

Article

Synthesis of Lithium Fluoride from Spent Lithium Ion Batteries

Daniela S. Suarez, Eliana G. Pinna, Gustavo D. Rosales and Mario H. Rodriguez *

Laboratorio de Metalurgia Extractiva y Síntesis de Materiales (MESiMat), Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Cuyo, Mendoza 5500, Argentina; martu2001@hotmail.com (D.S.S.); guadapinna@yahoo.com.ar (E.G.P.); gd_rosales@hotmail.com (G.D.R.)

* Correspondence: mrodriguez@uncu.edu.ar; Tel.: +54-9261-337-9329

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Abstract: Lithium (Li) is considered a strategic element whose use has significantly expanded. Its current high demand is due to its use in lithium ion batteries for portable electronic devices, whose manufacture and market are extensively growing every day. These days there is a great concern about the final disposal of these batteries. Therefore, the possibility of developing new methodologies to recycle their components is of great importance, both commercially and environmentally. This paper presents results regarding important operational variables for the dissolution of the lithium and cobalt mixed-oxide (LiCoO_2) cathodes from spent lithium ion batteries (LIBs) with hydrofluoric acid. The recovery and synthesis of Co and Li compounds were also investigated. The dissolution parameters studied were: temperature, reaction time, solid-liquid ratio, stirring speed, and concentration of HF. The investigated recovery parameters included: pH, temperature, and time with and without stirring. The final precipitation of lithium fluoride was also examined. The results indicate that an increase in the HF concentration, temperature, and reaction time favors the leaching reaction of the LiCoO_2 . Dissolutions were close to 60%, at 75 °C and 120 min with a HF concentration of 25% (v/v). The recovery of Co and Li were 98% and 80%, respectively, with purities higher than 94%. Co and Li compounds, such as Co_3O_4 and LiF, were synthesized. Furthermore, it was possible to almost completely eliminate the F^- ions as CaF_2 .

Keywords: LiF; cobalt; lithium; lithium ion batteries; LIBs

1. Introduction

Cobalt is widely dispersed in nature, however, commercially important sources are cobalt arsenides, oxides, and sulfides. There are several methods to extract cobalt, usually to separate it from copper and nickel. One traditional method produces a concentrate from cobalt ore. After roasting, the metal concentrates are converted to sulfate, removing the copper, aluminum, nickel, zinc, and iron via chemical precipitation. Finally, cobalt metal can also be recovered by electrowinning. Cobalt is a metal used in numerous commercial, industrial, and military applications. For example, superalloys are employed to make parts for gas turbine engines, cemented carbides, and diamond tools. Additionally, cobalt is used for manufacturing animal feed additives; producing catalysts for chemical, petroleum, and other industries; drying agents for inks, paints, and varnishes; dyes and pigments; glass decolorizers; ground coats for porcelain enamels; humidity indicators; magnetic recording media; rubber adhesion promoters for steel-belted radial tires; and vitamin B12 [1,2].

Lithium is present in many minerals, spring waters, and especially in salars. Spodumene [$\text{LiAl}(\text{SiO}_3)_2$] is the main source of Li, but since the exploitation of salars to extract the metal grows, other minerals, such as petalite [$\text{LiAl}(\text{Si}_4\text{O}_{10})$] and lepidolite [$\text{K}(\text{Li},\text{Al},\text{Rb})_4\text{O}_{10}$], are being used [1,3]. Industrially, Li is obtained by electrolysis of molten LiCl (with a melting point of 613 °C) or from

a mixture of LiCl and KCl 45–55% (with a melting point at 450 °C) [4]. This metal has a wide variety of industrial applications, such as in the production of lubricants and special alloys, manufacture of glass and ceramic materials, and in the development of psychiatric medications, among others.

Today, the main industrial applications of Li together with Co are as components of batteries in mobile phones, laptops, watches, pacemakers, etc., as well as in electric and hybrid cars [3,4].

Taking into account that the average life of lithium ion batteries (LIB) is about two years, and that their market is rapidly growing, it is easy to predict that they will soon become a serious environmental problem unless proper actions are taken, regarding the disposal of electronic waste [5,6].

Therefore, we believe that the recycling of spent lithium ion batteries (LIBs) is a matter of major importance, not only because of the presence of flammable and toxic elements in them, but also due to the possibility of economic and environmental benefits which can be achieved from the recovery of their main components [7,8].

