Separation of Co(II), Mn(II), and Ni(II) by solvent extraction with Cyanex 272 and D2EHPA from the sulfuric acid leaching solution of spent lithium-ion batteries

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Abstract: Spent lithium-ion batteries contain valuable metals such as cobalt, lithium, manganese and nickel. Smelting reduction of spent LIBs at high temperature results in metallic alloys. Therefore, it is necessary to recover the valuable metal ions present in the sulfuric acid leaching solutions of the metallic alloys. In this work, solvent extraction experiments were performed to separate the three metal ions, Co(II), Mn(II) and Ni(II) present in the leaching solutions of the metallic alloys. Synthetic sulfate solutions were prepared and commercial organophosphorous extractants were employed. First, both Co(II) and Mn(II) were completely extracted in one stage by using 40% saponified 0.3 M Cyanex 272, leaving Ni(II) in the raffinate. The small amount of Ni(II) co-extracted into Cyanex 272 was removed by two stages of cross-current scrubbing using pure $CoSO_4$ solution. The effect of pH and $CoSO_4$ concentration of the scrubbing solution on the scrubbing of Ni(II) was investigated. The Co(II) and Mn(II) present in the scrubbed Cyanex 272 were completely stripped by 0.05 M H_2SO_4 solution. Batch simulation experiments for the three stage of counter-current extraction with 1 M D2EHPA verified that Mn(II) and Co(II) were completely separated by selective extraction of Mn(II) into D2EHPA, leaving Co(II) in the raffinate. By consecutive extraction with Cyanex 272 and D2EHPA, pure solutions of Co(II), Mn(II) and Ni(II) with purity higher than 99.9% can be recovered from the starting solutions. A process was proposed for the treatment of sulfuric acid leaching solutions of spent LIBs containing Co(II), Mn(II) and Ni(II) by solvent extraction.

Keywords: hydrometallurgy, spent lihtium-ion batteries, separation, solvent extraction, commercial extractants

1. Introduction

Lithium-ion batteries have excellent energy storage capability and thus are extensively used in the portable vehicles and portable electronics (Bajolle et al., 2022). According to the report of Natarajan and Aravindan, the production of LIBs was valued at $30.4 billion in 2020 and is predicted to reach $304.7 billion by 2030 (Natarajan and Aravindan 2018). Moreover, the grade of the valuable metals (cobalt, lithium, manganese and nickel) present in LIBs is much higher than that of primary ores (Tawonezvi et al., 2023). It is anticipated that an enormous amount of waste products containing spent LIBs will be phased out during the next five years, resulting in waste of resources and negative effects on the local ecosystem. Therefore, it is essential to develop an appropriate method for the recovery of these valuable metals from spent LIBs (Shin and Sohn 2010; Cerrillo-Gonzalez et al., 2024; He et al., 2024). In general, hydrometallurgy and pyrometallurgy are the two main technologies utilized for recovering valuable metals from spent LIBs (Zanoletti 2024). Pyrometallurgy has some advantages such as large-scale treatment capacity and simple operation. However, low selectivity for target metals, waste gas emissions, and energy consumption from high temperature operation are some drawbacks of pyrometallurgy (Bellemans 2018; Liu et al., 2019; Makuza et al., 2021). Although the scale of hydrometallurgical process is relatively small and waste liquid is generated, it has the advantages of low process temperature, low hazardous gas emissions, and excellent metal extraction selectivity (Li et

al., 2019). Namely, hydrometallurgical operations such as leaching, chemical precipitation, solvent extraction, cementation, and ion exchange could efficiently and selectively recover target metals with high-purity from spent LIBs (Jha et al., 2016). Among these operations, precipitation can be performed using simple equipment at low cost. Although precipitation can effectively remove metal ions with high concentration, its selectivity for the target metal ions is not good owing to the possibility of adsorption of impure metal ions. Therefore, the purity of the precipitated metal may be low, requiring further purification (Rabah and Barakat 2001). Moreover, ion exchange has the advantage of providing high selectivity for specific metal ions, but the initial installation cost of the ion exchange resin is high (Wang et al., 2010). Solvent extraction provides high selectivity and separation efficiency (Verhoef et al., 2013; Habashi 2013). It also has some advantages in recovering high purity metals (Swain 2017). Therefore, to process spent LIBs on an industrial scale, combined processes of both pyrometallurgical and hydrometallurgical operations have been investigated. Namely, reduction smelting of spent LIBs powders at high temperature results in metallic alloys containing copper, cobalt, iron, manganese, and nickel (Tran et al., 2022). Our previous study indicated that dissolution of these metallic alloys by sulfuric acid solution containing an oxidizing agent results in a leaching solution containing Co(II), Cu(II), Fe(III), Mn(II), and Ni(II). Among these ions, Cu(II) and Fe(III) can be separated by cementation with iron powders and solvent extraction with D2EHPA after oxidation of Fe(II) to Fe(III), respectively (Wen et al., 2024; Jing et al., 2024). Therefore, the raffinate contained only Co(II), Mn(II) and Ni(II) and the concentrations of these metal ions in the resulting solution are represented in Table 1.

Table 1. The concentration of Co(II), Mn(II) and Ni(II) in the resulting solution after removal of Cu(II) and Fe(III) from the sulfuric acid leaching solution of spent LIBs (Tran et al., 2022).

