**RESEARCH REPORT**

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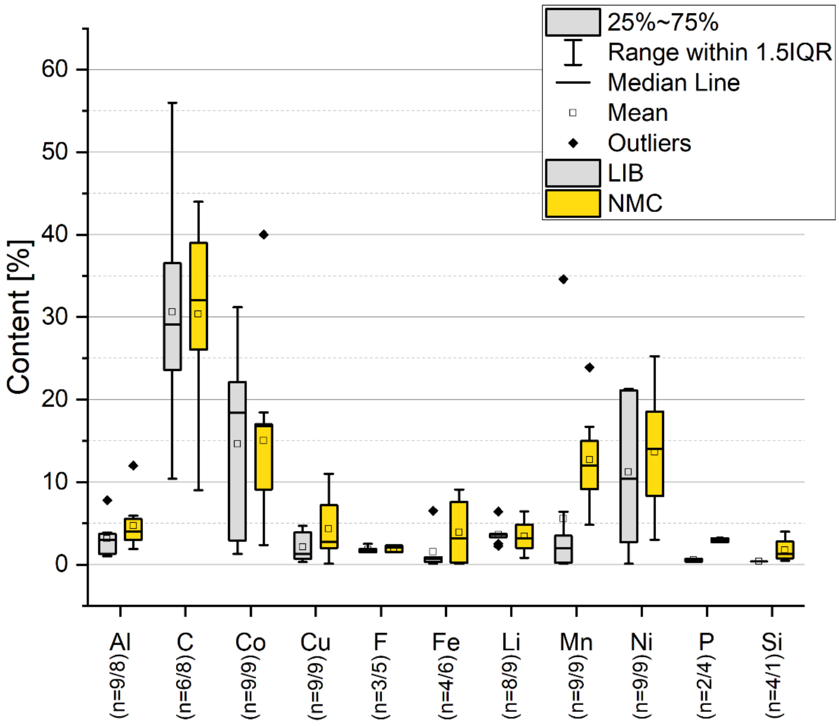

# Secondary raw materials for primary processing

## D2.1.2 Literature report on pre-treatment

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beyond the obvious

**Report's title**

Secondary raw materials for primary processing

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**Summary**

As the societies are striving towards carbon neutrality, energy storage and especially lithium-ion batteries have become one of key enabling technologies. Raw material demand for the batteries will increase in multifold at which time all possible material sources should be utilized. At the moment, recycling of end-of-life batteries are often separate from primary raw materials processors. Partly this is due to the complex, heterogenous and different nature of the feed. However, integrating secondary raw materials to primary production has gained interest to produce broader metallurgical capacity.

The aim of this study is to understand the aspects in pre-treatment of EV batteries which are crucial when secondary raw materials are fed to primary processing. The approach in the study composed of a literature review and black mass composition assessment.

The literature review on pre-treatment processes revealed differences between commercial actors leading to variation in the composition of active material rich fraction called black mass. Even though the pre-treatment processes may compose of same unit processes, differences in equipment type and configuration of the unit processes among other things affects the black mass composition. This variation can be enhanced through poor feed handling to the pre-treatment. In addition, lack of standard for the composition of black mass fraction may also enable wider fluctuation.

When reflecting the black mass composition with the feeds utilized in primary production, most disparity is generated by lithium, fluoride and organics which are not found in sulphidic concentrates from mines or in the intermediate mixed precipitates. This leads to the challenge related to element compatibility and the stage of the flowsheet at which the black mass would be fed into. As an example, the process must at the point in question have similar impurities as to be capable of handling the addition without complications or process modifications. Various treatment methods has been studied to remove or separate one or more of these materials/compounds from the black mass fraction. While mechanical treatment of black mass focus on the separation of graphite and metals such as iron, copper and aluminium from the black mass, thermal treatment aims at removal of fluorides including the binder.

In order to have a comprehensive view on the total effectiveness of integrating secondary pre-treatment and primary metals refining, further studies where these has been merged is needed.

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# 1. Introduction

In the battle against the climate change, decoupling from fossil fuel has been defined as one of the main actions. This decoupling requires not only energy production from new climate friendly sources but also electrification of transportation. However, the momentary supply and demand of energy might not balance out when electricity is produced with the renewable energy production systems due to variability in their availability (wind and solar). Therefore, energy storage is required as a solution to alleviate these balancing issues. Battery technology has evolved during the past several decades and can be nowadays considered as the key technology for storing energy. Development in other secondary battery technologies has proceeded in leaps when comparing to the common lead-acid batteries. Currently, lithium-ion batteries have become the dominant battery technology which are used both in consumer appliances, electric vehicles (EV) as well as in industrial heavy-duty applications.

As car manufacturers are electrifying their car fleet, high increase in demand of the battery raw materials is expected to occur. Based on a study by Xu et al., where future raw material demands for batteries was modelled in different scenarios, the lithium nickel cobalt manganese oxide (NMC) dominated battery scenario forecast which showed that the demand of lithium, cobalt, and nickel would increase by factors[1] of 18–20, 17–19, 28–31 respectively during a period of time spanning from 2020 to 2050. In addition, for other materials such as aluminium, copper, graphite and manganese, the increase caused by the demand from new batteries is estimated to be a factor of 15–20. (Xu et al. 2020) Another study by Alves Dias et al. forecasted with various scenarios the demand of cobalt to increase between 2.3 and 5.1 times the demand in 2017 by 2030 (Alves Dias et al. 2018). McKinsey & Company projected the demand of lithium and cobalt to increase by factors of 3, 1.6 respectively from 2017 to 2025. As for nickel the demand is forecasted to increase 1.25 times the annual demand in 2016 by 2025. However, the demand for high-purity class 1 nickel (suitable for battery manufacturing) may increase up to 10 times the demand in 2017 by 2025. (Azevedo et al. 2018; Campagnol et al. 2017)

At the moment, most of the battery raw materials are produced from primary sources (Neidhart et al. 2022). Degree of recycling of the raw materials from batteries varies greatly depending on the target elements. For example, Umicore recycles lithium-ion and nickel metal hydride batteries while recovering mostly nickel and cobalt from them (Pinegar et al. 2019). In addition, most of the current EV batteries are still in use and are not expected to return to recycling soon. However, this will change in future. Even though recycling of battery materials won’t solve the imbalance between the supply and demand, it can to some extent alleviate the need to produce more virgin raw materials. Xu et al. estimated that recycling, at best, has the potential to reduce 20–23 % of the cumulative material demand for lithium until 2050, 26–44 % for cobalt and 22–38 % for nickel, 26–44 % for manganese and 22-38 % for graphite (Xu et al. 2020).

Currently, main end-of-life operations for traction EV batteries include collection, sorting and possible discharge, followed up by mechanical and thermal pre-treatment and pyro- and/or hydrometallurgical treatment. Each end-of-life operation have their own limitations and requirements which makes the operation chain a multidimensional and complex entity. Current metallurgical processes for end-of-life (EOL) batteries are often separate from primary raw materials processors. This is partly due to the complex, heterogenous and dissimilar nature of the feed. However, in order to broaden the metallurgical capacity, it could be of interest to investigate whether feeds from end-of-life treatment chain could be utilized in primary raw materials processing.

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[1] The factors refer to the increase of material demand in battery industry and do not take into account demand in other industries/total demand.

# 2. Goal and approach

The aim of this study is to understand the aspects in pre-treatment of EV batteries which are crucial when secondary raw materials are fed to primary processing. In the work following issues are looked at:

- Current battery feed
- Current pre-treatment methods and their produced concentrates
- Factors in the pre-treatment affecting the output fraction quality
- Requirements for primary production

The approach in the study composes of a literature review and black mass composition assessment. The black mass assessment is based on reported results published in scientific journals or similar sources.

# 3. Li-ion battery waste pre-treatment and its characteristics

## 3.1 Different type Li-ion batteries

Lithium-ion battery technology is under constant development. As the visible changes relate to the geometry of the cell, perhaps the most relevant changes in terms of the performance of the battery are related to the chemistry of the cathode material. The most common cathode material chemistries and their characteristics are presented in Table 1. As the performance of the various lithium-ion battery chemistries are non-identical, they are used in different end-user applications. For example, lithium cobalt oxide (LCO) based batteries are often used in portable electronics where energy density is an important factor whereas LFP batteries are more commonly used in larger and heavier applications such as e-busses, EVs and stationary energy storage where energy density is not as critical or where it can be compensated by increasing amount/mass of the battery. NMC battery type has been predicted to become significantly more commonplace in future as it is currently the dominating chemistry for EVs (Yogo and Soler, 2019; Neidhart et al. 2022; Xu et al. 2020). However, analysis about the competition between LFP, NMC and NCA for the future lead technology has been presented (Pacios and Careaga, 2022) and it is yet uncertain which chemistry will become commonplace and favoured.

