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Partinen, Jere; Halli, Petteri; Wilson, Benjamin P.; Lundström, Mari The impact of chlorides on NMC leaching in hydrometallurgical battery recycling

Published in: Minerals Engineering

DOI: 10.1016/j.mineng.2023.108244

Published: 01/11/2023

Document Version Publisher's PDF, also known as Version of record

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Please cite the original version:

Partinen, J., Halli, P., Wilson, B. P., & Lundström, M. (2023). The impact of chlorides on NMC leaching in hydrometallurgical battery recycling. *Minerals Engineering*, *202*, Article 108244. https://doi.org/10.1016/j.mineng.2023.108244

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The impact of chlorides on NMC leaching in hydrometallurgical battery recycling



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ARTICLE INFO

ABSTRACT

Keywords: Battery materials recycling Dissolution mechanism Sulfate--chloride leaching MnO₂ Cl₂ The current paper studies the impact of chlorides on NMC111 (LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂) leaching mechanism. Experiments were conducted in chloride (HCl) and mixed sulfate-chloride (H₂SO₄-NaCl) solutions as well as in sulfate solution (H₂SO₄, reference), in the absence of external reductants. The results suggest no major differences in the leaching performance between studied lixiviants at 30 °C (~75% for Li, ~35% for Co, Ni, Mn), and increasing the temperature to 80 °C mainly improved the dissolution of lithium (>90% in all lixiviants). However, the leaching behavior of manganese was found to be different - in sulfate solutions, Mn precipitated as MnO₂ with only 6% Mn left in solution after 2 h (at 80 °C), whereas in chloride-containing solutions, dissolved Mn remained soluble (30-40% extraction). The presence of chlorides also supported cobalt and nickel extraction, the mixed H₂SO₄-NaCl system resulting in extractions of 55% for Co and 58% for Ni at 80 °C. The increase in the dissolutions is suggested to be explained by the experimentally verified reaction between Cl⁻ ions and NMC111, resulting in Cl₂ formation and simultaneous NMC dissolution. The results indicate that hydrometallurgical battery recycling processes may face challenges with manganese extraction to solution when operating at increased temperatures, and that the presence of chloride ions can help to mitigate such difficulties by inhibiting unwanted precipitation of manganese compounds, producing Cl₂ gas as a result. Nevertheless, as the final extractions were low even in the most effective lixiviant (55% Co, 58% Ni, 39% Mn at 80 °C), the use of additional reductants is necessary to ensure high metal leaching efficiencies also in such chloride-containing systems.

1. Introduction

Due to an increasing number of electric vehicles and the progressive electrification of societies, the associated utilization of lithium-ion batteries (LIBs) is rapidly expanding (IEA 2022). Such batteries will eventually reach the end of their useful life (EoL) and consequently, must be recycled to allow their valuable materials to be reclaimed for further use. Currently, pyrometallurgical processes are the prevalent means to recycle waste LIBs in industrial scale due to advantages related to operational ease and high throughput (Makuza et al., 2021). The disadvantages of such smelting processes are that elements like lithium, manganese and aluminum mainly report to the slag phase from which they can be difficult to reclaim, and recovery of electrolytes, graphite and plastics is typically not considered (Harper et al., 2019; Castro et al., 2022). Nonetheless, due to upcoming changes to EU regulations as a part of the updated European Battery Directive, there will be an increased emphasis on the total amount of battery waste to be recycled as well as recovery of specific individual elements e.g., lithium (European Commission, 2020). Furthermore, the directive will set additional targets related to the recycled content of Co, Ni, Cu and Li required in new battery cells that are placed on sale within the EU market area. This will likely emphasize the importance of hydrometallurgical LIB recycling methods due to their ability to recover a larger variety of battery elements with high purity – either as separate operations or in combination with pyrometallurgical ones – when the unit process operations are optimized accordingly (Zhang et al., 2018).

Hydrometallurgical recycling routes usually commence with the discharging and crushing of the battery waste, after which the fragmented waste is typically leached in sulfuric acid (Harper et al., 2019). Previous research has shown that the structure of LIB cathode materials allows for easy lithium dissolution via a deintercalation mechanism whereas the subsequently oxidized transition metals require a reductant for efficient extraction (Joulié et al., 2017; Porvali et al., 2020). One of the most extensively used reductants in leaching studies is hydrogen peroxide (Harper et al., 2019) which decomposes into water and oxygen during the leaching process, introducing no additional ions into the

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https://doi.org/10.1016/j.mineng.2023.108244

Received 7 December 2022; Received in revised form 21 June 2023; Accepted 10 July 2023 Available online 14 July 2023

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solution (Sohn et al., 2006). Nevertheless, due to the high energy consumption and toxic by-products associated with hydrogen peroxide production (Che et al., 2022), a plethora of alternative reductants have been investigated (Jena et al., 2021).

