

Hydrometallurgical process for recovery of cobalt from waste cathodic active material generated during manufacturing of lithium ion batteries

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Abstract

The paper presents a new leaching-solvent extraction hydrometallurgical process for the recovery of a pure and marketable form of cobalt sulfate solution from waste cathodic active material generated during manufacturing of lithium ion batteries (LIBs). Leaching of the waste was carried out as a function of the leachant H_2SO_4 concentration, temperature, pulp density and reductant H_2O_2 concentration. The 93% of cobalt and 94% of lithium were leached at suitable optimum conditions of pulp density: 100 g L^{-1} , $2 \text{ M H}_2\text{SO}_4$, 5 vol.% of H_2O_2 , with a leaching time 30 min and a temperature 75°C . In subsequent the solvent extraction study, 85.42% of the cobalt was recovered using 1.5 M Cyanex 272 as an extractant at an O/A ratio of 1.6 from the leach liquor at pH 5.00. The rest of the cobalt was totally recovered from the raffinate using 0.5 M of Cyanex 272 and an O/A ratio of 1, and a feed pH of 5.35. Then the co-extracted lithium was scrubbed from the cobalt-loaded organic using 0.1 M Na_2CO_3 . Finally, the cobalt sulfate solution with a purity 99.99% was obtained from the cobalt-loaded organic by stripping with H_2SO_4 .

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1. Introduction

Lithium ion batteries (LIBs) are extensively used as electrochemical power sources in modern electronic equipment due to their favorable characteristics such as high energy density, high cell voltage, long storage life, low self discharge rate and wide temperature range of use. In Korea, about 67 million cells and 122 million cells were used in 2000 and 2003, respectively [1]. During last 3 years, the demand for LIBs has doubled. Total worldwide rechargeable battery demand is predicted to reach 4.6 billion cells by 2010 [2]. Therefore, it is expected that a massive amount of waste generated during LIB manufacturing process in industry will cause a serious environmental problem. The increasing trend of the waste flux generated, ever increasing energy demand, rapid decrease in primary resources and strict

environmental regulations stimulate the need for improved waste recycling.

Several studies have been carried out to recover valuable metals from the waste cathodic active material (LiCoO_2) by pyro-metallurgical and hydrometallurgical processes. The methods reported commonly include crushing, physical separation, acid leaching, and precipitation or solvent extraction to recover the cobalt and lithium from the battery waste [1,3–12]. The recovery of cobalt from the waste LIB using crushing, physical separation, acid leaching followed by precipitation as Co(OH)_2 [3,4], CoC_2O_4 [1,5,6] has been reported. But such precipitation processes have inherent problems such as solid–liquid separation, high cost, low purity and slow kinetics [7].

Solvent extraction has been widely used for the recovery and separation of metals from the leach liquor, effluents, and the waste. Recovery of metal from waste LiCoO_2 by leaching-solvent extraction by different routes and using different extractants such as PC-88A [8], D2EHPA and PC-88A [9], and Cyanex 272 [10] have been reported [8–12]. A thorough

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Nomenclature

D_{Co}	distribution coefficient of cobalt
D_{Li}	distribution coefficient of lithium
β	separation factor
Aq.	aqueous
Org.	organic

literature review indicates that no detailed information has been reported yet for recycling of waste cathodic material generated during the battery manufacturing process by solvent extraction using Cyanex 272. In our earlier work, separation of cobalt and lithium by solvent extraction using Cyanex 272 from synthetic solution has been reported [11,12].

The objective of the present work is to develop an effective hydrometallurgical process for recovery of a pure and marketable form of cobalt sulfate solution/salt from the waste of the LIB industry. This process consists of mainly acid leaching, solvent extraction, scrubbing and stripping. The waste LiCoO_2 was leached in H_2SO_4 and from the leach liquor solvent extraction studies has been carried out for the separation of cobalt and lithium using Cyanex 272. During these leaching studies, various process parameters viz. concentration of leachant (H_2SO_4), concentration of reductant H_2O_2 , pulp density and temperature have been optimized. To recover cobalt from the leach liquor by solvent extraction, studies have been carried out using different process parameters viz. equilibrium pH, Cyanex 272 concentrations and O/A ratio. Small amounts of co-extracted lithium from cobalt-loaded Cyanex 272 have been scrubbed using a Na_2CO_3 solution. Finally, the cobalt has been stripped from the metal-loaded organic, using dilute H_2SO_4 .

2. Experimental

2.1. Materials

LIB industry waste LiCoO_2 generated during the manufacturing process was supplied by a Korean industry. The waste LiCoO_2 is an amorphous black colored powder having a particle size of 8.3 μm . The waste LiCoO_2 contains about 60.2 wt.% of cobalt and 7.09 wt.% of lithium. Chemical reagents such as H_2SO_4 , NaOH and Na_2CO_3 used for the experiment were analytical grade (A.R.) reagents. The extractant Cyanex 272 was supplied by Cytec Korea Incorporation and was used without further purification [13]. The low boiling point kerosene (180–270 °C) was used as the diluent and tri-*n*-butyl-phosphate (TBP) was used as the phase modifier.

