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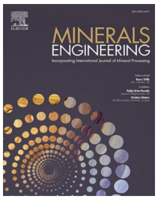

Investigating battery black mass leaching performance as a function of process parameters by combining leaching experiments and regression modeling

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ABSTRACT

The current paper investigates the leaching phenomena of industrially produced Li-ion battery waste in hydrometallurgical recycling processes. Specifically, it studies the leaching reactions of NMC111-type ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) black mass, as well as the statistical behavior of cathode material leaching yields under varying process conditions. The investigated process variables include reductive agent concentrations (Fe^{2+}, Cu, H_2O_2) as well as process temperature, whereas S/L ratio (200 g/L) and initial acidity (2 M H_2SO_4) were kept constant. At lower temperatures ($T = 30$ °C), copper was found to act as the predominant reductant, enabled by the presence of sufficient solution iron concentrations (≥0.4 g/L Fe). Conversely, at higher temperatures ($T \geq 50$ °C), the reductive capability of aluminum was substantially increased due to its decreased tendency for passivation. In contrast to copper, dissolved iron did not notably affect the reductive behavior of aluminum. The efficiency of metallic reductants initially present within the black mass was high, reaching cathode metal leaching yields above 90 % at 70 °C. A predictive leaching model for black mass leaching yields was built via regression analysis and can be used to indicate pregnant leach solution (PLS) composition – via leaching yields – after two hours of processing as a function of the investigated process variables. The model showed leaching temperature to be the most impactful parameter, while also indicating a higher reductive efficiency of copper when compared to equimolar additions of H_2O_2. As a case example, LFP ($LiFePO_4$) cathode powder was also investigated as an alternative reductant/catalysis species (Fe^{2+}) source in the system and was found to increase cathode metal leaching yields almost as much as $FeSO_4$ while also resulting in a remarkable increase in Al dissolution in the process.

1. Introduction

As countries all over the world are implementing more green technologies to phase out fossil fuels to achieve carbon neutrality, the requirement for energy storage applications is continuously increasing. For example, the estimated total number of electric vehicles (EV) globally grew threefold between 2018 and 2021 (IEA, 2023). Furthermore, the transition towards renewable energy sources also requires higher levels of energy storage capacity – like large-scale battery energy storage systems – to account for weather-related fluctuations, especially in the case of wind and solar power (Yuan et al., 2022; Kojima et al., 2023). After serving for their intended duration, batteries will eventually reach their End-of-Life (EoL) and must be recycled to bring their valuable contents back into circulation. Currently, most EoL batteries are recycled either via pyro-hydrometallurgical or hydrometallurgical methods (Shi et al., 2023). Smelting processes like the Umicore process can, in some cases, handle entire battery units, whereas hydrometallurgical processes always require the battery unit to be discharged, dismantled, crushed, and sieved to separate the cathode active material-rich fractions for recovery (Dobó et al., 2023). In addition, the use of efficient separation methods also allows for the majority of casing and current collector materials to be directed to their respective recycling processes. In addition to smelting, also recycling methods combining roasting and leaching have recently gained increasing interest (Pan and Shen, 2023).

Hydrometallurgical recycling typically starts with acid leaching of the underflow fraction of crushed and sieved battery waste rich in cathode materials and graphite – also known as black mass, the

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composition of which can greatly vary depending on the mechanical treatment the material has undergone (Wilke et al., 2023). In the leaching step, layered oxide-type cathode materials – such as $LiCoO_2$ (LCO) and $LiNi_xMn_yCo_zO_2$ (NMC) – partially react with hydrogen ions (H^+), to produce water and oxygen gas (Eq. (1), Nan et al., 2005). This dissolution reaction has previously been suggested to be enabled by water oxidation acting as the anodic reaction, albeit without experimental confirmation (Cerrillo-Gonzalez et al., 2022). Nonetheless, this reaction does not proceed to completion as total dissolution typically requires the use of an external reductant to transform the remaining cathode metal oxides to a soluble form.

$$4LiCoO_{2(s)} + 6H_2SO_{4(aq)} \rightarrow 2Li_2SO_{4(aq)} + 4CoSO_{4(aq)} + 6H_2O_{(l)} + O_{2(g)} \quad (1)$$

Considerable research in recent years has focused on hydrometallurgical recycling of lithium-ion batteries (LIBs), especially on various reductants that can be used to improve the leaching efficiency of cathode metal oxides like LCO and NMC (Castro et al., 2022). Of the various additives tested, the most common reductant used in black mass leaching has been hydrogen peroxide (Harper et al., 2019) as this decomposes into water and oxygen gas when it reacts with NMC-type cathode materials and has the added benefit of no impurity ions being introduced into the solution (Eq. (2).

$$6LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2(s)} + 18H^+_{(aq)} + 3H_2O_{2(aq)} \rightarrow 6Li^+_{(aq)} + 2Ni^{2+}_{(aq)} + 2Mn^{2+}_{(aq)} + 2Co^{2+}_{(aq)} + 12H_2O_{(l)} + 3O_{2(g)} \quad (2)$$

Nevertheless, in addition to its reductive properties, hydrogen peroxide is also a powerful oxidant. Consequently, it has been found to have negative effects during cathode material leaching in the presence of metallic Cu, Al, and Fe (Chernyaev et al., 2022) by preventing these elements, typically found within industrial black masses, from also acting as reductants toward battery cathode materials. Peroxide can oxidize Cu, Al, and Fe, resulting in overconsumption of both peroxide and the reductant metals, leading to a decrease in their collective reductive power. Furthermore, the anthraquinone process – commonly used in the production of hydrogen peroxide – requires high amounts of energy and generates toxic byproducts (Che et al., 2022). These shortcomings have motivated research toward finding alternative reductants for waste battery leaching. As mentioned above, metals typically associated with black mass can act as reductants, and promising results have been obtained using metallic Cu and Al fragments originating from battery current collector foils – either contained within the black mass in question or added as a separate feed composed of production scrap (Joulié et al., 2017; Chernyaev et al., 2021a). Nonetheless, previous studies (Peng et al., 2019; Porvali et al., 2020) have suggested that both Cu and Al require a catalyst, for example, aqueous species of iron or another suitable element, to enable efficient electron transfer with cathode metal oxides (Eqs. (3) and (4). *N.B.,* although Eqs. (3) and (4) are presented here for the leaching reaction of LCO, NMC-type cathode materials exhibit a similar oxidation–reduction behavior and reductant requirement (Lv et al., 2018).