*Table 1. Summary of the most common cathode chemistries and their characteristic features. ++ ideal, - - poor. (Harper et al. 2019; Pinegar et al. 2019)*

| Cathode chemistry | Safety | Cost | Energy density | Cycle life (times) | Applications |
|---|---|---|---|---|---|
| LCO ($LiCoO_2$) | - | - - | + | 0 | Consumer electronics |
| LFP ($LiFePO_4$) | ++ | + | 0 | + | EVs and e-busses, energy storage |
| LMO ($LiMn_2O_4$) | + | + | 0 | 0 | EVs, power tools, consumer electronics |
| NCA ($Li(Ni_{1-x-y}Co_xAl_y)O_2$) | 0 | 0 | ++ | + | EVs, power tools, smartphones, tablets, energy storage |
| NMC ($LiNi_xCo_yMn_zO_2$) where $x+y+z=1$ | 0 | 0 | ++ | 0 | EVs, e-busses, power tools, smartphones, tablets, energy storage |

Even though chemical composition may differ between the cathode materials significantly, the distribution of the other parts and components between the different battery types are somewhat similar (Figure 1). The dominating component in a battery is the battery pack and module periphery, constituting of *ca.* 35 w% of the battery. Anodes present roughly 20 w% of the entire battery in both NMC/NCA and LFP cases whereas the share of cathode differ between battery type. For NMC/NCA battery pack the cathode presents 23.2 w% whereas for LFP the share is 14.8 w%. This is the largest difference between different batteries. Electrolytes, separators, and other present slightly below 17 w% in both battery types followed by the cell housing presenting roughly 8 w% of the battery.

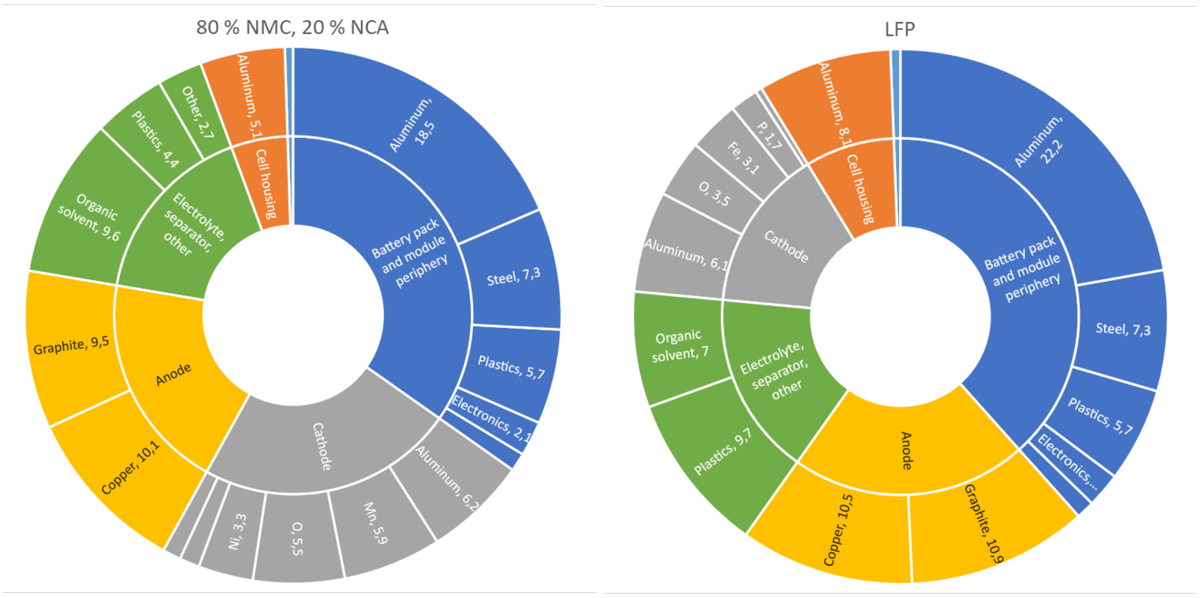

*Figure 1. A general composition of NMC/NCA and LFP battery. Modified from Elwert et al. 2018.*

A more detailed analysis on the active material composition of batteries of different cathode chemistries is presented below (Table 2). It can be noted that important differences exist between different battery types. In particular, cobalt, nickel, manganese, iron and phosphate concentrations vary significantly, which is expected as these are the structural elements in the cathode active material. The contents of the rest of the materials, substances and elements are somewhat on the same level as differences in these components should be somewhat limited.

*Table 2. Different type of lithium-ion cell compositions. (Gaines et al. 2018)*

| Element/material | NMC 111 | NMC 622 | NMC 811 | LCO | NCA | LMO | LFP |
|---|---|---|---|---|---|---|---|
| Active cathode material | 34.1 | 31.8 | 31.1 | 35.3 | 30.4 | 40.1 | 32.2 |
| Li | 7.86 | 7.82 | 7.79 | 7.09 | 7.22 | 3.84 | 4.4 |
| Co | 20.2 | 12.1 | 6.02 | 60.2 | 9.2 | | |
| Ni | 20.1 | 36.1 | 47.9 | | 48.9 | | |
| Mn | 18.8 | 11.3 | 5.61 | | | 60.8 | |
| Al | | | | | 1.4 | | |
| Fe | | | | | | | 35.4 |
| P | | | | | | | 19.63 |
| O | 33 | 32.8 | 32.7 | 32.7 | 33.3 | 35.4 | 40.6 |
| Graphite | 19 | 20.7 | 20.6 | 18.5 | 22 | 13.8 | 16.6 |
| Carbon black | 2.3 | 2.1 | 1.7 | 2.4 | 2.1 | 2.7 | 2.2 |
| Binder: PVDF | 2.9 | 2.9 | 3.6 | 3 | 2.9 | 3 | 2.7 |
| Copper | 16.4 | 16.8 | 15.7 | 16.1 | 16.9 | 15.7 | 14.5 |
| Aluminium | 8.2 | 8.4 | 8 | 8.1 | 8.4 | 7.9 | 7.5 |
| Electrolyte: $LiPF_6$ | 2.2 | 2.2 | 2.6 | 2.2 | 2.3 | 2.2 | 3.3 |

| Element/material | NMC 111 | NMC 622 | NMC 811 | LCO | NCA | LMO | LFP |
|---|---|---|---|---|---|---|---|
| Electrolyte: EC | 6.2 | 6.3 | 7.2 | 6 | 6.3 | 6.1 | 9.4 |
| Electrolyte: DMC | 6.2 | 6.3 | 7.2 | 6 | 6.3 | 6.1 | 9.3 |
| Plastic | 2.5 | 2.5 | 2.5 | 2.4 | 2.5 | 2.4 | 2.3 |

Beside chemistry, the cells can differ in geometry. Three different types of geometry, namely cylindrical, pouch and prismatic, are used in cells. The pouch and prismatic cell types are commonly used in EV batteries. A notable exception is Tesla who utilizes cylindrical cells. In Figure 2, an illustration of the different cell geometries and how they are placed within a module and further on in a pack is presented. The smallest cylindrical cell (18650) is 65 mm high and has a diameter of 18 mm. In the example of Tesla, one module contains 444 cylindrical cells while a single pack contains 18 modules, making in total 7 992 cells. This is significantly more than in prismatic or pouch cell configurations. The prismatic cell is commonly the heaviest cell geometry type whose dimensions are 173 mm (l) x 45 mm (w) x 123 mm (h). One module contains 12 cells and a pack 8 modules, making in total 96 cells in the case of BMW i3. Finally, pouch cells are thin but wide with the dimensions of 260 mm (l) x 225 mm (w) x 7.9 mm (h). One module is composed of 4 cells, contained in a pack of 48 modules, making it in total 192 cells in the case of Nissan Leaf. The geometry can be relevant from processability point of view as the cells with different geometries can behave uniquely in the crusher. Therefore, crusher configurations and operating parameters have a great role. In addition, cell geometry has been shown to affect the power and energy consumption in shredding as well as having impact on the gas formation as heavier cells will increase the loading of crusher (Pinegar and Smith, 2019; Diekmann et al. 2016).

Different pack configurations affect especially the dismantling phase in which housing, electronics and cables among other things are separated from each other. Robotic dismantling has been researched in order to facilitate the dismantling phase (Gerbers et al. 2018). However, at the moment robotic dismantling is not yet a common practice.

