D6.2 Literature assessment of Li-ion battery recycling steps

Project	Green Transport Delta - Electrification
Project number	MOB21011
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Version	3.0
Date	20 August 2024

Revision index

Version	Description	Date
1.0	Final draft for review technical coordinator	04-03-2024
2.0	Feedback GTD-E technical coordinator processed – final version	25-07-2024
3.0	Final version	20-08-2024

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The Green Transport Delta – Electrification project has received financial support from the Ministry of Economic Affairs and Climate, under the grant ‘ R&D Mobility Sectors’ carried out by the Netherlands Enterprise Agency.

Contents

Summary

This report aims to give a detailed description of the field of lithium ion batteries (LiBs) recycling in Europe, including a proposal for (a combination of) recycling technologies. Over the past decades, different technologies for the recovery of (critical) raw materials have been explored and some of them have reached high TRL (i.e., industrial scale). These can be divided in physical and chemical separation technologies. The first ones rely on differences in physical properties such as conductive properties, magnetic properties, density, amongst others. Whereas chemical separation technologies rely on differences in chemical properties such as acid-base properties, redox properties, amongst others.

Pre-treatment processes are technologies that separate materials based on differences in physical properties. Before such process steps are applied, LiBs may be discharged and/or dismantled. Pre-treatment technologies are usually applied before chemical separations. Pre-treatments for the retrieval of black mass from LiBs is a crucial step in the recycling process of batteries. Due to the non-standardised composition of the batteries, the pre-treatment step is not a standardised process and will vary depending on the battery type and chemistry, as well as the selected downstream recycling process. The general flow schemes of the pre-treatment processes are the same, however, the applied methods and technologies for each step will differ depending on the company applying them. Although the pre-treatment process has been optimised by different companies, there is still a need to optimize the recovery of black mass because losses of black mass can still be significant, mainly due to the black mass adhering to the foils of the batteries.

Amongst the chemical separation technologies, pyrometallurgy is a mature and predominant technology at industrial scale and has been employed for many decades now for various waste streams. Moreover, its simplicity and flexibility with respect to the feed materials is one of its main advantages against other technologies. Nevertheless, light materials such as lithium and manganese are retained in the slag and further separation steps are required to isolate metallic metals.

Direct recycling of the cathode active material could be a promising method for the production of new batteries, without having to reduce black mass to its elemental composition. However, direct recycling is only applicable to batteries that have a fixed/standard chemistries, such as lithium iron phosphate (LFP). The quality of the end product relies heavily on the pre-treatment process as it is essential to ensure the desired purity for the cathode active material for the process.

Hydrometallurgy is another separation technology based on differences in chemical properties. In this case, the separation of the elements is performed in aqueous media. Different chemical properties are considered when designing a hydrometallurgical recycling approach, such as acid-base/redox properties, affinity of metals towards selective coordination ligands, etc. This technology can give rise to high recovery efficiencies and selectivity. However, it usually relies on the use of different chemical reagents and sometimes it is a challenge to reuse them in more than one cycle. Moreover, each separation step may yield waste streams that require further treatment.

For this report, five patented hydrometallurgical processes, from four different companies were analysed in detail. The five processes are being developed by Li-Cycle, Northvolt, Duesenfeld and BRUNP. The former three were selected as these processes are to be implemented in Europe, while BRUNP was selected to also represent the Chinese recycling market.

These processes are classified in mixed precipitation and solvent extraction processes. The mixed precipitation processes (i.e., Li-cycle, Northvolt, BRUNP) are less complex, because these are all based on leaching of the metal ions from the black mass with a strong acid, followed by addition of a strong base to precipitate a mixed CAM-hydroxide cake as final product. Typically, copper ions are removed first from the acidic solution by solvent extraction, before the mixed CAM-hydroxide cake is precipitated. Furthermore, a lithium carbonate salt is obtained by precipitation from the residual solution. Typically, these processes co-produce large residual salt solution streams that require further treatment.
The solvent extraction processes (i.e., Northvolt, Duesenfeld) rely predominantly on selective ligands to separate metal ions by solvent extraction from the acidic metal ion solution obtained after leaching the black mass with a strong acid and peroxide. Each solvent extraction step is followed by a back-extraction step with a strong acid, to transfer the captured metal ions and subsequently recover the metals in the form of a metal salt (foremostly as metal-sulphate salts). These processes have as benefit that the metals can be recovered selectively as separate metal salt products with potentially better commercial value, instead as a mixed precipitate. However, the metal salts are recovered at the expense of an overall process including more process steps and several recycle streams in the process. These types of processes also yield a lithium-ion containing residual stream that can be further processed to obtain a lithium (carbonate) salt.

It was observed that none of the reviewed patents describe what are the further steps to use the final products for the production of new batteries. Considering some of these companies also manufacture batteries (e.g., Northvolt), from a techno-economic viewpoint it is possible that, within a manufacturing line, an intermediate product, such as a mixed metal hydroxide cake, might have advantages as a secondary raw material over isolated metallic salts (e.g., such as $CoSO_4$, $MnSO_4$, $NiSO_4$). However, such a mixed metal-hydroxide cake obtained from processing end-of-life batteries may have a composition different from the composition required for new batteries.

Finally, an assessment of the selected hydrometallurgical processes was performed in order to obtain a combination of the most favourable process steps. These processes were selected over pyrometallurgical ones considering the latter's disadvantages, such as Li losses in the slag, high energy consumption and high CO_2 emissions due to high temperature melting processes.

For this assessment, the processes were broken down to their specific process steps, because the processes vary in techniques that are applied and in their configuration. Using a systematic semi-quantitative approach, four of the specific process steps were evaluated on their characteristics and on their process conditions, to identify the potentially most favourable techniques. The information available from the process descriptions for leaching and recovery of the cathode metals was sufficient to perform a first preliminary evaluation. However, for the copper recovery and for lithium recovery steps the available data was insufficiently detailed, and the processes were too similar. In this way, it has been proven to be very difficult to give a proposal for a recycling process based on the most favourable combination of process steps. For a more complete evaluation, it is therefore recommended to obtain more detailed information and data on the various processes, for example by interviews with the process developers. It is noted that the latter was not in scope of this task. Furthermore, it is recommended to do a business case analysis for the processes, based on estimates of the feedstock and end product, of end product composition, yield and value and of major cost contributing factors, like use of energy and use of process chemicals and treatment of residual side streams.

1. Introduction

The goal of this report is to investigate battery recycling processes and to identify the specific process steps in these battery recycling process that are advantageous. An analysis is obtained by desk research on industrial scale recycling processes to recover materials from end of life (EOL) lithium ion batteries (LiBs). Subsequently based on selected recycling processes, an assessment of different recycling steps of these processes is executed to determine an optimal battery recycling process.

LiBs have become important to our daily life: most electronics are powered by LiBs. In addition, LiBs have become indispensable for the energy transition. In the case of electric vehicles (EV), a remarkable growth in sales is forecasted for 2030, expected to reach 88 million units in comparison to 10 million units sold during 2022. (ETC, 2023) Besides, new vehicles put on market from 2035 onwards must be electric.(Commission, 2021) However, such numbers of LiBs, necessary for daily life and the energy transition, require significant amounts of key materials and the estimated supply growth for them is not sufficient enough to meet the target demands by 2030. Figure 1 shows the estimated supply against the demand growth for key materials by 2030. As it is depicted, the demand baseline is higher than the estimated mine supply.

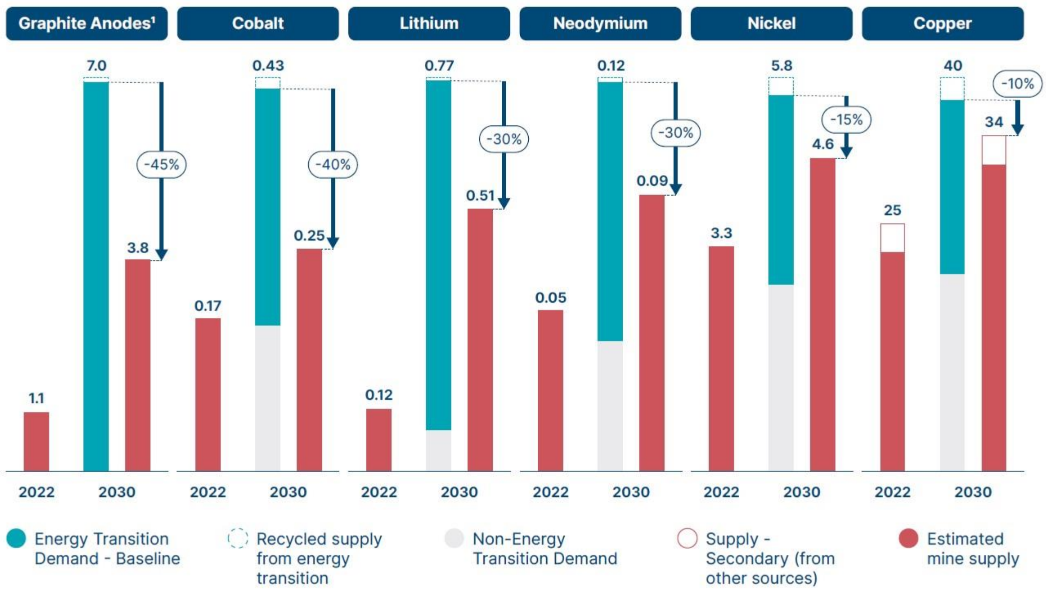
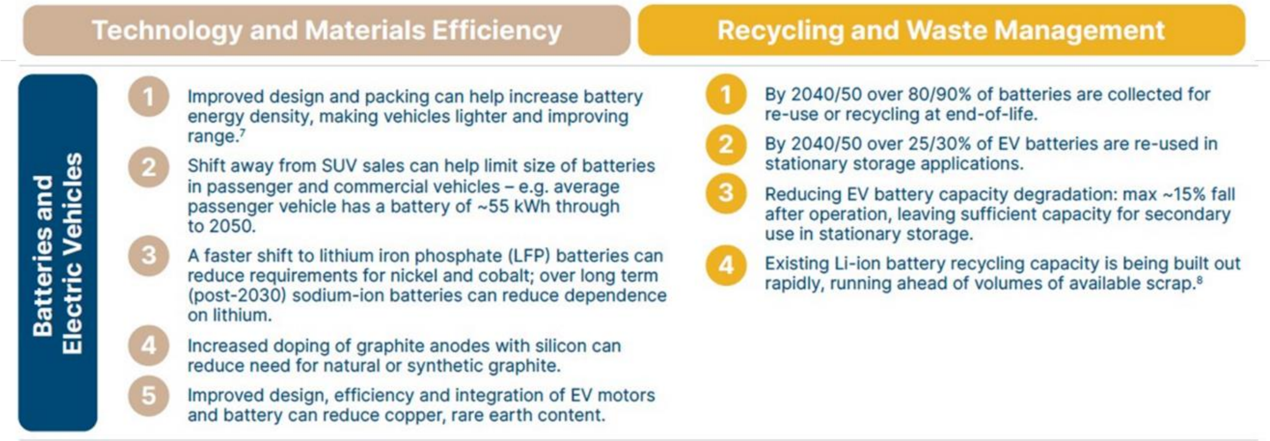


Figure 1: Estimated supply vs demand growth for key materials by 2030. (ETC, 2023)

All the elements presented in Figure 1 are required for the energy transition and for all of them the demand is higher than the supply requirements. Although recycling can become a relevant supply source of key materials in the future, recycled materials from clean energy technologies will play a minimal role until 2030, considering few EV will have reached EOL before 2030.

Over the long-term, pressure on the primary sources of materials can be significantly reduced by increasing technology efficiency and reducing total material requirements, by means of improving product design. Moreover, an increase in recycling will help meet the demand of these materials by secondary supply (Figure 2). These actions will have the following impacts in the short, medium, and long term:

- In the short term, improving technology efficiency utilizing smaller amounts of materials will have the strongest impact on materials demand reduction. This will help to meet production goals and diminish already existing supply gaps to 2030.
- In the mid-to-long term, primary sources demand can be remarkably reduced if a shift to next-generation of battery technologies and scale-up recycling is achieved from the mid-2030s onwards.
- For late-2030s onwards, because of EVs reaching EOL and scale-up of recycling, secondary supply will play a relevant role in meeting the forecasted materials demand (e.g., cobalt (Co), lithium (Li), graphite).
- For late-2040s, recycled supply of key materials - such as Li, Co and graphite - could cover over 50% of the forecasted energy transition demand. This scenario would be the result of an increased EOL batteries collection (over 80%) as well of high recycling rates (as high as 90%).



Technology and Materials Efficiency

Batteries and Electric Vehicles

1. Improved design and packing can help increase battery energy density, making vehicles lighter and improving range.[7]
2. Shift away from SUV sales can help limit size of batteries in passenger and commercial vehicles – e.g. average passenger vehicle has a battery of ~55 kWh through to 2050.
3. A faster shift to lithium iron phosphate (LFP) batteries can reduce requirements for nickel and cobalt; over long term (post-2030) sodium-ion batteries can reduce dependence on lithium.
4. Increased doping of graphite anodes with silicon can reduce need for natural or synthetic graphite.
5. Improved design, efficiency and integration of EV motors and battery can reduce copper, rare earth content.

Recycling and Waste Management

1. By 2040/50 over 80/90% of batteries are collected for re-use or recycling at end-of-life.
2. By 2040/50 over 25/30% of EV batteries are re-used in stationary storage applications.
3. Reducing EV battery capacity degradation: max ~15% fall after operation, leaving sufficient capacity for secondary use in stationary storage.
4. Existing Li-ion battery recycling capacity is being built out rapidly, running ahead of volumes of available scrap.[8]

Figure 2: Technology trends and actions to drive innovation, efficiency and recycling. (ETC, 2023)

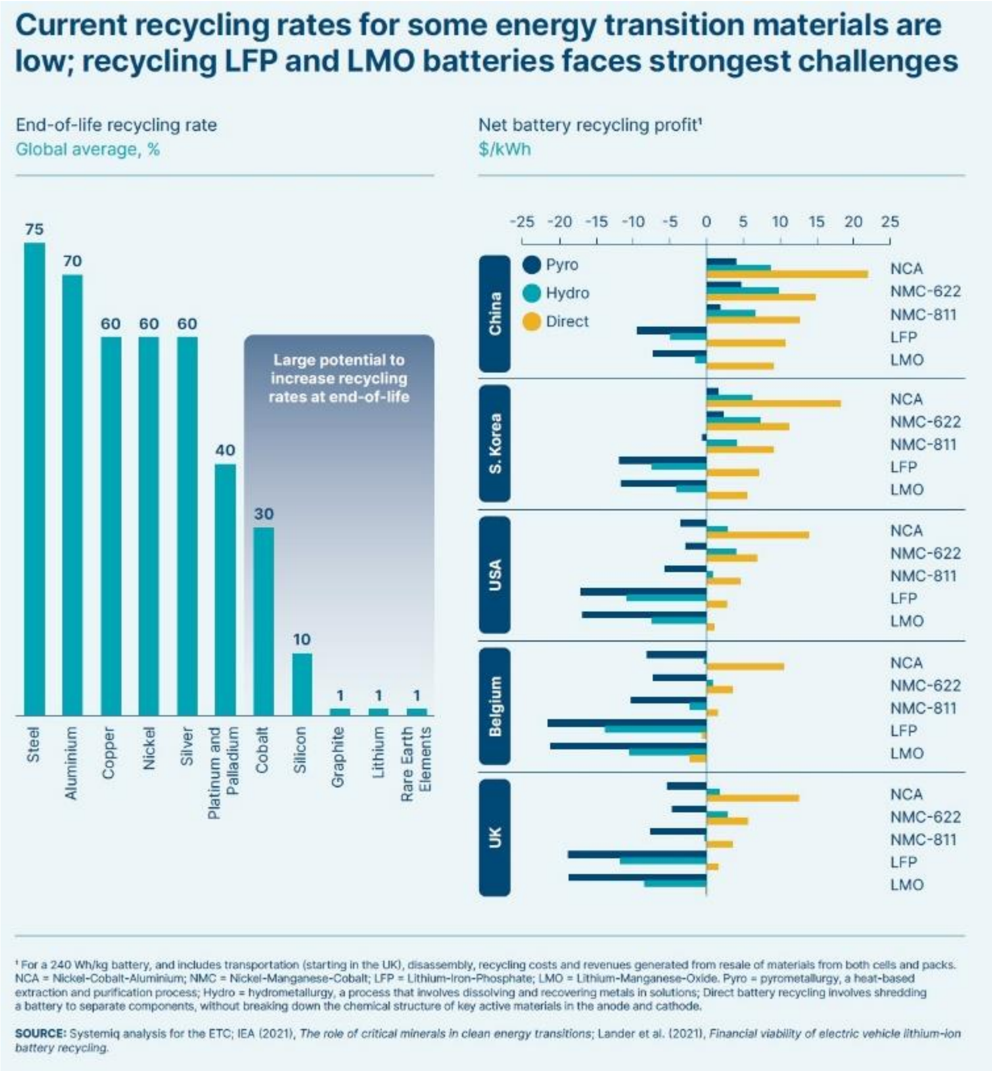
The battery chemistry can have an impact on the recovery rates, based on the complexity of the battery's materials. In this regard, the chemical and physical properties of materials and how these properties are related have a key role when designing a recycling process. The technologies selected for the recovery of materials (i.e., the recycling process itself) also has an impact on the recovery rates. Moreover, it has an impact on the waste production along the process, that should also be considered. Finally, the location can affect the overall recycling efficiency if there are limitations such as potential transport barriers of these materials to the final destinations where recycling takes place.