2.2. Leaching procedure

All batch-leaching experiments were carried out in a 0.5 L three necked, round bottomed thermostatic Pyrex reactor with temperature control facility. The reactor was fitted with an impeller stirrer, a vapor condenser and thermometer, and is described elsewhere [14]. The reflux condenser was used to

avoid vapor loss at high temperature, heating was provided by an electrical mantle and the temperature was controlled. A known strength and amount of H_2SO_4 was poured into the reactor and allowed to reach thermal equilibrium. Then the measured amount of waste LiCoO_2 powder and H_2O_2 solution were added into the reactor with agitating by the impeller stirrer. Leach liquor samples of 4 mL were drawn periodically at desired time intervals (between 5 and 90 min). Various process parameters such as H_2SO_4 concentration, H_2O_2 concentration, pulp density and temperature were optimized.

2.3. Solvent extraction procedure

The extractant Cyanex 272 was partially saponified up to 65% by adding a stoichiometric amount of concentrated NaOH solution to the extractant in kerosene under constant stirring of the mixture [11,12,15,16]. The kerosene was used as the diluent and 5 vol.% TBP was used as a phase modifier. The requisite pH for the aqueous leach liquor feed was adjusted with addition of NaOH or H_2SO_4 solution. Suitable amount of aqueous leach liquor was equilibrated with organic Cyanex 272 for 10 min, and then the phases were separated by the separating funnel. Ten minutes was found to be sufficient time to attain the equilibrium which was verified in preliminary tests. The aqueous raffinate was analyzed to determine the amount of Co(II) and Li(I) extracted by organic extractant. All experiments were carried out at ambient temperature (25 ± 1 °C). The solvent extraction was carried out in a cross-current solvent extraction manner. The same stock aqueous leach liquor was used in each set of experiments, but the raffinate from the first stage of extraction was used as the aqueous feed in the second stage for solvent extraction. The scrubbing and stripping tests were carried out using Na_2CO_3 solution and H_2SO_4 solution, respectively.

2.4. Analytical procedures

Analyses of the samples were carried out by a conventional titration method using murexide and instrumental analysis using atomic absorption spectrometer (Varian SpectraAA-400). The cobalt concentration in the feed, raffinate and stripped solution were determined by titration with 0.05 M EDTA in presence of Murexide indicator. To avoid the analytical error in low parts per million range metallic solutions, analyses of the samples were also carried out using an atomic absorption spectrometer. The lithium concentration in the feed, raffinate and stripped solution were determined using atomic absorption spectrometry (AAS) after suitable dilution of the samples with 5 vol.% of HCl. Both the cobalt and lithium concentrations in the organic phases were determined by a mass balance calculation method. The maximum deviations were permitted were about $\pm 3\%$.

3. Results and discussion

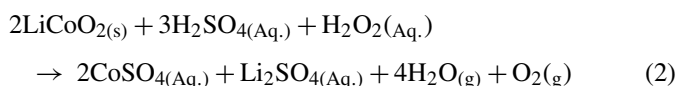
3.1. Leaching of waste LiCoO_2

Theoretically, the leaching efficiency of LiCoO_2 is better in the lower concentration range of H_2SO_4 as Co(II). The

leaching efficiency of cobalt is lower in strong acid solution because Co(III) is more unstable than Co(II) [17,18]. The leaching reaction of the waste LiCoO_2 with H_2SO_4 solution can be represented as follows [10]:



From chemical equation (1), it can be predicted that the addition of a reductant can facilitate the forward reaction, since Co(III) in the reactant reduces it to Co(II). Thus, the studies for improving the leaching efficiency of cobalt by adding reductant H_2O_2 solution during the acid leaching of waste LiCoO_2 were conducted [5,17,19]. The chemical reaction equation in the presence of H_2O_2 solution can be represented as:



In the leaching reaction cobalt and lithium were leached as CoSO_4 and Li_2SO_4 , respectively.

3.1.1. Effect of H_2O_2

The effect of reductant H_2O_2 concentration on leaching efficiencies of the waste cathode active materials was studied. The volume percent of H_2O_2 was calculated as supplied in the original bottle. The waste LiCoO_2 material was leached with 2 M H_2SO_4 solution at pulp density of 100 g L^{-1} . During leaching, the temperature was maintained at 75°C , and the leaching time was 30 min. The results are presented in Fig. 1 and show only 34% of cobalt was leached in the absence of H_2O_2 solution, whereas 74% of lithium was leached at the same condition. It was observed that the leaching efficiency of cobalt increased with the increase in concentration of reductant significantly, in comparison to the leaching efficiency in absence of reductant. The leaching efficiencies of cobalt and lithium increased from 34 to 99.99% and 74 to 99.99%, respectively, with the increase in H_2O_2 concentration from 0 to 25 vol.%. The results show that

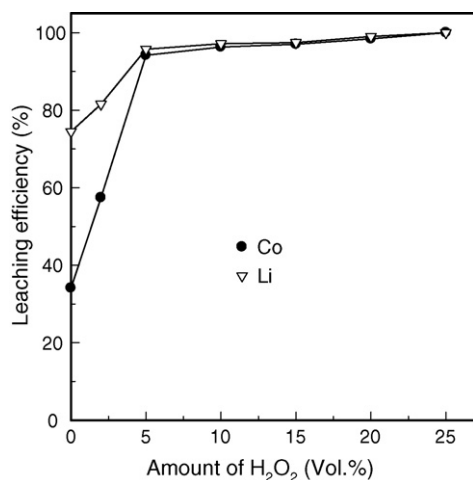


Fig. 1. Effect of H_2O_2 amount on the leaching of waste LiCoO_2 with 2.0 M H_2SO_4 solution at 75°C for 30 min (pulp density = 100 g L^{-1} , agitation speed = 300 rpm).

the increases in leaching efficiencies of cobalt and lithium with increase in volume percent H_2O_2 from 5 to 25 were insignificant. In the presence of 5 vol.% H_2O_2 reductant, the leaching efficiencies of cobalt and lithium were 94 and 95%, respectively. The figure shows that initial leaching efficiency for lithium is higher in comparison to cobalt up to 10 vol.% H_2O_2 .

