

Recovery of Cobalt as Cobalt Sulfate from Discarded Lithium-Ion Batteries (LIBs) of Mobile Phones



Pankaj Kumar Choubey, Archana Kumari, Manis Kumar Jha, and Devendra Deo Pathak

Abstract Cobalt, an exceptional cathode material present in lithium-ion batteries (LIBs), is an essential element for the production of energy storage devices. But, the lifespan of rechargeable batteries is decreasing day-by-day, which become obsolete after reaching their end of life. Therefore, an enormous amount of discarded LIBs are generated. Keeping in mind the above, a novel approach has been made to selectively recover cobalt from sulfate leach liquor of discarded LIBs containing 1.4 g/L Cu, 1.1 g/L Ni, 11.9 g/L Co, 6.9 g/L Mn, and 1.2 g/L Li. Initially, Cu and Ni were extracted by solvent extraction techniques using 10% LIX 84-IC. Almost complete precipitation of cobalt occurred from leach liquor at pH ~3 using ammonium sulfide solutions. Cobalt from the precipitated product was further dissolved in H₂SO₄ in presence of H₂O₂ at elevated temperature. The leach liquor obtained was evaporated to get the cobalt sulfate with a purity of more than 98%.

Keywords Spent LIBs · Leach liquor · Precipitation · Cobalt · Cobalt sulfate

Introduction

Lithium-ion batteries (LIBs) are extensively used in portable electronic devices as well as in electric vehicles to store energy. The unique properties of LIBs such as their high energy storage capacity and high specific energy have increased their demand to fulfill various technological applications [1, 2]. But with the passage of time, the energy storing capacity of LIBs decreases, thus resulting in the huge generation of waste LIBs. In 2017, ~12 billion units of obsolete LIBs were generated, which is expected to reach ~25 billion units by the end of 2020 [1]. Presently ~10% spent LIBs are reported to be recycled by the formal sector while the rest of the

P. K. Choubey · A. Kumari · M. K. Jha (✉)

Metal Extraction and Recycling Division, CSIR-National Metallurgical Laboratory, Jamshedpur 831007, India

e-mail: mkjha@nmlindia.org

P. K. Choubey · D. D. Pathak

Department of Chemistry, Indian Institute of Technology (ISM), Dhanbad 826004, India

batteries remains untreated or recycled in an illegal manner. This illegal treatment of scrap batteries results in the loss of valuable metals [2]. These discarded batteries contain a significant amount of cobalt (Co) and manganese (Mn) along with other valuable metals like lithium (Li), nickel (Ni), etc. Hence, it is necessary to develop sustainable recycling routes for the recovery of Co from these discarded LIBs due to a lack of abundant natural resource and to mitigate their demand–supply gap. Several researchers studied different techniques but generally, pyro- and hydro-metallurgical routes were employed for the recovery of Co from discarded LIBs [3–5]. Hanisch et al. (2015) treated the spent LIBs at high temperature (600 °C) to get the roasted product and further leached them in 2 M H₂SO₄ at 60 °C in the presence of 10% hydrogen peroxide to leach out Co [3]. 4 mol/L HCl is reported to be used to enhance the Co leaching efficiency up to 99% at 80 °C in 60 min keeping the pulp density at 20 g/L. But a quite long reaction time (180 min) was required to get the same leaching efficiency of Co in 3 mol/L H₂SO₄ at 90 °C in the presence of 0.25 g/L Na₂S₂O₃ (reductant) [4, 5]. Apart from this, organic acids like citric acid, malic acid, and ascorbic acid have also been used to leach out Co from spent LIBs. Almost 98% cobalt was leached in 1.0 mol/L oxalic acid at 80 °C in the presence of hydrogen peroxide. The advantage of this leaching system lies in the selective precipitation of Co as oxalate salt (CoC₂O₄), while other metals Li, Mn, Ni, and Al remained in the leach liquor [6, 7]. Ascorbic acid also acts as a self-reductant and hence eliminates the requirement of any other reducing agent during Co leaching [8].

