# Early-stage lithium recovery: Comparative analysis of oxalic acid efficacy in recycling end-of-life NMC batteries from electric vehicles

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The hydrometallurgical recovery of metals, especially from lithium-ion batteries (LIBs), usually begins with leaching processes that bring valuable metals into solution for efficient extraction. These techniques are typically followed by separation processes such as precipitation, extraction, and stripping to isolate the individual metals. This paper introduces a method for selectively leaching lithium by oxalic acid. By comparing the leaching ratios of thermally-treated and untreated black mass, we determined optimal conditions: roasted material, a leaching duration of 0 minutes at 20°C, using 0.6M oxalic acid with a solid-to-liquid ratio of 100 g/L. Under these conditions, the lithium leaching efficiency was 81.08%, while the leaching efficiencies for Co, Mn, and Ni were 1.63%, 1.69%, and 5.98%, respectively. This paper presents a novel approach to the selective recovery of lithium from spent LIBs, advancing green acid methodologies and contributing to the progress of sustainable recycling technologies.

**Keywords:** selective leaching, oxalic acid, ESLR, NMC 622, black mass

## INTRODUCTION

Recycling processes are essential in managing end-of-life electric vehicle (EV) batteries, providing a method to recover valuable metals and reduce environmental impact. As the market share of electric vehicles continues to grow along with increasing environmental awareness, the demand for efficient recycling methods to manage battery waste becomes ever more crucial. Consequently, this has led to a surge in demand for lithium-ion batteries(LIBs) (International Energy Agency 2023). Within the EV battery market, nickel-manganese-cobalt (NMC) batteries have emerged as a leading choice due to their high energy density, electrochemical performance, and cost-performance ratio (Link, Neef & Wicke 2023). NMC batteries thus hold a significant share of the market, highlighting the importance of efficient and sustainable recycling methods to manage the growing volume of spent batteries and recover valuable materials (Davis & Demopoulos 2023). A typical battery comprises four key components: cathode active material, anode material, separator, and electrolyte. Among these, the cathode materials hold the highest recycling value and potential due to inclusion of critical metals. Current recycling methods are generally divided into three categories: pyrometallurgical, hydrometallurgical, and biometallurgical processes. Biometallurgy, while environmentally friendly with mild leaching conditions, is hindered by lengthy treatment times and challenges in bacterial cultivation (Zhuang *et al.*, 2015). Pyrometallurgy is noted for its simplicity and rapid processing with high metal recovery rates, but it is energy-intensive and produces harmful emissions (Makuza, Tian, Guo, Chattopadhyay & Yu 2021). Conversely, hydrometallurgy offers a straightforward, mild, and eco-friendly approach with a high recovery rate, making it the primary focus of both laboratory research and industrial applications (Davis & Demopoulos 2023). The widespread adoption of NMC batteries in modern EVs has underscored the importance of efficient recycling strategies to recover critical raw materials such as lithium (Maisel, Neef, Marscheider-Weidemann & Nissen 2023).

However, traditional late-stage lithium (LSL) recycling processes in hydrometallurgy often face challenges, including material losses and complexities in recovering valuable constituents from spent batteries (Gao *et al.*, 2023). LSL recycling confronts the additional obstacle of sodium-lithium separation during precipitation, leading to material losses and insufficient lithium purities at the end product. In contrast, early-stage lithium recovery presents a promising avenue for improving overall recycling efficiency by yielding a purer product with reduced losses (Bae & Kim 2021). One innovative approach within ESLR is the use of oxalic acid for selective lithium leaching (Li *et al.*, n.d.; Rouquette, Petranikova & Vieceli 2023; Gómez-Garrido, Mora Navarro, Murcia Navarro & Faz Cano 2018; Zeng, Li & Shen 2015). This method enhances lithium recovery while minimising the co-leaching of other metals. By optimising leaching conditions, it is possible to achieve high lithium extraction rates with minimal extraction of other valuable metals, thereby streamlining the recovery process and enhancing the overall sustainability of battery recycling efforts.