Metal ions	Co(II)	Mn(II)	Ni(II)
mg/L	1869	258	9258

Cobalt(II) and nickel(II) ions are difficult to separate from weakly acidic solutions owing to their similar chemical properties. The presence of Mn(II) would complicate the separation of Co(II) and Ni(II). Chemical precipitation by using Na_2S and oxidative precipitation using NaClO are employed to separate Co(II), Mn(II) and Ni(II) from weakly acidic solutions (Qasem et al., 2021). Namely, Co(II) and Ni(II) can be selectively co-precipitated as metal sulfides over Mn(II) due to their lower solubility product, leaving Mn(II) in the filtrate (Ichlas et al., 2020). In this case, CoS and NiS in the precipitates need to be re-dissolved and then the metal ions should be separated from the leaching solution. On the other hand, in the oxidative precipitation of Mn(II) and Co(II) by NaClO from the sulfuric acid solution, its operating parameters should be strictly controlled to achieve separation (Wen et al., 2024). Although solvent extraction is easier to run in industrial scale compared to precipitation, the pH of the solution and the concentration of the extractants should be strictly controlled to achieve high degree of separation.

Generally, solvent extraction with organophosphorous extractants like D2EHPA, PC88A, and Cyanex 272 is employed to separate Co(II), Mn(II) and Ni(II) from weakly acidic solutions due to their excellent separation performance (Liu et al., 2015). When these acidic extractants are employed alone in solvent extraction, the equilibrium pH of the solution would be decreased, resulting in low extraction percentage of the target metal ions. Furthermore, co-extraction of impure metal ions reduces the purity of the target metal ions in the loaded organic phase. Therefore, in order to overcome the above drawbacks, saponification of the extractant, scrubbing and counter-current extraction are commonly employed for selective separation of metal ions by solvent extraction (Sole et al., 2005; Gajda and Bogacki 2006).

In this study, solvent extraction experiments were done to separate Co(II), Mn(II) and Ni(II) from the solutions with the same composition as Table 1. Since the concentration of Ni(II) was the highest in the solution, separation of Ni(II) was investigated by complete extraction of Co(II) and Mn(II) from the solution by using Cyanex 272. For this purpose, the concentration of Cyanex 272, its saponification degree, and scrubbing of the co-extracted Ni(II) was investigated. In order to separate the Co(II) and Mn(II) present in the loaded Cyanex 272, they were stripped by using sulfuric acid solutions. Then selective extraction of Mn(II) over Co(II) from the stripping solution was investigated by employing

counter-current extraction with D2EHPA. A process on the basis of solvent extraction was proposed for the recovery of pure Co(II), Ni(II), and Mn(II) solutions from the synthetic sulfuric acid leaching solution of spent LIBs.

2. Experimental

2.1. Reagents and chemicals

The synthetic solutions with the same composition as Table 1 were prepared by dissolving the corresponding salts of $CoSO_4(CoSO_4 \cdot 7H_2O$, Junsei Chemical Co., >98%, Japan), $MnSO_4(MnSO_4 \cdot nH_2O$, Duksan Pure Chemical Co., >98.5%, Korea), and $NiSO_4$ ($NiSO_4 \cdot 6H_2O$, Daejung Co., >98.5%, Korea) in the distilled water. The pH of the synthetic solutions was adjusted by adding either sulfuric acid solution (H_2SO_4, Daejung Co., >95%, Korea) or sodium hydroxide (NaOH, Duksan Pure Chemical Co,.LTD, >95%, Korea). Cyanex 272 (Cytec Inc., 85%, Canada), and D2EHPA (Daihachi Chem. Inc., 95%, Japan) were employed as extractants in the solvent extraction experiments. Commercial grade kerosene (Daejung Co., >90%, Korea) was employed as a diluent for the extractants. NaOH and H_2SO_4 solutions were used as a saponification and stripping agent in extraction and stripping experiments, respectively. All the chemicals used in this study were employed without any further purification.

2.2. Procedure and analytical methods

Plastic screw bottles (100 mL) were used to hold equal volume (20 mL) of the aqueous and the organic solutions in the solvent extraction experiments. Both phases were shaken for 30 mins using a wrist action shaker (model 75, USA), and then separated by using separatory funnels. The pH of the aqueous solution was measured using a pH meter (Orion Star A211, Thermo Fisher Scientific, USA). The concentrations of Co(II), Ni(II), and Mn(II) in the aqueous solution were measured by Inductively Coupled Plasma-Optical Emission Spectometer (ICP-OES, Spectro Arcos, Cleve, Germany), and those in the organic were calculated by mass balance. Extraction, stripping, and scrubbing percentage were calculated as follows.

$$\text{Extraction percentage} = \frac{(m_{initial} - m_{aq}) \times 100}{m_{initial}} \tag{1}$$

where $m_{initial}$ and m_{aq} are the mass of the metal ions in the aqueous before and after extraction, respectively.

$$\text{Stripping percentage} = \frac{m_{aq} \times 100}{m_{org}} \tag{2}$$

where m_{org} and m_{aq} are the mass of the metal ions in the organic phase before stripping and that in the aqueous phase after stripping, respectively.

$$\text{Scrubbing percentage} = \frac{m_{aq} \times 100}{m_{initial,org}} \tag{3}$$

where, m_{aq} and $m_{initial,org}$ are the mass of the metal ions in the aqueous phase after scrubbing and that in the organic phase before scrubbing, respectively.

Extraction percentage of a metal ion is based on the ratio of its mass, while the distribution coefficient of a metal ion is defined as the ratio of its concentration in the organic to that in the aqueous after extraction. Separation factor between Co(II) and Ni(II) is defined as the ratio of distribution coefficients of two metal ions.

$$\text{Separation factor} = \frac{D_{Co(II)}}{D_{Ni(II)}} \tag{4}$$

where $D_{Co}(II)$ and $D_{Ni}(II)$ represent the distribution coefficients of Co(II) and Ni(II), respectively.