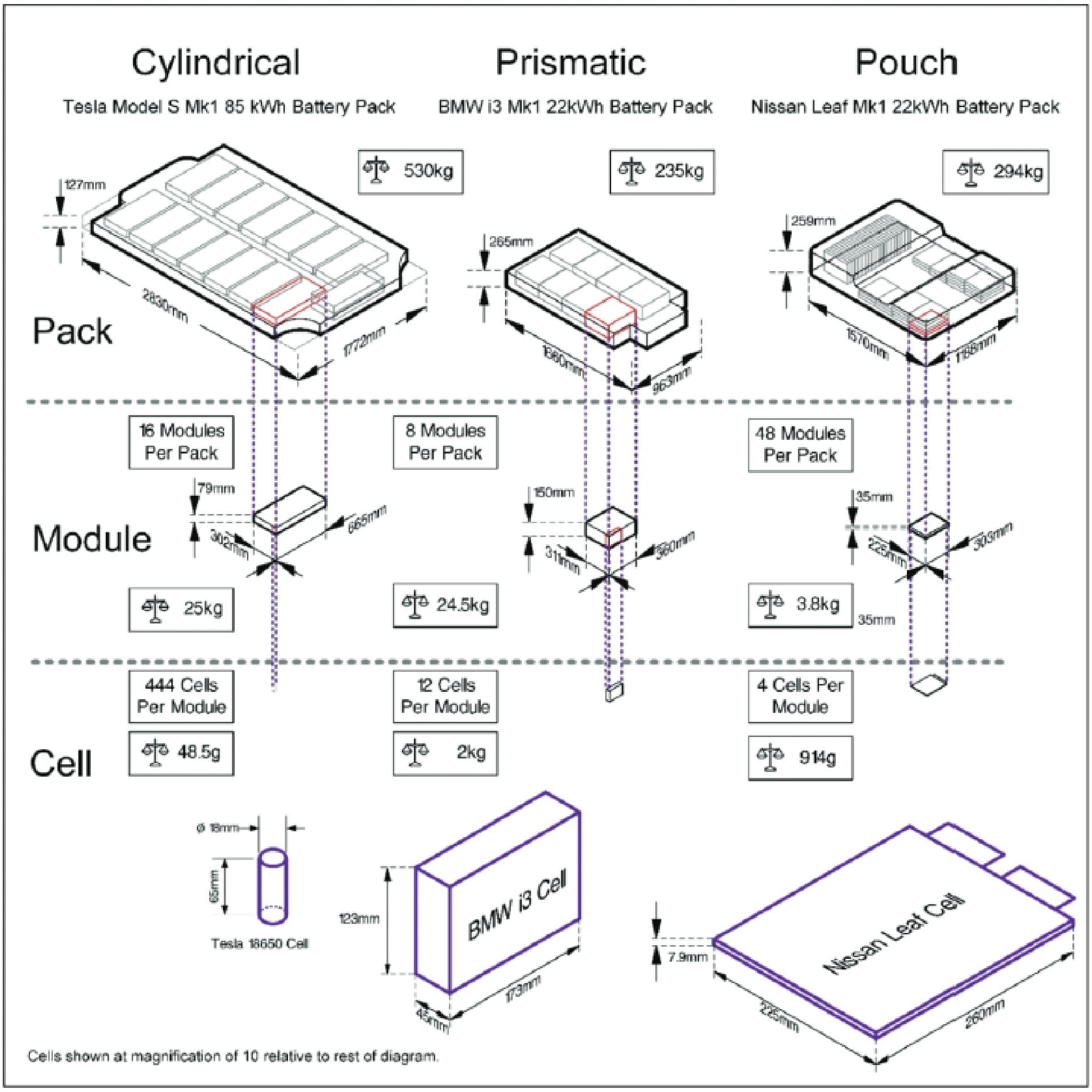

*Figure 2. Example of different battery systems and cell geometries. (Thompson et al. 2020[2])*

## 3.2 General description of Li-ion battery waste pre-treatment

The pre-treatment step is commonly tailor designed, making them unique processes. The implication is that entirely similar process configurations seldom exist. However, pre-treatment is often composed of similar type of unit processes which then may be positioned in different order while having different specifications and parameters. In Figure 3, an overall description of different pre-treatment unit processes is presented. In this work, pre-treatment was divided into three different stages, stages being namely pre-sorting, mechanical and thermal pre-treatment. Each of these stages have their own purpose, from making the feed material safe to handle, to improve liberation or removal of electrolyte.

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[2] https://creativecommons.org/licenses/by-nc/3.0/

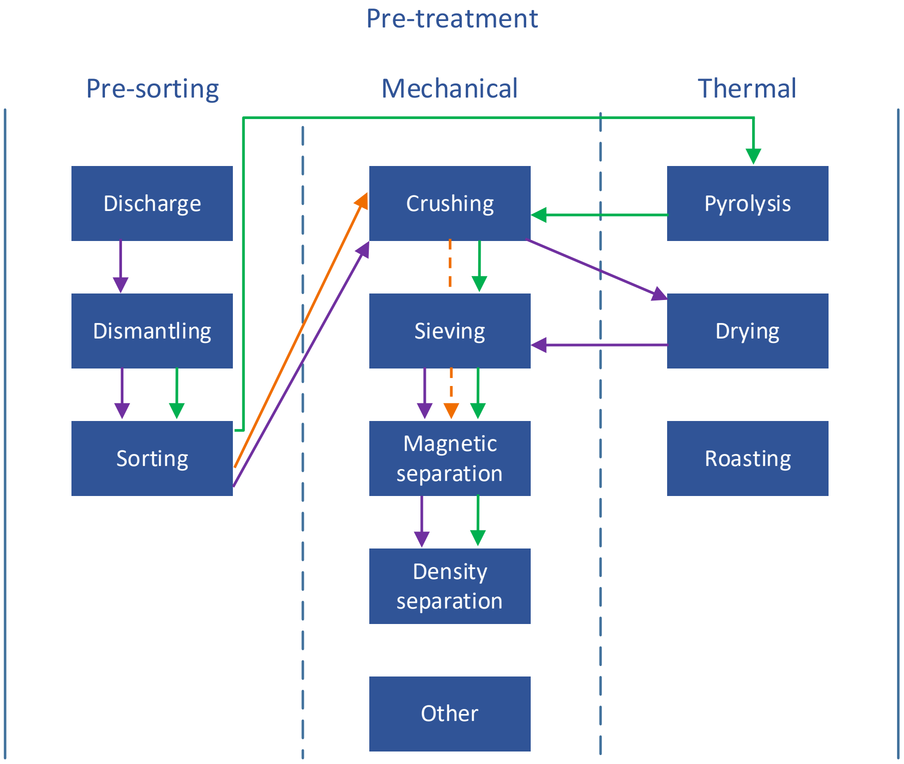

*Figure 3. A schematic figure of most common unit operations and processes under pre-treatment of waste batteries. Purple: Duesenfeld, Green: Accurec, Black: Akkuser*

Pre-sorting aims to produce a safe and treatable feed for the mechanical or thermal pre-treatment. Pre-sorting activities may also contribute to re-use of batteries if the business of an actor involves dismantling of proper cells. Generally, when a battery is received it will be first discharged. Various methods such as brine or Ohmic discharge can be applied to render the batteries safer for further treatment and to recover unused energy (Harper et al. 2019). After the discharging process, battery packs are often dismantled to modules and cells which may then be sorted further prior to the mechanical pre-treatment. As previously mentioned, dismantling is mainly conducted manually but research and development in robotic dismantling is on-going. Dynamic and heterogenous feed in which screws can, for example, be destroyed creates challenges to robotic dismantling.

