



# Article The Effect of a Molasses Reductant on Acetic Acid Leaching of Black Mass from Mechanically Treated Spent Lithium-Ion Cylindrical Batteries

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Abstract: Recovery of valuable metals from end-of-life cylindrical lithium-ion batteries (LiBs) by leaching using acetic acid in the presence of an organic reductant is a promising combination to overcome environmental concerns that arise from employing inorganic reagents. This study investigated the effect of using molasses as a reductant in acetic acid leaching of a mixture of cathode and anode materials (black mass) prepared using mechanical treatments from spent LiBs. The effects of temperature, solid/liquid ratio, stirring speed, and acid concentration on the leaching of target metals (Co, Ni, Mn, and Li), current collector metal foil elements (Al and Cu), and Fe from the battery casing, with and without reductant, were investigated to obtain the optimum leaching conditions. The effect of adding the molasses at the start of leaching and after 1 h of leaching was tested. Acid leaching without molasses extracted the target metals Li, Ni, Co, and Mn with an efficiency <35% for all leaching parameters. However, the Al and Fe extractions increased as the acid molarity increased. Molasses addition at the start of leaching increased the extraction of the target metals to >96% at temperatures >50 °C. This is likely due to oxidation of the reducing sugars in the molasses that reduced the insoluble Co(III), Ni(III), and Mn(IV) components to soluble Co(II), Ni(II), and Mn(II) species, respectively. The kinetics of Co extraction in the presence of molasses were analysed, which has indicated that the rate-determining step in the Co leaching process is the reduction of Co(III) on the surface of particles in the black mass. Excess molasses can precipitate out target metals, especially Co, due to the presence of oxalic acid in the molasses. The reducing effect precipitated Cu(II) to Cu<sub>2</sub>O, and could further reduce Co to metal, which suggests that leaching with the optimum dosage of acetic acid and molasses may selectively precipitate copper.

Keywords: recycling; LiB; acetic acid; molasses; precipitation; environmentally friendly

# 1. Introduction

Recycling end-of-life lithium-ion batteries (LiBs) has the potential to create a sustainable resource of metals for new batteries. This closed-loop recycling system would complement the demand for lithium (Li), cobalt (Co), nickel (Ni), and manganese (Mn) from primary sources for cathode materials [1]. Recovery of other battery metals (aluminium [Al], iron [Fe], and copper [Cu]) can also support a circular economy based on LiB recycling [2]. LiB recycling also reduces the environmental impacts of disposing of spent battery waste in landfills [3].

Current industrial-scale LiB recycling predominantly uses a pyrometallurgy process, which is a mature, simple-to-operate, and high-productivity approach. The hightemperature process (>1400 °C) [4] typically uses a smelting furnace to burn off materials from the battery outer casing, the carbon anode, the plastic separator, the binder, and electrolytes [5]. The process can be used for any battery chemistry configuration and eliminates the need for mechanical pre-treatment to dismantle or shred the LiBs [3]. Products



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). from the process are nickel (Ni), cobalt (Co), copper (Cu), and iron (Fe) alloys and slags of Li, Al, Mn, Fe, and Ca. Further slag treatment involving salt-roasting followed by water leaching can recover Li from the slag [6,7]. However, lithium recovery from slag is not yet economical, and the slag is currently often used in building aggregate [8]. In summary, the pyrometallurgical LiB recycling process is capital-intensive, has high energy use, requires treatment of the off-gas, and does not recover all the elements.

To address issues with pyrometallurgical recycling, hydrometallurgical processing of LiBs is being investigated. The technique is less energy-intensive, has lower capital cost [9], and recovers more valuable materials [10]. Lithium is relatively easy to extract in a hydrometallurgy process [3]. Pre-treatments, including discharging of residual battery charge and mechanical treatment, such as milling or shredding, are required prior to the leaching process in order to obtain a high recovery [11]. Although the whole hydrometallurgy-based process is longer than the pyrometallurgical ones, this technique has the potential to produce high-purity elements from the cathode and also from the foil current collectors as side products.

Recent literature has reported on the use of organic acids for leaching metals from the cathode material of spent LiBs. This is being investigated because leaching with inorganic acids results in high recoveries of target metals (>90%), which predominantly employed  $H_2SO_4$  1–2 M,  $H_2O_2$  1–5% v/v, and 40–50 S/L in a 1–2 h process [5]. However, the process has disadvantages, such as low metal selectivity, mineral acid waste, and generation of hazardous gases (Cl<sub>2</sub>, NOx, SOx) [12]. Recent studies have investigated citric acid [13], iminodiacetic acid, maleic acid [14], DL-malic acid [15], nitrilotriacetic acid, and adipic acid [16] as alternative lixiviants due to their ability to be recycled [12] and to avoid toxic gas emissions during the leaching process [17]. However, the high cost of these acids has stimulated studies using glycine [18] and lemon juice [19] as natural acid resources. Another study used acetic acid due to its low cost and selectivity to Al remaining in its element form after leaching rather than dissolving [12].

