

SEPARATION OF Co(II), Mn(II) AND Ni(II) FROM THE SULFURIC ACID LEACHING SOLUTION OF A LITHIUM-ION BATTERY BY SOLVENT EXTRACTION

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Abstract

Lithium-ion batteries (LIBs) contain valuable metals such as cobalt, lithium, manganese, and nickel. Therefore, the recycling of spent LIBs is important to meet the demand for the above-mentioned metals. In combined process for the treatment of spent LIBs, the smelting reduction of LIBs results in metallic alloys containing cobalt, manganese, nickel, and a small amount of other metals. These metallic alloys can be dissolved using sulfuric acid solutions containing oxidizing agents. In this work, solvent extraction experiments were done to separate Co (II), Mn(II), and Ni(II) from synthetic sulfate solution, the composition of which was similar to the leaching solutions of spent LIBs. The concentrations of Co(II), Mn(II) and Ni(II) in the sulfate solutions were 2, 0.3, and 8 g/L, respectively. First, it was possible to completely separate Mn(II) from Co(II) and Ni(II) by selective extraction using two stages of counter-current extraction with 10% saponified 0.3 M D2EHPA. Then, the pure $MnSO_4$ solution was recovered by stripping the loaded D2EHPA with 0.05 M H_2SO_4 solution. From the Mn (II) free raffinate, Co(II) was completely separated over Ni (II) by two stages of counter-current extraction with 15% saponified 0.3 M Cyanex 272. The purity of Ni (II) in the raffinate was higher than 99.9% and pure $CoSO_4$ solution was recovered by stripping the loaded Cyanex 272 with 0.05 M H_2SO_4 solution. A process on the basis of solvent extraction with commercial organophosphorus extractants was proposed to recover pure $CoSO_4$, $MnSO_4$, and $NiSO_4$ solutions from the sulfuric acid leaching solutions of spent LIBs.

Keywords: Hydrometallurgy; Lithium-ion batteries; Recycling; Separation; Solvent extraction

1. Introduction

Lithium-ion batteries (LIBs) are in high demand as rechargeable batteries for portable electronic devices and electric vehicles due to their advantages such as high power and energy density, long shelf life, low self-discharge rate, high cell voltage, and wide operating temperature range [1,2]. Consequently, as the global production of LIBs increases, so does the amount of spent LIBs, with an estimated 4.4 million tons of spent LIBs from electric vehicle battery packs by 2040 [3]. These spent LIBs contain valuable metals such as cobalt, nickel, lithium, and manganese, with concentrations significantly higher than those found in primary ores. Thus, landfilling these batteries could lead to serious environmental pollution due to the accumulation of these metals in soil and groundwater [4,5]. Furthermore, the demand for the above-mentioned metals is increasing and they are employed for the manufacture of cathode materials such as $LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$ [6,7]. Therefore, to

ensure a stable supply of the critical metals for LIBs and to protect the environment, the recycling of spent LIBs is essential.

The recycling methods for LIBs can be roughly divided into pyrometallurgical and hydrometallurgical processes. While pyrometallurgy can process large quantities, it involves high initial setup and process costs. On the other hand, hydrometallurgy is suitable for treating dilute solutions with low metal contents and can efficiently and selectively recover high-purity metals. In hydrometallurgy, several operations such as solvent extraction, ion exchange, and precipitation are employed to separate metal ions from the leaching solutions [8-11]. Metallic alloys containing cobalt, manganese, and nickel can be obtained by smelting reduction of spent LIBs at high temperature. According to our previous work, dissolution of these metallic alloys by a sulfuric acid solution in the presence of H_2O_2 as an oxidizing agent results in a leaching solution containing Co(II), Cu(II), Fe(III), Mn(II), and Ni(II) [12]. Among these metal ions,

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Cu(II) can be removed by cementation with iron powder [12]. After oxidizing Fe(II) to Fe(III), Fe(III) can be removed by solvent extraction with D2EHPA [12]. Then the raffinate contains Co(II), Mn(II) and Ni(II) and the composition of the raffinate is listed in Table 1.

The separation of Co(II), Mn(II), and Ni(II) from weakly acidic sulfate and chloride solutions has been widely reported due to their similar chemical properties. Of the three metal ions, the reduction potential of Mn(II) is the lowest and thus Mn(II) can be separated by oxidative precipitation of MnO₂ by adding some oxidizing agents [13]. The solubility products of CoS and NiS are much smaller than MnS and thus Co(II) and Ni(II) can be simultaneously separated from Mn(II) by precipitating the mixed sulfide of Co(II) and Ni(II) [14]. Although precipitation is easy to operate, filtration of the slurries after precipitation and washing of the precipitates are necessary. In contrast, solvent extraction can lead to pure solutions from which the pure compounds can be recovered by crystallization. In general, organophosphorus extractants such as D2EHPA, PC 88A, and Cyanex 272 are employed to separate the three metal ions from weakly acidic solutions. However, careful control of solution pH is necessary to obtain complete separation of the metal ions by using the above-mentioned extractants.