The objective of mechanical pre-treatment is to enrich target materials from a material matrix for further metals recovery. This processing occurs in particle domain where the separating force affects over the averaged property of particle's volume or surface in particle size class. Usually physical properties such as density, magnetic susceptibility and shape are utilized in the separation technologies. First, discharged cells are crushed to liberate materials from each other and making the feed suitable for mechanical separation unit processes. The crushing can be carried out in normal atmospheric conditions or under inert gas such as Ar, $CO_2$ or $N_2$ to increase the safety. In some cases, the battery cells can be first introduced to cryogenic cooling prior shredding or carrying the shredding in water medium to catch the electrolyte solvent (Sojka et al. 2020). Slow rotating shears or high-speed hammer mills are often used as the primary crushing technology whereas high-speed mills such as impact mills in secondary crushing (Velazquez-Martinez et al. 2019). After crushing, sieving/screening is commonly carried out to separate the fine material from coarse particles. The active material from crushed battery cells end up mostly to this fine fraction which is usually called black mass. Common screen sizes are between 200 and 840 µm (Pinegar et al. 2019; Smith and Swofer, 2013; Sojka et al. 2020; Velazquez-Martinez et al. 2019). Foils, plastics and metallic casing particles on the other hand end up in the coarse fraction which is introduced to further separation which may include magnetic and density (shaking table, zig-zag) separation. If wet processing is carried out during the pre-treatment, filtration is utilized to separate solids from liquid. Concentrates from mechanical pre-treatment are further treated by means of hydro- and pyrometallurgical methods to recover valuable elements.

Thermal pre-treatment aims at removing electrolytes, solvents and volatile hydrocarbons from the battery waste. In addition, the target has also been on the binder removal and detachment of cathode active material from the aluminum foils. Thermal pre-treatment can be carried out for dismantled cells or for a fraction from mechanical pre-treatment. Reported thermal pre-treatment methods are vacuum pyrolysis, drying and rotary kiln and reductive melting (Pinegar et al. 2019; Sojka et al. 2020; Velazquez-Martinez et al. 2019). Some actors such as Umicore, Nickelhütte Aue, Dowa and Kyoei Seiko operate thermal treatment solely, namely pyrometallurgical unit processes together with hydrometallurgical process technologies. These processes don’t necessary require discharging and pre-treatment prior the processing, allowing the utilization of the battery cells as a direct feed to the metallurgical process.

Examples on process configurations can be seen in Figure 3 where Accurec (green) relies on a combination of thermal and mechanical treatment where a rotary kiln cracks and pyrolyzes the organic components after which mechanical treatment takes place. Mechanical treatment in their process includes sieving, crushing, magnetic and density separation separates materials to different fractions (Sojka et al. 2020; Sommerville et al. 2021). Duesenfeld (Purple) also combines both thermal and mechanical pre-treatment to produce concentrates for further treatment/recovery. Duesenfeld specializes on electrolyte recovery through drying and evaporation, condensation and collection.

Akkuser (black) process on the contrary is composed of solely of mechanical treatment where two-stage crushing is carried out, followed up by magnetic separation. As mentioned previously, each process concept is a unique configuration of unit processes. In Table 3 a summary of some of the actors around the globe has been presented. It should be noticed that many companies are planning or investing in battery recycling plants at the moment, which makes the summary table a present-day snapshot of the situation. One observation of the data presented in Table 3 is that the capacities of the plants in Asia seem to be larger than in either Europe or North America. In addition, in many cases the mechanical pre-treatment is complemented with hydrometallurgical treatment by the same actor.

*Table 3. Summary of some actors within battery pre-treatment stage.*

| Company | Location | Capacity [t/a] | Treatment method | Ref |
|---|---|---|---|---|
| Accurec | EU | 3 000 | Mechanical + thermal -> hydrometallurgical | Sojka et al. 2020; Pinegar et al. 2019; Sommerville et al. 2021; Velazguez-Martinez et al. 2019; Meshram 2014 |
| Akkuser | EU | 4 000 | Mechanical | Huhtala, 2010; Sojka et al. 2020; Velazguez-Martinez et al. 2019 |
| Batrec | EU | 200 | Mechanical + thermal -> hydrometallurgical | Pinegar et al. 2019; Salojee et al. 2015 |
| Brunp | Asia | 10 000 | Mechanical + thermal -> hydrometallurgical | Sojka et al. 2020; Wang et al. 2020 |
| Duesenfeld | EU | 2 000 | Mechanical + thermal -> hydrometallurgical | Kwade at al. 2018; Velazguez-Martinez et al. 2019 |
| EDI | EU | 5 000–6 000 | Mechanical | Sojka et al. 2020 |
| Fortum | EU | 3 000 | Mechanical -> hydrometallurgical | Fortum news; Fortum news |
| Ganzhou Highpower | Asia | 10 000 | Mechanical -> hydro- and pyrometallurgical | Sojka et al. 2020 |
| GEM | Asia | 5 000/2 000 | Mechanical -> hydrometallurgical | Sojka et al. 2020 |
| Guanghua | Asia | 10 000 | Mechanical -> hydrometallurgical | Sojka et al. 2020 |
| Huayou Cobalt / Huayou Recycling | Asia | 65 000 (battery packs) -> 15 000–35 000 | Mechanical -> hydrometallurgical | Sojka et al. 2020 |
| Hydrovolt | EU | 12 000 (t of packs) | Mechanical | Hydro news; Hydrovolt |
| JX Nippon | Asia | 600 | Mechanical -> hydrometallurgical | Sojka et al. 2020; Haga et al. 2018 |
| Kobar | Asia | 900 | Mechanical -> hydrometallurgical | Sojka et al. 2020 |
| Li-Cycle | North America | 5 000 | Mechanical -> hydrometallurgical | Youtube; Blog post |
| OnTo / Ecobat | North America | Low | Mechanical -> hydrometallurgical | Velazquez-Martinez et al. 2019; Pinegar et al. 2019 |
| Promesa – Ecobat | EU | <1 000 | Mechanical -> hydrometallurgical | Sojka et al. 2020; Ecobat |
| Recupyl / TES-AMM | EU | 110 | Mechanical -> hydrometallurgical | Tedjar and Foudraz 2007; Pinegar et al. 2019; Saloojee et al. 2015; Sommerville et al. 2021; Velazquez-Martinez et al. 2019 |
| Redux | EU | 10 000 | Mechanical + thermal | Sojka et al. 2020 |

| Company | Location | Capacity [t/a] | Treatment method | Ref |
|---|---|---|---|---|
| Retriev LIB | North America | 4 500 | Mechanical -> hydrometallurgical | Pinegar et al. 2019; Saloojee et al. 2015; Sommerville et al. 2021; Velazquez-Martinez et al. 2019; Harper et al. 2019 |
| SungEel High Tech | Asia | 8 000 | Mechanical -> hydrometallurgical | Sojka et al. 2020 |
| Telerecycle | Asia | 3 000 | Mechanical -> hydrometallurgical | Sojka et al. 2020 |

## 3.3 Concentrates from pre-treatment

Depending on the pre-treatment configuration, different types and quantities of output fractions are generated. Commonly reported output fractions are steel, aluminum foils, copper foils, plastics, electronics and black mass/fines. In Figure 4, the mass balance of LithoRec pre-treatment process with lithium-ion traction batteries as the feed has been presented. From Figure 4 it can be seen that the aluminum fraction is the largest with 34.5 w%, followed up by black mass, copper and plastic fractions with shares of 23.1, 11.5 and 11.0 w% respectively. Steel, volatile compounds and electronics present solely less than 10 w% of the output fractions. The pre-treatment process is composed of both dismantling and mechanical treatment. Black mass and volatile compounds are the only fractions which are produced solely in the mechanical treatment stage, whereas steel and electronics are in turn produced solely in the dismantling stage. Rest of the fractions are generated in both stages with different division.