## BACKGROUND

Traditional hydrometallurgical processes for battery recycling typically involve the dissolution of the cathode active material in the black mass (after mechanical treatment) using sulfuric acid, augmented by reducing agents like hydrogen peroxide to enhance the dissolution of valuable metals such as cobalt, lithium, manganese, and nickel. Once these metals are brought into solution, they can be selectively recovered through methods such as solvent extraction, precipitation, and crystallisation. These steps are critical for isolating and purifying each metal for the resynthesis of new cathodes. However, the use of sulfuric acid in these processes poses environmental concerns. The chemical reactions involved might lead to the evolution of hydrogen sulfide ($H_2S$), which poses serious health risks and environmental hazards if not properly managed (Mohamed 2022). Organic acids have been explored as alternative leaching agents in the recycling of LIBs (Musariri, Akdogan, Dorfling & Bradshaw 2019; Golmohammadzadeh, Rashchi & Vahidi 2017; Li *et al.* 2013; Sun & Qiu 2012). In particular, acids like citric and oxalic acid are biodegradable and less toxic than traditional mineral acids (Sharma *et a*l., 1996). They have shown potential in effectively extracting valuable metals such as lithium, cobalt, and nickel from spent battery materials, supporting the development of more sustainable and safer recycling processes (Gómez-Garrido *et al.*, 2018; Joo *et al.*, 2016). Oxalic acid is widely recognised for its strong chelating effect, as numerous authors have reported (Gómez-Garrido *et al.*, 2018; Goel & Gautam 2010; Lee, Tran, Jung, Kim & Kim 2007). This compound forms stable complexes with various metal ions, making it an effective chelating agent in different applications. The metal oxides are dissolved at the beginning of the leaching reaction and then precipitate as a metal oxalate due to their low solubility as a solid. Based on the different solubilities of the metal oxalate species from the literature (Table ), mainly lithium oxalate is stable in aqueous solution. Due to the high solubility of 66 g/L, this is an ideal candidate for separating lithium from other metal oxalates. Cobalt oxalate, manganese oxalate and nickel oxalate have a very low to almost no solubility in aqueous media. Given our black mass composition, neither copper nor aluminum oxalate species were investigated.

*Table I. Solubility and $K_{sp}$ of Oxalate Compounds (Gestis Stoffdatenbank 2024; Sigma-Aldrich Chemie GmbH 2023; Haynes, Lide & Bruno 2013)*

| | Cobalt Oxalate ($CoC_2O_4$) | Lithium Oxalate ($Li_2C_2O_4$) | Manganese Oxalate ($MnC_2O_4$) | Nickel Oxalate ($NiC_2O_4$) |
|---|---|---|---|---|
| Solubility (20°C, g/L) | 0.037 | 66.0 | 0.032 | 0.012 |
| $K_{sp}$ | $6.639 \times 10^{-8}$ | 0.543 | $5.011 \times 10^{-8}$ | $5.308 \times 10^{-9}$ |

The experimental parameters were chosen based on previous publications on lithium leaching with oxalic acid from NMC Material (Verma, Johnson, Corbin & Shiflett 2020; Verma, Corbin & Shiflett 2021; Li, Fung, Xu, Wibowo & Ng 2019; Zhang *et al.*, 2018; Zeng *et al.*, 2015; Sun & Qiu 2012; Sohn, Shin, Yang, Kim & Lee 2006). The aim is to develop a robust, energy-efficient leaching system, which is why the temperature varied between room temperature 20°C and 60°C. The concentration of oxalic acid was selected to range from 0.1 to 0.6 mol/L, and the leaching time varied between 30 and 60 minutes. The S/L rate was fixed at 100 g/L due to potential economic efficiency. Furthermore, the influence on the leaching will be investigated; whether a thermal pretreatment step can improve the leaching efficiency.

## METHODOLOGY

### Material and Reagents

In this research, NMC 622 black mass was sourced from Duesenfeld GmbH, Germany. The black mass was provided with a residual moisture content, i.e., residues of electrolyte and lithium hexafluorophosphate conducting salt. For the removal of heavy boiling point electrolytes, the black mass was treated by the two options mentioned. The reagent used in this study - oxalic acid dihydrate - was analytical grade and purchased from Carl Roth (Karlsruhe, Germany).

### Methods

In this paper the two black masses with different treatments were used. The thermally untreated black mass was dried at 110°C to remove all low boiling electrolytes. The thermally treated black mass was subjected to controlled heat treatment under atmospheric conditions to remove residual organic compounds and possibly the binder to facilitate the recovery of valuable metals. Black mass was placed in a Nabertherm muffle furnace at ambient temperature and gradually increased the heat at a rate of 200°C per hour. Upon reaching 450°C, the temperature was maintained for 90 minutes to ensure thorough decomposition. Following this, the treated material was allowed to cool down to 80°C within the closed oven to prevent rehydration by residual moisture, which could potentially react with the NMC material. To further reduce contamination risks, particularly from residual cathode and anode foil particles, the cooled material was then sieved to yield a fraction smaller than 100 µm. This sieving step is crucial for removing larger contaminant particles and preparing the black mass for the subsequent hydrometallurgical processing.

