Recovery of valuable metals from cylindrical 18650-type spent lithium-ion batteries

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Abstract

The objectives of this work were to devise a flowchart of recycling processes for cylindrical 18650-type of spent lithium ion batteries (LIBs) and determine the optimal operating conditions that can be scaled up in an existing, but idled recycling plant for verification. After the pretreatment, the samples of screen undersize of the said LIBs were collected from a local spent battery recycling plant. The contents of major elements in the sample were determined to be 29-33 wt% of Ni, 30-32 wt% of Co, and 17-29 wt% of Mn. Then, various hydrometallurgical methods (including reductive acid leaching and solvent extraction) and electrowinning were employed to obtain their respective optimal operating conditions. Under the optimal operating conditions, the overall recoveries of 93% for high-purity Co and 95% for high-purity Ni were obtained for the said LIBs in this study. Based on the overall test results obtained, a technically feasible recycling scheme for valuable metals contained in cylindrical 18650-type of spent LIBs was devised. To verify this recycling scheme further, a semi-full scale testing has been planned.

Keywords: Spent lithium ion battery; Cylindrical 18650 cell; Metal recovery; Solvent extraction; Electrowinning

1. Introduction

Presently, various types of lithium ion batteries (LIBs) have been widely used in many kinds of consumer electronics and even electric vehicles. According to the differences in cathode active material, commonly used LIBs can be divided into the following types: (1) lithium cobalt oxide ($LiCoO_2$); (2) lithium manganese oxide ($LiMn_2O_4$); (3) lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$ or NMC); (4) lithium iron phosphate ($LiFePO_4$); (5) lithium nickel cobalt aluminum Oxide ($LiNiCoAlO_2$); and (6) lithium titanate ($Li_4Ti_5O_{12}$) [1]. As for the design shape, there are four configurations for LIBs: cylindrical, coin, prismatic, and thin and flat [2]. However, cylindrical cells (e.g., 18650 and 2170) and prismatic cells are two of the most popular options on the market. The former type is commonly used in laptops and electric vehicles, whereas the latter is used in mobile phones.

When the life span of LIBs is over, they need to be discarded and replaced. It was reported that in 1998 the world-wide production of LIBs was about 250 million cells. The annual production of spent LIBs containing 5–15 wt% cobalt (Co) and 2–7 wt% lithium (Li) was estimated to be 200–500 metric tons [3]. It was reported that about five million units of LIBs have been spent in 2000. This quantity was further estimated to be in the range of 200-500 metric tons, containing 2-15 wt% of cobalt (Co) and 2-7 wt% of lithium (Li) [4]. UNdata [5] further showed that during 2000-2010 about 12.7 billion mobile phones, 94.4 million laptops and 768.9 million digital cameras were produced [6]. Based on the latest statistics and models and prediction of booming of the electric vehicle industry, the quantity and weight of discarded LIBs in 2020 can exceed 25 billion units and 500 thousand metric tons, respectively [4]. It has been reported that about 5000 cells of $LiCoO_2$ battery are used in a Tesla electric vehicle [7]. However, it has been a general guess that about 7000+ cells of Panasonic NCR-18650A (3.1 Ah) are used in a Tesla car with an 85 kWh battery system [8].

Focusing on metallic values in spent LIBs, to date a tremendous amount of researches concerning the resource recovery and recycling of spent LIBs have been conducted and published [4,9,10]. Among various processes and technologies have been studied, roughly, they can be categorized into pyrometallurgical methods, hydrometallurgical, and bioleaching methods. But hydrometallurgical methods have gained their popularity due to the ease of studying in any wet chemistry lab. Basically, after the pretreatment (e.g., electricity discharging, crushing, and screening), the undersize fraction of LIBs is subjected to a series of combined processes such as acid leaching [11,12], solid/liquid separation, chemical precipitation [12,13], solvent extraction [12,14,15] and electrowinning [4,10,16].