Some studies have circumvented the need for external reductants by carrying out the leaching in hydrochloric acid. Chloride-based solutions have been assumed to be able to act as reductants by forming chlorine gas in the process, although so far, such claims have often been made without analyzing the presence of Cl₂ (Takacova et al., 2016; Porvali et al., 2019). Moreover, LIB scrap typically contains metallic aluminum, iron and copper particles that can act as reductants towards the cathode material, and the reductive capabilities of these metals - especially copper - are further enhanced by the presence of chloride ions. Chloride ions stabilize Cu⁺ species *i.e.*, cuprous chloride complexes in the solution (Fritz, 1980; Muir, 2002), allowing for reductive leaching of battery cathode materials without necessarily generating Cl₂ gas (Partinen et al., 2022). In addition, some studies have also been conducted using pure cathode material powders instead of LIB scrap, most commonly LCO (LiCoO₂) and various types of NMC (LiNi_xMn_vCo_zO₂), where the stoichiometric ratios of Ni, Mn and Co are denoted by a corresponding number (for example, NMC111 or NMC811). For example, Xuan et al. (2019) have investigated leaching NMC811 in 4 M HCl solution and reported formation of Cl₂ gas corresponding to cathode material dissolution. They later expanded this research to also cover other NMC-type cathode chemistries and concluded that the cathode composition greatly affects the leaching kinetics, with leaching rates in the order of NMC811 > NMC622 >> NMC532 >> NMC111 (Xuan et al., 2021).

Chloride media have also been utilized in various industrial battery metal processes, for example, the Bulong process in Australia refined nickel using sulfate-chloride media from 1999 to 2003 (Donegan, 2006), and currently, the Glencore Nikkelverk facility in Norway utilizes a sulfate-chloride-based process for nickel production (Agarwal et al., 2019). In addition to the use of chloride-containing methods by industry, recovery of battery metals from similar sulfate-chloride solutions is also an emerging field of research (Linneen et al., 2019; Wesselborg et al., 2021; Avdibegović et al., 2022). Due to the industrial relevance of both sulfate and chloride media, it is important to have a detailed understanding of battery material leaching behavior within such lixiviants. Consequently, this paper provides new understanding on NMC leaching in the presence of chlorides, which can provide the basis for further process developments for emerging hydrometallurgical battery recycling operations.

2. Materials and methods

The battery cathode material utilized throughout the experiments comprised of commercial $\rm LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ powder (NMC111, 7.5 \pm 2.5 μm D50, MSE Supplies, USA). Other chemicals used were H₂SO₄ (95–97%), NaCl (\geq 98%), HCl (37%) and HNO₃ (65%) provided by VWR Chemicals, Belgium. All solutions were prepared using deionized water (15 M\Omega·cm, Merck Elix Essential, France).

Leaching experiments were conducted in three different lixiviants: sulfate (1 M H₂SO₄), chloride (1 M HCl) and mixed sulfate–chloride (1 M H₂SO₄, 1 M NaCl), all prepared to an equivalent volume of 400 mL at room temperature. Leaching in each media was performed at temperatures of 30, 50, 70 and 80 °C, resulting in a total of 12 leaching experiments. Each experiment used 0.07 mol (6.75 g) NMC111 powder, and the setup, chemical amounts, and sampling procedures were similar to those outlined in our earlier study of LiCoO₂ leaching (Partinen et al., 2022), the main differences being in the reactor type (submersible cylindrical vs. jacketed round-shaped) and heating method (submersible vs. circulating water bath). Experiments were performed in a 500 mL cylindrical glass reactor with the temperature regulated by a thermostatic water bath (Lauda AQUAline AL 25, Germany). Solution was agitated with an overhead stirrer at 300 RPM (VWR VOS 16, USA, with a four-blade 5 cm diameter PTFE stirrer shaft with 45° blade angle, VWR,

USA) to keep solids in a suspension.

Solution samples (~4 mL) were taken at 5, 15, 30, 45, 60, 90 and 120 min and filtered with polyethersulfone syringe filters (0.45 μ m pore size, VWR, USA). Redox potential of the solution was determined at each sampling interval using a saturated calomel electrode (SCE, B521, SI Analytics, Germany) and platinum wire (Kultakeskus Oy, Finland) attached to a multimeter (Wavetek 5XL, TEquipment, USA) – results were subsequently converted to the SHE (standard hydrogen electrode) scale. Chlorine gas formation was monitored with a Cl₂ detector (WatchGas UNI mp100, 0.1–50 ppm Cl₂, the Netherlands) by placing the sensor on top of a reactor opening for 10 s directly following each sampling. Additionally, the initial lixiviant redox potential and reactor Cl₂ concentration were measured after preheating the lixiviant to reaction temperature, prior to the commencement of each experiment.

After 2 h of leaching, the pregnant leach solution (PLS) was vacuum filtered (Whatman, grade 50 filter paper, UK) and the obtained leach residue was dried overnight in an oven at 60 °C under atmospheric conditions. Leach residues were characterized with X-ray diffraction (XRD, PANalytical X'Pert Pro with Cu-K α radiation source, the Netherlands) and the obtained spectra were assessed with a characterization software (HighScore PLUS, the Netherlands). Solution samples were diluted with 2% HNO₃ and analyzed with an atomic absorption spectrometer (AAS, Thermo Scientific iCE 3000, USA).