LiBs chemistries have been changing and evolving since the 90s, driven by the achievement of a higher energy density and cycle lifespan. The cathode active material (CAM) is the battery component that has been investigated the most, in this regard. A detailed description of the CAM developed so far and how these have evolved within the last decades was presented in Deliverable 6.1 The higher the complexity of the battery chemistry (i.e., the amount of elements with different physic-chemical properties), the higher the challenge of developing an efficient recycling approach, with high recovery rates for all elements. The market share and value of the materials used for the CAM production is also a driving force for battery's recycling.

Battery recycling capacity is quickly becoming larger and, even though an over-capacity is possible, with 750 kt per year of possible recycling capacity by 2030, only 320 kt per year of manufacturing waste is available. This means that, currently, the available amount of manufacturing waste is below the forecasted recycling capacity for 2030. This is due to the fact that battery manufacturers are committed to reduce waste from production.

According to the Regulation of the European Parliament and of the Council concerning batteries and waste batteries, producers have an extended producer responsibility for the management at the EOL stage of the batteries they have put on market. This means that they should cover the costs related to collection, treatment and recycling of EOL batteries. Moreover, they should provide relevant information to end-users and waste operators about appropriate management of waste batteries. (Parliament, 2023) With respect to LiBs, a recycling of 70% by average weight is targeted by December 2031. For the materials itself, such as cobalt (Co), copper (Cu), lead (Pd), lithium (Li) and nickel (Ni), a 95% recycling efficiency is targeted.

Currently, recycling rates for some energy transition materials are quite low. Figure 3 shows the potential for certain elements to increase their current recycling rates (e.g., Co, Li, rare earth elements (REE)) once products reach their EOL.



Current recycling rates for some energy transition materials are low; recycling LFP and LMO batteries faces strongest challenges

¹ For a 240 Wh/kg battery, and includes transportation (starting in the UK), disassembly, recycling costs and revenues generated from resale of materials from both cells and packs. NCA = Nickel-Cobalt-Aluminium; NMC = Nickel-Manganese-Cobalt; LFP = Lithium-Iron-Phosphate; LMO = Lithium-Manganese-Oxide. Pyro = pyrometallurgy, a heat-based extraction and purification process; Hydro = hydrometallurgy, a process that involves dissolving and recovering metals in solutions; Direct battery recycling involves shredding a battery to separate components, without breaking down the chemical structure of key active materials in the anode and cathode.

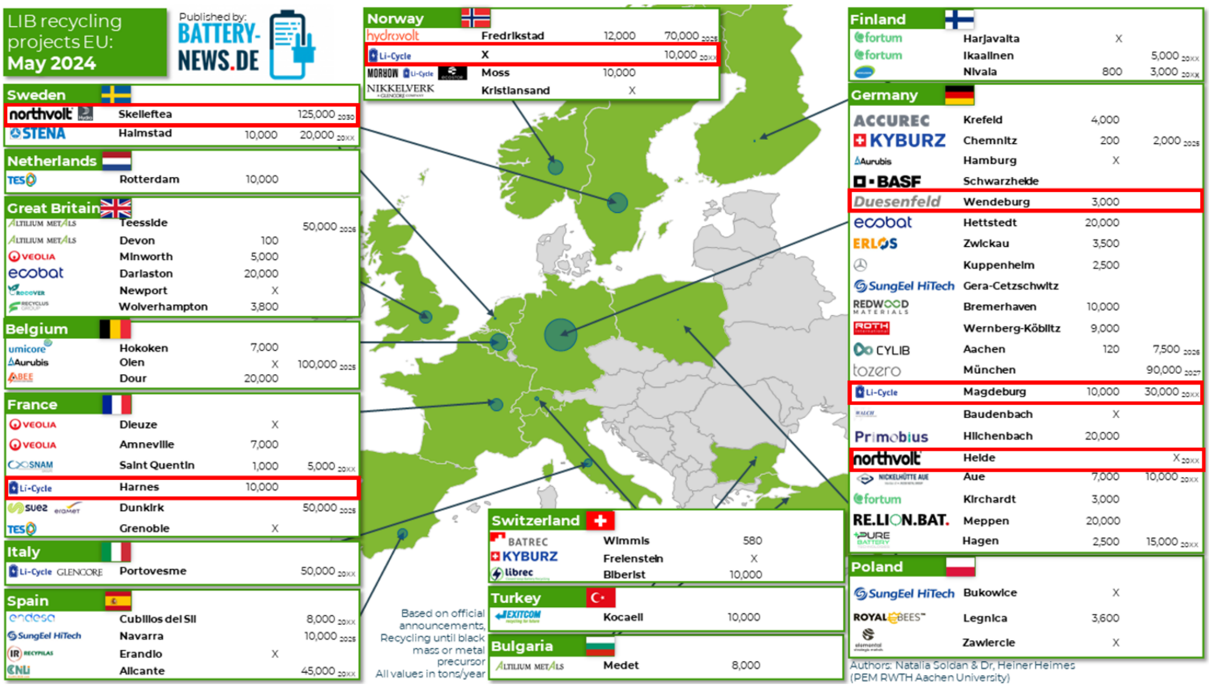
SOURCE: Systemiq analysis for the ETC; IEA (2021), *The role of critical minerals in clean energy transitions*; Lander et al. (2021), *Financial viability of electric vehicle lithium-ion battery recycling.*

Figure 3: Current recycling rates for some energy transition materials and technologies mainly employed at industrial scale, for the recycling of different batteries chemistries.(ETC, 2023)

Figure 3 also depicts that in countries such as China, South Korea, USA, Belgium and UK, direct recycling of LiBs (i.e., NCA, NMC-622, NMC-811, LFP, LMO) is more profitable than pyrometallurgy and hydrometallurgy, taking into account transportation, disassembly, recycling costs and revenues generated from resale of materials.(ETC, 2023)

1.1 Objective of this report

This report aims to give a detailed description of the field of battery recycling in Europe. Moreover, a number of processes outside Europe are briefly considered as well to bring a broader analysis perspective of current industrial processes. Figure 4 shows an overview of the most recent project announcements regarding Li-ion battery recycling and is updated multiple times a year as a result of a quickly developing field. At the time of starting work package 6, the companies highlighted in the red squares, Northvolt, Duesenfeld and Li-Cycle, had announced the most advanced processes to be developed in the EU. For this reason, the processes of these companies have been selected for the detailed description and subsequent analysis.



Sweden

northvolt Hydro	Skelleftea		125,000 2030
STENA	Halmstad	10,000	20,000 20XX

Netherlands

TES	Rotterdam	10,000	

Great Britain

ALTILIUM METALS	Teesside		50,000 2026
ALTILIUM METALS	Devon	100	
VEOLIA	Minworth	5,000	
ecobat	Darlaston	20,000	
RECOVER	Newport	X	
RECYCLUS GROUP	Wolverhampton	3,800	

Belgium

umicore	Hokoken	7,000	
Aurubis	Olen	X	100,000 2025
ABEE	Dour	20,000	

France

VEOLIA	Dieuze	X	
VEOLIA	Amneville	7,000	
SNAM	Saint Quentin	1,000	5,000 20XX
Li-Cycle	Harnes	10,000	
suez eramet	Dunkirk		50,000 2025
TES	Grenoble	X	

Italy

Li-Cycle GLENCORE	Portovesme		50,000 20XX

Spain

endesa	Cubillos del Sil		8,000 20XX
SungEel HiTech	Navarra		10,000 2025
IR RECYPILAS	Erandio	X	
CNLi	Alicante		45,000 20XX

Norway

hydrovolt	Fredrikstad	12,000	70,000 2025
Li-Cycle	X		10,000 20XX
MORROW Li-Cycle ECOSTOR	Moss	10,000	
NIKKELVERK A GLENCORE COMPANY	Kristiansand	X	

Finland

fortum	Harjavalta	X	
fortum	Ikaalinen		5,000 20XX
	Nivala	800	3,000 20XX

Germany

ACCUREC	Krefeld	4,000	
KYBURZ	Chemnitz	200	2,000 2025
Aurubis	Hamburg	X	
BASF	Schwarzheide		
Duesenfeld	Wendeburg	3,000	
ecobat	Hettstedt	20,000	
ERLOS	Zwickau	3,500	
	Kuppenheim	2,500	
SungEel HiTech	Gera-Cetzschwitz		
REDWOOD MATERIALS	Bremerhaven	10,000	
ROTH International	Wernberg-Köblitz	9,000	
CYLIB	Aachen	120	7,500 2026
tozero	München		90,000 2027
Li-Cycle	Magdeburg	10,000	30,000 20XX
WALCH	Baudenbach	X	
Primobius	Hilchenbach	20,000	
northvolt	Heide		X 20XX
NICKELHÜTTE AUE	Aue	7,000	10,000 20XX
fortum	Kirchardt	3,000	
RE.LION.BAT.	Meppen	20,000	
PURE BATTERY TECHNOLOGIES	Hagen	2,500	15,000 20XX

Poland

SungEel HiTech	Bukowice	X	
ROYAL BEES	Legnica	3,600	
elemental	Zawiercie	X	

Switzerland

BATREC	Wimmis	580	
KYBURZ	Freienstein	X	
librec	Biberist	10,000	

Turkey

EXITCOM recycling for future	Kocaeli	10,000	

Bulgaria

ALTILIUM METALS	Medet	8,000	

Based on official announcements, Recycling until black mass or metal precursor
All values in tons/year

Authors: Natalia Soldan & Dr, Heiner Heimes
(PEM RWTH Aachen University)

Figure 4: Map of announcements of plans and current activities by Li-ion battery recycling companies in Europe. (Battery-News.de, 2024)

The content of this report is divided in three chapters. Chapter 2 describes industrial technologies for battery recycling such as: pre-treatments; pyrometallurgy; direct recycling and hydrometallurgy. Examples of current industrial recycling processes are also discussed in this chapter. Chapter 3 is focused on a technology assessment of the different recycling steps of selected hydrometallurgical processes (i.e., Li-Cycle, Northvolt, BRUNP and Duesenfeld) to establish an optimal battery recycling process. Finally, Chapter 4 discusses final conclusions and outputs of the technology assessment.

2. Recycling technologies

This report focusses on recycling technologies for the recovery of batteries materials. Figure 5 depicts the four technologies that are described in detail in the following sections, with its main advantages and disadvantages.

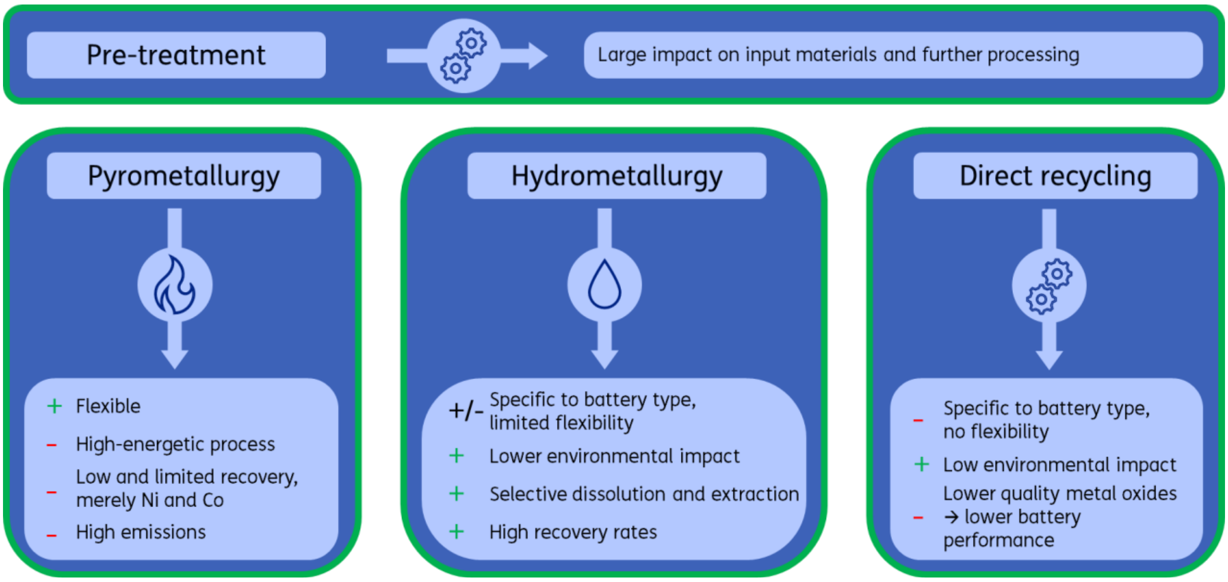


Figure 5: Li-ion battery recycling technologies described in this report.

The main differences of these technologies rely on the flexibility towards treating different batteries chemistries simultaneously, the selectivity for material recovery, the environmental impact with regards to direct emissions, the amount of reagents used and the energy consumption. For this report, only industrial-scale technologies, thus high Technology Readiness Level, were used for the description and analysis of the pre-treatment processes, pyrometallurgy, hydrometallurgy and direct recycling processes. Although some technologies are flexible to different batteries chemistries, this report mainly focuses on NMC chemistry, considering the demand growth for the key materials contained in these batteries. Figure 6 shows a basic scheme that represents a process and its major materials flows: inputs, such as reagents, energy requirements; outputs, such as final products; auxiliaries, such as any extra material required for the process; and waste, such as wastewater or any other waste stream generated during the process.

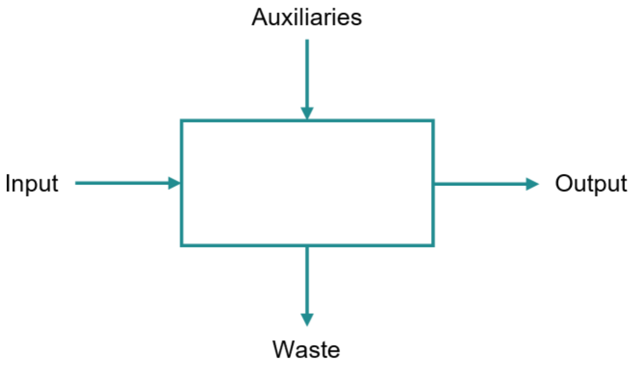


Figure 6: General diagram of process.

For the technology assessment, a thorough analysis of the material flows of each of the selected hydrometallurgical processes to be assessed is performed. This is also taken into account for the comparison of these processes and to draw up final conclusions.

2.1 Pre-treatment of LiBs

The first step in recycling of LiBs is the pre-treatment, which generally involves discharging and dismantling of the batteries, followed by crushing, shredding, and separation of the different components. The goal of pre-treatment is to optimize the recovery of the black mass (as already defined in Deliverable 6.1: consists of, but is not limited to, cathode active material.) for the recovery of valuable components in the subsequent recycling steps. Pre-treatment enables the safe handling, transportation, storage, and recycling of LiBs. It also reduces the volume of the recycle stream by recovering components that can either be discarded or recycled. (Yu et al., 2021) The pre-treatment process does not consist of standardized steps, but differs depending on the size of the LiBs units, the downstream recycling process (hydrometallurgical or pyrometallurgical) and the chemistry of the batteries. The size of the batteries determines if they are directly crushed without firstly discharging and dismantling them. For small format LiBs, used for portable devices such as laptops, tablets, smartphones, and power tools, no sorting and dismantling is performed, and the batteries are crushed directly. This is because the sorting process for smaller formats is more complex than for larger format batteries and challenging from a logistic and economic perspective. For example, a ton of small format batteries is comprised of > 20 000 cells, while a ton of large format LiBs is comprised of 3 to 5 battery packs (27 000 to 45 000 cells). For large format LiBs such as for electrical vehicles (EV), the batteries are first discharged and disassembled before being crushed or shredded, which is also related to safety of the process. (Latini et al., 2022) The non-standardized chemistry of the battery, makes it difficult to standardize the pre-treatment process and therefore many companies have developed and patented their own processes and technologies to effectively pre-treat the batteries to recover a purified black mass stream. (Latini et al., 2022; Yu et al., 2021) In the sections below a general overview and description of the pre-treatment steps is given along with which processes are applied for which industry. A general block flow diagram containing the general steps for the pre-treatment of large format LiBs is given in Figure 7.

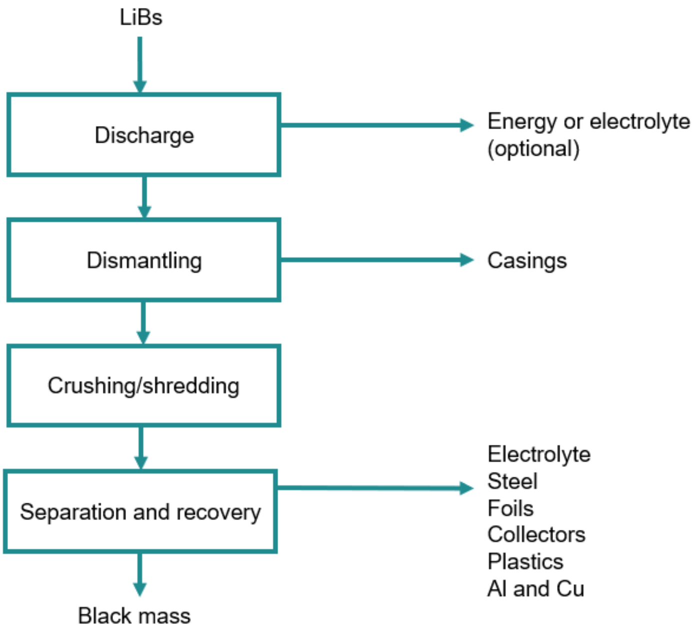


Figure 7: General process steps for pre-treatment of LiBs and the recovered materials in the subsequent steps.