Recoveries from organic acid leaching can potentially be increased with the addition of a reductant that reduces insoluble higher-valence oxides to a soluble compound, such as Co(III) to Co(II) [20]. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is the most common reductant used in current research, but it can be over-consumed due to its natural decomposition at a temperature higher than 60 °C [21]. Hydrogen peroxide also oxidises metals from the current collectors and the casing [22] when the concentration is in excess [23]. Sulphurbased salt (NaHSO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, or Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>) reductants are an alternative, which in a solution can generate SO<sub>2</sub> and introduce Na into the system [21,24]. Ascorbic acid, a weak acid and a mild reducing agent, can also be used as a reductant [16,25]. However, reducing agents like H<sub>2</sub>O<sub>2</sub>, NaHSO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and ascorbic acid are relatively costly [26]. Iron from the battery casing is a potential reductant that is already available in the system. It can also catalyse reactions in which Al and Cu from current collector foils act as reductants [26]. A pH below 2.5 is required to use iron as a reductant, as it precipitates at a higher pH [27]. This low pH would require a large quantity of neutralisation chemicals to be added before purification, which typically occurs at a pH of 4–9 [28].

Glucose has also been reported to be a good reducing agent for leaching the cathode materials in inorganic acids [29–31]. It is a low-cost, non-hazardous [32], and stable reducing agent [33]. Glucose could potentially be sourced from food factories' waste [30] or from cane molasses, which is a byproduct of sugar production [34]. A study has reported the use of molasses in reductive leaching of manganese ores [35], which also increased the dissolution of trace metals (Co, Ni, and Zn) [36]. These results indicate that molasses could be a potential reductant for the reductive leaching of cathode material.

Optimum leaching conditions are required to obtain high extraction of valuable metals for an economically viable cost and energy input [37]. In general, increasing the lixiviant and reductant concentrations [13,38], leaching temperature [25], and stirring speed [39] lead to the acceleration of chemical reactions, which enhances the leaching efficiency. However, the literature has reported that using organic acids in a solid/liquid (S/L) ratio <50 g/L

is required to obtain high metal extractions [16,19,40]. This low pulp density is not likely to result in economically feasible industrial applications [41]. A higher pulp density of up to 100 g/L was found to achieve the complete extraction of Li, 80% of Co, and 31% of Ni when citric acid in excess of 1.3 was used [17]. Further investigation is needed into the conditions under which a high pulp density in organic acid leaching can result in near complete extraction of all metals from cathode material.

Most studies in the literature have reported manually dismantling the batteries to avoid leach feed contamination from metals in the current collector foils and the steel casing (Al, Fe, and Cu) [42,43]. However, the manual technique is not economically viable for industrial-scale recycling [31,44]. Thus, this study used black mass (a mixture of cathode and anode materials) from mechanically treated, spent cylindrical LiBs that also contained metals from the current collectors (Al and Cu) and the casing steel, as this is more likely to reflect the product of economically viable industrial-scale pre-treatment. Acetic acid and molasses were used as the leaching lixiviant and reductant, respectively. To the best of our knowledge, there are no reports in the literature of using this combination for leaching mechanically produced black mass. The study investigated the effect of molasses on the extraction efficiency of the valuable cathode metals and, in particular, the leaching mechanism of Co. This study also investigated the effect of adding molasses to the leaching process at the beginning of the process and an hour after the start of leaching. The acetic acid-leaching behaviours of both the Li, Co, Ni, and Mn from the cathode material and the other metal components (Al, Cu, and Fe) at a S/L ratio >50 g/L, with and without reductant, were compared.

## 2. Materials and Methods

#### 2.1. Preparation and Characterisation of Leach Feed

A total of 18650 spent cylindrical batteries from laptops from a range of manufacturers were supplied by a local WEEE processing facility (Total Green Recycling Co., Ltd., Perth, WA, Australia). The mixed LiB waste was first discharged and then mechanically treated to obtain a black powdered mass of combined cathode and anode material for leaching. The leach feed preparation process involves discharging whole batteries by immersion in NaOH solution for 24 h, followed by a cut milling and attrition process to liberate the active electrode materials from current collector foils and plastic separators, and separation of the fine fraction by sieving. The particle size of the black mass powder used as feed in the leaching tests was  $<180 \mu m$ . Representative powder masses were obtained by sampling the bulk black mass with a rotary sample divider (SGS Australia). The samples used in the leaching tests had no heating pre-treatment before the leaching process. The mineral composition of a sample of the feed material was examined using an X-ray diffractometer (XRD CuK $\alpha$ -GBC Emma). Surface morphology studies and detection of trace elements were performed using an ultrahigh-resolution SEM, Tescan Clara. To determine the chemical composition, a sample was digested using aqua regia and diluted in an HCl solution. The Co, Li, Mn, Ni, Cu, Fe, and Al content in the sample was assayed with an ICP OES instrument (Thermo Fisher Scientific iCAP 7600 Duo). Carbon content was measured using a Thermo Scientific EA isolink without IRMS.

#### 2.2. Leaching Tests

The acid-leaching tests in this study used acetic acid from UNIVAR (Ajax Finechem). The leaching conditions used to assess the effect of using molasses as a reductant were determined by conducting initial leaching tests without a reductant and determining the process parameters that produced the highest leaching efficiency of valuable metals (Li, Co, Ni, and Mn) from the ranges: temperature (50, 70, 90 °C); solid/liquid (S/L) ratio (50, 100, 150 g/L); stirring speed (200, 400 rpm); and molarity (1, 2, 3 M). All leaching tests were conducted in a 250 mL three-neck round-bottom glass reactor for two hours. The reactor was placed in an oil bath to maintain the required temperature and connected to a condenser to minimise evaporation. During the leaching process, a magnetic stirring

bar set to the required stirring speed was used. The optimum leaching conditions were then used in leaching tests with local cane molasses (Blue Label) also added, with a fixed concentration of 75% w/v. An additional stirring speed of 300 rpm was assessed for the reductive leaching tests. In one set of tests, the molasses was added to the leach reactor at the start of leaching, and in the second set of tests, the molasses was added 60 min after the start of leaching.