3. Results and discussion

Leaching experiments were initially conducted in sulfuric acid to establish reference values, which would allow the role and effects of chloride ions on NMC111 leaching at different temperatures to be more clearly determined. Identical experiments were carried out in hydrochloric acid to study the presence of chloride ions and potential impact of chlorine gas evolution on the leaching system. Lastly, leaching was also performed with sulfuric acid that contained added chloride (from NaCl) to investigate whether the presence of chloride ions in mixed leaching is a significant factor during the leaching process. All experiments were conducted without additional reductants in order to study the leaching behavior of the mentioned lixiviants in the absence of such external reductants.

3.1. Sulfuric acid leaching in the absence of chlorides

In sulfuric acid media (1 M), metals dissolved primarily during the first 30 min after which the leaching rate was observed to decrease significantly (Fig. 1). As no additional reductants were used in the experiments, the final extractions of Co, Ni, Mn, and Li to pregnant leach solution (PLS) were determined to be relatively low (35%, 37%, 37% and 79% at 30 °C, respectively). When the experimental temperature of the leaching solution was increased to 80 °C it was found that the level of Li dissolution increased to approximately 90% whereas, in contrast, only a marginal increase in Co and Ni extraction was observed. Such results were expected due to the arrangement of metals in the cathode material: the NMC111 structure consists of layered lattices comprised of transition metals (Ni, Mn, Co) with oxygen, and the lithium ions are found in the interstitial spaces between these lattices. This configuration allows for the easy structural intercalation/deintercalation of Li⁺ during battery charging and discharging (Sun and Zhao, 2017). In addition, the lithium ions are also more easily dissolved during leaching via this deintercalation mechanism. Conversely, transition metals typically remain within the lattice structure, and previous studies have demonstrated that extraction of these metals from such layered cathode materials - like LCO and NMC111 - only achieves about 30 to 40% when leached without a reductant, and further increase in dissolution seems to require the use of a reduction agent (Ferreira et al., 2009, Joulié et al., 2017, Porvali et al., 2020, Chernyaev et al., 2021).

The leaching results of Mn showed a markedly different behavior when compared to Co, Ni and Li. At 30 $^\circ\text{C},$ Mn dissolution demonstrated



Fig. 1. Dissolution of a) Co, b) Ni, c) Mn and d) Li from NMC111 in 1 M H₂SO₄ solution at 30, 50, 70 and 80 °C.

an increasing trend up to 30 min of leaching, after which the curve plateaued (final yield 37% after 2 h). At temperatures > 30 °C, however, the Mn concentration of the PLS was found to decline after 5–15 min of initial dissolution, with only a 6% final yield at 80 °C. A possible explanation for this observation is MnO₂ precipitation as this becomes thermodynamically more favorable with increasing temperature (Eq. (1)).

$$MnO_{2(s)} + 4H^{+}_{(aq)} + 2e^{-}_{(aq)} \rightleftharpoons Mn^{2+}_{(aq)} + 2H_2O_{(l)}$$
(1)

The reduction potential for the MnO_2/Mn^{2+} redox pair (Eq. (1)) between 30 and 80 °C is E = 1.20-1.23 V vs. SHE, when calculated with HSC 9.4.1 (Metso Outotec, Finland). In leaching experiments at temperatures 50–80 °C, these thermodynamical precipitation potentials were exceeded by a substantial margin as the measured redox potentials reached values close to 1.4 V vs. SHE (Fig. 2). This indicates that the solution conditions during leaching were highly oxidative and supports the hypothesis of Mn precipitation as MnO₂. Theoretically, such high redox potentials should not be possible due to the water stability limit, *i. e.*, decomposition into oxygen gas at around E = 1.2 V (Eq. (2); Figure S1).

$$O_{2(g)} + H^{+}{}_{(aq)} + e^{-}{}_{(aq)} \rightleftharpoons H_2 O_{(l)}$$
 (2)

In practice however, depending on the conditions the oxygen gas formation reaction can require up to several hundreds of millivolts of overpotential (Ivanov et al., 2000), allowing the solution redox potential to substantially exceed this theoretical maximum. Reaching such a high redox potential to facilitate oxidation of Mn^{2+} and subsequent precipitation as MnO_2 (Eq. (1)) requires the presence of a strong oxidant. This requirement was clearly met by NMC111, as it was able to induce MnO_2 precipitation by accepting electrons from Mn^{2+} as a part the dissolution reaction (Eq. (3)), therefore simultaneously leading to a slight increase



Fig. 2. Redox potential vs. SHE in H_2SO_4 leaching of NMC111. The equilibrium potential for MnO_2 precipitation at 30 and 80 °C is indicated by horizontal dashed lines.

in Co and Ni dissolution at 80 °C (Fig. 1).