2.1.1 Discharge

The first step of pre-treatment is discharging the batteries for functionality and safety purposes. Industrially there are three manners in which batteries are deactivated, namely: thermal pre-treatment, salt-water baths, and controlled discharging via external circuits.(Latini et al., 2022; Neumann et al., 2022; Yu et al., 2021) Thermal deactivation involves subjecting the batteries to vacuum thermal recycling at temperatures of $\leq$ 250°C, thereby evaporating the electrolyte and discharging the battery. The electrolyte can be condensed afterwards but is contaminated with decomposition products (due to high temperature). The decomposition products are mainly from the plastics and binders. The advantage of decomposing the binder is that the recovery of black mass will be higher as the main reason for black mass loss is adhesion to the current collector foils due to the binders.(Yu et al., 2021) This method of discharging has been adopted by Accurec, with the advantage being a controlled deactivation while eliminating the risk of emitting toxic gases and metals. The drawback is that a fractional degree of lithium and graphite is lost during the process, apart from the loss of binders and plastics.(He et al., 2021; Latini et al., 2022; Yu et al., 2021)

Alternatively, batteries are discharged by submerging them in salt-water baths (typically (NaCl or Na_2SO_4). (Neumann et al., 2022) When submerged in the conductive solution, the positive and negative electrodes are short-circuited and the energy can be absorbed in a safe manner. This method is widely used as it is relatively cheap and easy to implement. The drawbacks are that the discharge speed is low and that damaged cells (corrosion of the cells) and batteries can contaminate the solution. (Yu et al., 2021)

The third option is discharging via external circuits using an Ohmic resistor. An electronic load is applied to offer resistance to discharge the spent LiBs. Typically, the energy is dissipated as heat and therefore cooling is required. Alternatively, the discharged energy could be recovered and stored (energy recycling) using modern electronic banks that enable energy recovery as alternating current (AC). (Harper et al., 2019; Windisch-Kern et al., 2022; Yu et al., 2021) Due to the wide variety of the batteries, automation of this process is difficult and it thus needs to be done manually which poses a health and safety risk to personnel.(Yu et al., 2021)

An alternative to discharging batteries, is to directly crush/shred the batteries in an inert atmosphere or under cryogenic cooling. This step is usually applied when the batteries are not dismantled after discharging and saves process costs as the discharge step is omitted. (Or et al., 2020) Companies that directly crush/shred are: Recupyl and Li-Cycle.(Depicker, 2022; Yu et al., 2021)

2.1.2 Disassembly (dismantling)

Once safely discharged, the batteries are either disassembled manually or crushed/shredded directly. (Neumann et al., 2022; Yu et al., 2021) During manual disassembly, components of the batteries are removed to reduce the recycling input materials stream for further recycling, by reducing them to cell or module level.(Yu et al., 2021) The plastic casings, the aluminium covering, and the connection interface of the battery are removed. Apart from the plastics and aluminium (Al) other valuable components such as steel, Cu, and precious materials can be recovered from the battery housing, as well as cable harnesses, cooling systems, and other electronic parts. These components can all be recycled for the production of new batteries.(Windisch-Kern et al., 2022; Yu et al., 2021) The advantage of manual disassembly is that recovered fractions are less contaminated (generates more homogenous streams). Moreover, when the battery configurations are non-standardized, manual disassembly is the most effective way to recover the materials. The drawbacks of manual disassembly are high labour costs, safety hazards and lower efficiency. (Kim et al., 2021; Kwade, 2018; Windisch-Kern et al., 2022; Yu et al., 2021) Processes in which manual disassembly is incorporated are: Hydrovolt (pre-treatment for the Northvolt recycling process)(Hydrovolt, 2022), Duesenfeld (Duesenfeld, 2022), Umicore (Latini et al., 2022), LithoRec (Latini et al., 2022; Yu et al., 2021), and Retriev (Latini et al., 2022).

2.1.3 Comminution: Mechanical crushing and shredding

The next step after either deactivation and/or dismantling is mechanical disintegrating of the batteries. The process step is known as comminution (mechanical treatment) and can involve multiple steps (with intermediate separation steps) to reduce the particle size and maximize the separation efficiency of the battery components. The first crushing step is usually a rough crushing step, after which the aluminium and steel casings, plastics, black mass, and non-ferrous materials are separated via different methods (see Section 2.2.4). The recovered black mass subsequently undergoes a second (fine) crushing step to liberate the different elements, mainly the cathode active material from the foils and to avoid that particles from the current collector attaching to the black mass (purer stream).(Neumann et al., 2022; Yu et al., 2021) Industrially, different methods of crushing are being applied namely inert/cryogenic crushing and wet crushing in water or an alkaline brine.(Latini et al., 2022)

Inert crushing or cryogenic crushing entails crushing the batteries under an inert atmosphere or very low temperatures, respectively. As mentioned above, this step can be already implemented as an alternative to the discharging and dismantling steps. Under an inert/cryogenic atmosphere the risk of fire or explosions is reduced by lowering the reactive nature of lithium. Lithium is reactive in air and water, resulting in the generation of hydrogen gas which in this approach is avoided. (Windisch-Kern et al., 2022; Yu et al., 2021) Additionally, the emission of toxic gases is eliminated. (Or et al., 2020) For inert crushing, the inert atmosphere usually consists of argon (Ar), nitrogen (N_2), or carbon dioxide (CO_2). Industrially, cryogenic crushing (T = -160 °C, with liquid N_2) was applied in the Retriev process after manual disassembly to avoid short circuiting because of the volatile electrolyte, however, due to the high operating cost this step is no longer applied (only for batteries with a large content of flammable Li). Currently, for the Retriev process the disassembled batteries are shredded and wet milled. (Latini et al., 2022) Industrial processes that apply inert crushing are Batrec (shredding under CO_2 atmosphere) and Duesenfeld (shredding under N_2 atmosphere).

Wet crushing, as the name suggests, entails crushing the batteries in water or aqueous solutions. During wet crushing, lithium is converted to an unreactive state so that it does not react with the electrolyte.(Yu et al., 2021) The advantage is that the solution/water eliminates dust emission and subsequent clogging of equipment, which is usually the case with dry crushing. Additionally, water acts as a fire retardant and absorbs the heat generated during crushing, thereby preventing high temperatures and explosions. Wet crushing is also advantageous for subsequent separation process such as froth floatation, as the surface roughness, particle agglomeration, and surface oxidation is lower for wet crushing compared to inert crushing. Wet crushing is usually done in combination with deactivation in a brine solution. (Latini et al., 2022) Companies that industrially apply wet crushing methods are Retrieve (lithium hydroxide (LiOH) brine), Li-Cycle, Lithion, and Neometals. (Latini et al., 2022)

Regardless of the crushing process chosen, gases are still emitted which need to be cleaned before being released as off-gas. In general, the gas is sent to a condenser to recover evaporated electrolytes, after which the gas goes to carbon filters and wet scrubber to remove volatile organic components and toxic HF which originates from the binder and lithium salt decomposition.(Latini et al., 2022)

The advantage of directly crushing (without disassembly) is that the processing capacity is higher and it omits the safety risks to personnel. The disadvantage is that the volume of the recycling stream is larger, which will lead to larger equipment and higher energy consumption. Furthermore, the purity of the stream is lower. (Yu et al., 2021) Processes that adopt directly crushing the batteries without manual disassembly are Li-cycle, Recupyl (2010), and Batrec. (Depicker, 2022; Kwade, 2018; Neumann et al., 2022; Yu et al., 2021)

2.1.4 Separation and recovery

Crushing and shredding are usually accompanied by intermittent separation steps to recover the liberated materials. Typically, the first component to be separated after crushing is the electrolyte, however, it is not the case for all processes. Thermal drying is the process that is typically industrially applied for the recovery of the electrolyte, such as for the Duesenfeld process. (Latini et al., 2022) For the process of Duesenfeld, thermal drying is carried out under vacuum (100 – 300 mbar) at temperatures between 80 and 140 °C, thereby avoiding the formation of HF gas. The organic solvent of the electrolyte evaporates and is either recovered for recycling or combusted for energy recovery.(Bussmann, 2022; Latini et al., 2022)

After the recovery of the electrolyte and the first crushing step, the heavy fraction namely the casings (aluminium and steel), electronic conductors, and steel screws are separated from the lighter fraction namely the current collectors, active material, and separators. Separation is typically done via air classification (zigzag-shifter). Air classification has been adopted by many industrial processes namely Duesenfeld, Accurec, Redux, and Neometals. (Kim et al., 2021; Latini et al., 2022) Afterwards the heavy fraction is further separated via magnetic separation to recover the steel. The lighter fraction undergoes a second crushing step to liberate the black mass, thereby increasing the yield of black mass. (Kim et al., 2021; Latini et al., 2022) For the separation of current collector foils from the separators, companies such as Duesenfeld, Accurec, and Redux, apply a second stage air classification step, while Euro Dieuze Industrie, Li-Cycle, and Lithion uses Eddy current separation (prototype stage). Subsequently for the separation of copper from aluminium foils, Lithion adopted a second stage air classification, while Duesenfeld uses optical separation. (Latini et al., 2022)

The purpose of the second crushing step is to liberate the black mass from the collector films to enable a better separation and recovery of the black mass. The liberated black mass is separated from the current collectors and foils through sieving. The large particles (> 2 mm) consist of the aluminium and copper foils, metal scraps and plastics. The smaller particles (typically < 2 mm or even smaller) consist mainly of the black mass material, but also contain impurities such as aluminium, copper, and plastics. Depending on the process and the purity of the stream, the black mass is either further grinded and sieved to increase the purity of the stream before the subsequent recycling process. (Kim et al., 2021; Latini et al., 2022; Yu et al., 2021) For example, for the process of Duesenfeld the black mass is recovered using a vibrational sieve (500 µm mesh size) after the second crushing step.(Kwade, 2018; Latini et al., 2022) Multiple sieving steps can be applied however, with each step there is a fractional loss of black mass. For the Li-Cycle process the LiBs are directly shredded and the shredded material is then sent to multiple screens (industrial sieves) to separate the plastics and foils from the black mass. (Depicker, 2022)

The typical recovery efficiency of black mass for the pre-treatment section ranges between 75 and 90 wt.% (of black mass entering the system). The reason of the loss of black mass is mainly due to adhesion to current collectors and foils. (Latini et al., 2022)

In Table 2.1 an overview of each pre-treatment step and the industrial processes is given.

Table 2.1: Overview of pre-treatment processes.

Pre-treatment step	**Process**	**Advantage**	**Disadvantage**	**Recovered materials**	**Material lost/damages**	**Industrial implementation**	**Ref.**
Discharge	Thermal deactivation	• Limits the risk of emitting toxic and harmful gases. • Controlled discharge • Improves recovery of black mass.	• Fractional loss of Li and graphite • High-temperature requirements • Decomposition of binders and plastics	• Electrolyte	• Loss of electrolyte if there is no recovery. • Li and graphite loss • Loss of plastics and binders	• Accurec	(Latini et al., 2022; Neumann et al., 2022; Windisch-Kern et al., 2022)
	Salt-water baths	• Cheap process • Easy to implement	• Possible corrosion of metal casing • Possible contamination of solution from damaged cells and batteries • Slow process	• None	• Corrosion of metal casing	• Retriev	(Harper et al., 2019)
	External circuit	• Eliminates the risk of toxic or harmful has emission. • Possible energy recovery	• Low efficiency • Manual operation and gives safety risks	• Energy	• Damage to cell due to overheating if cooling is not applied	• Duesenfeld • Redux • Ascend Elements	(Latini et al., 2022; Yu et al., 2021).
Disassembly	Manual	• Recovery of purer components • Effective recovery of non-standardized battery components	• Labour costs • Safety risks • Lower efficiency	• Plastics • Al • Cu • Steel • Precious metals • Cooling systems • Other electronics		• Duesenfeld • Hydrovolt • Umicore • LithoRec • Retriev	(Kim et al., 2021; Latini et al., 2022; Windisch-Kern et al., 2022; Yu et al., 2021)

Crushing/ Shredding	Inert/ cryogenic crushing	• Eliminates emission of toxic gases • Reduces risk of fire and explosions • Enables easy breaking of plastic casings (cryogenic)	• High operating cost (cryogenic)	• Liberation of cathode and anode material	• Loss of black mass due to adhesion to collectors and foils	• Batrec (CO_2 atmosphere) • Duesenfeld (N_2) • Recupyl (CO_2 and Ar)	(Latini et al., 2022; Yu et al., 2021)
	Wet crushing	• Elimination of dust emission, clogging • Prevents explosions, by acting as a fire retardant. • Can be combined with discharging in salt-water baths. • Lower surface roughness, particle agglomeration and surface oxidation	• Wastewater needs to be treated afterwards (increase in operational cost)	• Liberation of cathode and anode material	• Possible loss of binder, electrolyte when cutting LiBs directly with highly pressurised water • Loss of black mass due to adhesion to collectors and foils	• Neometals • Retrieve ($LiOH$ brine) • Li-Cycle ($Ca(OH)_2$ and $NaCl$ brine) • Euro Dieuze Industrie (E.D.I) • Lithion	(Latini et al., 2022; Yu et al., 2021)
	Inert crushing/ shredding (no prior disassembly)	• No safety risks. • Increased processing capacity	• Higher volume of material to recycle downstream. • Loss of purity of the recycle stream	• Liberation of cathode and anode material	• Loss of material purity		(Latini et al., 2022; Neumann et al., 2022; Yu et al., 2021)
Separation	Sieving	Mature separation method		• Black mass • Foils • Plastics	• Fractional loss of black mass which increases with multiple stages	• Standard step in all pre-treatment processes	(Latini et al., 2022)
	Air-classification	Mature separation method		• 1st classification - heavy and light fractions • 2nd classification – current	• Foils • Binders	• Duesenfeld • Accurec • Redux • Neometals	(Latini et al., 2022)

				collectors foils from separator			
	Magnetic separation	Mature method of separation		• Steel components		• Duesenfeld • Accurec • Redux • Akkuser • Euro Dieuze • Ascend Elements • Recupyl • Li-Cycle • Lithion	(Latini et al., 2022)
	Thermal vacuum drying	Improves recovery of black mass		• Electrolyte		• Duesenfeld	(Latini et al., 2022)
	Optical separation			• Cu from Al foils		• Duesenfeld	(Latini et al., 2022)

The pre-treatment steps applied are often dependent of the downstream recycling process. For the pyrometallurgical process, pre-treatment is kept to a minimum and usually only consists of the deactivation and disassembly steps (for large format LiBs), after which the stream is smelted in a high-temperature furnace (1500 °C) to recover an alloy. Components such as electrolyte, plastics and separator material are combusted and thus cannot be recycled or re-used. The alloy and slag then undergo further treatment (typically hydrometallurgical) to obtain higher purity products.

For the hydrometallurgical route the pre-treatment is more extensive, to ensure that a purer black mass stream is fed to the process. The more extensive pre-treatment process results in the recovery of different components, such as aluminium and copper, plastics, binders, electrolyte etc. which can be recycled to produce new batteries or burned to produce heat (energy recovery). The purity of the product after the recycling process will be high and thus minimal to no downstream processing is required to purify the products further.