A 1 mL sample of leach solution was withdrawn 5, 15, 30, 45, 60, 90, and 120 min after the start of leaching, and the pH and oxidation–reduction potential (ORP) were measured. The sample was then diluted and syringe-filtrated for elemental analysis using ICP-OES. Solid residues were filtered from the pregnant leach solution (PLS) at the end of each leaching test using a Whatman filter paper and washed with water before being dried overnight. The residues were examined by SEM-EDS for surface morphology. The valence of Co, Ni, Mn, and Cu on the surface of residue particles was determined using the X-ray photoelectron spectroscopy (XPS) machine from Kratos AXIS Ultra DLD (Kratos Analytical). The chemical composition of the dried residues was determined using the same method as for the feed material.

The leaching efficiency ( $\eta$ L) was calculated using Equation (1), where C<sub>d</sub> is the concentration of metal d dissolved in the leach solution after 120 min; V is the volume of leach solution after 120 min; W<sub>d</sub> is the wt% of metal d in the leach feed; and m is the total weight of the leach feed, and d represents that of Li, Ni, Co, Mn, Al, Fe, and Cu in the sample.

$$\eta L_d = (C_d \times V) / (W_d \times m) \times 100\%$$
<sup>(1)</sup>

## 2.3. Thermochemical Modelling

The thermochemical stability area of different species in the aqueous solution from the leaching process without and with reductant was determined by constructing Eh-pH diagrams using HSC software 7.1. The chemical system was specified for the diagram calculation by selecting elements and species of each element, and the preferred temperature range was determined. The diagram was calculated using actual concentrations of the observed elements determined by the AAS analyses of leach solutions samples in mg/L, which were converted to mmol/kg H<sub>2</sub>O. Eh-pH measurements recorded during the leaching process were then plotted onto the Eh-pH diagrams to establish the likely species of the elements present in the leaching system.

#### 3. Results and Discussion

#### 3.1. Characterisation of the Leach Feed

The identification of peaks in the XRD spectrum in Figure 1a shows that the leach feed contained carbon from the anode, materials from the various cathodes (which were lithium cobalt oxide (LiCoO<sub>2</sub>–LCO) and lithium-nickel-cobalt-manganese oxide (NMC)), and a trace of aluminium. The surface morphology of the sample in Figure 1b confirms the presence of the material detected using XRD, as well as some copper (Cu) and trace amounts of Fe, Si, and Al. Table 1 shows that the dominant element in the sample was Co (24%), which is consistent with the majority of cathode types in the sample being LCO. Lithium content was most likely from the element present in the cathode material powder, as the lithium salts from electrolytes in the batteries were mostly dissolved in the water during the mechanical pre-treatment. Iron in the sample was most likely from the LiFePO<sub>4</sub> cathode material and the battery casing steel. Other materials, namely, oxygen, binder (PVDF), and trace elements, are likely present in the feed and are counted as others in Table 1.

Table 1. Chemical composition of the <180 µm black powder.

Element	Al	Fe	Cu	Со	Ni	Mn	Li	С	Others
Wt%	1.6	2.5	1.1	24.6	3.9	2.9	3.9	33	26.5



Figure 1. Sample identification using (a) XRD and (b) SEM-EDS analysis.

## 3.2. Leaching in the Absence of Reductant

In the initial leaching experiments, the leaching behaviours of Li, Co, Ni, Mn, Al, Fe, and Cu were determined in the absence of molasses as a reductant for different process parameters.

## 3.2.1. Effect of Molarity and S/L Ratio

Leaching efficiencies of metals from cathode materials were not significantly affected by the molarity and S/L ratio, as can be seen in Table 2. However, the acid concentration and S/L ratio had a notable effect on Al and Fe leaching efficiencies, which increased as the acid concentration increased or the S/L ratio decreased. Figure 2a shows that the 1 M acetic acid solution had a higher pH value (up to 3.9) than the other molarities. Al and Fe start to precipitate in this pH range, as reported from a previous precipitation study of those metals from spent LiB material [45]. The 1 M acetic acid solution had the lowest Eh values, as shown in Figure 2b, which indicates a lower oxidation reaction occurred at this molarity than at higher acid concentrations. This likely means that the Al and Fe did not dissolve well at the high pH of the 1 M solution. The increasing Eh value (Figure 2b) as the acid concentration increased indicates higher oxidation of Al and Fe in the solution, as the Eh value would not have been different due to the target cathode metals, whose extraction was not significantly affected by the molarity.

Molarity (M)	Temp (°C)	S/L (g/L)	Stirring Speed (rpm)	pH Final	%Li	%Co	%Ni	%Mn	%Al	%Fe	%Cu
1				3.92	30	20	26	29	33	1	95
2		100	100	3.41	31	20	28	29	77	32	92
3	90	100	400	3.12	31	20	31	30	80	39	92
4				2.83	30	20	33	29	80	44	85
2	50	100	100	3.29	25	17	23	28	77	31	86
3	70	100	400	3.12	27	19	26	30	76	37	86
2	00	50	100	2.83	29	19	36	32	83	42	85
3	90	150	400	3.25	30	20	33	31	73	20	88
3	90	100	200	3.02	29	19	32	30	81	39	84

**Table 2.** Leaching efficiency (%) of metals from cathode material, current collector foils, and Fe in the absence of reductant.



