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Published in: RESOURCES CONSERVATION AND RECYCLING

DOI: 10.1016/j.resconrec.2018.11.023

Published: 01/03/2019

Please cite the original version:
Porvali, A., Aaltonen, M., Ojanen, S., Velazquez Martinez, O., Eronen, E., Liu, F., ... Lundström, M. (2019). Mechanical and hydrometallurgical processes in HCl media for the recycling of valuable metals from Li-ion battery waste. RESOURCES CONSERVATION AND RECYCLING, 142, 257-266. https://doi.org/10.1016/j.resconrec.2018.11.023
Mechanical and hydrometallurgical processes in HCl media for the recycling of valuable metals from Li-ion battery waste

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ARTICLE INFO
Keywords: Recycling Characterization Hydrochloric acid leaching Solvent extraction Lithium carbonate precipitation

ABSTRACT
The present work offers a study on the engineering implications of the recovery of valuable fractions from industrially collected lithium battery (LIB) waste by mechanical and hydrometallurgical processes in HCl media. Direct leaching of LIB waste provides a possibility for Li extraction, a component that is lost into the slag fraction in the state-of-art high temperature processes. The challenges arising from the heterogeneous composition of industrial battery waste are highlighted, and the behavior of main metals present such as Co, Cu, Li, Mn, Ni and Al is observed. It is shown that mechanical separation processes can form fractions rich on Cu and Al, although subsequent refining stages are necessary. Regarding direct leaching, fast kinetics were found, as complete Li dissolution can be achieved in ca. 120 min. Furthermore, high solid/liquid ratio (> 1/10) is required to increase metal value concentrations, resulting in a viscous slurry due to the graphite, plastics and other undissolved materials, which challenges filtration and washing of leach residue. Neutralization of the product liquid solution (PLS) result in co-precipitation of valuable battery metals along with Fe and Al. The highest value of LIBs lies in Co, subjected for solvent extraction (SX) or direct precipitation to make an intermediate product. SX can provide selectivity whereas Na2CO3 precipitation provides a fast route for Co-Ni bulk production. Li2CO3 precipitation from the remaining PLS is possible as zabuyelite - however, due to heterogeneity of the battery waste, the recovery of Li2CO3 with battery-grade purity remains a difficult task to be achieved by direct precipitation route.

1. Introduction
Secondary lithium-ion batteries (LIB) are the most widespread reusable batteries in consumer products, being mainly used in portable electronics, mobile phones, electric vehicles (EVs) and, more recently, in large-scale grid energy storage (Chagnes and Swiatowska, 2015). The consumption of batteries is drastically growing, as modern societies increasingly rely on equipment requiring the use of mobile on-demand electricity. Although predictions of the Li market beyond 2020 are difficult, the global demand for Li is steadily growing due to the development of EVs and the increasing production of glass and ceramics (Martin et al., 2017). However, it is still uneconomical to recover sufficient quantities of Li using the state-of-the-art technologies for battery recycling. It is therefore necessary to research new processing schemes capable to address the impending future demand of Li and offer a more efficient recovery of valuable metals confined in LIBs.

In general terms, the LIB cells consist of i) electrodes that store the chemical energy; ii) electrolyte, which facilitates the movement of ions between electrodes and iii) a non-conductive, but ion-permeable polymeric separator that prevents short-circuit in the battery. Current LIBs use various lithium oxides (e.g., LiCoO2, LiFePO4 and nickel-manganese-cobalt oxide, or NMC oxide) as cathode materials, typically coated on aluminum foil. The anode commonly consists of a graphite layer coated on copper foil, onto which Li intercalates during the charging cycle. Various Li-salts are used currently as electrolytes, usually contained in organic solvents such as ethylene carbonate (EC) in order to avoid water electrolysis. The heterogeneous design and complex chemistries of these types of batteries result in significant challenges to the mechanical and refining processing of LIBs for an effective recovery of all its valuable components.

The Co contained in LIB cathode materials is an element that requires particular attention. Co is largely obtained as a by-product of Ni and Cu production, with only around 3% of Co globally acquired as the main product (Sverdrup et al., 2017). As a consequence, Co production is relatively inflexible, posing risks to the supply chain of battery materials. Co is therefore considered to be a strategic and valuable metal, a
fact reflected by its classification as a critical raw material by the European Union (European Comission, 2017). In contrast, Li is abundant in the Earth’s crust with several exploitable deposits around the globe with a production expected to increase in the coming years to meet growing demands (Ciez and Whitacre, 2016). Nevertheless, the recycling of Li is nowadays minimal (i.e., < 1% in 2011) and due to ever shorter lifetimes of consumer products powered by LIBs, immense quantities of Li are currently being lost to various waste fractions (Reuter et al., 2013). These are not sustainable practices and represent a senseless waste of raw materials, especially as the production of battery-grade chemicals require energy intensive and laborious refining processes (Chagnes and Swiatowska, 2015). The development of Li recycling processes or integration of Li-rich waste streams into primary processes is crucial in order to preserve raw materials, energy and the environment. In order to recycle Li in particular, a low temperature techniques such as hydrometallurgy is needed. However, battery waste is extremely heterogeneous and problematic to treat consistently via hydrometallurgical means (Etacheri et al., 2011). Consequently, research in the field of LIB recycling is intensive, including exploration of different leaching media for solvent extraction or chemical precipitation (Chen and Zhou, 2014; Guo et al., 2016; Ku et al., 2016; Li et al., 2009; Pranolo et al., 2010; Sun and Qiu, 2012; Wang et al., 2016, 2009; Zhu et al., 2012). A commonly used method for Li recovery after solution purification is carbonate precipitation in the form of Li2CO3, which can be used in preparation of precursor battery materials. Solvent extraction and precipitation can be utilized in selective recovery of various additional metals such as Ni and Co. (Lv et al., 2018)

