

Article

Application of Co and Mn for a Co-Mn-Br or Co-Mn- $C_2H_3O_2$ Petroleum Liquid Catalyst from the Cathode Material of Spent Lithium Ion Batteries by a Hydrometallurgical Route

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Abstract: We investigated the preparation of CMB (cobalt-manganese-bromide) and CMA (cobalt-manganese-acetate) liquid catalysts as petroleum liquid catalysts by simultaneously recovering Co and Mn from spent Li-ion battery cathode material. To prepare the liquid catalysts, the total preparation process for the liquid catalysts consisted of physical pre-treatments, such as grinding and sieving, and chemical processes, such as leaching, solvent extraction, and stripping. In the physical pre-treatment process, over 99% of Al was removed from material with a size of less than 0.42 mm. In the chemical process, the leaching solution as obtained under the following conditions: 2 mol/L sulfuric acid, 10 vol % H_2O_2 , 0.1 of solid/liquid ratio, and 60 °C. In the solvent extraction process, the optimum concentration of bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), the equilibrium pH, the degree of saponification, the organic phase/aqueous phase ratio isotherm, and the stripping study for the extraction of Co and Mn were investigated. As a result, Co and Mn were recovered by 0.85 M Cyanex 272 with 50% saponification in counter current two extraction stages. Finally, a CMB and CMA liquid catalyst containing 33.1 g/L Co, 29.8 g/L Mn, and 168 g/L Br and 12.67 g/L Co, 12.0 g/L Mn, and 511 g/L $C_2H_3O_2$, respectively, was produced by 2 M hydrogen bromide and 50 vol % acetic acid; it was also found that a shortage in the concentration can be compensated with cobalt and manganese salts.

Keywords: CMB; CMA; cobalt; manganese; Li-ion battery

1. Introduction

The demand for lithium-ion batteries (LIBs) has been growing continuously, and the original use of batteries as energy sources for portable electronic devices has been extended to their application as power sources in hybrid electric vehicles (HEVs) and electric vehicles (EVs). The amount of cobalt used in Li-ion batteries has been increased to 42 wt % [1]. Therefore, recycling of Li-ion batteries is important from economic and environment standpoints. Therefore, many researchers have studied the recovery of Co from Li. However, these investigations have demonstrated the recovery of Co and Li from $LiCoO_2$ cathode material. Currently, recovery of Co content has gradually declined and is replaced by the recovery of Ni and Mn due to the differences in metal prices, voltage capacities, and safety of operation at high temperatures. Therefore, valuable metals, such as Co, Mn, and Ni need to be recovered via an economically sustainable process. The separation/purification of cobalt and manganese is hardly achieved by the hydrometallurgical

method because cobalt and manganese have similar chemical properties. However, several methods, such as leaching by ammonia–ammonium carbonate [2,3], precipitation [4–6] and solvent extraction [7–13], have been reported for the separation/purification of cobalt and manganese.

In particular, a mixture of extractants has been employed for the separation and purification of Co and Mn [14–18]. Based on the reported studies, many researchers have been interested in the individual separation of Co and Mn for applications in a field that is different from the final product. However, if an application for Co and Mn is found, the problem of separating Co and Mn for the recycling of Li-ion batteries will be solved; such a method would also be economically viable due to the elimination of the separation and purification stages during processing. One of the possible applications of cobalt and manganese compounds is in a cobalt-manganese-bromide (CMB) or cobalt-manganese-acetate (CMA) liquid catalyst.

CMB and CMA catalysts represent a major use of cobalt and manganese; these two metals are used in mixed cobalt acetate/manganese bromide homogeneous catalysts for the production of terephthalic acid (TPA) and di-methylterephthalate (DMT). TPA and DMT are used to make polyethylene terephthalate from p-xylene. The catalytic reaction proceeds with cobalt acetate or bromide, with manganese present during the TPA process. South Korea is a major TPA supplier and produced 2.281 thousand tons of TPA in 2014; moreover, South Korea, Taiwan, Thailand, and Mexico comprise approximately 94% of the global TPA ion product capacity [19].

