



Imam Khomeini International University

Vol. 7, No. 2, Summer 2022



نشریه مهندسی منابع معدنی

Journal of Mineral Resources Engineering  
(JMRE)

## Research Paper

# Recycling of Precious Metals from the Waste of Lithium-Ion Batteries

Asadi Dalini E.<sup>1</sup>, Karimi Gh.R.<sup>2</sup>, Zandevakili S.<sup>3\*</sup>

1- M.Sc, Dept. of Mining Engineering, Imam Khomeini International University, Qazvin, Iran

2- Assistant Professor, Dept. of Mining Engineering, Imam Khomeini International University, Qazvin, Iran

3- Assistant Professor, Dept. of Mining Engineering, Vali-e-Asr University of Rafsanjan, Kerman, Iran

Received: 02 Nov. 2020

Accepted: 02 Mar. 2021

**Abstract:** The process of recovering metals from spent lithium-ion batteries is difficult due to the complexity of the metal components. Therefore, the separation and extraction of metal ions from the leaching solution of spent lithium-ion batteries requires a set of hydrometallurgical processes. In this research, precipitation and solvent extraction processes have been used to the final recovery of metals. Initially, 96.5% of manganese ions were precipitated by applying potassium permanganate with the molar ratio of manganese ions to potassium permanganate: 2 and pH: 2. Then, via dimethylglyoxime in molar ratio of nickel ions to dimethylglyoxime: 0.5, and pH: 5, 96% nickel recovered, approximately. Subsequently, using 30 v/v% D2EHPA and 5 v/v% TBP respectively as an extractant and a modifier of the organic phase, and under optimal conditions of Vo/Va: 1, pH: 5, temperature 25 °C, time 20 min and mixing speed 400 rpm, it is possible to achieve 93.38% cobalt extraction efficiency and also control the loss of lithium at 16.74%. Finally, in the molar ratio of lithium ions to sodium carbonate: 0.7, temperature 100 °C, time 40 min, mixing speed 400 rpm and the pH: 12, the lithium precipitation efficiency reached to 98.84%.

**Keywords:** Hydrometallurgical processes, Lithium-ion battery, Treatment of leach solution, Precipitation, Solvent extraction.

### How to cite this article

Asadi Dalini, E., Karimi, Gh. R., and Zandevakili, S. (2022). "Recycling of precious metals from the waste of lithium-ion batteries". Journal of Mineral Resources Engineering, 7(2): 157-177.

DOI: 10.30479/JMRE.2021.14489.1463

\*Corresponding Author Email: [s.zandvakili@vru.ac.ir](mailto:s.zandvakili@vru.ac.ir)

### COPYRIGHTS



©2022 by the authors. Published by Imam Khomeini International University.

This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution 4.0 International (CC BY 4.0) (<https://creativecommons.org/licenses/by/4.0/>)

## INTRODUCTION

The widespread and rapidly increasing production and consumption of LIBs, as well as the development of consumer electronics and hybrid and electric vehicles, has led to increased demand metals and generation of battery scrap [1-3]. Compared to other chemical batteries, lithium-ion batteries are relatively harmless. Still, some environmental considerations about their production, consumption, and expiration are the challenges of LIBs. Spent LIBs contain many toxic substances, such as heavy metals like copper, cobalt, lithium and nickel, and organic chemicals like electrolytes and separators [4-7]. Also, LIBs can regularly release toxic organic compounds that are very corrosive and pose an unavoidable risk in causing damage to the environment and public health [8,9]. Hydrometallurgy process has attracted much attention in academic research and industrial applications because of effective metal recovery, relatively low energy consumption, and low gas emissions [10]. In this paper, the recovery of manganese, nickel, cobalt and lithium metals from the leaching solution of spent lithium-ion batteries using hydrometallurgical method has been studied. The main focus of this study is the selective separation of metals from leaching solution of spent lithium-ion batteries, the investigation of the factors influencing cobalt solvent extraction and control of loss of lithium in the previous stages of metals separation.

