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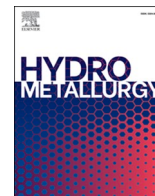
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The efficiency of scrap Cu and Al current collector materials as reductants in LIB waste leaching

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ABSTRACT

This current study addresses the role of copper and aluminum - typical major components of current collector scrap from battery manufacturing plants - in the leaching of pre-treated LiCoO₂-rich battery waste concentrate at industrially relevant process conditions ($T = 60\text{ }^{\circ}\text{C}$, $[\text{H}_2\text{SO}_4] = 2\text{ M}$, $S/L = 200\text{ g/L}$). An empirical model has been constructed which demonstrates that the effects of both copper and aluminum are significant. Both elements have independent and linear impacts on cobalt extraction and acid consumption. The model predicts that either 11 g of copper (0.75 Cu/Co, mol/mol), 4.8 g of aluminum (0.7 Al/Co, mol/mol) or a combination of both are required for full cobalt extraction from 100 g of sieved industrial battery waste concentrate. Aluminum was shown to influence cobalt leaching although it was less effective (47%) when compared to copper (66%) in terms of current efficiency due to associated side reactions, such as excess H₂ formation. Aluminum has several possible reaction routes for LiCoO₂ reduction; in parallel or in series via H₂ formation, Cu²⁺ cementation and/or Fe³⁺ reduction, whereas copper acts solely through Fe³⁺ reduction. These results indicate that by using copper scrap, in preference to the more typical hydrogen peroxide, the CO₂ footprint of the battery leaching stage could be decreased by at least 500 kg of CO₂ per ton of recycled cobalt. In contrast, the use of aluminum, although promising, is less attractive due to the challenges related to its removal during subsequent solution purification.

1. Introduction

Transition from a carbon-intensive (oil-based) economy to a clean energy economy necessitates a rise in the use of technological applications that are increasingly dependent on mineral and metal-rich resources. For example, the amount of copper required for an electric vehicle (EVs) is 5 times higher compared to the equivalent market-dominating internal combustion engine (ICE) car (Inoue et al., 2012). The ever-growing variety of applications of lithium-ion batteries (LIBs) such as EVs, mobile devices, and energy storage, requires a significant increase in the levels of lithium-ion battery manufacturing. In Europe alone, factories with a capacity of over 200 GWh/a are expected to be in operation by 2028 (Constantinescu, 2019). LIBs comprise of an anode, separator and a cathode, with an organic electrolyte that contains dissolved Li⁺ species either in the form of LiPF₆ or LiBF₄ (Meng et al., 2020). The anode typically comprises of graphite coated Cu foils, whereas the active materials based on Li oxides - such as LiCoO₂ (LCO), LiMn₂O₄, LiNi_xMn_yCo_zO₂ (NMC), and LiFePO₄, are coated on Al

cathodes (Meng et al., 2020).

The LiCoO₂ battery chemistry was first introduced commercially in 1991 and has since become the basis for a majority of Li-ion battery technologies (Helbig et al., 2018). In 2005, LiCoO₂ had a total market share of 94% and to date, such materials still dominate the LIB chemistries found within spent battery waste (Melin, 2019). More recently, chemistries like lithium nickel manganese cobalt oxide (NMC/NCM) have been introduced primarily in order to lower the amount of high-cost Co present within battery cells (Helbig et al., 2018). The rapid growth in LIB use and the incremental refinement of the various battery technologies has ultimately resulted in a complex battery waste that needs new industrial approaches to optimize battery metal recoveries.

Europe, in particular, faces an increasing challenge to ensure the availability of sustainably sourced critical metals required for battery production (Wang et al., 2014). In 2017, the global Co supply was estimated to be 126,000 t and the demand is predicted to increase up to 390,000 t by 2030, resulting in an overall global Co deficit of 150,000 t (Alves Dias et al., 2018). According to a recent report by the EU Joint

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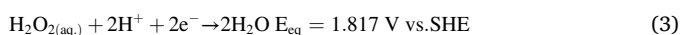
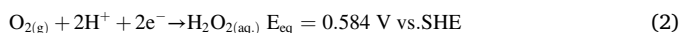
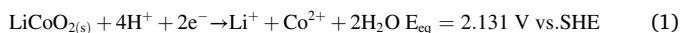
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Research Centre, 51% of the Co currently mined is supplied by the Democratic Republic of Congo (DRC), followed by China, Russia, Canada and Australia (Lebedeva et al., 2016). Of this global supply, approximately 60% (78,000 t) of all Co consumption is related to battery industries (Liu et al., 2020). This scarcity of primary cobalt mineral resources (Helbig et al., 2018; Huang et al., 2019), high price and associated political uncertainties highlight the importance of Co recovery from secondary raw material sources, such as spent batteries. Consequently, to increase the availability of these valuable metals and enhance circular economy principles, it is critical to develop a holistic understanding of the behavior and phenomena related to actual industrial battery waste in recycling processes. Metal recovery from battery waste typically includes unit processes like mechanical treatment, smelting, pyrolysis, leaching, solvent extraction, precipitation, and crystallization. Leaching of waste batteries has been investigated in both mineral - HCl, HNO₃, H₂SO₄ - and organic - citric, malic, ascorbic, oxalic - acids (Liu et al., 2019a; Meshram et al., 2020; Zhao et al., 2020). Of these, sulfuric acid is both the most common and the predominant industrially relevant lixiviant.