The technical literature contains many papers related to the recycling of the materials that compose batteries, either by using physical or chemical methods [9]. Physical treatments are generally used to separate the LiCoO_2 which adheres to the cathode surface. Later, oxides are subjected to a chemical procedure that allows the recovery of the components. Among the physical processes used, mechanical and thermal separation may be included, as well as the dissolution of the adhesive which joins the oxide to the film. The chemical processes, as mentioned above, are used to solubilize and/or to recover metals contained in the LiCoO_2 . These methods can be pyro- and/or hydrometallurgical [9]. Regarding the latter, LiCoO_2 leaching of spent batteries has been done by using both organic and inorganic acids, such as citric acid, malic acid, aspartic acid, H_2SO_4 , HCl , HNO_3 , H_2SO_3 , and H_3PO_4 , as leaching agents. Experimental results have indicated that most Co dissolution is achieved with HCl . Moreover, increasing the temperatures and concentrations of the leaching agent promote the recoveries of Li and/or Co independently of the acid [10–17]. In addition, the effect of the reducing agent (H_2O_2) on the dissolution of LiCoO_2 (from LIBs) with the inorganic acids, such as HNO_3 , H_3PO_4 , and H_2SO_4 , were studied in other investigations [17–25]. Lee and Rhee reported extraction values over 93% for cobalt and lithium, when working with $\text{HNO}_3\text{--H}_2\text{O}_2$ [18], whereas Dorella and Mansur used H_2SO_4 and obtained leaching values of around 95% for lithium and 80% for cobalt [23]. Pinna et al. obtained dissolutions of the mixed lithium cobalt oxide of nearly 100% working with $\text{H}_3\text{PO}_4/\text{H}_2\text{O}_2$ [17]. Zhang et al. studied the use of chemical agents that produce leaching and reduction at the same time and, working with H_2SO_3 , achieved lithium and cobalt dissolutions of about 60% [14], while when working with HCl , the dissolution of both metals were close to 99%.

In the literature, there are several studies in which the Co is precipitated as hydroxide, using sodium or ammonium hydroxide [8,10,20,26], and as cobalt oxalate, employing sodium or ammonium oxalate [17,21,27,28]. In addition, some studies report the recovery of Li from LIBs as carbonate [8,14,21,29] using $\text{Na}_2\text{CO}_{3(s)}$ or $\text{CO}_{2(g)}$ as the precipitating agent to obtain, in both cases, $\text{Li}_2\text{CO}_{3(s)}$ [30,31].

One of the most commonly used lithium salts is LiF , which is utilized as a flux in ceramics and glass industry, as well as in light metal welding [4,32]. It is also used in the manufacture of optical components for analytical equipment (IR and UV spectroscopy). More recently, it has been employed in the fabrication of new cathodes for Li batteries, e.g., LiF-Fe [33]. A potentially important use of LiF is represented by atomic fusion, where it would be employed as a source of ^6Li isotopes [34,35].

The industrial process to manufacture LiF is carried out by preparing a concentrated solution of a lithium salt, e.g., Li_2CO_3 , obtained from brines or rock deposits through well-known industrial processes [4,12,21]. This lithium-containing solution is then treated with fluorine salts or HF to obtain LiF as the final product.

In order to avoid the reprocessing of Li salts when obtaining LiF , research was carried out through a direct process using LIBs as a raw material. The objectives of this work were to study the influence of operational parameters on the dissolution of LiCoO_2 with HF (in a closed vessel) and to synthesize

Co_3O_4 and LiF . Furthermore, a new process for their synthesis was developed, taking into account environmental and economic benefits.

2. Materials and Methods

The leaching reagent used was analytical-grade HF.

A sample of LiCoO_2 was obtained from the cathodes of spent lithium ion batteries from mobile phones of different brands. These batteries were dismantled manually, the cathode was separated, and the LiCoO_2 was removed from the aluminum film by scraping.

Characterization of the sample was performed by X-ray diffraction (XRD) with a Rigaku D-Max III C diffractometer (Osaka, Japan), operated at 35 kV and 30 mA using $\text{K}\alpha$ radiation of Cu and Ni filter at $\lambda = 0.15418$ nm. Morphological analysis was done by SEM in a LEO 1450 VP (Zeiss, Jena, Germany).

The XRD and SEM characterization of the cathode material are shown in Figure 1a,b, respectively. Determination of cobalt and lithium content in the LIBs was performed by atomic absorption spectroscopy (AAS) using a Varian SpectrAA 55 spectrometer (Palo Alto, CA, USA) with a hollow cathode lamp (analytical error 1.5%). The quantitative composition of the sample was 6.7% Li and 40.1% Co, expressed in mass percentage.