Currently, there is only one EPA-licensed recycling plant (designated “Plant Y”) for dry batteries and LIBs in Taiwan. (Note: To the best knowledge of the present authors, there is one plant for LIBs recycling is under construction.) Through the technology transfer from Industrial Technology Research Institute (ITRI), Taiwan in 2014, Plant Y has become fully equipped based on a sound flowchart of recycling processes for LIBs developed by ITRI. Due to unknown situations, however, Plant Y has only operated its low-end technology section for the processing of spent dry batteries while the recycling and processing equipment for spent LIBs has been idled ever since the said technology transfer. One main reason is that there is a subsidy from a recycling fund managed by Taiwan EPA. The primary objective of this research was to make good use of such an already built LIBs recycling facility for its resurrection to recover valuable metals from cylindrical 18650-type spent LIBs. Based on the principle of technically feasible reverse implementation, through this study a flowchart of recycling processes can be re-devised and the lab-scale optimal operating conditions determined can be implemented in this existing recycling plant for spent LIBs in the near future.

2. Experimental

2.1 Source of spent LIBs and their pretreatment

Spent LIBs of cylindrical 18650 cells were first collected by a local batteries recycling plant (i.e., Plant Y). Then they were subjected to electricity discharging, crushing, and screening. The screen undersize (minus 0.27 mm fraction) was then subjected to roasting at 400 °C before its hydrometallurgical processing.

2.2 Reductive acid leaching

After the pretreatment, the powders of spent LIBs were subjected to leaching of sulfuric acid (2-4 M) with a pulp density of 33 g/L at an elevated temperature (30°C, 55°C, and 80°C) for 60 min to determine the optimal concentration of H_2SO_4 and operating temperature. To further enhance the acid leaching performance, reductive leaching was conducted using H_2SO_4 accompanied by H_2O_2 (30% in concentration) with a dose of 5 vol% or 10 vol% for comparison. After each leaching test, solid/liquid separation followed.

2.3 Separation of metallic ions in the leached solution

In this study of spent LIBs recycling, the valuable metals of concern included Co, Ni, Li, and Mn. To better recover these valuable metals, the following scheme of recycling processes was proposed and tested: (1) selective precipitation of Fe and Al in the hydroxide form using NaOH at pH 3.8; (2) recovery of Mn by solvent extraction (i.e., extraction by 0.45 M di-(2-ethylhexyl) phosphoric acid (in short, D2EHPA) with a saponification degree in the range of 25-70% under the phase ratio O/A = 1 and stripping by 0.1 M H_2SO_4 to form $MnSO_4$); (3) recovery of Co and Ni by solvent extraction (i.e., extraction by kerosene diluted bis-(2,4,4-tri-methyl-pentyl) phosphinic acid (known as Cyanex 272) with a saponification degree in the range of 10-70% under the phase ratio O/A =1 while adjusting the aqueous phase to neutral pHs and then stripping by 0.1 M H_2SO_4 to form $CoSO_4$ and $NiSO_4$); and (4) selective precipitation to form Li_2CO_3 for Li recovery using oversaturated potassium carbonate. In this stage, solid/liquid separation was conducted whenever needed.

2.4 Recovery of metals by electrowinning

Cobalt and nickel recovered from the solvent extraction stage (in the forms of $CoSO_4$ and $NiSO_4$) were further subjected to electrowinning in an electrochemical cell using titanium plate as the anode and SS 316L as the cathode. Different operating conditions were tested to attain the optimal performance in recovery of Co and Ni.

2.5 Analysis of metal concentrations in solutions and characterization of solid specimens

In this work concentrations of different metals in aqueous solutions were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES; PerkinElmer Optima 7000, USA). Metal sheets obtained from electrowinning were analyzed by environmental scanning electron microscopy with energy-dispersive X-ray spectroscopy (ESEM-EDS; ESEM: FEI Quanta-200, Czech Republic & EDS: EDAX Genesis XM 4i, USA) and X-ray diffractometry (XRD; Bruker D8 Discover, USA), whereas the residual elements in the electrolyte after electrowinning were analyzed by ICP-OES.

3. Results and discussion

3.1 Metal contents in the pretreated specimen of spent LIBs

In this study Ni, Co, and Mn were found to be the major elements contained in cylindrical 18650-type LIBs that have been subjected to the pretreatment. Their corresponding contents were determined to be 28.9-32.5 wt%, 29.5-32.4 wt%, and 17.2-29.1 wt% (varied with analytical methods and with or without roasting). As for the contents of minor elements, they were determined and shown as follows: (1) Fe, 3.65-7.49 wt %; (2) Al, 3.71-6.87 wt%; (3) Li, 4.44-5.85 wt%.