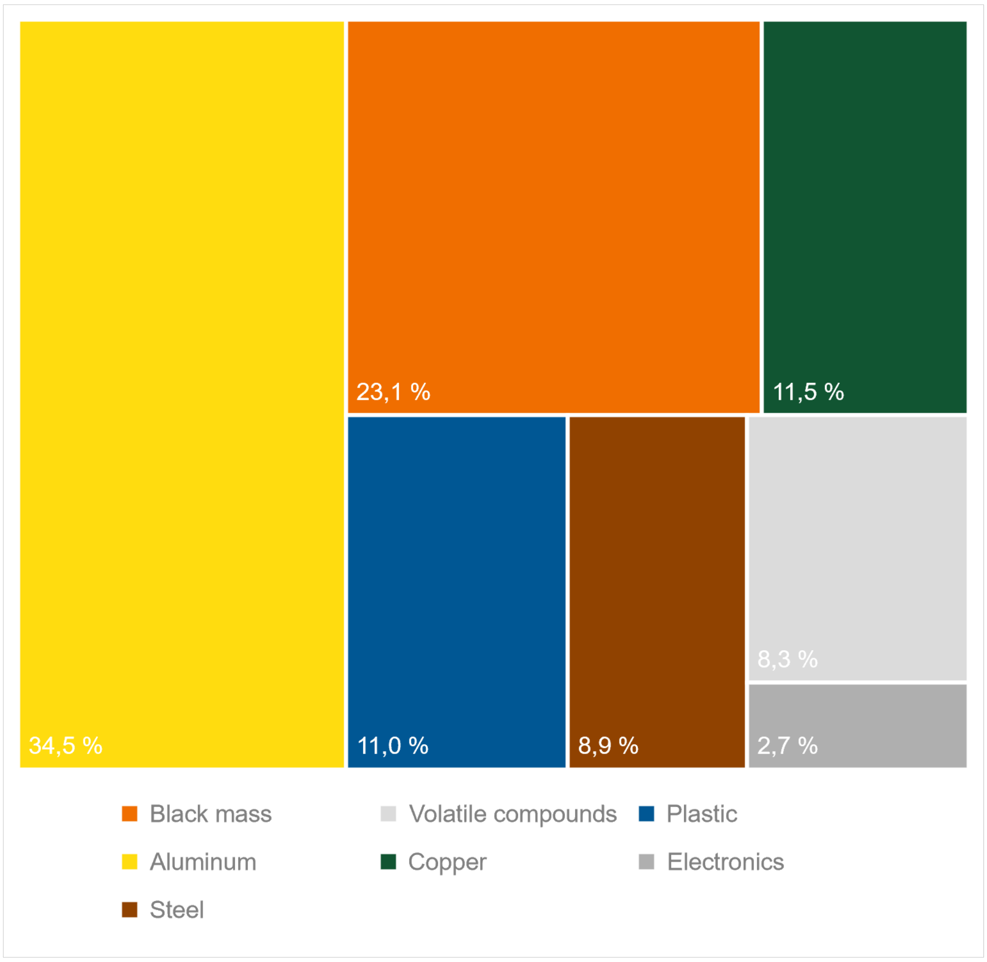

*Figure 4. Mass balance of output fractions in LithoRec/Duesenfeld process. (Modified from Gerdas et al. 2018)*

Main valuable fractions in the mechanical pre-treatment are black mass, copper, aluminum, electronics and steel. In another study of LithoRec-process by Diekmann et al. the composition of output fractions has been reported, which are presented in Table 4 (Diekmann et al. 2016). It should be noted that to the reported quantities of output fractions are different than what was shown in Figure 4, perhaps due to the development of the process which has occurred between the published research works. However, Table 4 shows how battery system periphery, which is composed of the battery pack, contains mostly steel originating from casing/structure and in smaller shares electronics and cables. Heavy parts from mechanical pre-treatment were composed mostly of aluminum particles, presenting 74.3 % of the fraction followed by steel, copper, plastics and inclusions. Separator fraction from density separation is rather clean fraction where 97.8 % of the fraction was composed of separators. The foil fraction which was enriched of both of Al- and Cu-foils contained a high share of black mass: 44.8 %. This high share has been one driver to further treat foil fraction to separate the remaining black mass. As for black mass fraction copper and aluminum impurities can be detected.

*Table 4. Composition of output fractions from LithoRec process. Battery system periphery fraction originates from dismantling while the rest of fractions are from mechanical pre-treatment. (Diekmann et al. 2016)*

| **Material** | **Battery system periphery [%]** | **Heavy parts [%]** | **Foil fraction [%]** | **Separator fraction [%]** | **Black mass fraction [%]** |
|---|---|---|---|---|---|
| Steel | 88.1 | 13.8 | | | |
| Iron | | | | | 0.1 |
| Electronics | 3.9 | | | | |
| Aluminum | 1.5 | 74.3 | | | 0.6 |
| Al-foil | | | 16.6 | 1.6 | |
| Copper | | 5.0 | | | 1.8 |
| Cu-foil | | | 29.8 | | |
| Plastics | 0.6 | 4.0 | 5.9 | 0.6 | |
| Cables | 5.9 | | | | |
| Inclusions | | 2.9 | | | |
| Separator | | | | 97.8 | |
| Black mass | | | 44.8 | | 97.6 |

When the black mass compositions are examined in more detail from various sources (Figure 5), it can be seen that black masses are composed mostly of carbon (graphite) followed by cobalt, nickel and manganese. Other elements which are used in the compounds found within batteries, such as fluoride and lithium, are observed in lower quantities. Fluoride can originate from electrolyte salt ($LiPF_6$) and from the PVDF binder. As for elements which do not originate from the active materials itself, such as aluminum, copper and iron, are presumably impurities or leftovers from foils and other parts in the battery cell. It should be noted that in Figure 5 the black mass compositions were compiled from sources involving both end-of-life and process waste treatment. The analysis methods differ from XRF to ICP and therefore should not be looked at individual values but more as distributions.

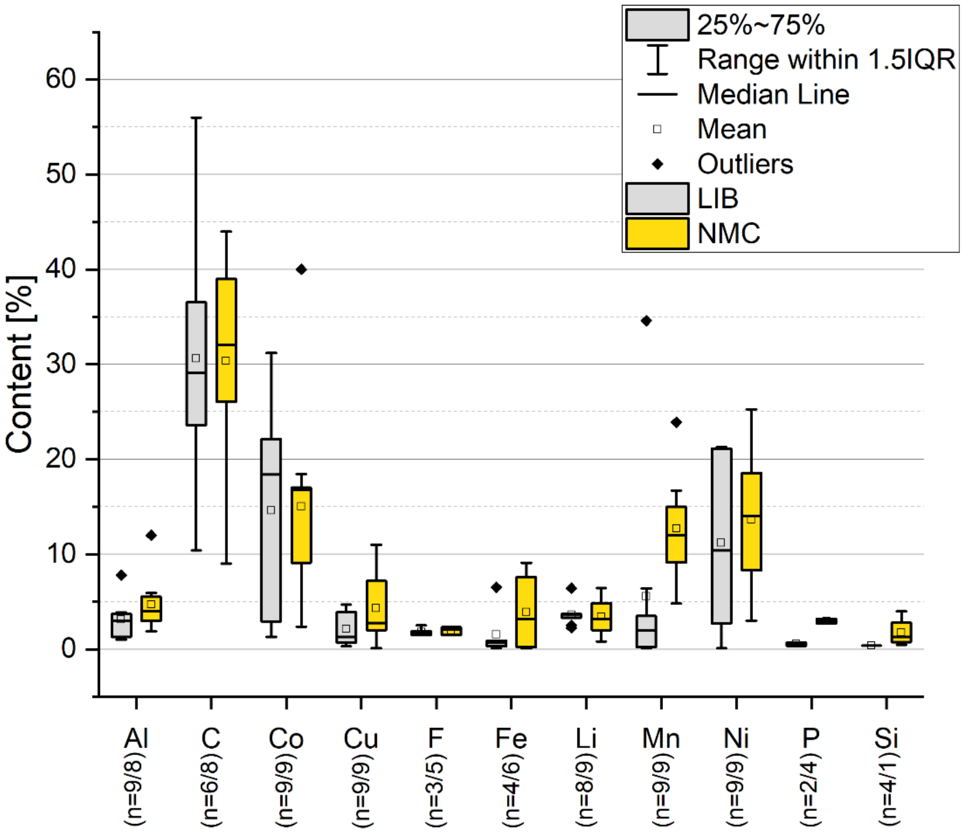

*Figure 5. End of life and production waste lithium-ion battery black mass composition based on various literature sources, n refers to the amount of sources separately for LIB first number and NMC second number.*

It can be noted that rather large variation could be detected, especially for graphite, cobalt, copper, iron, manganese and nickel, independent of the battery chemistry reported. The variations in cobalt, manganese and nickel concentrations are logical as the fluctuation in feed material is most likely due to the different chemistries being present, as was discussed in Section 3.1. This variation is transferred also as a fluctuation to other components of the black mass fraction. Interestingly rather high variations in copper and iron concentrations can be detected which could indicate different removal efficiencies of pre-treatment processes. Lower fluctuations in fluoride and lithium occurs due to their occurrence in active material. Their concentrations are rather similar independent of the cell chemistry. In addition, they are embedded in the active material which makes them hard to separate by means of mechanical pre-treatment. As there are no standards for black mass composition, fluctuations are expected occur.

## 3.4 Factors in pre-treatment affecting the output concentrate quality

Several aspects in the pre-treatment stage affect the qualities and compositions of produced concentrates. These can be roughly divided to feed handling, operational parameters and process configuration. Feed handling refers in this study to all actions which occur before the mechanical and thermal pre-treatment processes. As an example, using a mixed battery feed vs. pre-sorted battery waste could be considered as a feed handling procedure whereas selecting the specific mesh size for screening is an operational parameter.