## METHODS

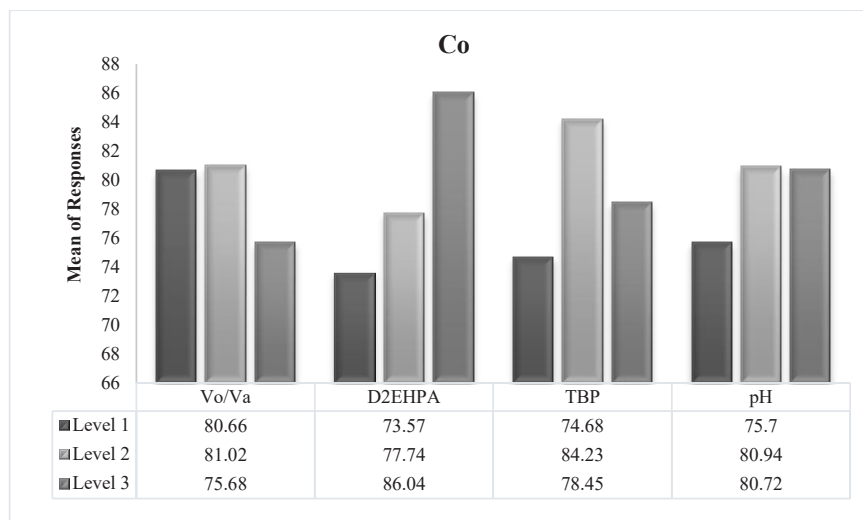
The recycling of metals was carried out through the various process, including pre-treatment, crushing, leaching and final recovery. The process was initiated by neutralizing the material in the 5 wt% solution of sodium chloride to completely discharge the batteries within 36 hours. Then, after initial crushing and manual separation of the different components of the batteries from each other, the solution of 10 wt % sodium hydroxide was used to remove and alkali dissolution of aluminium foil from other accompanying cathode materials. Subsequently, the resulting solution was filtered and the remaining solids material was dried in an oven at 80 °C for 12 h. Finally, in order to remove associated impurities, especially carbon and Polyvinylidene fluoride (PVDF) from cathodic valuable materials, calcination was carried out at the temperature of 610 °C in a vacuum furnace for 3 h. The cathode material leaching process was also carried out, in the presence of 2 M sulfuric acid at 60 °C for 80 min, 4 v/v% of H<sub>2</sub>O<sub>2</sub>, and the solid-to-liquid ratio of 30 g/L. Precipitation operations were used to separate manganese and nickel metals from the leaching solution. Potassium permanganate (KMnO<sub>4</sub>) and dimethylglyoxime (DMG) were added to the leaching solution, for precipitation manganese and nickel, respectively. The solvent extraction process was developed to concentration and extraction of the cobalt from lithium ion in the remaining solution. The SX operation was designed using the design expert software (version 10) following the conditions and results listed in Table 1 using the Taguchi L<sub>9</sub> orthogonal array method for 4 variables at 3 different levels, and the effect of parameters such as D2EHPA concentration, TBP concentration, pH and the phase ratio of organic to aqueous on cobalt extraction was investigated. Lithium precipitation experiments were performed in different molar ratios of lithium ions to sodium carbonate.

**Table 1.** Conditions and results of Co and Li solvent extraction experiments

Run	O/A ratio	pH	TBP	D2EHPA	Co Recovery (%)	Li Recovery (%)
1	1	6	5	20	86	13.47
2	1.5	4	10	20	75.56	7.46
3	1.5	6	0	30	85.1	17.18
4	1	4	0	10	67.26	8.58
5	2	4	5	30	84.3	13.14
6	1	5	10	30	88.74	15.88
7	1.5	5	5	10	82.4	8.12
8	2	5	0	20	71.68	7.31
9	2	6	10	10	71.06	6.82

## FINDINGS AND ARGUMENT

By calculating the mean of responses at different levels, we can determine the optimal levels of parameters during these experiments according to Figure 1. As shown in Figure 6, the optimal SX conditions to achieve the highest percentage of cobalt extraction can be obtained in the presence of 30 v/v% D2EHPA, 5 v/v% TBP, pH: 5 and  $V_o/V_A = 1.5$ .



**Figure 1.** The mean responses of Co solvent extraction at different levels of parameters

**Effect of VO/VA :** Increasing the phase ratio of organic to aqueous from 1 to 2 due to increasing the viscosity of the solution leads to a decrease in the cobalt extraction efficiency from 93.38% to 88.94%. Also, in these conditions, a slight decrease in lithium loss from 16.74% to 13.56% was obtained. Due to the results obtained, the maximum efficiency of cobalt extraction and the minimum rate of lithium loss occurs in the  $V_o/V_A = 1.5$ .

**Effect of D2EHPA:** D2EHPA is the most common and useful extractor for separating cobalt from leaching solutions. The reaction of cobalt ion exchange with D2EHPA is following equation 1 [11].



The results show that as the concentration of D2EHPA increases from 10 to 30 v/v%, the extraction efficiency of cobalt and lithium increases from 81.26% and 7.47% to 93.38% and 16.74%, respectively.

**Effect of TBP:** The results show that TBP has a positive effect on cobalt extraction efficiency. The result of increasing the cobalt extraction efficiency from 84.02% to 93.38% while adding 5 v/v% of TBP to the solution can be observed.

**Effect of pH:** According to results, by increasing the pH from 4 to 6, the cobalt and lithium extraction efficiency increase from 88.34% and 14.43% to 93.05% and 18.58%, respectively. Since the rate of lithium loss at pH: 5 less and the efficiency of cobalt extraction is similar to the experiment condition at pH: 6, the optimal pH: 5 was selected to the separation of cobalt from the leaching solution.

Analyzing the results of SX experiments show that the optimal conditions for cobalt extraction were provided at 30 v/v% D2EHPA, 5 v/v% TBP,  $V_o/V_A=1$ , pH:5, temperature 25 °C, time 20 min and mixing speed 400 rpm. Under these conditions, the efficiency of cobalt extraction is 93.38% and lithium loss is 16.74%.