**Figure 2.** Changes of pH (**a**) and Eh (**b**) during the leaching in the absence of reductant in various acid concentrations, and plots of Eh-pH (colored lines and circles) for leaching in 1 M acid on diagram of Cu (**c**) and Fe (**d**). The blue dotted lines indicate the stability area of water and the black solid lines outline the stability region of ions.

Plausible reactions during the leaching process of LCO and NMC material are described in Equations (2) and (3). Both equations are proposed from balancing the relevant chemical reactions, in which partial dissolution of Co, Ni, and Mn occurred, as reported in Table 2. The detected higher oxidation state of Co, Ni, and Mn after leaching in the absence of reductant will be reported in the XPS analysis. Equations (4)–(6) are the proposed reactions of current collector foils (Cu and Al) and Fe from the casing with the acetic acid using chemical balance equations of HSC 7.1.

$$4LiCoO_{2} + 6CH_{3}COOH(aq) \rightarrow 4CH_{3}COOLi(aq) + Co(CH_{3}COO)_{2}(aq) + Co_{3}O_{4} + 0.5O_{2} + 3H_{2}O$$
(2)

$$12\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2(s) + 22\text{CH}_3\text{COOH}(aq) \rightarrow 12\text{CH}_3\text{COOLi}(aq) + 2\text{Ni}(\text{CH}_3\text{COO})_2 (aq) + \text{Co}(\text{CH}_3\text{COO})_2 (aq) + 2\text{Ni}(\text{CH}_3\text{COO})_2 (aq) + (3)$$

$$2\text{Mn}(\text{CH}_3\text{COO})_2 (aq) + \text{Co}_3\text{O}_4 + \text{Mn}_2\text{O}_4 + \text{Ni}_2\text{O}_3 + \text{O}_2(g) + 11\text{H}_2\text{O}(aq)$$

 $2Cu + 4CH_3COOH(aq) + O_2(g) \rightarrow 2Cu(CH_3COO)_2(aq) + 2H_2O(aq)$ (4)

$$2Al + 6CH_3COOH(aq) \rightarrow 2Al(CH_3COO)_3 (aq) + 3H_2(g)$$
(5)

$$Fe + 2CH_3COOH(aq) \rightarrow Fe(CH_3COO)_2(aq) + H_2(g)$$
(6)

The copper leaching efficiency was the highest (84–95%) of all the metals in the leaching process without reductant (Table 2). Copper leaching requires oxygen to be dissolved in the acid (Equation (4)). Based on reactions 2 and 3, oxygen gas is likely generated during oxidation of the cathode material as a result of the lithium dissolution. The highest extraction of copper (for 1 M acid) indicates that the oxidative environment of the leaching system supports copper dissolution. The Eh-pH diagram in Figure 2c for Cu in 1 M acetic acid indicates a thermochemically suitable condition for Cu dissolution in the acid where the plot of Eh-pH on the chart shows that Cu is in the aqueous form of Cu(CH<sub>3</sub>COOH)<sub>2</sub>. On the contrary, the plot of Eh-pH on the diagram in Figure 2d shows that Fe can be expected to precipitate as  $Fe_2O_3$ . The moderately decreasing Cu extraction with increasing acid concentration is likely because Al and Fe metal dissolution was enhanced at the lower pH.

However, the increasing molarity did not significantly affect the leaching efficiency of target metals (Li, Ni, Co, Mn), which ranged from 20 to 31%, as shown in Table 2. A previous study reported that the LiB waste-leaching process consumed significant amounts of acid [46]. Lithium dissolution during the leaching process increases as the acid concentration increases [28] because the hydrogen (H<sup>+</sup>) ions oxidise lithium easily [47]. The high pKa of acetic acid (4.8 at 25 °C) [29] results in partial dissociation of the acid in water into acetate ions to donate the H<sup>+</sup> ions. The plausible reactions of metal foils (Al and Cu) and Fe during the leaching with acetic acid in Equations (4)–(6) shows that those metals likely consumed the available H<sup>+</sup> ions. An enhanced leaching efficiency of those metals as the acid concentration increases (see Table 2) shows the high consumption of H<sup>+</sup> ions. Thus, the partially dissociated acid is seemingly insufficient to leach all the elements from the cathode material.

Moreover, different oxidation states of the target cathode metals Co, Mn, and Ni in the leach feed were detected based on the fitted peaks for the XPS spectra in Figure 3. The fitted peaks (coloured) in the XPS spectra for Co, Mn, and Ni (Figure 3a,c,e) indicate a high oxidation state ((III) or (IV)), which is resistant to acid leaching. A previous study [48] also reported high oxidation states of those elements from XPS analysis of NMC batteries. The higher intensity of Co peaks in Figure 3 compared to other elements is due to the dominance of LCO in the feed sample, which is consistent with the chemical compositions in Table 1. In the leach residue, the cobalt valence increased, and there was a shift from Co(II) to  $Co_3O_4$ , as indicated by the broad satellite (blue curve) in Figure 3b, which is a typical spectral characteristic of  $Co_3O_4$  in LCO batteries [49]. The increasing intensity and decreasing binding energy of all fitted peaks in Figure 3b,d,f after leaching indicates the changes in the element's valence electron charge to a higher state. Apart from the issue that a lack of H<sup>+</sup> ions causes low dissolution of these metals, the high oxidation state of target metals points to the need for a reductant to reduce the high-valence elements to valence states that are more readily dissolved in the acid.