Therefore, Co and Mn used in Li-ion batteries present a possible source for the manufacturing of CMA and CMB liquid catalysts. In this study, the simultaneous recovery of cobalt and manganese was performed from lithium-ion battery scrap cathodic material by solvent extraction to prepare aqueous CMB and CMA liquid catalysts.

2. Materials and Methods

2.1. Materials

Scrap cathodic material was subjected to physical treatment involving cutting and grinding steps to detach the cathodic active material from Al foil. After classification, the ground cathodic material was separated into powders of five different size fractions—greater than 2.38 mm, between 1.0 mm and 2.38 mm, between 0.42 mm and 1.0 mm, between 0.25 mm and 0.42 mm, and less than 0.25 mm—to concentrate the cathodic active material, except from Al foil. The fraction of the material with a size of less than 0.42 mm was selected for reductive leaching. Table 1 shows the chemical composition of the cathodic material and to separate the Al foil.

Table 1. Chemical composition of cathodic material scrap of lithium-ion battery (wt %).

Elements	Co	Mn	Ni	Li	Al
Content	18.2	17.3	19.1	6.8	11.1

2.2. Solvent Extraction for Cobalt-Manganese-Bromide (CMB) and Cobalt-Manganese-Acetate (CMA) Aqueous Catalysts

For the preparation of the feed solution, leaching tests were conducted using 1 M H₂SO₄ and 10 vol % H₂O₂ at a reaction temperature of 60 °C, an agitation speed of 250 rpm, a solid/liquid ratio (S/L ratio) of 100 g/L, and a reaction time of 2 h. Removal of Al from the leach liquor was performed by adjusting the pH to 5.5.

A commercial extractant, bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), was supplied by Cytec Industries Inc. (Woodland Park, NJ, USA) and was used without further purification. Commercial grade extra-pure kerosene (Boiling point: 180–270 °C; Junsei Chemical Co., Ltd., Tokyo, Japan) was used as the diluent for all experiments. ACS (American Chemical Society, Washington, WA, USA)

reagent HBr (Sigma-Aldrich Corporation, St. Louis, MO, USA) was utilized for solvent extraction as a stripping solution.

Stock solutions of Cyanex 272 were prepared by diluting Cyanex 272 in kerosene at a predetermined mass ratio and were saponified to 50% Na-Cyanex 272 of different compositions in the 30–70% range by adding stoichiometric amounts of the concentrated NaOH solution. All of the preliminary experiments were carried out at ambient temperature (25 ± 1 °C) to examine the effect of the pH, saponification%, and Cyanex 272 concentration over the 0.7–0.95 M range. The aqueous Al-free phase was equilibrated with different volumes of 50% saponified 0.85 M Cyanex 272 by shaking in a separating funnel for 5 min in a shaking machine (Jeio tech, Deajeon, Korea). The equilibrium pH and metal concentrations in the aqueous phase were measured after the separation of the aqueous and organic phases.

The McCabe-Thiele diagrams involve both extraction and stripping studies in which the organic phase/aqueous phase ratio (O/A ratio) varied between 1/5 and 5/1. The stripping of cobalt and manganese from the loaded organic phase for the aqueous CMB catalyst was carried out with dilute HBr (0.5–3.0 M).

All samples were analyzed via an atomic absorption spectrometer (Perkin Elmer Model 400; Perkin Elmer, Waltham, MA, USA), bromine was analyzed via ion chromatography (Dionex ICS-3000; Dionex, Sunnyvale, CA, USA), and the acetate was analyzed via gas chromatography (Hewlett Packard 5890 II series plus; Hewlett Packard, Palo Alto, CA, USA).

3. Results and Discussion

3.1. Physical Separation of Cathodic Material Scrap

Table 2 lists the wt % of different fractions obtained after the physical separation of cathodic material scrap and the metal concentrations in each fraction. The fraction with a size of less than 0.42 mm; high cobalt and manganese concentrations of 17.8% (95.8% concentrated) and 16.8% (96.4% concentrated), respectively; only 0.4% Al was NaOH, adding up to a pH of 5.5, and formed precipitation was removed by filtration.