The leaching experiments were conducted using a conventional glass beaker placed on a heating plate magnetic stirrer (Hei-Tec, Heidolph Instruments, Schwabach, Germany). The temperature of the solution was controlled using an external PT100 temperature sensor connected to the heating plate. 200 mL of the desired organic acid solution was added to the beaker, and the system was heated to the target temperature. Different experimental conditions were investigated such as a concentration of oxalic acid (0.1M and 0.6M), temperature (20°C and 60°C), and leaching durations of either 30 or 60 minutes at a fixed solid to liquid ratio of 100 g/L. Once the desired temperature was reached, the black mass was gradually added to the beaker under continuous stirring at 600 rpm. After and while leaching, samples for analysis were collected with an Eppendorf pipette and were filtered with a syringe filter (Berrytec, cellulose acetate, 0.45 µm particle size retention) and rinsed to 20 mL in volumetric flasks and acidified with 1% $HNO_3$ to avoid changes in pH and associated precipitation.

Leaching efficiency, η (%) was calculated for each element according to the following equation:

$$\eta\ (\%) = \frac{C_i \times V_L}{x_i \times m_{MB}} \times 100\ \%$$

where $C_i$ is the concentration of element i in leach solution of sample (in g/l); $V_L$ is the total volume of the leach solution (in L); $x_i$ is the concentration of the element i in the black mass sample (in wt %); $m_{BM}$ is the weight of the input material (in g).

### Characterisation

The chemical composition of the liquid samples obtained during the laboratory experiments, as well as the starting and final solid samples, were analysed by ICP-OES using an ICP 5100 from Agilent Technologies, USA. One acid digestion was made of each solid sample, 100 mg weighed out and 2.5 mL of $H_2SO_4$, 2 mL of $HNO_3$ and 2 mL demineralised water added to each. The digestion is carried out in PTFE (polytetrafluoroethylene) reaction vessels in a TurboWave digestion autoclave from MLS

Mikrowellen-Labor-Systeme GmbH, Germany. With an upstream pressure of 40 bar argon, the temperature is heated to 250°C and maintained for 45 minutes. After cooling, the digestion solutions are transferred to 50 mL volumetric flasks and filtered off before measurement. From the resulting solutions of the acid digestion and the liquid samples from the leaching experiments, different dilutions with a 0.5% $HNO_3$ as matrix are prepared and measured with Agilent's ICP-OES 5100. The calibration covers a measuring range from 0.05 mg/L to 10 mg/L; the calibration solutions are also prepared with 0.5 % $HNO_3$. Different wavelengths are measured for each element, and these are compared with each other.

X-ray diffraction (XRD) was employed to determine the main phases present in the leaching residues. This technique involves directing monochromatised Cu Kα radiation at the sample and analysing the resulting diffraction patterns to identify crystalline structures. For this purpose, a Bruker D4 Endeavor diffractometer equipped with a one-dimensional LYNXEYE detector (Bruker Corporation, Billerica, MA, USA) was utilised.

## RESULTS AND DISCUSSION

### Characterisation of the material

Two samples of identical NMC black mass were used in this study, one thermally treated and one untreated. It was investigated whether a thermal treatment of the black mass in a moderate temperature improves the leaching efficiency. The composition of the individual elements of the NMC black mass is presented in Table II. The elemental analysis of the two black mass samples, NMC 622 unroasted and NMC 622 roasted reveals distinct differences in their chemical compositions. In comparison to the unroasted NMC 622 black mass, the roasted NMC 622 black mass exhibits higher concentrations of aluminum (Al), cobalt (Co), lithium (Li), manganese (Mn), and nickel (Ni). This increase in elemental concentrations can be attributed to the thermal treatment process, which leads to loss of graphite and the removal of high boiling point electrolytes such as propylene carbonate and ethylene carbonate, as well as residues of the conducting salt lithium hexafluorophosphate ($LiPF_6$). The graphite is reported to act as a reductant in the roasting process under atmospheric conditions to break the $LiNi_xCo_yMn_zO_2$ active material into different compositions such as $Li_2CO_3$, $LiCoO_2$, $LiNiO_2$ and MnO (Mousa *et al.*, 2022; Liu et al. 2019).