$$2LiCoO_{2(s)} + Cu_{(s)} + 8H^+{}_{(aq)} \xrightarrow{Fe(II)/Fe(III)} 2Li^+{}_{(aq)} + 2Co^{2+}{}_{(aq)} + 4H_2O_{(l)} + Cu^{2+}{}_{(aq)} \quad (3)$$

$$3LiCoO_{2(s)} + Al_{(s)} + 12H^+{}_{(aq)} \xrightarrow{Fe(II)/Fe(III)} 3Li^+{}_{(aq)} + 3Co^{2+}{}_{(aq)} + 6H_2O_{(l)} + Al^{3+}{}_{(aq)} \quad (4)$$

In addition to acting as a reductant when in the presence of a suitable catalyst, aluminum has also been hypothesized as being able to act via another route due to H_2 gas formation (Eq. (5), which could also potentially reduce cathode materials and aid their dissolution (Joulié et al., 2017).

$$2Al_{(s)} + 6H^+{}_{(aq)} \rightarrow 2Al^{3+}{}_{(aq)} + 3H_{2(g)} \quad (5)$$

However, hydrogen gas is generally not a very reactive molecule under typical leaching conditions due to its high bond strength (Baade et al., 2001). This passivity has been demonstrated by the experiments of Huang et al. (2022) who found that direct hydrogen reduction of an NMC-type cathode material requires a temperature above 500 °C. Moreover, efficient hydrogen reduction of metals in solution normally requires aggressive conditions – in industrial hydrogen reduction processes, the temperature and pressure can be up to 180 °C and 30 bar (Crundwell et al., 2011). Therefore, reactions of H_2 with other components present in a leaching system can be considered unlikely, and any hydrogen gas formed during leaching is predominantly lost into the ambient atmosphere along with potential reductive power.

This research attempts to provide a deeper understanding on the topic of utilizing reductants found within real, industrially produced black masses by means of experimental work and regression modeling. Specifically, this study focuses on the impacts that temperature and solution iron concentration have on the reductive efficiency of Cu and Al and aims to ascertain the effects of these parameters on black mass leaching efficiency with regression modeling. The target is to build a robust model able to predict target metal leaching yields in order to support future process development, lab-scale test planning, and feed composition optimization – with varying transition metal and impurity concentrations – with respect to process conditions.

2. Materials and methods

The following chemicals were used throughout the experiments: H_2SO_4 (95–97 %, Merck, Germany), HNO_3 (65 %, VWR Chemicals, Belgium) $FeSO_4 \cdot 7H_2O$ (≥99.0 %, Sigma-Aldrich, USA), H_2O_2 (50 %, Sigma-Aldrich, USA) $LiFePO_4$ powder (MSE Chemicals, USA) and HCl (37 %, VWR Chemicals, Belgium). All solutions were prepared using deionized water (15 MΩ·cm, Merck Elix Essential 15, Germany). Certain experiments also used metallic Cu reclaimed from EoL EV batteries, supplied by KYBURZ Switzerland AG. For experiments using this material, the reclaimed copper was shredded to 1 mm flakes using a cutting mill (Retsch SM 300, Germany). The chemical analysis of the shredded Cu can be found in the Supplementary material (Table S1).

Black mass (mainly composed of NMC111-type battery waste) was obtained as a crushed and sieved fraction (<1 mm) from the Industrial Materials Recycling group at Chalmers University of Technology, Sweden, and originates from batteries provided by Volvo Cars AB, Sweden. The black mass pre-treatment process entailed dismantling and mechanical treatment including two-stage crushing, sieving, and magnetic separation as described in Pudas et al. (2015) and Vieceli et al. (2023). No further pre-treatment was carried out on the material. To determine the elemental composition of the black mass, total dissolution was carried out on four samples – 5.0 g each – of the bulk material. Samples were taken from the bulk and digested in 200 mL of concentrated aqua regia solution (156 mL 37 % HCl, 44 mL 65 % HNO_3) under a boiling temperature for 60 min, and the resulting solution elemental concentrations were analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5900 SVDV, USA) with average concentration and standard deviation of each element calculated based on the analysis (Table 1). The high standard deviation relative to the

Table 1
Average concentrations and standard deviation values (g/100 g) of studied elements in black mass.

Element	Li	Co	Ni	Mn	Cu	Al	Fe
Average	3.3	10	8.8	7.9	7.5	3.5	0.1
Standard deviation	0.08	0.55	0.36	0.21	1.35	0.18	0.02

average, especially for Cu and Fe, highlight the inhomogeneous nature of the raw material.

All leaching experiments were conducted in a 1 L jacketed glass reactor, heated with a circulating thermostatic water bath (Haake C1, Germany). Each experiment used 500 mL of 2 M H_2SO_4 solution and 100 g of black mass, amounting to a S/L ratio of 200 g/L – a value relevant in the context of industrial leaching processes. Cu, $LiFePO_4$ (LFP) powder, and $FeSO_4$ – where applicable – were added along with black mass at the start of each experiment. In experiments using H_2O_2, the peroxide amount was steadily added throughout the first hour of leaching to avoid excessive foaming caused by gas evolution and reduce the risk of reactor overflow. All experiments used 300 RPM agitation with an overhead stirrer (VOS 16, VWR, USA) with a 45° angled four-blade PTFE (polytetrafluoroethylene) impeller that was 5 cm in diameter.

The total leaching time was 2 h, and sampling was performed at intervals of 5, 15, 30, 45, 60, 90, 120 min from the start of experiments by extracting a solution sample from the reactor with a hose attached to a syringe. Individual samples were subsequently processed by percolation through a filter paper (Grade 41, Whatman, UK); filtration with syringe filters was also tested but proved unsuccessful due to membrane clogging caused by the presence of solid particles. Resultant solution samples were diluted with 2 % HNO_3 and analyzed for dissolved metal concentrations with ICP-OES. At the end of each experiment, the final solid/liquid separation for the pregnant leach solution (PLS) was undertaken via vacuum filtration with Whatman grade 50 filter papers to measure the final solution volume.

In addition to the separate effects attributable to the different experimental factors tested, the combined impacts of various reductant additions and temperatures were investigated with a Design of Experiments (DoE) approach to create a predictive leaching model. The test series utilized a two-level full factorial design with three center point experiments and four variables: solution iron concentration (adjusted with $FeSO_4 \cdot 7H_2O$ additions), Cu addition, H_2O_2 addition, and temperature (Table 2). The reductant amount columns (g, mL) in Table 2 refer to chemical amounts added to 500 mL of leaching solution, whereas the columns labeled "reductant/TM" refer to the ratio of available reductant present in the leaching system; added chemical amount + amount originally present within the black mass vs. molar amount of transition metals (TM) in the system. For example, 100 g of black mass contains 0.1 g of Fe and 7.5 g of Cu, both of which can also provide reductive power toward cathode materials (Porvali et al., 2020). Monitored responses for inclusion in the model included the leaching yields of Co, Ni, Mn, and Li after 2 h of leaching. These experimental results were subsequently used to create a regression model using MODDE 13 software (Sartorius, Germany).

