



Extraction of manganese by alkyl monocarboxylic acid in a mixed extractant from a leaching solution of spent lithium-ion battery ternary cathodic material



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HIGHLIGHTS

- Antagonistic effect was proofed for Co and Mn extraction in Versatic 10 acid/D2EHPA.
- Antagonistic effect made a decrease of loading capacity for D2EHPA.
- Separation factor of Mn over Co was maximum in Versatic 10 acid/D2EHPA.
- In loaded organic, over 98% of Mn was extracted and impurities were removed by EDTA.
- Mn in loaded organic phase was stripped by 0.5 mol L⁻¹ H₂SO₄.

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ABSTRACT

We investigate the separation of manganese by an antagonistic effect from a leaching solution of ternary cathodic material of spent lithium-ion batteries that contain 11,400 mg L⁻¹ Co, 11,700 mg L⁻¹ Mn, 12,200 mg L⁻¹ Ni, and 5300 mg L⁻¹ Li using a mixture of alkyl monocarboxylic acid and di-(2-ethylhexyl) phosphoric acid extractants. pH isotherm, distribution coefficient, separation factor, McCabe–Thiele diagram, selective scrubbing, and countercurrent extraction tests are carried out to prove an antagonistic effect and to recover manganese using alkyl monocarboxylic in the mixed extractant. Slope analysis is used to determine the extraction mechanism between a mixture of extractants and valuable metals. An increasing concentration of alkyl monocarboxylic acid in the mixture of extractants results in a decrease in distribution coefficient of cobalt and manganese, however, the separation factor value ($\beta_{(Mn/Co)}$) increases at pH 4.5. This is caused by slope analysis where alkyl monocarboxylic acid disrupts the extraction mechanism between di-(2-ethylhexyl)phosphoric acid and cobalt. Finally, continuous countercurrent extraction in a mini-plant test demonstrate the feasibility of manganese recovery from cobalt, nickel, and lithium.

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1. Introduction

The development of a recycling process for spent lithium-ion batteries is very important from an environmental and economic point of view. To date, several solvent–extraction processes have been reported to achieve this aim. Cobalt and lithium are usually recovered from the spent lithium-ion batteries of LiCoO₂ electrodes

[1–8]. However, some of the cobalt in the lithium-ion battery has been replaced by nickel and manganese because of high cobalt prices and the safe operation of lithium-ion batteries at high temperatures [9]. Manganese recovery from a mixed cobalt/manganese solution should be studied for cobalt purification.

Di-(2-ethylhexyl)phosphoric acid (D2EHPA) is the most suitable extractant for manganese separation from cobalt. Devi et al. [10] compared (D2EHPA), 2-ethylhexyl phosphonic mono-2-ethylhexyl ester (PC88A), and bis(2,4,4-trimethylpentyl)phosphonic acid (Cyanex 272) to extract manganese from cobalt and found that D2EHPA extracts manganese from cobalt more selectively than

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Cyanex 272 and PC88A. Sato and Nakamura [11] investigated manganese, cobalt, nickel, copper, zinc, cadmium, and Hg extraction by D2EHPA and reported metal extraction in the order of $Zn > Cd > Mn > Cu > Co > Ni > Hg$. Cheng (2000) [12] reported a similar extraction order ($Zn \sim Ca > Mn \sim Cu > Co \sim Ni > Mg$) for zinc, manganese, copper, cobalt, and nickel with D2EHPA in the presence of Ca and Mg. Wang and Nagaosa [13] investigated the extraction of cadmium, manganese, copper, cobalt, and nickel by di-2-methylnonylphosphoric acid (D2MNP) in heptane. They reported that the extraction of metals is according to $Cd \approx Mn > Cu > Co > Ni$ at an aqueous ionic strength of $0.10 \text{ mol L}^{-1} \text{ NaClO}_4$.

Dreisinger and Cooper [14] investigated the pH isotherm by PC88A in sulfate and chloride media. In sulfate medium, manganese is extracted prior to cobalt, but in chloride medium, cobalt is extracted prior to manganese. In both media, the difference in pH_{50} (pH at the 50% extraction efficiency of metal) is small.

Cole [15] investigated the pH_{50} using Cyanex 272 in sulfate medium and reported a pH_{50} value for manganese and cobalt of 4.60 and 4.65, respectively. Ahn et al. [16] reported that cobalt can be extracted selectively by tri-octyl/decylamine (Alamine 336) from a hydrochloric leaching solution of manganese nodules, however, copper, iron, manganese, and zinc were co-extracted. Application of Co-D2EHPA for manganese removal from cobalt electrolyte solution has been investigated by Alam et al. [17]. However, 10% cobalt was co-extracted above pH 5. These literature studies indicate that manganese is extracted in preference to cobalt, and *vice versa*, however, the former separation is difficult because of small differences in pH_{50} .