*Table II. NMC black mass composition*

| | Al (%) | Co (%) | Cu (%) | Li (%) | Mn (%) | Ni (%) |
|---|---|---|---|---|---|---|
| NMC 622 untreated | 1.28 | 3.61 | 0.53 | 3.22 | 4.56 | 17.64 |
| NMC 622 roasted | 2.08 | 5.10 | 0.67 | 4.4 | 6.78 | 24.11 |

This results in an initial elemental composition of $LiCo_{0.13}Mn_{0.2}Ni_{0.65}O_2$, while the variation of the initial NMC622 is likely to be attributed to losses in the preceding mechanical processes.

### Leaching experiments

Introducing oxalic acid leaching offers a strategic pathway to enhance the selective recovery of lithium from the commercial black mass samples. The experiments involved comparing unroasted and roasted samples for their leaching efficiencies of aluminum (Al), cobalt (Co), copper (Cu), lithium (Li), manganese (Mn), and nickel (Ni).

The leaching results are displayed in Table *III*III. Three experimental parameters were investigated, each both with roasted (R) and unroasted (U) materials, resulting in the experiments named GU1, GR1, GU2, GR2, GU3 and GR3 – varying in terms of oxalic acid concentration (0.1M vs 0.6M), leaching. Comparing the results, displayed in the experiments GU1 (unroasted) and GR1 (roasted), there are notable differences in leaching efficiencies across various metals under identical conditions of oxalic acid concentration (0.1M), temperature (20°C), and time (30 minutes). It can be observed that roasting significantly increased the leaching efficiency of Li from 29.70% in the unroasted sample to 41.33% in the roasted sample while maintaining similar experimental conditions. Similar trends can be observed for the Al (7.64% unroasted, 12.68% roasted), Co (0.17% unroasted, 2.58% roasted), Mn (2.43% unroasted, 3.5% roasted) and Ni (0.26% unroasted, 1.23% roasted). However, the copper leaching efficiency decreased significantly from 28.19% in the unroasted sample to 6.68% in the roasted sample. This decrease is likely due to the conversion of elemental copper from the anode foils to copper oxide during the roasting process, which might be less amenable to leaching at the low oxalic acid concentration of 0.1M. In the leaching experiments designated as GU2 (unroasted) and GR2 (roasted), conducted under conditions of 0.6M oxalic acid concentration, 20°C temperature, and 60 minutes duration, a noticeable difference is observed in the leaching rates of various metals. For aluminum, the leaching rate substantially increases from 12.50% in the unroasted sample to 26.77% in the roasted sample, indicating that roasting and increased acid concentrations significantly enhance aluminum's susceptibility to leaching by modifying its physical and chemical properties. Cobalt also shows an increase, albeit smaller due to the solubility limit, from 0.20% to 1.63%, suggesting a similar enhancement in reactivity post-roasting. The most dramatic transformation is seen in copper, which has a low leaching rate in its unroasted state but leaps to 17.54% when roasted. Conversely, manganese is an exception where roasting slightly reduces its leaching rate from 2.04% to 1.69%, suggesting that the roasting process might generate forms of manganese less amenable to leaching, such as manganese (II) oxide (MnO), which can form when roasting at 450°C with a carbon (graphite) source as a reductant under these conditions. Lithium and nickel show significant improvements in their leaching efficiencies due to roasting. Lithium leaching rate jumps from 55.26% to 81.08%, and nickel from 0.13% to 5.98%, underscoring the effectiveness of roasting in enhancing their chemical reactivity and solubility in the leaching solution. In GU3 and GR3, roasting clearly influences the leaching efficiencies of the metals investigated, though the changes vary by metal. For aluminum, leaching efficiency rises from 14.33% in the unroasted sample to 22.85% in the roasted one, indicating a positive impact of roasting on aluminum's reactivity. Cobalt's efficiency slightly decreases from 2.77% to 1.76% with roasting. Nickel shows an improvement, increasing from 6.23% to 8.81%. Manganese decreases from 2.18% in the unroasted sample to 0.68% in the roasted sample. Lastly, lithium and copper increased in leaching efficiencies with lithium rising from 80.42% to 84.63%, and copper significantly from 4.64% to 25.77%. These increases suggest that roasting breaks down the NMC matrices into different oxide species enclosing these metals, enhancing their dissolution during leaching.

