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Selective extraction and separation of nickel from cobalt, manganese and lithium in pre-treated leach liquors of ternary cathode material of spent lithium-ion batteries using synergism caused by Versatic 10 acid and LIX 84-I

Sung-Ho Joo [a,b], Dong ju Shin [b], ChangHyun Oh [b], Jei-Pil Wang [c], Gamini Senanayake [d], Shun Myung Shin [a,b,]*

[a] *Resource Recycling Department, Korea University of Science & Technology (UST), Republic of Korea*
[b] *Extractive Metallurgy Department, Korea Institute of Geoscience & Mineral Resources (KIGAM), 92 Gwahang-no, Yuseong-gu, Deajeon 305-350, Republic of Korea*
[c] *Department of Metallurgical Engineering, Pukyong National University, Republic of Korea*
[d] *Chemical & Metallurgical Engineering & Chemistry, School of Engineering & Information Technology, Murdoch University, 90, South Street, Perth, WA 6150, Australia*

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ABSTRACT

The extraction of nickel from a leach liquor containing cobalt, manganese and lithium of Li-ion batteries cathode material using a mixture of Versatic 10 acid and LIX84-I was investigated. The leach liquor of LiB cathode material obtained with H_2SO_4/H_2O_2 as the lixiviant was purified by precipitating the leached aluminum, iron and copper as hydroxides by adjusting the pH to ~5. To extract nickel, the effect of Versatic 10 acid concentration was the experimental variable in the mixture of extractants. The pH-isotherms revealed the synergistic effect on nickel caused by the increasing concentration of Versatic 10 acid which decreased the pH_{50} for nickel extraction and pH 5 was chosen as the most suitable pH for solvent extraction. A loading isotherm at pH 5 was constructed by changing the O/A ratio. The McCabe Thiele diagram predicted the possibility of using three stages to extract over 98% nickel, which was confirmed experimentally. The stripping test was carried out from loaded organic of Versatic 10 acid alone, LIX 84-I alone and the combination of Versatic 10 acid and LIX 84-I. Slow stripping of nickel from LIX 84-I indicated that LIX 84-I and Versatic 10 acid acted as the extractant and synergist, respectively.

1. Introduction

Resource quality and economic treatment of low grade ores can be challenging for producers in mining and metallurgical industry. Global nickel and cobalt reserves are distributed in nickel–iron–copper (Ni–Fe–Cu) sulfide ores and nickel laterites (30% and 70%, respectively). The nickel content in Ni–Fe–Cu sulfide ores and laterites is 1–3% and 1–2%, respectively. However, the mining cost of Ni–Fe–Cu sulfide is considerably high due to the deep underground locations. The cost of the laterite processing is also high due to the difficulty in upgrading (Bacon and Mihaynov, 2002). The spent batteries are secondary resources of high metal grades. Legislations passed in many countries are meant to prohibit the discard of the spent batteries to landfills and to promote recycling. The recovery of nickel from secondary, resources such as spent nickel–cadmium (Ni–Cd), nickel–metal hydride (Ni–MH) and lithium-ion (Li-ion) batteries is valuable from economic and environmental points of view due to their increased domestic and industrial applications which cause increased global production as well as the pollution caused by improper discarding of the spent batteries. Many studies have addressed the recovery of nickel from spent Ni–Cd and Ni–MH batteries (Reddy et al., 2005; Fernandes et al., 2012, 2013; Rudnik and Nikiel, 2007; Li et al., 2009). The pre-treatment, leaching, separation and recovery of metals from spent Li-ion batteries (LiBs) have also been extensively reviewed (Meshram et al., 2014).

The separation of metal ions from cobalt rich leach liquors of spent LiBs has been largely based on solvent extraction and precipitation (Kang et al., 2010a, 2010b; Meshram et al., 2014). The major component, cobalt, in the Li-ion battery has been partially substituted with nickel and manganese by the manufacturing companies due to an increase of cobalt price and safe operation of LiBs at high temperature (Lu et al., 2013). Therefore, it is important to investigate the selective recovery of nickel from $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ type spent LiBs. This study aims to briefly review the previous work on solvent extraction for the separation of relevant metal ions from leach liquors and mainly focus on selective extraction of nickel from a leach liquor of spent $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ type Li-ion battery ternary cathode material which contained cobalt, manganese and lithium ions.

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* Corresponding author at: Extractive Metallurgy Department, Korea Institute of Geoscience & Mineral Resources (KIGAM), 92 Gwahang-no, Yuseong-gu, Deajeon 305-350, Republic of Korea.
E-mail address: shin1016@kigam.re.kr (S.M. Shin).