3.2 Reductive acid leaching

Among various concentrations of H_2SO_4 tested, 3 M was found to outperform the others. Then acid leaching was conducted using 3 M H_2SO_4 under different temperatures and reaction time. Test results showed that the leaching efficiencies of selected metals increased with increasing temperature and reaction time. This finding is in line with that of reported by others [17]. Such test results are not surprising because that the acid leaching of metals is an endothermic reaction. An increase in reaction temperature influenced the leaching of Fe and Ni the most, followed by Co and Li, and the least for Al and Mn. In addition, the leaching efficiencies of selected metals increased as the reaction time elapsed, but leveled off around 20 min. Thus, the optimal conditions for acid leaching of cylindrical 18650-type spent LIBs at this stage were determined to be 3M H_2SO_4, reaction temperature of 80 ºC, and reaction time of 20 min. Under the circumstances, the leaching efficiencies of selected metals are given as follows: (1) Fe, 100%; (2) Ni, 92%; (3) Al, 83%; (4) Li, 82%; (5) Mn, 76%; and (6) Co, 63%. To further increase the leaching efficiencies of Co and Li, two different doses of H_2O_2 (i.e., 5 vol% and 10 vol%) were used in reductive leaching experiments separately to study the influence of this reducing agent. It was found that by adding 10 vol% H_2O_2 to the H_2SO_4 leaching system a remarkable increase in leaching efficiencies of Co, Ni, and Li were obtained in 10 min of reaction time, particularly for Co. The H_2O_2-enhanced leaching efficiencies of selected metals became 100% for Fe, 91% for Ni, 82% for Al, 97% for Li, 95% for Mn, and 97% for Co. A similar trend of findings were also reported other researchers [9, 13]. Such a marked increase in leaching efficiency of Co was verified by the comparison of X-ray diffraction (XRD) patterns (Note: Not shown) of the original specimen of cylindrical 18650-type spent LIBs and the specimen subjected to reductive leaching by 3 M H_2SO_4 and 10 vol% H_2O_2. As noticed, the relative intensities of $LiCoO_2$, Co_3O_4, and CoO are greatly reduced in the latter XRD pattern as compared with the former. This is an indication that a great portion of Co_3O_4 and CoO in the specimen of cylindrical 18650-type spent LIBs were dissolved by H_2O_2. Thus, 10 vol% of H_2O_2 was further selected and added to the aforementioned optimal leaching conditions. The leached metal contents thus obtained were used as the basis for the calculations of metal recovery when needed.

3.3 Separation of metallic ions in the leached solution

After acid leaching, NaOH was used to form metal hydroxides for the removal of Fe^{3+}/Fe^{2+} and Al^{3+} from the leached solution. Since H_2SO_4 was used for leaching of LIBs, ferrous ions formed would be oxidized to ferric ions by H_2O_2 when the said reductive acid leaching was performed. Under a proper pH condition Fe^{3+} in contact with OH^- would form $Fe(OH)_3$ precipitate. In a recycling study of LIBs, it was reported that 100% removal of Fe was obtained under the condition of pH ranging from 3.8 to 5.2 [18]. To avoid the loss of valuable metals of concern due to their co-precipitation with $Fe(OH)_3$ at a higher pH (e.g., > 4.5), pH = 3.8 was thus selected in this work. Test results showed that 100% Fe and 22% Al contained in the leached solution were removed. Nevertheless, 4% Li, 2% Co, and 2% Ni were also reported to the loss due to co-precipitation.