The chemical equations (1) and (2) suggest that the lithium leaching efficiency is independent of the H_2O_2 concentration and the cobalt leaching efficiency is dependent on H_2O_2 concentration. The leaching efficiencies results of both the metals from without addition of H_2O_2 to a 10 vol.% H_2O_2 shows that the leaching efficiency of both the metals increases significantly. In the presence of 5 vol.% H_2O_2 , the leaching efficiency of cobalt increases nearly threefold, whereas the leaching efficiency of lithium is only about 0.3-fold. This signifies that the leaching efficiency of cobalt depends on the reductant concentration. In the presence of H_2O_2 , the quantitative leaching and the increases in leaching efficiency of cobalt supports the proposed chemical equation (2). Hence, the reaction mechanism follows Eq. (2) in the presence of H_2O_2 and follows Eq. (1) in absence of reductant H_2O_2 .

3.1.2. Effect of temperature

The effect of temperature on the leaching efficiency was studied using 2 M H_2SO_4 at a pulp density of 100 g L^{-1} , concentration of reductant 5 vol.% and leaching time 30 min. The results are presented in Fig. 2 and indicate that 67% of cobalt and 84% of lithium can be leached at 25°C . The leaching efficiency of the metals increased with increase in leaching temperature. At 60°C , 92% of cobalt and 93% of lithium were leached. When the temperature was increased to 75°C , the recovery of cobalt and lithium were found to be 93 and 94%, respectively. Further increase in temperature did not show any significant increase in the recovery of cobalt and lithium. Fig. 2 clearly indicates the leaching efficiency as a function of temperature and the same has no significant change above temperature of 75°C . This is because of the minimal availability of reactant, i.e. the waste LiCoO_2 is significantly low

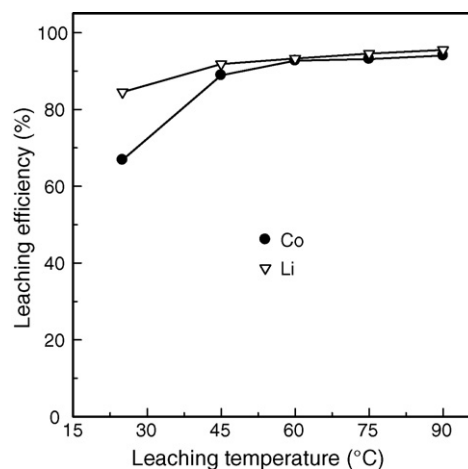


Fig. 2. Effect of leaching temperature on the leaching of waste LiCoO_2 with 2.0 M H_2SO_4 for 30 min ($\text{H}_2\text{O}_2 = 5 \text{ vol.}\%$, pulp density = 100 g L^{-1} , agitation speed = 300 rpm).

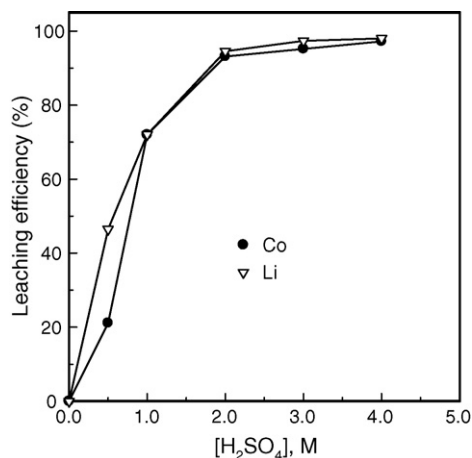


Fig. 3. Effect of H_2SO_4 concentration on the leaching of waste LiCoO_2 at 75°C for 30 min ($\text{H}_2\text{O}_2 = 5$ vol.%, pulp density = 100 g L^{-1} , agitation speed = 300 rpm).

3.1.3. Effect of H_2SO_4 concentration

The effect of H_2SO_4 concentration on the leaching efficiency of the waste LiCoO_2 was studied. The concentration of H_2SO_4 was varied from 1 to 4 M at a pulp density 100 g L^{-1} , temperature 75°C , reductant concentration at 5 vol.% H_2O_2 and leaching time 30 min (Fig. 3). Fig. 3 depicts that the leaching efficiencies increase from 21 to 97% for cobalt and 46 to 98% for lithium as the H_2SO_4 concentration increases from 0.5 to 4 M. Leaching efficiency of metals rapidly increased up to 2 M with the increase in concentration of H_2SO_4 . In the presence of 2 M H_2SO_4 , the leaching efficiency of cobalt and lithium is 93 and 94%, respectively. With further increase in the H_2SO_4 concentration from 2 to 4 M, the leaching efficiency for both the metal increases slowly in comparison to lower H_2SO_4 concentration leaching, i.e. 0.5–2 M H_2SO_4 . The leaching efficiency of cobalt was increased slowly from 95 to 97% and leaching efficiency of lithium was also increased from 97 to 98% with increase in H_2SO_4 concentration from 3 to 4 M, respectively. As shown in Fig. 3, to increase only about 4% of leaching efficiency for both the metals, another 2 M of H_2SO_4 is required. Subsequently, also more NaOH is required for increasing the pH of leach liquor before solvent extraction process. From the economical point of view, it is necessary to reduce the acid consumption during leaching and which subsequently reduces the consumption of NaOH in solvent extraction studies. So, in further studies for the leaching of the waste was carried out using 2 M H_2SO_4 .