$$\frac{6LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2(s)} + 24H^{+}{}_{(aq)} + 6e^{-}{}_{(aq)} \rightarrow 6Li^{+}{}_{(aq)} + 2Ni^{2+}{}_{(aq)}}{+ 2Mn^{2+}{}_{(aq)} + 2Co^{2+}{}_{(aq)} + 12H_2O_{(l)}}$$

$$(3)$$

Thus, the dissolved Mn^{2+} acts as an *in-situ* reductant for further NMC111 leaching as suggested by Billy et al. (2018), although the reductive efficiency and subsequent increase in Ni and Co dissolutions were relatively low due to the low Mn^{2+} concentration in the PLS. At 30 °C, the redox potential exhibited a different behavior as there was a distinct decline between 5 and 30 min. Although the potential steadily

increased afterwards until the end of the experiment, the values stayed below 1.1 V vs. SHE, and no related decline in Mn concentration was observed (Fig. 1c).

The NMC111 dissolution mechanism in a H₂SO₄ medium has previously been studied by Billy et al. (2018) who suggested that the leaching proceeds via two steps: the first step comprises Li deintercalation and subsequent related transition metal dissolution, whereas the second step is governed by Mn^{2+} oxidation to MnO_2 that results in a further reduction and dissolution of the NMC111 material. Their results indicated that in this second step, MnO2 precipitation was initially associated with additional Li dissolution (up to approximately 85%) and then with improved Ni and Co dissolution during prolonged - 43 days leaching at 30 °C. The results outlined in the current study correlate with such findings, as increases in the temperature to 50 and 70 °C improved Li dissolution to 83% and 86%, whereas slightly improved Ni and Co dissolutions were only observed at 80 °C (44% and 42%, respectively). The temperature increases in our study effectively caused the same phenomena (Billy et al., 2018) to occur over a much shorter time due to enhanced reaction kinetics.

XRD analyses of the leach residues showed that the cathode material exhibits increasing degrees of delithiation as the reaction temperature is increased (Fig. 3). The major phase identified after leaching at 30 °C is Li_{0.4}Ni_{1/3}Mn_{1/3}Co_{1/3}O₂, which further transforms to Li_{0.24}Ni_{1/3}Mn_{1/3}Co_{1/3}O₂ at 50 and 70 °C. After leaching at 80 °C, any remaining NMC111 is almost completely delithiated and replaced by Mn_{0.33}Co_{0.33}Ni_{0.33}O(OH). The suggested formation of MnO₂ (Fig. 1c) in the leach residues (T \geq 50 °C) was also confirmed by XRD diffractograms (Fig. 3). Furthermore, at 30 °C, a lithium-containing birnessite-type compound – Li₄Mn₁₄O₂₇·xH₂O – was found to be present in the residue, as previously reported by others (Billy et al., 2018; Lv et al., 2020). Even

though the solution redox potential at 30 °C did not reach the value required for MnO_2 precipitation (Fig. 2), several types of manganese oxides have been observed to have significantly lower oxidation potentials (Liu et al., 2009), which can explain formation of such a birnessite-type compound at this temperature. In contrast, the birnessite phase was not detected at higher temperatures, presumably due to its complete conversion to MnO_2 – such a transformation has been reported earlier in acidic media in the presence of dissolved Mn^{2+} (Tu et al., 1994).

Overall, the findings presented here indicate that in sulfate solutions an increase in the reaction temperature can cause extensive precipitation of manganese as MnO_2 , and this reaction can further act as a reductant towards NMC111 dissolution. Increased temperature significantly improves Li dissolution, whereas Ni and Co extractions are only slightly improved, highlighting the need for an additional reductant for more complete transition metal dissolution. During leaching at 30 °C, manganese was found to precipitate as $Li_4Mn_14O_{27}\cdot xH_2O$, which transformed into MnO_2 as the temperature was increased. Such precipitated manganese compounds would become a part of the leach residue and be mixed with other insoluble species like plastics and graphite.

3.2. Hydrochloric acid leaching

Identical NMC111 leaching experiments were also conducted under similar conditions using a 1 M HCl solution as lixiviant. At 30 °C, the dissolutions of all metals reached their final values at a slightly faster rate when compared to H_2SO_4 media – levels of maximum yield were found within 15 min (Fig. 4) – with final leaching efficiencies of 35%, 37%, 35% and 75% for Co, Ni, Mn, and Li, respectively. Although the



Fig. 3. XRD diffractograms of pristine NMC111 and leach residues after leaching in 1 M H₂SO₄ at 30, 50, 70 and 80 °C.