In several papers, the focus has been on the treatment of a single specific battery type, obtained from dismantling batteries by hand, using synthetic solutions or through simulated crushing processes (Barik et al., 2016; Chen et al., 2011; Jha et al., 2013). Nevertheless, such narrow scope does not reflect the realities of contemporary industrial battery sorting and mechanical processing capabilities. For example, it is not possible to ascertain the specific chemistry of a battery by simple visual inspection on its casing. As a consequence, industrial scale mechanical processes will inevitably process a mixture of the various types of LIB batteries available in the market. This drastically increases the heterogeneity of input material to recycling systems and causes limitations to what is sensibly achievable with hydrometallurgical processes. Since recycling is already practiced at industrial level by several companies, it has befallen to these companies to understand these issues. However, these developments have not translated to spread of engineering information, and this specialty knowledge is still difficult to obtain outside the recycling industry. In this paper, we aim to provoke spread of knowledge in this important subject. As the purpose of leaching is to dissolve the metals present in LIB waste, its selectivity can be improved by properly chosen preliminary treatment operations. Pre-treatment, either mechanical or pyrometallurgical, is mandatory to hydrometallurgy. Several methods have been employed in-mechanical pre-treatment, including crushing and shredding, magnetic separation and sieving (Xiao et al., 2017). For example, pyrometallurgical processes have often been incorporated in various forms in recent studies on battery recycling (Barik et al., 2016; Sun and Qiu, 2012), as it offers advantages like the ability to deal with difficult-to-handle plastics within the waste stream – primarily due to the separators and battery casings – via pyrolysis burning. However, Li is easily lost into the resulting slag under, e.g., copper converting conditions (Tirronen et al., 2017).

In this study, various aspects related to recycling of extraction of metals from LIB waste are addressed by experimental means. Industrially collected LIB waste was used to gain insight into recycling of industrial LIB waste. Currently, the contemporary literature is lacking in insight to waste processing that has not been manually dismantled nor subjected to thermal treatment. The elemental composition in regards to different particle size fractions and density fractions with its associated implications on mechanical pre-processing was investigated. Furthermore, leaching as well as solution purification and metals extraction phenomena were analyzed in HCl media. HCl has been successfully applied in active material leaching (Takacova et al., 2016; Zhang et al., 1998), however these studies have been conducted at much lower S/L ratios than in the present work. It has also been shown recently to work with very high S/L ratios (Barik et al., 2017). Li recovery was demonstrated from the product liquid solution (PLS) as Li2CO3 via precipitation route. Li2CO3 preparation is a topic with wide scale of studies being composed and published and in general, wide array of reviews on Li recovery and LIB recycling have been conducted by several researches very recently (Swain, 2017; Lv et al., 2018; Yun et al., 2018; Ordoñez et al., 2016). Hydroxide and carbonate precipitation of other transition metals was investigated. The work aims at revealing issues, such as gas evolution during LIBs leaching, which may affect the feasibility of future LIBs treatment processes.

2. Experimental

2.1. Materials

An industrial scale operator provided the crushed and sieved battery waste used in the investigations. The LIB waste received had undergone two preliminary separation stages: i) sieving after crushing using a mesh with openings of ca. 1 mm, and ii) magnetic separation for the removal of steel casings. As both underflow and overflow were provided, a 1:1 mixture was used when simulating crushed battery waste streams. The chemicals used were HCl (37%, Merck Millipore, Finland), oxygen (O2, 99.99%, AGA Oy, Finland), NaOH (97%, Caesar & Loretz GmbH, Germany) and Na2CO3 (99.5%, Fluka, Germany) and were used without further purification.

2.2. Characterization of battery waste

Particle size analyses were performed by separating the crushed LIB waste in a vibrating sieving machine (Retsch AS 50), using sieves with the following nominal opening sizes: 8 mm, 4 mm, 2 mm, 1 mm, 500 µm, 250 µm and 125 µm. A total of 20 min of sieving was performed for each experiment and the resultant fractions were weighed.

Density measurements for the crushed LIBs were performed for each particle size fraction with a Quantachrome ULTRAPYC1200 pycnometer. 10 tests per sample were performed and the average value was calculated within a set deviation range. An additional sorting process was performed by hand and the separated fractions generated were analyzed for their chemical contents.

The solid analysis (after total leaching into Aqua Regia) and the solution analysis were carried out using flame atomic adsorption spectroscopy (FAAS, Varian AA240) and inductively coupled plasma – optical emission spectroscopy (ICP-OES, Perkin Elmer 7100 DV). The metals analyzed were the major elements expected in LIBs: Cu, Co, Mn, Fe, Ni and Li were analyzed by FAAS, and Al by ICP-OES.