For the direct recycling route (still in the prototype phase), the required pre-treatment is more extensive as the black mass is not separated into its comprised components, but rather recycled as a whole. The purity of the black mass therefore needs to be very high to enable the re-use of the recycled cathode material for new battery production. In

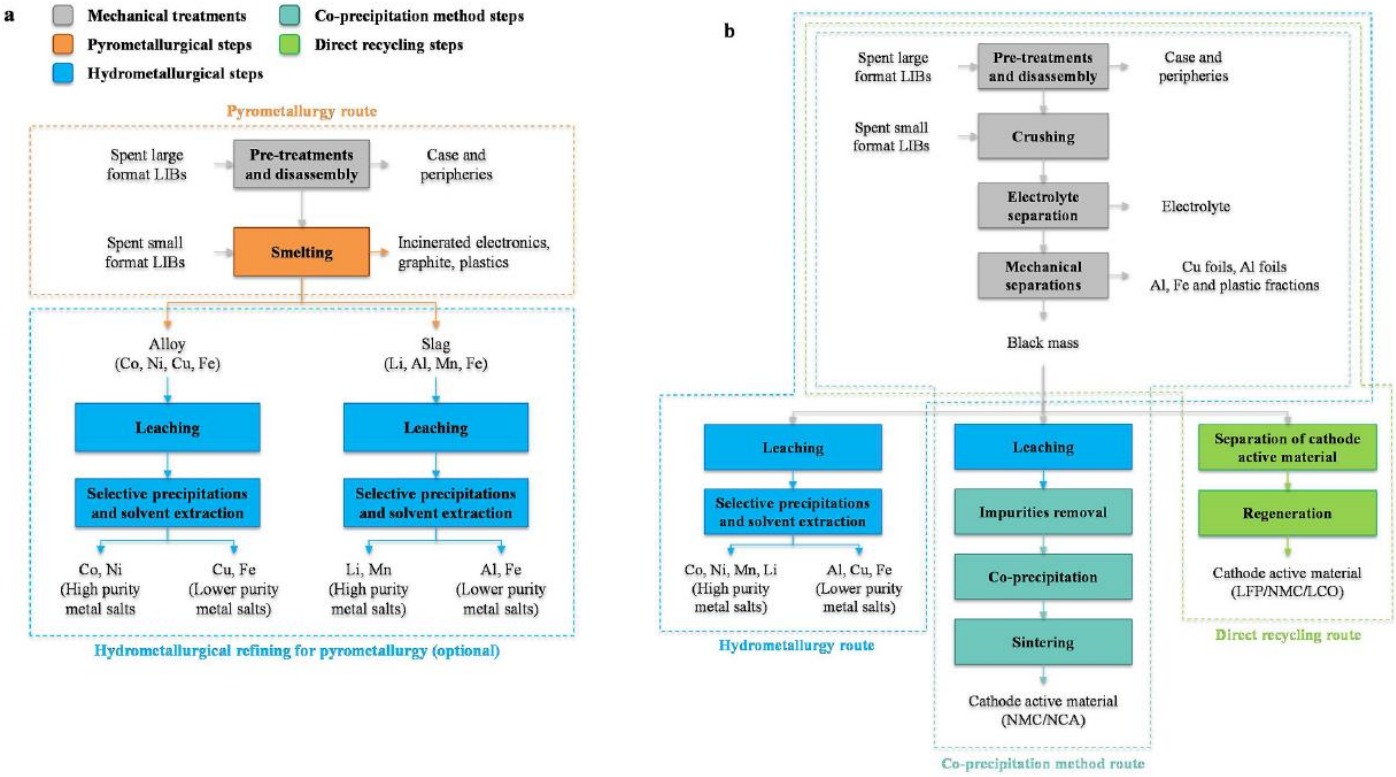


Figure 8: General flow scheme indicating which pre-treatment steps are applied for which recycling route (taken from (Latini et al., 2022).

2.2 Pyrometallurgical methods

Pyrometallurgy finds its origin in the processing of conventional mined ores. Currently, it is also quite dominant for metal recovery from e-waste. Its main advantages are its simplicity, its flexibility towards the feed materials, and its high processing rate. Another advantage is the negligible environmental impact coming from the dross/slag, which is further on treated to recover Li. However, toxic gases may be generated and these must be neutralized by an off-gas treatment, such as the one incorporated in Umicore's plant, removing all volatile organic compounds as well as dust. (Makuza et al., 2021) This technology is mostly used to concentrate target components into an intermediate product, such as an Ni-Co alloy for EOL LiBs, and to remove unwanted materials, such as graphite and fluorine, that may have a negative impact on the efficiency of further refining processes (i.e., hydrometallurgical treatments). (Reiner Sojka, 2020)

The process itself consists of feeding spent LiBs together with additives (i.e., coke) into a furnace. Three types of reactions occur in different temperature zones: 1st zone (< 300˚C, pre-heating), the electrolyte is evaporated at lower temperatures, therefore avoiding the risk of explosion of the fed material; 2nd zone (< 700 ˚C, pyrolysis), plastics are pyrolyzed; 3rd zone (1200-1450˚C), the smelting and reducing of metal oxides occur, giving rise to a Ni, Co, and Cu alloy that is further refined by hydrometallurgical treatments, whereas Mn, Al and Li are slagged. A gas cleaning installation is used to treat the off gas produced as part of the process and, therefore, avoid the release of toxic gases into the environment.(Windisch-Kern et al., 2022)

Various aspects influence pyrometallurgical processes, being temperature, processing time, flux addition, and types of purge gas, the most relevant ones.(Reiner Sojka, 2020) One of the main advantages of this process is that pre-treatment steps (e.g., dismantling) are not required unless batteries exceed the size requirements for material feeding. Moreover, carbon rich compounds (i.e., graphite from active anode material and plastics) can act as both reducing agent and energy source (i.e., the resulting energy released from these reactions heats up the smelter), therefore minimizing the need of additives or extra energy input.

A great variety of pyrometallurgical treatments exist, such as incineration, pyrolysis, roasting, and smelting. Since incineration and pyrolysis are mostly considered pre-treatments to remove the organic content (e.g., binder), this chapter will address roasting and smelting in more detail, to have a more a clear understanding of the chemical reactions involved for the metals recovery.

2.2.1 Roasting

Roasting is an exothermic gas-solid reaction that occurs at high temperatures, to convert metal oxides into a mixed metal alloy. In the case of LiBs, active cathode material components are recovered by means of a carbothermic reduction (CTR) process.(Makuza et al., 2021) The latter consists of heating the active cathode material with a reducing agent, such as carbon or coke, under vacuum or an inert atmosphere, to reduce the metal oxides into a mixed metal alloy. The alloy then contains Co, Ni, and possibly other metals such as Cu and Fe, whereas Li and Al remain in the slag. Metal alloys are further refined by means of hydrometallurgical treatments.(Baum et al., 2022). Moreover, it is possible to combine other LiBs related waste into the feed (i.e., as secondary raw materials) to recover its metal content.(Windisch-Kern et al., 2022)

Nevertheless, this process has certain disadvantages such as low selectivity towards metal recovery; therefore, further refining steps are required for isolation and purification of extracted metals. Moreover, Li usually ends up in the slag (i.e., as lithium carbonate, Li_2CO_3) and though upstream processing to recover Li is under research, it is not yet industrially implemented.(Windisch-Kern et al., 2022)

An alternative to CTR roasting is salt-assisted roasting. The transition towards this roasting option is, due to the fact that Li_2CO_3 obtained from CTR roasting has a low solubility, giving rise to low leaching efficiencies. Another relevant aspect about salt-assisted roasting is that it requires less acid consumption (i.e., in further refining steps), which has a positive environmental impact in terms of less toxic gas emissions.(Makuza et al., 2021) There are three types of salt-assisted roasting processes: chlorination, sulfation, and nitration. Different reagents can be used to obtain more soluble Li salts (Table 2.2).

Table 2.2: Salt-assisted roasting reagents.(Makuza et al., 2021)

Chlorination	**Sulfation**	**Nitration**
HCl (g), NH_4Cl, NaCl, Cl_2 (g)	SO_2 (g), $MgSO_4$, NH_4SO_4, $NaHSO_4.H_2O$, Na_2SO_4, H_2SO_4	HNO_3

By means of chlorination roasting it is possible to produce soluble metal chlorides, with solubilities higher than 800 g/L (20˚C). In the case of sulfation, sulfuric acid (H_2SO_4) has been adopted as a sulfation agent for spent LiBs recycling. The resulting salt, lithium sulphate (Li_2SO_4), is easily soluble in water (257 g/L, 20˚C). Another advantage is that, from a viewpoint of the resulting products, it is a cleaner and less environmentally harmful reagent than others. With a controlled amount of H_2SO_4 during the sulfation roasting, sulfur produced in the process can be recycled as SO_4^{2-} instead of SO_x emission, thereby minimizing secondary pollution.

Finally, nitration agents in contact with spent LiBs give rise to soluble lithium nitrate ($LiNO_3$), with a solubility of 623 g/L, at 35˚C.

2.2.2 Smelting

The smelting process consists of heating the feed material above its melting point; metals are reduced and separated into a liquid phase. In this case, the carbon and Al content of spent LiBs act as reducing agents, no extra reducing agents are added, as in smelting. This process can be carried out with different spent LiBs chemistries and these can be fed into the furnace without the need for pre-treatment.

The process comprises two phases: in phase 1, the electrolyte is evaporated by means of heating the feed material at a low temperature, thus avoiding the risk of explosion that may occur at higher temperatures; in phase 2, the feed is heated at a higher temperature until melting of the material. Part of the energy required for the smelting process is supplied by the combustion of the organic material, whereas the carbon and Al from spent LiBs act as reducing agents. The Al is slagged as aluminium oxide (Al_2O_3) and its recovery is not economically feasible. Moreover, lithium oxide (Li_2O) is not reduced and it is also slagged, whereas the remaining metals are further recovered from the mixed alloy by means of hydrometallurgical processes.

One of the main disadvantages of the smelting process is its high energy consumption, with low selectivity (i.e., metal alloys need to be refined). Also, it is more economically feasible for batteries with Co and Ni content; for other battery chemistries, such as LFP and LMO, metals are slagged and therefore it is difficult to recover them.(Makuza et al., 2021) Moreover, this process is not suitable to recover Li; salt-assisted roasting process would be more convenient for this purpose.

2.2.3 State of the art of industrial processes

Pyrometallurgical processes are predominant at industrial scale due to the fact that it is a mature and relatively simple process. An overview of companies practicing pyrometallurgical treatments within Europe is presented in Table 2.3.

Table 2.3: Overview of the companies that practice pyrometallurgical treatments.(Makuza et al., 2021)

Company	**Location**	**Pre-treatment**	**Type of treatments**	**Capacity, t/y**	**Final products**
Umicore	Belgium	Not required (dismantling only for batteries that exceed size requirements)	Smelting, shaft furnace	7000	• Slag: Li, Al • Alloy: Ni, Co, Cu
Accurec	Germany	Dismantling → pyrolysis → mechanical treatments	Pyrolysis and smelting	6000	• Slag: Li • Alloy: Co, Ni • Li concentrated fraction
Glencore	Switzerland	Not required	Smelting, electric arc furnace	7000	• Slag • Alloy: Ni, Co, Cu
LithoRec	Germany	Dismantling → crushing → air classification	Drying and calcination	100	• Li_2CO_3
GRS Batteries	Germany	Not reported	Vacuum distillation	Not reported	• Co, Ni, Cu
Battery resources	Germany	Discharging → shredding → magnetic separation → sieving → dense medium separation	Sintering	Not reported	• Li_2CO_3 • Metal oxides
Nickelhütte Aue GmbH	Germany	Not reported	Smelting	Not reported	• Co, Ni, Cu

Different industrial pyrometallurgical processes are already being implemented for the recovery of Ni and Co from spent LiBs. These processes include further refining steps to enhance the purity of the recovered products. For some companies, LiB recycling is an expansion of the already existing Ni-Cd/ Ni-MH recycling facilities. Moreover, some battery manufacturing companies are including recycling of spent LiBs within their own facilities.

2.3 Direct recycling of LiBs

Direct recycling involves the removal of the cathode and anode material from the respective electrodes for reconditioning and re-use, without separating the material into the separate elements. A general layout of the direct recycling steps is given in Figure 9.

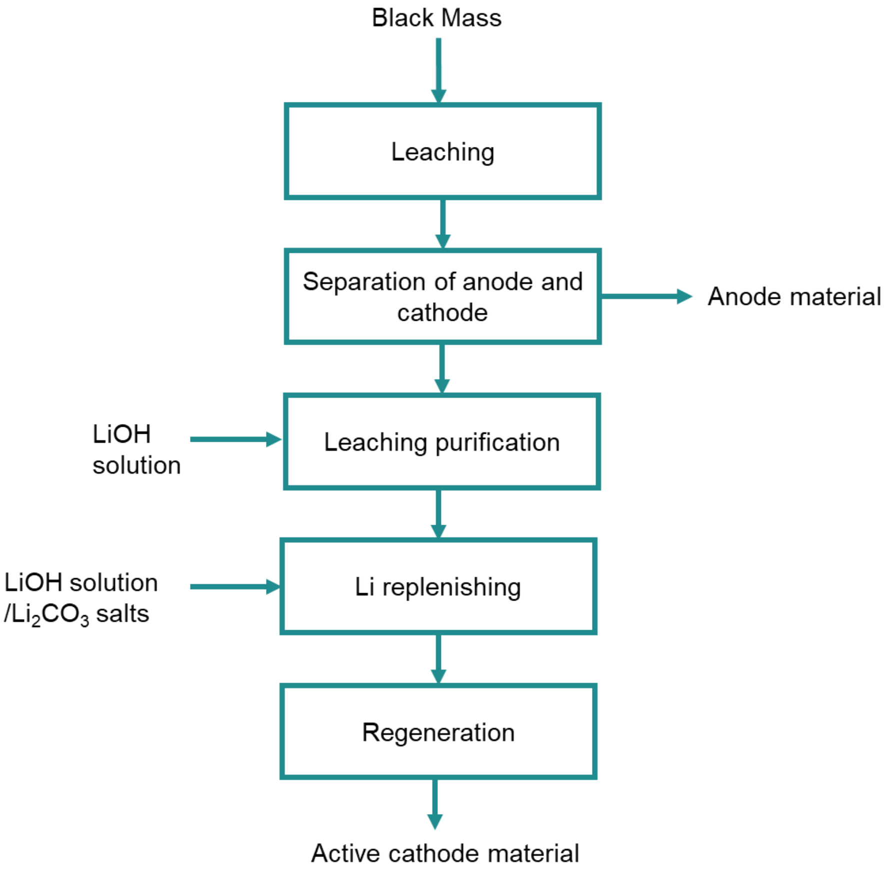


Figure 9: General concept layout of a direct recycling process.

After disassembly of the battery and the subsequent pre-treatment steps to recover and purify the black mass (see Section 2.1), an additional separation step is added to separate the cathode active material from the anode material (graphite). The cathode material is then purified by firstly dissolving the polyvinylidene difluoride (PVDF) binder in a basic LiOH solution (leaching purification step in Figure 9) and afterwards the solid is filtered and washed with acetone or ethanol, to produce a stream with a purity of 99%. The cathode material is dried in a vacuum oven, milled, and sieved. (Golmohammadzadeh et al., 2023; Latini et al., 2022) The next step in the direct recycling process is replenishing the lithium content. This is due to losses of the material, caused by degradation and the materials not being fully recovered during disassembly. (Baum et al., 2022; Harper et al., 2019) Replenishing is done by adding Li_2CO_3 salts to the mixtures or using a LiOH solution. (Forte et al., 2021; Sloop et al., 2020). The process finishes regenerating the material by heating the mixture to temperatures between 650 and 900 °C, for several hours under a H_2/Ar, N_2 or air/O_2 atmosphere (last step in Figure 9). This is done to restore the crystalline structure and morphology of the cathode active material for battery use. (Forte et al., 2021; Harper et al., 2019; Sloop et al., 2020) After regeneration, the cathode material is suitable to be directly used to produce new batteries.

Currently, direct recycling is not applied industrially as this technology is still in the development/prototype stage. (Latini et al., 2022) Companies which look at the development of direct recycling for LiBs are OnTo (also known as EcoBat) and Botree Cycling.(Wang, 2022) For the patented OnTo process, the separation of the anode and cathode material (see Figure 9 – separation of anode and cathode) is done via dense media separation. The retrieved cathode material then undergoes leaching purification, after which it is mixed with a LiOH solution to replenish the Li content. The mixture is then filtered, dried, and washed with either deionized water or LiOH solution. After washing the material is dried (150 – 160 °C) and ground. The last step in the regeneration phase is to sinter the powder under an air/O_2 atmosphere at 900 °C for eight hours. (Latini et al., 2022) For the OnTo process the recovered graphite (anode material) also undergoes a high temperature treatment to purify the graphite for re-use.

Investigations regarding the direct recycling of batteries have mainly focused on LCO and LFP batteries. Direct recycling is a promising route for recycling of LFP batteries as the stoichiometry of LFP batteries are fixed (in contrast to lithium nickel cobalt aluminium oxide (NCA) and NMC batteries), ensuring universal applicability of recovered material for the production of new LFP cathodes. (Baum et al., 2022; Neumann et al., 2022) Currently, LFP batteries are not recycled commercially due to the low value of the recovered materials (iron and phosphorus) as opposed to the recovery of metals such as nickel, cobalt, and manganese from NCA and NMC batteries. (Forte et al., 2021; Maagoe, 2022) Recycling of LFP batteries is thus not economically feasible using conventional processes such as pyrometallurgy or hydrometallurgy, but with direct recycling the process could become economically feasible. Recently a European project named ACROBAT (Advanced critical raw materials recycling from spent LFP batteries), was started that aims to recycle end-of-life LFP lithium-ion batteries. (VITO, 2022)

2.4 Hydrometallurgical methods

Hydrometallurgical processing of batteries focusses on leaching of metals in aqueous media to bring them into solution to be able to separate the metal ions. The combination of H_2SO_4 and hydrogen peroxide H_2O_2, as leaching agent, is being employed to a great extent, though other alternatives are also being investigated. The following reaction conditions have the most significant impact on a leaching process in terms of yield and rate: concentration of leaching agent, temperature, reaction time, solid-to-liquid ratio and stirring rate (Harper et al., 2019; Or et al., 2020).