Fig. 4. Dissolution of a) Co, b) Ni, c) Mn and d) Li from NMC111 in 1 M HCl solution at 30, 50, 70 and 80 °C.

two acids (1 M HCl vs. 1 M H₂SO₄) contain a different amount of H⁺ ions in their structure, a likely explanation for faster dissolutions in HCl is the higher activity coefficient of chloride solutions when compared with corresponding sulfate solutions (Puvvada et al., 2003). Increasing the reaction temperature to 50 and 70 °C did not significantly improve either the Co or Ni dissolutions, however, Li extraction increased to 81% at 50 °C and 87% at 70 °C. Nonetheless, apart from faster initial dissolutions recorded at 30 °C, final Co, Ni and Li extractions were of a similar magnitude as those achieved in H₂SO₄ media (Fig. 1) over the same temperature range. Statistical integrity of the results was confirmed by repetition experiments (Supplementary material; Figure S3, Tables S1-S2). Although the effects of solution chloride ion concentration were not investigated in this study, previous results by others (Xuan et al., 2019) have shown that increasing the HCl concentration leads to a remarkable increase in reaction kinetics.

Interestingly, manganese exhibited a significantly different leaching behavior in HCl solutions when compared to sulfate media as no extensive precipitation of manganese compounds was observed (Fig. 4c), and increased reaction temperatures resulted in only a minor decrease in dissolution – 30% at 80 °C *cf.* 35% at 30 °C. Therefore, the slightly improved Ni and Co dissolutions achieved at 80 °C cannot be explained in terms of electrons released by manganese species precipitation (Eq. (1)), but rather by an alternative mechanism. It is suggested that that the presence of chlorides can provide a reduction process that involves the oxidation of Cl⁻ ions to form chlorine gas, releasing electrons to support active material leaching (E = 1.29 V vs. SHE at 80 °C, Eq. (4)).

$$Cl_{2(g)} + 2e^{-}{}_{(aq)} \Rightarrow 2Cl^{-}{}_{(aq)}$$
 (4)

A comparison of the reactions for MnO_2 precipitation (Eq. (1)) and Cl_2 evolution (Eq. (4)) shows that the reduction potential of the former is lower (1.20 V vs. 1.29 V (SHE) at 80 °C, HSC 9.4.1). This difference in the potentials implies that Cl_2 gas evolution would not be favored when there are Mn^{2+} ions present in the solution, although the prevailing conditions can significantly affect the stability of various species in the leaching system. For example, the presence of chloride ions can promote formation of complexed species like $MnCl^+$ (Suleimenov and Seward, 2000), and the reduction potentials of both MnO_2 precipitation and Cl_2



Fig. 5. Cl₂ concentration in the reactor gas phase as a function of time in 1 M HCl media.

evolution are dependent on pH, as illustrated by the corresponding Pourbaix diagram (Supplementary material, Figure S2). To identify the dominant reaction in the system, chlorine gas concentration in the reactor was monitored with a Cl_2 detector during leaching (Fig. 5). These measurements showed considerable Cl_2 evolution during experiments especially at 70 and 80 °C, indicating that Cl^- ions present in the solution can be oxidized in the presence of NMC111 active material, releasing Cl_2 gas and donating electrons to NMC111 in the process. This reaction can also further enhance active materials leaching (Eq. (5)).

$$3LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2(s)} + 12HCl_{(aq)} \rightarrow 3LiCl_{(aq)} + NiCl_{2(aq)} + MnCl_{2(aq)} + CoCl_{2(aq)} + 6H_2O_{(l)} + 1.5Cl_{2(g)}$$
(5)

Due to detector limitations, the Cl_2 concentration results are only semiquantitative, although a more precise determination of Cl^{-} consumption and Cl_2 evolution would be possible by analyzing the solution chloride concentration after leaching (Xuan et al., 2019) or by capturing and reacting the evolved Cl_2 gas with NaOH solution and determining the amount of NaClO formed as a result (Yi et al., 2021). However, such measurements were not performed in this study.

The presence of Cl₂ formation reaction at temperatures \geq 50 °C was also reflected by changes in the solution redox potential (Fig. 6), which quickly stabilized at approximately 1.3 V vs. SHE – close to the value corresponding to Cl₂ gas evolution. Together with the Cl₂ concentration results (Fig. 5) the measured redox potentials indicate that the presence of chlorides and subsequent Cl₂ evolution may prevent the solution redox potential from reaching equally high values as measured in sulfate media (Fig. 2). Alternatively, it is possible that the electrode is only measuring the potential of the prevalent Cl₂ formation reaction instead of the entire solution. Conversely, at 30 °C the redox potential showed a similar behavior to sulfate media with an initial decrease between 5 and 30 min followed by a steady increase until the end of the reaction. These values were higher than those measured in H₂SO₄ solution, reaching the theoretical MnO₂ precipitation potential in 2 h.