Feed handling

Besides of pre-sorting the waste battery cells based on their chemistry, which quite directly affects the output compositions, although it may be somewhat challenging. Other actions, such as removal of residue charge of the cells prior crushing, or pre-sorting cells based on cell geometry can affect the compositions as well.

In the research by Wuschke et al., the correlation of remaining state of charge (SoC) of a battery cell to the temperature increase in crushing was investigated. They recognized that increasing the SoC from 2 % to 10 % caused a temperature increase of between 27 °C and 54 °C, reaching the highest measured temperature of 75 °C with 10 % SoC. (Wuschke et al. 2019) For safe treatment a low SoC is recommended as otherwise there exists a danger of fire as well as explosion and generation of toxic gases. However, depending on the discharge practice at different operators, various temperatures during crushing can be encountered. This might result in variations of remaining electrolyte and fluoride content in black mass fraction as electrolyte solution ($LiPF_6$ and solvent). Diekmann et al. reported that high local temperatures in crushing may cause $LiPF_6$ to start decomposing at around 60 °C (Diekmann et al. 2017). When reflecting this with the outcomes from the study performed by Wuschke et al. it can be noticed that already with 6 % SoC the maximum temperature nearly reaches the 60 °C limit. Furthermore, if temperatures increase up to 90 – 120 °C the decomposition of the solid electrolyte interface (SEI) on the anode is initiated (Doose et al. 2021). This in turn will create an exothermic reaction sequence where the intercalated lithium begins to react first with the electrolyte in temperature above 120 °C and further on the components of electrolyte starts to decompose at temperature of above 200 °C. After this the exothermic reactions of embedded lithium in binder and the decomposition of cathode active material starts at 240 °C and 250 °C respectively.

Pre-sorting of battery cells prior crushing can be carried out also by the geometry of the cell, namely cylindrical, prismatic and pouch. As the design and geometry is different between these cells they behave differently in crushing process as well. Pinegar et al. separately crushed cylindrical, pouch and prismatic cells with a slow rotating (28 rpm) laboratory scale twin-shaft shredder and investigated how the geometry affected the quality of output fractions (Pinegar et al. 2019). They noted that some variation could be detected, especially between the cylindrical cell and the other two cell geometries. The share of particles with size of below 500 µm were 14.7 w%, 12.4 w% and 16.4 w% for prismatic, cylindrical and pouch cells respectively. In addition, large particles with a size above 8 mm were identified more for cylindrical cells than for the other two ones. Pouch cell in turn seem to have more particles in size fraction 2 – 4.75 mm compared with prismatic and cylindrical cell samples.

The study by Pinegar et al. investigated further how different components of battery cells were distributed after crushing. When comparing how easily active material disengages from aluminium or copper foil it was noted that the graphite tend to disenage easier than lithium metal oxide for all cell types. This is in correlation with other published research (Bachér et al. 2021; Vanderbruggen et al. 2021; Wuschke et al. 2019,). While examining the differences between the cell types it was seen that lower share of fine active cathode material (<500 µm) was generated with pouch cells namely 14.3 w% compared with prismatic and cylindircal cells which produced 27.36 w% and 29.6 w% of fine active cathode material respectively. For the anode active material, cylindrical cell produced more fine material material 71.9 w% compared to prismatic and pouch cells which generated 57.5 w% and 54.9 w% of fine active material respectively.

Distribution of foils from crushing of cells of different geometries were in line with active material distribution as large part of aluminum foils concentrated to size fraction between 2 and 8 mm. As for other components and materials they tended to concentrate to the larger particle size fractions. Cell casing, plastic and paper seemed to concentrate to larger size fractions with cylindrical cell samples, in contrast to the other two.

The overall composition of different type of cells from the crushing experiment can be seen in Table 5. While the composition between prismatic and cylindrical cells are somewhat similar, greater fraction of active material and metal foils are present in pouch cells due to lighter cell and pack casing.

*Table 5. Mass composition of different cell type after crushing experiment. (Pinegar et al. 2019)*

| Cell type | Lithium metal oxide [%] | Graphite [%] | Al-foil [%] | Cu-foil [%] | Cell casing [%] | Paper & plastic [%] | Separator [%] | Pack casing [%] |
|---|---|---|---|---|---|---|---|---|
| Prismatic | 19.9 | 12.8 | 1.6 | 5.9 | 21.6 | 2.6 | 6.4 | 29.2 |
| Cylindrical | 16.5 | 10.3 | 1.5 | 6.0 | 17.0 | 3.9 | 17.2 | 27.6 |
| Pouch | 33.0 | 18.1 | 3.4 | 12.1 | 8.3 | 3.0 | 9.5 | 12.7 |

Operational parameters and process configuration

Size reduction is a crucial stage in the mechanical pre-treatment of batteries as the liberation of materials which will be separated in the sub-sequent processes is determined here. In addition, suitable particle size for sub-sequent processes is also determined in this stage. In order to minimize material inclusions, crushing with low deformation and compression is proposed, of which rotary shears have been highlighted. In a study by Diekmann et al. five different rotary shears with different crushing mechanism (RRS: radial rotary shear and ARS: axial rotary shear) and additional mesh openings were investigated (Diekmann et al. 2018). The study revealed that axial rotary shear - which crushes material with interdigitating tools – generate larger particle output compared to radial rotary shear which crushes with a geared rotor and a stator.

Diekmann further studied the effect of having a secondary crushing stage with a cutting mill (10 mm discharge screen) on the light fraction after first air separation of crushed batteries by zig-zag separator. The experiment showed that the yield of black mass fraction can be increased from 60 % to 75 % (Figure 6). Notably the secondary crushing did not increase the copper and aluminium content in the black mass fraction.

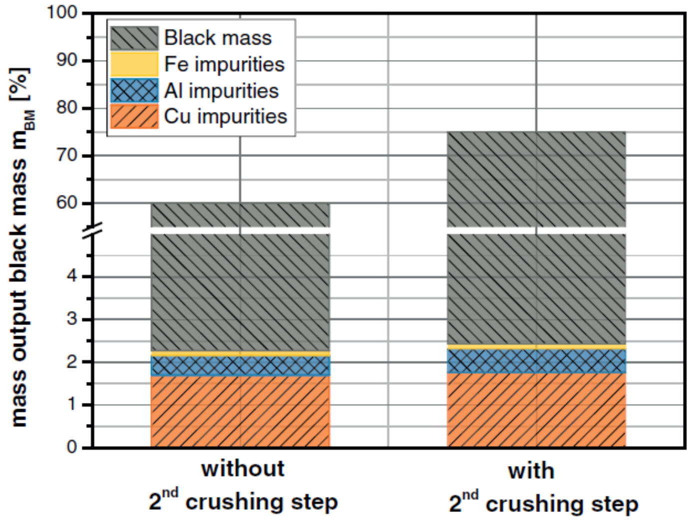

*Figure 6. Yield of black mass fraction with and without second crushing step. (Diekmann et al. 2017[3])*

Perhaps the most common method to affect the composition and quality of black mass fraction is to introduce it to screening as size dependent concentration differences between materials exist in the black mass (Figure 7). With various screening cut sizes the content of materials such as copper and aluminum can be reduced in the black mass. In proportion, the share of graphite and cathode active material would increase in the underflow. However, when screening also valuable active material will be removed and the recovery of them will decrease if no treatment is introduced for the overflow. As an example, if 30 % of

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active cathode material ends up in an overflow, around 70 % of them need to be recovered in order to reach the proposed recovery targets with the assumption that all active material from underflow is later recovered downstream. It should be noted that impurities attached to the active material grains, for example by coating such as the PVDF binder, cannot be separated with mechanical separation unit processes but requires instead some kind of chemical, thermal or mechanical (attrition etc.) treatment.