2.3. Leaching experiments in HCl media

HCl was chosen as a leaching medium due to its ability to reduce Li2O2, circumventing the need to use oxidant such as H2O2 or other organic reductant in H2SO4 leaching (Peng et al., 2018). Through calculation with HSC Chemistry 9.4.1 (Outotec), we can show that reduction of chloride ions and release of chlorine gas is thermodynamically a viable reaction:

\[
2\text{LiCoO}_2(s) + 8\text{HCl}(aq) = 2\text{LiCl}(aq) + 2\text{CoCl}_2(aq) + \text{Cl}_2(g) + 4\text{H}_2\text{O}(aq)
\]

The \(\Delta G^\circ\) for the reaction at T range of 0–100 °C is -155.625 kJ/mol -191.941 kJ/mol. This is contrary to the result what Takacova et al. calculated (Takacova et al., 2016). This could be due to the error in their equation, which is not balanced in their study, however the source of...
difference could as well be the use of older database (HSC 6.1 vs. HSC 9.4.1). Chlorine gas is a toxic molecule, which can be treated via adsorption and electrolysis (Jüttermann et al., 2000). It is also industrially possible to reuse chlorine gas directly in hydrometallurgical processes (Anderson, 2014). In addition to Cl₂(g), it is also possible that H₂(g) will evolve due to the oxidation of Al foils by hydrogen ions (Zoski, 2006):

\[
\text{Al}^{3+} + 3e^- = \text{Al}(s) \rightarrow -1.662 \text{ V (vs. SHE)}
\]  

\[
2\text{H}^+ + 2e^- = \text{H}_2(g) \rightarrow 0 \text{ V (vs. SHE)}
\]

\[
2 \text{ Al} + 6\text{H}^+ = 2\text{Al}^{3+} + 3\text{H}_2(g)
\]

\[
\text{EMF} = 0 - (-1.662 \text{ V}) = 1.662 \text{ V}
\]

However, this is uncertain as there exists other metals and dissolved ions that could potentially be the source of the oxidative power instead of H⁺ ions.

The direct acid leaching by HCl media was investigated in a 1 l glass reactor vessel immersed within a water bath with controlled temperature (Haake DC 10 heater) ad stirred with a four-blade agitator. Direct leaching of LIB waste provides a possibility for Li extraction which currently is not subjected to recovery. A 4 M concentration of HCl was used (Contestabile et al., 2001). In addition, O₂ purging (0.133 dm³/s) was used throughout the leaching experiments in order to guarantee Cu dissolution. In contrast, reductive conditions in sulfuric acid leaching was used throughout the leaching experiments in order to guarantee Cu dissolution. Initial and final redox potentials were measured. Two parameters were varied in the leaching: temperature (T) and solid-to-liquid ratio (S/L). Leaching duration was fixed at 180 min as it has been shown by others to have been an enough for reaching good leaching results (Zhang et al., 1998; Barik et al., 2017) The parameters used in the experiments are presented in Table 1. Basis for the leaching series was 2² full factorial matrix with 2 center points (Bezerra et al., 2008) with experiments 7 L and 8 L intended to show whether dissolution is possible at T = 50 °C. The purpose was not to create regression models, but to screen how T and S/L affect the responses (Yield of Li and Co and redox potential).

### 2.4. Neutralization of the PLS

The neutralization stage in hydrometallurgical processes focuses on Fe removal. In the work hereby presented, neutralization was accomplished by NaOH (2 M). Neutralization was investigated in terms of T and pH with values outlined in Table 2. Droplets of 2 M NaOH solution was added to PLS and the PLS was left stirring for 30 min prior to sampling. In addition, the pH of these solutions was constantly measured during the equilibration phase. Finally a combination of vacuum and syringe filtration was used in order to separate the supernatant (PLS) and precipitates. Similarly, the pH ranges here used were determined by referring to prior study on sulfate media (Wang and Friedrich, 2015).

Solvent extraction experiments were performed by using 200 mL separatory funnels. Shaking water bath (Stuart SBS40) was utilized as a mixer under constant 30 °C temperature. 15-minute contact time was used in both extraction and stripping. Cyanex 272 (20 vol.%) was used as an extractant and tributyl phosphate (TBP, Sigma-Aldrich, > 99%) as a phase modifier (10 vol.%). Kerosene (Sigma-Aldrich, > 95%) was used as a diluent (70 vol.%). The diluent was sulfonated by mixing concentrated sulfuric acid with kerosene at ratio of 1:1 (vol.%/vol.%) for ca. 10 min, separated and subsequently washed with H₂O at 1:1 for ca. 10 min. The phases were then separated and sulfonated kerosene used in SX experiments. Cyanex 272 was saponified prior to the preparation of the organic phase by using stoichiometric amount of NaOH to reach 40% saponification degree. The saponification has been shown to improve the uptake of Co and Mn. O:A = 1 and 2 were used in the experiments and the PLS sample was neutralized to target pH of 5 prior to the SX experiments. O:A ratio of 1 has been shown to be enough for Co recovery in 2 extraction stages, albeit from sulfate media (Swain et al., 2006).