According to Table 1, the concentration of Mn(II) is the lowest and therefore it is efficient to extract Mn(II) over Co(II) and Ni(II). D2EHPA shows a selectivity for Mn(II) over Co(II) and Ni(II) from weakly acidic solutions [15-17]. Moreover, Cyanex 272 can selectively extract Co(II) over Ni(II) from weakly acidic solutions [18-20]. Once Mn(II) is separated from Co(II) and Ni(II) by extraction with D2EHPA, then Co(II) and Ni(II) can be separated by extraction with Cyanex 272. In solvent extraction, co-extraction of impure metal ions is inevitable and thus it is important to employ scrubbing and counter-current extraction to achieve a high degree of separation. In this work, solvent extraction experiments were done to find the optimum conditions to separate Co(II), Mn(II), and Ni(II) from the sulfate solution with the composition in Table 1. By using D2EHPA and Cyanex 272, optimum conditions were obtained to separate the three metal ions by investigating the effect of solution pH, extractant concentration and saponification degree of

the extractants. A process was proposed to recover CoSO₄, MnSO₄, and NiSO₄ solutions with a purity higher than 99.9% from the sulfate solution by solvent extraction.

2. Experimental

2.1. Reagents and Chemicals

In this work, the synthetic solutions with the same composition as in Table 1 were employed to investigate the separation of these metal ions by solvent extraction. For this purpose, cobalt sulfate (CoSO₄·7H₂O, Daejung Chemical & Metals Co., >98%, Korea), manganese sulfate (MnSO₄·H₂O, Daejung Chemical & Metals Co., >98.5%, Korea), and nickel sulfate (NiSO₄·6H₂O, Daejung Chemical & Metals Co., >98.5%, Korea) were dissolved in distilled water. Sulfuric acid (H₂SO₄, Daejung Chemical & Metals Co., >95%, Korea) and sodium hydroxide solution (NaOH, Daejung Chemical & Metals Co., >99%, Korea) were added to the synthetic solutions to adjust solution pH. The scrubbing solutions were prepared by dissolving the target metal ions in distilled water. D2EHPA (Cytec Ind., 95%, Canada) and Cyanex 272 (Cytec Ind., 85%, Canada) were employed in solvent extraction experiments, and kerosene (Daejung Chemicals & Metals Co. Ltd., Korea, >90%) was used as a diluent. All reagents used in this study were of analytical grade and were used without further purification.

2.2. Procedure and analytical methods

The solvent extraction experiments were performed with equal volumes (20 mL) of the aqueous and organic phase in plastic screw cap bottles sealed with parafilm. The mixture of both phases was shaken for 30 mins at room temperature using a Burrell wrist action shaker (model 75, USA), and then was separated by using a separatory funnel. The pH of the aqueous solution was measured by a pH meter (Orion Star A211, Thermo Fisher Scientific, USA), and the concentrations of the metal ions in the aqueous were measured using inductively coupled plasma-optical emission spectrometer (ICP-OES, Acros, Spectro, Germany).

The concentrations of the metal ions in the organic phase were calculated by mass balance. The percentages of extraction, scrubbing, and stripping of the metal ions were calculated using the following equations.

$$\text{Extraction percentage (\%E)} = \frac{M_{ini} - M_e}{M_{ini}} \times 100 \quad (1)$$

Table 1. The concentration of the metal ions in the sulfuric leaching solution of spent LIBs after separation of Cu(II) and Fe(III)

Metal ions	Co(II)	Mn(II)	Ni(II)
Concentration, mg/L	2000	300	8000



$$\text{Scrubbing percentage}(\%S) = \frac{M_{aq}}{M_{org}} \times 100 \quad (2)$$

$$\text{Stripping percentage}(\%S^*) = \frac{M_e^*}{M_{ini}^*} \times 100 \quad (3)$$

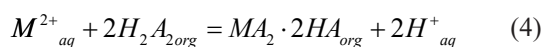
where M_{ini} and M_e are the mass of the metal ions in the aqueous before and after extraction, respectively. M_{org} and M_{aq} are the mass of the metal ions in the loaded organic and aqueous solution before and after scrubbing, respectively. Moreover, M_{ini}^* and M_e^* are the mass of the metal ions in the organic and aqueous phases before and after stripping, respectively.

3. Results and discussion

3.1. Separation of Mn(II) from the synthetic sulfate solution

3.1.1. Separation of Mn(II) by extraction with D2EHPA

The concentration of Mn(II) in the synthetic sulfuric acid solution was 0.3 g/L. Although Mn(II) can be separated from Co(II) and Ni(II) by oxidative precipitation [21], solvent extraction was employed to separate Mn(II) in this work. According to the extraction data of Co(II), Mn(II), and Ni(II) by organophosphorus extractants, D2EHPA can selectively extract Mn(II) over Co(II) and Ni(II) from weakly acidic solutions [22]. When the D2EHPA concentration is higher than 0.01 M, the dimeric form of D2EHPA participates in the extraction reaction and thus the extraction reaction of divalent metal ions by D2EHPA can be represented as Eq. (4) [23,24].



where M^{2+} and H_2A_2 represent divalent metal ions and the dimer of D2EHPA, respectively. Moreover, subscripts *aq* and *org* denote the aqueous and organic phases, respectively. First, the effect of D2EHPA concentration on the extraction of the three metal ions was investigated by varying D2EHPA concentration from 0.1 to 1.0 M. In these experiments, the initial pH of the synthetic solution was fixed at 4 and the volume ratio of the two phases was unity. Fig. 1 shows that the extraction percentage of Mn(II) increased from 30% to 86% as D2EHPA concentration increased from 0.1 to 1.0 M. When D2EHPA concentration was 1.0 M, the extraction percentages of Co(II) and Ni(II) reached 6% and 2%, respectively. In these experiments, the equilibrium pH of the aqueous phase decreased from 2.45 to 1.84 as D2EHPA

concentration increased to 1.0 M. The decrease in equilibrium pH is related to the release of hydrogen ions from D2EHPA into the aqueous phase as shown in Eq. (4). The initial pH of the synthetic solution was varied from 4 to 6 to investigate its effect on the