As reported in the literature, solvent extraction has proven its excellence in extraction of valuable metals from the acid leached solution of LIBs [12-15]. Thus, solvent extraction was also adopted for the recovery of Mn, Co, and Ni using selected organic solvents with various saponification degrees (SD) at equal phase ratio (i.e., O/A = 1). Here extraction of Mn was studied using 0.45 M D2EHPA with SD in the range of 25-70%. Results of preliminary tests showed that adjusting pH value for the aqueous phase alone seemed to be of no help in reducing the co-extraction of other valuable metals beside Mn. As for the effect of SD of D2EHPA on metal separation, it was found that co-extraction of valuable metals became more obvious in the cases of 45% to 70% of saponification degree under pH = 3 (see **Fig. 1**). However, when D2EHPA with a SD = 25% was employed, zero extraction of Mn was found. Thus, to yield a result of minimum co-extraction of other valuable metals while obtaining a good extraction of Mn, D2EHPA with a SD of greater than 25% was considered. When SD was increased to 35%, it was found that 79% extraction of Mn was obtained without co-extraction of Co. During the stripping step, 0.1 M H_2SO_4 as the stripping agent was found to be capable of yielding 100% stripping efficiency for Mn.

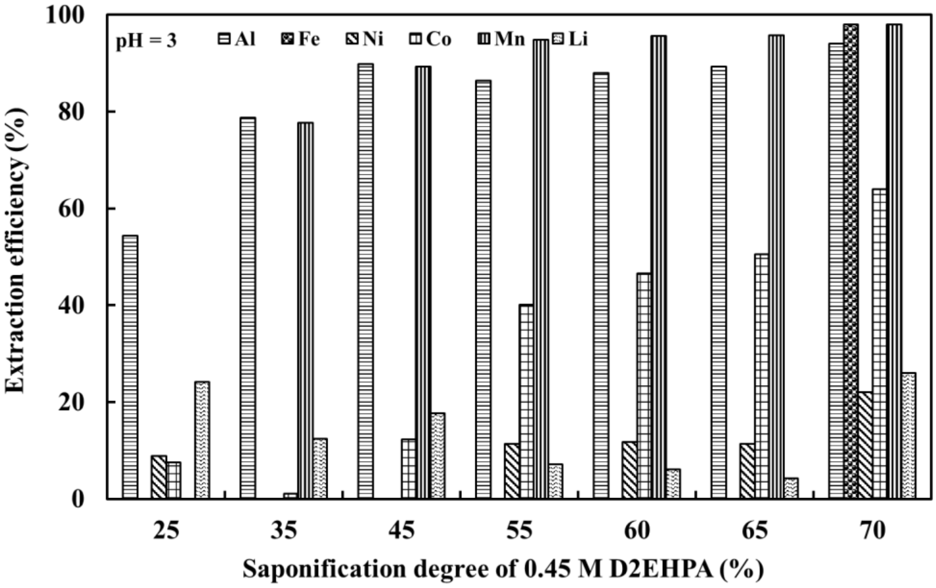


Fig. 1. Variation of extraction efficiency with saponification degree of D2EHPA for solvent extraction of various metals contained in cylindrical 18650-type spent LIBs

After the separation of Mn has been achieved, further separation of Co and Ni were studied. In this work solvent extraction of Co was conducted using 0.3 M Cyanex 272 of various saponification degrees at pH 6, whereas 0.1 M H_2SO_4 was used for stripping (see **Fig. 2**). Cyanex 272 with a SD of 50% was found to be the optimal condition in this study yielding 100% extraction efficiency of Co and only 10% co-extraction of Ni. This finding is in very good agreement with that of reported by others [19]. When a lower SD of Cyanex 272 was used, it yielded a much poor extraction (28-65%) of Co along with co-extraction of other valuable metals. Oppositely, when a higher SD of Cyanex 272 was used, a serious co-extraction of Ni (up to 84%) was found.

In this study the solvent extraction and stripping conditions used for Ni were the same as for Co except pH at 7 was used. To obtain a high extraction efficiency of Ni, however, two-stage solvent extraction and stripping were employed. In so doing, 100% extraction efficiency and 99% stripping efficiency of Ni were obtained. Since the metals partitioned into Cyanex 272 can be almost completely stripped out, this organic solvent thus can be regenerated via new saponification for re-use in later experiments.