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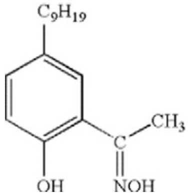
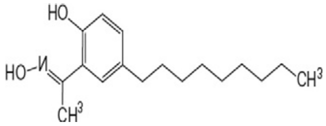
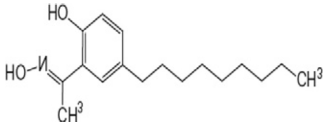
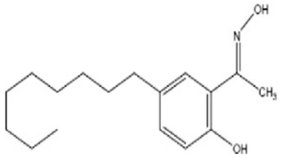
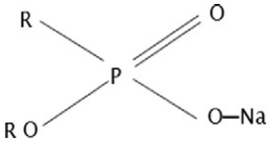
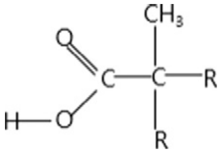
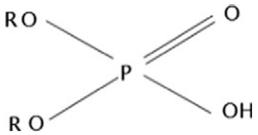
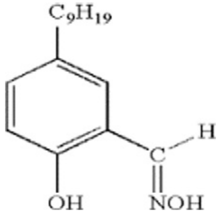
Table 1
Extraction of nickel using various extractants.

Extractant	Structure	Important aspects	
LIX84		• Co-extraction of Cu and Ni by LIX 84-I. • Ni was selectively stripped by spent electrolyte at pH 1.7. However, 26 g/L Ni was lost.	Parija and Bhaskara Sarma (1998)
LIX84-I		• Recovery of nickel by LIX 84-I from ammonium sulfate solution containing only nickel.	Parija and Bhaskara Sarma (2000)
LIX84-I		• The order of extraction: Cu (pH 4.0) > Ni (pH 7.5) > Zn (pH 9.0). • The solution did not contain cobalt and manganese.	Reddy and Priya (2005)
LIX984N		• Extraction of copper from pregnant solution by LIX 984N. • Extraction of nickel from copper raffinate solution by LIX 984N.	Sridhar et al. (2011)
NaPC-88A		• Extraction of Co from mixed sulfate/chloride leach liquor, by NaPC-88A. • Extraction of nickel from cobalt raffinate solution, by NaPC-88A.	Parhi et al. (2011)
Versatic 10 acid		• Co- extraction over 99% Co and Ni from Ca and Mg using Versatic 10 acid at pH 6.5. • Extraction of Co from co-extracted Co and Ni, mixture using Cyanex 272.	Tsakiridis and Agatzini (2004)
TOPS 99		• Recovery of Cd from Co and Ni solutions by Cyanex 923. • Extraction of Co from Cd raffinate by Cyanex 272. • Extraction of Ni from cobalt raffinate, using TOPS 99.	Reddy et al. (2005)
ACORGA M5640		• Simultaneous extraction of Ni and Cu from ammonia/-ammonium carbonate solution by ACORGA M5640. • Removal of ammonia by scrubbing solution of pH 3.0 at equilibrium pH 7.4. • Selective stripping of Ni. But low stripping efficiency of Ni. • No cobalt and manganese in the solution.	Sridhar et al. (2010)

2. Previous studies

A review of the general recovery methods of nickel by solvent extraction using LIX, Versatic 10 acid, TOPS, ACORGA M5640, and PC 88A as extractants is presented in Table 1. The LIX reagent coextracted copper and nickel which was then separated by selective stripping of nickel from copper in the loaded organic sample, however, as the aqueous base was an ammoniacal solution, ammonia was scrubbed from the loaded organic before selective stripping of nickel for electrowinning. A loss of nickel occurred in the step for ammonia scrubbing (Parija and Bhaskara Sarma, 1998). It is important to note that the feed aqueous solution used in above studies did not contain cobalt and manganese (Parija and Bhaskara Sarma, 2000; Liqing et al., 2011; Reddy and Priya, 2005). Preferential extraction of cobalt from metal ion mixtures has been accomplished using other extractants, such as NaPC-88A, Versatic 10 acid and TOPS, where nickel has been recovered from the raffinate solution (Parhi et al., 2011; Tsakiridis and Agatzini, 2004). Likewise, separation of nickel from copper involves the selective stripping of the ammoniacal/ammonium carbonate solution (Sridhar et al., 2010). However, as described above, ammonia was scrubbed from the loaded organic phase and the stripping efficiency of nickel was low due to the losses during scrubbing.

Table 2 summarizes the previous studies which have addressed the recovery of nickel using mixtures of extractants which promoted synergism. Versatic 10 acid has been used most often, reflecting its synergistic activity. Preferential extraction of cobalt has been achieved, followed by the recovery of nickel after removing impurities including Cu, Al and Fe by using a mixture of Ionquest 801 and Acorga M5640 (Pranolo et al., 2010). Preferential extraction of cobalt has also been achieved using Cyanex 302 and D2EHPA (Darvishi et al., 2005). The synergistic effect during extraction of nickel from calcium and magnesium from solutions free of cobalt and manganese has also been reported (Ndlovu and Mahlangu, 2008).