Subsequently, precipitation studies were carried out to recover the metals from leach liquor of LIBs using a number of precipitating agents [4, 9]. Initially, Mn was precipitated with potassium dichromate (KMnO₄) at pH 2. After the separation of manganese, Ni and Co were removed as nickel-dimethylglyoxime (Ni-DMG) and cobalt hydroxide complex, respectively [4]. Finally, lithium was precipitated as lithium carbonate using sodium carbonate as a precipitant at 90 °C in a range of pH 11 to 12 [9].

In this paper, a novel process flow-sheet has been reported to selectively recover Co as hydrated cobalt sulfate (CoSO₄·7H₂O) from leach liquor of spent LIBs using precipitation followed by sulfate leaching and evaporation. Various process parameters were optimized for the recovery of pure Co in sulfate form.

Experimental

Materials

Spent LIBs supplied by the local market were used for experimental purposes. The spent LIBs are mainly composed of cathode, anode, separator, and electrolyte. The cathodic materials contain lithium, cobalt, manganese, and nickel in the form of their oxides such as lithium cobalt oxide (LiCoO₂), lithium cobalt manganese nickel and oxide (LiCoMnNiO₂). Initially, sodium chloride solution was used to discharge

Table 1 Typical composition of spent LIBs (wt %)

Li	Co	Mn	Ni	Cu	Graphite	Others
2.1	13.4	7.1	2.3	2.5	55.1	~20

Table 2 Chemical composition of leach liquor (g/L)

Li	Co	Mn	Ni	Cu
1.2	11.9	6.9	1.1	1.4

the LIBs prior to pre-treatment. Thereafter, LIBs were crushed using the scutter crusher, and separated into different components such as black powder, metallic concentrate, and plastic materials. The obtained black powder was dissolved in sulfuric acid at optimized leaching conditions [10]. The detailed composition of spent LIBs and leach liquor used in this study are presented in Tables 1 and 2, respectively. Ammonium sulfide (Analytical grade, supplied by Loba Chemie Pvt. Ltd., Mumbai, India), sulfuric acid, hydrogen peroxide, and sodium hydroxide supplied by E. Merck, Mumbai India were used during the experiments (E. Merck, Mumbai, India, analytical Grade).

Methodology

Precipitation Procedure

Bench-scale studies were carried out in a beaker (capacity 200 mL) containing 100 mL leach liquor with the addition of different amounts of ammonium sulfide (2–10% v/v) under a constant stirring facility to uniformly mix the solution. During precipitation, the pH of the solution was kept constant ~3.0 throughout the experiments by adding ammonium sulfide and sulfuric acid solution. Solution temperature was also kept constant (30 °C) with the help of a temperature-controlling sensor. The slurry was filtered and metal content in the filtrate was analyzed using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (VISTA MPX, CCD Simultaneous, Make: Australia) and Atomic Absorption Spectrometer (AAS) (Model no. AAS 200, Make Perkin Elmer, USA).

Leaching Procedure

The leaching experiments were carried out in a temperature-controlled leaching reactor fitted with a reflux condenser to avoid loss of solution during the experiments. Different concentrations of sulfuric acid were used as a leaching agent at pre-selected temperature (30–60 °C) with the help of temperature-sensitive hot plate

having a magnetic stirring facility to maintain the stable temperature. On reaching the set temperature, the desired amount of sample was charged into the leaching reactor under a stirring speed of 400 rpm, which was found sufficient to ignore the effect of mass transfer on leaching. Sampling was carried out at different time intervals during experiments to observe the effect on leaching of metals. Once the leaching was completed, the solution was filtered and the residue left was dried in a vacuum oven and kept for further analysis.

Results and Discussion

Leach liquor of spent LIBs containing 1.4 g/L Cu, 1.1 g/L Ni, 11.9 g/L Co, 6.9 g/L Mn, and 1.2 g/L Li was used for the recovery of cobalt. At first, Cu and Ni were removed by a solvent extraction process using 10% LIX 84-IC as an extractant. Thereafter, the precipitation process was used to selectively precipitate the cobalt from the raffinate obtained after the separation of Cu and Ni. The detailed discussion is presented below.