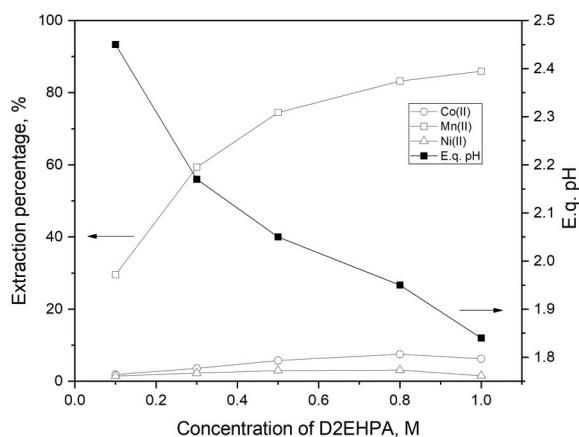


Figure 1. Effect of D2EHPA concentration on the extraction of the metal ions from synthetic solutions and on the equilibrium pH. (Aqueous: [Co(II)] = 2.0 g/L, [Mn(II)] = 0.3 g/L, [Ni(II)] = 8.0 g/L, initial pH = 4.0. Organic: [D2EHPA] = 0.1-1.0 M. O/A = 1)

extraction of the metal ions. In these experiments, 1.0 M D2EHPA was employed at unity phase ratio. According to Fig. 2, the effect of the initial pH of the solution was negligible, which is attributed to the similar equilibrium pH. When the initial pH was 6, the extraction percentages of Mn(II), Co(II), and Ni(II) were 87%, 6%, and 3%, respectively.

Our data clearly indicates that there is a large difference in the extraction percentage by D2EHPA

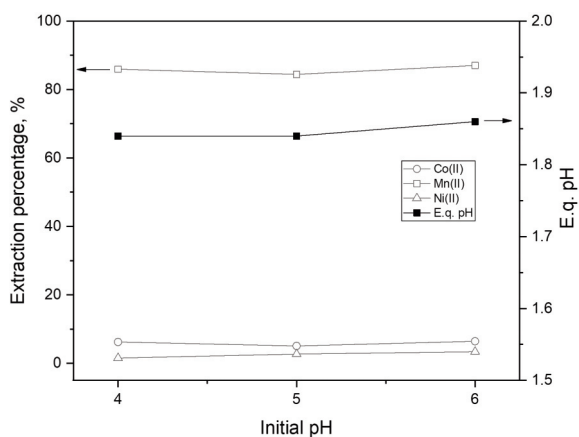


Figure 2. Effect of initial pH of the solution on the extraction of the metal ions and on the equilibrium pH. (Aqueous: [Co(II)] = 2.0 g/L, [Mn(II)] = 0.3g/L, [Ni(II)] = 8.0 g/L, initial pH = 4.0-6.0. Organic: [D2EHPA] = 1.0 M. O/A = 1)



between Mn(II) and Co(II)/Ni(II). By utilizing this difference, it might be possible to separate Mn(II) from the solution by counter-current extraction. In doing counter-current extraction, employment of an optimum concentration of an extractant is of importance to reduce the co-extraction of the impurity metal ions. Moreover, the viscosity of the organic phase would be increased with extractant concentration, resulting in a decrease in the mass transfer of the extractant [25]. Therefore, counter-current extraction experiments were done by employing 0.3 M D2EHPA and the initial pH of the aqueous solution was fixed at 6. In multi-stage counter-current extraction, the number of stages can be estimated by using the following equation [26].

$$C_n = \frac{W_n}{V_{aq}} = \frac{W}{V_{aq}} \left(\frac{1}{1 + D \frac{V_{org}}{V_{aq}}} \right)^n = C_{initial} \left(\frac{1}{1 + D \frac{V_{org}}{V_{aq}}} \right)^n \quad (5)$$

where n represents the number of extraction stages, C_n and W_n are the concentration and the mass of a metal ion discharged from the n th stage, respectively. V_{aq} and V_{org} are the volumes of the aqueous and organic phases, respectively. D is the distribution coefficient of a metal ion and $C_{initial}$ represents the initial concentration of the target metal ion. When the distribution coefficient of a metal ion is assumed to be constant, Eq. (5) can be solved to estimate the number of counter-current extraction stages required to extract the metal ion by inserting the necessary values.

When D2EHPA concentration was 0.3 M, the extraction percentage of Mn(II) was 66% and the distribution coefficient of Mn(II) was 1.94. Since the initial concentration of Mn(II) in the solution was 0.3 g/L, manipulation of Eq. (5) indicates that the concentration of Mn(II) in the raffinate would be less

than 5 mg/L when the number of counter-current stages is 4. Therefore, batch simulation experiments of four stages of counter-current extraction were done and the results are shown in Table 2. The extraction percentages of Mn(II), Co(II), and Ni(II) at the 4th stage were 98%, 4% and 2%, respectively. Although complete extraction of Mn(II) could be achieved with an additional 5th stage counter-current extraction, a small amount of Co(II) and Ni(II) were co-extracted with Mn(II). In order to increase the recovery percentage of Co(II) and Ni(II) from the solution and to recover pure Mn(II) solution, the Co(II) and Ni(II) present in the loaded D2EHPA should be removed by scrubbing.