### 2.5. Ni, Co recovery

Ni and Co recovery was investigated both by direct precipitation and alternatively by solvent extraction after neutralization stage. Direct precipitation by Na₂CO₃ aimed at the production of a nickel-cobalt rich precipitate by Na₂CO₃. The final goal was to produce PLS suitable for Li recovery. Precipitation was investigated in terms of both temperature, T and pH with the experimental parameters used outlined in Table 2. Droplets of 2 M Na₂CO₃ solution was added and the solution was let to equilibrate for 30 min with magnetic stirring prior to sampling. In addition, the pH of these solutions was constantly measured during the equilibration phase. Finally a combination of vacuum and syringe filtration was used in order to separate the supernatant (PLS) and precipitates. Similarly, the pH ranges here used were determined by referring to prior study on sulfate media (Wang and Friedrich, 2015).

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### 2.6. Li₂CO₃ recovery

Finally, Li₂CO₃ recovery was pursued for solution which was neutralized (pH = 5) and from which Ni and Co was extracted by precipitation (pH = 8), both at T = 50 °C. Table 3 outlines the parameters utilized in the purification stages, evaporation and Li recovery. As Li₂CO₃ has a relatively large solubility of 15.4 g/L (Seidell and Linke, 1952), it was necessary to increase the concentration of Li₂CO₃ by evaporation of PLS in order to recover Li, a common practice in industry (Zeng et al., 2014; Wilkomirsky, 1999). As a result, the solution volume was reduced by two-thirds to reach a Li concentration equal to 3249 mg L⁻¹. After the evaporative concentration of Li, a stoichiometric addition of Na₂CO₃ was performed (stoichiometric ratio of 1:1.2, [Li⁺]: [CO₃²⁻]) in order to initiate Li₂CO₃ precipitation (Zhu et al., 2012). The final Li₂CO₃ precipitation was carried out at pH = 8.5. The Li₂CO₃

### Table 1
Leaching test series with 4 M HCl, and O₂ purging.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>T (°C)</th>
<th>S/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1L</td>
<td>60</td>
<td>1/20</td>
</tr>
<tr>
<td>2L</td>
<td>80</td>
<td>1/20</td>
</tr>
<tr>
<td>3L</td>
<td>60</td>
<td>1/15</td>
</tr>
<tr>
<td>4L</td>
<td>80</td>
<td>1/15</td>
</tr>
<tr>
<td>5L</td>
<td>70</td>
<td>1/10</td>
</tr>
<tr>
<td>6L</td>
<td>70</td>
<td>1/10</td>
</tr>
<tr>
<td>7L</td>
<td>50</td>
<td>1/20</td>
</tr>
<tr>
<td>8L</td>
<td>50</td>
<td>1/10</td>
</tr>
</tbody>
</table>

### Table 2
Neutralization test series (1 P).

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Precipitation stage</th>
<th>pH</th>
<th>T (°C)</th>
<th>Precipitator</th>
</tr>
</thead>
<tbody>
<tr>
<td>1P1</td>
<td>1</td>
<td>5, 5.5, 6</td>
<td>30</td>
<td>NaOH</td>
</tr>
<tr>
<td>1P2</td>
<td>1</td>
<td>5, 5.5, 6</td>
<td>40</td>
<td>NaOH</td>
</tr>
<tr>
<td>1P3</td>
<td>1</td>
<td>5, 5.5, 6</td>
<td>50</td>
<td>NaOH</td>
</tr>
</tbody>
</table>

### Table 3
Ni and Co recovery by precipitation in experimental series (2 P).

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Precipitation stage</th>
<th>pH</th>
<th>T (°C)</th>
<th>Precipitator</th>
</tr>
</thead>
<tbody>
<tr>
<td>2P1</td>
<td>2</td>
<td>7, 7.5, 8</td>
<td>30</td>
<td>Na₂CO₃</td>
</tr>
<tr>
<td>2P2</td>
<td>2</td>
<td>7, 7.5, 8</td>
<td>40</td>
<td>Na₂CO₃</td>
</tr>
<tr>
<td>2P3</td>
<td>2</td>
<td>7, 7.5, 8</td>
<td>50</td>
<td>Na₂CO₃</td>
</tr>
</tbody>
</table>
precipitates were filtered, washed and analyzed by x-ray diffraction (XRD, PANalytical X’Pert Pro Powder, Almelo, Netherlands) with a CuKα radiation source at a scan rate of 2°/min (acceleration potential 45 kV, current 40 mA). Additionally, chemical analysis was performed in order to determine the purity and confirm the formation of Li2CO3 (Table 4).