3. Results and discussion

Lots of work have been reported on the extraction of Co(II), Mn(II) and Ni(II) from weakly acidic solutions by using organophosphorous extractants such as D2EHPA, PC 88A and Cyanex 272 (Nathsarma and Devi 2006; Wang et al., 2022).

In the synthetic sulfate solutions employed in this work, the concentration of Ni(II) was the highest. Therefore, separation of the minor components, Co(II) and Mn(II), would result in raffinate containing

only Ni(II). According to the extraction data of divalent metal ions by the above three extractants, Cyanex 272 can extract Co(II) and Mn(II) together, leaving Ni(II) in the raffinate(Guimarães et al., 2014). Therefore, Cyanex 272 was first employed in this work to separate Co(II) and Mn(II) from the solution.

3.1 Simultaneous separation of Co(II) and Mn(II) from Ni(II) by solvent extraction with Cyanex 272

3.1.1. Comparison of extraction behavior of the metal ions between Cyanex 272 and saponified Cyanex 272

The extraction behaviour of the three metal ions by Cyanex 272 was first investigated by varying the concentration of Cyanex 272 from 0.1 to 1 M. In these experiments, the initial pH of the synthetic solution was fixed at 6. The extraction reaction of divalent metal ion by Cyanex 272 can be represented as (Tang and Steenari 2015)

$$M^{2+}_{aq} + 2H_2A_{2,org} = M(HA_2)_{2,org} + 2H^+_{aq} \tag{5}$$

where M^{2+} and H_2A_2 represent divalent metal ions and dimeric Cyanex 272, respectively. Moreover, subscripts aq and org represent aqueous and organic phases. Fig. 1 shows that Ni(II) was not extracted at all in the Cyanex 272 concentration ranges employed in this work. Although Co(II) and Mn(II) were co-extracted by Cyanex 272, their extraction percentages were less than 10%. The lower extraction percentage of Co(II) and Mn(II) might be ascribed to a decrease in solution pH during the extraction. As shown in Fig.1, the equilibrium pH of the aqueous solution decreased to 2.8 as Cyanex 272 concentration increased to 1 M. The decrease in solution pH is related to the liberation of hydrogen ions from Cyanex 272 during the extraction of the metal ions.
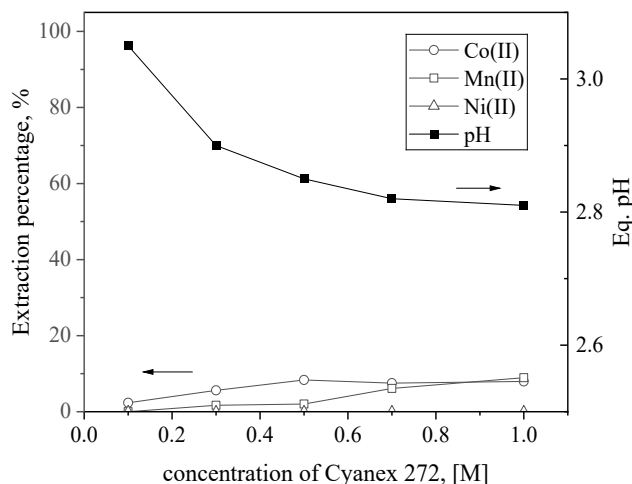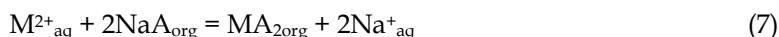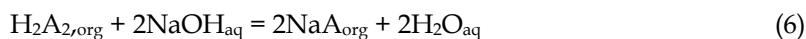

Fig. 1. Effect of Cyanex272 concentration on the extraction of Co(II), Ni(II) and Mn(II) from synthetic sulfate solution with initial pH 6 at unity phase ratio. (reaction time: 30mins and temperature: 25°C)

Therefore, saponified Cyanex 272 was employed to suppress the decrease in solution pH owing to the liberation of hydrogen ions from Cyanex 272. The saponification reaction of Cyanex 272 and the extraction of divalent metal ion by the saponified Cyanex 272 can be represented as (Kim et al., 2016).

$$H_2A_{2,org} + 2NaOH_{aq} = 2NaA_{org} + 2H_2O_{aq} \tag{6}$$

$$M^{2+}_{aq} + 2NaA_{org} = MA_{2org} + 2Na^+_{aq} \tag{7}$$

Comparing the extraction reactions, Eqs. (5) and (7) indicates that there is some difference in the extraction reaction of metal ions between Cyanex 272 and saponified Cyanex 272. Dimeric form of Cyanex 272 takes part in the extraction, while monomeric form of saponified Cyanex 272 takes part in the reaction. Since sodium ions are liberated instead of hydrogen ions during the extractions, the decrease in solution pH would be reduced, which would enhance the extraction of metal ions. In order to investigate the effect of saponification degree on the extraction of the metal ions, saponification degree of 0.3 M Cyanex 272 was varied from zero to 50% and extraction experiments were done employing the synthetic solution with initial pH 6. Fig. 2 shows that extraction percentages of Co(II)

and Mn(II) increased rapidly from 6% to 97% and 2% to 99%, respectively, as the saponification degree of Cyanex 272 increased from zero to 30%, while the equilibrium pH was gradually increased from 2.9 to 4.64. The extraction capacity of the saponified extractant for the target metal ion is much higher than that of the unsaponified extractant on the basis of the concentration of the extractant. Moreover, this figure shows that the extraction percentage of metal ions was increased with the final pH of the raffinate because the reduction in solution pH is lessened owing to the transfer of sodium ions instead of hydrogen ions, which is in good agreement with Eq. (7). When the saponification degree of Cyanex 272 was 40%, Co(II) and Mn(II) were completely extracted together with a small amount of Ni(II). The separation factors between Co(II) and Ni(II) by the 30% and 40% saponified 0.3M Cyanex 272 were 2184 and 1790, respectively, indicating that 30% saponified 0.3 M Cyanex 272 was more effective than 40 % saponified 0.3 M Caynex 272 in terms of separation factor.