After the 4th stage extraction, the concentrations of Co(II), Mn(II) and Ni(II) in the loaded D2EHPA were 76, 293, and 139 mg/L, respectively. In the scrubbing experiments, pure Mn(II) solution was employed and the scrubbing reaction can be represented as Eq. (6) [27,28].



where M refers to divalent metal ions such as Co(II) and Ni(II). In general, the pH and the concentration of the metal ions in the scrubbing solution affect the scrubbing behavior of the target metal ions. In our preliminary experiments, when the pH of the scrubbing solution was 1.5, Mn(II) was stripped from the loaded D2EHPA. Therefore, it was necessary to maintain the pH of the scrubbing solution at around 2. First, the effect of Mn(II) concentration in the scrubbing solution on scrubbing was investigated by varying the Mn(II) concentration from 2.0 to 3.0 g/L, while the pH of the scrubbing solution was fixed at 2. According to the experimental results, most of the Ni(II) in the loaded D2EHPA was completely scrubbed, while about 86% of the Co(II) was

Table 2. The variation in the concentration and extraction percentage of the metal ions during four stages of counter-current extraction of the sulfate solution with 0.3 M D2EHPA

Stage	Concentration of metal ions in the loaded D2EHPA, mg/L			E.q. pH
	Co(II)	Ni(II)	Mn(II)	
Feed	2000	8000	300	-
1st	64	128	198	2.45
Extraction percentage, %	3.2	1.6	66.1	
2nd	18	0	250	2.33
Extraction percentage, %	0.9	0	83.5	
3rd	18	0	278	2.26
Extraction percentage, %	0.9	0	92.6	
4th	76	139	293	2.14
Extraction percentage, %	3.8	1.7	97.6	

*Operating condition: Initial pH of the aqueous = 6.0, O/A = 1

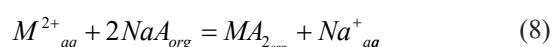
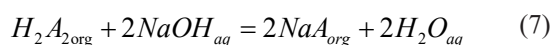


scrubbed in the Mn(II) concentration ranges (see Table 3). As the Mn(II) concentration in the scrubbing solution increased, the extraction percentage of Mn(II) was also increased, indicating that 0.3 M D2EHPA was not saturated with the metal ions. Considering the stoichiometry of the scrubbing reaction and scrubbing percentage, the extraction of Mn(II) occurred through scrubbing as well as extraction by the free D2EHPA present in the loaded D2EHPA. In this case, the equilibrium pH would be decreased to less than 2, resulting in the stripping of the Mn(II). Therefore, it is important to keep the concentration of Mn(II) in the scrubbing solution within 3.0 g/L. Although Ni(II) was completely scrubbed, around 10 mg/L of Co(II) remained in the scrubbed D2EHPA. Therefore, four stages of cross-current scrubbing experiments were done by using scrubbing solution with 2.0 g/L Mn(II) and pH 2. Table 4 shows the variation in the scrubbing percentage of Co(II) and Ni(II), and the purity of Mn(II) in the scrubbed D2EHPA with the number of cross-current scrubbing stages. According to the experimental results, Co(II) and Ni(II) were completely scrubbed by two stages of cross-current scrubbing (see Table 4). After the scrubbing experiments, the purity of Mn(II) in the scrubbed D2EHPA was higher than 99.9%.

3.1.2. Separation of Mn(II) by extraction with saponified D2EHPA

According to the results of the extraction with D2EHPA, it was difficult to completely extract Mn(II) from the solution using even 1.0 M D2EHPA in one stage. This might be ascribed to the decrease in the

solution pH due to the release of hydrogen ions from D2EHPA, reducing the driving force for the extraction of the metal ions [29]. In order to overcome the decrease in solution pH, D2EHPA was saponified by using NaOH solution. Namely, a specific amount of NaOH solution was added to the organic phase and then reacted at room temperature according to the reported method [30,31]. The saponification reaction of D2EHPA with sodium hydroxide and the subsequent extraction reaction by saponified D2EHPA are shown in Eqs. (7) and (8) [32].



As represented in Eq. (8), the saponified D2EHPA takes part in the extraction reaction as a monomer. First, the effect of saponification degree of 0.3 M D2EHPA was investigated by varying saponification degree to 40%. The experiments were done from the solution with an initial pH of 6. Fig. 3 shows that Mn(II) was completely extracted by saponified D2EHPA. Namely, the extraction percentage of Mn(II) increased from 84% to completeness when the saponification degree increased from 5% to 30%. In these saponification ranges, the equilibrium pH of the raffinate increased from 2.15 to 3.71. Hence, the extraction percentage of Co(II) and Ni(II) also rapidly increased when the saponification degree was higher than 10%.