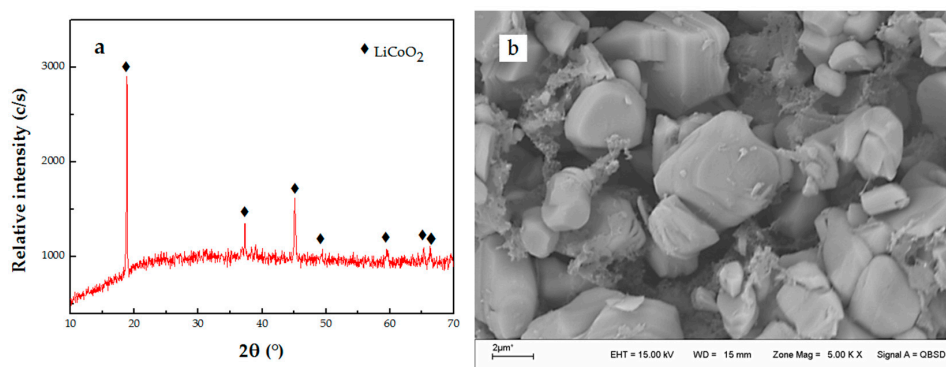


Figure 1. (a) XRD and (b) SEM of LiCoO_2 from cathodes of LIBs.

The diffractogram in Figure 1a shows that the cathode contains lithium cobalt oxide (JCPDS 01-075-0532). The micrograph of Figure 1b shows that LiCoO_2 particles have irregular shapes with rounded edges.

2.1. Leaching Assays

The leaching tests were performed in a closed vessel of 500 mL capacity, constructed of polyvinyl chloride (PVC), immersed in a thermostatic bath, fitted with a mechanical stirrer and temperature control. The operational variables studied were temperature, reaction time, stirring speed, solid-liquid ratio and leaching agent concentration. The dissolution reaction was calculated by the expression:

$$X(\%) = \frac{m_0 - m_r}{m_0} \times 100 \quad (1)$$

where X is the conversion; m_0 is the initial mass of LiCoO_2 , and m_r is the mass of LiCoO_2 unreacted after the reaction [17,34]. Each experiment was replicated three times. The average conversion efficiency is presented in the experimental results.

2.2. Recovery Assays

In the tests of separation and synthesis, the cobalt solution was prepared by dissolving LiCoO_2 with HF, using the best leaching conditions determined in Section 3.1. The operating parameters studied were pH, temperature, and reaction time, with and without stirring.

The recovery of Li from the resulting solution, after the precipitation of Co, can be carried out by several known methods. In this case, lithium was precipitated as LiF, evaporating the solvents above the solubility product constant (K_{sp}) of LiF [30,36,37]. Finally, the resulting solutions were stored to eliminate the content of F^- ions.

Lithium and cobalt were analyzed by atomic absorption spectroscopy to calculate the recovery percentage in all of the experiments:

$$R(\%) = \frac{E_s}{E_m} \times 100 \quad (2)$$

where E_m is the initial amount of each element in the sample and E_s is the quantity of each element in the leach liquor obtained after precipitation.

3. Results

3.1. Dissolution of $LiCoO_2$ with HF

The following reaction was proposed as the most probable for the dissolution of $LiCoO_2$ with HF:



3.1.1. Effect of the Leaching Temperature

Figure 2 shows the effect of temperature on the dissolution of $LiCoO_2$ with HF at a concentration of 15% (v/v), a solid-liquid ratio 2% (w/v), reaction time of 120 min, and a stirring speed of 330 rpm. The temperature range tested was between 25 °C and 95 °C.

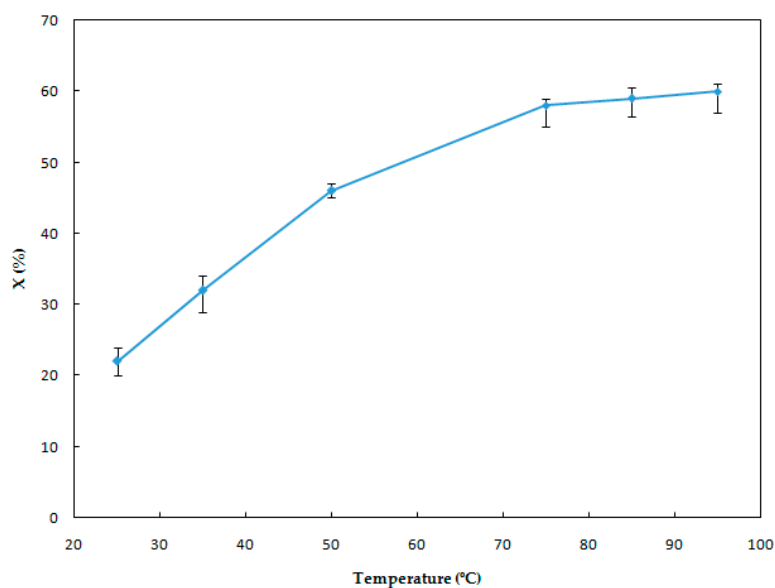


Figure 2. Effect of temperature on the dissolution of $LiCoO_2$.