**Figure 3.** Fitted photoelectron spectra of Co, Mn, and Ni, respectively, on the feed (**a**,**c**,**e**) and residue after leaching in 3 M acetic acid without reductant (**b**,**d**,**f**). The black curve represents the raw data, and coloured curves correspond to fitted peaks.

## 3.2.2. Effect of Temperature

Increasing the temperature of the leaching process did not significantly affect the dissolution of target metals. However, the slight increases with temperature of the leaching

efficiencies in Table 2 show that the leaching process involves endothermic reactions. A previous leaching study with acetic acid reported a similar result on the effect of temperature [12]. Moreover, acids dissociate more at a higher temperature, releasing more H<sup>+</sup> ions to enhance metal dissolution. The Li extraction increased as the acid concentration rose, resulting in some oxygen more likely released (Equations (2) and (3)) from the oxides at higher temperatures. The process supported the Cu oxidation being higher at 90 °C. Given the observed effect of temperature, the subsequent leaching test work with a reductant was conducted at 90 °C.

## 3.2.3. Effect of Stirring Speed

Increasing the stirring speed only affected the leaching efficiencies of Li and Cu, as reported in Table 2. The high stirring speed did not significantly affect the extraction of target metals, as discussed in Section 3.2.1. Partial dissociation of acetic acid can only leach the target metals to a maximum value range of 20–33%. Applying agitation during the leaching process can enhance liquid film diffusion, which can increase the transference rate of the solution to a particle's surface [38]. The position of lithium in the LCO structure between the Co-O octahedral configurations (Figure 4) [50] and the weaker interaction of lithium with oxygen ions compared to the Co-O interaction [51] leads to higher dissolution of Li, which contributes to the higher oxidation of Co. The higher agitation speed likely enhanced the contact of H<sup>+</sup> ions from the solution with Li on the surface. In the dissolution of Cu, the higher stirring speed increases the mass transfer of the oxygen gas [52] generated from reactions 2 and 3 to the liquid phase for copper oxidation. Although low Cu dissolution is preferred in general, given the cathode materials are the main target of LiB recycling, a stirring speed at 400 rpm was selected for subsequent leaching work in the presence of a reductant to minimise the impact of low diffusion through the liquid film on the efficiencies.



Figure 4. The structure configuration of LiCoO<sub>2</sub>.

## 3.3. Leaching with Reductant Addition

The leaching results without reductant indicate that a temperature of 90 °C and a stirring speed of 400 rpm are likely to produce the greatest extraction efficiencies for the target metals. The molarity does not have a major impact on the target metal leaching efficiencies, but as the aim is to achieve high efficiencies at a higher S/L ratio (100 g/L), the molarity of 3 M acetic acid was selected for the test work with a reductant, as this produced slightly higher efficiencies for all target metals. An initial comparison of 75% *w*/*v* molasses amounts (10, 20, and 30 mL) was conducted to determine which amount results in the highest Co extraction. Molasses was added to the leaching system after one hour, until which point the leaching reaction of the feed was with acetic acid solution only. The increased leaching efficiency of Co after the molasses addition reflects that the reductant effectively reduced the relatively more stable high-oxidation-state Co to a more readily

dissolved lower-oxidation-state species. Further explanation of the molasses effect on the target metal extraction is reported in the following discussion.

The comparison in Figure 5 shows that Co dissolution decreased as the molasses amount increased. The molasses composition in Table 3 shows that the reductant contained reducing sugar and organic acids, as detected using HPLC analysis. The oxalic acid content in molasses likely partially precipitated Co, as sediment containing Co was formed in the PLS after filtering out the residue and allowing the solution to cool down. The sediment formation was greatest at the highest molasses amount (30 mL), as shown in Figure 5b. The sediment was dissolved in a HCl solution for ICP analysis, which determined the sediment composition was mostly Cu (21 g/L) and Co (10 g/L), with < 2 g/L of each of Li, Ni, and Mn and < 1 g/L of each of Fe and Al. The results indicate that an excess amount of molasses can precipitate out not only Co, but also Cu. Thus, further investigations were performed with 10 mL of molasses slurry as the reductant.



**Figure 5.** (a) Co leaching efficiency during the reductive leaching in 3 M acetic acid with 10, 20, and 30 mL molasses added after 1 h of acid leaching at 90  $^{\circ}$ C, 400 rpm, and 100 g/L, and (b) filtered sediment from the leaching using (1) 10 mL, (2) 20 mL, and (3) 30 mL.

Component	Content				
Total Sugars	61.3 g/100 g				
Oxalic Acid	29 g/L				
Malic Acid	144 g/L				
Lactic Acid	46 g/L				
Citric Acid	109 g/L				

**Table 3.** Content of sugar and organic acids in the 75% w/v molasses.

In the next experiments, 10 mL of diluted molasses (75% w/v) was added to the leaching system at the beginning of the leaching, and in a second experiment, the molasses was added after an hour of acidic leaching. The results indicated that postponing the molasses addition until after an hour of acidic leaching did not have a significant effect. The leaching efficiency of Co, Li, Ni, and Mn ranged from 96 to 99% for both reductant addition times, as shown in Figure 6a–d. The highest metal extraction was reached within 30 min of the start of the leaching process for all target metals when the molasses was added at the beginning. When the molasses was added 60 min after the start of acid leaching, the maximum metal extractions were not reached until 45 min after the addition of the molasses. The results potentially indicate that different mechanisms were occurring during the two leaching processes.