When the saponification degree of 0.3 M D2EHPA was 10%, the extraction percentage of Mn(II), Co(II) and Ni(II) was 95%, 15% and 4%,

Table 3. The effect of Mn(II) concentration in the scrubbing solution on the scrubbing of Co(II) and Ni(II) from the loaded D2EHPA and on the purity of Mn(II) in the scrubbed D2EHPA

Conc. of Mn(II), g/L	Before scrubbing, mg/L			After scrubbing, mg/L			Scrubbing percentage, %		Purity, %
	Org _{Co(II)}	Org _{Ni(II)}	Org _{Mn(II)}	Org _{Co(II)}	Org _{Ni(II)}	Org _{Mn(II)}	Co(II)	Ni(II)	
2	76	139	293	11	0	548	86	100	98.1
2.5	76	139	293	10	0	641	87	100	98.5
3	76	139	293	12	0	683	85.7	100	98.3

*Operating condition: Initial pH of the scrubbing solution = 2.0, O/A = 1

Table 4. Variation in the composition and in the purity of the scrubbed D2EHPA during four stages of cross-current scrubbing by pure Mn(II) solution with 2 g/L and pH 2 at unity phase ratio

Stage	Before scrubbing, mg/L			After scrubbing, mg/L			Scrubbing percentage, %		Purity, %
	Org _{Co(II)}	Org _{Ni(II)}	Org _{Mn(II)}	Org _{Co(II)}	Org _{Ni(II)}	Org _{Mn(II)}	Co(II)	Ni(II)	
1	76	139	293	11	0	548	86	100	98.1
2	11	0	548	0	0	638	100	-	99.9
3	0	0	638	0	0	668	-	-	99.9
4	0	0	668	0	0	671	-	-	99.9



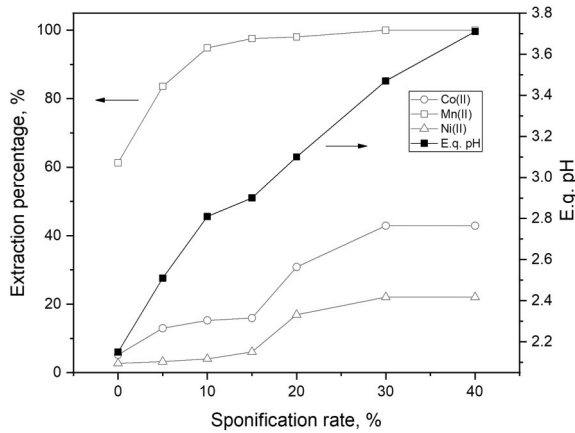


Figure 3. Effect of saponification degree of D2EHPA on the extraction of the metal ions from the synthetic solution and on the equilibrium pH. (Aqueous: $[Co(II)] = 2.0$ g/L, $[Mn(II)] = 0.3$ g/L, $[Ni(II)] = 8.0$ g/L, initial pH = 6.0. Organic: $[D2EHPA] = 0.3$ M, saponification degree = 0-40%, $O/A = 1$)

respectively. Therefore, it can be said that employment of D2EHPA with a lower saponification degree is more effective in suppressing the co-extraction of Co(II) and Ni(II) with Mn(II). Therefore, batch simulation experiments of four stages of counter-current extraction were done from the solution with pH 6 by using 10% saponified 0.3 M D2EHPA. Fig. 4 shows that Mn(II) was completely extracted after two stages of counter-current extraction. When the number of counter-current extraction stages was 2 and 3, no Co(II) and Ni(II) were extracted into the organic phase, while about 8% of Co(II) was co-extracted with Mn(II) after four

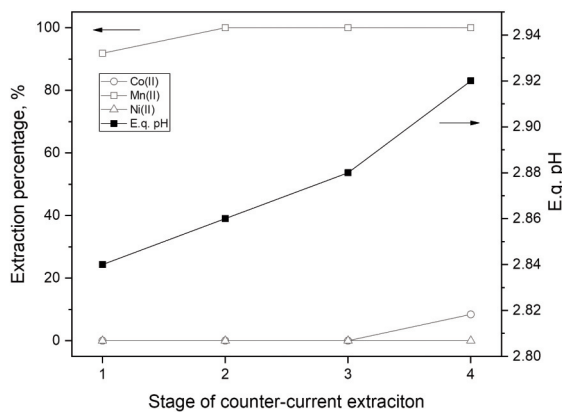
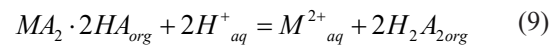


Figure 4. The change in the extraction of the metal ions and equilibrium pH during batch simulation experiments for the four stages of counter-current extraction with 10% saponified 0.3 M D2EHPA. (Aqueous: $[Co(II)] = 2.0$ g/L, $[Mn(II)] = 0.3$ g/L, $[Ni(II)] = 8.0$ g/L, Initial pH = 6.0. Organic: $[D2EHPA] = 0.3$ M, saponification degree = 10%. $O/A = 1$)

stages of counter-current extraction by 10% saponified 0.3 M D2EHPA. Therefore, two stages of counter-current extraction using 10% saponified 0.3 M D2EHPA was selected as the optimum condition to completely separate Mn(II) over Co(II) and Ni(II).

The loaded D2EHPA after two stages of counter-current extraction with saponified D2EHPA contained only Mn(II). Therefore, stripping experiments of Mn(II) from the loaded D2EHPA were done by using sulfuric acid solutions. The stripping reaction of metal ion with sulfuric acid can be described as follows [33].



Stripping experiments were done by varying sulfuric acid concentration from 0.01 M to 0.5 M at unity phase ratio of the two phases. Fig. 5 shows that Mn(II) was completely stripped from the loaded D2EHPA when H_2SO_4 concentration was higher than 0.05 M. Extraction with saponified D2EHPA and subsequent stripping with sulfuric acid solution, Mn(II) solution with a purity higher than 99.9% was recovered.