Figure 2 indicates that the dissolution of $LiCoO_2$ increases while increasing the temperature, which agrees with the known fact that, in solid-liquid heterogeneous reactions, a rise in temperature causes an increase in the reactivity of the solids [38,39]. The maximum value of $LiCoO_2$ dissolution was obtained at 95 °C, but 75 °C was selected as the best for studying other operational parameters. In addition, in this working range, a plateau was verified in the dissolution of the oxide between 75 °C and 95 °C.

3.1.2. Effect of HF Concentration

Tested HF concentrations were 5%, 10%, 15%, 20%, and 25% (*v/v*) with the other variables held constant: temperature, 75 °C; reaction time, 120 min; solid-liquid ratio, 2% (*w/v*); stirring speed, 330 rpm. Figure 3 shows the dissolution values obtained.

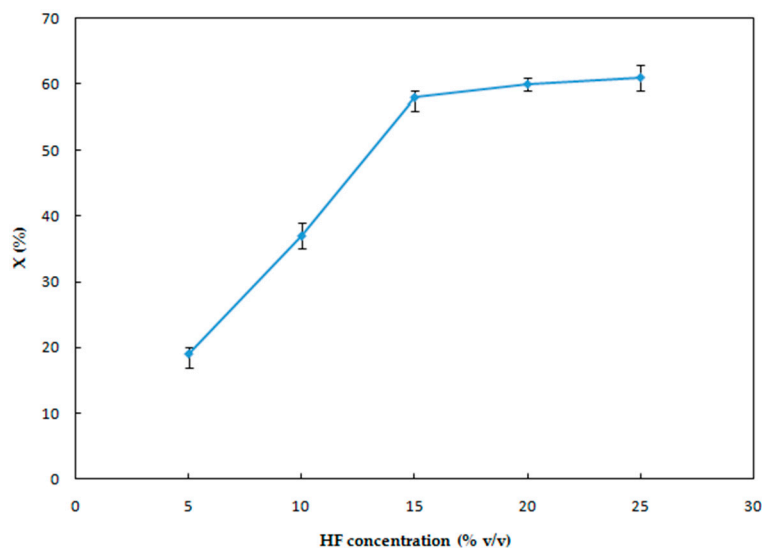


Figure 3. Effect of HF concentration on the dissolution of LiCoO₂.

The results in Figure 3 show that when leaching agent concentration (HF solution) increases so does the dissolution of the mixed oxide up to a HF concentration of 15% (*v/v*); after that, a plateau is observed in the dissolution value. This is because increasing the leaching agent concentration gives rise to a larger amount of F[−] and H⁺ ions, available to react with LiCoO₂. From these results, the optimum HF concentration was selected to be 15% (*v/v*), which was used for the rest of the assays, although the maximum dissolution value for the oxide (61%) was achieved by working with HF 25% (*v/v*).

3.1.3. Effect of Reaction Time

Figure 4 shows the dissolution values obtained at 75 °C, a HF concentration of 15% (*v/v*), a solid-liquid ratio of 2% (*w/v*) and stirring speed of 330 rpm. The reaction time range tested was 5–240 min.

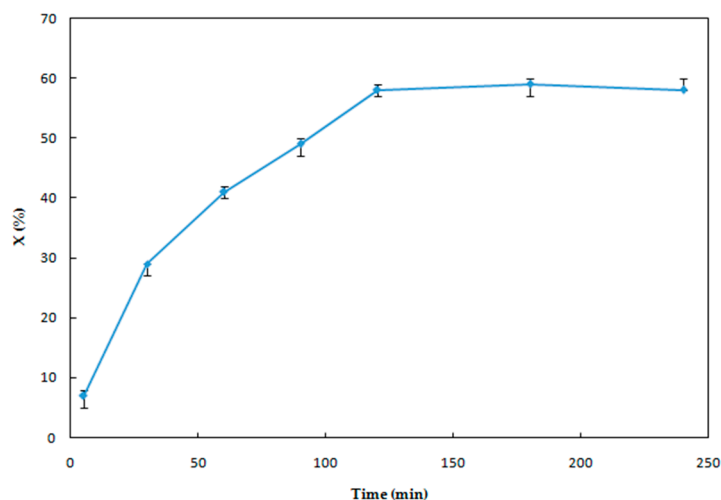


Figure 4. Effect of reaction time on the dissolution of LiCoO₂.