Tsakiridis and Agatzini(2004a) [18] found that cobalt and nickel can be separated from manganese by bis (2,4,4- trimethylpentyl) dithiophosphinic acid (Cyanex 301). Cyanex 301 has a high selectivity for cobalt and nickel separation from manganese. Tsakiridis and Agatzini (2004b) [19] studied cobalt and nickel separation from magnesium by bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) and the cobalt pH_{50} was pH 3. Devi and Mishra [20] reported on the extraction of manganese by Cyanex 302. The pH_{50} value was 5.75 by 0.025 mol L^{-1} Cyanex 302. Considering the above two studies, cobalt could be extracted in preference to manganese and there is a significant possibility of cobalt separation from manganese because of the significant difference in pH_{50} by Cyanex 302. Unfortunately, Cyanex 301 and Cyanex 302 are expensive. Cheng(2006) [21] used a mixture of monocarboxylic acid (Versatic 10 acid) and aliphatic hydroxyoxime (LIX 63) for cobalt and nickel separation from a synthetic solution to simulate a laterite leach solution. The cobalt and nickel extraction curve shifted to a lower pH, which results in a $\Delta\text{pH}_{50}(\text{Mn}-\text{Ni})$ value of 1.96 and a $\Delta\text{pH}_{50}(\text{Mn}-\text{Co})$ value of 2.53 with a 0.5 mol L^{-1} Versatic 10 acid/ 0.35 mol L^{-1} LIX 63 system.

In this study, for commercial application purposes, we consider the combination of D2EHPA and Versatic 10 acid for the extraction and separation of cobalt, manganese, nickel, and lithium. The mixed extractant, Versatic 10 acid/D2EHPA, reduced the extraction behavior of cobalt and manganese, which is an opposite response to the synergistic effect obtained in the study by Cheng (2006). This study will contribute to the refining and recovery of cobalt.

2. Experimental methods

2.1. Reagents and materials

The extractant di-(2-ethylhexyl)phosphoric acid (molecular weight: 322.43 g, density: 0.96 g cm^{-3} , purity: 95% weight, commercial name: D2EHPA) was supplied by Mobil Chemicals and alkyl monocarboxylic acid (molecular weight: 175 g, density:

0.91 g cm^{-3} , purity: 90%, commercial name: Versatic 10 acid) was supplied by Shell Chemicals. Both extractants were used without further purification. The organic diluent kerosene was obtained from Junsei. Leaching tests were conducted using a solution of $2 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and 5 vol.% H_2O_2 at $60 \text{ }^\circ\text{C}$, 300 rpm, a solid/liquid ratio of 100 g L^{-1} , and a reaction time of 2 h. Impurities including aluminum, iron, and copper were removed by precipitation at pH 4.8, adjusted by the addition of 4 M NaOH. The filtered liquor was diluted prior to solvent extraction.

2.2. Solvent extraction

2.2.1. pH isotherms

Metal ion extraction from the clarified leach liquor of the ternary cathode material of spent lithium-ion batteries for the construction of pH isotherms were carried out using 0.43 mol L^{-1} D2EHPA and a mixture of 0.43 mol L^{-1} D2EHPA and 0.7 mol L^{-1} Versatic 10 acid, with an organic/aqueous (O/A) ratio of 1:1 at room temperature. To determine the extraction behavior of valuable metal ions, pH isotherms were obtained for different compositions of mixed extractants (0.1, 0.3, 0.5, and 0.7 mol L^{-1} Versatic 10 acid and 0.43 mol L^{-1} D2EHPA), with an O/A ratio of 1:1, an agitation speed of 250 rpm, and at room temperature. The two phases were contacted with rapid stirring and the pH was measured using a Thermo ORION 5 STAR and controlled by the addition of 5 mol L^{-1} NaOH. Samples were collected at pH intervals of 0.5, 10 min after equilibration, and separated into organic and aqueous phases using a separating funnel.

2.2.2. McCabe–Thiele diagram test

In order to determine the number of stages that are required at chosen volume phase ratio, the extraction isotherm was obtained at a different O/A phase ratios 7, 5, 3, 2, 1, 0.5 and 0.3 with 0.43 mol L^{-1} D2EHPA/ 0.7 mol L^{-1} Versatic 10 acid. All the experiments were carried out at room temperature and mixing time was optimized within 5min. Aqueous and organic phase was separated after equilibration, that aqueous samples was used for analysis.

2.2.3. Countercurrent simulation extraction and stripping test

To obtain a manganese solution from the loaded organic, stripping was carried out at different concentrations of sulfuric acid, an O/A of 2, and at room temperature using a separation funnel.

In the countercurrent extraction and stripping experiment, a shakeout test was carried out using a separation funnel and the raffinate and stripping aqueous samples were collected.

All shakeout tests were carried out with automatic shaker (model SI-600R) to maintain the agitation speed.

The collected all aqueous samples and all analyses were performed by atomic absorption spectrometer (Perkin Elmer Model 400).

2.2.4. Continuous current simulation extraction

Continuous tests were carried out in a laboratory solvent-extraction unit. The effective volume was 253 mL for each mixer and 764 mL for the settler. Table 1 shows the operating conditions for manganese recovery.

3. Results and discussion

3.1. Extraction behavior with Versatic 10 acid addition

Fig. 1 shows the extraction behavior of manganese, cobalt, nickel, and lithium by 0.43 mol L^{-1} D2EHPA alone, 0.7 mol L^{-1} Versatic 10 acid alone and 0.43 mol L^{-1} D2EHPA + 0.7 mol L^{-1}

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