3. Results and discussion

3.1. Effect of temperature

To investigate the effect of temperature on black mass leaching performance, leaching experiments were conducted without added reductants at temperatures of 30, 50, and 70 °C (Fig. 1). The reaction temperature was found to remarkably affect the leaching yields of all metals of interest. Lithium leaching efficiency rose steadily with increases in temperature, reaching approximate yields of 70 % at 30 °C, 80 % at 50 °C, and > 90 % at 70 °C. The leaching yields of Ni, Co, and Mn all followed a similar trend as the reaction temperature was increased – the final metal yields were 50 % at 30 °C, 70 % at 50 °C, and > 90 % at 70 °C. Based on these results, 70 °C would seem to be the optimal leaching temperature, however, the maintenance of such a relatively high temperature in an industrial leaching process could lead to an increased energy consumption that could negatively impact the economic and environmental aspects of the process.

The almost complete dissolution (>90 %) of Li, Co, Ni, and Mn achieved by leaching at 70 °C (Fig. 1c) can be ascribed to the black mass Cu and Al contents (7.5 % Cu, 3.5 % Al; Table 1). In fully discharged cathode material, the transition metals in NMC111 are predominantly in the oxidation states of Co^{3+}, Ni^{2+}, Mn^{4+} (Shaju et al., 2002), and therefore, Co and Mn must be reduced to the + 2-oxidation state to enable dissolution. This reduction is achieved by simultaneous oxidation and dissolution of the current collector metals Cu and Al (Eqs. (3) and (4). Calculation based on the raw material composition (Eqs. S1–S3, Supplementary material) shows the total amount of electrons required for complete dissolution of Co and Mn to be 0.46 mol per 100 g black mass (1 e^- per Co, 2 e^- per Mn), whereas the amount of available electrons from reductant metals is 0.63 mol/100 g (2 e^- per Cu, 3 e^- per Al), *i. e.*, the black mass components contain almost a 40 % surplus of electrons compared to the requirement for complete cathode material dissolution.

This calculation supports the observed result that the current collector metal concentrations in the raw material investigated are sufficiently high to allow for high leaching yields of cathode metal oxides to be achieved over the course of the chosen reaction time. Therefore, the main factor limiting cathode metal dissolution appears to be related to reaction kinetics rather than the potential number of electrons available

Table 2
Design of Experiments (DoE) used as a basis for the regression model. Reductant amounts are shown both as added amounts and total molar amounts (raw material + addition) divided by the total molar amount of reducible transition metals (TM; Ni, Co, Mn) in 100 g of black mass.

Exp. Code	Target Fe conc. (g/L)	Added $FeSO_4 \cdot 7H_2O$ (g)	Fe/TM (mol/mol)	Added Cu (g)	Cu/TM(mol/mol)	Added H_2O_2 (mL)	H_2O_2 /TM (mol/mol)	*T* (°C)
A1	0.2	0	0.004	0	0.25	0	0	30
A2	0.4	0.5	0.008	0	0.25	0	0	30
A3	0.2	0	0.004	7.5	0.51	0	0	30
A4	0.4	0.5	0.008	7.5	0.51	0	0	30
A5	0.2	0	0.004	0	0.25	6.7	0.25	30
A6	0.4	0.5	0.008	0	0.25	6.7	0.25	30
A7	0.2	0	0.004	7.5	0.51	6.7	0.25	30
A8	0.4	0.5	0.008	7.5	0.51	6.7	0.25	30
A9	0.2	0	0.004	0	0.25	0	0	50
A10	0.4	0.5	0.008	0	0.25	0	0	50
A11	0.2	0	0.004	7.5	0.51	0	0	50
A12	0.4	0.5	0.008	7.5	0.51	0	0	50
A13	0.2	0	0.004	0	0.25	6.7	0.25	50
A14	0.4	0.5	0.008	0	0.25	6.7	0.25	50
A15	0.2	0	0.004	7.5	0.51	6.7	0.25	50
A16	0.4	0.5	0.008	7.5	0.51	6.7	0.25	50
A17	0.3	0.25	0.006	3.75	0.38	3.35	0.13	40
A18	0.3	0.25	0.006	3.75	0.38	3.35	0.13	40
A19	0.3	0.25	0.006	3.75	0.38	3.35	0.13	40