**Figure 6.** Leaching efficiency of (a) Co, (b) Li, (c) Ni, (d) Mn, (e) Al, (f) Fe, and (g) Cu during the reductive leaching using 3 M acetic acid and 10 mL of 75% w/v molasses in comparison to molasses addition time, at the beginning and after 60 min of leaching. The black dotted lines in each figure represent the addition time of molasses in the system.

The rapid increase in Li extraction to ~99% when molasses was added at the beginning of the leaching indicates the presence of a significant number of  $H^+$  ions in the leaching system. The dependency of the lithium dissolution on hydrogen ions is shown by Equations (2) and (3), which are proposed for this system.  $H^+$  ion sources could include the fructose, glucose, and organic acids in the molasses.

The reducing sugars, fructose, and glucose are commonly found in cane molasses [34]. The oxidation reactions of glucose and fructose likely reduce the metal oxides. Both sugars are reducing sugars [36,53] because their aldehyde functional group is easily oxidised to carboxylic acid in an acidic solution in the presence of strong oxidants. The milled LiB black powder contains Co(III), Mn(IV), and Ni(III), which can act as strong oxidants for aldehydes. During the oxidation of aldehydes, metal oxide reduction occurs, producing the readily dissolved elements (+2). Plausible reduction reactions for Co, Mn, and Ni with aldehydes are given in Equations (7)–(9).

$$RCHO + Co_3O_4 + 6H^+ \rightarrow RCOOH + 3Co^{2+} + 3H_2O$$
(7)

$$RCHO + Mn_2O_4 + 6H^+ \rightarrow RCOOH + 2Mn^{2+} + 3H_2O$$
(8)

$$RCHO + Ni_2O_3 + 4H^+ \rightarrow RCOOH + 2Ni^{2+} + 2H_2O$$
(9)

XRD spectra of the leaching residue from the 3 M acetic acid leaching with molasses addition at the beginning of the leaching in Figure 7a did not detect any cathode oxide materials. Graphite is the dominant mineral phase in the residue, with a very high intensity compared to the leaching feed (Figure 1a). The composition of the residue in wt% is 0.03% Li, 0.27% Co, 0.26% Ni, 0.04% Mn, 1.2% Cu, 0.54% Al, 1.75% Fe, and 83% C. This result demonstrates that the molasses component has succeeded in reducing the high-valence metals to be dissolved.



**Figure 7.** Identification of leaching residue of acetic acid 3 M with molasses using (**a**) XRD analysis, and (**b**) EDS mapping detection on aluminium oxide and aluminium silicate.

Apart from metals in the cathode material, the molasses addition did not affect the Al dissolution. Figure 6e shows that Al had no further dissolution after molasses addition. The maximum leaching efficiency of Al to about 80% was because of the presence of aluminium oxides and silicates (Figure 7b), which hardly dissolved in a weak acidic solution. A previous study also found similar minerals in the leaching residues of the black mass with sulphuric acid [47]. The results show that 3 M of acetic acid dissolved Al easily, with or without reductant (Figure 6e).

Iron and Cu dissolution profiles behave differently after molasses addition. Iron dissolution increased after the reductant addition to the highest extraction of 70% (Figure 6f), but the dissolved Cu reduced to about 20% (Figure 6g) simultaneously. In the leaching with the absence of reductant, Cu was dissolved, as the oxygen was likely generated (Equations (2) and (3)) from the partial Li dissolution (30%) process, as reported in Table 2. After molasses addition, the aldehydes from reducing sugars (glucose and fructose) in molasses can reduce Cu(II) to Cu(I) with the proposed reaction in Equation (10) [54].

$$RCOH + Cu^{2+} \rightarrow ROOH + Cu_2O \tag{10}$$

It is, therefore, proposed that the reductant addition intensified the Li dissolution and oxygen generation (according to Equations (2) and (3)). The additional oxygen could partly

oxidise the unstable Cu(I) to Cu(II). A subsequent reaction between Cu(II) and Fe possibly occurs due to ionic transfer, which results in the sedimentation of Cu(II) to Cu metal and the dissolution of Fe to Fe(II). This could explain the enhanced iron dissolution after the molasses addition.

The final pH of the reductive leaching environment increased to 4 (Figure 8a), and the Eh value decreased to around 150 mV (Figure 8b). The Eh-pH simulation for Fe (Figure 8c) shows the ferrous ions regions, which represents Fe dissolution. The Cu Eh-pH simulation in Figure 8d indicates the possibility of the formation of cuprous Cu in the reductive environment. From SEM images, the Cu metal was not detected in the residue after leaching without reductant (Figure 8e), but it was detected in the residues of reductive leaching (Figure 8f). The copper in the residue after leaching without reductant was 0.2%, and with reductant, it was 1.2%. This supports the proposed reaction series for Cu precipitation during the leaching process with molasses reductant.

The final extraction of the target metals was similar for molasses addition at the start of leaching and one hour after the start of leaching, but the times after molasses addition to reach maximum extraction were different. The Eh values (Figure 8b) dropped rapidly from 600 mV to about 150 mV when molasses addition was an hour after the start of acid leaching. When molasses was added at the start of leaching, a lower Eh (400 mV) was measured after 5 min of leaching, and this fell to a similar ORP potential (150 mV). However, the time for this decrease was 15 min less than the time when molasses was added an hour after the start of leaching. These results indicate that after the addition of molasses, a minimum oxidation time is required before the aldehyde component starts reducing the high-valence metal oxides.

As discussed earlier, the weak acid content in molasses (Table 3) may supply H<sup>+</sup> ions for oxidation, which could increase lithium dissolution. Therefore, it may be possible to achieve similar results to those obtained with 3 M acetic acid as the lixiviant using a lower strength of 2 M.