In Figure 4 it can be observed that an increase in the reaction time led to an increase in the dissolution of the LiCoO_2 . That is, the increase in the contact time between the reactants led to an increase in the dissolution of the solid, which is consistent with the literature [38,39]. It is worth noting that after 120 min of reaction, the LiCoO_2 dissolution remained constant (plateau of the figure), which is why this value was selected for the study of the other operational parameters.

3.1.4. Effect of Stirring Speed

The effect of the stirring speed on the dissolution of LiCoO_2 was tested between 110 rpm and 550 rpm, and the other variables were kept constant: temperature, 25 °C; reaction time, 120 min; solid-liquid ratio, 2% (w/v), and HF concentration, 15% (v/v). Figure 5 shows the dissolution values obtained.

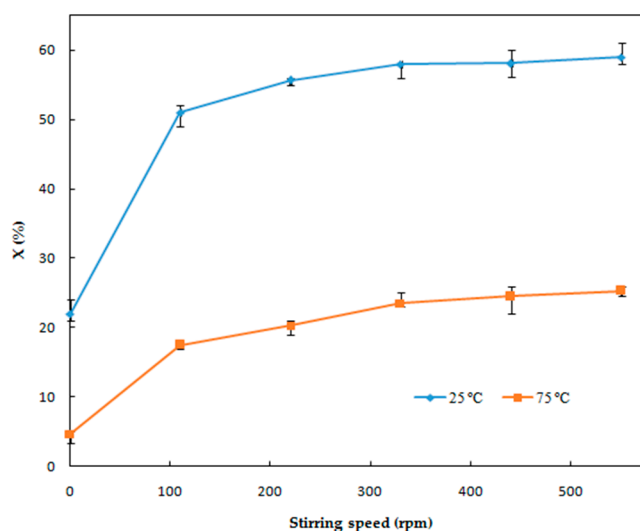


Figure 5. Effect of stirring speed on the dissolution of LiCoO_2 .

Figure 5 shows that, below 300 rpm, the stirring speed affects the dissolution rate of the LiCoO_2 , these results are more remarkable at higher temperatures, which would indicate that the reaction has diffusion control. Above 300 rpm, the stirring speed slightly affects the leaching rate. The latter is because the film thickness around the solid, through which the HF must flow in order for the solid to make contact and react, does not change when increasing the stirring speed. This suggests that HF transfers from the bulk of the solution to the solid, through the boundary layer, and plateaus at a maximum stirring speed. Therefore, the film thickness is minimal. These results would indicate that there is not a diffusive control over the global dissolution rate of the process due to the film thickness.

3.1.5. Effect of Solid-Liquid Ratio

Figure 6 shows the dissolution values obtained at 75 °C, HF concentration of 15% (v/v), stirring speed of 330 rpm, and a reaction time 120 min. The solid-liquid ratio range tested was between 1% and 5% (w/v).

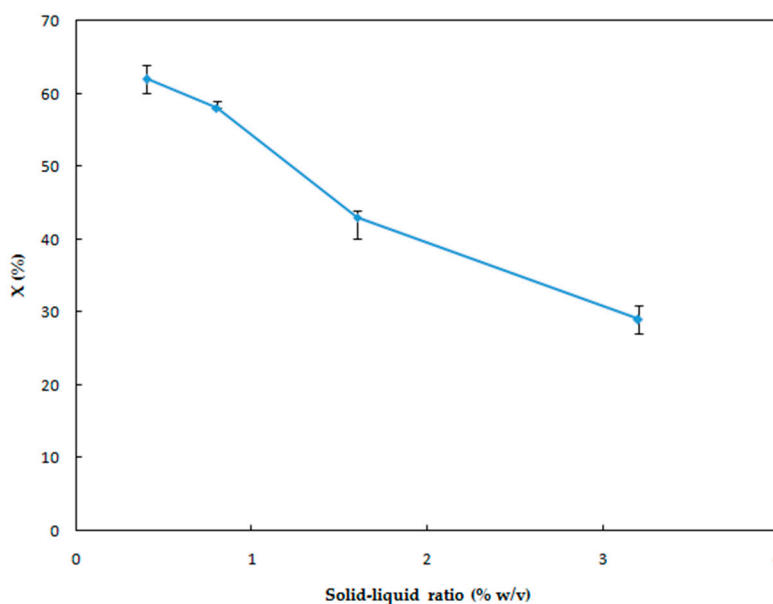


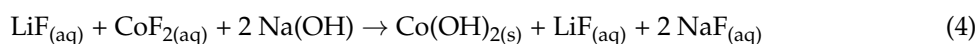
Figure 6. Effect of solid-liquid ratio on the dissolution of LiCoO₂.