Despite the redox potentials exceeding the value required for MnO_2 precipitation at all temperatures, the only recognizable peaks corresponding to the presence of manganese-containing materials in the XRD diffractograms were related to Li₄Mn₁₄O₂₇·xH₂O (Fig. 7). This compound was found in the residue after leaching at 30 °C, although the peaks were of much lower intensity than those in the corresponding H₂SO₄ experiment. No MnO₂ was identified in any of the leach residues, which contradicts with the hypothesis based on the reduction potentials that would suggest Cl₂ to act as an oxidant towards Mn^{2+} , producing MnO_2 and Cl⁻ in the process (Eq. (6)).

$$Cl_{2(g)} + Mn^{2+}{}_{(aq)} + 2H_2O_{(l)} \Longrightarrow MnO_{2(s)} + 2Cl^{-}{}_{(aq)} + 4H^{+}{}_{(aq)}$$
(6)



Fig. 6. Redox potential vs. SHE in HCl leaching of NMC111. The equilibrium potentials for MnO_2 precipitation and Cl_2 evolution are indicated by horizontal dashed lines.

However, this reaction is strongly dependent on an alkaline pH (Li et al., 2019), and it has been found to be dramatically inhibited when the solution pH decreases to the value of 7 and below (Hao et al., 1991). Conversely, Cl⁻ ions can reduce MnO_2 to Mn^{2+} when the pH is below 1, *i. e.*, when HCl concentration is above 0.1 M (Tu, 1993). Therefore, any MnO_2 precipitated in the current study is likely to have redissolved into the solution through a reaction with HCl, resulting in the output of Cl₂ gas as one of the products (Eq. (7)).

$$MnO_{2(s)} + 4HCl_{(aq)} = MnCl_{2(aq)} + 2H_2O_{(l)} + Cl_{2(g)}$$
(7)

Notwithstanding, the presence of the birnessite phase in the 30 °C leach residue and the corresponding lack of chlorine gas formation during the experiment indicate that such dissolution either does not occur at low temperatures or the reaction kinetics are restricted. Furthermore, despite the tendency of Cl⁻ ions to reduce MnO₂ under acidic conditions and elevated temperatures as described above, Joulié et al. (2017) have previously reported the presence of MnO₂ in leach residue after 3 h of leaching in a 1 M HCl solution at 90 °C, although no clear explanation for this finding was included in the discussions.

Apart from differences in Mn behavior, the XRD diffractograms of the leach residues revealed similar leaching behavior in HCl media compared to H_2SO_4 . The extent of NMC111 delithiation is enhanced with increased temperature, decreasing from 0.4 times the stoichiometric amount at 30 °C to 0.24 at 50 °C and 70 °C, and reaching almost complete delithiation at 80 °C as demonstrated by the presence of a predominant $Mn_{0.33}Co_{0.33}Ni_{0.33}O(OH)$ phase (Fig. 7).

Based on the findings detailed above, it is suggested that NMC111 dissolution in HCl solutions progresses faster than in sulfate media during the first 15 min of leaching, but results in similar final dissolution levels of Li, Co, and Ni, whereas MnO_2 precipitation is clearly inhibited by the presence of chloride ions. The leaching process begins with active material dissolution without an external reductant as the redox potential of the system is not sufficient for either Mn^{2+} or Cl⁻ to act as reductants (Fig. 6). Instead, the reaction presumably proceeds by producing oxygen gas via a reaction analogous to that reported by Lv et al. (2018) (Eq. (8)).

$$\frac{6LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2(s)} + 18H^{+}_{(aq)} \rightarrow 6Li^{+}_{(aq)} + 2Ni^{2+}_{(aq)} + 2Mn^{2+}_{(aq)}}{+ 2Co^{2+}_{(aq)} + 9H_2O_{(l)} + 1.5O_{2(q)}}$$
(8)

As the solution redox potential increases, dissolved manganese species start to precipitate as MnO_2 (Eq. (1)), which provides electrons for NMC111 reduction and thereby further drives dissolution. Upon formation, MnO_2 rapidly reacts with the Cl⁻ ions present and is reduced back to soluble Mn^{2+} , forming Cl₂ gas in the process (Eq. (7)). Alternatively, Cl⁻ ions can react directly with the cathode material without Mn^{2+} involvement (Eq. (5)) as was observed when leaching a manganese-free cathode material – LiCoO₂ – under identical conditions (Supplementary material, Figures S4–S6). Furthermore, if implemented into an industrial battery recycling process the leaching system would also contain considerable amounts of copper and aluminum, which could have significant effects on the leaching performance due to copper complexation with chloride ions (Partinen et al., 2022) and chlorideinduced aluminum corrosion phenomena (Abdel-Gaber et al., 2006).

3.3. Sulfuric acid leaching in the presence of chlorides

Identical leaching experiments were carried out in 1 M H_2SO_4 –NaCl solutions to clarify the effects of the chloride ion source on the sulfatebased leaching process. At 30 °C, Co, Ni, Mn, and Li reached their final leaching efficiencies of 36%, 37%, 36% and 76% within 15 min (Fig. 8) – both the kinetics and extractions being of a similar magnitude when compared to HCl experiments. Nonetheless, increasing the temperature to 80 °C considerably increased the dissolution of Co (55%) and Ni (58%) when compared to the respective results achieved in H₂SO₄ or HCl solutions, which suggests that the chloride ion source has a significant impact on the leaching process. Such improved leaching behavior



Fig. 7. XRD diffractograms of pristine NMC111 and leach residues after leaching in 1 M HCl at 30, 50, 70 and 80 °C.

could be explained by the solution composition as various chloride salts have been reported to increase the activity coefficient of the chloride ion in HCl solutions – the effect of metal salts being stronger than an equivalent increase in HCl concentration (Puvvada et al., 2003). This chloride salt effect may also explain why an identical leaching experiment performed in 1 M HCl–Na₂SO₄ solution yielded much lower dissolutions of Co, Ni and Mn – with associated manganese precipitation and less prominent Cl₂ evolution – despite containing equal concentrations of Cl⁻ and SO₄^{2–} ions (Supplementary material, Figures S7 and S8).