Table 4 indicates that using 2 M acetic acid, the highest leaching efficiencies of the target metals Li, Ni, and Co were >98%, and for Mn, it was >96% (at 90 °C, 100 g/L solid/liquid ratio, and 400 rpm stirring speed). The composition of the leach solution is 26 g/L Co, 4.1 g/L Li, 3.7 g/L Ni, 2.6 g/L Mn, 1.4 g/L Al, 2.1 g/L Fe, and 0.3 g/L Cu. In a test with the pulp density increased to 150 g/L, the Co, Ni, and Mn extractions were reduced to 69%, 25%, and 72%, respectively. However, Li extraction was still above 97%, which indicates that the number of H<sup>+</sup> ions was still sufficient for delithiation. An insufficient amount of reductant for this amount of black mass likely caused the lower extractions of Co, Ni, and Mn. Reducing the stirring speed to 200 rpm also reduced the leaching efficiencies for Co, Ni, and Mn by about 11%. This result is consistent with the earlier discussion on the non-reductive leaching process, where it was suggested that a higher stirring speed increased the contact of reagents and particles by minimising the boundary layer on the surface of the particles. Lowering the leaching temperature to 70 °C decreased the leaching efficiency of Li, Co, Ni, and Mn, with the greatest reduction observed for Li and Co, which had a leaching efficiency of 50% after 180 min of leaching. A higher temperature may enhance the extraction of metals by promoting the oxidation of the aldehydes functional groups in the reducing sugars [55].

**Table 4.** Leaching efficiency of Li, Co, Ni, Mn, Al, Fe, and Cu using 2 M acetic acid and 10 mL of molasses 75% *w/v* added at the beginning of the leaching.

Temp (°C)	S/L (g/L)	Stirring Speed (rpm)	Li %	Co %	Ni %	Mn %	Al %	Fe %	Cu %
90	100	400	99.8	99.8	99.3	96.4	71.4	56.5	25.6
90	150	400	97.4	69.7	26.5	72.2	2.8	23.3	3.3
90	100	200	92.1	88.0	88.8	83.3	65.8	51.7	23.8
90	100	300	93.8	89.6	84.1	94.2	54.4	56.3	21.9



Table 4. Cont.

**Figure 8.** Solution (**a**) pH values and (**b**) Eh values during leaching for the two molasses addition times, the Eh-pH simulation of Cu (**c**) and Fe (**d**) for reductive leaching, and EDS Cu mapping on residues after leaching without reductant (**e**) and with molasses (**f**).

From the best results in Table 4, a flow chart for the leaching process of prepared feed with discharging and mechanical treatment is presented in Figure 9. The leaching process generated residue predominantly comprising carbon, as reported in the earlier discussion. This residue can be processed further to extract the carbon for potential reuse as the anode material. Further separation of impurities elements, including Al, Fe, Cu, and others, is recommended to recover the target elements from the leach solution of sufficiently high purity that meets the requirement for cathode material manufacture. Precipitation of Al and Fe with NaOH solution [43,45,56] is widely employed. However, a new precipitant than NaOH, namely, diammonium hydrogen phosphate (DAP) [57], and complexation with phytic acid after precipitation with NaHCO<sub>3</sub> [58] are reported as the alternative. The copper concentration in the solution in this study is lower than Al and Fe, which may decrease during the precipitation of Al and Fe. An electrodeposition process using a stainless steel cathode and alloy electrode as anode material can selectively recover copper from Ni, Co, and Mn in the leach solution of spent LiB [45].





3.4. Analysis of the Leaching Kinetics

Kinetic analysis of metal dissolution in acetic acid and molasses can assist in determining the rate-limiting step that controls the reaction. Co, the primary target metal from black mass, was selected for the kinetic study. The dissolution reaction of solid particles in a solution containing acid and reductant is a non–catalytic heterogeneous reaction. During the reductive leaching process, the leaching efficiency of Co increased as the temperature increased (Table 4 and Figure 10a). Under the most efficient reductive leaching conditions, no Co was detected in the residue (Figure 7a). These results suggest that Co-containing particles shrink with time during the leaching process. The surface morphologies of particles in the residues after the leaching process at 30, 50, 70, and 90 °C in Figure 10b show that the surface of particles containing Co exfoliated to different degrees, and slits were created. The slits on the particle surface are more profound at higher temperatures. The exfoliation continued during the leaching process until most particles had shrunk to the point where they were no longer detected. Thus, the kinetic analysis for the leaching process of the black mass in the mixture of acetic acid and molasses used the shrinking core model (SCM) with a shrinking small particle approach.



**Figure 10.** (a) Leaching efficiency profiles of Co at 30, 50, 70, and 90 °C using 2 M acetic acid and 10 mL of molasses 75% w/v; (b) surface morphology of particles in the residues after leaching at 30, 50, 70, and 90 °C; (c) illustration of two mechanisms involved in the reaction between a lixiviant and a reductant with a particle (shaded area)—(1) diffusion through a liquid film (dotted line), (2) chemical reaction, (3) diffusion through liquid film; (d) linear fits of plots from leaching at different temperatures for the shrinking particle model equation for diffusion through a film; (e) linear fits of plots from leaching at different temperatures for the shrinking particle; and (f) linear fit of the calculated chemical reaction constant rates for temperatures from 30 to 90 °C.