3. Results and discussion

3.1. Heterogenous nature of the raw material

The chemical analysis of the sieved LIB waste material (Fig. 1 and Fig. 2) shows that the content varies widely in the different particle size fractions. The “others” fraction consisted mainly of organic residues (Chen and Zhou, 2014; Barik et al., 2016). The coarsest particle fraction showed the lowest metal content, likely as the plastic casings and the thin plastic form foil-like particles that accumulate in this fraction. Interestingly, the metal content also has a decreasing trend in the smallest particle size fractions. A reasonable explanation for this is the presence of fine graphite powder used on the anode materials in LIBs. The chemical analysis shows the presence of Ni and Mn, suggesting that e.g. NMC oxides and LiMn2O4 type batteries are present in the industrially crushed LIB waste stream. This highlights the necessity of using proper safety measures, including respiratory protection, gloves and protective during raw material handling. As seen, Cu and Al were present in higher concentrations in particle sizes > 500 μm. It is worth noting that there exist several LIB cathode chemistries, and a variety of components such as Li, Co, Mn and Ni are mostly expected to be finesized particles, as they are expected to proceed from the brittle cathode material (Zeng et al., 2014). Although Co is also part of the cathode materials, a significant presence of Co reported to the overflow, perhaps due to the material remaining adhered to the electrodes (Xu et al., 2008). From Fig. 3, it is possible to ascertain that Fe is also concentrated into the underflow, indicating the presence of LiFePO4 type batteries in the raw material received from industrial operator. It is notable that the Al size distribution closely follows that of Cu, likely indicating the lack of Al-containing anode active materials in the raw material feed.

Density measurements were combined with elemental analyses in order to determine the feasibility of density-based separation and enrichment of metals present in LIBs waste (Fig. 4). As seen, the plastic-containing “Others” fraction was poorly separated from any of the fractions. A sharp increase in Al and Cu share was observed at a density of 2 g cm⁻³. The overall separation efficiency in density separation remained relatively low, containing 62% of total Al and 75% of total Cu at 2.036 g cm⁻³. Other metals ranged between 16–22% of their total wt.% in raw material feed. These results suggest that a density-based separation may present a relatively simple method for Al and Cu separation from the rest of the materials.

Characterization of chemical composition and density of manually sorted metallic particles following visual inspection was also performed to determine the intrinsically attached components in the battery waste particles. Table 5 shows the results of Al and Cu-rich fractions. As seen, Al foils contain 11 wt.% of Co which is likely due to the organic binder used with the cathode active material. This confirms that some quantities of Ni, Co, Li and Mn may report to the coarse fraction even after crushing and sieving, and will be lost if subjected to Cu or Al smelting process. The reported densities are not for pure elements, but for the material sample that was used in the analysis.

Based on the distribution of elements presented above, one of the
major challenges with physical separation of LIBs is highlighted. While both particle size and density-based separation results in concentrated fractions of Cu and Al, the resulting products are still contaminated with plastics or even other valuables, such as Co. This emphasizes the need for hydrometallurgical treatment of battery waste to obtain high purity secondary raw materials, as this approach allows the recovery of Li and Co that are otherwise lost in the slag of copper smelter (Tirronen et al., 2017). Properly chosen mechanical separation operations however, represent a useful pre-processing stage as it permits the concentration of particular metallic species into streams with lower flow-rate that could be more easily handled in subsequent refining processes.

3.2. Leaching of LIBs fraction

The underflow of ca. 1000 μm sieve was used as case raw material fraction in hydrometallurgical treatment. The chemical composition of the main metals present in this fraction is presented in Table 6. The raw materials were analyzed and the results are presented in Table 6. In total, 5 parallel samples were analyzed. There’s large variance in the results of Co, Cu and Al. This is due to the larger Al and Cu foil pieces, causing variations in the composition. Co has large variability and Mn, Ni and Li are experiencing only 1–4 % variations in mean vs. mean standard deviation of sample, whereas Al, Co and Cu show variation of 9–14 %. It is known that Co can be adhered to Al and Cu foils due to the organic binder, as shown by our results. This may in part explain the variability of Co. However, it is hard to explain why Mn, Ni and Li show less variability. Regardless, this is detrimental to comparability of the leaching results. In order to obtain solutions with high Co concentration, a relatively high amount of solids must be used: 100 g of raw material per 1 L of the solution would result in maximum of ca. 28.62 g/L of Co and 3.6 g/L of Li.

The extraction of Li, Co, Mn and Ni into HCl solution during leaching series (Table 1) are presented in Table 7 as metal concentrations in the solution. This was done due to the sampling having uncertainty. No clear trends were observed within the investigated range of leaching parameters, perhaps attributable to the heterogeneity of the samples as shown in Table 6. In addition to variation caused by sampling, other sources of error are analytical (± 3% in AAS). To overcome the issues related to statistical representativeness of the sample in leaching tests, the raw material could be ground to finer particle sizes before sampling. This can allow a more homogeneous distribution of Al, Cu and other elements into samples used in leaching experiments (Sun et al., 2015). However, in doing so, the particle size distribution will change, along with a possibility of mecanochemical changes occurring. Since the intention of the present work was to evaluate the crushed samples produced, this was not attempted hereby. Also, the leach residue analysis can provide future tools to increase the amount of data points gained from the leaching experiments.

In each experiment at minimum ca. 40 wt.% of the initial raw material feed remained in the leach residue, necessitating expansive leach residue treatment. Kinetics of metals dissolution were fast in each experiment in HCl media, maximum extractions being achieved already before 120 min. Furthermore, during and after the leaching experiments it was also observed that the associated slurry has a relatively high viscosity, most likely due to undissolved graphite and polymer residues, thus challenging the S/L separation after leaching. The oxidation-reduction potential (ORP) of the solution after leaching is also shown in Table 7. At T = 80 °C and sample mass = 40 g (4 L), the redox potential was decreased to 851 mV (vs. Ag/AgCl). However, at T = 80 °C and sample mass = 80 g (6 L), the redox potential decreased further to 645 mV (vs. Ag/AgCl). The pronounced effect of higher temperature on ORP could be due to the evaporation of HCl, and not only due to the consumption by dissolution reactions. Decrease in ORP signifies decrease in oxidative potential of the solution. This may affect the efficiency of the chloride processes and the effect of temperature must therefore be considered not only from the perspective of dissolution kinetics, but also HCl losses.