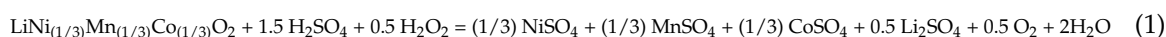
Table 2. Metal composition of different fractions.

Division (mm)	Co	Li	Ni	Mn	Al	Mass (%)
+2.38	0.29	0.0	0.34	0.14	8.33	18.72
−2.38 + 1.0	0.08	0.3	0.08	0.13	0.54	1.49
−1.0 + 0.42	0.02	0.10	0.22	0.22	1.88	4.63
−0.42 + 0.25	2.81	0.30	1.99	2.43	0.25	12.18
−0.25	15.0	6.10	16.47	14.38	0.10	61.78
Total	18.2	6.80	19.1	17.30	11.10	98.80 (1.2) ¹

¹ The value inside parentheses is loss during physical treatment.

3.2. Leaching and Removal of Al

Equation (1) describes the reductive leaching of the cathodic active material caused by H₂O₂.



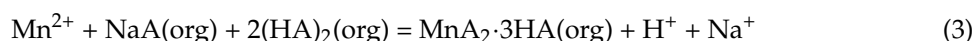
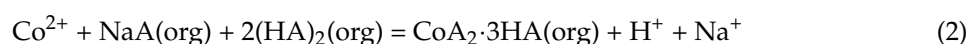
All metals were leached with an efficiency of 99% at a high S/L ratio of 100 g/L at 60 °C. After leaching, impurities, such as Al, were removed in the leachate, 5 M NaOH. An aqueous solution containing 12.9 g/L Ni, 12.8 g/L Co, 12.1 g/L Mn, and 4.3 g/L Li was prepared for solvent extraction (Table 3).

Table 3. Metal concentration of leachate by reductive leaching and pH controlled liquor (mg/L) (1 M H₂SO₄, 10 vol % H₂O₂, a reaction temperature of 60 °C, an agitation speed of 250 rpm, a solid/liquid ratio of 100 g/L, and a reaction time of 2 h).

Element	Ni	Co	Mn	Li	Al	pH
Leach liquor	18,860	17,740	16,700	7020	830	0.97
pH 5.5 solution	17,530	16,400	16,380	6912	-	5.5
After dilution prior to solvent extraction	12,910	12,800	12,130	4320	-	5.7

3.3. Solvent Extraction with Saponified Cyanex 272

The acidic form of Cyanex 272 exists as a dimer (HA)₂, whereas the saponified form exists as a monomer. The existence of the disolvated species in the organic phase for a sulfate medium has been reported by other investigators. The extraction of cobalt by partially saponified Cyanex 272 can be expressed by Equations (2) and (3) [20–23], where (HA)₂ and NaA represent Cyanex 272 and sodium-Cyanex 272, respectively:



Considering the equilibrium constant, taking the logarithm and rearranging Equation (4), we obtain:

$$\log D = \log K_{\text{ex}} - \log[\text{Na}^+] + \log[\text{NaA}(\text{org})] + 2\log[(\text{HA})_2(\text{org})] + \text{pH} \quad (4)$$

D is defined as distribution ratio and K_{ex} is defined as equilibrium constant:

$$D = \frac{\text{Concentration of metal in the organic}}{\text{Concentration of metal in the aqueous}} \quad (5)$$

To choose the optimum extractant concentration and equilibrium pH for a high percentage extraction of Co and Mn, the effect of a 50% saponified Cyanex 272 concentration in the 0.7–0.95 M range and an aqueous phase equilibrium pH in the 4.5–6.5 range was studied at an aqueous phase/organic phase ratio (A/O ratio) of 1/2.

The results are shown in Figures 1 and 2, demonstrating that the percentage of extraction of Co increases with the increasing equilibrium pH of the aqueous phase and with the extractant concentration. The optimum equilibrium pH of the aqueous phase appears to be in the 5.0–6.0 range with a >95–98% Co extraction and low co-extraction of Ni (~10%). The separation factors for Co/Li and Co/Ni for extraction using 50% saponified 0.85 M Cyanex 272 at equilibrium pH of 6 were close to 772.7 and 725.7, respectively (in Figure 2, the arrow presents pH at different concentration Cyanex 272).