When compared to other metals, Mn dissolution was observed to be less affected by the reaction temperature. Mn leaching efficiency decreased to 30% at 50 °C in a similar way to that previously found for H₂SO₄ and HCl lixiviants, whereas further increases in temperature to 70 °C and 80 °C slightly improved Mn dissolution, reaching 39% at both temperatures. As in HCl solution, the dissolution results in H₂SO₄–NaCl (Fig. 8c) indicated some manganese precipitation at an early stage of leaching at 80 °C. The precipitated manganese oxides can subsequently dissolve back into solution (Eq. (9)) in a similar way to HCl media (Eq. (6)).

$$4NaCl_{(aq)} + 2H_2SO_{4(aq)} + MnO_{2(s)} \Rightarrow 2Na_2SO_{4(aq)} + MnCl_{2(aq)} + 2H_2O_{(l)} + Cl_{2(g)}$$
(9)

In addition to higher metal dissolutions, the experiments in H_2SO_4 -NaCl media were also associated with more prominent Cl_2 gas evolution (Fig. 9). Although the measured values between the two lixiviants differed only during leaching at 50 °C, the concentration reading of the Cl_2 gas detector was observed to reach its maximum value much faster in all H_2SO_4 -NaCl experiments compared to HCl media. The

evolution of chlorine gas was also reflected in the measured solution redox potentials, which quickly reached the value of 1.3 V at 50, 70 and 80 °C (Fig. 10) – the reaction seemingly limiting the redox potential in a similar way as in HCl media. Furthermore, the observed potential drop between 5 and 30 min at 30 °C was significantly smaller in NaCl–H₂SO₄ solution in contrast to either sulfate or chloride media.

Despite the similarities between redox potentials in H_2SO_4 –NaCl and HCl solutions, XRD diffractograms showed a significant difference with respect to manganese compounds found to be present in the resultant leach residues (Fig. 11). The birnessite peak intensities in the residue formed at 30 °C were substantially higher than in HCl media (Fig. 7) and slightly higher in comparison to H_2SO_4 (Fig. 3). Remnants of these peaks were also detected in the 50 °C residue, unlike in the corresponding residues from other lixiviants. This occurrence of the birnessite-type phase indicates that manganese may be more likely to precipitate out of the solution in the initial leaching stages when leached in the presence of both sulfate and chloride ions compared to either H_2SO_4 or HCl alone. Regarding the peaks related to NMC111, the leach residue diffractograms are like those obtained from sulfate and chloride media, *i.e.*, the Li content within the cathode material decreased with increasing temperature and reached almost complete delithiation after leaching at 80 °C.

Based on the results outlined here, the chloride ion source has a significant impact on the leaching process, as the dissolution of Ni and Co significantly improved throughout the reaction time when using a H_2SO_4 -NaCl lixiviant in preference to either sulfuric acid or hydrochloric acid alone. This enhanced active material dissolution was also associated with increased chlorine gas evolution when compared to HCl solutions.



Fig. 8. Dissolution of a) Co, b) Ni, c) Mn and d) Li from NMC111 in 1 M H₂SO₄-NaCl solution at 30, 50, 70 and 80 °C.



Fig. 9. Cl₂ concentration in the reactor gas phase as a function of time in 1 M $\rm H_{2}SO_{4}\text{-}NaCl$ media.

3.4. Significance of chloride-ions in NMC111 leaching

It appears that so far in chloride-based hydrometallurgical leaching studies, Cl₂ gas evolution has only been measured in studies using pure cathode chemicals – commercial products or active material powders manually separated from LIB cathodes – as a raw material (Takacova et al., 2016; Porvali et al., 2019), and there is limited evidence that the reaction occurs in the presence of other reductant species. Thus, it is



Fig. 10. Redox potential vs. SHE in H_2SO_4 -NaCl leaching of NMC111. The equilibrium potentials for MnO_2 precipitation and Cl_2 evolution are indicated by horizontal dashed lines.

uncertain whether Cl_2 evolution occurs to a significant extent in chloride leaching of industrial black mass.