3.3. Neutralization of the PLS

Leachates obtained in Exp. 1 L – 8 L were combined to produce PLS for the solution purification investigations. The solutions were combined in order to ensure that a large volume of solution was available for all the future experiments, ensuring a stable baseline unlike in leaching experiments. The chemical analysis of the solution used as the initial PLS for Li recovery is presented in Table 8. It can be seen that in the PLS the concentration of Co is remarkably high (> 16 g/L), and the concentrations of other metals (Li, Ni, Mn, Cu, Al) are of the same magnitude 1500–2550 mg L⁻¹, whereas Fe is present at smaller quantities (741 mg L⁻¹).

Firstly, iron removal from leachate was investigated with neutralization by hydroxide precipitation and the results at different temperatures are outlined in Fig. 5. As can be seen, iron was completely removed at every temperature when pH ≥ 5, which signifies that ferric iron (Fe³⁺) was present in the solution as it starts to precipitate at pH ca. > 2 (Wang and Friedrich, 2015). Overall, the results suggest that by using T = 50 °C and pH = 5, it is possible to remove most of the iron (ca. 99%), aluminum (ca. 80.5%) and copper (ca. 80%) with hydrolysis, however, it was evident that part of the valuable battery metals are lost in neutralization stage: Ni (9.6%), Co (1.6%) and Li (2.28%). This loss is most likely due to mechanism unrelated to e.g. Ni hydrolysis, such as adsorption to the mixed hydroxide precipitate of Fe-Al-Cu. The loss in molarity is calculated to be Ni = 3.2 mM, Co = 4.57 mM, Li = 8.37 mM, when initial concentration based on Table 8 was Li = 0.367 M,

Table 5
The chemical analysis of hand-picked metallic samples of LIB waste.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g cm⁻³)</th>
<th>Fe (%)</th>
<th>Ni (%)</th>
<th>Co (%)</th>
<th>Al (%)</th>
<th>Cu (%)</th>
<th>Mn (%)</th>
<th>Li (%)</th>
<th>Other (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>6.14</td>
<td>3.9</td>
<td>0.4</td>
<td>1.9</td>
<td>0.2</td>
<td>73.8</td>
<td>0.2</td>
<td>0.4</td>
<td>19.3</td>
</tr>
<tr>
<td>Sample 2</td>
<td>2.87</td>
<td>0.4</td>
<td>1.0</td>
<td>11.4</td>
<td>61.3</td>
<td>1.6</td>
<td>1.5</td>
<td>1.2</td>
<td>21.6</td>
</tr>
</tbody>
</table>
Co = 0.285 M and Ni = 0.034 M. However, the behavior of Mn and Li is anomalous. Experimental results suggest some Mn and Li precipitation at 30 °C, however E-pH diagrams created with HSC reveal that if anything, decreasing temperature should support Mn precipitation, Fig. 6. Lithium should not precipitate at all at this pH range.

### 3.4. Ni, Co recovery

In order to conduct a direct Ni and Co bulk precipitation, PLS was neutralized (T = 50 °C and pH = 5) and subjected for carbonate precipitation experiments (Fig. 7). In general, carbonate precipitation is assumed to function by Eq. (6):

$$2yM^{2+} + yCO_3^{2−} \rightarrow M_{2y}(CO_3)_y$$  \hspace{1cm} (6)

Nearly complete metals separation was achieved at pH = 7 when T = 50 °C. These conditions allowed removal of 94.7% Ni and 94.8% Co from the solution along with removal of Mn (97.2%). This suggests that carbonate precipitation can produce Ni and Co mixed carbonate precipitate with almost no losses of Li into the solids. The effect of pH is confounded with the effect of CO3 concentration as Na2CO3, a weak base, was used as a precipitating agent. It is therefore possible that there is precipitation of mixed (oxy)hydroxide-carbonates. Again, increasing temperature decreased the solubility of the carbonates, causing improved precipitation at higher temperatures.

Solvent extraction of Co, Mn, Ni and Li was investigated also with sodium saponified Cyanex 272 in sulfonated kerosene with TBP phase modifier at O:A 1:1 and 2:1, shown in Fig. 8. The extraction follows the following generalized reaction equation (Wilson et al., 2014):

$$nLH_{org} + M^{n+} \leftrightarrow [M(L)_n]_{org} + nH^+$$  \hspace{1cm} (7)

where L is the organic, complexing ligand.

### Table 6

Chemical analysis of the main elements of LIBs, from five parallel raw material samples.