3.1.4. Effect of pulp density

The effect of pulp density on the leaching efficiencies of cobalt and lithium was studied in range of 10–125 g L^{-1} . The experimental conditions were 75°C , 2 M H_2SO_4 and 5 vol.% H_2O_2 . The results obtained are presented in Fig. 4 and indicate that the leaching efficiencies of cobalt and lithium decreases as the pulp density increases. The figure also shows that the total recovery of cobalt and lithium possible at the pulp density 10–20 g L^{-1} . However, 93% of cobalt and 94% of lithium were leached at pulp density 100 g L^{-1} . At higher pulp density, the fil-

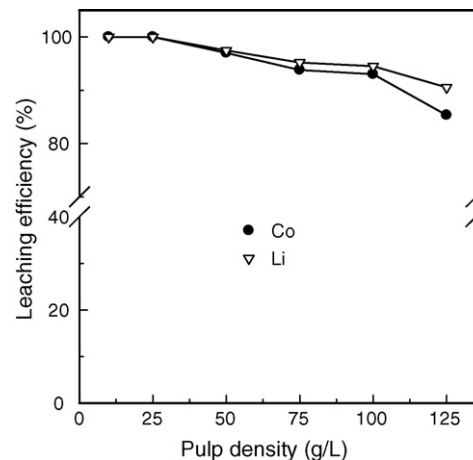


Fig. 4. Effect pulp density on the leaching of waste LiCoO_2 with 2.0 M H_2SO_4 for 30 min ($\text{H}_2\text{O}_2 = 5$ vol.%, agitation speed = 300 rpm).

tration problem was observed. So, the pulp density of 100 g L^{-1} is considered to be the suitable for the leaching of waste LiCoO_2 .

From the above-studied parameters, considering the lower energy consumption, lower chemical consumption and relatively better leaching efficiency the best suitable condition for leaching of cobalt and lithium from the waste LiCoO_2 was decided. The result showed 93% of cobalt and 94% of lithium can be leached under optimized experimental conditions, i.e. a 100 g L^{-1} pulp density, a 2 M concentration of leachant, a 5% concentration of reductant H_2O_2 , a 30 min leaching time and a 75°C temperature. The residual LiCoO_2 was reused for leaching. The same leaching behavior was observed for leached residue.

3.2. Solvent extraction of cobalt

A sufficient amount of leach liquor was generated in the optimized conditions using a 2 L three-necked thermostatic Pyrex reactor similar to the leaching study mentioned above. The leach liquor generated in the optimized condition contained 44.72 g L^{-1} cobalt and 5.43 g L^{-1} lithium at pH of 5.00, and has been used for the separation and recovery of cobalt and lithium using solvent extraction process. In order to recover cobalt from the sulfate leach liquor, the solvent extraction studies were carried out using Cyanex 272 as the extractant, 5 vol.% TBP as phase modifier and kerosene as diluent.

3.2.1. pH-extraction isotherm

The pH-extraction isotherm of cobalt and lithium was studied using 1 M Cyanex 272 at different equilibrium pH values with an A/O ratio of 1:1. The percentage of extraction, distribution coefficient and separation factor at different equilibrium pH were determined. The effect of equilibrium pH on the extraction and separation of cobalt and lithium is shown in Fig. 5. The pH isotherm presented in Fig. 5 indicates that the recovery of cobalt and lithium increases with increase in equilibrium pH. In the equilibrium pH range of 4.46–5.35 which corresponds to an initial pH of 1.60–5.05, the cobalt extraction ranged from 25 to 51% and the lithium extraction from 5 to 8%. It was observed that the recovery of lithium was very low in compari-

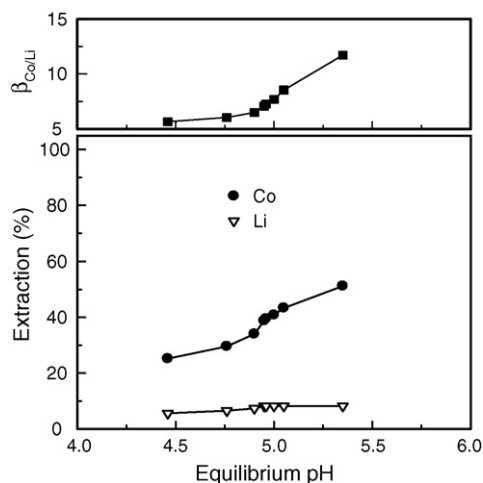


Fig. 5. Effect of equilibrium pH on extraction and separation of Co and Li from H_2SO_4 leach liquor of waste LiCoO_2 using 1.0 M Cyanex 272 (initial aqueous solution 44.72 g L^{-1} Co and 5.43 g L^{-1} Li, O/A = 1).

son to cobalt extraction. No significant increase in the extraction of lithium was observed at an equilibrium pH higher than 4.75. Above the equilibrium pH of 5.35, the extraction behavior could not be determined accurately as the precipitation of cobalt was started. As shown in Fig. 5, the separation factor for cobalt over lithium ranged from 5.65 to 11.74 as the equilibrium pH ranged from 4.46 to 5.35. The separation factor increased in between the range of pH 4.90–5.35, significantly. The maximum separation factor for cobalt over lithium was 11.74 and the maximum extraction for cobalt was 51.23% at equilibrium pH = 5.35 (initial feed pH = 5). In this equilibrium pH, only 8% of the lithium was co-extracted. Hence, the initial pH of 5 was considered as suitable for further studies.