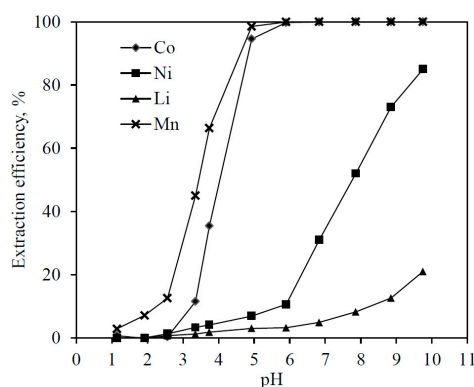


Figure 1. pH isotherm of lithium ion batteries leaching solution with Cyanex 272.

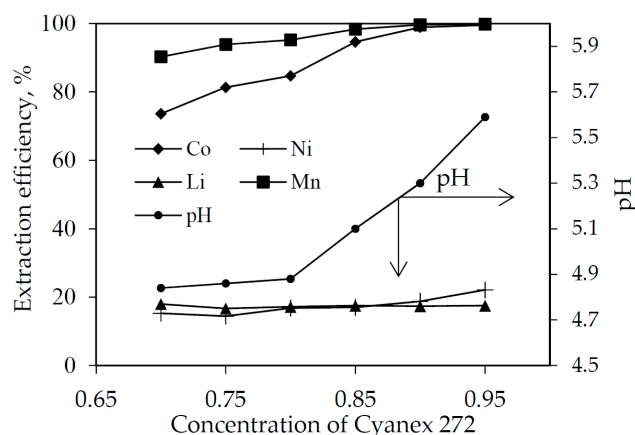


Figure 2. Effect of concentration of 50% saponified Cyanex 272 on metal extraction and pH.

The effect of the saponification ratio of Cyanex 272 (30–70%) on the extraction of metals from clarified leach liquors at an initial pH of 5.5 using 0.85 M Cyanex 272 is presented in Figure 3. The cobalt extraction increases from 48.7% to 100%, with an increase in the saponification ratio from 30% to 70%, which also causes an increase in the equilibrium pH from 4.2 to 6.8 (in Figure 3, the arrow presents pH at different saponification concentration of Cyanex 272). The extraction of nickel and lithium was also observed at higher saponification ratios and higher pH levels.

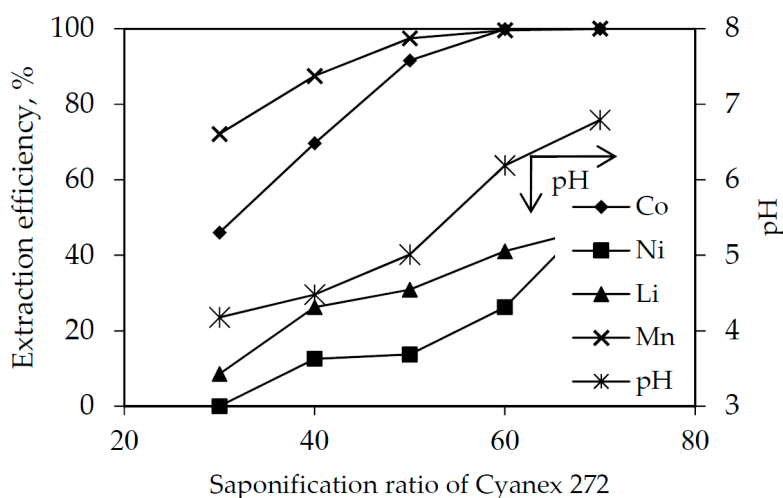


Figure 3. Effect of saponification% of 0.85 M Cyanex 272 on metal extraction and pH.