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Co</th>
<th>Mn</th>
<th>Ni</th>
<th>Fe</th>
<th>Cu</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>3.60</td>
<td>28.62</td>
<td>2.75</td>
<td>2.74</td>
<td>0.72</td>
<td>3.02</td>
<td>2.15</td>
</tr>
<tr>
<td>Std. Deviation</td>
<td>± 0.031</td>
<td>± 2.653</td>
<td>± 0.131</td>
<td>± 0.043</td>
<td>± 0.034</td>
<td>± 0.353</td>
<td>± 0.304</td>
</tr>
<tr>
<td>Coefficient of Variation (%)</td>
<td>± 1.10%</td>
<td>± 9.27%</td>
<td>± 4.76%</td>
<td>± 1.59%</td>
<td>± 4.81%</td>
<td>± 11.68%</td>
<td>± 14.14%</td>
</tr>
</tbody>
</table>

### Table 7

Extraction of Li, Co, Mn, Ni, Al and Cu into the 4 M HCl solution, reported as concentration (mg L⁻¹), during the LIBs raw material leaching. The experimental parameters are outlined in Table 1. Redox reported as mV vs. Ag/AgCl.

<table>
<thead>
<tr>
<th>L/S</th>
<th>T (°C)</th>
<th>Li</th>
<th>Co</th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Al</th>
<th>Redox</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>50</td>
<td>2858</td>
<td>17663</td>
<td>2670</td>
<td>2552</td>
<td>2799</td>
<td>1785</td>
<td>1045</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
<td>2472</td>
<td>16486</td>
<td>3451</td>
<td>2949</td>
<td>2572</td>
<td>2435</td>
<td>1057</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
<td>3069</td>
<td>20480</td>
<td>3766</td>
<td>2626</td>
<td>2884</td>
<td>2379</td>
<td>645</td>
</tr>
<tr>
<td>15</td>
<td>70</td>
<td>2364</td>
<td>16372</td>
<td>2487</td>
<td>1908</td>
<td>1833</td>
<td>1460</td>
<td>1069</td>
</tr>
<tr>
<td>15</td>
<td>70</td>
<td>2426</td>
<td>16364</td>
<td>2324</td>
<td>1827</td>
<td>1803</td>
<td>1416</td>
<td>1076</td>
</tr>
<tr>
<td>20</td>
<td>50</td>
<td>1595</td>
<td>10199</td>
<td>1408</td>
<td>1230</td>
<td>1415</td>
<td>972</td>
<td>1031</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
<td>1334</td>
<td>9466</td>
<td>2189</td>
<td>1301</td>
<td>1383</td>
<td>1053</td>
<td>1025</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>1223</td>
<td>8757</td>
<td>2408</td>
<td>1138</td>
<td>1281</td>
<td>1057</td>
<td>851</td>
</tr>
</tbody>
</table>

### Table 8

Chemical analysis of the PLS, obtained from LIBs leaching in HCl media. The solution was combined from the leachates of tests 1 L–8 L.

<table>
<thead>
<tr>
<th>Li (mg L⁻¹)</th>
<th>Co (mg L⁻¹)</th>
<th>Ni (mg L⁻¹)</th>
<th>Mn (mg L⁻¹)</th>
<th>Cu (mg L⁻¹)</th>
<th>Al (mg L⁻¹)</th>
<th>Fe (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2548</td>
<td>16817</td>
<td>1996</td>
<td>2146</td>
<td>2145</td>
<td>1519</td>
<td>741</td>
</tr>
</tbody>
</table>

Fig. 5. Neutralization of PLS originating from HCl leaching of libs at T = 30, 40 and 50 °C, experiments 1 P1 – 1 P3.
Fig. 6. E-pH diagram of Mn-Cl-O-H system. [Mn] = 0.039 M, [Cl] = 4 M. Two diagrams superimposed on each other, created at T = 30 °C and T = 50 °C.

Fig. 7. Total Recovery of metals from PLS by carbonate precipitation (T = 30, 40 and 50 °C in experiments 2 P1 – 2 P3). The PLS was neutralized (pH = 5, T = 50 °C) prior to this precipitation stage.
The solution was neutralized (pH = 5) and the solution composition used in SX experiments is shown in Table 9.

It was possible to obtain most of the Mn and Co residing in the solution at O:A = 1:1, however just one step will not be enough for their complete extraction. Conversely, at O:A of 2:1 co-extraction of nickel was drastically increased, but this may be also attributed to increased pH (Cytec, 2008). The end pH for extraction was 4 in O:A = 1:1 whereas it was 5.3 in O:A = 1:2. Co-extraction of Li in SX is a common problem as it is very easy to lose a significant portion of the Li into the organic phase (Chen et al., 2011). With multi-stage SX process, it is possible to selectively extract Mn and Co from Ni and Li. In this paper, we did not investigate the subsequent recovery steps. However, there exists different methods for their separation. One potential way for the separation of Mn from Co is oxidative precipitation of Mn (Zhang et al., 2002), followed by oxalate precipitation of Co (Chen et al., 2011). In the case of Li and Ni, pH adjustment to 11 could guarantee the precipitation of Ni along with impurities, as shown in present research, followed by e.g. carbonate recovery of Li (Han et al., 2018).

Solvent extraction can be superior compared to precipitation method employed. The extractant can be reused and can offer higher selectivity compared to precipitation when optimized. However, both methods are dependent upon pH control, necessitating neutralization reactions that produce large volumes of neutralization residues. Solvent extraction is also a cost intensive process with open intensive organic reagents as well as safety and flammability issues related. However, the extent of required neutralization agent could be addressed in future by designing leaching processes operating at relatively high pH or alternatively by developing extractants operating at low pH.