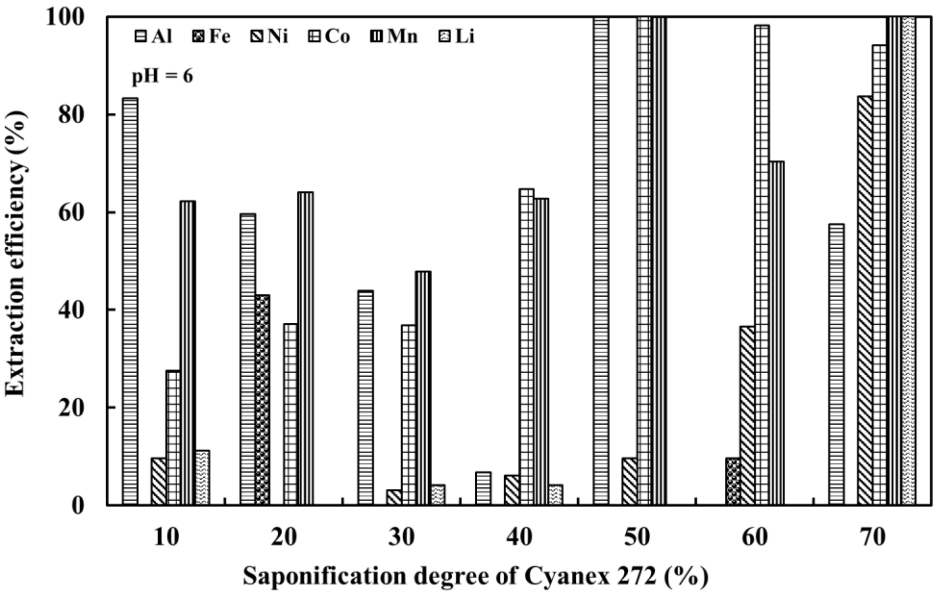


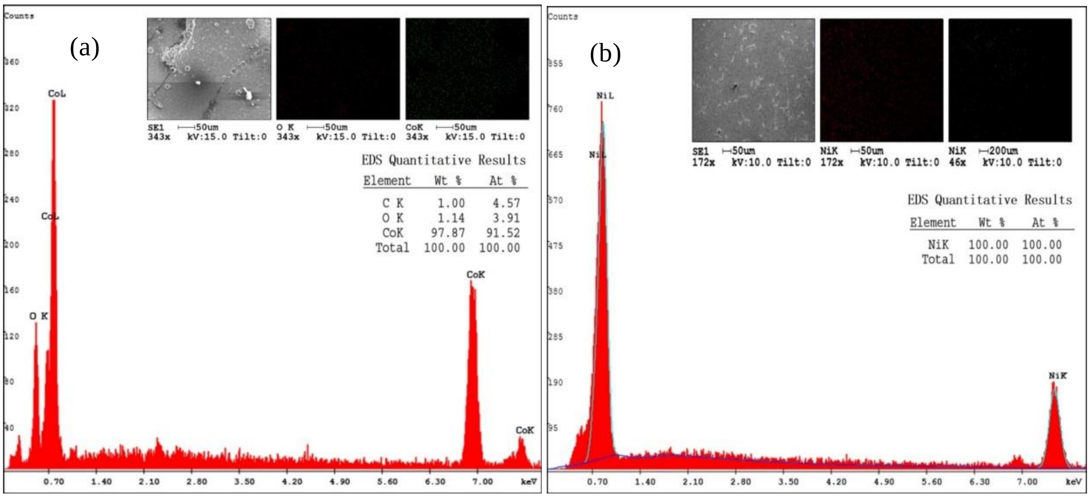
Fig. 2. Variation of extraction efficiency with saponification degree of Cyanex 272 for solvent extraction of various metals contained in cylindrical 18650-type spent LIBs

3.3.4 Recovery of Li^+ from raffinates

The raffinate that remains after removal or extraction from each of the aforementioned separation processes might still contain lithium ions worth recycling. To meet this end, an equal volume of oversaturated potassium carbonate solution was mixed with each of raffinates to form Li_2CO_3 precipitates. It was determined that 42-94% of lithium ions were precipitated depending on the residual concentration of Li^+ in each raffinate.