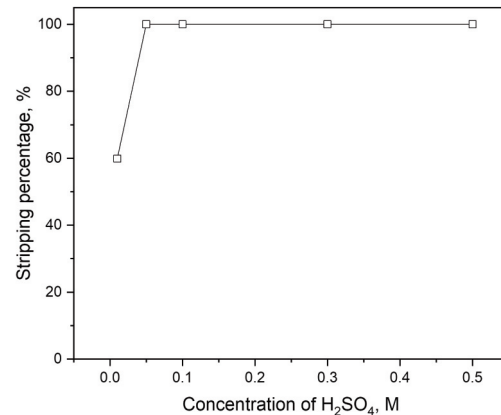


Figure 5. Effect of the concentration of H_2SO_4 in the stripping solution on the stripping of Mn(II) from the loaded D2EHPA. (Loaded D2EHPA: $[Mn(II)] = 300$ mg/L, $O/A = 1$)

3.2. Separation of Co(II) from the Mn(II) free raffinate

3.2.1. Extraction of Co(II) over Ni(II) by Cyanex 272

Two stages of counter-current extraction with 10% saponified 0.3 M D2EHPA resulted in a raffinate containing Co(II) and Ni(II). The concentration of Co(II) was much lower than that of Ni(II) in the raffinate. Therefore, it is better to selectively extract Co(II) over Ni(II) from the raffinate. Among the organophosphorus extractants, Cyanex 272 can

selectively extract Co(II) over Ni(II) from weakly acidic solutions [20,34]. The extraction reaction of divalent metal ions by Cyanex 272 can be represented as Eq. (4). First, extraction experiments were done by varying Cyanex 272 concentration from 0.1 to 1.0 M. In these experiments, the pH of the raffinate was controlled to 6 and the phase ratio was unity. Fig. 6 shows that extraction percentages of Co(II) and Ni(II) slightly increased with Cyanex 272 concentration, which can be ascribed to a low equilibrium pH.

Further extraction experiments were done by varying the saponification degree of Cyanex 272. For

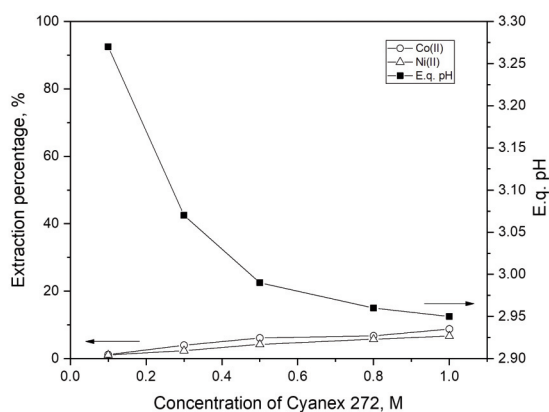


Figure 6. Effect of Cyanex 272 concentration on the extraction of Co(II) and Ni(II) from the raffinate after separation of Mn(II) and on the equilibrium pH. (Aqueous: [Co(II)] = 2.0 g/L, [Ni(II)] = 8.0 g/L, initial pH = 6.0. Organic: [Cyanex272] = 0.1-1.0 M, O/A = 1)

this purpose, the saponification degree of 0.3 M Cyanex 272 was varied to 40% and extraction experiments were done by using the raffinate with initial pH 6. Fig. 7 shows that the extraction percentage of Co(II) rapidly increased to completeness as the degree of saponification increased to 20%. When the saponification degree was 20%, 11% of Ni(II) were co-extracted with Co(II). When the saponification degree was 15%, the extraction percentages of Co(II) and Ni(II) were 90% and 7%, respectively. Therefore, batch simulation experiments for three stages of counter-current extraction were done with 15% saponified 0.3 M Cyanex 272. Fig. 8 shows that the extraction percentage of Co(II) gradually increased from 80% to completeness as the number of counter-current stage increased from 1 to 3. In the counter-current extraction experiments, Ni(II) was not extracted and thus Co(II) could be selectively extracted over Ni(II). After three stages of counter-current extraction using saponified Cyanex 272, Co(II) was completely extracted leaving Ni(II) in the raffinate and the equilibrium pH of the raffinate was 5.24.

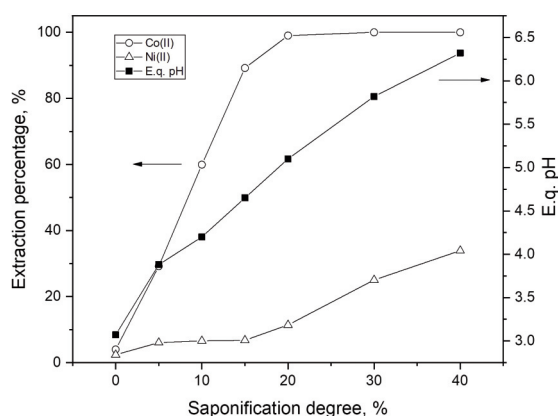


Figure 7. Effect of saponification degree of 0.3 M Cyanex 272 on the extraction of Co(II) and Ni(II) from the raffinate after the separation of Mn(II). (Aqueous: [Co(II)] = 2.0 g/L, [Ni(II)] = 8.0 g/L, initial pH = 6.0. Saponification degree = 0-40%, O/A = 1)