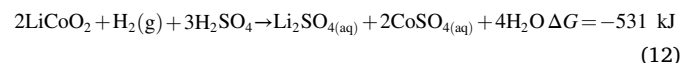
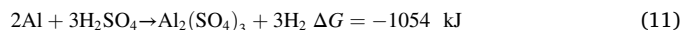
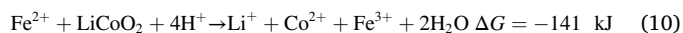
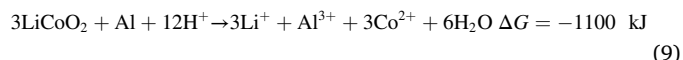
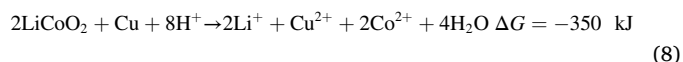
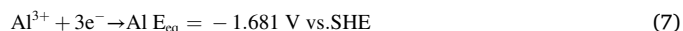
In order to achieve the complete dissolution of LiCoO₂, a reduction agent - with a lower standard electrode potential to that of LiCoO₂ - is required. The standard electrode potential for LiCoO₂ reduction is relatively high at 2.13 V vs. SHE (Eq. 1), which suggests that several elements like Fe, Cu and Al, that are already present in the raw material, could act as reductants for LiCoO₂. On the other hand, hydrogen peroxide (Eq. 2) has been widely used as a reducing agent in hydrometallurgical LIB leaching (Joulié et al., 2017; Meng et al., 2018; Peng et al., 2019), as O₂ and H₂O are the only decomposition products, and therefore, theoretically no further solution impurities result from the treatment. For instance, Bertuol et al. (2016), leached LCO, obtained from dismantled batteries, in 2 M H₂SO₄ with 4 vol% of H₂O₂ at 75 °C for 60 min and extracted over 95% of Li and Co. Zou et al. (2013), leached mixed cathode materials composed of LCO, NMC 111, LiMn₂O₄ and LiFePO₄ in 4 M H₂SO₄ and 30 wt% H₂O₂, which resulted in the successful leaching of all cathode materials except LiFePO₄. Zheng et al. (2017), leached a mixture of LCO, NMC 111, LiMn₂O₄ and LiNiO₂ that had been manually separated from dismantled battery packs. Metal extraction of 99% was achieved in 2.5 M H₂SO₄, with a H₂SO₄/H₂O₂ ratio of 5 (vol/vol) and L/S ratio of 10 mL/g, although some LiFePO₄ was found to remain undissolved. On the other hand, He et al. (2017), also achieved 99% extraction of Ni, Co, Mn and Li from pure NMC 111 and LCO using H₂O₂ as reducing agent in the following sulfate-based system (1 M H₂SO₄, 1 vol% of H₂O₂ and pulp density of 40 g/L). Nonetheless, H₂O₂ is also a strong oxidant (Eq. 3) and can also end up being consumed for the oxidation of Cu, Al (current collector materials) and Fe (steel casings) within industrial battery waste (Aaltonen et al., 2017; Porvali et al., 2019). As hydrogen peroxide is known to decompose in the presence of sulfuric acid at elevated temperatures (Wu et al., 2008), concentrations that exceed the theoretical amount are required to ensure complete reduction (Yang et al., 2016). Consequently, not only is there an increase in the chemical consumption, environmental impact and costs related to H₂O₂, but also an associated degradation of the reductive capabilities of Cu, Al, and Fe.



In addition to H₂O₂, several other materials have been investigated as possible reduction agents for LCO dissolution. For example, Meshram et al. (2015) investigated the use of sodium bisulfite (NaHSO₃) as a reductant for the leaching of manually dismantled battery packs. The resulting NMC powder was leached in 1 M H₂SO₄ with varying (0–0.25 M) concentrations of NaHSO₃, which lead to approximately 97% of Li,

92% of Co, 96% of Ni and 88% of Mn being extracted. Although NaHSO₃ could be a suitable alternative to H₂O₂, the addition of the extra Na⁺ would circulate within the process streams and would therefore require extra stages to ensure removal. Chen et al. (2016), used citric acid and glucose as lixiviant and reductant, respectively, to extract over 90% of Li, Ni, Mn, and Co from NMC powder obtained from hand disassembled LIBs. Moreover, tea waste (0.3 g/g of NMC powder) has also demonstrated to effectively leach over 90% metals in 2 M H₂SO₄ (Chen et al., 2019). However, the NMC powder was calcined at 550 °C for 1 h prior to leaching and the use of tea biomass alone could be insufficient to support an industrial scale process.

Another alternative approach that has been studied in the use of nickel-metal hydride (NiMH) battery waste as a reductant for waste LIBs. In this case, the presence of oxidized rare earth metals result in the synergistic dissolution of metals from both battery waste types without the need for additives (Liu et al., 2019b), although access to a stable supply of NiMH materials is crucial. Peng et al. (2018), have also demonstrated that the overflow of crushed LiCoO₂ batteries—rich in Cu and Al foils—can improve the extraction of Co and Li when added to the leaching process, therefore potentially minimizing the need for H₂O₂. Furthermore, it has also been shown that the surfaces of handpicked Al foils can contain up to 11 wt% of Co (Porvali et al., 2019), which suggests that a holistic approach to Co extraction could also be supported by feeding Al-rich battery waste to the leaching process, rather than separating it prior to leaching. Investigations by Ghassa et al. (2020) proved that iron from battery casing scrap can effectively assist in the dissolution of the active materials, whereas Porvali et al., (2020) studied the combined effect of metallic Cu particles and ferric iron on the leaching kinetics of pure LiCoO₂ in a sulfate-based system. In both cases, it was determined that Fe²⁺ (Eq. 4) acted as a reductant for LiCoO₂ (Eq. 10) and that the formed Fe³⁺ could be reduced back to Fe²⁺ by the converse oxidation of metallic Cu to aqueous Cu²⁺ (Eq. 4 and 5). The effect of Cu and Al current collectors on the dissolution of LiCoO₂ and NMC cathodes has also been researched by Joulié et al. (2017) and their findings suggest that the reducing power of Al may result from the formation of H₂ within sulfate-based systems (Eq. 6 and 7). In this instance, Al can react with the acidic medium to produce gaseous H₂ (Eq. 11), which has the thermodynamic capability to reduce not only LiCoO₂ (Eq. 12), but also Fe³⁺ (Eq. 4 and 7) and Cu²⁺ (Eq. 5 and 7), all of which can potentially transfer their reductive power to the LiCoO₂ dissolution.



Currently, much of the research related to the hydrometallurgical recycling of LIBs is focused on use of additive reducing agents to treat manually disassembled LIB packs, where the current collectors have been separated and the active material stripped from Al foils. In contrast, industrial scale recycling processes make use of battery black mass -

produced by crushing - that contains plastics, organics, current collectors, and steel casing. Consequently, it is essential to also study the effect of the impurities, commonly present in waste LIB concentrates, on the dissolution of the active material as it can allow for the efficient utilization of their chemical power in active material dissolution. For example, > 15% of Cu and Al current collectors are discarded as process scrap during the battery manufacturing (Hanisch et al., 2015). Therefore, the main aim of this work is to study the role and efficiency of Cu and Al current collectors (from scrap production) as reductants in LIB waste leaching, in preference to the introduction of new process chemicals like H_2O_2 , to enhance the circular economy of materials. Empirical models were developed for *Co extraction*, *final acid concentration* and *acid consumption rate*, and response surface modeling was utilized in order to build a regression equation that allowed the optimization of the Cu-Al ratio for the leaching of industrial LIB waste rich in LCO materials.

2. Materials and methods

2.1. Raw materials

The waste battery concentrate investigated originated primarily from mobile phones and laptops was sourced from an industrial battery recycler. Spent batteries were initially pre-sorted manually based on chemistry, followed by a two-step crushing, magnetic separation of ferromagnetic material and sieving process to produce a cobalt-rich with minor impurities such as Ni, Mn, Cu and Al. the concentrate investigated (Pudas et al., 2015). As a result of this methodology, any $LiPF_6$ present in the concentrate is more than likely to have reacted with atmospheric moisture during the processing and transportation prior to any leaching step (Eq. 13).



Consequently, due to the risks for potential hydrofluoric acid formation, appropriate safety measures related to personal protection and waste handling were undertaken.