In order to completely extract Co(II) and Mn(II) by saponified Cyanex 272, cross-current extraction experiments were done. In these experiments, 30% saponified 0.3 M Cyanex 272 was employed and Table 2 shows the results of two stages of cross-current extraction. In the first stage, 97% of Co(II) and 99% of Mn(II) were extracted and both metal ions were completely extracted at the second stage of cross-current extraction. But 26.8% of Ni(II) was co-extracted at the second stage of cross-current extraction. Therefore, it is necessary to remove Ni(II) from the loaded Cyanex 272.
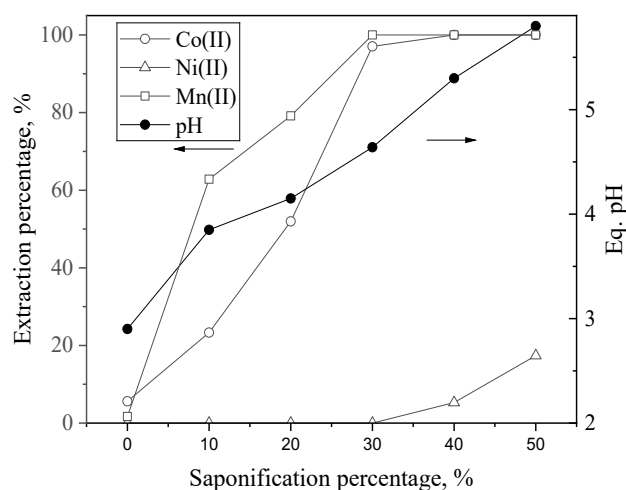

Fig. 2. Effect of saponification degree of 0.3 M Cyanex 272 on the extraction of Co(II), Ni(II) and Mn(II) from synthetic sulfate solution with initial pH 6 at unity phase ratio.(reaction time: 30mins and temperature: 25°C)

Table 2. Variation in the extraction percentage of Co(II), Ni(II) and Mn(II) during two stages of cross-current extraction with 30% saponified 0.3 M Cyanex 272 at unity phase ratio. (Initial pH of aqueous solution: 6, reaction time: 30min, temperature: 25°C)

	stage	Mn(II)	Co(II)	Ni(II)	Eq. pH
Extraction percentage, %	1	88.4	97.2	2.3	4.77
	2	99.9	99.9	26.8	5.82

3.1.2. Scrubbing of Ni(II) from the loaded Cyanex 272 with pure cobalt sulfate solution

According to the results in previous section, the separation factor between Co(II) and Ni(II) by 30% saponified 0.3 M Cyanex 272 was higher than that by 40% saponified 0.3 M Cyanex 272. However, two stages of counter-current extraction were necessary to completely extract Co(II) and Mn(II) from the solution by 30% saponified 0.3 M Cyanex 272. In this cross-current extraction, about 26% of Ni(II) was co-extracted after two stages. By contrast, complete extraction of Co(II) and Mn(II) in one stage was possible by employing 40% saponified 0.3 M Cyanex 272. In this case, about 5% of Ni(II) was co-extracted in one stage. On the basis of the process simplification and the suppression of the co-extraction of Ni(II), 40% saponified 0.3 M Cyanex 272 was selected for further experiments. For scrubbing

experiments, the loaded Cyanex 272 was prepared by using 40% saponified 0.3 M Cyanex 272. When 40% saponified 0.3 M Cyanex 272 was employed, the concentrations of Co(II), Ni(II), and Mn(II) in the loaded Cyanex 272 were 1949, 487 and 314 mg/L. Scrubbing experiments were done by using pure CoSO$_4$ solution. In scrubbing experiments, the concentration of Co(II) in the scrubbing solution and solution pH would affect the scrubbing behavior of the metal ions present in the loaded organic. Table 3 shows the effect of the initial pH of the scrubbing solution on the scrubbing of Ni(II) from the loaded Cyanex 272. In these scrubbing experiments, the concentration of Co(II) in the scrubbing solution was fixed at 2 g/L. The Ni(II) in the loaded Cyanex 272 was completely removed from the loaded Cyanex 272 irrespective of the initial pH of the scrubbing solution. When the initial pH of the scrubbing solution was 1.5, the concentration of Co(II) as well as Mn(II) in the loaded Cyanex 272 decreased, indicating that both ions were stripped from the loaded Cyanex 272 due to the low pH of the scrubbing solution. When the initial pH of the scrubbing solution was higher than 2, there was no change in the concentration of Mn(II), while that of Co(II) in the scrubbed solution increased, indicating that scrubbing reaction occurred. In these experiments, scrubbing of Ni(II) from the loaded Cyanex 272 by CoSO$_4$ scrubbing solution can be expressed as

$$Co^{2+}_{aq} + NiA_{2,org} = CoA_{2,org} + Ni^{2+}_{aq} \tag{8}$$
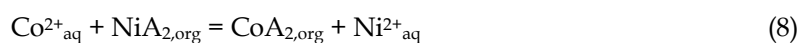
According to Table 3, when the initial pH of the scrubbing solution was 2, the increase in the concentration of Co(ll) in the loaded Cyanex 272 was about 11 mg/L, while the decrease in the concentration of Ni(II) in the loaded Cyanex 272 was 487 mg/L. This change in the concentration of Co(II) and Ni(II) during scrubbing indicates that stripping as well as scrubbing of Ni(II) by Eq. (8) occurred together when the pH of the scrubbing solution was 2. When the pH of the scrubbing solution was higher than 3, pure scrubbing of Ni(II) by Co(II) occurred. The data in Table 3 indicates that Ni(II) can be removed from the loaded Cyanex 272 by using pure CoSO$_4$ solution as a scrubbing solution. Since there was little change in the concentration of Mn(II) in the Cyanex 272, the purity of Co(II) in the scrubbed Cyanex 272 was rather constant when the pH of the scrubbing solution was in the ranges from 2 to 5.

