# Study on a Reductant-assisted Hydrometallurgical Process for Lithium Recovery from Wastewater in Lithium Carbonate Production

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Lithium-ion batteries are increasingly being utilized as eco-friendly energy storage systems due to their high power density and excellent electrochemical performance. In particular, with the rapid growth of electric vehicles (EVs) and renewable energy storage systems (ESS), global demand for lithium-ion batteries is continuously increasing and is projected to exceed 11 million tons by 2030 (Gruber and Medina, 2010).

The primary lithium sources used in lithium-ion secondary batteries are lithium carbonate ($Li_2CO_3$) and lithium hydroxide (LiOH). Among them, lithium carbonate, which accounts for approximately 50% of the lithium compound market, is generally produced from low-grade brines (Alekseyev and Alekseyeva, 2008). It is also used as a raw material for the production of lithium chloride, lithium hydroxide, lithium bromide, lithium nitrate, lithium sulfate, lithium niobate, and other lithium compounds. As the demand for high-performance batteries—particularly those using lithium hydroxide—increases, the demand for lithium carbonate is also rapidly rising (Vikström et al., 2013). While lithium carbonate prices are expected to decline to around $15,000 per ton of lithium carbonate equivalent (LCE) by the mid-2020s due to increased supply during 2022–2023, prices are forecasted to rise again and surpass $50,000 by around 2030 due to projected supply shortages (Baylis, 2013). Currently, South Korea imports 100% of both raw and intermediate lithium materials, resulting in unstable material supply. Although lithium hydroxide is directly imported for battery manufacturing, there is a growing need for domestic production and processing technologies for lithium carbonate (USGS, 2022).

In the production of lithium carbonate from low-grade brines, lithium is typically precipitated as a carbonate salt. High overall lithium recovery is largely dependent on the recovery efficiency of residual lithium remaining in the filtrate. Among common lithium precipitates, lithium phosphate ($Li_3PO_4$) has the lowest solubility product ($Ksp = 2.37 \times 10^{-9}$), making it a key target for reprocessing (Zhao et al., 2013). Therefore, recent technologies have focused on precipitating trace lithium from post-production wastewater as lithium phosphate and recovering it to enhance lithium utilization (Yunfeng Song et al., 2019).

Acid leaching is the most commonly employed method for lithium recovery from lithium phosphate. However, this process involves high energy consumption and extensive use of chemical solvents, leading to environmental concerns (Flexer et al., 2018). To address these issues, this study aims to minimize the use of acidic and alkaline reagents and reduce by-product and wastewater generation by adopting an acid–reductant combination extraction method. Various acid–reductant combinations were evaluated under different experimental conditions, including concentration, contact time, temperature, and reaction duration, in order to identify the most effective combination for leaching lithium from insoluble lithium phosphate ($Li_3PO_4$) (Yu et al., 2019).

In this study, hydrochloric acid (HCl), sulfuric acid ($H_2SO_4$), and nitric acid ($HNO_3$) were used as leaching agents, and hydrogen peroxide ($H_2O_2$), potassium permanganate ($KMnO_4$), and potassium persulfate ($K_2S_2O_8$) were employed as reductants. Lithium leaching efficiencies were compared based on different combinations of reagent concentrations and temperature conditions. A pre-test was conducted using hydrochloric acid, sulfuric acid, and nitric acid at concentrations of 0.5 M, 1 M, and 3 M. To assess the effect of temperature, experiments were performed at 25°C and 80°C, with a reaction time of 90 minutes, agitation at 200 rpm, a solution volume of 40 mL, and a solid dose of 0.5 g. The results indicated that there was minimal difference in leaching efficiency between the two temperatures. Based on these results, the main experiment was conducted under the same conditions, and the outcomes are presented in Figure 1.After the reaction, the slurry was filtered using a 0.45 µm PVDF membrane filter, and lithium concentration in the filtrate was analyzed by inductively coupled plasma–optical emission spectrometry (ICP-OES) to calculate leaching efficiency. The remaining solid residues were filtered using a 1.2 µm GF/C filter, washed with deionized water (DIW), and dried. The physical characteristics before and after leaching were subsequently examined to assess changes in material properties.

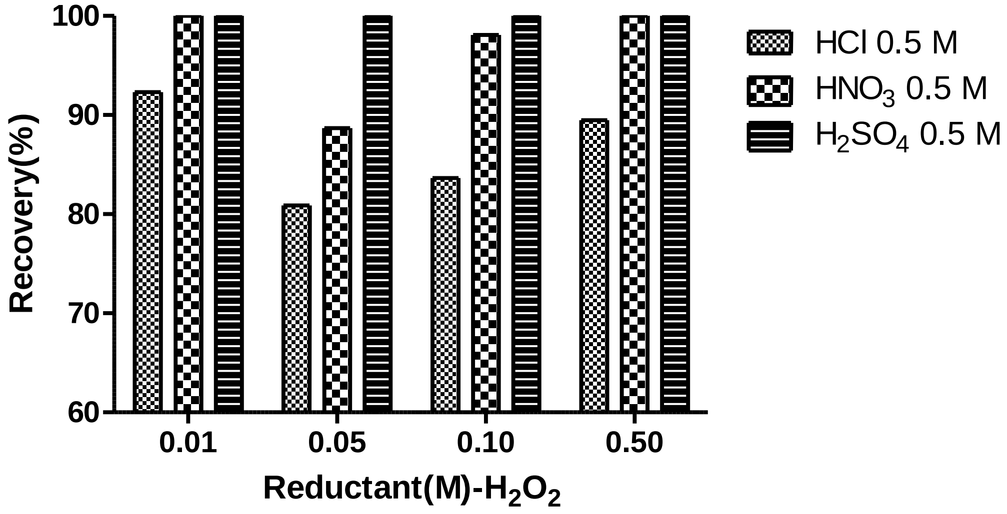

Figure 1. Comparison of leaching efficiency based on acid–reductant combinations (volume : 40 mL, dosage : 1 g, leachant conc. : 0.5 M , reductant conc. : 0.01, 0.05, 0.1, 0.5 M, temp. : 80°C)

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