*Table III. Results of the leaching experiments*

| Exp. Name | Treatment | Al (%) | Co (%) | Cu (%) | Li (%) | Mn (%) | Ni (%) | Temp (°C) | Time (min) | Oxalic Acid Conc. (Mol/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| GU1 | Unroasted | 7.64 | 0.17 | 28.19 | 29.70 | 2.43 | 0.26 | 20 | 30 | 0.1 |
| GR1 | Roasted | 12.86 | 2.58 | 6.68 | 41.33 | 3.51 | 1.23 | 20 | 30 | 0.1 |
| GU2 | Unroasted | 12.50 | 0.20 | 0.00 | 55.26 | 2.04 | 0.13 | 20 | 60 | 0.6 |
| GR2 | Roasted | 26.77 | 1.63 | 17.54 | 81.08 | 1.69 | 5.98 | 20 | 60 | 0.6 |
| GU3 | Unroasted | 14.33 | 2.77 | 4.64 | 80.42 | 2.18 | 6.23 | 60 | 60 | 0.6 |
| GR3 | Roasted | 22.85 | 1.76 | 25.77 | 84.63 | 0.68 | 8.81 | 60 | 60 | 0.6 |

In the course of our experiments, changes were observed in the residue post-leaching. Specifically, there was an increase in the weight of the residue, accompanied by a color change from dark black to dark grey. These observations suggest a transformation in the material composition, likely due to the conversion of nickel-manganese-cobalt (NMC) material into single oxalate species with low solubilities. Specifically, the transition metal ions present in the black mass, such as cobalt and nickel, form mostly insoluble metal oxalate complexes upon reaction with oxalic acid. Only lithium oxalate has a higher solubility of 66 g/L. Further analytical support for this hypothesis is provided by XRD, Figure 1, of the residue from experiment GR3, which shows the obvious presence of nickel oxalate. These results indicate that the leaching process may selectively dissolve nickel and leads to a crystalline precipitation of nickel oxalate hydrate. The discovery that only nickel oxalate hydrate forms crystalline precipitates while leaching, while cobalt and manganese likely form amorphous precipitates, suggests distinct behaviors of these metals in response to oxalic acid leaching that need further investigation. In the leaching experiments, the comparison between roasted and unroasted materials shows a clear trend: roasting generally enhances the leaching efficiency of metals. During the roasting process the graphite in the black mass is suspected to act as a reductant for Co, Mn and Ni, favouring the leaching. In the context of the NMC 622 compound ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$), the oxidation states of the elements are reported to be as follows: lithium (Li) is in the +1 oxidation state, nickel (Ni) exists in a mixed valence state averaging around +2.5, manganese (Mn) is in the +4 state, and cobalt (Co) is in the +3 state, with oxygen (O) in the -2 state (White, Gittleson, Homer & El Gabaly 2020; Jung *et a*l., 2019). During the roasting process, the carbon present in the black mass likely plays a significant role in reducing these elements. Specifically, the carbon acts as a reductant, facilitating the reduction of nickel from its +3 to +2 oxidation state, cobalt from +3 to +2, and manganese from +4 to +2. This reduction process during roasting is crucial as it enhances the reactivity and solubility of these metals during the leaching process, thereby improving the overall efficiency of metal recovery. In conventional leaching, this reduction is achieved using a reductant such as hydrogen peroxide ($H_2O_2$). Oxalic acid can also act as a reductant in the leaching process, being oxidised to carbon dioxide ($CO_2$).