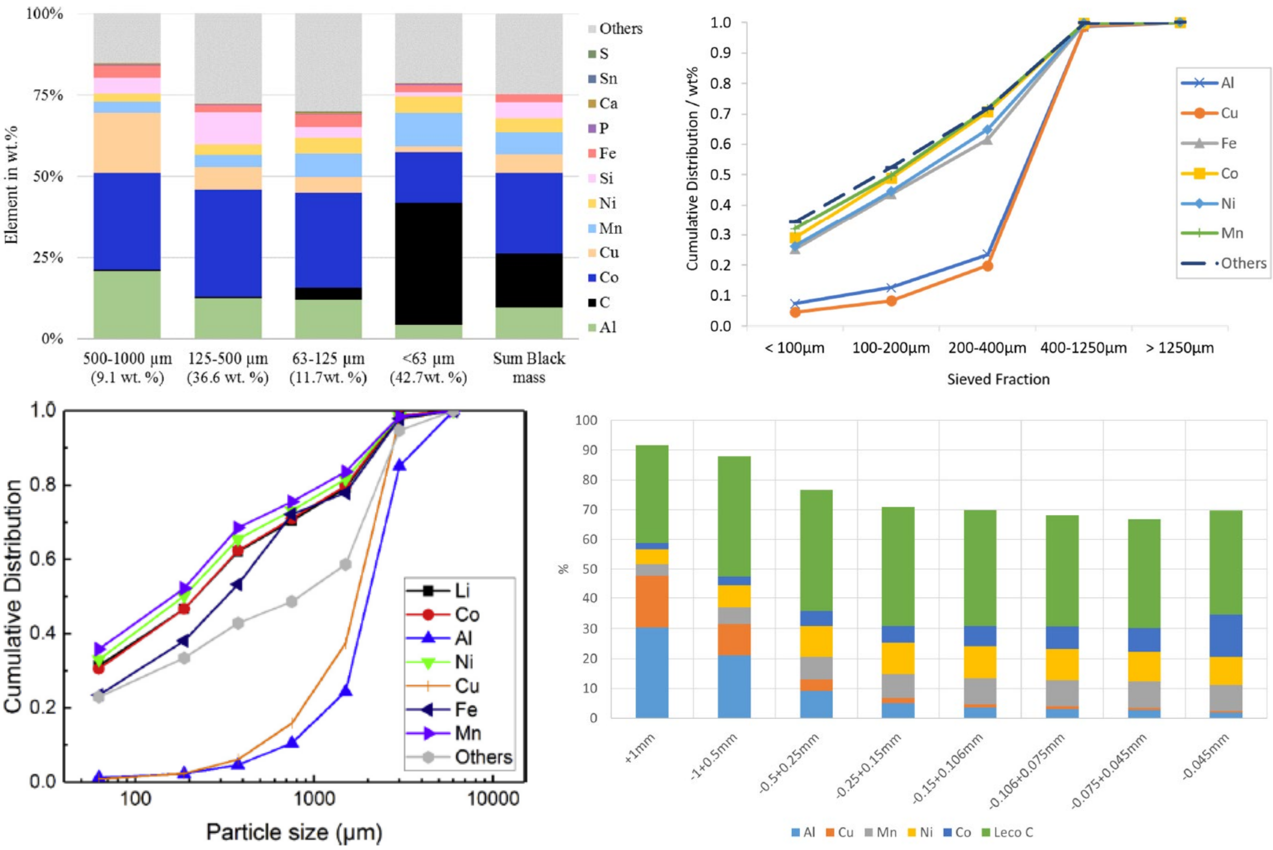

*Figure 7. Distribution of materials in various research. (Porvali et al. 2019[4] (left down row); Ruismäki, et al. 2020[5] (right up row); Vanderbruggen et al. 2021a[6] (left up row); Yang et al. 2021[7] (left down row))*

Until this date, intensive industrial scale mechanical treatment of black mass has not been commonplace. Thermal treatment has been introduced on the other hand in industrial scale, not directly on black mass fraction, but on entire battery or crushed battery to remove electrolyte as in the case of Duesenfeld or Accurec process and as such affect the black mass fraction in addition to safety issues (Pinegar et al. 2019; Sojka et al. 2020; Velazquez-Martinez et al. 2019).

Destination options and their requirements on black mass fraction

Depending on the post treatment method whether it is pyrometallurgical or hydrometallurgical different type of considerations for the black mass composition can be taken. It has been reported that pyrometallurgical treatment can deal better fluctuations in the feed composition compared to the hydrometallurgical treatment (Karlsson and Lindström, 2018; Sojka et al. 2020). This may affect the strategy of pre-treatment operation.

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# 4. Achieving requirements for primary production

## 4.1 Typical feeds in primary production

Production of cobalt and nickel from primary raw materials are composed of mining and beneficiation/mineral processing producing a concentrate which can be treated to extract metals either by a combination of process technologies such pyrometallurgy and hydrometallurgy. Commonly, different types of cobalt and nickel bearing sulphide ores and minerals are treated. Another source of these elements are laterites, an oxidic material source. In this section, selected Finnish primary raw material as well as process intermediate compositions are explored and compared to black mass compositions.

In short, production of cobalt and nickel from sulphide ore begins with blasting and mining, after which the ore is crushed and milled to liberate with optimum degree the desired sulphides. The milled ore is then commonly fed to a flotation circuit to separate the desired sulphide minerals from the gangue and from unwanted sulphides, such as pyrite and pyrrhotite and/or sulpharsenides (Törmänen et al. 2021). Flotation process produces various types of concentrates depending on the deposit and the beneficiation process. Common sulphide concentrates are nickel-, copper- and zinc concentrates where cobalt can also be present. In Finland, 2021 operating mines and their nickel and cobalt containing products are as follows (Tukes 2022):

- Kevitsa/Boliden: Ni-PGE-Co concentrate
- Sotkamo/Terrafame (no flotation): Ni sulphate and Co sulphate
- Talc mines/Elementis: Ni-Co concentrate or Mixed hydroxide precipitate (MHP)

Sulphide concentrates are commonly fed to a smelter facility where the concentrate is smelted and converted to produce a matte. Matte contains the valuable metals as well as iron and sulphur which is then fed to a sequence of leaching processes which is operated either under atmospheric or pressurized environment to extract the elements into the solution. The pregnant leach solution is then subjected to further impurity removal, recovery and refining. Common leaching methods are pressure oxidative leaching with sulphuric acid, ammoniacal (e.g., Sherritt-Gordon process) or chlorine-chloride (e.g., Nikkelverk) leaching system, (Törmänen et al. 2021). After leaching, in general, sequential removal of impurities takes place, depending on the individual process technology and the feed which the technology has been adapted to treat. Recovery, separation and refining of values such as cobalt and nickel from the intermediate concentrate can take place on-site or at another facility.

Another route to treat sulphide concentrates would be direct leaching without the pyrometallurgical stage. This can take place with both pressure oxidative leaching as well as direct atmospheric leaching. The method of direct leaching is somewhat common for Cu and Zn sulphide concentrates because of their reactivity and amenability to dissolution. It is also common for refractory Au bearing minerals, such as pyrites and arsenopyrites. It is however seldomly used for Ni-Cu-Co sulphide concentrates. An example of sulfatic atmospheric leaching process technology is the Albion process (Hourn and Turner, 2012). In the hydrometallurgical process, the re-ground concentrate is fed to either atmospheric or pressure oxidative leaching to extract the elemental values to solution. The metal-containing leach liquor is separated from solid residue and sent to solution purification, metal recovery and refining, which can include precipitation, solvent extraction, ion-exchange as well as electrochemical purification by electrowinning. Instead of an end product, a facility could potentially produce an intermediate, such as a mixed hydroxide precipitate (MHP) or mixed sulfide precipitate (MSP). (Törmänen et al. 2021, (Willis, 2007). The intermediate can then be redissolved with pressure oxidative leaching (MSP) or direct leaching (MHP) to produce a concentrated solution from which values can be further separated and refined with e.g., precipitation, solvent extraction and crystallization processes to produce battery grade chemicals.

Bioleaching can be also an option to treat sulphide minerals. In this method iron and sulphur-oxidizing micro-organisms are utilized in the leaching stage. In the case of large-scale heap, dump or pad leaching which are used for low-grade ores, the leaching time can be several years or even decades. As an example, biological heap leaching is undertaken at Terrafame facility. After leaching, the metals can be recovered as in traditional hydrometallurgy: for example, as mixed hydroxide precipitate. (Törmänen et al. 2021)

Considering the cobalt containing sulphide concentrates composition from various Finnish deposits, intermediate MHP and MSP products as well as black mass from LIB recycling (Table 6) it can be noticed that differences exist in both concentrations and typical major elements present in the concentrates/fractions. Lowest element concentrations are typically found in sulphide concentrates, with the notable exception of iron and sulphur. Iron is a typical element part of the minerals that bear Ni and Co, and sulfur is naturally sourced from the sulfide compound. In the case of cobalt, highest concentrations can be found in MSP followed by MHP and black mass. As for nickel black mass have the highest concentrations, although it needs to be acknowledged that the compositions of the MHP and MSP may vary based on the preceding process and the raw material composition being treated. However, it should be noticed that variations in the concentrates are largest for black mass. Sulphur is a central element for the concentrates as well as for MSP, which is not traditionally found in black mass, at least in high concentrations. From black mass point of view aluminium, carbon/graphite (as well organic electrolytes), fluoride and lithium are elements which are not typically found in the other fractions, at least in significant quantities. These may have an effect on the processability. For example, fluoride may generate toxic gas emissions and might present corrosive challenges as well as act as an impurity in subsequent processes (Beak et al. 2022; Brückner et al. 2020; Sojka et al. 2020). As for lithium, for which recycling targets has been set in the proposal for new battery legislation, adaption in current primary processes which do not commonly recover lithium may be required. In addition, lithium may attack the refractories if black mass is co-processed in a secondary Co-, Cu-, Ni-smelter (Brückner et al. 2020).