Metal content in the concentrate was obtained by performing the total leaching of the battery waste material, followed by atomic absorption spectroscopy (AAS, Thermo Fisher, ICE 3000, USA) with an air-acetylene flame of the resulting solution. **N.B.** it is possible that part of Li remains in the undissolved graphite after the aqua regia treatment. Aluminum content was determined with an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer, Optima 7100 DV, USA), whereas the level of fluorides was ascertained by a standardized fusion method (ASTM D3761–96) - the sample was fused with carbonate flux, then dissolved in pH-buffered citric acid before the fluoride content was measured with an ion-selective electrode. The average elemental composition of the concentrate is presented in Table 1. Excess of Al and Cu present in the material were removed by sieving the concentrate with a 500 μm mesh screen for 5 min using a vibratory sieve shaker (Fritsch Analysette 3, Idar-Oberstein, Germany) and most current collector fragments remained in the >500 μm overflow (supplementary material, Fig. S1). The <500 μm underflow was used as the main raw material in the leaching experiments. In addition, manganese was found to exist as a separate oxide (Fig. 1 and Fig. S2, supplementary material).

The underflow (< 500 μm) was characterized by X-ray Diffraction

(XRD, X'Pert Pro MPD Powder, USA, equipped with PIXcel1D detector, Co K α source operated at 40 kV, 40 mA, along with Fe beta filter without monochromator). Analyses were performed for the initial concentrate and leach residue. Separate Cu and Al foil sheets from discarded production scrap were obtained from an EV battery manufacturing site, crushed in a cutting mill (Retsch SM 300, GMB, Finland), and sieved with a 2 mm diameter screen to remove the larger fragments. The effect of this sieved scrap on battery waste leaching was investigated via an experimental series, the focus of which was the final extraction as a function of the weight of the current collectors added, as outlined in Table 2.

The lixiviant (2 M H_2SO_4) was prepared from sulfuric acid (95–97%, Merck Emsure), and its concentration was confirmed by titration. Ferric iron was added as $Fe_2(SO_4)_3 \cdot nH_2O$ (VWR, GPR RECTAPUR) to the acid prior to the addition of the concentrate (in exp. E12 and E13). Nitric acid for sample dilution was prepared from concentrated HNO_3 (65%, Merck Emsure). Hydrochloric acid for sample dilution for Li determination was prepared from concentrated HCl (37%, Merck Emsure). Saturated KCl was prepared by dissolving salt (Riedel-de Haën, 99.5% purity) in water and was used to prevent the ionization of Li during the analysis with AAS. Sodium hydroxide solution (2 M NaOH Alfa Aesar, standardized) was used to ascertain lixiviant concentration. The same solution was further diluted to 0.2 M and used to analyze the leaching samples. Methyl orange (Schering AG) was used as an indicator. Additionally, the reduction potentials (E_{eq}) and Gibbs free energies (ΔG) were calculated at 60 °C (Eq. 1–12) using HSC Chemistry software (version 9.4.1, Outotec, HSC, 2019).

2.2. Leaching experiments

The extraction of cathode metals from the sieved underflow (< 500 μm) battery fraction was investigated at $T = 60$ °C, initial $[H_2SO_4] = 2$ M, agitation speed of 350 rpm and S/L = 200 g/L. In the leaching series (Table 2), current collectors were introduced to the system after 30 min of leaching, and the response surface model was derived.

Leaching was carried out in a 1 L glass jacketed reactor that included a 4-blade impeller agitator (90 mm diameter) and a reflux condenser. Temperature control was provided by a heating bath (Haake C1, Thermo Electronics, Germany). 100 g of concentrate was added to 500 mL of the lixiviant (S/L ratio = 1:5) and current collectors (Cu and/or Al) were used as external reductants, added at leaching time $t = 0.5$ h. Sampling was carried out with a Finnpiptette F2, which was used to obtain aliquots of slurry (6 mL) that were subsequently filtered prior to analysis (filter paper grade 005, Ahlstrom-Munksjö). Redox potential was measured from within the reactor vessel with an ORP electrode (Pt vs. Ag/AgCl in 3 M KCl, Mettler Toledo, USA).

Prior to the analyses of Co, Cu, Mn, Ni, Li and Fe by AAS, sample solutions were diluted with 0.3 M HNO_3 . The acid concentration of the pregnant leach solution (PLS) was determined from samples taken at 5 min, 1 h, 2 h, and 3 h. These samples were diluted with 50–80 mL of water and treated by the addition of $Na_2S_2O_3 \cdot 5H_2O$ (VWR, 99.8% pure) – to reduce Fe^{3+} to Fe^{2+} to prevent precipitation of ferric iron prior to the endpoint.

The metal extraction Y_{Me} (in %) in the solution was calculated using Eq. 14.

Table 1

Average metal content (mg/g) in the investigated waste battery concentrate as well as sieved fractions, < 500 μm fraction used as the raw material for leaching experiments.

Concentrate	Ratio	Li	Ni	Mn	Co	Al	Fe	Cu	F
As-received	–	37.1	22.8	26.3	259	34.1	5.9	40.1	33.7
> 500 μm	19	27.1	21.6	19.5	185.5	158.6	11.2	132.8	n/a
< 500 μm	81	38.1	25	27.6	260	23.1	4.7	15.4	n/a

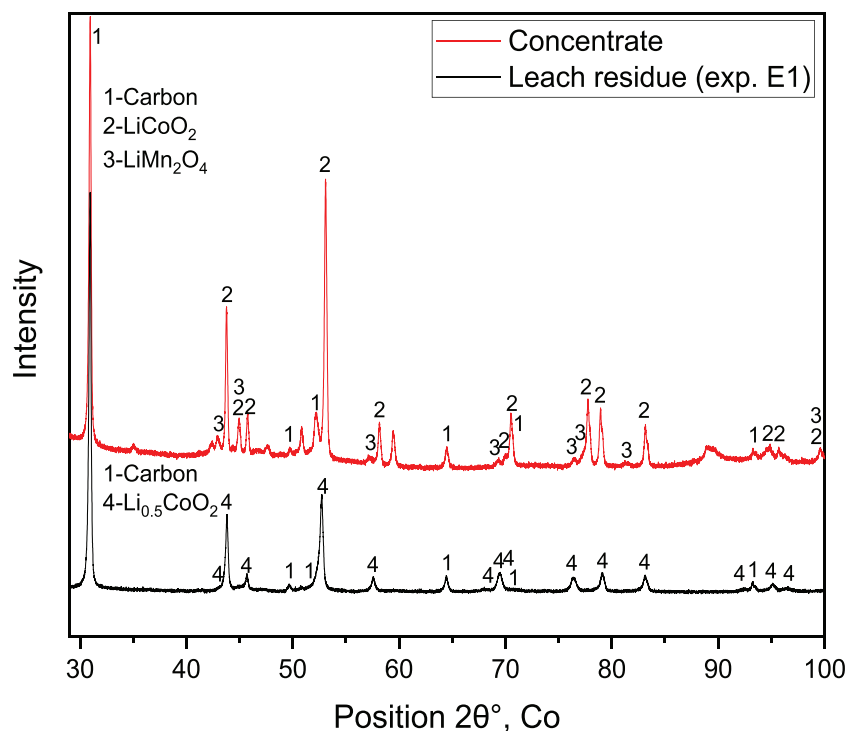


Fig. 1. XRD diffractograms of battery waste concentrate and leach residue (from experiment E1).