### 3.5. Demonstration of Li_{2}CO_{3} precipitation

The solution purification was performed in two steps: Neutralization (NaOH precipitation, pH = 5, T = 50 °C) and Ni and Co removal (Na_{2}CO_{3} precipitation, pH = 8, T = 50 °C). Combination of these two stages provided solution high in Li (1119 mg L⁻¹) and low in impurities (< 10 mg L⁻¹), as displayed in Table 10. These results suggest that by straightforward precipitation, some selectivity between Li and other metals present can be achieved, although rather anomalously, Co showed an increased precipitation at neutralization stage when compared to results observed previously in experimental series 1P (Fig. 5).

In the final stage, Li was recovered by evaporation combined with precipitation and an extensive chemical analysis of the white lithium carbonate powder produced is presented in Table 11. The results show that it was possible to obtain a relatively pure lithium carbonate precipitate of 95.3% purity. Nonetheless, this more detailed precipitate analysis demonstrates the difficulties associated with the processing of mixed LIB battery waste as, in addition to major battery elements (Li, Ni, Co, Mn, Al, Cu, Fe), also minor quantities of other impurities were found in the precipitate, even after neutralization and Ni&Co carbonate precipitation steps. As a consequence, it is unrealistic to expect a pure precipitation route to provide high purity Li_{2}CO_{3}. The purity of Li_{2}CO_{3} was calculated based on the assumption that all Li in the precipitate was in the form of Li_{2}CO_{3}, resulting in a purity of 95.3%. This can be considered as an intermediate as new battery production is reported to require > 99.5% pure material (Chagnes and Swiatowska, 2015).

Moreover, due to the relatively high solubility product of lithium carbonate, achievement of suitable supersaturation levels is energy intensive even though it results in a mediocre precipitation efficiency of ca. 50%. Further evaporation would be required in order to induce a higher state of saturation in the solution, though energy efficiency of the process could be improved by use of higher initial S/L ratios in the leaching. In addition, higher temperature could also be utilized in order to obtain better Li_{2}CO_{3} precipitation efficiencies (Zhu et al., 2012). The amount of impurities in real industrially collected and crushed raw material is remarkable and further purification is required, either prior or post precipitation. Washing of the precipitate would improve the purity, but would also lead to valuable lithium carbonate dissolution.

Finally precipitates were subjected to XRD, where the formation of lithium carbonate in the crystallographic form of zabuyelite (Reference Number: 98-010-0324) was confirmed (Fig. 9). This analysis clearly demonstrated the presence of lithium carbonate, however, a number of weak unidentified signals corresponding to unknown compounds and impurities were also observed.

Taking together the XRD and chemical analysis, results strongly indicate that it is possible to obtain a relatively pure (> 95%) Li_{2}CO_{3} product via pure precipitation route after leaching of industrially crushed LIBs waste. In terms of circular economy of Li, further refining stages are required to produce battery-grade Li_{2}CO_{3}.
Cyanex 272. At end pH = 4 and A:O = 1, the saponification (97.1%), Co (97.2%) and Mn (97.3%) or alternatively by SX with nitrates precipitation (at T = 50 °C and pH = 8) with extraction of Ni (81.3%) and Al (80.5%) could be removed at optimal conditions. Large part of solids remained in the leach residue, challenge the dividing of identical homogenous samples. Large standard deviations of Al (14%), Cu (11%) and Co (9%) were measured in parallel raw material analysis. In the leaching, plastics and graphite present in the LIB waste caused viscous slurry conditions. Relatively large portion of solids remained in the leach residue, ca. 40 wt.% of the input solids were undissolved.

Impurity removal was performed by neutralization at pH (5–6) with NaOH at different temperatures (30–50 °C). Most of the Fe (99.6%), Cu (81.3%) and Al (80.5%) could be removed at optimal conditions (pH = 5, T = 50 °C). Neutralization was followed by Ni and Co carbonate precipitation (at T = 50 °C and pH = 8) with extraction of Ni (97.1%), Co (97.2%) and Mn (97.3%) or alternatively by SX with Cyanex 272. At end pH = 4 and A:O = 1, the saponified extractant in sulfonated kerosene provided efficient separation of Ni (3.15%) and Li (5.26%) from Mn (80.3%) from Co (56.17%). Additional processing steps would be required in order to reach higher extraction efficiency.

Finally, Li2CO3 was produced at relatively high purity (95%) and at yield of ca. 50% via precipitation route. However, improving the yield is a matter of increasing supersaturation. In this turn may necessitate further evaporative concentrating of the solution in order to maximize the Li2CO3 recovery.

Acknowledgements

Authors would like to thank Petteri Halli and Chao Peng for the help in performing XRD analyses. Authors would also like to thank Alexander Chernyayev for performing leaching experiments. The authors of this research paper are grateful to the METYK-project (grant number 3254/31/2015), funded by Business Finland (BF). The research was also supported by the Strategic Research Council at the Academy of Finland, project CloseLoop (grant number 303454), RawMatTERS Finland Infrastructure (RAMI) funded by Academy of Finland and CMEco (grant number 7405/31/2016), also funded by BF.

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