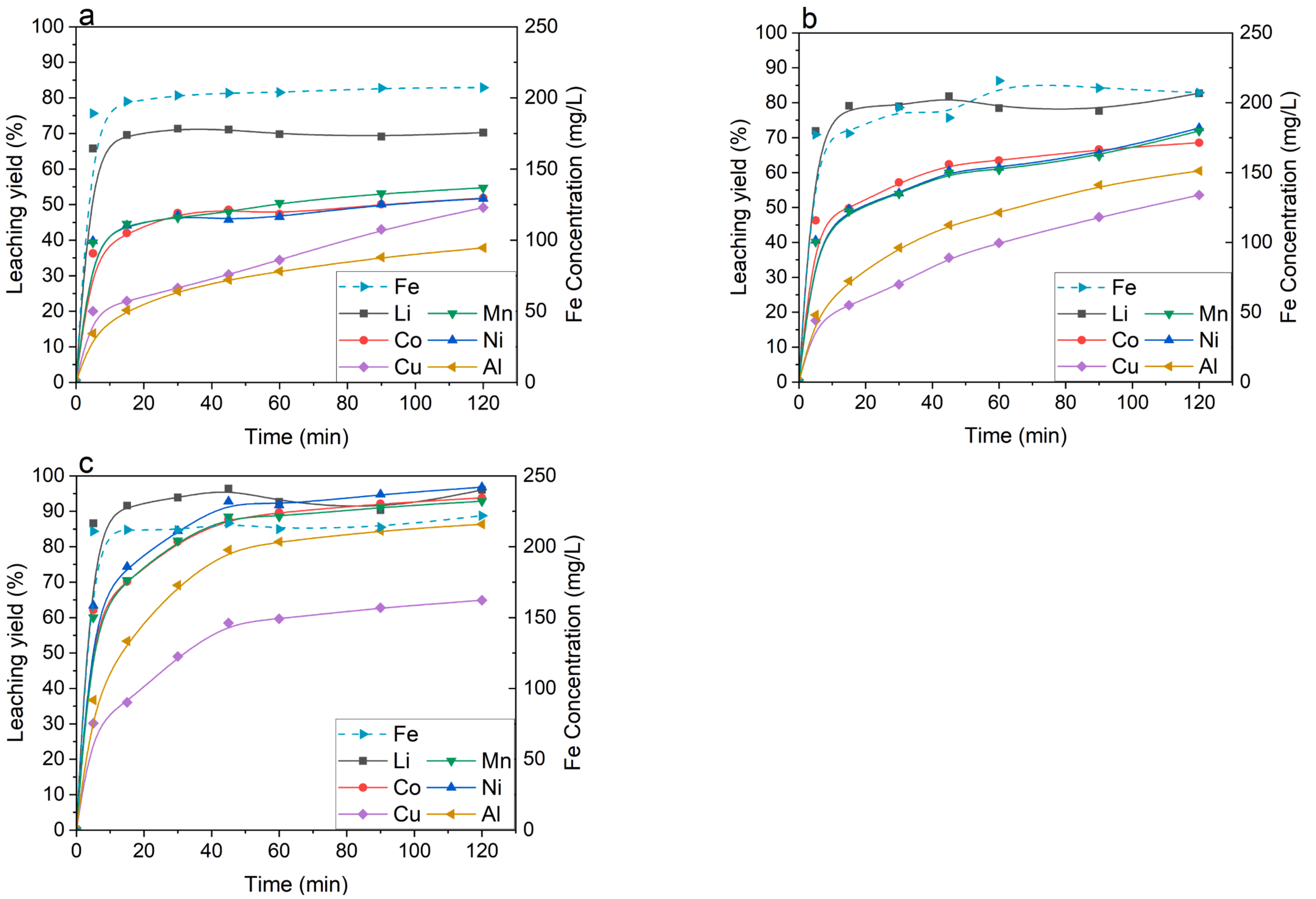

Fig. 1. Leaching results under the temperatures of a) 30, b) 50, and c) 70 °C without reductants in 2 M H_2SO_4. Leaching yields of studied metals are illustrated by solid lines (left Y-axis), whereas solution iron concentration is indicated by a dashed line (right Y-axis).

for cathode metals reduction. Consequently, further reductant additions may not be necessary when processing this particular battery waste at $T = 70$ °C. Nonetheless, in these experiments (Fig. 1) the solution iron concentration was low (~200 mg/L), which may have impeded electron transfer between Cu, Al, and cathode metal oxides, resulting in suboptimal leaching kinetics. This hypothesis is supported by the previous study of Porvali et al., (2020) where the authors concluded that the rate-limiting step in a $LiCoO_2$ leaching system is related to reactions between metallic copper and dissolved iron rather than $LiCoO_2$ reduction. Furthermore, results of the same study suggest that efficient dissolution of an LCO-type cathode material using Cu as reductant can be obtained with a solution iron concentration of around 560 mg/L – calculated based on the reported parameters – which is more than double the Fe level of the experimental results outlined in Fig. 1.

A comparison of Cu and Al behavior indicates Cu to be the more active reductant toward battery waste, as it dissolves more readily under lower temperatures when compared to Al (50 % Cu yield vs. 40 % Al under $T = 30$ °C), despite the thermodynamically higher driving force for NMC reduction by aluminum (Chernyaev et al., 2023). In contrast, Al is more strongly affected by temperature increases, and is a more active reductant at higher temperatures, exceeding the Cu leaching yield at $T = 50$ °C (60 % Al; 55 % Cu) and $T = 70$ °C (85 % Al; 65 % Cu). This behavior is related to the characteristics of Al, which although is electrochemically less noble than Cu, forms a strong oxide layer on the surface that renders it less amenable to acid dissolution at low temperatures (Shukla et al., 2023). As temperature is increased, the oxide layer breaks down increasing surface reactivity, which allows Al to dissolve more readily (Amer, 2002). This also enables aluminum to act as a reductant toward cathode metal oxides more efficiently, consequently enhancing the leaching yields of Co, Ni, Mn, and Li. Interestingly, Al dissolution in the battery waste leaching experiments outlined here were determined to occur at a higher rate when compared to previous research of Al leaching using H_2O_2 as an oxidant (Shukla et al., 2023), where similar Al leaching yields required high temperatures, large H_2O_2 doses, and long reaction times. This highlights the highly reactive nature of waste NMC materials toward Al, whether because of the oxidative power of cathode metal oxides or the presence of other species contained within the material – like fluorine or other halogens that are known to vigorously react with Al to form aluminum trihalides (Sanders, 2012).

From a theoretical leaching yield perspective, Al may be considered a more desirable reductant than Cu in black mass leaching, as Al can donate much more electrons per mass unit, owing to the low atomic weight and favorable electron configuration of the element. The molar mass of Al (27.0 g/mol) is less than half of that of Cu (63.5 g/mol), amounting to more than twice the number of moles per mass unit. Furthermore, Al can donate three electrons upon dissolution cf. to two available from Cu. As a result, Al can donate around 3.5 times the number of electrons during dissolution per mass unit. Nevertheless, a major disadvantage of aluminum as a reductant is the lack of feasible Al recovery methods as high-value products from hydrometallurgical solutions, as evidenced by the lack of commercial hydrometallurgical recycling operations (Sristava and Meshram, 2023). Therefore, Al is typically recovered as an impurity precipitate in the subsequent solution neutralization and impurity removal steps, which has been shown to result in valuable battery metal losses. More specifically, battery leach solutions have been found to suffer losses of Ni, Co, and Li in the range of

2–10 % as co-precipitates upon hydroxide precipitation when the solution contains more than 2 g/L Al (Chernyaev et al., 2021b) – a value greatly exceeded in the experiments of the current study (up to 6 g/L Al). In addition, a study by Wang and Friedrich (2015) also reports that complete removal of Al from solution by hydroxide precipitation results in Ni, Co, and Mn losses in the range of 14–21 %. Due to these shortcomings, it may be more beneficial to separate Al from black mass prior to leaching and compensate for the subsequently diminished reducing power by the addition of another reductant like metallic copper. This approach is also supported by the findings of Rinne et al. (2021), whose simulations suggest that efficient metallic Al separation before metallurgical processing could decrease the greenhouse gas (GHG) emissions of recycling by over 60 % when compared with the corresponding production of virgin battery raw materials.