Figure 6 shows that a decrease in the solid-liquid ratio led to an increase in the dissolution of the LiCoO₂. Data obtained from this figure displays that, for the solid-liquid ratio of 1% (*w/v*), the dissolution of LiCoO₂ is high, and it begins to decrease with the further increase in the solid-liquid ratio. This is due to the fact that, for a fixed concentration of HF acid, there is more acid available to react with the LiCoO₂ at a lower solid-liquid ratio.

3.2. Recovery of Co and Li

3.2.1. Recovery of Co

The following reaction was proposed as the most probable for the precipitation of Co(OH)₂:



The effects of pH, temperature, and reaction time on the precipitation reaction of Co were studied. After reaching the desired agitation value, the stirring was stopped, and the obtained solid was filtered. In the resulting solutions, cobalt concentrations were determined, and then the solid was dried in an oven at 120 °C for 2 h for further characterization.

Effect of pH

Several aliquots of 25 mL were taken from the solution and were kept with constant stirring at 110 rpm and without stirring, for two minutes of reaction time. The pH range studied was between 2 and 12 using 2 M NaOH solution. Figure 7 shows the results of the effect of pH changes on the precipitation reaction of Co, indicating that the increase in pH led to an increase in the formation of Co(OH)_{2(s)}, which agrees with the literature that reports the formation of such solids at an alkaline pH. The maximum recovery value of Co(OH)_{2(s)} occurred at pH = 9 and 10 with and without stirring, respectively. This slight difference between the pH values at which the maximum recovery of Co is obtained could be due to the agitation, which accelerates the mixing of the reactants and, thus, the precipitation of Co(OH)₂.

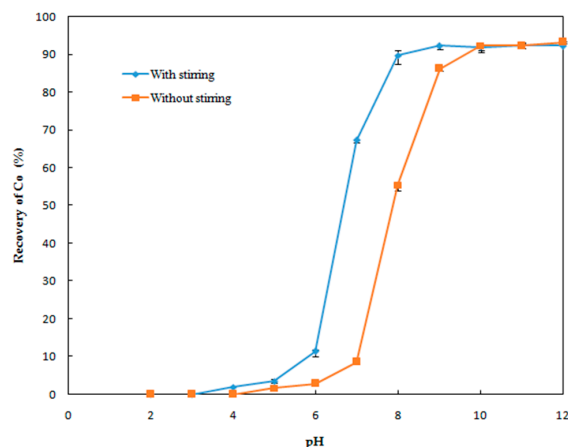


Figure 7. Effect of pH on the recovery of Co.

Effect of Temperature

Figure 8 shows the effect of temperature on the precipitation of Co for several aliquots of 25 mL of the solution, each one adjusted to pH = 9 or 10 (considered optimum, Section “Effect pH”) with and without stirring, respectively. The reaction system was kept with constant stirring (at 110 rpm) and without stirring, for two minutes of reaction time. The tested temperatures were 25, 35, 50, 60, and 75 °C during two minutes of time reaction. After each test, the obtained precipitate was filtered, and then dried in an oven.

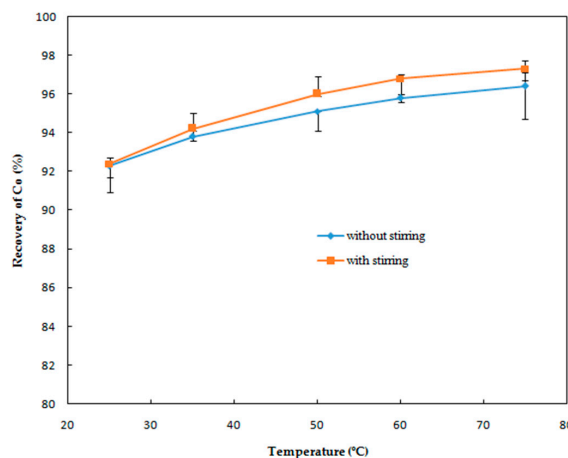


Figure 8. Effect of temperature on the recovery of Co.

From the results in Figure 8, it can be inferred that temperature changes do not have a marked effect on the precipitation reaction of $\text{Co}(\text{OH})_{2(s)}$, given that the slight increase in the recovery of Co when increasing temperature could be explained by taking into account that the solubility of $\text{Co}(\text{OH})_{2(s)}$ ($K_{sp} 1.6 \times 10^{-15}$ at 25 °C) increases when the temperature decreases. This effect is less important when the experiments are agitated, since the stirring increases the solubility and, thereby, decreases the amount of obtained solid.

Effect of Reaction Time

The effect of reaction time on the precipitation of Co was studied using several aliquots of 25 mL of the solution, each of them adjusted to pH = 9 or 10 (considered optimum, with and without stirring, respectively). Stirring speed and temperature were kept constant at 110 rpm at 25 °C and 75 °C. These results are shown in Figure 9, for a time range between 1 min and 60 min.