3.4. McCabe-Thiele Extraction Isotherm Study

The McCabe-Thiele study was conducted to determine the number of theoretical extraction stages or stripping stages for the target metals via O/A ratio isotherm experiments. Firstly, the equilibrium curve is drawn by connecting points of extraction or stripping of O/A ratio. Then, a feed line is drawn vertically on the x -axis. Thirdly, a random slope can be drawn within the range of the equilibrium curve and the feed solution. This slope is the operating line. Fourthly, a horizontal line is drawn from the feed solution line to the equilibrium curve, and a vertical line is then drawn from the equilibrium curve to the operating line. Finally, this operation is repeated until a horizon line cannot draw.

Figure 4 shows the loading isotherm and the O/A ratio isotherm, the McCabe-Thiele diagram, for the extraction of Co and Mn from the clarified leach liquor using 50% saponified 0.85 M Cyanex 272. It also shows that the quantitative extraction stage of cobalt and Mn occurs in a two-stage counter-current extraction using an O/A ratio of 2 (operating line = 0.5). It can be seen that, at the first

stage, the total concentration of Co and Mn is 12 g/L in the organic phase and 7 g/L in the aqueous phase. At the second stage, the total concentration of Co and Mn is 3 g/L in the organic phase and 0 g/L in the aqueous phase.

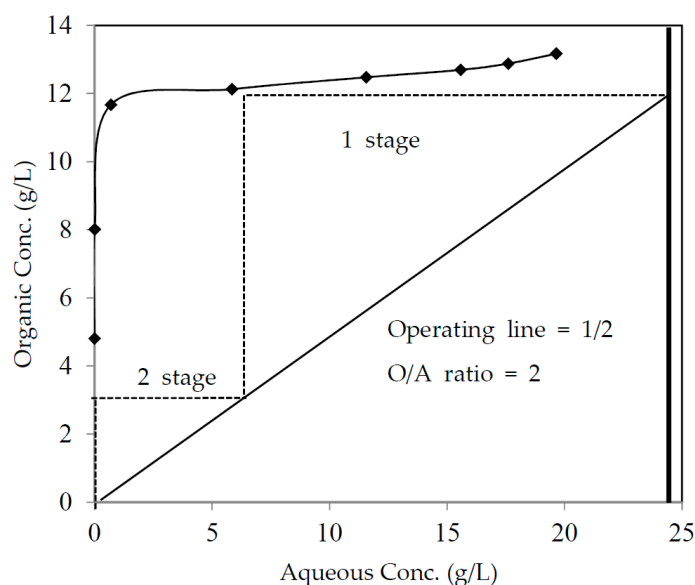


Figure 4. McCabe-Thiele diagram for cobalt extraction using 50% saponified 0.85 M Cyanex 272.

3.5. Two Stages Counter-Current Extraction Batch Simulation

Considering the minimum number of stages and the better extraction efficiency of cobalt, an O/A ratio of 2 was selected to carry out a two-stage counter-current extraction batch simulation with 40% saponified 0.85 M Cyanex 272 to confirm the McCabe-Thiele predictions. A two-stage CCES resulted in a raffinate containing 0.5 mg/L of Co (>99.9% extraction efficiency) and a loaded organic phase containing 6.4 g/L Co and 6.0 g/L Mn. The co-extraction amounts of Li and Ni were 0.4 mg/L and 0.6 mg/L into the loaded organic phase, respectively (Table 4). Additionally, at the first extraction stage, the concentrations of impurities, such as Ni and Li, in the aqueous phase were higher than those of Ni and Li in the feed solution due to the crowding effect.

Table 4. The results of the counter current simulation extraction batch tests by 0.85 M Cyanex 272 with 50% saponification. Unit: g/L.