Table 2

Experimental leaching series on LCO concentrate (< 500 μm fraction).

Experiment	Electrode foil additions, g	
	Cu	Al
E1	0	0
E2	2	0
E3	2	2.5
E4	1	1.25
E5	0	2.5
E6	2	0
E7	1	1.25
E8	1	0
E9	1	2.5
E10	0	1.25
E11	2	1.25
E12 ^a	10	0
E13 ^b	2	0

During leaching, the concentration of Fe was 0.8–0.9 g/L.

^a Fe added to the solution (2 g/L).

^b Fe added to the solution (2.6 g/L).

$$Y_{Me} = \frac{C_{Me} \cdot V_L}{x_0 \cdot m_0} \cdot 100\% \quad (14)$$

where C_{Me} is the concentration of metal (g/L) in solution, V_L is the volume of the leach solution (L), x_0 is the fraction of metal in the concentrate (%), and m_0 is the initial weight of the concentrate introduced to the leaching reactor (g).

2.3. Regression modeling

Regression modeling was applied to investigate the effects of Cu and Al in leaching. Design of Experiment (DoE) software (Modde, Version 8, Umetrics, Sweden), was utilized for data analysis and a response surface methodology (RSM) was selected to fit the data into a central composite face-centered design (Cheng et al., 2019; Hung et al., 2020). The selected design requires 3 levels of each factor, which subsequently

allows the quadratic relationship and interactions to be analyzed. The coded levels of the current collector addition and the corresponding amount of foils added to ~490 mL of slurry at $t = 0.5$ h are presented in Table 3. The Co extraction ($t = 3$ h), acid consumption rate ($t = 0.5$ – 3 h) and final acid concentration ($t = 3$ h) of the leachate were fitted to the model. It should be noted that ~50% of Co dissolution occurs spontaneously, but this ceases after $t = 0.5$ h, prior to the addition of the reducing agents.

3. Results

3.1. Characterization of LCO battery waste

Several authors have characterized industrial Li-ion battery cathode scrap using XRD (Maroufi et al., 2020; Peng et al., 2018; Xie et al., 2020). The crystalline phases identified via this methodology display some slight variations between the published works; in general, the XRD peak identification of these materials is not straightforward due to the presence of amorphous phases, high backgrounds, uneven particle sizes and low x-ray peak intensities. The X-ray diffractogram (Fig. 1) obtained in this work suggests that in addition to LiCoO₂ (ICDD: 01–070-2685) and carbon (ICDD: 00–041-1487), a compound that contains Ni and Mn in a similar ratio (Table 1) was also present, which is indicative of minor amounts of LiMn_{0.5}Ni_{0.5}O₂ (ICSD: 98–005-5376) or LiMn₂O₄ (PDF: 01–088-0589) in the LCO battery waste. According to SEM-EDS analyses, Mn exists as a separate oxide (supplementary material, Fig. S2) as shown by the peaks on the diffractogram. This is not unexpected, as the raw material investigated comprised of industrially collected and manually pre-sorted battery waste from real world sources. After 3 h of

Table 3

Coded levels and corresponding values of current collector additions.

Factor	Levels		
	–1 (low)	0 (center)	+1 (high)
Copper, g	0	1	2
Aluminum, g	0	1.25	2.5

leaching (E1) in the absence of externally added reducing agents (i.e. current collector scrap), ~ 52% of Co was found to dissolve, whereas 91% of Ni, 70% of Mn and 86% of Li were also co-extracted. Analysis of the solid residue after leaching showed that it contained delithiated LiCoO_2 in the form of $\text{Li}_{0.5}\text{CoO}_2$ (ICSD: 98-015-9792, Fig. 1), thereby confirming the results found for the leach solution and the fate of the remaining, unleached Co material.

This observation is similar to previous results obtained for synthetic LiCoO_2 leaching (Porvali et al., 2020), where also ~50% Co extraction and the presence of $\text{Li}_{0.5}\text{CoO}_2$ was observed in the residue. Billy et al. (2018) investigated the dissolution of NMC type of cathode in acidic conditions and hypothesized that the delithiation may be dependent on the presence of acid as Li^+ is exchanged with H^+ ions. Furthermore, it was demonstrated that the delithiation causes structural rearrangements on the surface, which may be the case for LCO as well. The formation of cobalt oxide (Co_3O_4) on the surface of LCO in leaching has been previously shown by Ferreira et al. (2009). Due to the delithiation in LCO, Co_3O_4 , which is a semiconductor, forms on the surface of LCO hindering the electron transfer between the core of the particle and lixiviant, therefore LCO requires a reducing agent to be dissolved. In contrast, the peaks related to Mn and Ni containing oxides could no longer be detected in the leach residue diffractogram (Fig. 1).

3.2. Leaching of LCO battery waste with controlled Cu and Al addition

With the addition of Cu only (E2), a minor improvement in LiCoO_2 dissolution (Eq. 8) was observed, up to ~60% extraction (Fig. 2A) vs. ~52% obtained for the dissolution of Co in the absence of added reductants. Furthermore, the simultaneous oxidation of copper was also evident, shown by the significant rise in Cu concentration after $t = 0.5$ h (Fig. 2B). Additionally, LiMn_2O_4 and nickel oxide were dissolved with 78% and 97% of Mn and Ni extracted, respectively (supplementary material, Fig. S3A-B). Addition of Al and Cu scrap together (E3, 2 g Cu and 2.5 g Al) resulted in improved cobalt extraction of up to 88%. The effect of Al was further confirmed by the addition of 2.5 g Al only (E5), which yielded Co dissolution of ~80%. Overall from the results of experiments E2–E10 (Fig. S3A-C) it could be ascertained that the extraction of Ni, Mn, and Li - were all improved when compared to leaching in the absence of reduction agents (E1).