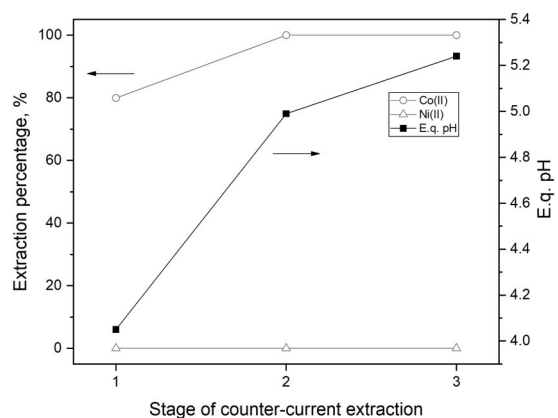


Figure 8. Changes in the extraction of Co(II) and Ni(II) during batch simulation experiments for three stages of counter-current extraction with 15% saponified 0.3 M Cyanex 272. (Aqueous: [Co(II)] = 2.0 g/L, [Ni(II)] = 8.0 g/L, initial pH = 6.0, O/A = 1)

3.2.2. Stripping of Co(II) from the loaded Cyanex 272 by sulfuric acid solution

When two stages of counter-current extraction using 15% saponified 0.3 M Cyanex 272 were employed, complete extraction of Co(II) was possible, leaving all the Ni(II) in the raffinate. The concentration of Co(II) in the loaded Cyanex 272 was about 2.0 g/L. Therefore, stripping experiments were done by varying the concentration of H₂SO₄ from 0.01 M to 0.5 M. The stripping reaction of Co(II) with sulfuric acid can be described as Eq. (9). Fig. 9 shows that 96% of Co(II) was stripped by 0.01 M sulfuric acid solution, and all the Co(II) was completely stripped when the H₂SO₄ concentration was higher



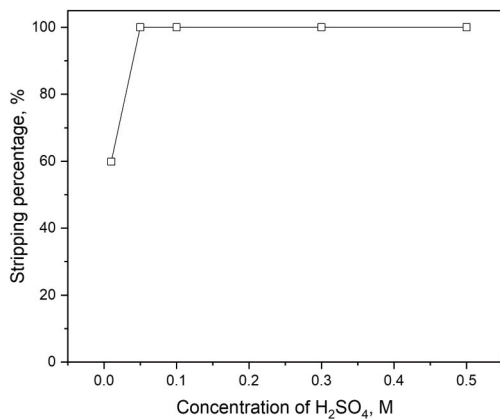


Figure 9. Effect of H_2SO_4 concentration in the stripping solution on the stripping of Co(II) from the loaded Cyanex 272. (Loaded Cyanex 272: $[Co(II)] = 2.0$ g/L, $O/A = 1$)

than 0.05 M. The purity of Co(II) in the stripping solution was higher than 99.9%, while that of Ni(II) in the raffinate was also higher than 99.9%.

3.3. A flowchart of the separation of Co(II), Mn(II), and Ni(II) from the sulfuric acid leaching solution of spent LIBs by solvent extraction

Fig. 10 is a proposed flowchart for the separation of the Co(II), Mn(II), and Ni(II) from the sulfuric acid leaching solutions of metallic alloys obtained from the

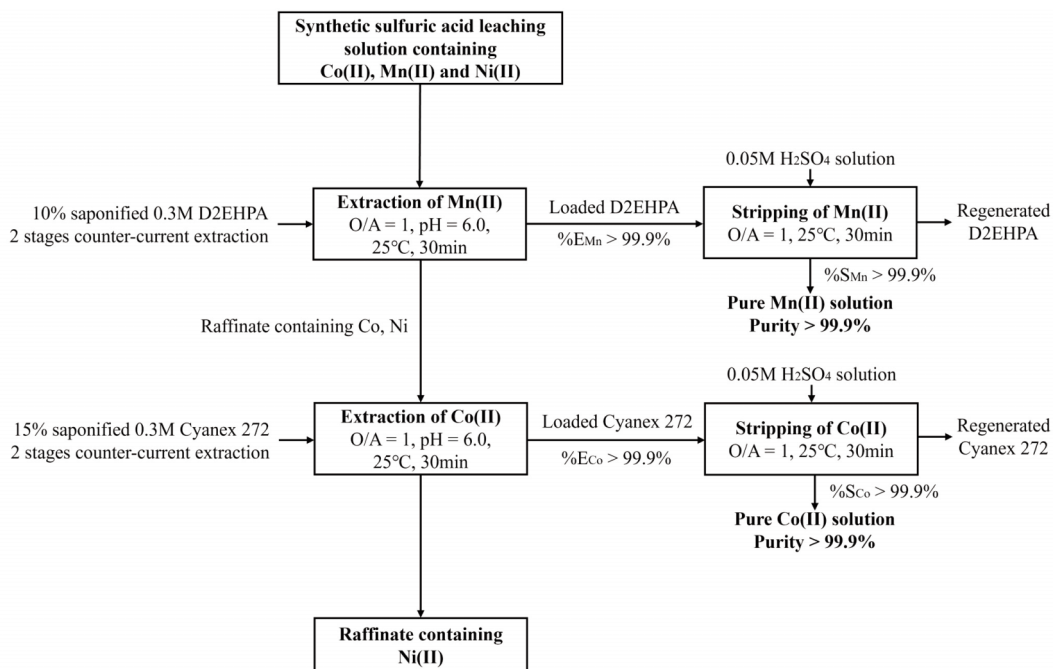


Figure 10. A proposed flowchart for the separation of Co(II), Mn(II) and Ni(II) from the synthetic sulfuric acid leaching solution of spent LIBs by solvent extraction

smelting reduction of spent LIBs. Mn(II) was completely separated by two stages of counter-current extraction using 10% saponified 0.3 M D2EHPA from the solution containing Co(II) and Ni(II). Then $MnSO_4$ solution with purity higher than 99.9% was recovered by stripping the loaded D2EHPA with 0.05 M sulfuric acid solution. Thereafter, the Co(II) present in the raffinate was separated from Ni(II) by two stages of counter-current extraction using 15% saponified 0.3 M Cyanex 272. Then stripping of the loaded Cyanex 272 with 0.05 M sulfuric acid solution resulted in a $CoSO_4$ solution with purity higher than 99.9%. By sequential extraction of Mn(II) and Co(II) with D2EHPA and Cyanex 272, only Ni(II) remained in the raffinate. Therefore, it is possible to separate Co(II), Mn(II), and Ni(II) by extraction with commercial organophosphorus extractants.