The reaction in the SCM shrinking small particle model is controlled by two sequential mechanisms, as illustrated in Figure 10c: (1) diffusion through liquid film around the particle and (2) chemical reactions at the particle surface. The rate equations for those steps are represented by Equations (11) and (12) [59], respectively.

$$t/\tau = 1 - (1 - X)^{2/3} \tag{11}$$

$$t/\tau = 1 - (1 - X)^{1/3} \tag{12}$$

where X is the reacted solid fraction, t is the leaching time (min), and  $\tau$  is the required time (min) for a complete dissolution of the target metal. The  $\tau$  (=1/k) is obtained by determining the slope (k) of a line fitted from a plot of t versus the right-hand sides of Equations (11) and (12) calculated from X.

Table 5 shows the values of slope,  $\tau$ , and R<sup>2</sup> calculated from linear fits of the plots in Figure 10d,e. In all cases, the value of R<sup>2</sup> was > 0.9. A comparison of the  $\tau$  values in Table 5 shows that chemical reactions had a longer completion time than the diffusion process. This result means the chemical reactions are likely to be the rate-determining mechanism in Co dissolution.

**Table 5.** The value of  $R^2$  and slope from the linear fitting of leaching data plots at 30, 50, 70, and 90 °C; calculated  $\tau$ ; and k".

T (°C)	Diffusion	n Film (r1)	Chemical <b>F</b>	τ (r	nin)	. //	
	R <sup>2</sup>	Slope	R <sup>2</sup>	Slope	r1	r2	<b>k</b> ''
30	0.969	0.0016	0.970	0.0008	641	1250	$1.51  imes 10^{-20}$
50	0.971	0.0025	0.949	0.0011	407	926	$2.15 imes10^{-20}$
70	0.936	0.0040	0.938	0.0021	250	476	$4.27 imes10^{-20}$
90	0.964	0.0191	0.976	0.0143	52	70	$2.91  imes 10^{-19}$

According to Levenspiel [59], the rate constant for a surface chemical reaction (k'') can be calculated from the  $\tau$  value according to Equation (13).

$$\tau = \rho \mathbf{B} \cdot \mathbf{R}_0 / (\mathbf{b} \cdot \mathbf{k}'' \cdot \mathbf{C} \mathbf{A} \mathbf{g}) \tag{13}$$

where  $\rho B$  is the molar density of the article (mole/m<sup>3</sup>), R<sub>0</sub> is the initial radius of the particles, CAg is the concentration of the reactant (mole/L), and b is the mole ratio of solid to reactant.

The slope of a linear fit of -lnk'' versus 1000/T in Figure 10f represents the value of Ea/R, where Ea is the activation energy for the reaction mechanism to occur. This is calculated by multiplying the slope by R = 8.3145 J/mol·K (see Equation (14)).

$$K'' = Ae^{-Ea/RT}$$
(14)

The Ea for the fitted line, 42 kJ, represents the activation energy for the surface chemical reaction. Earlier studies [12,29] have reported an identical rate-controlling reaction when leaching LiB material using acetic acid as the lixiviant with different reductants, including hydrogen peroxide and bagasse pith. This analysis indicates that the rate-controlling step in the leaching is the reduction of a higher valence Co(III) to Co(II) on the surface of particles in the black mass.

#### 4. Conclusions

Extraction of target metals (Li, Ni, Co, and Mn) from spent LiB black mass without a reductant reached maximum efficiencies of between 20 and 30% using 3 M acetic acid. Leaching efficiencies of between 96 and 99% for the same elements was obtained by employing 2 M acetic acid as the lixiviant and diluted molasses (75% w/v) as the reductant, with a 100 g/L slurry at 90 °C and 400 rpm stirring speed. The benefit of molasses in the leaching process was due to the reducing sugars and organic acid traces contained

in the molasses. A temperature of >50 °C and a 15 min reaction time were required for the oxidation of aldehyde groups in the reducing sugars, which resulted in reduction of the high-valence metals Co(III), Ni(III), and Mn(IV) to the easily dissolved corresponding metals with valence (+2). The H<sup>+</sup> ions from the lixiviant and the additional ions from molasses components are both proposed to enhance the Li dissolution, as significant Li dissolution was observed after the addition of molasses, This process contributes to the reduction reaction of the molasses component on Co(III), Ni(III), and Mn (IV) to soluble Co(II), NI(II), and Mn(II).

Molasses in an excess amount precipitated out target metals, especially Co, likely due to the presence of oxalic acid. The reducing sugars in molasses also precipitated out Cu(II) to Cu<sub>2</sub>O, which was further reduced to Cu metal due to ionic transfer involving Fe, resulting in sedimentation of Cu metal. The enhanced Fe dissolution after the addition of molasses also indicates a sedimentation process. The precipitation of Cu was confirmed by the detection of Cu metal in the residue by EDS SEM mapping following reductive leaching. The increase of Cu in the leaching results. However, Al dissolution was not affected by the addition of molasses. The results demonstrate that molasses enhanced the target metal dissolution and suppressed the Cu(II) dissolution, which minimised the Cu content in the pregnant solution. A further investigation without an acetic acid lixiviant, i.e., using just molasses, could investigate the effect of natural acid traces in the molasses.

The required completion times ( $\tau$ ) for the two kinetic mechanisms involved in Co metal dissolution, namely, diffusion of lixiviant and reductant through a liquid film around a particle containing Co and chemical reactions at the particle surface, indicate that chemical reaction is the rate-determining step for the leaching process. The rate-controlling mechanism of Co leaching in the presence of molasses is a surface chemical reaction with an activation energy of 42 kJ.

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