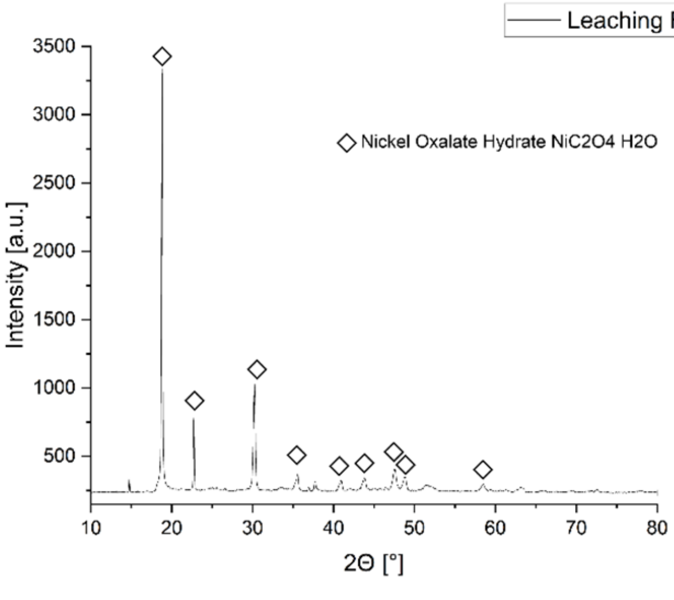

*Figure 1. XRD pattern of leached NMC black mass.*

The leaching experiments focused on extracting lithium from black mass underscored several insights regarding the influence of roasting, acid concentration, leaching time and temperature on the process efficiency. Among various tested conditions, roasting the material combined with a 0.6M concentration of oxalic acid at 20°C for 60 minutes demonstrated notable effectiveness in leaching lithium. While this set of conditions did not achieve the absolute highest efficiency observed in the experiments—falling short by only a slight margin of 3.55% compared to the most efficient condition—it stands out as significantly advantageous. The low operational temperature of 20°C is highly desirable due to its lower energy requirements in the leaching process, which can lead to savings in energy costs and a reduced environmental impact. However, it is important to note that the roasting process itself does contribute to the overall carbon footprint, as it involves significant energy consumption and the release of carbon emissions. Roasting at 450°C requires substantial energy input, which not only increases operational costs but also results in higher $CO_2$ emissions, thereby impacting the environmental sustainability of the process. Despite the benefits of a low-temperature leaching process, it is essential to weigh these against the environmental footprint associated with roasting. While the roasting process enhances the leaching efficiency of lithium, it also introduces additional carbon emissions and energy consumption. Therefore, one must carefully evaluate whether the increased lithium recovery justifies the higher energy requirements and associated $CO_2$ emissions from roasting. In conclusion, prioritising a lower temperature process such as the one achieved at 20°C with roasted material in a 0.6M oxalic acid solution for 60 minutes presents a practical balance between efficiency and operational sustainability. This approach ensures an effective lithium recovery while adhering to energy efficiency and environmental sustainability goals, making it an optimal choice despite the slight difference in maximum achievable efficiency.

## CONCLUSION

In conclusion, the research presented in this paper clearly demonstrates the effectiveness of roasting as a pre-treatment method to enhance the leaching efficiency of lithium, particularly when derived from secondary materials such as recycled batteries. Our experiments indicate that roasting, with leaching under low-temperature conditions significantly improves lithium recovery rates, highlighting a potential reduction in both energy consumption and environmental impact compared to higher temperature processes. The increase in leaching efficiencies observed at 20°C with roasted samples compared to unroasted ones underscores the potential of roasting. This method not only supports the extraction of lithium more efficiently but also aligns with the commercial objectives of cost reduction and environmental sustainability. However, the impact of roasting, including its carbon footprint and associated emissions, needs to be carefully considered to ensure a truly green process.

Optimising low-temperature roasting processes for lithium recovery from secondary sources offers numerous benefits, including lower operational costs, reduced energy requirements, and minimised environmental degradation. These improvements are crucial for scaling up production processes and enhancing the economic viability of lithium recycling operations. In future work, we plan to investigate the potential of counter-current leaching operations to improve the efficiency of the lithium extraction process from black mass. Counter-current leaching, which involves the movement of the solid and liquid phases in opposite directions, can enhance the efficiency of the extraction process by maximising the concentration gradient throughout the leaching operation. This method is expected to optimise the contact time and solution concentrations, potentially leading to higher lithium yields and more efficient use of reagents. By implementing and refining this technique in the near future, we aim to advance the operational efficacy and sustainability of the leaching process in lithium recovery.

Future investigations should focus on refining low-temperature techniques, exploring their limits and potential optimisations to further enhance lithium recovery while maintaining potential commercial feasibility. Moreover, it is essential to consider several other factors to ensure a comprehensive approach to optimising the process. Tracking the consumption of oxalic acid during the leaching process could provide useful insights into its effectiveness as a reductant and help optimise its usage. The carbon footprint associated with the roasting process should be carefully evaluated, as roasting enhances leaching efficiency but also generates $CO_2$ emissions. Monitoring and managing gaseous emissions during the roasting process is crucial to minimise environmental impact and comply with regulatory standards. Understanding the speciation and behaviour of different fractions of each element during roasting and leaching can provide deeper insights into the mechanisms at play and help refine the process for better efficiency. The adoption of these technologies has the potential to transform the battery recycling industry and make substantial contributions to sustainable resource management practices. By continuously improving and optimising these techniques, we aim to enhance the operational efficiency and environmental sustainability of the lithium recovery process.

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