3.2. *Effect of iron*

As highlighted in Section 3.1., iron deficiency may have impeded the leaching kinetics in experiments without added reductants (Fig. 1). To overcome this drawback, experiments were conducted with added iron (in the form of $FeSO_4 \cdot 7H_2O$) to increase the concentration to the level found suitable (~560 mg/L) by Porvali et al. (2020). Experiments with target solution Fe concentrations of 400 mg/L and 600 mg/L were conducted to improve the reductive capabilities of metallic Cu and Al contained within black mass. As iron was added in divalent form, it can directly act as a reductant, however, is also further regenerated in the process by metallic impurities and consequently acts as a catalyst for the NMC leaching process (Eqs. (3) and (4). This behavior is shown by the results, which demonstrate how increases in solution Fe concentration have a marked effect on the dissolution of almost all studied metals (Fig. 2). At 30 °C, increasing the solution iron concentration from 0.2 g/L to 0.4 g/L improved the final leaching yields of Ni, Co, and Mn from around 50 % (Fig. 1a) to 70 % (Fig. 2a), and Li from 70 % to 85 %. A similar trend was also seen at 50 °C as Co, Ni, and Mn leaching yields increased from ~ 70 % (Fig. 1b) to ~ 85 % (Fig. 2c) as the solution Fe concentration was increased from 0.2 to 0.4 g/L. Furthermore, Li leaching efficiency also increased from 83 % to 94 %.

The concurrently increased Cu dissolution rates show that cathode material dissolution was improved because of enhanced electron transfer between Cu and the cathode material – due to the increased solution Fe concentration – as detailed in Eq. (3). Moreover, it is also evident that even a relatively small iron addition into the system at $T = 50$ °C resulted in almost a similar level of leaching when compared with the results at $T = 70$ °C in the absence of added iron. It is worth noting that the current study used a different strategy when compared with a previous study on a similar topic (Chernyaev et al., 2021a), where black mass leaching was instead improved by the addition of metallic Cu and Al, reaching similar cathode metal leaching yields. The applicability of these different approaches can be explained by differences in black mass compositions, as the raw material used in the current study was

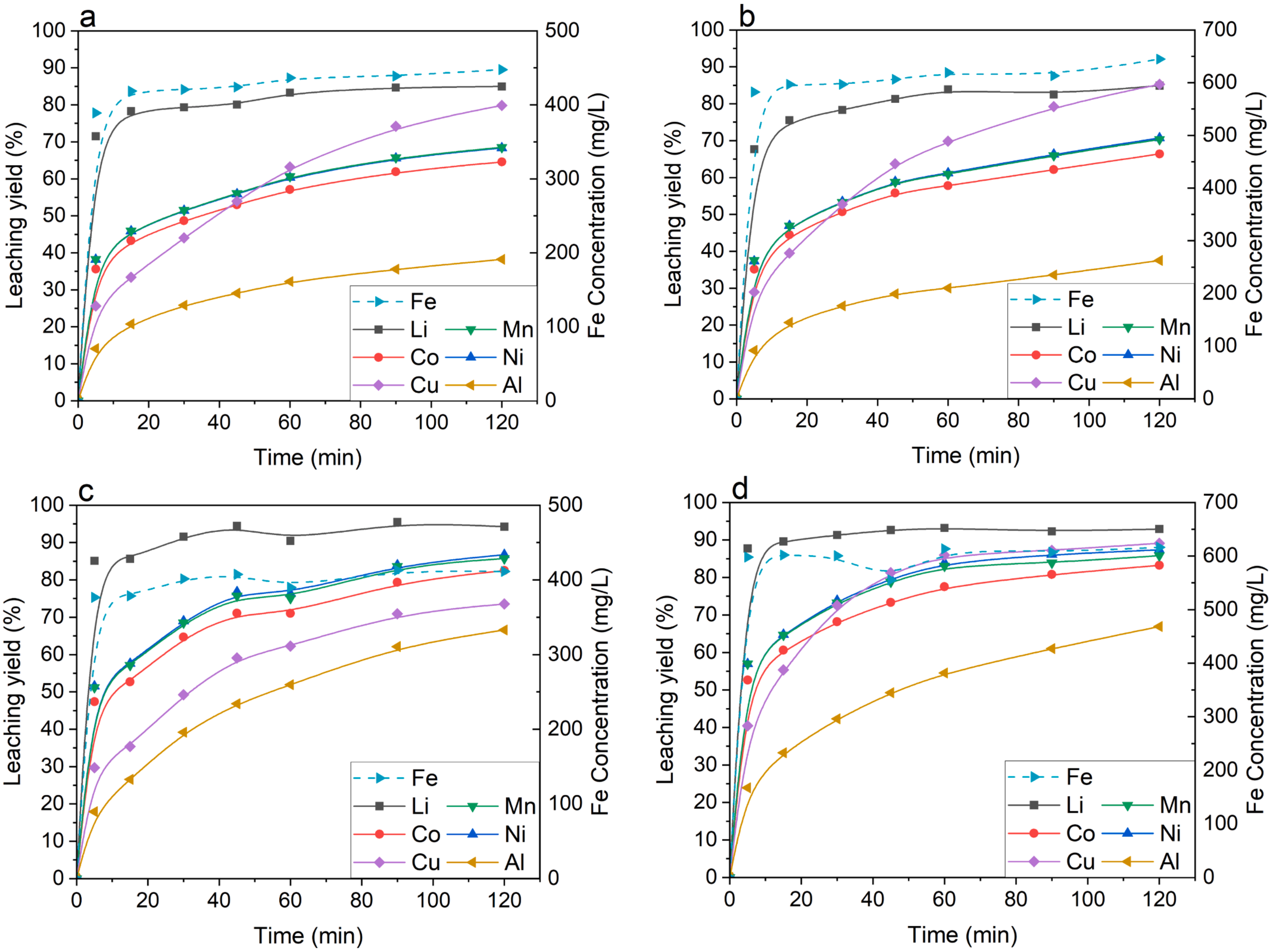

Fig. 2. Leaching results with iron additions a) 30 °C, 0.4 g/L total Fe, b) 30 °C, 0.6 g/L total Fe, c) 50 °C, 0.4 g/L total Fe, d) 50 °C, 0.6 g/L total Fe in 2 M H_2SO_4. Leaching yields of studied metals are illustrated by solid lines (left Y-axis), whereas solution iron concentration is indicated by a dashed line (right Y-axis).

remarkably higher in Cu and Al and much lower in Fe. The success of these leaching strategies for such different raw material compositions underlines the importance of a thorough understanding of the raw material composition and reaction mechanisms for the successful design and operation of black mass recycling processes.

In contrast to solution iron concentration, the impact of temperature increase (from 30 to 50 °C) on copper dissolution – even in the presence of added iron – was low. This indicates that the reaction between the cathode material and Cu is most likely not controlled by the rate of chemical reaction, as such rates are known to approximately double for each 10 °C increase in temperature, even in the case of low activation energy reactions (Levenspiel, 1999). Therefore, mass transfer or mixed control may be the prevalent mechanism in this reduction reaction, which likely occurs between Cu and Fe^{3+} ions, as the reaction between Fe^{2+} and battery cathode powder has been reported to be very fast (Porvali et al., 2020).