Once in solution, the metals are separated by means of precipitation, by adjusting the pH of the solution, or solvent extraction, making use of selective extractants towards the target metals to be recovered. Usually, Co is isolated as carbonate, hydroxide, sulphate, or oxalate salt ($CoCO_3$, $Co(OH)_2$, $CoSO_4$, CoC_2O_4, respectively), whereas Li is often precipitated as Li_2CO_3 or lithium phosphate (Li_3PO_4).(Harper et al., 2019) Moreover, Co can also be isolated as metallic Co by means of electrowinning.(Makuza et al., 2021)

Hydrometallurgical treatments have the advantage of high recovery rates and selectivity towards dissolution and extraction of elements. As a disadvantage, these can carry environmental and human risks related to the acid corrosiveness. Other issues to be addressed are the high volumes of solvents required, the speed of dissolution of the CAMs from the current collector foils, the costs of neutralization, and the likelihood of cross-contamination of materials (Harper et al., 2019).

For hydrometallurgical treatment of black mass, several companies have developed their own process, varying in type of end product and level of sustainability. For this report, five processes developed by four companies have been selected to be described in high detail, divided into two main process routes: mixed precipitation of the CAMs versus separate recovery through solvent extraction. Below, an overview of the hydrometallurgical routes is given for every company. In the paragraphs following the descriptions, the various hydrometallurgical routes will be compared.

2.4.1 Selected hydrometallurgical processes

Five patented hydrometallurgical processes, from four different companies, were analysed and are described in detail below. The five processes are developed by Li-Cycle, Northvolt, BRUNP and Duesenfeld. Li-Cycle, Northvolt and Duesenfeld are companies present in Europe, whereas BRUNP was selected to also represent the Chinese recycling market.

Li-Cycle

Li-Cycle has four recycling facilities in North America, with an operational capacity to process 51000 tons/year of spent LiBs. By the end of 2023, a new recycling facility will be processing up to 35000 tons/year of black mass, being the first commercial hydrometallurgical plant in North America to also recover battery grade Li_2CO_3 from spent LiBs (https://li-cycle.com/about/). Figure 10 depicts the full process of spent LiBs, which comprises both mechanical and hydrometallurgical treatments.

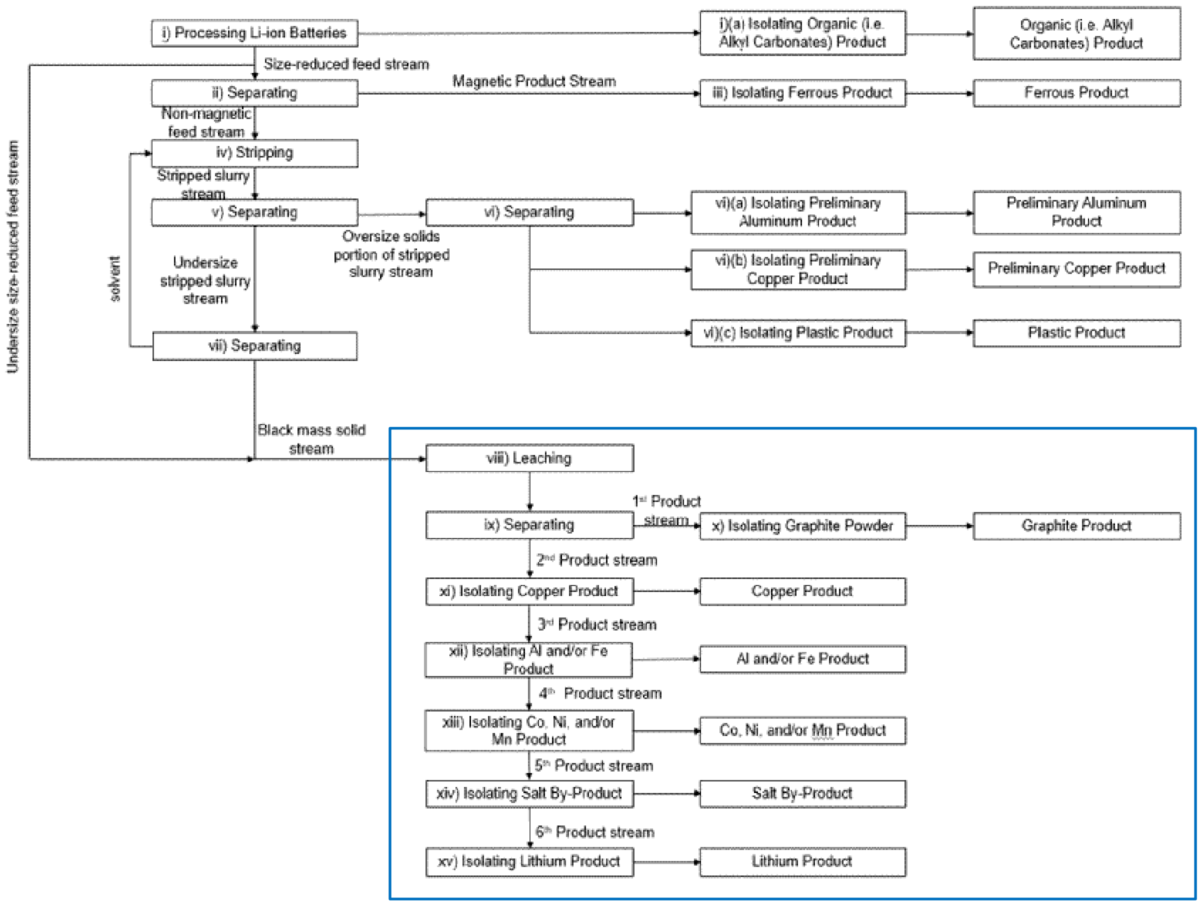


Figure 10: Li-Cycle, Example 3 of Process 2 as explained in the patent (the hydrometallurgical method is highlighted in a blue square).(Kochhar, 2019)

A zoom in on the hydrometallurgical method (Process 2, Example 3) shows that the black mass obtained after mechanical treatments is subjected to an acid leaching, making use of H_2SO_4 and H_2O_2, being the latter a reducing agent to guarantee cobalt dissolution. This process achieves a 95% leaching efficiency. After a series of steps to isolate impurities - such as Cu, Al, Fe, graphite -, the pregnant leach solution containing nickel, cobalt, manganese, and lithium is subjected to a mixed precipitation process, by addition of a hydroxide salt (e.g., sodium hydroxide (NaOH)) to precipitate the corresponding metal hydroxides. From the resulting filtrate, after isolating the cobalt, nickel, and manganese hydroxides (i.e., by filtration), a sulphate salt by-product is isolated to achieve a lithium enriched solution. Subsequently, Li_2CO_3 is isolated by addition of sodium carbonate (Na_2CO_3).

BRUNP Industry

The company was founded in 2005 in Fushan, China. Its core business is the recycling of spent batteries and cars. From 2013 to 2015, BRUNP continuously supplied materials to CATL, a LiBs manufacturer, and the company finally became a subsidiary of CATL. Therefore, it can be considered that BRUNP not only treats EOL batteries but also waste materials from manufacturing lines. Nevertheless, the amount of production scrap being treated is unknown (Reiner Sojka, 2020).

The company's battery recycling facilities have a total area of 130,000 square meters, with an operational capacity of 6000 tons/year of waste batteries and a production of 4500 tons of nickel manganese cobalt hydroxides (ternary precursor), nickel manganese acid lithium cobalt (ternary material), lithium cobalt oxide, cobalt chloride, nickel sulphate, cobalt sulphate, and cobalt oxide, reaching 98% yields. BRUNP is Asia's first recycling company of spent batteries (https://en.brunp.com.cn/intro/14.html). The company recycles different spent batteries streams: NMC, LMO, and LFP. As an example, Figure 11 depicts the recovery process of CAMs of NMC, from black mass.

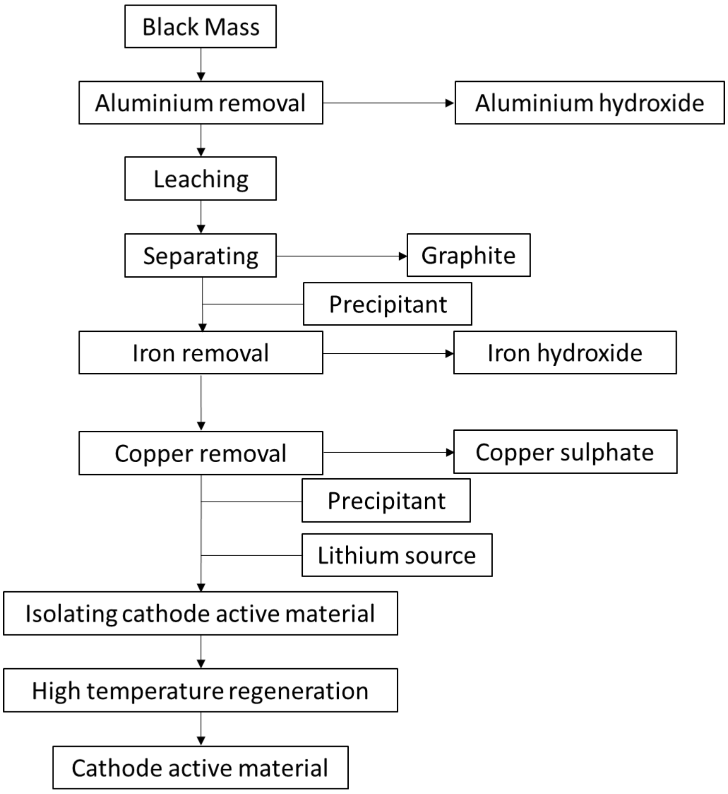


Figure 11: BRUNP process for the recovery of NMC from black mass (translated from the original Chinese version) (Ltd., 2009).

After a first sorting step, the batteries undergo mechanical treatments until a black mass is retrieved. Subsequently, the black mass is treated with NaOH to remove aluminium content. Further on, the resulting material is subjected to an acid leaching to dissolve metal oxides. After filtration, graphite is isolated as a solid residue. From the resulting filtrate, Fe is removed as iron hydroxide ($Fe(OH)_3$), after addition of yellow modumite and filtration. Further on, copper sulphate ($CuSO_4$) is extracted from the filtrate by means of solvent extraction. From the resulting solution, after increasing the pH (i.e., adding NaOH and Na_2CO_3), an NMC-hydroxide precipitates and is isolated. The Li content is recovered from the filtrate. The recovered material is subjected to drying and then mixed with a Li source and regenerated in the oven, after two heating cycles (500˚C and 900˚C, respectively). A recovery yield of 95% for nickel, 96% for cobalt and 95% of manganese is obtained. The patent also covers the recovery process for other battery chemistries, such as LMO and LFP.

Duesenfeld GmbH

The full patented process developed by Duesenfeld combines mechanical and hydrometallurgical treatments for the recovery of metals contained in spent LiBs. The patent describes the recovery of spent LFP, LMO, LCO, and NCA batteries. Figure 12 depicts the process flow diagram for the recycling of NMC spent batteries.

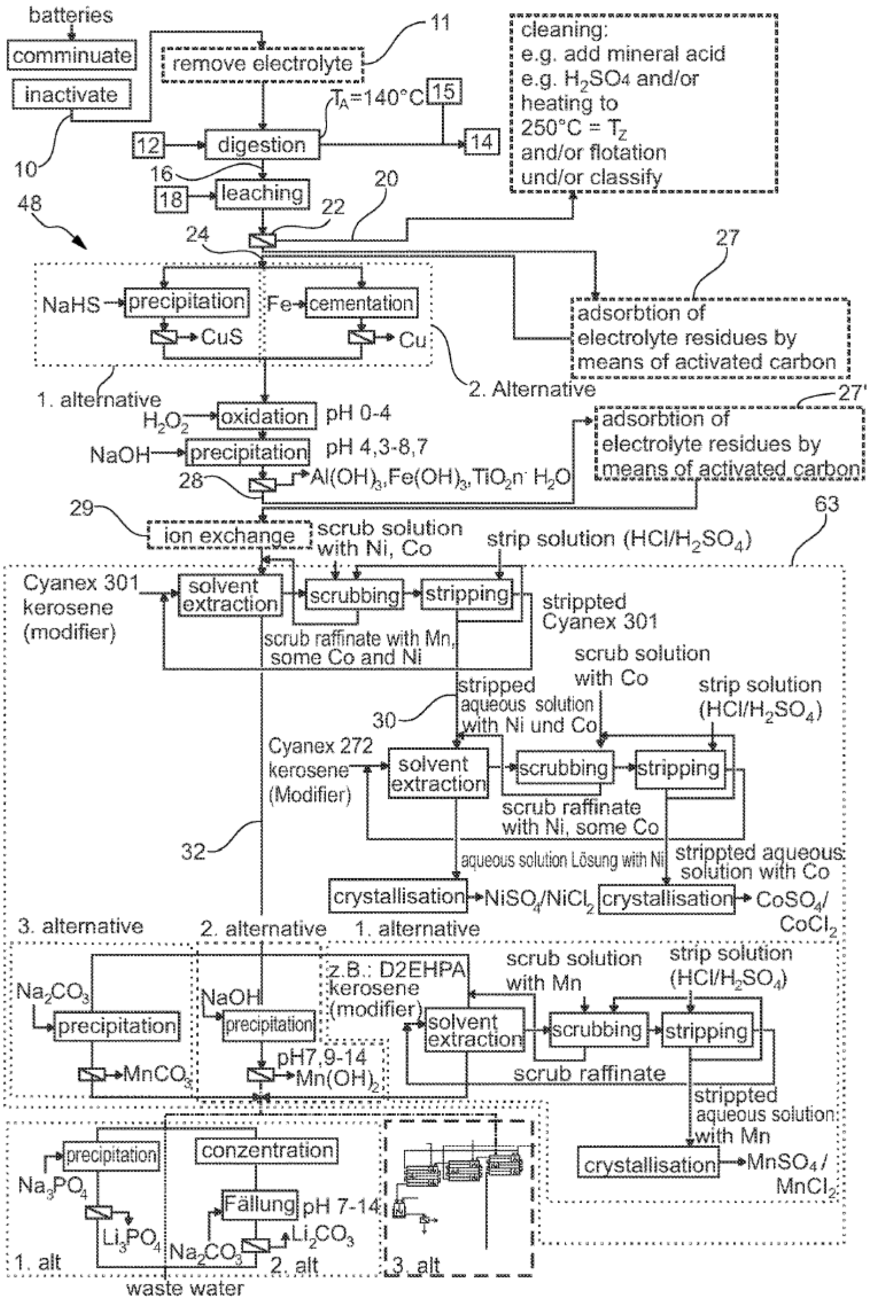


Figure 12: Duesenfeld process flow diagram for the recycling of NMC batteries (Hanisch, 2022).

After mechanical treatments, an acid digestion is carried out to guarantee a safe removal of fluoride (F) content. Fluorine compounds can give rise to HF, being extremely hazardous to human health, besides the fact that it is highly corrosive. Therefore, an acid digestion step making use of concentrated H_2SO_4, removes the F content and reduces safety precautions on subsequent steps of the recovery process. The resulting hydrogen fluoride is then captured by precipitation as calcium fluoride.

Once the hydrogen fluoride is removed, the black mass is leached to bring all metals to solution. Afterwards, impurities such as Al, Fe and Cu are removed by precipitation and ion exchange. Then, the leachate - enriched in nickel, cobalt, and manganese - is subjected to a solvent extraction step, making use of different extractants selective to Co and Ni. Two streams - rich in Co and Ni - are obtained, from which cobalt sulphate ($CoSO_4$) and nickel sulphate ($NiSO_4$) are isolated, respectively.

From the resulting solutions after extraction of Ni and Co, Mn can be isolated by solvent extraction and finally precipitated as manganese sulphate ($MnSO_4$), manganese carbonate ($MnCO_3$), or manganese hydroxide ($Mn(OH)_2$). From the final solution, Li is precipitated as lithium phosphate (Li_2PO_4) or Li_2CO_3. The combined process (mechanical and hydrometallurgical) achieves a material recovery yield of 91%.

Northvolt AB

Established in 2017, the company's core business is the development and manufacturing of LiBs. As part of the value chain, the company has an ongoing program for battery recycling: Revolt. This plant will operate with an annual capacity of 125,000 tons of spent batteries to be recycled and a 95% recovery efficiency of Ni, Co and Mn from spent batteries to battery-grade levels of purity. The company patented three processes:

1) Process for the recovery of cathode materials in the recycling of batteries: (Mahmood ALEMRAJAB, 2020)

This process is mainly focused on the removal of impurities - such as copper, aluminium, and iron - from the resulting leachate of the black mass, and subsequently the mixed precipitation of NMC-hydroxides. Figure 13 shows a flow diagram of the process described in this patent.