3.4 Recovery of Co and Ni by electrowinning

As stated in Subsection 3.3, while using Cyanex 272 for solvent extraction of Co and Ni, 0.1 M H_2SO_4 was used as the stripping solution yielding aqueous solutions containing $CoSO_4$ and $NiSO_4$ separately. Each of these solutions was used as the electrolyte in the electrochemical cell by applying an electric current (110 A/m^2 in current density) to recover the metal therein via electrodeposition. It was found that recovery of Co and current efficiency increased with increasing reaction temperature and time, but with decreasing concentration of sulfuric acid. Under the optimal operating conditions, the maximum recovery of cobalt and current efficiency both reached 100%. This is in good agreement with the general findings reported for spent LIBs even though the present study employed a much lower current density as compared with other studies (i.e., 110 A/m^2 vs. 240-250 A/m^2) [20,21]. Similar experimental findings were also obtained for Ni. The maximum recovery of nickel and current efficiency were determined to be 100% and 65%, respectively. Metal sheets thus obtained were further examined and analyzed by ESEM-EDS. As shown in **Fig. 3** and XRD patterns (not shown), these electrodeposited metal sheets were determined to be high-purity Co and high-purity Ni, respectively. Further, the residual concentrations of Co and Ni in the electrolytes after electrowinning were found to be undetectable.



EDS Quantitative Results

Element	Wt %	At %
C K	1.00	4.57
O K	1.14	3.91
CoK	97.87	91.52
Total	100.00	100.00

EDS Quantitative Results

Element	Wt %	At %
NiK	100.00	100.00
Total	100.00	100.00

Fig. 3. SEM micrographs and the relevant EDS results for the metal sheets obtained from (a) 0.1 M $CoSO_4$ and (b) 0.1 M $NiSO_4$ subjected to electrowinning, respectively

3.5 Summary and overall evaluation of technical feasibility

In this work the technical feasibility was evaluated based on the pre-treated specimen of screen undersize (< 0.27 mm fraction) of cylindrical 18650-type spent LIBs. During the acid leaching stage it yielded the leaching efficiencies of greater than 90% for all target metals except Mn. During the hydroxide precipitation stage it yielded the removal efficiencies of 100% for Fe and 22% for Al. However, 29% of Mn was also removed due to co-precipitation. During the solvent extraction stage using D2EHPA, it yielded 82% extraction efficiency for Mn. During the solvent extraction stage using Cyanex 272, it yielded 100% extraction efficiency for Co and 29% co-extraction of Ni. Using 0.1 M H_2SO_4 as the stripping agent the subsequent stripping efficiency for Co was determined to be 100%, which is beneficial to Co recovery by electrowinning. In a separate operation of the 2-stage solvent extraction using Cyanex 272, it yielded 100% extraction efficiency for Ni. Using 0.1 M H_2SO_4 the subsequent 2-stage stripping efficiency for Ni was determined to be 99%. During the carbonate precipitation stage the removal of lithium ion up to 92% was attainable. Finally, during the electrowinning stage it yielded 100% recovery for both Co and Ni. Based on the metal contents determined by ICP-OES analysis of the acid leachate, the devised flowchart of recycling processes (see **Fig. 4**) in this lab-scale study could yielded the following overall recoveries: (1) Ni, 95%; (2) Co, 93%; (3) Li, 72%; and (4) Mn, 69% or 55% depending on in the form of $MnSO_4$ (after solvent extraction) or in the form of Mn_3O_4 (after electrowinning). It is worth noting that in this work the overall recovery for each target metal refers to the screen undersize specimens of entire spent LIBs of 18650-type, which has been subjected the said pretreatments, reductive acid leaching, chemical precipitation, solvent extraction, and electrowinning. Inevitably, there would be a certain degree of metal loss in almost every unit operation. In comparison with other studies, however, the present study still yielded a comparable or even better recovery for each target metal. In the literature, most researchers used only the specimens of the cathodic active materials of LIBs in their studies for reporting the recovery of metals. Besides, most of studies did not have a complete recycling route to recover very pure cobalt and nickel as compared with the present study. Thus, the recycling scheme devised as shown in **Fig. 4** is considered to be technically feasible. More specifically, there is a great potential for this scheme of metal recycling processes for spent LIBs of cylindrical 18650 cells to be scaled up and implemented in an actual battery recycling plant (i.e., Plant Y).