Table 3. Effect of initial pH of the scrubbing solution on the scrubbing of Ni(II) from the loaded Cyanex 272 at unity phase ratio.(Concentration of Co(II) in the scrubbing solution: 2 g/L, loaded organic : 40% saponified 0.3 M Cyanex 272, reaction time: 30mins, temperature: 25°C)

pH	Before Scrubbing, mg/L			After Scrubbing, mg/L			Scrubbing %	Purity of Co(II) in organic, %
	Org$_{Co(II)}$	Org$_{Ni(II)}$	Org$_{Mn(II)}$	Org$_{Co(II)}$	Org$_{Ni(II)}$	Org$_{Mn(II)}$	Ni(II)	Co(II)
1.5	1949	487	314	523	0	187	100	73.6
2	1949	487	314	2059	0	314	100	86.8
3	1949	487	314	2577	0	314	100	89.1
4	1949	487	314	2642	0	314	100	89.3
5	1949	487	314	2673	0	314	100	89.4

The effect of Co(II) concentration in the scrubbing solution was investigated by fixing the pH of the scrubbing solution at 2. In these experiments, the concentration of Co(II) in the scrubbing solution was varied from 1 to 2 g/L. The initial concentrations of Co(II), Ni(II), and Mn(II) in the loaded Cyanex 272 were 1953, 463 and 343 mg/L which are slightly different from those data in Table 3. Table 4 shows that Ni(II) was completely scrubbed regardless of the concentration of Co(II) in the scrubbing solution. There was little change in the concentration of Mn(II) in the loaded Cyanex 272 during the scrubbing experiment, while the concentration of Co(II) in the loaded Cyanex 272 was slightly decreased when the concentration of Co(II) in the scrubbing solution was 1 g/L. Therefore, it can be inferred that all the Ni(II) together with some of Co(II) was stripped during scrubbing. This data might indicate that pure sulfuric acid solution with pH 2 can remove the Ni(II) from the loaded Cyanex 272 by selective stripping. But our data clearly shows that Co(II) can be also stripped when the pH of sulfuric acid solution is 2.

Presence of Co(II) in the scrubbing solution would suppress the stripping of Co(II) from the loaded Cyanex 272. Therefore, it can be said that control of the pH of the scrubbing solution is important in suppressing the stripping of Co(II) during scrubbing. Scrubbing experiments with pure CoSO$_4$ solution led to the scrubbed Cyanex 272 containing only Co(II) and Mn(II). Since the concentration of CoSO$_4$ in the scrubbing solution did not greatly affect the scrubbing percentage of Ni(II), scrubbing solution with Co(II) concentration of 1 g/L was selected as an optimum condition.

Table 4. Effect of Co(II) concentration in the scrubbing solution on the scrubbing of Ni(II) from the loaded Cyanex 272 at unity phase ratio. (Loaded organic: 40% saponified 0.3 M Cyanex 272, reaction time: 30mins, temperature: 25°C)

Co(II) conc. in scrubbing solution, mg/L	Before Scrubbing, mg/L			After Scrubbing, mg/L			Scrubbing %	Purity of Co(II) in organic, %
	Org$_{Co(II)}$	Org$_{Ni(II)}$	Org$_{Mn(II)}$	Org$_{Co(II)}$	Org$_{Ni(II)}$	Org$_{Mn(II)}$	Ni(II)	Co(II)
1000	1953	463	343	1932	0	336	100	85.1
1300	1953	463	343	2174	0	336	100	86.6
1500	1953	463	343	2353	0	336	100	87.5
1700	1953	463	343	2388	0	334	100	87.6
2000	1953	463	343	2538	0	333	100	88.3

3.2. Separation of Co(II) and Mn(II) from the scrubbed Cyanex 272

3.2.1. Stripping of Co(II) and Mn(II) using H$_2$SO$_4$ solution

One stage extraction of the sulfate solution with 40% saponified 0.3 M Cyanex 272 led to complete extraction of Co(II) and Mn(II), leaving Ni(II) in the raffinate. Therefore, pure Ni(II) compounds can be recovered from this raffinate. Scrubbing of Ni(II) from the loaded Cyanex 272 with CoSO$_4$ solution resulted in the scrubbed Cyanex 272 containing only Co(II) and Mn(II). Since the extraction behavior of Co(II) and Mn(II) by Cyanex 272 is similar to each other, it would be difficult to separate these two metal ions present in the scrubbed Cyanex 272 by selective stripping. Therefore, Co(II) and Mn(II) were completely stripped from the scrubbed Cyanex 272 by using sulfuric acid solution. Since stripping reaction is the reverse of the extraction reaction, stripping of divalent metal ions from the loaded Cyanex 272 with 40% saponification degree can be represented as follows

$$MA_{2,org} + 2H^+{}_{aq} = M^{2+}{}_{aq} + H_2A_{2,org} \qquad (9)$$
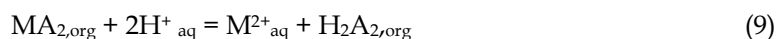
Stripping experiments were done by varying H$_2$SO$_4$ concentration from 0.01 to 1 M at unity phase ratio of the two phases. Fig. 3 shows that the stripping percentages of Co(II) and Mn(II) were 66% and
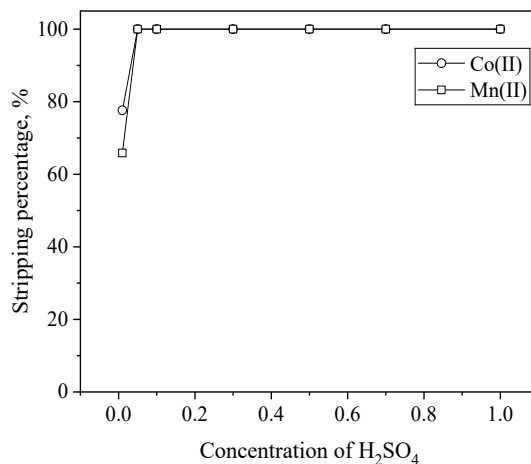