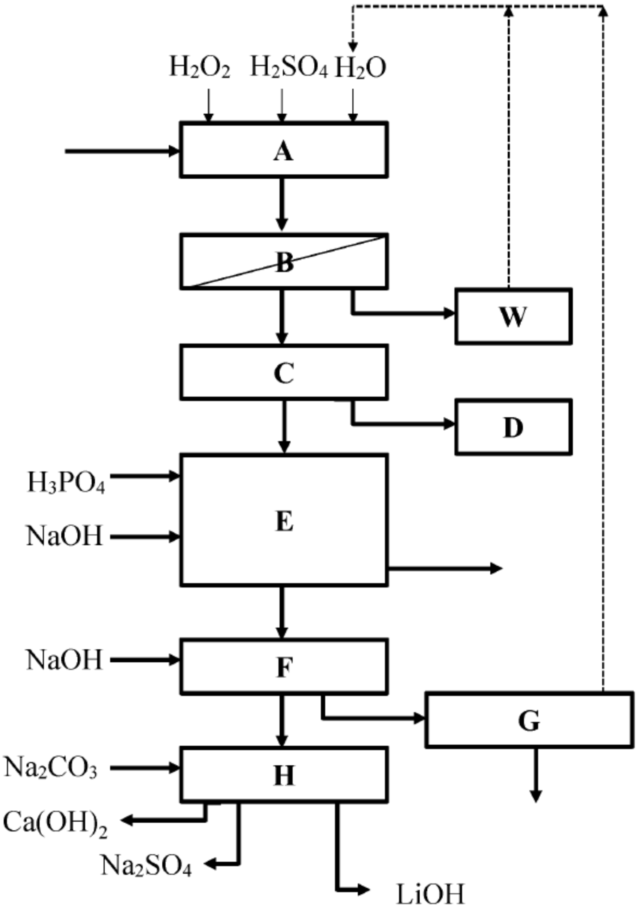


Figure 13: Flow chart for the Northvolt process for the recovery of cathode metals from spent batteries.(Mahmood ALEMRAJAB, 2020)

After subjecting the black mass to a leaching process making use of H_2SO_4 and H_2O_2 (A) and removing the graphite by filtration (B), the leachate undergoes two purification steps to remove impurities such as:

- Cu, removed by solvent extraction (C), giving rise to a copper product (D);
- Al and Fe, removed by precipitation as phosphate salts (E).

From the resulting filtrate, a cake of nickel-manganese-cobalt hydroxide is obtained by addition of NaOH (F). After filtration, lithium hydroxide is isolated by addition of Na_2CO_3 to the filtrate (H).

2) *Process and method for producing crystallized metal sulphates:*(Robert John Fraser, 2022)
This patent describes a process to produce Ni, Mn, Co and Li sulphate. For this purpose, seven examples are presented in this patent. An overview of two of them will be described here. Figure 14 depicts a flow chart of *Example 1* mixed precipitation process.

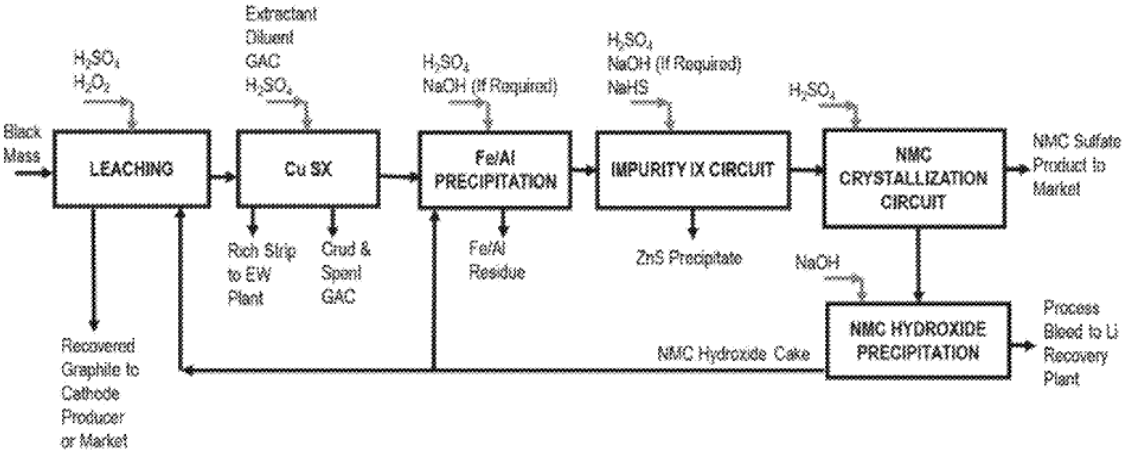


Figure 14: Flow chart of Example 1 process of the Northvolt process (Robert John Fraser, 2022).

A first leaching step is carried out using H_2SO_4 and H_2O_2. After filtration of the solid residue, the filtrate is subjected to a first purification step, consisting in solvent extraction of copper impurities. The resulting raffinate solution is then treated with NaOH to remove iron and aluminium impurities. Further on, a next purification step is carried out to remove zinc (Zn) and residual copper (Cu) from the purified pregnant leach solution. This step is performed making use of an ion exchange resin. The final step is the crystallization of Ni, Mn, and Co sulphates, by water evaporation at 65˚C and later on cooling at 0˚C to give rise to metal sulphates crystals. After a filtration step, a metal sulphate cake is obtained which can be used for the synthesis of new CAMs. Lithium remains in the filtrate and can be isolated subsequently from this solution.

In the process described as *Example 2*, metals are separated by solvent extraction. Figure 15 depicts a flow chart of the full process described as *Example 2*.

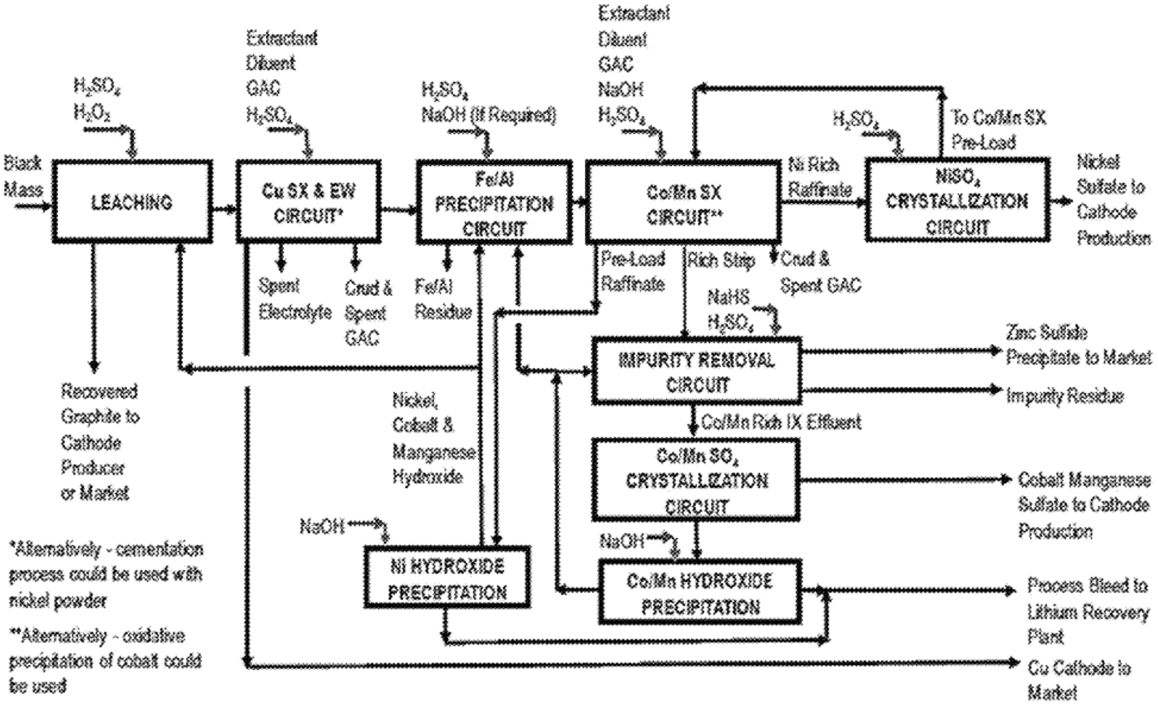


Figure 15: Flow chart of Example 2 process of the Northvolt process (Robert John Fraser, 2022).

After removal of impurities - such as copper and iron -, cobalt and manganese are extracted from the pregnant leach solution by a solvent extraction process, using a selective extractant - such as Cyanex (bis(2,2,4 trimethylpentyl)phosphinic acid) - towards these metals. From the resulting extractant solution, cobalt and manganese are stripped from the organic phase with a H_2SO_4 solution, at pH 1. After evaporating and cooling down the solution, cobalt and manganese sulphates are obtained and removed by filtration. Lithium can be recovered from the resulting filtrate. The nickel rich raffinate from the cobalt-manganese extraction process is acidified making use of H_2SO_4 prior to crystallization, cooling down and filtration, to obtain nickel sulphate.

3) *Process for cathode active material precursor preparation:*(Mahmood ALEMRAJAB, 2022)

This patent describes a process to obtain a CAM precursor from spent LiBs. The leaching step is carried out under the same conditions as previously described. The leaching residue, consisting of graphite, plastics, and undissolved metals, is filtrated and the resulting filtrate is subjected to a purification step to remove impurities, such as Cu, Al, Fe, and Zn. Cu is removed by means of solvent extraction, whereas the remaining impurities (i.e., Al, Fe, Zn) are removed by precipitation, once the pH is increased. After a second filtration step, the nickel, manganese, and cobalt concentration of the filtrate is adjusted to the desired level of total concentration of ions in solution for the target ratio of the active material to be obtained. Further on, the pH of the solution is increased to precipitate one or more active materials, preferably in the form $Ni_xCo_yMn_z(OH)_2$. The desired target molar ratio Ni:Co:Mn may be: 0.8:0.1:0.1 / 0.83:0.085: 0.085 / 0.85:0.075:0.075 / 0.90:0.05:0.05. The resulting solid is filtrated and, from the filtrate, lithium may be recovered by precipitation after addition of Na_2CO_3 to give rise to Li_2CO_3.

2.4.2 Other hydrometallurgical processes

Two other companies recover CAMs at industrial scale: TES and Aurubis. TES recovers the CAM by mixed precipitation, whereas Aurubis process first isolates a lithium salt and later on, a nickel salt.

TES

TES is a worldwide waste management company. A commercial battery recycling facility operates in Singapore, with a capacity to handle 14 tons of spent LIBs or the equivalent of 280.000 smart phones each day, for the recovery of CAMs. The final treatment process of TES is based on the technology developed by Green Li-ion.(GreenLi-ion) The recycling process greatly resembles other mixed precipitation processes: black mass is leached using an acidic solution after which graphite is removed from the mixture by filtration. Subsequently, a solution of sodium hydroxide is added to treat impurities such as aluminium and copper. The impurities are removed by filtration; however, also for this process, copper is most probably reclaimed by electrowinning. The CAMs are recovered by the addition of a 'formulated solution' and the precipitated $NiMnCo(OH)_2$ is removed from the solution by filtration. Finally, Li_2CO_3 is recovered by the addition of Na_2CO_3 and filtration. The great benefit reported by Green Li-ion is the very fast process: the CAMs are recovered within 10 hours when starting the process with leaching black mass.

However, this process may be similar to the Li-Cycle process also reporting on a fast precipitation of the CAMs by operating at relatively high pH, implying the use of large amounts of chemicals.

Aurubis

Aurubis is a German metal recycling company with expertise in pyrometallurgical processes as well as electrolytic copper refining. In 2022, a pilot line was built based on the ASPA technology developed by Aurubis.(Aurubis) The process approaches the recovery of the materials differently as lithium is first leached selectively. The patented process (Suriano, 2023) for the recovery of CAMs from LiBs commences with the preparation of a slurry: black mass is mixed with water for the addition of ozone. Under heavy mixing, lithium is leached in 3 hours at $T = 70 - 95$ °C while maintaining the pH around 7. By addition of NaOH, LiOH can be recovered after which the process resembles the majority of recycling processes again as the remaining black mass is leaching using H_2SO_4.

However, the patent only describes the recovery of nickel in a later stadium: ozone is added to the mixture as an oxidizing agent and nickel sulphate is precipitated upon increase of H_2SO_4 concentration to 5 mol/L. The patent does not describe removal of impurities such as aluminium and copper or the recovery of cobalt and manganese.

In the following sections, a more detailed description of each process is presented, including process flow diagrams and comparative tables with process parameters. Further on, a technology analysis is presented. TES and Aurubis processes were not considered for the technology comparison and analysis (described in the following sections). TES process is quite similar to the Li-cycle one, except for the copper removal step (i.e., in the Li-cycle process, copper is removed by solvent extraction whereas in the TES process, copper is removed by precipitation). As for Aurubis process, since the patent does not describe the impurities removal nor the recovery steps for cobalt and manganese, there is not enough information to perform a step-by-step comparison with respect to the other selected processes, described in this report.

2.4.3 Process flow diagrams

Each of the processes analysed in this chapter consist of a series of steps until recovering the CAM, as metal hydroxides or sulphates cakes, or metal sulphates saltsThe flow diagram for each process is presented in Figure 16 - Figure 20. Each starting material for each step is represented by boxes. Inputs (i.e., chemical reagents) are next to arrows, and resulting products follow the arrows. Auxiliaries and waste streams are represented in orange colour. Finally, the most relevant products (based on commercial value and criticality) - graphite, Cu, CAM product, Li product - are also framed in boxes.

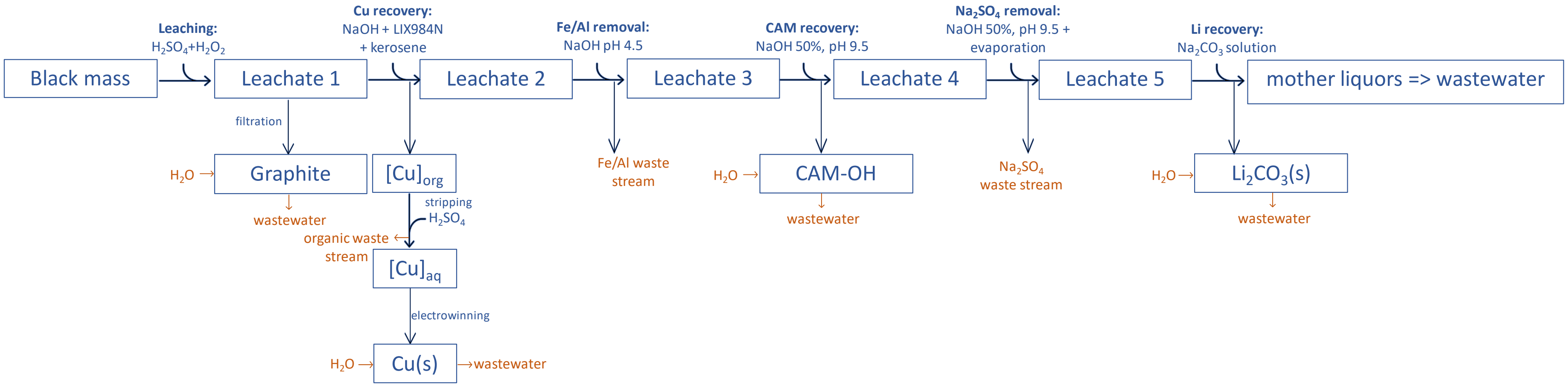


Figure 16: Process flow diagram of Li-cycle (mixed precipitation) hydrometallurgical process.

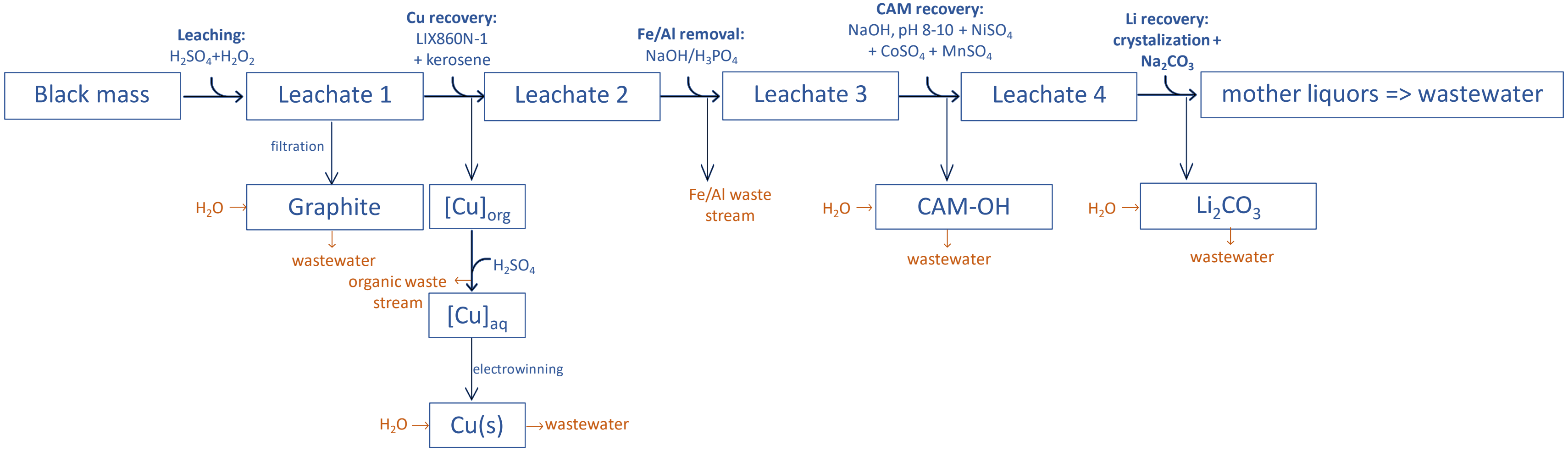


Figure 17: Process flow diagram of Northvolt (mixed precipitation) hydrometallurgical process.