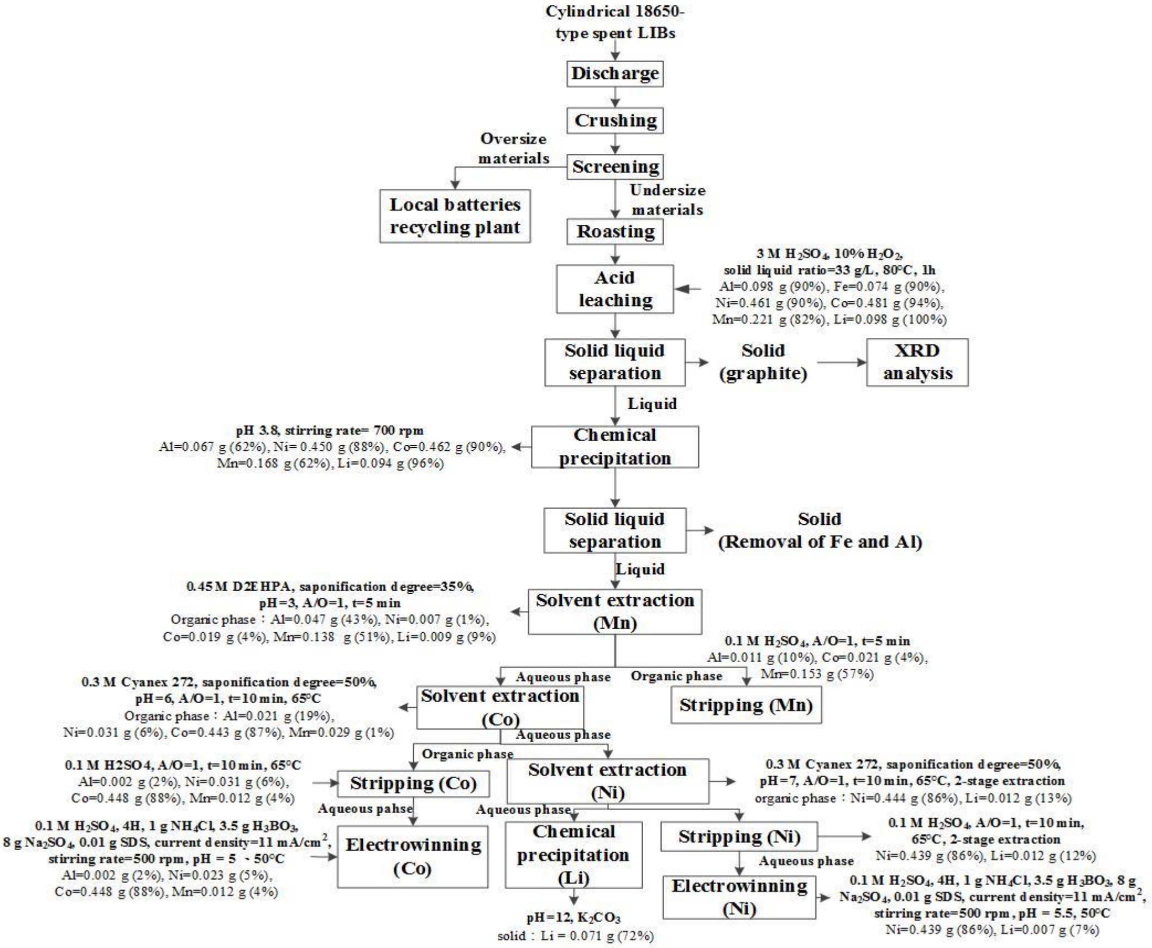


Fig. 4. Flowchart of cylindrical 18650-type spent LIBs recycling processes

4. Conclusions

In this lab-scale study the devised flowchart of recycling processes for spent LIBs of cylindrical 18650 cells has been found to be technically feasible. This recycling scheme includes pretreatment, acid leaching, separation of metals in leached solution, hydroxide precipitation, solvent extraction, carbonate precipitation, and electrowinning. Under the optimal operating conditions the overall recoveries were 95% for Ni, 93% for Co, 72% for Li, and 69% for Mn were obtained. Thus, a scale-up study has been planned for future implementation in an already built and almost fully equipped battery recycling plant in Taiwan.

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