No. of Counter-Current Extraction Stages	O: Organic Phase A: Aqueous Phase		Co	Mn	Ni	Li
2	1	O1	6.4	6.0	0.0006	0.0004
		A1	7.7	2.7	13.8	4.8
	2	O2	3.7	1.3	0.45	0.25
		A2	0.005	0.002	12.9	4.3

3.6. Stripping Test for Preparing Aqueous CMB and CMA Catalyst

3.6.1. Preparation of CMB Liquid Catalyst by Stripping with HBr

A sufficient amount of the loaded organic was generated from counter-current extraction simulation tests containing 6.4 g/L Co, 6.0 g/L Mn, 0.6 mg/L Ni, and 0.4 mg/L Li. The stripping of Co and Mn resulted in complete stripping by a 2 M HBr solution from the loaded organic phase at the first O/A ratio stage. The McCabe-Thiele diagram experiment was conducted to examine the concentration of Co and Mn obtained by 2 M HBr. Figure 5 shows that the concentrations of Co and Mn can be

increased by 5 times during the two stripping stages. To confirm this, a counter-current simulation batch stripping test was conducted. This obtained a CMB liquid catalyst that contains approximately 60 g/L Co and Mn from 2 M HBr in a two stage stripping process.

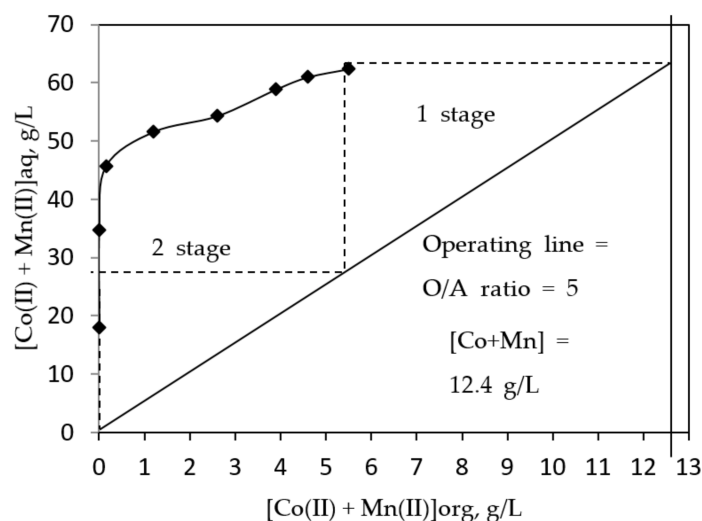


Figure 5. McCabe-Thiele diagram for Co and Mn stripping by 2 M HBr.

The commercial CMB specification is presented in Table 5. Compared to the commercial CMB, the concentration of Mn in the produced CMB was insufficient; however, the low concentration of Mn can be remedied by the formation of 0.55 M MnBr_2 . It is necessary to add MnBr_2 salt to prepared CMB.

Table 5. Specifications of CMB (Cobalt-Manganese-Bromide) and CMA (Cobalt-Manganese-Acetate) aqueous catalyst as an industrial grade and the concentration of prepared stripped solution. Unit: g/L.

Type	Experimental Condition	Co	Mn	Br	$\text{C}_2\text{H}_4\text{O}_2$	Ni	Li
CMB specification	-	30	60	153	-	<10 mg/L	<10 mg/L
CMA specification	-	22	11	-	37	<10 mg/L	<10 mg/L
Re-manufactured CMB	Stripping ratio: O/A = 5	33.1	29.8	168	-	7.2	4.1
Re-manufactured CMA	Stripping ratio: O/A = 2	12.67	12.0	-	511	-	-

3.6.2. Preparation of CMA Catalyst by Stripping with $\text{C}_2\text{H}_4\text{O}_2$

To prepare the CMA liquid catalyst, Co and Mn were stripped by 30 vol %–80 vol % of acetic acid at the first stage of the O/A ratio. As a result, the optimum concentration of acetic acid was found to be 50 vol %, with a stripping efficiency of 68.4% for Co and 62.9% for Mn. The McCabe–Thiele diagram experiment was conducted to determine whether the stripping stage was necessary for the purification of Co and Mn by 50 vol % $\text{C}_2\text{H}_4\text{O}_2$. Figure 6 shows that a third stage was necessary for stripping Co and Mn at the second state of O/A ratio, meaning that Co and Mn can be concentrated up to 2 times. Therefore, Co and Mn were stripped by 50 vol % of acetic acid in a counter current simulation of the 3-stage stripping batch test at an O/A ratio of 2. The obtained results are shown in Table 5 and are compared with the commercial CMA specifications. In the produced CMA, the concentration of Co does not meet the commercial CMA specifications. Therefore, the shortage in the concentration of Co can be addressed adding cobalt to obtain 0.15 M $\text{Co}(\text{C}_2\text{H}_3\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$. It is necessary to add $\text{Co}(\text{C}_2\text{H}_3\text{O}_4)_2$ salt to prepared CMA.