3.2.2. Effect of the concentration of Cyanex 272

The optimization of the extraction conditions was essentially carried out in terms of the extractant concentration at an initial pH of 5.00. The leach liquor at an initial pH of 5, containing 44.72 g L^{-1} cobalt and 5.43 g L^{-1} lithium was used for this purpose. The concentration of the extractant Cyanex 272 was varied from 0.5 to 2 M, the percentage extraction and separation factor for the cobalt and lithium was calculated. The organic:aqueous ratio (O/A) was maintained at 1 for each set of studies. The results are presented in Fig. 6 which shows the increase in percentage extraction of cobalt and lithium with the increase in the concentration of extractant. As the extractant concentration increases from 0.5 to 2 M, the extraction of cobalt ranges from 20 to 77% and the extraction of lithium ranges from 2 to 15%. From Fig. 6, it was observed that the extraction of cobalt increased rapidly with increasing extractant concentration, but the extraction of lithium was relatively lower than the cobalt. The loading of cobalt ranged from 9.27 to 34.52 g L^{-1} with respect to extractant concentration range from 0.5 to 2 M. As the extractant concentration increased to fourfold, the extraction of cobalt increased only about 1.92-fold. The extractant investment per unit of gram of cobalt extraction was high at higher concentration of the extractant and the extractant investment per unit

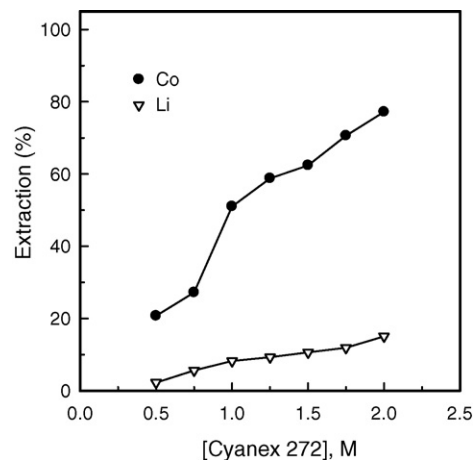


Fig. 6. Effect of Cyanex 272 concentration on extraction of Co and Li from H_2SO_4 leach liquor of waste LiCoO_2 at an initial pH of 5.0 (initial aqueous solution 44.72 g L^{-1} Co and 5.43 g L^{-1} Li, O/A = 1).

of gram of cobalt extraction was lower at lower concentration. Hence, higher concentrations of extractant were not efficient and effective for the extraction and separation. This is because of the viscosity of the extractant. The viscosity of the organic phase increased with the increase in molar concentration of extractant in the organic phase. The problem related with phase disengagement was observed at higher concentrations of extractant having a molar concentration more than 1.5 M because of the viscosity of the extractant. The same problem also has been reported by Nogueira and Delmas [20]. The results also show that the extraction of lithium increased from 0.5 to 1 g L^{-1} with the increase in the concentration of Cyanex 272 from 1.5 to 2 M. The higher concentration of lithium in the organic phase created a problem in complete scrubbing. The separation factors under all the conditions were similar. Due to all the above problems, viz. viscosity, phase disengagement, scrubbing difficulties, further experiments have been carried out using 1.5 M Cyanex 272.

3.2.3. Effect of O/A ratio

The studies of the effect of the O/A ratio on the extraction of cobalt and lithium from leach solution at an initial pH of 5 have been carried out using the 1.5 M extractant Cyanex 272 by varying the O/A ratio. The distribution coefficient, separation factor and percentage extraction were calculated. The results presented in Fig. 7 show the recovery of cobalt and lithium increases with the increase in O/A ratio. The extraction of cobalt ranged from 62 to 99% as the O/A ratio increases from 1 to 2. The extraction of lithium ranged from 10 to 39% as the O/A ratio ranged from 1 to 2. Fig. 7 indicated that the extraction of cobalt increased steadily and consistently. The extraction of lithium was slowly increased in the O/A ratio range of 1–1.6, and the extraction was increased rapidly in the range of 1.6 to 2. At an O/A ratio 1.6, about 17% of lithium was extracted. At this ratio, the loaded organic contains 23.87 g L^{-1} of cobalt and 0.58 g L^{-1} of lithium. At the O/A ratios of 1.8 and 2, about 28% and about 40% of lithium was extracted, respectively. With increase in O/A ratio, it was observed that the percentage cobalt with respect to total metallic content present in the organic phase decreased as the concentra-

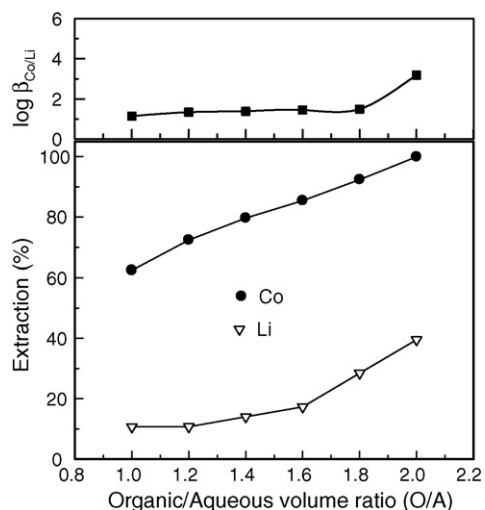


Fig. 7. Effect of O/A volume ratio of Cyanex 272 on extraction of Co and Li from H_2SO_4 leach liquor of waste $LiCoO_2$ at an initial pH of 5.0 and 1.5 M of Cyanex 272 (initial aqueous solution 44.72 g L^{-1} Co and 5.43 g L^{-1} Li).