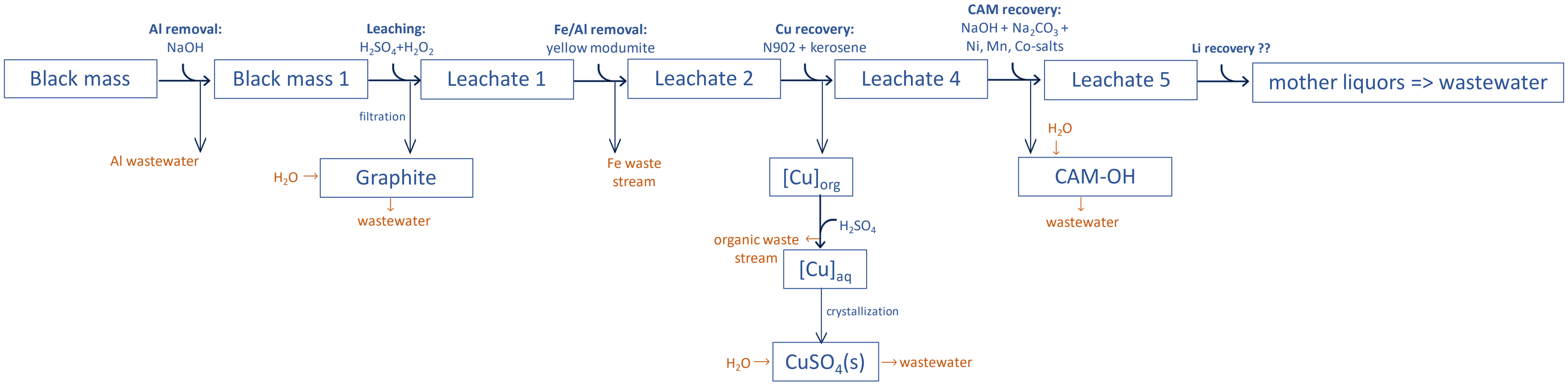


Figure 18: Process flow diagram of BRUNP (mixed precipitation) hydrometallurgical process.

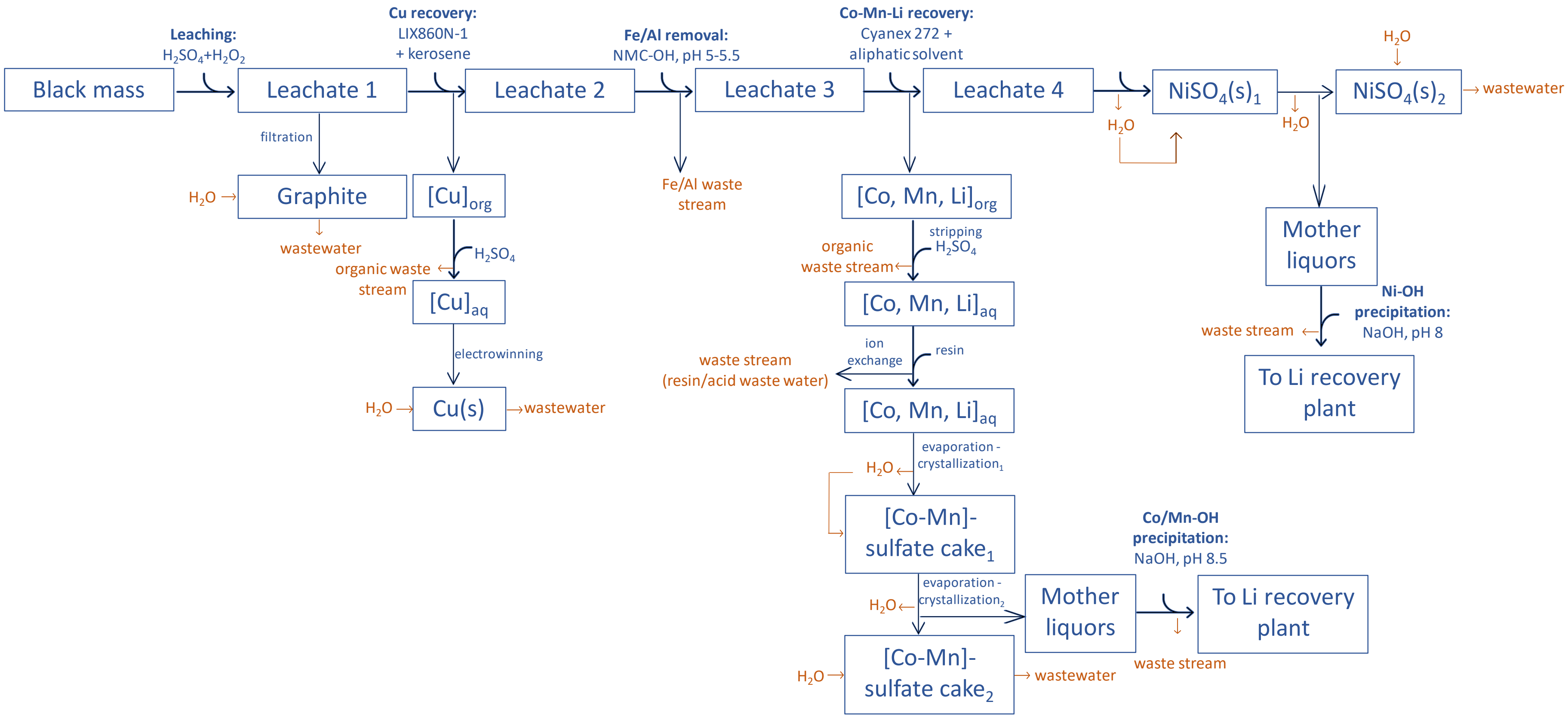


Figure 19: Process flow diagram of Northvolt (solvent extraction) hydrometallurgical process.

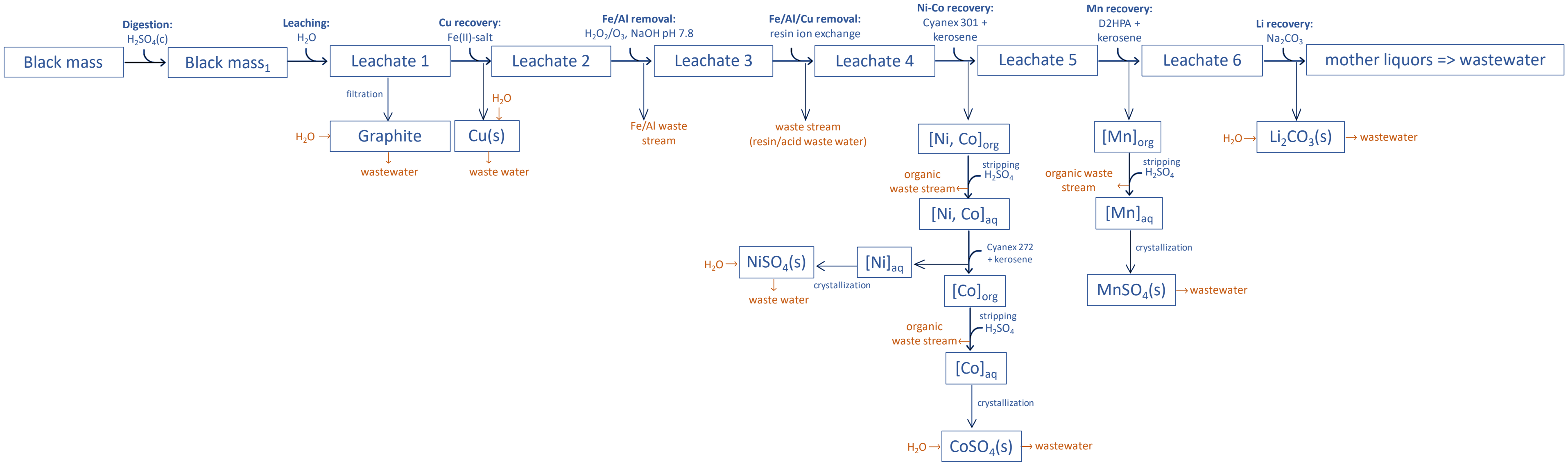


Figure 20: Process flow diagram of Duesenfeld (solvent extraction) hydrometallurgical process.

A thorough description of each step for both mixed precipitation and solvent extraction processes is presented in the following sections. Finally, tables with all the quantitative available data for each step are presented at the end of the process's description, for comparison reasons (Section 2.4.9.).

2.4.4 Leaching of target metals

Hydrometallurgical methods generally start with leaching of the target materials: cobalt, nickel, manganese, and lithium in the case of battery recycling. Most industrially scaled processes, if not all, use a solution of H_2SO_4. Optionally, H_2O_2, is used as a reductant. However, there are some differences in the reaction conditions which are listed in Table 2.4.

Table 2.4: Leaching conditions for the patented processes.

	Li-Cycle	**BRUNP**	**Northvolt**	**Northvolt**	**Duesenfeld**
Type of hydrometallurgy	Mixed precipitation	Mixed precipitation	Mixed precipitation	Solvent extraction	Solvent extraction
Leaching agent	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
Concentration leaching	0.5 M	4.4 M	2-5 M	not specified	Digestion: 40 kg of H_2SO_4 (c) to 1 kg of comminute material. Then, 1:2 - 1:20 of digestion material to water (~0.9-9 M H_2SO_4)
Reducing agent	H_2O_2	H_2O_2	H_2O_2	H_2O_2	not specified
Target pH	2.5	not specified	0.5	0.5	minus 0.7 - 4
Temperature	80 ˚C	60 ˚C	65 ˚C	65 ˚C	R.T.
Leaching time	360 min	not specified	not specified	not specified	Max. 10 h
S/L (solid/liquid)	10% (1:10)	not specified	1:6	1:6	1:2 -1:20

*All processes operated at atmospheric pressure.

As depicted in Table 2.4, there are some similarities and differences between mixed precipitation and solvent extraction processes, and also among the same type of processes. All five patented processes make use of H_2SO_4 as leaching agent. Among mixed precipitation processes, H_2SO_4 concentrations range between 0.5 M and 5 M. In the case of solvent extraction process from Northvolt, though not specified, it is possible to assume that the leaching conditions are equal as the ones described for the mixed precipitation process, since the main differences, as described, arise in the further refining steps. In the Duesenfeld process, a first digestion step using concentrated H_2SO_4 is performed to eliminate the fluoride content. For the leaching step, the patent describes a weight ratio of digestion material to water of 1:2 -1:20. Therefore, it can be roughly estimated that H_2SO_4 range 0.9 - 9 M for the leaching step. All processes also make use of H_2O_2 as reducing agent, except the Duesenfeld process, whose patent does not specify if any reducing agent is being employed. With respect to pH, temperature, and S/L (i.e., the amount of solid per unit volume of leaching agent), all of these variables show differences among the five processes (e.g., room temperature < T < 80˚C). Moreover, only the Li-cyle and Duesenfeld patents report the leaching time, with a high variability between them.

With regard to the particle size, only Li-cycle and Duesenfeld patents define a black mass particle size for the leaching step: ≤ 10 mm and < 500 μm, respectively. However, there is no further discussion on how this variable may impact on the leaching efficiency. BRUNP and Northvolt patents do not specify the black mass particle size required for their leaching processes.

From an overview perspective and based on the available data compiled in Table 4, it is possible to point out that when higher concentrations of H_2SO_4 are being employed, the leaching process can be carried out at lower temperatures as well as higher S/L ratio. Reaction time can also fluctuate depending on the other variables (e.g., leaching time can take longer at lower temperatures than when heating, when the remaining variables are similar). Moreover, particle size has an impact on reactivity of black mass in acid media; the smaller the particle size, the higher the exposed surface and, therefore, the higher the reactivity. Other variabilities of reaction conditions of these processes may rely on differences in the black mass composition, as the starting material for the leaching process.

2.4.5 Removal of non-cathode materials

Pre-treatment processes focus on the isolation of black mass which should consist of CAMs mainly. However, as batteries are shredded and crushed, all components are reduced in similar size and materials are mixed. Black mass is obtained after magnetic separation, densimetric separation, air-sorting separation, sieving or a combination of these processes (see Section 2.1). Physical properties - such as magnetic properties, density, particle size - determine the pre-treatment processes. However, Shredded and crushed materials from batteries have similar size and can end up in the same material stream as the CAMs. In that way, materials such as aluminium and copper from electrode foils and graphite from the anode, are also present in black mass and steps must be taken to remove them as they are considered contaminants in the recovery process of CAMs. The following sections describe the most common methods of separation of such non-cathode materials.

Non-soluble materials

After leaching, some materials are not affected by the acidic environment and remain unaltered, such as trace amounts of plastics which were not fully separated during the pre-treatment step. However, the majority of the non-leached materials originates from the anodic material, namely graphite. Most industrially applied processes focus on removal of solid particles, including graphite, after leaching.

Li-Cycle approaches the removal of unreacted solids by filtration, making use of a filter press or bed filter. This step is performed directly after the leaching of black mass. The resulting solid can be purified by a two-step flotation process, to isolate a graphite product. In some cases, a solid-liquid separation is performed by a centrifuge. Subsequently, after separation, graphite is rinsed with hot water, resulting in a waste water stream that requires further treatment.

Northvolt and Duesenfeld have a similar strategy as Li-cycle. All three patents of Northvolt report a solid residue obtained after leaching of the black mass, mainly composed of graphite. Separation of the solid residue is followed by a filtration step, using a vacuum belt filter or a hydraulic filter press. Subsequently, the solid is rinsed with water to remove adsorbed or encapsulated mother liquors.

Alternatively, Duesenfeld also reports centrifugation, as another means of recovery of graphite. In this case, the isolated solid is rinsed with water or mineral acid (i.e., silicon is preferably removed in this way) until metallic impurities reach a concentration of at most 10.000 ppm. The patent reports that the resulting graphite can replace virgin graphite in many applications. Alternatively, other means of graphite purification may include flotation.

Finally, BRUNP reports the removal of the unreacted solid residue once the leaching step is over, to reclaim the graphite. However, the patent does not specify by which means the graphite is isolated.

Copper

Copper is a contaminant in the black mass fraction; however, it has a high value and is therefore recovered as a single material. Most processes recover copper at low pH after the removal of aluminium and iron.

Li-Cycle combines solvent extraction with electrowinning. Initially, the pH is increased to pH 2 using NaOH. Solvent extraction is done by using the LIX 984N extractant (1:1 vol mixture of 2-hydroxy-5-nonylacetophenone ketoxime (LIX 84-I) and 5-nonylsalicylaldoxime (LIX 860-I)) in kerosene and subsequent stripping with H_2SO_4. Finally, the copper is recovered by electrowinning with a combined efficiency of > 80%.

The process patented by BRUNP also describes a solvent extraction step using N902 as an extraction agent, specific for copper in acidic environment, whereas it also extracts nickel in basic medium. (Duan et al., 2020) Copper is stripped from the solution using H_2SO_4, yielding copper sulphate as a product.

The Northvolt process shows similarities with the Li-cycle and BRUNP processes, since copper is also removed by solvent extraction. However, in this case, 5- dodecylsalicylaldoxime (LIX860N-I) is used as an extractant, diluted in kerosene. Cu is then stripped using H_2SO_4 solution and sent to an electrowinning plant to produce copper cathode material. Alternatively, copper can be removed by cementation, reaching metallic Cu as a final product.

In the Duesenfeld process, the copper is removed by cementation: a ferrous salt is added to reduce the copper. The reaction is carried out at a temperature between 0 - 100˚C, for 1 - 720 min. Alternatively, Cu can be precipitated as copper sulphide (CuS) by addition of sodium hydrogen sulphide (NaHS).

Iron and aluminium

Iron and aluminium are recovered as a mixed hydroxide in the process developed by Li-Cycle. The metal salts are precipitated from the leachate by the addition of NaOH at a target pH of 4.5 and separated by filtration. This step has a recovery efficiency above 99% and the resulting mixed hydroxide purity is close to 85%.

BRUNP approaches the removal of aluminium and iron differently: the elements are recovered separately, but more importantly, aluminium is separated from black mass prior to the leaching step. Aluminium is leached by the addition of a NaOH solution and heating at 80 °C. Subsequently, $Al(OH)_3$ is recovered by filtration. The black mass residue, unaltered by NaOH, is then subjected to an acid leaching. After removal of the solid residue (i.e., graphite), iron is recovered from the leachate by addition of yellow modumite ($Na_2Fe_6(SO_4)_4(OH)_{12}$)(Jiang Kaixi, 2014), at pH 1-3. The latter acts as a flocculant and eases the removal of iron, as $Fe(OH)_3$.

Duesenfeld reports the removal of impurities, such as iron and aluminium, by precipitation of their corresponding hydroxides altogether. After leaching the black mass, a first step of oxidation of Fe(II) to Fe(III) is carried out, by addition of H_2O_2 or ozone (O_3). Subsequently, the pH is increased preferably to 7.8, using NaOH or Na_2CO_3, to precipitate $Fe(OH)_3$ and $Al(OH)_3$. If titanium is also present as an impurity, it can be precipitated as TiO_2. The precipitates are separated by filtration or centrifugation. After Cu, Fe, Al, and titanium (Ti) removal, an ion exchange process is carried out to remove remaining of these metals in solution and Zn, when present in the leachate. The ion exchanger may contain a chelating agent with aminophosponic acid groups as functional groups.