Despite the beneficial iron concentration effects on copper, aluminum dissolution was virtually unaffected by iron additions, which contradicts with the results previously obtained by Peng et al. (2019). Nonetheless, a notable increase in Al dissolution was again observed in response to the higher reaction temperature. These findings suggest that Al dissolution is controlled by the reactions related to the surface oxide layer and passivation rather than the chemical reaction rate between NMC and bulk Al. It can be hypothesized that at low temperatures, Al dissolution – and therefore the progress of related reduction reactions – may be strongly controlled by the Al_2O_3 passivation layer that hinders the kinetics of electron transfer, at least in the context of a black mass leaching process.

3.3. *$LiFePO_4$ as an iron source*

As an alternative to sulfate, iron can be added in any other readily soluble form. An optimal solution would be to utilize another waste fraction that must undergo leaching as a part of its recycling process, for example, another type of battery waste. Fractions of other battery waste types – namely nickel metal hydride (NiMH) and $LiFePO_4$ (LFP) – have previously been studied as reductants to achieve synergistic benefits for both waste types within the leaching system (Liu et al., 2019; Jiang et al., 2021). The market share of NiMH-based batteries is slowly declining (Cassayre et al., 2022) whereas LFP is constantly increasing in popularity, especially in electric vehicles (IEA, 2023). In addition to the increasing market share, LFP waste currently lacks viable commercial recycling process technologies and capacity (Zhao et al., 2024) and is thus an interesting prospect as a reductant in LCO/NMC battery waste recycling processes. LFP can also provide Fe for catalysis purposes, enhancing dissolution of cathode materials (Eq. (3). In contrast to LCO or NMC-type cathode materials, dissolution of LFP does not consume acid. Nonetheless, it requires a sufficiently high acid concentration for dissolution (Eq. (6) and to prevent subsequent iron precipitation as $FePO_4$ (Eq. (7) in the highly oxidizing conditions of a black mass leaching process.

$$LiFePO_{4\,(s)} + 3H^{+}{}_{(aq)} \rightarrow Li^{+}{}_{(aq)} + Fe^{2+}{}_{(aq)} + H_3PO_{4\,(aq)} \tag{6}$$

$$Fe^{3+}{}_{(aq)} + PO_4{}^{3-}{}_{(aq)} \rightarrow FePO_{4(s)} \tag{7}$$

In the current study, pure commercial LFP cathode powder was added as an additional iron source to investigate its impacts on NMC leaching. At $T = 30$ °C, the results (Fig. 3) showed a very similar leaching performance when compared with those obtained using iron sulfate ($FeSO_4 \cdot 7H_2O$; Fig. 2). Nonetheless, Al dissolution was remarkably higher in the presence of LFP, as 60 % of Al dissolved at this temperature (vs. 38 % with $FeSO_4$) – as was expected based on previous literature (Shukla et al., 2024). Al dissolution in the presence of LFP was also slightly higher at $T = 50$ °C, reaching a value of 73 %. However, despite the increased Al dissolution in the presence of LFP, the leaching yields of Li, Ni, Mn, and Co at $T = 50$ °C were lower when compared with the leaching yields obtained using $FeSO_4$, and the cause for this decrease in cathode metal leaching yields is currently unclear. However, it is unlikely that this would be caused by phosphate precipitation of the said metals under such acidic conditions, as at even higher pH, trivalent Fe and Al ions should precipitate preferentially over the dissolved ions of Ni, Co, Mn, and Li (Chernyaev et al., 2023).

Despite the slightly decreased cathode metal leaching yields, these results suggest that LFP waste could potentially be used as an iron source in a commercial LIB recycling process, allowing for the simultaneous recycling of both battery waste types, provided that any potential challenges arising from the increased solution Al concentration can be mitigated. On the other hand, mixing LFP-type battery waste to the feed would introduce phosphate ions into the leach solution, making it more complex and necessitating thorough phosphate removal at a later stage of the recycling process. Moreover, as some current industrial battery recycling processes recover Co, Ni, and Mn as a mixed hydroxide precipitate to be directly used as a raw material in new NMC-type cathode materials, the presence of phosphate ions would interfere with the process by precipitating the metals as insoluble phosphates (Latini et al., 2022). Nevertheless, the presence of phosphate ions could also prove beneficial for solution purification, as Fe and Al precipitation as

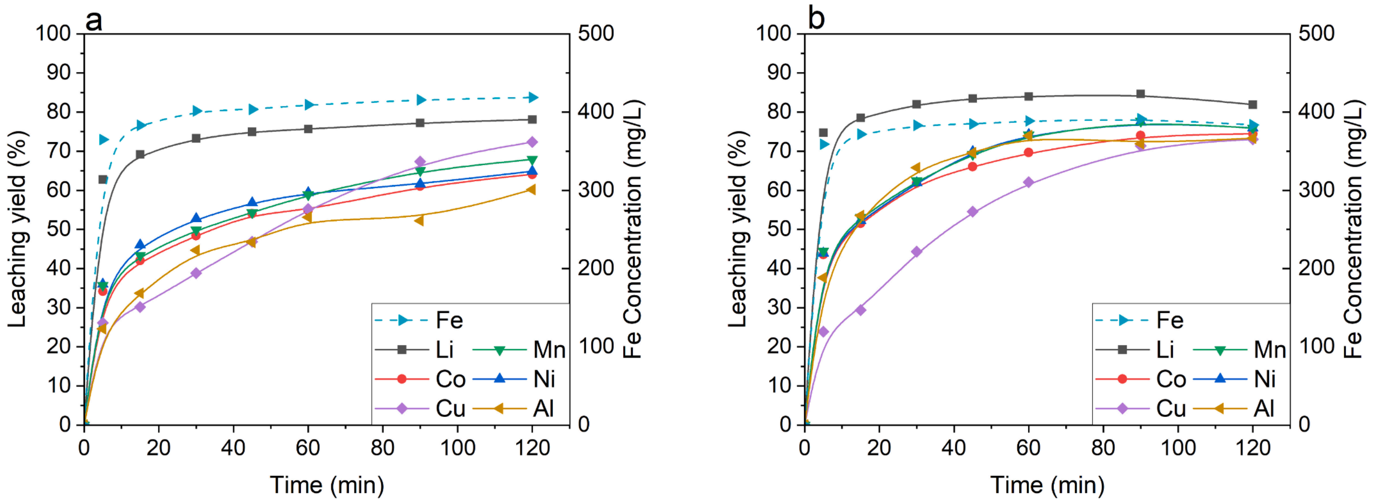

Fig. 3. Leaching results with LFP cathode material additions ($LiFePO_4$/TM = 0.004 mol/mol, *cf.* Table 2) under temperatures of a) 30 °C, b) 50 °C in 2 M H_2SO_4. Leaching yields of studied metals are illustrated by solid lines (left Y-axis), whereas solution iron concentration is indicated by a dashed line (right Y-axis).

phosphates has been shown to be associated with less co-precipitation of valuable battery metals when compared with hydroxides, and the resulting precipitate cake has been shown to have much better filterability characteristics (Twidwell and Dahnke, 2001; Chernyaev et al., 2023).