Nevertheless, it is also clear that the addition of aluminum leads to an increase in the level of acid consumption as indicated by the marked decrease in the sulfuric acid molarity in the presence of Al (Fig. 2C). The 2.5 g Al (0.092 mol) added could theoretically react with a maximum of 0.14 mol of H_2SO_4 to produce 0.14 mol of H_2 , according to Eq. 11. However, the difference in the final acid concentration between E1 (no Al added) and E5 (2.5 g of Al added) was 0.52 M, corresponding to ~0.26 mol. Consequently, a maximum of 57% of the acid consumed (difference

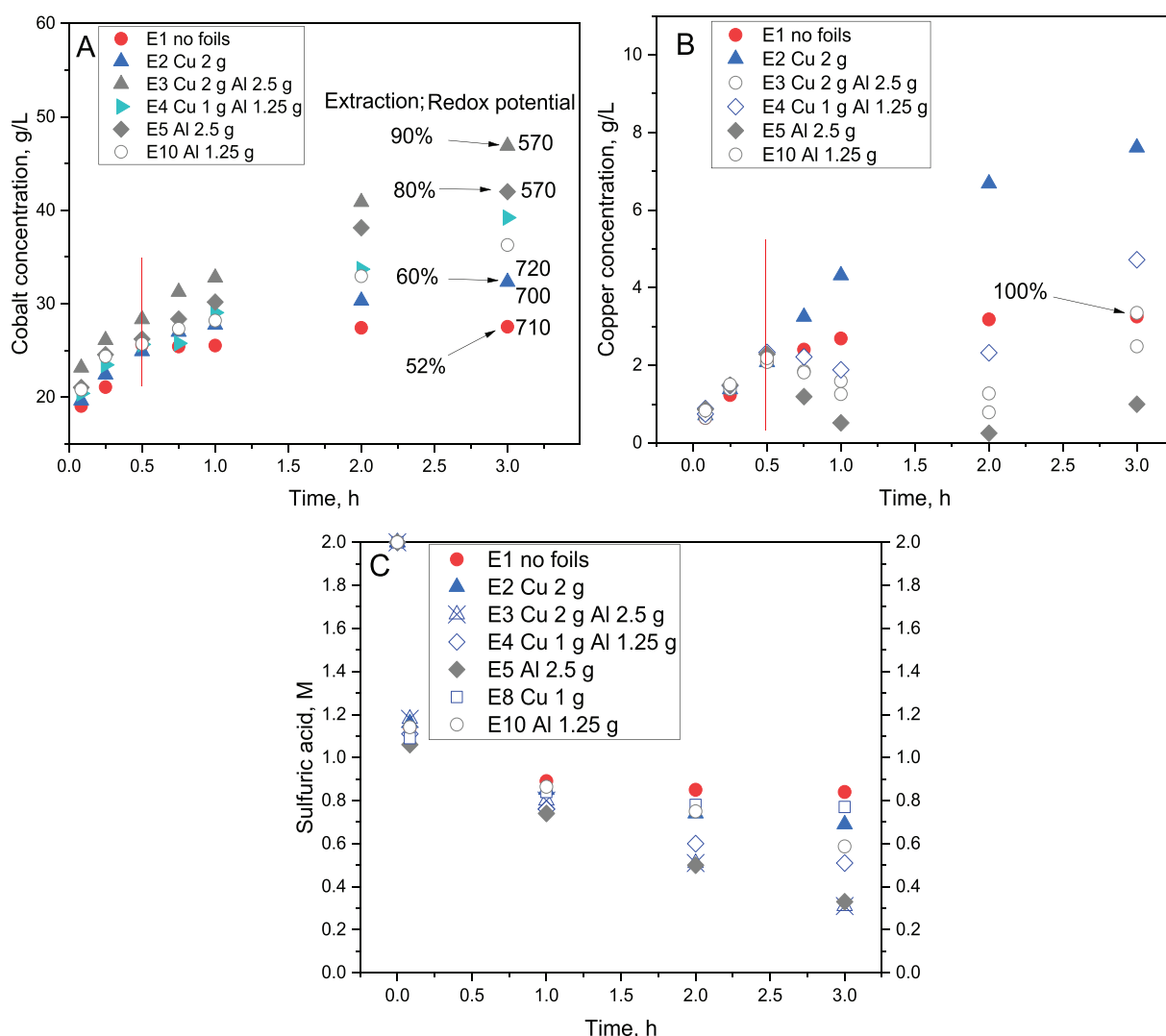


Fig. 2. Concentration and extraction of (A) cobalt, (B) copper, (C) acid concentration. $T = 60^\circ\text{C}$, 200 g/L of solids, $[\text{H}_2\text{SO}_4] = 2\text{ M}$.

between E1 and E5) could be caused by the addition of 2.5 g of Al. Furthermore, hydrogen gas generated can theoretically reduce LiCoO_2 , a phenomenon utilized widely by the hydrometallurgical industry (Crundwell et al., 2011). To reduce 0.22 mol of Co, 0.11 mol of H_2 would be required (Eq. 12), and a maximum of 0.14 mol of H_2 could be generated in the system.

Al can act also directly as a reductant as the standard reduction potential for Al lies below that of LiCoO_2 , $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Cu (Eq. 1, 4, 5 and 7). Therefore, thermodynamically, aluminum can reduce LiCoO_2 also via dissolved iron (Eq. 9) in a similar way to Cu. Moreover, Cu^{2+} was shown to retain the reductive power of Al, through the reduction of Cu^{2+} to metallic Cu in the presence of Al (Fig. 2B, experiments E3, E4, E5 and E10), via reduction by H_2 or direct cementation by Al. The cementation is thermodynamically possible (Ekmekyapar et al., 2012) due to the lower nobility of Al cf. Cu (Eq. 5 and Eq. 7). As a redox potential of 570 mV vs. Ag/AgCl (Fig. 2A) is not typical for Cu precipitation (Khoshkhoo et al., 2017), this suggests that cementation, rather than the precipitation, is the cause of the significant decrease in dissolved copper (Fig. 2B). In addition, cemented metallic Cu can act as a reductant for LiCoO_2 via the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple, therefore this route and its kinetics are more dependent on the concentration of dissolved iron and the selected leaching time, in contrast to direct LCO reduction by H_2 .

Although iron that originated from the raw material ($< 500 \mu\text{m}$) was not considered as a variable in the DoE, two separate experiments (E12 and E13) were conducted with ferric iron sulfate addition to ascertain the influence of Fe on leaching behavior. It was found that the presence of iron notably increased the dissolution kinetics of LiCoO_2 (supplementary material, Fig. S7). However, the addition of ferric iron did not improve either the holistic reductive efficiency or the current efficiency of copper, but rather was found to increase the leaching kinetics only.

3.3. Regression modeling

As the final Co extraction varied from 52 to 90% at $t = 3 \text{ h}$ (supplementary material, Fig. S5), experiments E1–E11 were statistically analyzed by response surface modeling (supplementary material, Table S1). The responses - Co extraction ($t = 3 \text{ h}$), final acid concentration ($t = 3 \text{ h}$) and acid consumption rate ($t = 0.5\text{--}3 \text{ h}$) were fitted to the model. In the experimental data, the variables included the current collector materials added: Cu and Al, whereas the dissolved iron was a constant, due to its default occurrence in the investigated battery waste fraction.