4. Conclusions

Solvent extraction experiments were done to separate Co(II), Mn(II), and Ni(II) from synthetic sulfate solutions. The composition of the synthetic sulfate solutions was similar to that of the sulfuric acid leaching solutions of metallic alloys obtained from the smelting reduction of spent LIBs at high temperature. First, Mn(II) was selectively extracted over Co(II) and Ni(II) by either single D2EHPA or saponified D2EHPA. In the four stages of counter-current extraction with 0.3 M D2EHPA, some of

Co(II) and Ni(II) were co-extracted with Mn(II) and thus scrubbing with Mn(II) solution was necessary to remove the Co(II) and Ni(II) from the loaded D2EHPA. In contrast, only Mn(II) was selectively extracted over Co(II) and Ni(II) by two stages of counter-current extraction with 10% saponified 0.3 M D2EHPA. Therefore, employment of saponified D2EHPA was more efficient than single D2EHPA in separating Mn(II) from the solution. The Mn(II) in the loaded D2EHPA was completely stripped by using 0.05 M H₂SO₄ solution, resulting in a MnSO₄ solution with purity higher than 99.9%. Secondly, Cyanex 272 was employed to separate Co(II) over Ni(II) present in the Mn(II) free raffinate. Compared to single Cyanex 272, saponified Cyanex 272 was more effective in extracting Co(II) from the raffinate. Two stages of counter-current extraction with 15% saponified 0.3 M Cyanex 272 resulted in complete extraction of Co(II), leaving all the Ni(II) in the raffinate. Pure CoSO₄ solution was recovered by stripping the loaded Cyanex 272 with 0.05 M H₂SO₄ solution. A process was proposed for the recovery of CoSO₄, MnSO₄, and NiSO₄ solutions with a purity higher than 99.9% from the sulfate solutions containing Co(II), Mn(II), and Ni(II) by solvent extraction.

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Author Contributions

Methodology and editing: Man Seung Lee; data support and writing-original draft preparation: Ji Hyeok Jeon and Jiang Xian Wen. All authors have read and agreed to the published version of the manuscript.

Data availability

The data of this work could be obtained by contacting with the corresponding author by e-mail.

Declarations of competing interest

The authors declare no conflict of interest.

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SEPARACIJA Co(II), Mn(II) I Ni(II) IZ RASTVORA SUMPORNE KISELINE DOBIJENOG LUŽENJEM LITIJUM-JONSKIH BATERIJA SOLVENTNOM EKSTRAKCIJOM

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Apstrakt

Litijum-jonske baterije (LIB) sadrže vredne metale kao što su kobalt, litijum, mangan i nikel. Stoga je reciklaža istrošenih LIB-ova važna za zadovoljavanje potražnje za gore navedenim metalima. U kombinovanom procesu za tretman istrošenih LIB-a, redukcija topljenja LIB-a rezultira metalnim legurama koje sadrže kobalt, mangan, nikel i malu količinu drugih metala. Ove metalne legure se mogu rastvoriti korišćenjem rastvora sumporne kiseline koji sadrže oksidacione agense. U ovom radu rađeni su eksperimenti solventne ekstrakcije za izdvajanje Co (II), Mn(II) i Ni(II) iz rastvora sintetičkog sulfata, čiji je sastav bio sličan rastvorima za luženje istrošenih LIB. Koncentracije Co(II), Mn(II) i Ni(II) u sulfatnim rastvorima bile su 2, 0,3 i 8 g/L, pojedinačno. Prvo, bilo je moguće potpuno odvojiti Mn(II) od Co(II) i Ni(II) selektivnom ekstrakcijom koristeći dve faze protivstrujne ekstrakcije sa 10% saponifikovanim 0,3 M D2EHPA. Zatim je čisti rastvor $MnSO_4$ dobijen uklanjanjem napunjenog D2EHPA sa 0,05 M rastvorom H_2SO_4 . Iz rafinata bez Mn (II), Co(II) je potpuno odvojen preko Ni (II) u dve faze protivstrujne ekstrakcije sa 15% saponifikovanim 0,3 M Cyanex 272. Čistoća Ni (II) u rafinatu je bila veća od 99,9% i čisti rastvor $CoSO_4$ je dobijen uklanjanjem napunjenog Cyanex 272 sa 0,05 M rastvorom H_2SO_4 . Predložen je postupak zasnovan na solventnoj ekstrakciji uz korišćenje komercijalnih organofosfornih ekstraktanata za oporavak čistih rastvora $CoSO_4$, $MnSO_4$ i $NiSO_4$ iz lužnih rastvora sumporne kiseline istrošenih LIB.

Ključne reči: Hidrometalurgija; Litijum-jonske baterije; Reciklaža; Separacija; Solventna ekstrakcija