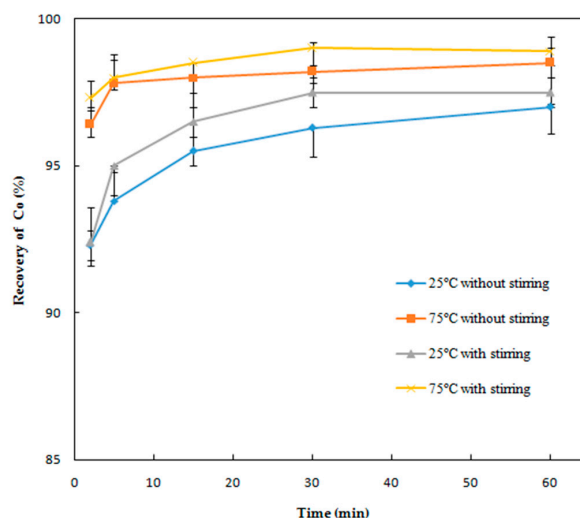


Figure 9. Effect of reaction time on the recovery of Co.

As shown in Figure 9, high recoveries of Co in every tested condition were obtained. In addition, the increase of the reaction time led to an increase in cobalt recovery, and this effect is more marked at 75 °C. For both temperatures, the maximum recovery of $\text{Co}(\text{OH})_2$ is obtained at a reaction time of 30 min. The best results were achieved at 30 min and 60 min with and without stirring, respectively, at 75 °C. Furthermore, increasing the reaction time led to the formation of a solid that was easier and quicker to filter.

Synthesis of Co_3O_4

Synthesis was performed by accumulating the $\text{Co}(\text{OH})_{2(s)}$ obtained in “Effect of pH” and “Effect of Temperature”. This solid was washed five times with 25 mL aliquots of hot doubly-distilled water to remove residual NaOH and impurities. Then the purified $\text{Co}(\text{OH})_{2(s)}$ was dried and calcined at 600 °C for 2 h. Co_3O_4 formation occurs through the following reaction:



In Figure 10 the diffractogram and the SEM micrograph of the obtained solid after calcination are shown. The XRD indicates the presence of Co_3O_4 (ICDD 01-080-1545) and SEM shows particles of this oxide with sharp edges, and different shapes and sizes.

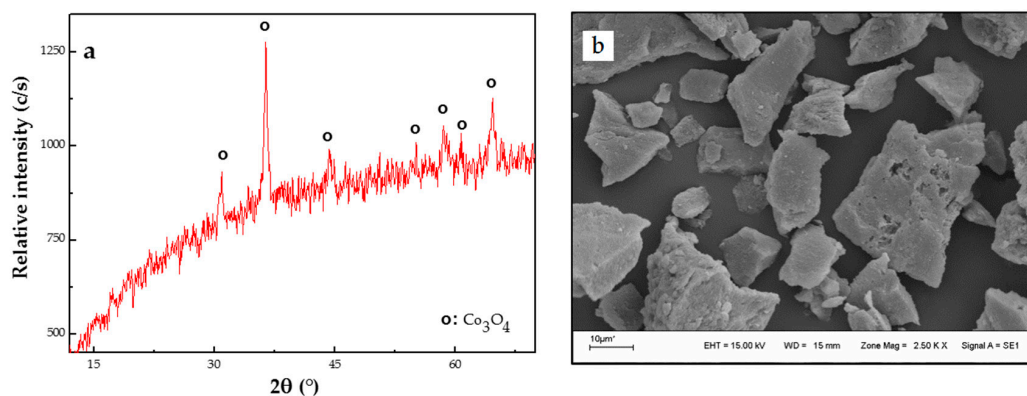


Figure 10. (a) XRD and (b) SEM of the precipitated solid by the addition of NaOH.

3.2.2. Recovery of Li

The liquor obtained after the recovery of Co was evaporated (60 °C) until the appearance of a gelatinous white precipitate. Figures 11 and 12 show the diffractogram and the SEM micrograph of the LiF precipitated, respectively.

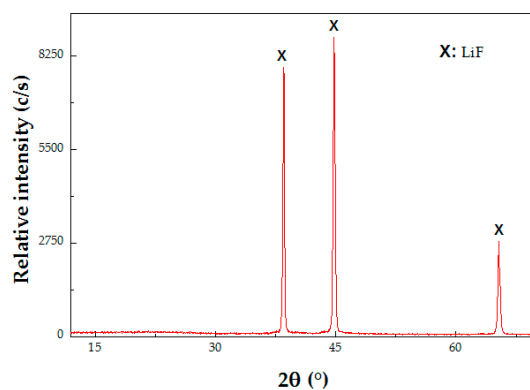


Figure 11. XRD of the precipitated solid by evaporation.