Experimental data were fitted to a second-order (Eq. 15) model (Montgomery, 2012) and the following regression coefficients were obtained:

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \varepsilon \quad (15)$$

where y is the response, X refers to the coded factors, β the unknown parameters that are estimated based on the experimental data, and ε is a random error that describes the experimental error.

In the initial model, all terms were considered as follows: linear - $[\text{Cu}]$ and $[\text{Al}]$ as well as quadratic - $[\text{Cu}^2]$ and $[\text{Al}^2]$ followed by the interaction term $[\text{Cu} \cdot \text{Al}]$. The interaction between copper and aluminum on Co extraction in the investigated leaching system displays parallel lines, which indicates an absence of interaction (supplementary material, Fig. S6). Additionally, no interaction was observed in acid consumption rate and final acid concentration. Subsequently, the insignificant terms were removed at the confidence level of 0.95 with low probability

Table 4

P-values of linear terms in the model equations.

Model	p-value $[\text{Cu}]$	p-value $[\text{Al}]$
Co extraction	0.002	< 0.001
Acid consumption rate	0.001	< 0.001
Final acid concentration	0.05	< 0.001

(p-value above 0.05), and only linear effects were found to be significant (Table 4).

These findings suggest that acid consumption rate also follows a linear relationship with Cu and Al. This is expected, as only the linear terms of $[\text{Cu}]$ and $[\text{Al}]$ were significant for Co extraction and these also have a direct impact on the acid consumption.

Over the experimental range investigated, aluminum was shown to have a larger contribution to cobalt leaching and acid consumption, which is indicated by the larger constant of the $[\text{Al}]$ term compared to $[\text{Cu}]$ in all the model equations (Eq. 16–18). This may be explained by the lower nobility of Al and thus its larger reductive power, which can concurrently reduce other components within the system including H^+ ions. Moreover, aluminum oxidation provides three moles of electrons per one mole of dissolved ion, whereas copper provides only two. Any interaction between Cu and Al does not seem to affect the final Co extraction, therefore it is most likely that Al could act as a reductant for LiCoO_2 independently of Cu, i.e. the presence of Al does not promote or inhibit the effect of copper.

The built regression equations and their fits are presented in Table 5. The model has a good fit as R^2 and R^2 (adj) are close to 1. Moreover, the predictive power (Q^2) of all models is high (ideally > 0.5).

3.4. Efficiency of current collector scrap in leaching

It was demonstrated that $\sim 50\%$ of Co can be dissolved spontaneously from industrially crushed and sieved ($< 500 \mu\text{m}$) concentrate. Furthermore, initial dissolution of the metal oxides in the sulfuric acid system is enhanced with the battery components present in the concentrate, such as Cu, Al and Fe (Peng et al., 2019). Nonetheless, an external reductant is required to dissolve the remaining cobalt, therefore current collector foil scrap additions were investigated. A response surface (Fig. 3) was built based on Eq. 16 and utilized a linear contour approach. This response surface enabled the final Co extraction to be predicted, with added reductants presented as mole per mole of undissolved cobalt in the solid phase at $t = 0.5 \text{ h}$.

In the experimental study, the copper ratios to the undissolved cobalt ($\text{Cu}/\text{Co}_{t=0.5\text{h}}$) used were 0.035–0.176 mol/mol and for aluminum $\text{Al}/\text{Co}_{t=0.5\text{h}} = 0.14\text{--}0.55 \text{ mol/mol}$. According to Eq. 8, 1 mol of Cu can reduce 2 mol of Co (ratio 1/2), thus the added Cu was stoichiometrically insufficient ($\text{Cu}/\text{Co}_{t=0.5\text{h}}$ ratio of 0.18, Fig. 3), as 0.5 Cu/Co would be required for total Co dissolution. With 36% of the stoichiometric amount of Cu (in the absence of added Al), i.e. $\text{Cu}/\text{Co}_{t=0.5\text{h}}$ ratio of 0.18, only $\sim 65\%$ Co extraction was achieved. As aluminum is a trivalent metal, therefore 1 mol of Al can support the reduction of 3 mol of Co. However, in the current study, the Al/Co ratio of 1/3 (0.33) was shown to be insufficient for maximum Co extraction (Fig. 3), which remained at $\sim 80\%$ when only Al was added. This suggests that Al is not very efficient for the reduction of LiCoO_2 (Eq. 7) and that part of Al was consumed also for reduction of the acid and other cathode metal oxides (supplementary material, Fig. S3A–B). Nevertheless, it is important to note that the reductive power of metallic copper can also be consumed by dissolved oxygen or reduction reactions involving the Mn and Ni oxides. In

Table 5

Central composite design and the responses for the leaching: Co extraction (Y_{Co}) in %, final acid concentration (C_A) in M and acid consumption rate (k_A) in M/h.

Model	Equation	Q^2	R^2	R^2 (adj)	Equation
Co extraction ($t = 3 \text{ h}$)	$Y_{\text{Co}} = 72.5455 + 3.56486 \cdot X_1 + 11.5909 \cdot X_2$	0.937	0.965	0.965	16
Acid consumption rate ($t = 0.5\text{--}3 \text{ h}$)	$k_A = -0.211427 - 0.0243315 \cdot X_1 - 0.0726901 \cdot X_2$	0.974	0.986	0.982	17
Final acid concentration ($t = 3 \text{ h}$)	$C_A = 0.544364 - 0.046232 \cdot X_1 - 0.180965 \cdot X_2$	0.913	0.966	0.958	18

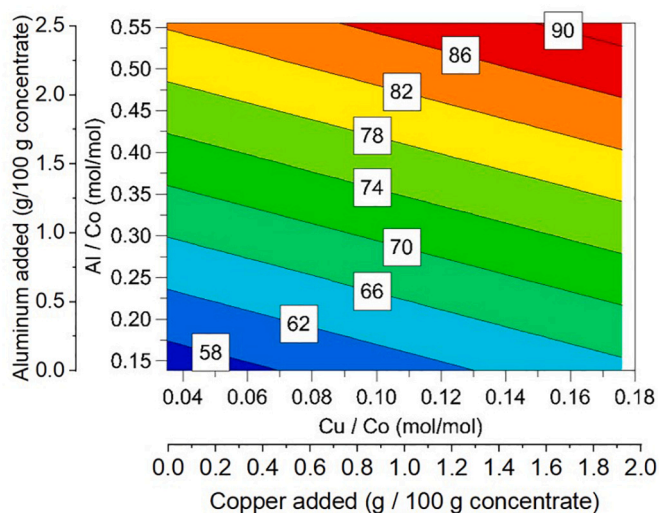


Fig. 3. Response surface of the model for predicting the cobalt extraction with the addition of Al (0–2.5 g) and Cu (0–2 g).

contrast, the presence of both excess Al ($\text{Al}/\text{Co}_{t=0.5\text{h}} = 0.55$) and additional Cu ($\text{Cu}/\text{Co}_{t=0.5\text{h}} = 0.18$) resulted in a total Co extraction of 90%.