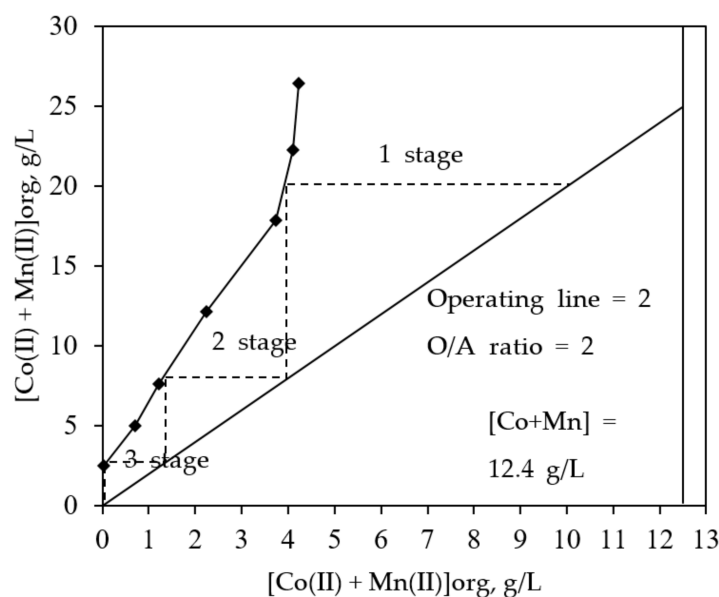


Figure 6. McCabe-Thiele diagram for Co and Mn stripping by 50 vol % acetic acid.

4. Conclusions

The results of preparing a CMB catalyst by solvent extraction of cobalt and manganese from cathodic material scrap to develop new applications for cobalt and manganese recovered from cathodic lithium-ion battery scrap material are as follows:

The physical treatment of cathodic material scrap produced a fraction that was separated into sizes of over and under 0.42 mm, with a high cobalt content of 17.8% (98.4% concentrated) and a high manganese content of 14.3% (98.6% concentrated) and only 0.1% Al. Under the leaching condition of 1 M H₂SO₄, 10 vol % H₂O₂, reaction temperature of 60 °C, agitation speed of 250 rpm, solid/liquid ratio of 100 g/L, and reaction time of 2 h, most of the cobalt, manganese, lithium and nickel were dissolved with 0.35% Al. The Al was then removed by NaOH. The optimum equilibrium pH of the aqueous phase in the 5.5–6.0 range led to a high Co extraction (95–98%) and low Ni extraction (~10%). A selective extraction of cobalt from leach liquor containing nickel and lithium was performed using 50% saponified 0.85 M Cyanex 272. Based on the McCabe-Thiele diagram, the extraction of cobalt could be estimated as 99.9%, with the cobalt and manganese extraction occurring in a two-stage counter-current operation with an O/A ratio of 2. From the loaded organic phase containing cobalt and manganese, the HBr solution stripping behavior was investigated. The cobalt and manganese were stripped with 2.0 M HBr at O/A = 1. The McCabe-Thiele diagram was estimated to be 99.9% cobalt stripping in a two-stage counter-current operation with an O/A ratio of 2. The stripping of the loaded organic phase with 2.0 M HBr and 50 vol % C₂H₄O₂ produced a CMB solution containing 33.1 g/L Co and 29.8 g/L Mn, and the CMA solution containing 153 g/L Br and 12.67 g/L Co, 12 g/L Mn and 511 g/L C₂H₃O₂. The produced solution could be used as aqueous CMB and CMA catalysts by compensating manganese salts to form 0.55 M MnBr₂ and 0.15 M Co(C₂H₂O₄)₂·4H₂O.

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Conflicts of Interest: The authors declare no conflict of interest.

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