Fig. 3. Effect of H$_2$SO$_4$ concentration on the stripping of Co(II) and Mn(II) from the scrubbed Cyanex 272 at unity

phase ratio.(Scrubbed organic : 40% saponified 0.3 M Cyanex 272, reaction time: 30mins, temperature: 25°C)

77%, respectively when the concentration of sulfuric acid was 0.01 M. Both metal ions were completely stripped when the concentration of sulfuric acid was higher than 0.05 M. Therefore, 0.05 M H_2SO_4 solution was selected as the suitable condition for the complete stripping of Co(II) and Mn(II) from the scrubbed Cyanex 272.

3.2.2. Selective extraction of Mn(II) over Co(II) by D2EHPA from the stripping solution

When 0.05 M H_2SO_4 solution was employed as a stripping solution, the concentrations of Co(II) and Mn(II) in the stripping solution were 1953 and 343 mg/L, respectively. According to the extraction data of divalent metal ions by organophosphorous extractants, D2EHPA shows some selectivity for Mn(II) over Co(II) from weakly acidic solution (Nguyen et al., 2020). Since the initial pH of the solutions affects greatly the extraction of metal ions by organophosphorous extractants, the initial pH of the stripping solution was varied from 3 to 6. **Fig. 4** shows the effect of initial pH on the extraction of the two metal ions by using 0.3 M D2EHPA at unity phase ratio. The extraction percentages of Co(II) and Mn(II) were rather constant at approximately 9% and 61% irrespective of the initial pH of the solution.
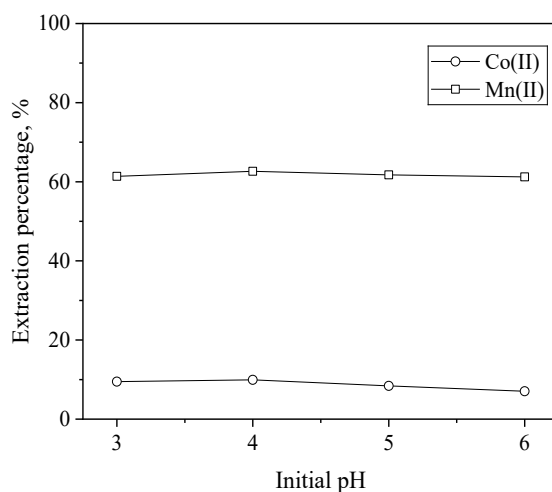

Fig. 4. Effect of the initial pH of the solution on the extraction of Co(II) and Mn(II) by 0.3 M D2EHPA at unity phase ratio.(reaction time : 30mins and temperature : 25°C)

In order to investigate the effect of D2EHPA concentration on the extraction of the two metal ions, D2EHPA concentration was varied from 0.1 to 1 M and extraction experiments were done by using the stripping solution with initial pH 6 at unity phase ratio. According to **Fig. 5**, when the concentration of D2EHPA increased from 0.1 to 1 M, the extraction percentage of Co(II) increased from 3 to 13%, while that of Mn(II) increased from 30 to 91%. **Fig. 6** shows that separation factor between Mn(II) and Co(II) was proportional to D2EHPA concentration and a separation factor of 66 was obtained when D2EHPA concentration was 1 M.

Our extraction data indicates that there is some difference in the extraction of the metal ions between Cyanex 272 and D2EHPA. The extraction percentage of Mn(II) by 1 M Cyanex 272 was less than 10% (see Fig. 1), while about 91% of Mn(II) was extracted by 1 M D2EHPA (see Fig. 5). This difference in extractability between D2EHPA and Cyanex 272 can be ascribed to the stronger acidity of D2EHPA than Cyanex 272. Since the acidity of D2EHPA is stronger than that of Cyanex 272, D2EHPA can extract well metal ions from the solution with low pH.

3.2.3. Separation of Mn(II) and Co(II) by either scrubbing or counter-current extraction

When 1 M D2EHPA was employed, 13% of Co(II) was co-extracted with Mn(II) into D2EHPA. Therefore, it is necessary to separate the Co(II) and Mn(II) present in the loaded D2EHPA. In this work, scrubbing with pure $MnSO_4$ solution was investigated to separate the two metal ions from the loaded D2EHPA. For this purpose, the initial pH of the scrubbing solution was fixed at 2 and the concentration of $MnSO_4$