The remaining Cu and Al present in the slurry at $t = 0.5$ h – when the current collector scrap additions took place – were estimated to be 0.49 g and 0.83 g, respectively, which is equal to 0.008 and 0.031 mol per mol Co. These minor amounts were considered when calculating the efficiency of the reductants per undissolved Co (at $t = 0.5$ h), but only the added quantities were considered as variables.

Fig. 4 depicts the prediction of the Co extraction model (based on the experimental data) of Cu and Al required for full Co extraction. For example, if Al addition is to be avoided, 11 g of Cu per 100 g of concentrate (dashed line, crossing x-axis) is required for full Co extraction (Fig. 4). This corresponds to 0.75 of $\text{Cu}/\text{Co}_{t=0.5\text{h}}$ (mol/mol), i.e. 66% current efficiency of Cu for Co reduction after $t = 0.5$ h of leaching (Eq. 8). Similarly, 4.8 g of Al per 100 g of concentrate (in the absence of Cu addition) would achieve full cobalt extraction, corresponding to 0.7 of $\text{Al}/\text{Co}_{t=0.5\text{h}}$ (mol/mol) – a current efficiency of 47% for Al in the reduction of LiCoO_2 .

These results suggest that in the leaching of industrially collected LIB

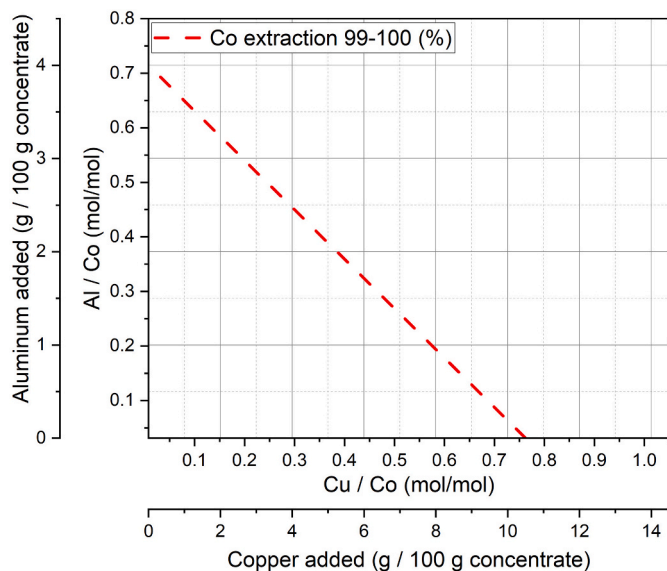


Fig. 4. Adjusted aluminum-copper ratio required for maximum cobalt extraction. $T = 60$ °C, 200 g/L of solids, $[\text{H}_2\text{SO}_4] = 2$ M, $t = 3$ h.

waste, the reductive power, i.e. electrons provided by Cu are more efficiently utilized for LiCoO_2 reductive dissolution compared to Al, as the copper efficiency is enhanced by the co-catalyzing effect of dissolved iron that originates from the battery waste itself (Porvali et al., 2020). Thermodynamically, Al has several alternative reduction reaction routes for LiCoO_2 , such as formation of H_2 , reduction of Cu^{2+} to Cu, Fe^{3+} to Fe^{2+} , reduction of Ni and Mn based oxides, or a combination of these reactions, therefore the chance for potential efficiency losses are increased. Nevertheless, Al reduced LiCoO_2 at a faster rate when compared to copper as Cu is highly dependent on the levels of dissolved iron within the leach solution. Consequently, metal oxide reduction by Cu can be improved by the introduction of more iron to the system, which increases the leaching kinetics – as demonstrated in the supplementary material (Fig. S7A).

3.5. Environmental impact of Cu, Al and H_2O_2

Net emissions per 1 kg of each reducing agent produced are summarized in Table 6. Primary metal production routes involve smelting, whereas the secondary production is based on scrap re-melting.

A similar LCO-rich waste concentrate as used in the current study, was previously leached by Aaltonen et al., 2017 (2 M H_2SO_4 , H_2O_2 concentrations: 0–5% (v/v), slurry density = 10% (w/v), $T = 70$ °C, $t = 5$ h). Over 95% of Co was extracted with 2% (v/v) of H_2O_2 added, equal to 3.59 g of 50% H_2O_2 per 3.45 g of Co. Based on the experimental results and Ecoinvent 3.6 database (Table 6), the amount of CO_2 (kg) emitted during the production of each reducing agent required to dissolve 1 metric ton of cobalt from industrially pre-treated LCO rich battery waste was estimated (Fig. 5). If current collector scrap is used as the reduction agent in LIB leaching, the secondary processing of current collector scrap (Cu or Al) can be avoided, i.e. the amount of CO_2 emissions related to their secondary processing would be reduced by 647 kg (copper) or 92 kg (aluminum) per ton of Co. Secondly, the additional environmental impact of leaching will be reduced by 1269 kg of CO_2 as the use of hydrogen peroxide can be avoided.

Nevertheless, challenges related to aluminum removal in solution purification stage could increase the overall environmental burden of the process despite its low associated CO_2 emissions (92 kg/ton of Co) in recycling (Fig. 5). Aluminum tends to form colloidal hydroxide precipitate at higher pH (Lottermoser, 2010) with amorphous gel-like properties (Dash et al., 2012; Meher et al., 2005). Al removal by precipitation as hydroxide is challenging due to the co-precipitation of Cu and Co, however, solvent extraction or a combination with hydroxide precipitation could potentially support selective aluminum removal (Or et al., 2020; Suzuki et al., 2012). Moreover, if the current collectors (Cu and Al) originate from the primary production, the environmental impact of Al would exceed that of H_2O_2 whereas Cu would have lower impact compared to H_2O_2 .

Use of copper pre-production scrap as a reductant in LIB waste leaching seems attractive; its current efficiency in reduction is high, and its recovery by electrowinning and solvent extraction is well known and already in use on an industrial scale (Sole and Tinkler, 2016; Stevanović et al., 2009). Furthermore, the level of CO_2 emissions from copper recovery from the battery leach solution is not likely to reach primary Cu production levels (744 kg/ton of Co) and therefore is significantly lower when compared to that of H_2O_2 (1269 kg/ton of Co). Consequently, the use of copper current collector scrap could help to decrease the total amount of emitted CO_2 by at least 500 kg/ton of cobalt extracted in leaching. Moreover, the secondary production of Cu via

Table 6

Emission intensity (kg CO_2 -eq/kg) for the manufacturing of copper, aluminum and 50% hydrogen peroxide (European aggregate, Ecoinvent 3.6 database).

