $^{-1}$ )	Gross margin (%)	Return of investment (%)	Payback time (y)
100	7.5	1,687,000	1,301,000	1,025,000	–	–	12
185	7.5	2,398,000	1,480,000	1,896,000	22	19.1	5.2
250	7.5	2,570,000	1,550,000	2,562,000	39.5	39.5	3.1
100	10	1,687,000	1,301,000	1,305,000	3.0	8.7	8.7
185	10	2,398,000	1,480,000	2,414,000	38.7	32.1	3.1
250	10	2,570,000	1,550,000	3,262,000	52.5	48.7	2.1
100	18	1,687,000	1,301,000	2,200,000	40.9	40.6	2.4
185	18	2,400,000	1,480,000	4,070,000	63.4	73.2	1.4
250	18	2,570,000	1,550,000	5,500,000	71.5	100	1.0

- the effect of the input flow rate for both processes (with and without solvent extraction)
- the effect of the selling price of low purity CoCO $_3$  obtained without solvent extraction.

As for the first point: simulations are performed for different input flow rate in order to understand the minimum amount of waste which should be processed to have a feasible process. Input amounts are based on real amounts of spent batteries which were collected in Italy in 2008. In particular, the chosen amount 100, 185 and 250 t y $^{-1}$  of input material correspond to the 20, 37 and 50% of the total collected wastes, respectively. Input material of the leaching section is about 50% in weight of the initial waste before physical pretreatment (experimental data not reported here).

As for the second point: since the international market of chemicals does not give any selling price for low purity CoCO $_3$  obtained without solvent extraction, several simulations are carried out for different selling prices of this product (from 10 to 18 \$ kg $^{-1}$ ). The aim of these simulations is to understand for which selling price of low purity CoCO $_3$ , the processes with and without solvent extraction give the same economical outputs (i.e. gross margin and payback time).

Process simulations show that for both processes the economical benefits (gross margin and payback time) are proportional to the input flow rate of treated wastes (see Fig. 9a for the process with solvent extraction and data reported in Table 4 for the process without solvent extraction). The diffusion of this kind of plants can be then favored by promoting collection strategies.

Process simulations also show that the total investment for the process including solvent extraction is significantly higher than that without solvent extraction (Table 3).

As for the effect of selling price of low purity CoCO $_3$ , fixing this price at 18 \$ kg $^{-1}$  and feeding the hydrometallurgical section with at least 250 t y $^{-1}$  of electrodic powder both processes reach the same economical benefits (see gross margin and payback time obtained in these conditions for both processes in Fig. 9).

If either the selling price of low purity CoCO $_3$  or the input flow rate of wastes decrease (i.e. price < 18 \$ kg $^{-1}$  or feed flow rate < 250 t y $^{-1}$ ), the economical outputs without solvent extraction become worst than those with solvent extraction.

#### 4. Conclusions

In this paper two hydrometallurgical processes to recover lithium and cobalt from lithium ion batteries were analyzed. Co and Li were extracted from an input material coming from a large scale mechanical route of pre-treatment of a recycling plant in the Northern Italy. This powder was successfully leached using 2 g g $^{-1}$  of sulphuric acid in the presence of an excess of 50% of a reducing agent as glucose, which could be also a waste of food factory. Iron, aluminum and copper (partially) were removed by precipitation as hydroxides at pH 5.0. When solvent extraction was performed high purity cobalt carbonate (47%, w/w of cobalt) was obtained by precipitation. Performing the same operation without solvent extraction a product containing 36–37% (w/w) of Co was obtained. Lithium was recovered by crystallization (yield 80%) with 98% purity. Solvent extraction allows to obtain high purity products but this operation is one of the most expensive in hydrometallurgical processes. Process simulations showed that, for the same input flow rate, process with solvent extraction gives economical outputs (gross margin and payback time) which are better than those for the process without solvent extraction. Processes present the same economical indices for a feed flow rate of at least 250 t y $^{-1}$  if low purity cobalt carbonate (produced without solvent extraction) could be sold at 18 \$ kg $^{-1}$ .

#### References

- [1] A.M. Bernardes, D.C.R. Espinosa, J.A.S. Tenório, J. Power Sources 130 (2004) 291–298.
- [2] P.V.D. Bossche, The Current Legislative Development in the EU Waste Policy: Challenge or Opportunities for Metal Industry, Cobalt Development Institute, January 2006.



- [3] S.M. Shin, N.H. Kim, J.S. Sohn, D.H. Yang, Y.H. Kim, *Hydrometallurgy* 79 (2005) 172–181.
- [4] G. Dorella, M.B. Mansur, *J. Power Sources* 170 (2007) 210–215.
- [5] B. Swain, J. Jeong, J.C. Lee, G.H. Lee, J.S. Sohn, *J. Power Sources* 167 (2007) 536–544.
- [6] D.A. Ferreira, L.M. Zimmer Prados, D. Majuste, M.B. Mansur, *J. Power Sources* 187 (2009) 238–246.
- [7] L. Li, J. Ge, F. Wu, R. Chen, S. Chen, B. Wu, *J. Hazard. Mater.* 176 (2010) 288–293.
- [8] J.S. Sohn, D.H. Yang, S.M. Shin, N.H. Kim, H.T. Sohn, in: K.I. Rhee, J.K. Oh (Eds.), *Proceedings of the International Symposium on Green Technology for Resources and Material Recycling*, 24–27 November, Seoul, Korea, 2004, pp. 316–320.
- [9] P. Zhang, T. Yokoyama, O. Itabashi, T.M. Suzuki, K. Inoue, *Hydrometallurgy* 47 (1998) 259–271.
- [10] M. Contestabile, S. Panero, B. Scrosati, *J. Power Sources* 92 (2001) 65–69.
- [11] S. Castillo, F. Ansart, C. Laberty-Robert, J. Portal, *J. Power Sources* 112 (2002) 247–254.
- [12] J.F. Paulino, N.G. Busnardo, J.C. Afonso, *J. Hazard. Mater.* 150 (2008) 843–849.
- [13] C.K. Lee, K.I. Rhee, *Hydrometallurgy* 68 (2003) 5–10.
- [14] J. Nan, D. Han, X. Zuo, *J. Power Sources* 152 (2005) 278–284.
- [15] G. Furlani, E. Moscardini, F. Pagnanelli, F. Ferella, F. Vegliò, L. Toro, *Hydrometallurgy* 99 (2009) 115–118.
- [16] D.C. Montgomery, *Design and Analysis of Experiments*, 4th edition, John Wiley & Sons, New York, 1997.
- [17] K. Sarangi, B.R. Reddy, R.P. Das, *Hydrometallurgy* 52 (3) (1999) 253–265.
- [18] S.K. Sahu, A. Agrawal, B.D. Pandey, V. Kumar, *Miner. Eng.* 17 (2004) 949–951.
- [19] B. Swain, J. Jeonga, J.C. Lee, G.H. Lee, *Sep. Purif. Technol.* 63 (2008) 360–369.