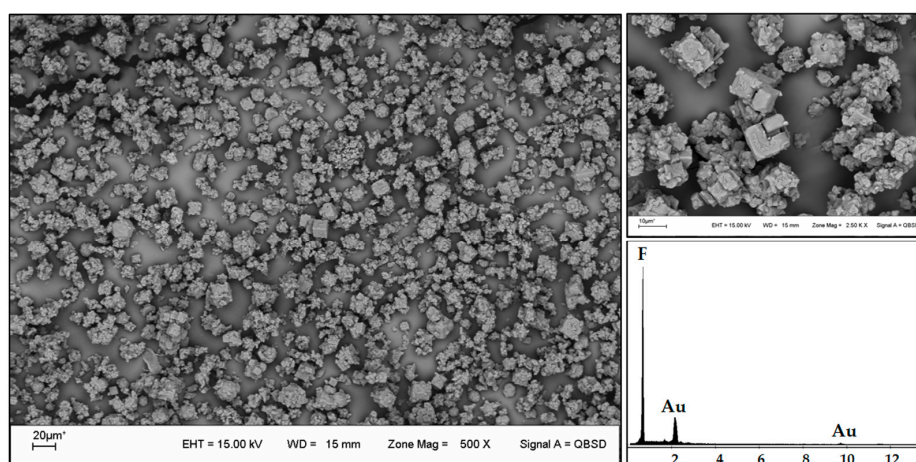


Figure 12. SEM of the precipitated solid by evaporation.

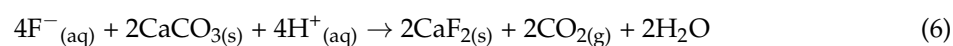
The XRD patterns in Figure 11 present the structure of LiF (ICDD 01-089-3610). Figure 12 exhibits the obtained particles, which have a well-defined crystal structure, coinciding with the cubic shape of LiF particles [36]. Gravimetric analysis showed that the recovery of Li as LiF was close to 80%. EDS analysis indicated that the purity of the LiF precipitate was 98.4 wt % (see Table 1). These results suggest that the solid LiF obtained by this route is of high purity.

Table 1. Purity of LiF.

Purity of LiF (wt %)	Elemental Composition (wt %)						
	Li	F	Na	K	Ca	Al	Others
98.4	26.5	71.9	0.42	0.26	0.08	0.05	0.78

3.3. Elimination of F^- Ion as CaF_2

The precipitation of F^- using $CaCO_3$ produces CaF_2 , which can be used for recycling:



This reaction was carried out using CaCO_3 ; the resulting precipitate was analyzed by XRD (see Figure 13). Figure 13 shows that, with the addition of CaCO_3 (ICDD 96-900-9669), precipitation of the CaF_2 compound (ICDD 96-900-9006) is achieved. By controlling the reaction time, most of the remaining F^- from previous stages can be eliminated.

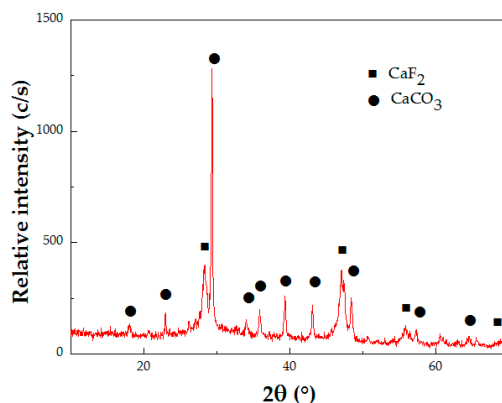


Figure 13. Diffractogram of the solid precipitated by the addition of CaCO_3 .

4. Conclusions

In this work, the effects of the operational parameters on the LiCoO_2 leaching process and on the recovery of Co were studied. The obtained results showed that the increase of temperature, reaction time, and leaching agent concentration (HF) favored the dissolution reaction of LiCoO_2 . The optimum value of dissolution was 58%, which was obtained working under the following conditions: temperature, 75 °C; HF concentration, 15% (v/v); reaction time, 120 min; solid-liquid ratio, 2% (w/v) and stirring speed, 330 rpm. The recovery of Co and Li as Co_3O_4 and LiF were 98% (without stirring at 30 min of reaction and pH 9) and 80%, respectively, with purities higher than 94%. Moreover, F^- was almost completely eliminated from the effluent with the addition of CaCO_3 .

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Conflicts of Interest: The authors declare no conflict of interest.

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