*Table 6. Composition of different feeds and fractions in primary and secondary processing of battery materials.*

| Element | Sulphide concentrate* [%] | MHP** [%] | MSP** [%] | NMC black mass*** [%] | LIB black mass*** [%] |
|---|---|---|---|---|---|
| Co | 0.3 – 1.5 | 30 – 39 | 55 – 61 | 8 – 19 | 3 – 21 |
| Ni | 0.1 – 9 | 2 – 5 | 3 – 6 | 9 – 17 | 3 – 22 |
| Mn | | 4 -9 | <0.1 | 9 – 15 | 0.2 – 4 |
| Cu | 0.1 – 23 | 1 – 4 | 1 – 5 | 2 – 7 | 0.5 – 4 |
| Al | | <0.5 | <0.1 | 3 – 6 | 1 – 4 |
| Fe | 20 – 45 | <0.5 | <0.8 | 0.25 – 7 | 0.4 – 1 |
| S | 31 – 46 | 3 – 5 | 34 – 36 | | |
| Mg | 2 – 5 | 3 – 5 | <0.1 | | |
| C | | | | 27 – 38 | 25 – 36 |
| F | | | | 1.8 – 2.2 | 1.5 – 1.9 |
| Li | | | | 2 – 4 | 3 – 4 |

* Estimates presented in Törmänen et al. 2021 for various Co containing concentrates either from research studies or production
** Example composition of MHP and MSP from Willis, 2007
*** 25th and 75th quartile in Figure 5

The challenge in integrating the black mass into a primary process are related to element compatibility and the stage of the flowsheet at which the black mass would be fed into the individual primary process. For instance, the process must at that point have similar impurities as to be capable of handling the additions without problems. For instance, if black mass would be leached in an autoclave with NiCoS concentrate, any impurity removal after this stage would need to be able to handle Li, Fe, Cu, Mn and Al.

The impact of the addition of foreign raw materials to any potential water circuits and their mass balances would need to be estimated.

## 4.2 Pre-treatment of black mass for subsequent processing

Studies on various type of treatment methods on black mass fraction either to recover materials or to condition and modify it has been carried out during the recent years. Mechanical treatment such as flotation, gravity and electrostatic separation has been introduced mainly to separate cathode active material from anode active material. This has been complemented with milling and attrition whose purpose is to modify the feed more suitable for the separation.  Thermal treatment on the other hand has focused on modification of black mass to be more suitable for subsequent processing for example through fluoride removal.

As an example of the mechanical treatment, flotation has been introduced as a method to recover graphite from black mass fraction or separate base metals such as copper and aluminium from the coarser part of black mass (Qiu et al. 2022; Rinne et al. 2022, Ruismäki et al. 2021; Vanderbruggen et al. 2022; Yang et al. 2021, Zhan et al. 2021). The PVDF binder in active material has been shown to decrease the selectivity of flotation as it makes the cathode active material hydrophobic and may also promote agglomeration of black mass particles, resulting in entrapment (Vanderbruggen et al. 2021b). Various types of pre-modification of black mass prior flotation have been studied, either to remove the binder from the surface of cathode particles or to affect its properties. Such methods can be thermal treatment such as pyrolysis and roasting, chemical treatment such as Fenton oxidation as well as mechanical treatment like attrition (Qiu et al. 2022; Vanderbruggen et al. 2022; Zhan et al. 2021; Yang et al. 2021). By introducing pre-treatment methods to the flotation feed both the grade and recovery of graphite and cathode active material can be increased with tens of percent achieving up to 90 % recoveries with grades of 77 % for graphite and 83 % for cathode active material (Qiu et al. 2022)

Density/gravity separation of graphite from cathode active material has been also studied (Kepler et al. 2016; Zhan et al. 2022; Zhang et al. 2018). As an example, Zhan et al. investigated the centrifugal gravity separation (Falcon UF) to separate graphite from cathode material. They studied both pristine sample (NMC 111 and graphite powder) and dismantled and delaminated black mass fraction from laptop batteries. The pristine sample were tested with both single and multistage approach. Single stage experiments revealed that the feed mass and solid content impacted separation significantly achieving over 90 % recovery and grade for the cathode material in the concentrate. In addition, increasing the G-force in the process increased the separation performance. The multistage approach was composed of one rougher, two sequential cleaner and two sequential scavenger stages which resulted in a concentrate of 99 % cathode material grade and tailings of a 99 % graphite grade. An experimental circuit composed of one rougher and two cleaners with two cycles for the black mass sample abled production of a concentrate with 98 % cathode material grade. However, the recovery was just *ca.* 40 – 50 %. (Zhan et al. 2022)

Mechanical processing options that would affect the black mass characteristics and properties are mainly limited to milling and attrition. In some studies, milling and attrition has been used as a pre-treatment for flotation (Liu et al. 2020; Vanderbruggen et al. 2022). In these studies, the main aim of the pre-treatment was to modify the particle surface to increase the selectivity in flotation, mainly through the removal of the organic binder. Another approach of using milling on black mass fraction modification is to trigger physicochemical changes including phase transformations, structural defects, strain, amorpholization, and even direct chemical reactions. This is called mechanochemical treatment. Commonly, black mass is mixed with one or several reagents and a grinding media after which milling is carried out for extended periods to produce water or acid soluble complexes. As an example, in a study by Dolotko et al. black mass was milled together with metallic aluminum which acted as a reducing agent. The study suggested that metallic cobalt was generated in the process, which is magnetic and could be removed with a magnetic separation process. (Dolotko et al. 2020) Also the use of PVC has been investigated as a chlorine donor to form soluble $CoCl_2$ and LiCl during the milling which can then be dissolved in water. The recovery efficiencies varied depending on the level of PVC usage, roughly 90 % recovery was achieved for cobalt (Saeki et al. 2004).

Thermal treatment of black mass mostly aims at removal of PVDF binder and other organic compounds. Several different technologies have been investigated and introduced such as pyrolysis, roasting and calcination. Pyrolysis and roasting has been introduced as a pre-treatment method prior flotation improving hydrophobicity of cathode active material by binder removal (Qiu et al. 2022; Zhan et al. 2021;) Investigations on different thermal treatment methods for binder removal and detachment of cathode active material from aluminium foils suggest incineration, for 90 minutes at temperature between 550 °C – 650 °C, more suitable compared to dynamic and vacuum pyrolysis which would require longer treatment times. (Lombardo et al. 2021) As a summary it has been reported that PVDF binders are decomposed at ~500 °C and the carbon conductive agents are burnt off at higher temperatures whereas electrolytes are volatized in lower temperature. (Kim et al. 2021)

## 5. Conclusions

As the societies are striving to reduce carbon emissions, energy storage and especially batteries have become one of the key technologies enabling the move towards carbon neutrality. Raw material demand for the batteries will increase in multifold at a time when all possible material sources should be utilized. Integrating secondary raw materials to primary production has gained interest to broaden metallurgical capacity by having both primary and secondary raw materials routes as an option for the black mass treatment.

After collection of waste lithium batteries typically they are mechanically pre-treated after the discharge step. As there are several actors providing this process step and each having their unique process, variations in the active material rich fraction called black mass is produced. In addition, changes in the battery feed may raise the fluctuation of the black mass composition. When reflecting the black mass composition with the feeds utilized in primary production, most disparity is generated by lithium, fluoride and organics which are not found in sulphidic concentrates from mines or in the intermediate products such as mixed precipitates. Various treatment methods have been studied to remove or separate one or more of these materials/compounds from the black mass fraction prior to hydrometallurgical treatment. While mechanical treatment of black mass focus on the separation of graphite from the black mass, thermal treatment aims at removal of fluorides including the binder. Proper understanding of the capabilities for integrating a given recycled battery fraction into primary metals refining requires proper mass balancing that takes into account both the impurity profile of all the feeds and their relevance in the perspective of the total mass flow,

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