in the scrubbing solution was varied from 1 to 3.5 g/L. Table 5 shows that the scrubbing percentage of Co(II) increased with the concentration of Mn(II) in the scrubbing solution. Complete scrubbing of Co(II) from the loaded D2EHPA was possible when the concentration of Mn(II) in the scrubbing solution was 2.5 g/L. Our scrubbing results indicate that it was possible to remove the Co(II) present in the loaded D2EHPA by scrubbing. After scrubbing, the scrubbing solutions contain Mn(II) and Co(II). Therefore, the scrubbing solutions can be a feed to the extraction stage to regenerate the pure scrubbing solution.
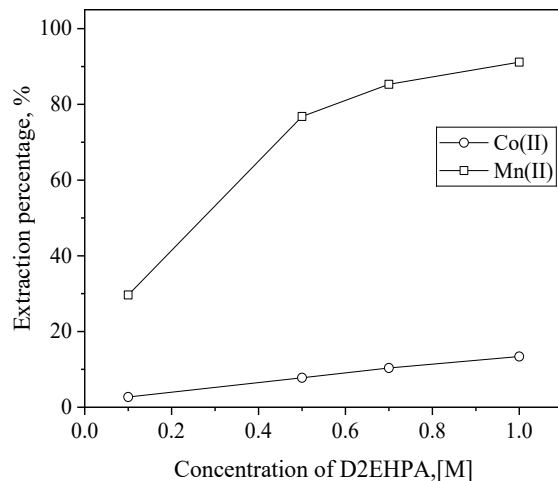

Fig. 5. Effect of D2EHPA concentration of the extraction of Co(II) and Mn (II) from the stripping solution with initial pH 6 at unity phase ratio.(reaction time: 30mins and temperature: 25°C)
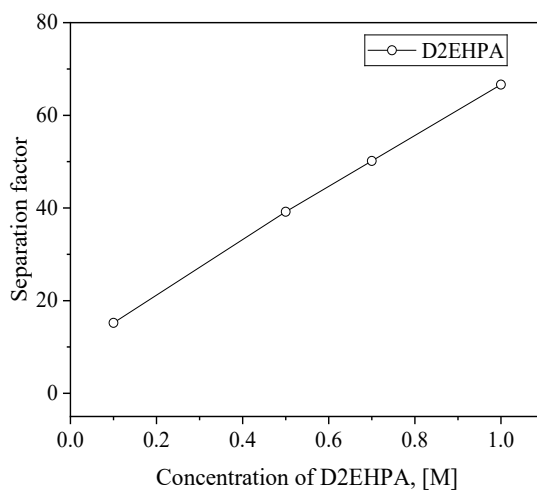

Fig. 6. Variation in the separation factor between Mn(II) and Co(II) with D2EHPA concentration from the stripping solution with initial pH 6 at unity phase ratio. (reaction time: 30mins, temperature: 25°C)

Table 5. Effect of the concentration of Mn(II) in the scrubbing solution on the scrubbing of Co(II) from the loaded D2EHPA at unity phase ratio.(Loaded organic : 1 M D2EHPA, reaction time: 30mins, temperature: 25°C)

Mn(II) conc. in scrubbing solution, mg/L	Before scrubbing, mg/L		After Scrubbing, mg/L		scrubbing, %	Purity of Mn(II) in organic, %
	$Org_{Co(II)}$	$Org_{Mn(II)}$	$Org_{Co(II)}$	$Org_{Mn(II)}$	Co(II)	Mn(II)
1000	253	312	23	680	90	96
1500	253	312	22	859	91	97.5
2000	253	312	0	922	97	99.2
2500	253	312	0	1021	100	>99.9
3000	253	312	0	1187	100	>99.9
3500	253	312	0	1390	100	>99.9

According to our extraction data of Co(II) and Mn(II) by D2EHPA, there is much difference in the extraction percentage between Co(II) and Mn(II). In this situation, counter-current extraction by employing an extractant with low concentration would minimize the co-extraction of an impure metal ion. Therefore, batch simulation experiments of 3 stages of counter-current extraction were done by employing 1 M D2EHPA at unity phase ratio. Table 6 shows the variation in the concentration of the two metal ions and their extraction percentages with the number of the stages of counter-current extraction. When 1 M D2EHPA was employed, the extraction percentages of Co(II) and Mn(II) in the first stage were 0.63% and 80.2%, respectively. However, as the number of counter-current extraction stages increased to 2 and 3, the small amount of Co(II) loaded in the D2EHPA was scrubbed into the aqueous, while Mn(II) was extracted into D2EHPA. It can be said that Co(II) and Mn(II) in the stripping solution can be completely separated by 3 stages of counter-current extraction with D2EHPA. Both scrubbing and counter current extraction can successfully separate Co(II) and Mn(II) from the solution containing Ni(II). However, in the case of scrubbing, the scrubbing solutions must be treated and thus are generally fed to the extraction circuit. On the other hand, in the case of counter current extraction, the loaded organic phase can be recycled after stripping without scrubbing. Therefore, counter current extraction was selected as the most suitable process in this study.

Table 6. Variation in the concentration and the extraction percentage of Co(II) and Mn(II) with the number of extraction stages during batch simulation of three stages of counter-current extraction with 1 M D2EHPA from the stripping solution with initial pH 6 at unity phase ratio. (reaction time: 30mins, temperature: 25°C)

	stage	Co(II)	Mn(II)
Stripping solution, mg/L	-	1779	249.4
Extraction percentage	1	0.6	80.2
	2	0	96.5
	3	0	100
Raffinate, mg/L	1	1767.7	49.5
	2	1785.6	8.9
	3	1788.3	0

3.3. A proposed process for the separation of Co(II), Ni(II), and Mn(II) from the sulfate solution by solvent extraction

Fig. 7 shows a proposed process for the separation of Ni(II), Co(II), and Mn(II) from the sulfuric acid leaching solution of spent LIBs. First, Co(II) and Mn(II) are completely extracted using saponified Cyanex 272 together with a small amount of Ni(II). Second, the small amount of Ni(II) present in the loaded Cyanex 272 can be separated by scrubbing with pure $CoSO_4$ solution. The scrubbing solution containing Co(II) and Ni(II) can be a feed to the extraction stage. Third, the Co(II) and Mn(II) present in the scrubbed Cyanex 272 are completely stripped by using dilute sulfuric acid solution. Fourth, counter-current extraction with D2EHPA would selectively extract Mn(II) from the stripping solution, leaving Co(II) in the raffinate. The Mn(II) in the loaded D2EHPA can be stripped by using sulfuric acid solution. When Co(II) and Mn(II) were completely extracted by Cyanex 272, Ni(II) remains in the raffinate and thus pure Ni(II) compounds can be recovered from the raffinate.