3.4. Regression modeling and prediction of leaching yields

In addition to laboratory experiments, regression modeling was conducted to compare the effects of various leaching parameters: temperature, solution Fe concentration, as well as Cu and H_2O_2 additions (Table 2). These variables were used as factors for the model, whereas the studied responses were the leaching yields (%) of Co, Ni, Mn, and Li at 120 min. The parameter levels for temperature and Fe concentration were selected based on results detailed in sections 3.1 and 3.2. Investigated Cu level was chosen to be 100 % higher than the amount contained in the original raw material *i.e.,* received black mass (7.5 g in 100 g of black mass), and H_2O_2 addition was chosen so that the calculated reductive power – electrons available for reduction – was stoichiometrically the same as that of the chosen Cu addition, *i.e.,* 6.7 mL of 50 % H_2O_2 solution per 100 g of black mass. The model was fitted in MODDE 13 software using the partial least squares method (Wold et al., 2001), considering only first order model terms (T, Fe, Cu, H_2O_2). Implementation of the interaction and square terms was also considered, but these terms were rejected due to the lack of statistical significance.

The coefficient plots for investigated factors and responses considering leaching results at $t = 120$ min indicate that reaction temperature is by far the most impactful factor for all investigated battery metals, having a value more than twice of that of any other variable (Fig. 4). It is also the only statistically significant factor for Li yield, as the error bars of all the other studied factors (Fe, Cu, H_2O_2) crossed the $y = 0$ level. This is likely since Li dissolves faster and easier compared to transition metals – at all conditions – and therefore the relative differences between other tested factors are small in terms of final yield at $t = 120$ min. For all transition metals, Cu and Fe additions also had significant effects on the final leaching yields. Finally, H_2O_2 had a smaller effect when compared to Cu and Fe, being statistically significant only for Co yield. Some of the model uncertainty is likely due to the use of industrially produced black mass as raw material, as it contains various impurities and is inhomogeneous by nature (Porvali et al., 2019), making it difficult to reliably determine the precise composition (Table 1).

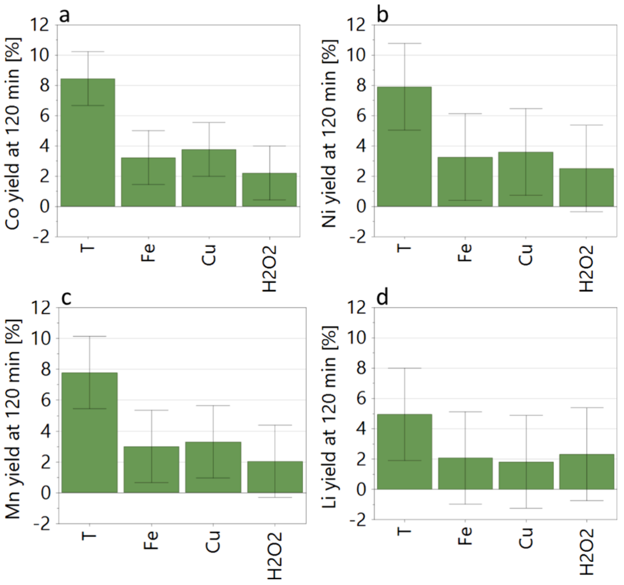

Fig. 4. Effects of investigated factors on the leaching yields of a) Co, b) Ni, c) Mn, and d) Li, with error bars showing the statistical significance of each factor.

The models for Co, Ni, and Mn exhibited a good fit, with decent statistical significance ($R^2 = 0.73$–0.91) and prediction precision ($Q^2 = 0.65$–0.85). The models also had a very good reproducibility (>0.94) and no significant problems (validity > 0.35 for all metals). A detailed summary of fit plot is shown in the Supplementary material (Fig. S1). After elimination of statistically insignificant factors, the software derived formulas for cathode metal leaching yields (Eqs. (8)–(10). For Li, no satisfactory model was achieved by insignificant factor elimination, and therefore, no equation for Li yield at $t = 120$ min is included in the equations. *N.B.,* the terms "reductant/TM" denote the molar amount of the reductant in question divided by the molar amount of transition metals in a 100 g of black mass, *cf.* Table 2.

$$Co\ yield(\%) = 0.90 \cdot [T] + 31.4 \cdot [Cu/TM] + 1800 \cdot [Fe/TM] + 18.5 \cdot [H_2O_2/TM] + 16.6 \tag{8}$$

$$Ni\ yield(\%) = 0.84 \cdot [T] + 30.1 \cdot [Cu/TM] + 1820 \cdot [Fe/TM] + 23.2 \tag{9}$$

$$Mn\ yield(\%) = 0.83 \cdot [T] + 27.6 \cdot [Cu/TM] + 1680 \cdot [Fe/TM] + 24.6 \tag{10}$$

From the Co yield equation (Eq. (8), it can be determined that the coefficient for H_2O_2/TM is substantially lower when compared with that of Cu/TM. This indicates that H_2O_2 has a lower impact on the final Co leaching yield when compared with an equal molar amount of Cu present in the system as illustrated in Fig. 5. It can be seen that a 0.25 mol/mol addition of Cu/TM results in a Co yield increase of ~ 8 percentage points, whereas an equimolar addition of H_2O_2 only increases Co yield by ~ 5 percentage points. Although the effect of H_2O_2 was only statistically significant for Co, a similar trend can also be assumed to apply to Ni and Mn, as these metals behaved almost identically to Co in all experiments performed in this study. There are several potential reasons as to why H_2O_2 reductive efficiency is statistically lower than that of Cu. In addition to acting as a reductant toward cathode metal oxides the compound is also a strong oxidant that can be consumed by side reactions with other black mass components like the oxidation of metallic Cu and Al. Moreover, H_2O_2 decomposition is known to be accelerated by the presence of various dissolved metals such as copper and iron (Haber and Weiss, 1934; Gil-Lozano et al., 2017), and the phenomenon is further exaggerated when ions of both Cu and Fe are present (Eul et al., 2001) – as in this case.