Cu primary	Cu secondary	Al primary	Al secondary	50% H_2O_2
1.76	1.53	7.59	0.5	1.22

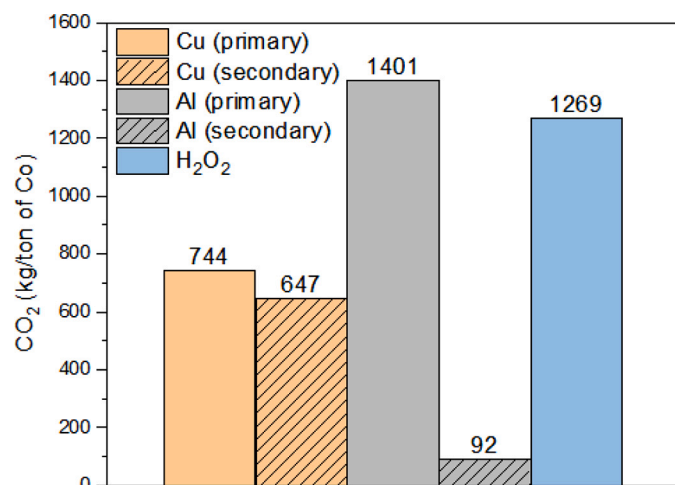


Fig. 5. CO₂ emissions related to the production of the required amount of each reducing agent.

pyrometallurgical routes could also be avoided. At this stage, the discussion of the carbon footprint related to this process are currently only indicative, as more extensive work on the solution purification is required to confirm the holistic effect of both aluminum and copper in more detail. Furthermore, the consumption of H₂O₂ that occurs during a peroxide-based approach to LIBs recycling also needs to be experimentally verified.

4. Discussion

The unique feature of this investigation is that both impure industrially produced battery waste concentrate and current collector scrap from an EV battery manufacturing site were used in the experiments, making the study highly relevant for realistic industrial-scale battery recycling process development. Nonetheless, industrially produced raw materials tend to be inhomogeneous in nature, which can cause challenges related to reproducible and consistent sampling. In this work the issue of inhomogeneity was addressed by using sieved (< 500 µm) raw material, with controlled additions of current collectors as reductants in leaching. This approach allowed a model to be developed that predicts Co recovery and its leaching kinetics from industrial battery waste as a function of the typical current collector materials (Cu, Al) present. The *final acid concentration* prediction (Eq. 18) can support the adjustment of the Cu-Al ratio for the maximum *Co extraction* (Eq. 16) for a selected initial acid concentration. Once the current collector ratio has been adjusted, the model can be used to predict the acid concentration that remains after leaching or the required initial acid concentration to achieve the target acid concentration for further solution purification processes.

Electrochemically, the primary advantages of aluminum are its high driving force for the reduction as well as its ability to provide three electrons per atom in comparison to the two possible from Cu. Additionally, aluminum current collectors obtained from battery production scrap typically include additional cobalt containing material attached to the surface with organic binders, therefore the use of Al current collectors could also potentially reduce the amount of cobalt wasted as a result of the manufacturing process. The main drawback to the use of aluminum scrap is that once dissolved, Al is known to form gel-like precipitates as solution pH is increased, which results in poor filtration performance and co-precipitation of other metals (Gella, 2007). This leads to subsequent solution purification challenges, and consequently, it is desirable to reduce the Al amount as much as possible. Nevertheless, Al cannot be fully removed from the black mass by sieving and the overflow fraction also contains a significant amount of Co, which also

needs to be recycled. Benefits of the model produced as part of this study is that it allows the target amounts of Cu and Al required for maximum metals leaching to be optimized as function of both the Al/Cu overflow fraction and amount of current collector scrap to be added.

Although more noble, copper may provide an efficient reduction power via the Fe³⁺/Fe²⁺ couple (Peng et al., 2019; Porvali et al., 2020), although due to the mode of action - in the case of an absence of Fe³⁺/Fe²⁺ - the overall reduction power attributable to Cu would be negligible. Also, pure copper itself has significant economic value and can be recovered as a by-product of battery recycling by current industrial state-of-the-art methods. If the presence of Al in the solution would not pose challenges to the solution purification process, then Al could also be added along with Cu to provide additional - and alternative - routes for successful leaching. The Cu-Al ratio can be adjusted depending on the amount of the current collectors present in the raw materials or available as scrap from a battery production site. Although Al has lower reduction efficiency compared to Cu, it may have a larger reductive power and can therefore be used to increase the leaching kinetics without the need to introduce additional iron.

During leaching, the level of iron concentration defines the leaching kinetics, i.e. whether it can catalyze the reduction of the active material by copper within the target leaching time. For example, if the iron concentration in the solution is insufficient, it may take longer for the active material to be dissolved. The most important factor is the availability of an electron source throughout the leaching process, e.g. metallic copper, or aluminum, which will ultimately determine whether the active material can be completely dissolved.

5. Conclusions

The findings in this investigation provide new tools that may assist the selection of leaching strategies for hydrometallurgical operations related to LIB battery wastes. Typically, H₂O₂ has been used as the reductant in battery leaching, however, the work outlined here presents an alternative strategy that involves the use of metallic reductants, which originate from the current collector scrap generated during EV battery manufacture. As a significant amount of current collector material is wasted during the fabrication of LIB cells, this investigation assesses the effect of the reductive power of Cu and Al foils on the leaching of industrially produced LIB waste concentrate in sulfuric acid media. The leaching was carried out in 2 M H₂SO₄, at 60 °C, with an agitation speed of 350 rpm and S/L ratio of 1:5.

These experimental results suggest that both current collector materials are effective alternative reductants to, for example, hydrogen peroxide. Aluminum was found to increase the leaching kinetics significantly but was overall less efficient than Cu due to the larger number of side reactions that occur like hydrogen evolution. In contrast, the effectiveness of Cu was determined to be strongly associated with the presence of dissolved iron within the leaching system - an insufficient level of Fe²⁺/Fe³⁺ in the leachate results in only modest levels of metal extraction (cf. leaching in the absence of added current collector scrap) due to the absence of the synergistic Cu-Fe pathway.

The model produced in this study suggests that for a complete Co extraction, 11 g of Cu per 100 g of concentrate (26 wt-% of Co) with 0.8 g/L of Fe in the final solution is enough to achieve full extraction of Co within 3 h. Additionally, it was demonstrated under experimental conditions that with 2 g/L of Fe and 10 g of Cu added, 100% of Co could be leached within 2 h. The models built for *Co extraction*, *final acid concentration* and *acid consumption rate* may offer support to future battery recycling operators in the optimization of reductants and battery production scrap use. Based on the associated preliminary environmental results, it can be concluded that the use of copper-rich current collector scrap from battery manufacturing in battery waste leaching could potentially decrease the CO₂ footprint of the battery leaching stage by at least 500 kg/ton of produced Co.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.hydromet.2021.105608>.

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