4. Conclusions

Solvent extraction experiments were conducted to separate Co(II), Mn(II) and Ni(II) present in the synthetic leaching solution of spent lithium-ion battery. The initial concentrations of Co(II), Mn(II) and Ni(II) in the solution were 1869, 258, and 9258g/L, respectively. Since the concentration of Ni(II) was the highest among the three metal ions present in the solution, it would be efficient to separate Co(II) and Mn(II) from the solution by one step operation. For this purpose, simultaneous extraction of Co(II) and Mn(II) from the solution was investigated by employing Cyanex 272 as an extractant. Although

Co(II) and Mn(II) were selectively extracted by Cyanex 272, their extraction percentages were less than 10% owing to a decrease in solution pH. Our results showed that complete extraction of Co(II) and Mn(II) together with 5.2% extraction percentage of Ni(II) was possible from the aqueous solution with initial pH 6 by using 40% saponified 0.3 M Cyanex 272 in one stage, leaving Ni(II) in the raffinate. The co-extracted Ni(II) in the loaded Caynex 272 was successfully removed by scrubbing with pure $CoSO_4$ solution with pH 2 and 1 g/L concentration. Scrubbing results with pure $CoSO_4$ solution indicated that the pH of the scrubbing solution was very important in suppressing the stripping of Co(II) from the loaded Cyanex 272. Extraction with saponified Cyanex 272 followed by scrubbing led to raffinate containing Ni(II) and pure scrubbed organic containing Co(II) and Mn(II). The Co(II) and Mn(II) present in the scrubbed Cyanex 272 were completely stripped by using an 0.05 M H_2SO_4 solution. Use of D2EHPA as an extractant led to selective extraction of Mn(II) over Co(II) from the stripping solution. Batch simulation experiments for the three stages of counter-current extraction with 1 M D2EHPA with the stripping solution of initial pH 6 led to complete extraction of Mn(II), leaving Co(II) in the raffinate. A process based on solvent extraction was proposed to separate Co(II), Mn(II) and Ni(II) in the sulfate solutions resulted from the sulfuric acid leaching solutions of spent LIBs. By this process, pure $CoSO_4$, $MnSO_4$ and $NiSO_4$ solutions can be recovered.
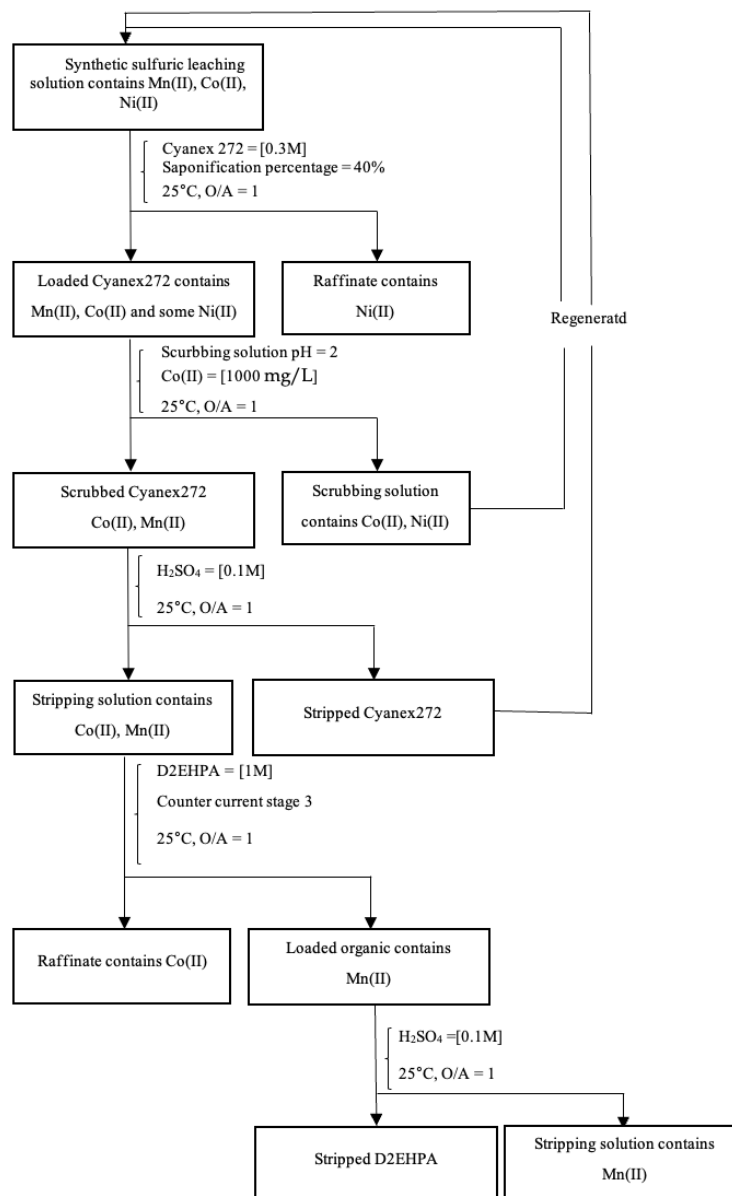

Fig. 7. A proposed process for the separation of Co(II), Ni(II), and Mn(II) present in synthetic sulfate solutions with solvent extraction

Acknowledgements

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