The developed model allows for the straightforward prediction of transition metal leaching yields in a leaching process. For example, at low temperatures $T = 30$ °C (without reductant additions) the model predicts leaching yields of 59 % for Co and 63 % for Ni and Mn, whereas the corresponding values at a higher process temperature $T = 50$ °C are 77 % for Co and 80 % for Ni and Mn. These predictions display a reasonable error margin (5–15 %) when compared with the results presented in Fig. 1, slightly overestimating yields at $T = 30$ °C, while underestimating them at $T = 50$ °C – likely since the model assumes the relationship between input parameters and responses as being linear. The predicted leaching yields can further be used to estimate the PLS metal compositions when the feed contents are known and thus be used to support experimental work design. Nonetheless, as the model is built based on one kind of industrial black mass, using a fixed S/L ratio, it may not be able to predict the leaching behavior of other systems and black mass compositions with absolute precision, especially as the cathode chemistry has been reported to affect the leaching system performance – cathode materials with higher nickel content generally being more reactive when compared with NMC111 (Xuan et al., 2021). However, the S/L ratio investigated here was rather high, 200 g/L, and since lower S/L ratios have previously been found to be associated with higher leaching yields (Peng et al., 2018), results achieved with other leaching systems are likely to be higher than predicted by the model.

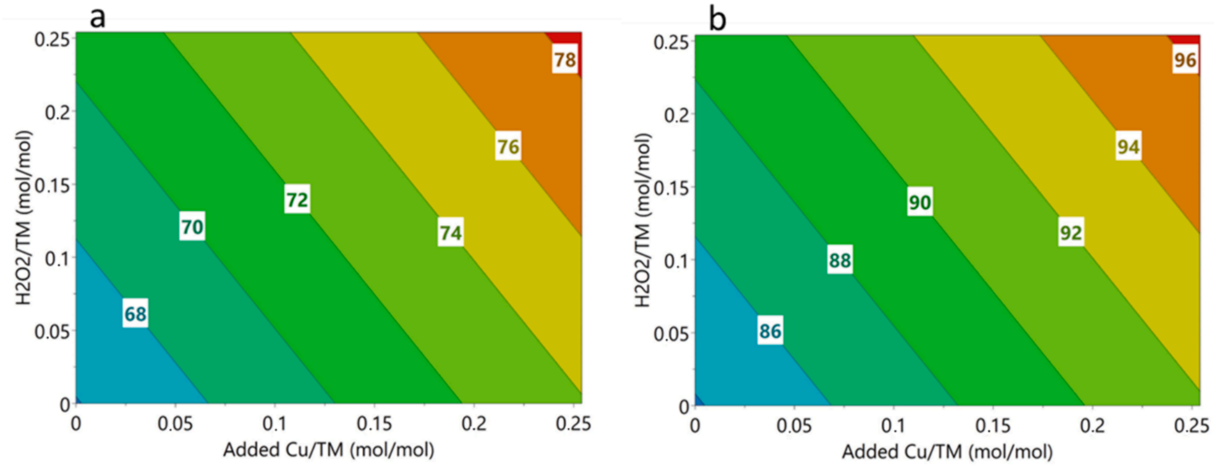

Fig. 5. Predicted Co yields (%) after 120 min leaching with added Cu and H_2O_2 under Fe concentration of 0.4 g/L and temperature of a) 30 °C, b) 50 °C.

4. Conclusions

The current study investigated the impacts of various parameters on the leaching performance of industrially produced NMC111-type black mass, focusing on the reductive efficiency of metallic Cu and Al contained within. The reductive efficiency of Cu was found to improve in accordance with PLS iron concentration increases up to 0.4 g/L, whereas that of Al only increased at higher ($T \geq 50$ °C) leaching temperatures. These differences between Cu and Al behavior can be hypothesized to be an indication of different limiting factors between the two reductants – Al leaching has been found to occur in sulfuric acid solutions by chemical reaction kinetics and formation of passivation layer, whereas Cu may be more strongly controlled by mass transfer effects. These differences could be exploited in a recycling process by using lower leaching temperatures to minimize Al dissolution and make the subsequent solution purification step less chemical intensive. Furthermore, ensuring a sufficient solution Fe concentration would allow for maximal Cu reduction efficiency and subsequent cathode metal leaching yields in the process.

It is important to note that this work has mainly considered Cu and Al dissolution values as consumption, *i.e.,* metal losses that should be minimized. Nevertheless, depending on technical and economic considerations, it may in some cases be beneficial to aim for total dissolution of also Cu and Al in the leaching step, especially if subsequent graphite recovery from the leach residue is desired. However, achieving total dissolution of Cu and Al would likely require even higher leaching temperatures than investigated here – potentially with additional use of strong oxidizing agents – or a secondary leaching step aiming to dissolve any metallic Cu and Al remaining in the residue. Regardless of the chosen strategy, implementation of such modifications could increase the costs and environmental footprint of the process.

Experiments investigating $LiFePO_4$ cathode material as an iron source exhibited higher Al dissolution levels and slightly lower cathode metal leaching yields when compared with $FeSO_4$. Nonetheless, the leaching yields could probably be improved with further research and thus, it is suggested that recycling of LFP-type black mass could potentially be incorporated into an NMC black mass recycling process as a reductant. Although, such implementation would likely require thorough phosphate removal in downstream process steps, while simultaneously increasing the production of Fe-rich process residues.

Based on the DoE leaching results, statistical models for Co, Ni, and Mn yields were built using *T*, *Fe*, and *Cu* as variables, whereas H_2O_2 addition only showed statistical validity for Co. The models indicated that Cu additions were more beneficial for improving cathode metal yields when compared to equimolar H_2O_2 additions despite the substantial copper content in the raw material itself. The efficiency of added copper versus H_2O_2 shown here underlines the benefits of utilizing metallic impurities found within black masses instead of relying on the often used peroxide as the reductant. Furthermore, these models allow for leaching performance prediction and reductant amount calculation for process design and experiment planning purposes.

Overall, the results of this study emphasize that thorough knowledge of raw material composition and careful leaching process optimization can help recycling operators adjust their processes to maximize leaching yields while minimizing chemical footprint and energy consumption. The authors believe that the results of this study will help to develop more efficient and environmentally friendly battery recycling processes and thereby positively contribute to the field of battery recycling – with the goal of increasing the share of EoL batteries becoming raw materials for new batteries and thereby bridging the gap between waste and raw materials in the battery value chain.

CRediT authorship contribution statement

Jere Partinen: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Petteri Halli:** Writing – review & editing. **Anna Varonen:** Writing – review & editing, Investigation. **Benjamin P. Wilson:** Writing – review & editing, Project administration. **Mari Lundström:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [Jere Partinen reports a relationship with Technology Industries of Finland Centennial Foundation that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.].

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mineng.2024.108828.

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