tion of lithium increased in the organic phase. The percentage extraction of cobalt was found to be high (more than 90%) with increase in O/A ratio from 1.6 to 2. From the data, it was also observed that the percentage of cobalt present in the organic phase with respect to the total metallic content in organic phase decreased from 96.5 to 94.77% with increase in O/A ratio from 1.6 to 1.8. The cobalt loading in organic phase was 27.90, 26.89, 25.45, 23.88, 22.96 and 22.34 g L^{-1} for O/A ratio of 1, 1.2, 1.4, 1.6, 1.8 and 2, respectively. However, the lithium loading in organic phase was ranged from 0.577 to 1.073 g L^{-1} with respect to O/A ratio as above. The total loading of metal in organic phase was 28.48, 27.47, 25.99, 24.46, 23.81 and 23.41 g L^{-1} for O/A ratio of 1, 1.2, 1.4, 1.6, 1.8 and 2, respectively. Since the loading of cobalt content decreased and the loading of the lithium content increased in the organic phase, the purity of the metal decreased in the organic phase with increase in O/A ratio. Simultaneously, the total loading of the metal decreased with increase in phase ratio. Thus, from efficient use of an organic extractant and organic extractant investment point of view, the higher phase ratio is not suitable for extraction and separation purposes. Again the higher contamination of lithium in organic phase leads subsequently to the scrubbing problem. The stoichiometric calculation of the cobalt–Cyanex 272 suggests that the lower concentration and lower volume ratio O/A is not suitable for quantitative extraction of cobalt. Hence, the O/A ratio of 1.6 was considered as the suitable condition for extraction study.

The higher loading of lithium at a higher phase O/A ratio and higher concentration is due to the more available sites or surface area of extractant for the metal extraction. As verified and explained in our earlier work at the lower O/A ratio and at the lower Cyanex 272 concentration, where there is competition between cobalt and lithium ions, the efficiency of cobalt extraction is dominant over lithium which leads the least extractability of lithium in organic phase. In contrast, when there are enough available sites in extractant, the lithium gets extracted to organic phase comparatively higher than earlier [11,12].

The obtained data was correlated with the separation factor shown in Fig. 7. Fig. 7 indicates that the separation factor also increases with increase in the O/A ratio. The separation factor varies from 13.93 to 1528.83 as O/A ratio varies from 1 to 2. In figure it is shown that separation factor is an abnormally higher value at O/A of 2 because the extraction of cobalt reaches 99.99%. From the above studies, the optimum condition for the extraction and separation of cobalt and lithium has been optimized. The initial aqueous feed pH of 5, extractant Cyanex 272 concentration of 1.5 M, and phase O/A ratio of 1.6 were found to be the suitable optimum condition for extraction. In this optimized condition 85% of cobalt was extracted from leach solution and the loaded organic phase contains 23.87 g L^{-1} cobalt and 0.59 g L^{-1} lithium.

3.2.4. Scrubbing of lithium

The studies for the scrubbing of small amount of co-extracted lithium from the cobalt-loaded organic were carried out using Na_2CO_3 solution. The metal-loaded organic phase for scrubbing test was conducted using 1.5 M Cyanex 272 at phase ratio O/A of 1.6 from the leach liquor of waste $LiCoO_2$ at pH of 5.00 in a single contact. The resulting loaded organic phase contains 23.87 g L^{-1} of cobalt and 0.59 g L^{-1} of lithium. Some scrubbing tests not presented in this paper were carried out using different scrubbing medium, i.e. double distilled water, $C_2H_2O_4$ and Na_2CO_3 at different concentration level. The Na_2CO_3 was found to be suitable reagent for scrubbing without any difficulties. The scrubbing studies were carried out similarly as our previous work to remove lithium from metal-loaded organic phase using 0.1 M Na_2CO_3 scrub solution [21]. The scrubbing study was carried out using the loaded organic and scrubbing solution with in the ratio of 1:5 to 5:1. The scrubbing isotherm is plotted in Fig. 8. The type of curve obtained showed that scrubbing of lithium is very efficient, whereas cobalt removal is not easy at this condition. The graphical simulation in Fig. 8 indicates that about three times scrubbing is required at O/A ratio of 3.8 for getting a quantitative scrubbing using 0.1 M of sodium carbonate. The result obtained from above simulation was verified by

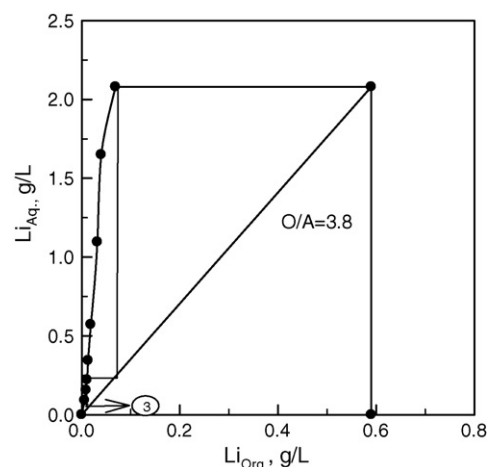


Fig. 8. Equilibrium isotherms for lithium scrubbing from loaded 1.5 M Cyanex 272 from leach solution at O/A = 1.6 (initial loaded organic solution 23.87 g L^{-1} Co and 0.59 g L^{-1} Li).