The findings of this study have shown that chloride ions can reduce NMC111 and dissolve the cathode material by forming Cl₂ gas in the process, however, the reaction is slow even at high temperatures when compared to other commonly used reductants like metallic copper (Joulié et al., 2017; Porvali et al., 2020). This indicates that utilizing a chloride-containing lixiviant alone as a reductant is not sufficient for NMC111-type battery waste, and the use of additional or alternative



Fig. 11. XRD diffractograms of pristine NMC111 and leach residues after leaching in 1 M H₂SO₄-NaCl at 30, 50, 70 and 80 °C.

reductants should be preferred. More positively, the presence of chlorides in the lixiviant can prevent manganese losses during leaching by providing an alternative reaction with a redox potential lower than that of MnO₂ precipitation. Chlorine gas is often associated with occupational and environmental hazards due to its toxic properties (Greenwood and Earnshaw, 1997), although with proper mitigation steps, the Cl₂ formed can be safely collected and utilized as an oxidant in other process steps (Crundwell et al., 2011), potentially lowering operating expenses and oxidative chemical usage of the overall process.

Nevertheless, if chlorine gas evolution is to be avoided, inhibitory approaches are also available. The findings detailed here indicate that there was no significant chlorine gas formation during leaching at 30 $^\circ\mathrm{C}$ as the solution redox potential did not reach a sufficient value for the reaction to occur. This can provide a further incentive for the development of low temperature leaching processes, in addition to lower energy consumption and operating expenses. Furthermore, earlier findings indicate that the solution redox potential can be decreased by the addition of external reductants (Peng et al., 2018), the presence of which has also been observed to prevent excessive manganese precipitation (Meshram et al., 2015; Wang et al., 2019), whereas the presence of metallic Fe, Cu and Al - which are often found entrained within LIB black mass - is also known to affect the redox potential and reaction pathway during leaching (Chernyaev et al., 2022). There is also evidence that a high concentration (4 M) of NH₄Cl within HCl media can efficiently inhibit chlorine gas evolution (Yi et al., 2021), although, the use of such a high amount of this type of additive may not be feasible from either economic or environmental standpoints.

4. Conclusions

The current study investigated the impact of chlorides on the leaching behavior of NMC111 cathode material. The dissolution results showed that the choice of lixiviant did not significantly affect leaching efficiencies of Li, Co, Ni or Mn at 30 °C. Nevertheless, considerable differences emerged at elevated temperatures – especially at 80 °C – as manganese precipitated out of H₂SO₄ solutions, whereas both HCl and H₂SO₄–NaCl solutions generated substantial amounts of Cl₂ gas, confirming the hypothesis of chlorine gas evolution as an interaction between battery cathode materials and Cl⁻ ions. Consequently, this chlorine gas evolution resulted in increased Co and Ni dissolutions, especially in H₂SO₄–NaCl solutions, presumably due to the higher reactivity of chloride salt solutions towards the cathode material compared to HCl.

XRD analyses of the leach residues showed a steady decrease in the NMC111 lithium content with respect to increasing temperature in all lixiviants. Furthermore, a manganese-containing compound – Li₄M- $n_{14}O_{27}$ ·xH₂O – was identified in all leach residues after 2 h of leaching at 30 °C, whereas in H₂SO₄ solutions, increased temperatures caused further manganese precipitation as MnO₂. In the context of a recycling process treating black mass, this could result in manganese losses as the precipitate would likely be mixed with other insoluble components like graphite and plastics in the leach residue, making subsequent Mn recovery difficult. In chloride-containing solutions, MnO₂ precipitation was not evident despite the calculated redox potentials predicting the opposite. This suggests that the presence of chloride ions inhibits manganese oxide precipitation by either (i) favoring soluble manganese due to complexation with chloride ions, (ii) allowing temporary

precipitation of manganese oxides followed by fast reduction back to Mn^{2+} via associated Cl₂ gas evolution, or (iii) providing an entirely alternative reductive reaction for the cathode material. This indicates that chloride additions to the lixiviant could prevent manganese losses by keeping the element soluble throughout the leaching process.

Despite the significantly increased Ni and Co extractions achieved with H_2SO_4 –NaCl solutions, the reductive power of chlorine gas evolution towards NMC111 was not great even at a high temperature of 80 °C, as less than 60% of transition metals dissolved over the course of the 2-hour reaction time. Moreover, maintaining such a high reaction temperature would require unnecessarily high amounts of energy compared to the associated benefits. Therefore, it is speculated that the use of high temperatures and chloride additions without external reductants may not provide the best holistic operation strategy for industrial NMC leaching, but rather that the use of additional reductants – in the presence or absence of chlorides – is a necessity. Thus, the use of lower reaction temperatures along with external reductants is suggested to be a more beneficial strategy for NMC leaching in terms of energy and material efficiency.

CRediT authorship contribution statement

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

Declaration of Competing Interest

The authors 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.

Acknowledgements

This research has been funded by BATCircle2.0 project (Business Finland grant number 44886/31/2020) and Finnish Steel and Metal Producers' Fund. This work also made use of RawMatters Finland Infrastructure (RAMI) based in Aalto University and funded by the Academy of Finland.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mineng.2023.108244.

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