Precipitation of Cobalt from Leach Liquor

In order to selectively precipitate cobalt from the leach liquor, precipitation studies were carried out using different concentrations of ammonium sulfide varying from 2 to 10% (v/v), while maintaining pH ~3. The result shows that (Fig. 1) the precipitation of cobalt increases with increase in ammonium sulfide concentration due to an increase in the content of sulfur ion which facilitates the formation of insoluble cobalt sulfide species resulting in the enhancement of cobalt precipitation. About 30.1%

Fig. 1 Effect of ammonium sulfide concentration on Co precipitation. [Solution: Leach liquor of spent LIBs; Precipitant: ammonium sulfide; pH: 3; Time: 30 min]. (Color figure online)

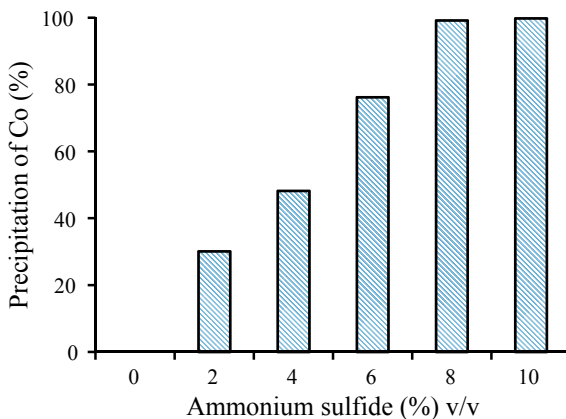
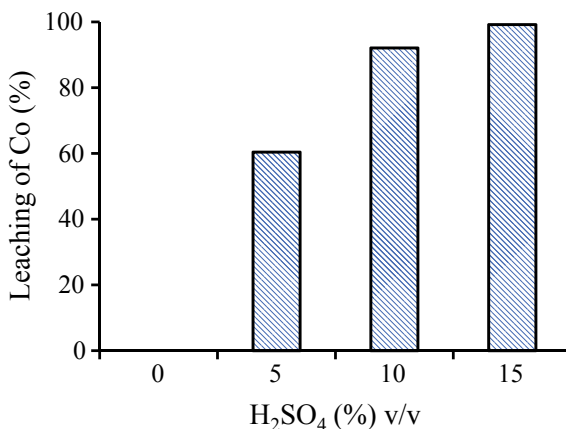


Fig. 2 Effect of sulfuric acid concentration on Co leaching. [Solid: Precipitated cobalt sulfide; Acid: H_2SO_4 ; Additive: 10% H_2O_2 ; Time: 30 min]. (Color figure online)



Co was precipitated with 2% ammonium sulfide (v/v) while 99.2% Co precipitated with 8% ammonium sulfide (v/v). Lithium and manganese remained in the filtrate. Hence, 8% ammonium sulfide (v/v) was chosen as the optimum concentration for the precipitation of cobalt from leach liquor of spent LIBs. Precipitated cobalt sulfide was further dissolved in sulfuric acid solution to recover the cobalt in the form of cobalt sulfate.

Leaching of Cobalt from the Obtained Precipitate/Cobalt Sulfide

In order to get Co as hydrated cobalt sulfate, the precipitate of cobalt sulfide was further leached in sulfuric acid in a range varying from 5 to 15% (v/v) in the presence of 10% (v/v) hydrogen peroxide at elevated temperature. Figure 2 shows that the leaching of cobalt was found to increase with the increase in the acidic strength of the solution, which facilitated the dissociation of the sulfide molecule of cobalt. As a result, cobalt leaching efficiency was increased. Further, the increase in the acid concentration above 15% had no significant effect on the leaching of cobalt. Hence, 15% H_2SO_4 was considered as optimum acid concentration for cobalt leaching from precipitated cobalt sulfide.