three-stage scrubbing. About 99.99% pure cobalt was obtained in organic phase. It was observed as the phase ratio of organic to scrubbing solution increases the phase separation became an important problem. Above the loaded organic versus scrubbing solution ratio 5:1, the phase disengagement time was more than 24 h and after that the phase separation was also incomplete. Thus, it is not possible to use higher O/A ratio more than 5:1 for scrubbing.

3.2.5. Stripping of cobalt

The purified cobalt-loaded organic obtained after the scrubbing of lithium has been used for the stripping experimental purpose. In all sets of stripping study, the O/A ratio was maintained at 1. The percentage of stripping and purity at different strip acid concentration was determined. The results presented in Fig. 9 shows the stripping of cobalt depends on the concentration of H_2SO_4 . The cobalt stripping was increased from 17 to 99.95% as the H_2SO_4 concentration increased from 0.1 to 0.75 M. At higher range of H_2SO_4 concentration, there was no change in metal recovery, as the stripping of cobalt reached about 99.999%. However, the lithium present as trace, i.e. 0.002 g L^{-1} in the loaded organic, was also stripped; completely at even lower concentration of H_2SO_4 . The lithium concentration was negligible in comparison to cobalt concentration in stripped solution. The change in purity with respect to stripping is presented in Fig. 9. Fig. 9 indicates that the purity of cobalt ranged from 99.951 to 99.992% as the strip acid concentration varied from 0.1 to 2 M. From the purified cobalt-loaded organic, the pure cobalt sulfate crystal could be produced by stripping with 5 M H_2SO_4 contacted at an O/A ratio of 5 [8].

3.3. Recovery of cobalt from the raffinate

Due to several problems like higher rate of contamination of lithium, purity concern, high content of cobalt and lithium in leach liquor and phase disengagement difficulties the total

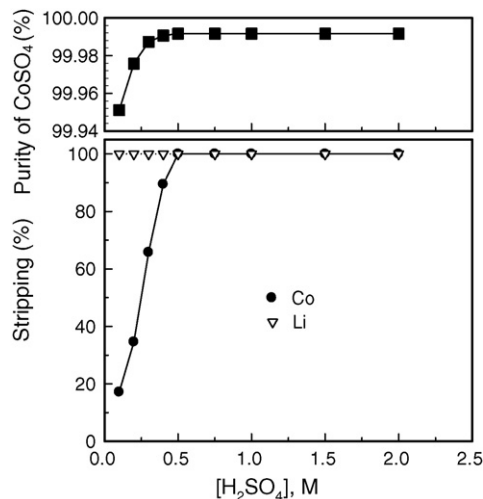


Fig. 9. Effect of H_2SO_4 concentration on stripping of Co and Li from the loaded organic generated from 1.5 M Cyanex 272 and O/A = 1.6 (initial loaded organic solution 23.87 g L^{-1} Co and 0.002 g L^{-1} Li, O/A = 1).

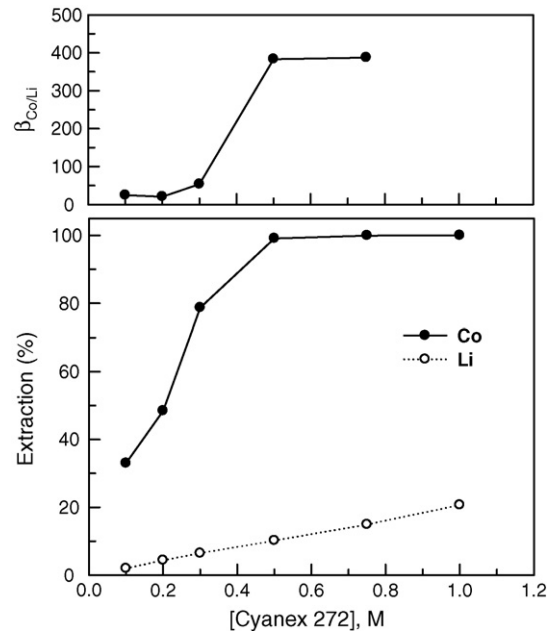


Fig. 10. Effect of Cyanex 272 concentration on extraction of Co and Li from raffinate at initial pH of 5.35 (initial aqueous solution 6.52 g L^{-1} Co and 4.49 g L^{-1} Li, O/A = 1).