**Li scrubbing:** Lithium scrubbing was investigated as a function of the concentration of the scrubbing agent using sodium hydroxide and sodium carbonate. With the increase in the concentration of NaOH and  $\text{Na}_2\text{CO}_3$  from 0.075 to 0.2 M, the efficiency of lithium scrubbing has increased to 88.65% and 98.04%. However, increasing the concentration of the scrubbing agent to more than 0.2 M has led to the stabilization and reduction of the scrubbing efficiency by sodium carbonate and sodium hydroxide, respectively. Therefore, 0.2 M of sodium carbonate was considered as the appropriate reagent concentration for lithium scrubbing.

Stripping of Co: As the concentration of sulfuric acid increases from 0.1 M to 1 M, stripping efficiency increased from 55.21% to 99.88%.

Precipitation of Li: Optimal conditions were obtained at the MRLN: 0.7 with the possibility of precipitation of 98.84% of lithium.

## CONCLUSIONS

Due to the increase in demand and consumption of lithium-ion batteries, the amount of waste of electrical and electronic equipment is growing. Lack of management of the recycling of lithium-ion batteries, on the one hand, means environmental pollution and on the other hand means ignoring the huge source of valuable metals such as manganese, nickel, cobalt, and lithium. In this study, an attempt has been made to use various hydrometallurgical techniques to recover valuable metals from the leaching solution of spent lithium-ion batteries.

The results showed that 96.5% of manganese ions in oxide form were separated from the leaching solution by the MRMK: 2 and pH: 2. In the same way, 96% of nickel in MRND: 0.5 and pH: 5 can be recovered under constant experimental conditions.

The optimal conditions for cobalt extraction (93.38%) were obtained at 30 v/v% D2EHPA, 5 v/v% TBP, Vo/Va:1, pH:5, temperature 25 °C, time 20 min and mixing speed 400 rpm.

Optimal conditions for lithium precipitation were obtained at the MRLN: 0.7 with the possibility of precipitation of 98.84% of lithium.

## REFERENCES

- [1] Choubey, P. K., Kim, M. S., Srivastava, R. R., Lee, J. C., and Lee, J. Y. (2016). "Advance review on the exploitation of the prominent energy-storage element: Lithium. Part I: From mineral and brine resources". *Minerals Engineering*, 89: 119-137.
- [2] Lv, W., Wang, Z., Cao, H., Sun, Y., Zhang, Y., and Sun, Z. (2018). "A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries". *ACS Sustainable Chemistry and Engineering*, 6: 1504-1521.
- [3] Kim, H., Hong, J., Park, K. Y., Kim, H., Kim, S. W., and Kang, K. (2014). "Aqueous rechargeable Li and Na ion batteries". *Chemical Reviews*, 114: 11788-11827.
- [4] Sole, K. C., Parker, J., Cole, P. M., and Mooiman, M. B. (2019). "Flowsheet Options for Cobalt Recovery in African Copper-cobalt Hydrometallurgy Circuits". *Mineral Processing and Extractive Metallurgy Review*, 40: 194-206.
- [5] Zeng, X., Li, J., and Singh, N. (2014). "Recycling of spent lithium-ion battery: A critical review". *Critical Reviews in Environmental Science and Technology*, 44: 1129-1165.
- [6] Zhang, Y., Wang, Y., Zhang, H., Li, Y., Zhang, Z., and Zhang, W. (2020). "Recycling spent lithium-ion battery as adsorbents to remove aqueous heavy metals: Adsorption kinetics, isotherms, and regeneration assessment". *Resources, Conservation and Recycling*, 156: 104688.
- [7] Choubey, P. K., Chung, K. S., seuk Kim, M., Chun Lee, J., and Srivastava, R. R. (2017). "Advance review on the exploitation of the prominent energy-storage element Lithium. Part II: From sea water and spent lithium ion batteries (LIBs)". *Minerals Engineering*, 110: 104-121.
- [8] Zheng, X., Zhu, Z., Lin, X., Zhang, Y., He, Y., Cao, H., and Sun, Z. (2018). "A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries". *Engineering*, 4: 361-370.
- [9] Yang, Y., Lei, S., Song, S., Sun, W., and Wang, L. (2020). "Stepwise recycling of valuable metals from Ni-rich cathode material of spent lithium-ion batteries". *Waste Management*, 102: 131-138.
- [10] Yang, Y., Xu, S., and He, Y. (2017). "Lithium recycling and cathode material regeneration from acid leach liquor of spent lithium-ion battery via facile co-extraction and co-precipitation processes". *Waste Manag*, 64: 219-227.
- [11] Olivier, M. C. (2011). "Developing a solvent extraction process for the separation of cobalt and iron from nickel sulphate solutions". In the Faculty of Engineering at Stellenbosch Un. Stellenbosch University, M.Sc Thesis.