In addition, reductant concentration (H_2O_2) was also varied from 5 to 15% at elevated temperature to leach out cobalt from the precipitated product (cobalt sulfide). It was found that 75.2% Co dissolved in 15% H_2SO_4 at 60 °C in 30 min when 5% H_2O_2 was added to the leachant, while cobalt leaching was enhanced up to 99.2% when 10% H_2O_2 was added to the solution under the same experimental conditions. The leaching of cobalt was found to increase with the addition of hydrogen peroxide due to the generation of sufficient dissolved oxygen or nascent oxygen, which might be responsible for the enhancement of cobalt leaching efficiency. Further, the role of

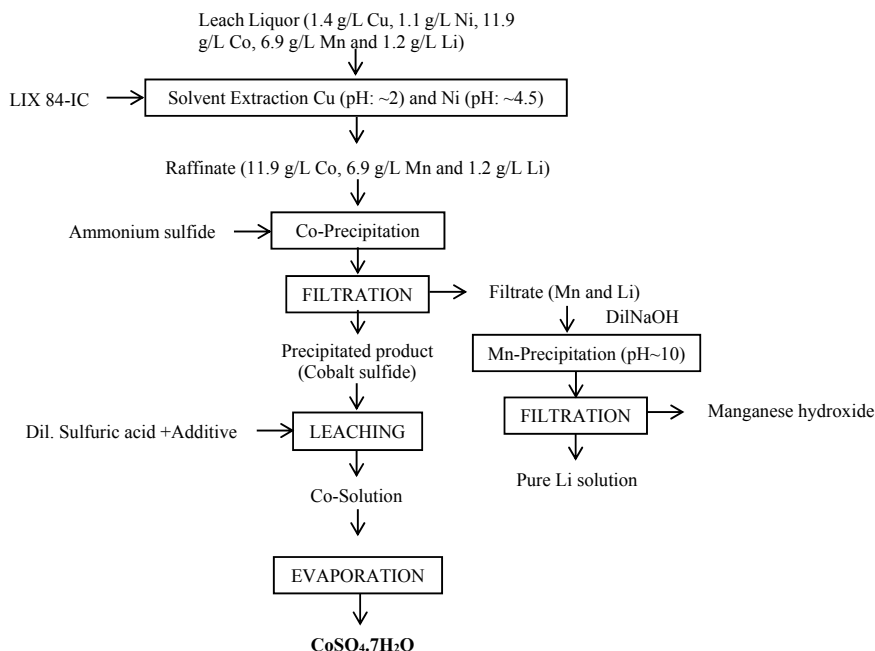


Fig. 3 Developed process flow-sheet for the recovery of cobalt from leach liquor of spent LIBs

temperature was also studied and found that leaching of cobalt gradually increased with an increase in solution temperature up to 60 °C due to an increase in the rate of reaction. But above 60 °C, the temperature had no significant effect on the enhancement of cobalt leaching efficiency. Therefore, 60 °C temperature was considered as the optimum temperature for cobalt leaching from precipitated cobalt sulfide. Finally, a process flow-sheet has also been developed for the separation of copper, nickel, cobalt, manganese, and lithium from leach liquor of spent LIBs as presented in Fig. 3.

Conclusion

Based on the lab-scale precipitation and leaching studies, the following conclusions have been drawn for the recovery of cobalt from leach liquor of spent LIBs.

1. 99.2% cobalt was precipitated from leach liquor of spent LIBs in 30 min at room temperature using 8% (v/v) ammonium sulfide as a precipitating agent, while lithium and manganese remained in the solution.
2. It was found that 60.4% cobalt dissolved from the precipitated product with 5% H₂SO₄ at 60 °C in 30 min in the presence of 10% H₂O₂ (v/v).
3. Complete leaching of cobalt (99%) occurred using 15% H₂SO₄ at 60 °C in 30 min with the addition of 10% H₂O₂ (v/v).

4. Finally, leach liquor of the precipitated product was evaporated to get cobalt sulfate of purity more than 98% as shown in Fig. 3.

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