cobalt could not be extracted from the leach liquor of waste LiCoO_2 . Because of the same problem the counter current simulation study is not suitable for quantitative extraction of pure cobalt. Since the maximum extraction was 85% in the above optimization process, in order to recover the rest of the cobalt from the raffinate the solvent extraction studies were carried out using Cyanex 272. The raffinate generated after the recovery of cobalt from the leach liquor in optimized condition contains 6.52 g L^{-1} cobalt and 4.49 g L^{-1} lithium. To simulate the process in continuous mode, cross-current extraction experiments were carried out to recover cobalt. Fig. 10 shows the effect of Cyanex 272 concentration on the extraction efficiency of cobalt and lithium from the raffinate. The initial pH of the aqueous phase was 5.35, and the O/A ratio was 1. As shown in the figure, the extraction of cobalt ranged from 33 to 99.99% and the lithium extraction ranged from 2 to 21% as the extractant concentration ranged from 0.1 to 1 M. The result presented in Fig. 10 shows the rapid increase in cobalt recovery with the increase in molar concentration of the extractant. The lithium extraction increases slowly in comparison to cobalt extraction. At 0.5 M Cyanex 272 concentrations, about 99% of cobalt was recovered. However, in this condition, only 10% of lithium was co-extracted with cobalt. As the concentration of the extractant increased for further studies, the co-extraction of the lithium also increased very rapidly in comparison to the increase in recovery of cobalt. The experimental results show 0.5 M concentration of Cyanex 272 is suitable for quantitative extraction of cobalt with little contamination of lithium. In the optimum condition, the loaded organic contained 6.5 g L^{-1} cobalt and 0.46 g L^{-1} lithium. As shown in Fig. 10, the separation factor also increases with the increase in concentration of Cyanex 272. The separation factor varies from 24.62 to 387.70 in the range of 0.1–0.75 M of Cyanex 272. The separation factor for 1 M Cyanex 272 is not shown in Fig. 10, since at this

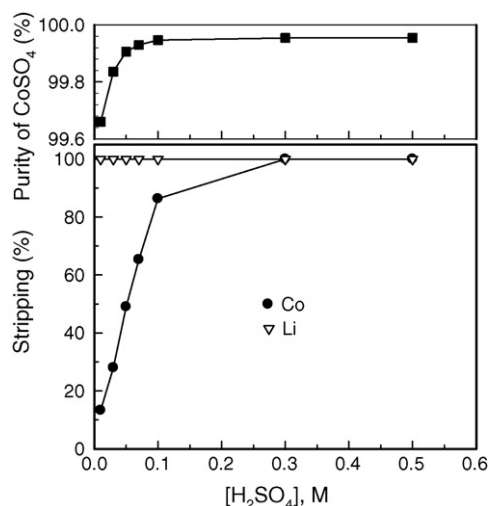


Fig. 11. Effect of H_2SO_4 concentration on stripping of Co and Li from the loaded organic generated from 0.5 M Cyanex 272. (Initial loaded organic solution 6.46 g/L Co and 0.003 g L^{-1} Li, O/A = 1).

point, almost all cobalt got extracted from aqueous solution. At this point, it is not possible to calculate distribution coefficient for cobalt.

The co-extracted lithium from the loaded organic was scrubbed using 0.1 M Na_2CO_3 , similar to above-mentioned optimized scrubbing condition in Fig. 8. Finally, the studies for the stripping of cobalt were carried out using different concentration H_2SO_4 at the O/A of 1. The result presented in Fig. 11 shows the stripping of metal increases with increase in H_2SO_4 concentration. The rapid increase in stripping of cobalt was observed even in small increase in concentration of H_2SO_4 . The stripping of cobalt ranges from 13.3 to 99.99% as the strip acid concentration ranged from 0.01 to 0.5 M. The traces of lithium about 0.003 g L^{-1} which are present in organic phase get stripped even at 0.01 M of strip acid. Hence, the purity of stripped cobalt varies. As presented in Fig. 11, the purity of cobalt varies from 99.66 to 99.99% when the strip acid concentration varies from 0.01 to 0.5 M. From the results, it was found that 0.5 M of sulphuric is suitable for stripping of cobalt.

For industrial interest, to enrich the strip solution generated from raffinate stream as same as the strip solution generated from fresh leach liquor stream was calculated. The calculation shows that the 0.5 M H_2SO_4 at an O/A ratio of 3.66 is required to generate the same concentrated cobalt sulfate solution from the raffinate. The feasibility of the result was also verified using the calculated condition and the expected result was also obtained. Complete extraction of cobalt with 99.99% purity as sulfate solution from the waste was achieved.

4. Conclusions

Based on the above studies, following conclusions have been drawn.

1. The best condition for leaching of cobalt from the waste LiCoO_2 was found to be 2 M H_2SO_4 at a leaching temper-

ature of 75 °C, pulp density of 100 g L^{-1} , and 5 vol.% of H_2O_2 for 30 min for our system. Under these conditions, the leaching efficiencies of cobalt and lithium were 93 and 94%, respectively.

2. The quantitative recovery of cobalt with a minimum lithium co-extraction was achieved using a Cyanex 272 concentration of 1.5 M, an initial pH of 5 and an O/A ratio of 1.6 in a single stage. Subsequently, the rest of the cobalt was extracted at a Cyanex 272 concentration of 0.5 M, an initial pH of 5.35 and an O/A ratio of 1 in a single stage. By this process, cobalt loss and solvent investment can be minimized.
3. Solvent extraction was followed by a three-stage lithium scrubbing using 0.1 M Na_2CO_3 solution with an O/A ratio of 3.8. Then it was stripped using 0.5 M H_2SO_4 . Complete extraction of cobalt with 99.99% purity as CoSO_4 solution was obtained by managing the suitable volume and concentration of H_2SO_4 solution. The obtained cobalt sulfate solution with high purity can be used for making salt/metal.
4. The selective and efficient separation/recovery of metal values from waste cathodic active material is feasible using Cyanex 272. This process is effective for recycling of waste, conservation of the natural resources and curtailing environmental pollution.

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