Northvolt also reports removal of impurities by precipitation, after black mass leaching. In this case, Fe and Al are removed together as phosphate salts or hydroxide salts. Hydroxide salts are precipitated by addition of NaOH or potassium hydroxide (KOH), after Cu removal, whereas phosphate salts - $FePO_4$ and $AlPO_4$ - are obtained by addition of H_3PO_4 to the leachate, until reaching pH 2.5.

The phosphate salts have two main advantages with respect to the corresponding hydroxide salts: they do not absorb NMC metals nor Li, and they are easier to separate by filtration and easier to wash than the hydroxides.

2.4.6 Separation and recovery of metals

Recycling processes for batteries focus on the recovery of the CAMs. When all the other elements contained in batteries have been removed, these materials can be recovered with high purity. The recovery process can be done in several ways: most companies make use of mixed precipitation, yielding a mixture of all CAMs, or recover the materials by precipitation following solvent extraction. Both methods are discussed and differences between companies are described below.

Mixed precipitation

Recovery of CAMs by mixed precipitation is a method designed to recover the materials for direct use as new CAMs. In this way, recycling processes are closely related to the production processes of new batteries. Companies such as BRUNP and Northvolt are highly linked to LiB manufacturing lines.

The recovery of the CAMs in the process of BRUNP is, similar to Northvolt, designed to obtain the desired composition for new CAMs. First, the NMC-ratio is adjusted using Co, Ni, and/or Mn salts to a total concentration of 2 mol/L. Example 6 of the BRUNP patent discusses the NMC 532-ratio. Subsequently, NaOH and Na_2CO_3 are added as precipitation agents, with a final concentration of 2 mol/L and 1 mol/L, respectively. The target pH of the mixture is 8. It appears that a NMC-hydroxide precipitate is recovered after 5 hours, as the concentration of the salts in the filtrate is increased by a concentration step for the recovery of Li. The resulting NMC-OH is dried at 100°C for 12 h. The dried precipitate is then mixed with an 1.05 Li_2CO_3 : 1 NMC-OH ratio and thermally treated at 550 °C for 5 h and another thermal treatment at 900 °C for 10 h, yielding a LiNMC-532 CAM. The patent reports an overall recovery efficiency of > 95%.

Li-Cycle describes a more vigorous method of recovering the CAMs: by addition of a 50 wt% NaOH solution, pH 9.5 is targeted, significantly higher than the process described by BRUNP. The operating temperature is kept in the range of 40 to 60˚C. The precipitation process is performed in a short time: the residence time reported in the patent is only 60 minutes. This is most probably possible as a result of high pH, but has the disadvantage of the use of large amounts of chemicals. Lithium is recovered separately from the filtrate (i.e., as Li_2CO_3), once the cobalt, manganese, and nickel are recovered as their corresponding hydroxides (see Section 2.4.4 for full description of Li recovery). The patent does not specify if the final product is similar in composition as the one obtained by BRUNP.

Northvolt also patented two processes for the recovery of CAM by mixed precipitation. Once obtained a leachate free of impurities, the concentration of each metal is adjusted by addition of concentrated solutions of Ni, Co, and Mn sulphates to meet the desired target ratio of the CAM. After targeting a pH of 8 - 9 (by addition of NaOH, LiOH) the NMC-hydroxide is precipitated. The precursor can subsequently be subjected to a CAM production process. As reported by Northvolt, the process allows a cost and resource saving production of a CAM precursor for the production of secondary LiBs.(Northvolt, 2021)

Solvent extraction based separation and recovery

Another method for the recovery of CAM is solvent extraction. This method consists of the removal of metals dissolved in aqueous media, using selective ligands to give rise to soluble complexes in organic solvents. After extraction of the metal into the organic phase, a stripping step is followed, making use of a H_2SO_4 solution to bring the metal back to aqueous media. Further on, precipitation or electrowinning of the target metal allows the isolation of a metal salt or metallic metal, respectively. From the processes reviewed in this report, Northvolt and Duesenfeld make use of solvent extraction to recover both, impurities (e.g., Cu) and CAM metals from the leachate.

In the Northvolt process, right after the removal of Fe and Al, the extractant Cyanex 272 (bis (2,4,4-trimethylpentyl)phosphonic acid), dissolved in an aliphatic solvent, is used to extract Mn and Co from the leachate. Then, the organic solvent is scrubbed to remove potential impurities, before stripping both manganese and cobalt by means of a H_2SO_4 solution. Subsequently, the Co-Mn liquor is subjected to an ion exchange process to remove other impurities, such as Zn. The resulting effluent solution coming from the ion exchange column is then transferred to an evaporative crystallization circuit, operated under vacuum to flash cool the solution to 30˚C. As the water is evaporated, the Mn and Co sulphate crystallize. The solid is then isolated by centrifugation. On the other hand, the nickel rich raffinate obtained after solvent extraction of manganese and cobalt, is acidified until achieving pH 1. Subsequently, the liquor undergoes the same crystallization process as the one previously described, to crystallize nickel sulphate. Therefore, the outputs of this process are nickel sulphate and a cake of Mn and Co sulphate.

In the Duesenfeld process, after removal of copper, aluminium and iron, cobalt and nickel are extracted from the leachate using Cyanex 301 (bis (2,4,4-trimethylpentyl)phosphinodithioic acid), dissolved in kerosene. Subsequently, both metals are stripped by means of a H_2SO_4 solution. Following further separation of cobalt using Cyanex 272 (also in kerosene), both metals are crystallized separately, as their corresponding sulphate salts. The raffinate of the nickel and cobalt extraction is enriched in manganese, which is also removed by solvent extraction, making use of DE2HPA (Di(2-ethylhexyl)phosphoric acid) dissolved in kerosene. Alternatively, Mn can be recovered by precipitation as $Mn(OH)_2$, adding NaOH, or $MnCO_3$, adding Na_2CO_3.

Another two companies have developed recovery processes of CAMs from spent LiBs, by solvent extraction: Mecaware and Solvay-Veolia. Mecaware (Metal and Carbon Waste Recycling) is a start-up company specialized in the recycling of technological products, such as batteries, for the recovery of critical metals and rare earths elements by means of environmentally friendly approaches.(Mecaware) (Network). The company patented a process for the recovery of metals by solvent extraction. The method varies remarkably with respect to the other solvent extraction processes reviewed in this section. In this case, carbon dioxide and amines are combined to give rise to carbamates, which can selectively coordinate target metals to be recovered. The resulting complexes precipitate in the organic media in which the extraction is carried out and are further isolated by filtration.(Julien Leclaire, 2016)

Solvay, Veolia, and Renault partnered to develop a recycling technology for the recovery of CAM from spent LiBs from powering electric vehicles, e-bikes, power tools, electronic devices, or stationary storage stations. Solvay’s hydrometallurgical process can purify cobalt, lithium, and nickel after Veolia's chemical extraction process from black mass.(Solvay) The process itself makes use of extractants, such as Cyanex, selective to the recovery of each metal, after a leaching step.(Syensqo) This joint collaboration began in 2020. The demonstration plant is planned to operate all the process steps, including the leaching of black mass, the separation, and purification of individual metals and their transformation into metal salts grade for CAM producers. The design, permits, utilities, and equipment of the plant was planned to begin in 2021. However, there is currently no more public access information up to date with regard to the progress of this joint collaboration.

Solvent extraction can give rise to individual battery grade sulphates/carbonates, instead of recovering a cake containing the three metals as sulphate or hydroxide salts, as in mixed precipitation. It can be selective and very effective; however, it is a relatively complex unit operation, it usually requires multiple reaction stages, scrubbing, and stripping, the use of inorganic acids as well as treatment systems for organic/aqueous waste streams, organic vapour recovery, and fire protection. This requires high capital costs, which can reach as much as 30% of the refinery cost on a commercial scale solvent extraction operation.

2.4.7 Recovery of lithium

The recovery of Li, mostly as Li_2CO_3, is usually performed as the last step of these recycling processes. Li is usually concentrated in the filtrate, once all the other metals from the cathode active material have been recovered, by precipitation or solvent extraction.

In the Li-cycle process, Li can be recovered from the filtrate, after recovery of the NMC-hydroxides. Before isolating a Li salt, the filtrate is evaporated at 95˚C to reduce the volume and concentrate the Na content. To increase the pH of the solution, a 50 wt% NaOH solution is added until reaching pH 9.5, and then the solution is cooled to 10˚C, to precipitate sodium sulphate decahydrate ($Na_2SO_4 \cdot 10\ H_2O$). The obtained solid is filtered. The resulting filtrate, free of impurities and enriched in Li, is subjected to a further evaporation step, to reach a higher lithium concentration in solution: 11 g/L. A saturated Na_2CO_3 solution is added to the concentrated filtrate and heated at 95 ˚C for 6 h. The resulting solid is filtrated and rinsed with hot water (70 ˚C), and then dried at 80 ˚C. A 90% recovery efficiency is achieved and a Li_2CO_3 with a purity of 89%, which needs to be further refined.

BRUNP reports the recovery of Li in a similar way, at the end of the process, once the metal hydroxides are precipitated. The pH of the resulting filtrate is adjusted to pH 8 and the solution is evaporated to increase the Li concentration. The resulting precipitate is filtered and dried. Subsequently, the solid is mixed with a stoichiometry amount of Li_2CO_3, and then subjected to a two-stage thermal treatment (500 ˚C and 900 ˚C), as explained in the previous section, to finally achieve a new CAM. In this case, no previous conditioning to remove sodium salts is reported.

In the Duesenfeld process, Li is also recovered by precipitation. In this case, the final product can be Li_2CO_3 or Li_3PO_4, depending on the precipitating agent (i.e., Na_2CO_3 or Na_3PO_4, respectively). In one case or the other, the filtrate is conditioned to pH 7-14 and preferably evaporated, to facilitate lithium precipitation. As a third alternative, lithium is extracted by solvent extraction, using Cyanex 936, then stripped with a mineral acid and subsequently precipitated or crystallized.

Finally, Northvolt process reports lithium recovery after coprecipitating the cathode material precursor, by precipitating Li_2CO_3 from the leachate, using Na_2CO_3. (Mahmood ALEMRAJAB, 2022) Then, Li_2CO_3 is converted to LiOH, using NaOH or KOH.

2.4.8 Recovery of non-battery materials

Li-cycle and Northvolt report non-battery materials recovery, such as sulphate salts, as part of the last stage of the LiBs recovery processes, once the Ni, Mn, and Co are isolated from the pregnant leach solution as already described in the previous sections.

In the case of Li-cycle, sodium sulphate is crystallized as $Na_2SO_4 \cdot 10H_2O$ and subsequently dried to produce anhydrous Na_2SO_4. Depending on the external neutralizer used in the Northvolt process for the recovery of Ni, Mn, and Co, different by-products can be recovered by the end of the process. In this regard, the type of external neutralizing agent can be selected based on the by-product's commercial value. For instance, if KOH is used as the external neutralizing agent, the resulting by-product would be potassium sulphate (K_2SO_4), a fertilizer; whereas if the external neutralizing agent is $Ca(OH)_2$, the resulting by-product would be gypsum ($CaSO_4 \cdot 2H_2O$), which can be used in construction. In case of using LiOH, Li_2SO_4 would be the final by-product, which is used in battery production. Moreover, the type of external neutralizing agent can be selected based on its ability to be recovered and converted to its hydroxide salt to be re-used in the process.

2.4.9 Process steps parameters

The steps involved in each process are classified as follows:

- Leaching;
- Graphite removal;
- Cu removal;
- Fe and Al removal;
- CAM recovery;
- Li recovery.

These steps were previously described. However, in order to perform a semi quantitative analysis to compare all processes (Section 3.1.), for each step, specific information related to inputs and outputs - such as reagents concentrations and volumes, temperature, pH, etc. - was collected from the patents and all this data was used to prepare comparative tables (Table 2.5: - Table 2.9). The latter were filled in with as much information as it was possible to gather from the corresponding patents.

In those cases in which the data is not available, “n.a.” indicates de lack of specific information for that step. The leaching step is excluded from this section since it's corresponding comparative table is already presented in Section 2.4.4.

This information is complementary to the processes flow diagrams (Section 0).

Table 2.5: Comparison of graphite recovery step between all processes.

Li-cycle		Other processes	
Graphite recovery		Graphite recovery	
Filtration/centrifugation + washing		Filtration/centrifugation + washing	
Parameters		Parameters	
solid-liquid separation (e.g., centrifugation)	1 ton water/ton cake solid	**solid-liquid separation (e.g., centrifugation)**	not specified

Table 2.6: Comparison of copper recovery step between all processes.

Mixed precipitation						Solvent extraction			
Li-cycle		Northvolt		Brunp		Northvolt		Duesenfeld	
Solvent extraction + electrowinning		Solvent extraction + electrowinning		Solvent extraction + precipitation		Solvent extraction + electrowinning		Precipitation	
Parameters		Parameters		Parameters		Parameters		Parameters	
C (NaOH)	18.9 M	**C (NaOH/NMC-OH)**	n.a.	**C (N902)**	n.a.	**NaOH/NMC-OH**	n.a.	**C(Fe(II)-salt)**	n.a.
pH	2	**pH**	1-1.4	**C (H_2SO_4)**	n.a.	**pH**	1-1.4	**T, ˚C**	0 - 100
C (LIX984N)	30%vol diluted in kerosene	**C (LIX860N-I), disolved in kerosene**	n.a.			**C (LIX860N-I), disolved in kerosene**	n.a.	**time, min**	1 - 720
Cu extraction efficiency	> 95%	**Cu extraction efficiency**	n.a.			**Cu extraction efficiency**			
C (H_2SO_4)	1 M	**C (H_2SO_4)**	n.a.			**H_2SO_4**	1 mol/ mol of Cu		
Cu conversion Cu(aq) to Cu(s)[3]	> 85%	**Cu conversion Cu(aq) to Cu(s)**[3]	n.a.			**Cu conversion Cu(aq) to Cu(s)**	n.a.		

Table 2.7: Comparison of iron and aluminium removal step between all processes.

Mixed precipitation						**Solvent extraction**			
Li-cycle		**Northvolt**		**Brunp[1]**		**Northvolt**		**Duesenfeld**	
Fe/Al removal		**Fe/Al removal**		**Al removal**		**Fe/Al removal**		**Fe/Al removal**	
Precipitation		**Precipitation**		**Dissolution**		**Precipitation**		**Precipitation**	
Parameters		**Parameters**		**Parameters**		**Parameters**		**Parameters**	
C (NaOH)	18.9 M, addition rate per batch (L): stoichiometric[2]	**First precipitation**		**C (NAOH)**	6 M	**1. First precipitation**		**1. Oxidation of Fe(II)**	
pH	4,5	**NaOH solid**	0.75 kg/h + 1.2 kg/h	**T, ˚C**	80	**NMC-OH**	n.a.	**C (H_2O_2)**	n.a.
T, ˚C	25-40[2]	**H_3PO_4 85%**	1.5 kg/h	**Filtration**	Filtrate rich in $Al(OH)_4^-$ and solid rich in BM.	**pH**	5-5.5	**pH**	8,7
				Fe removal		**2. Second precipitation**		**2. Precipitation**	
				Precipitation and filtration		**Mixing with H_2SO_4**	?	**pH**	7,8
		pH	2,5	**Parameters**		**pH**	1,5	**C (NaOH)**	n.a.
		T, ˚C	70	**Yellow modumite**	n.a.	**Addition of a base**	?	**3. Ion exchange on leachate**	
		time, min	1440			**pH**	4-5.5	**Ion exchanger with aminophosphonic acid groups**	n.a.
		Second precipitation							
		NaOH solid	n.a.						
		pH	5						
		T, ˚C	70						
		time, min	1440						

[1] Brunp removes Al and Fe separately. Al is removed before the leaching and Fe is removed after Cu recovery.

Table 2.8. Comparison of CAM recovery step between all processes.

Mixed precipitation						Solvent extraction							
Li-cycle		**Northvolt**		**Brunp**		**Northvolt**				**Duesenfeld**			
CAM-OH cake recovery		**CAM-OH cake recovery**		**CAM-OH cake recovery**		**Co-Mn sulphate cake recovery**		**Ni sulphate recovery**		**Ni-Co sulphate cake recovery**		**Mn sulphate recovery**	
Precipitation + washing		**Precipitation**		**Precipitation**		**Solvent extraction of Co and Mn**		**Precipitation of $NiSO_4$**		**Solvent extraction of Ni and Co**		**Solvent extraction of Mn from the resulting raffinate, after Ni-Co extraction**	
Parameters		**Parameters**		**Parameters**		**Parameters**		**Parameters**		**Parameters**		**Parameters**	
C (NaOH)	18.9 M, addition rate per batch (L): stoichiometric[2]	**C (NaOH)**	n.a.	**C (NaOH)**	2 M	**Solvent extraction**		**Crystalization**		**1. First solvent extraction**		**1. Solvent extraction**	
pH	9.5	**CAM concentration adjusted with: $NiSO_4$, $CoSO_4$ and $MnSO_4$ (s)**	Depending on concentration of metals on the leachate	**C (Na_2CO_3)**	1 M	**Cyanex 272, disolved in aliphatic solvent**	n.a.	**H_2SO_4 (added to the raffinate)**	n.a.	**C (Cyanex 301), disolved in kerosene**	n.a.	**C (D2EHPA), disolved in kerosene**	n.a.
T, ˚C	50	**pH**	8-10	**Ni, Mn and Co salts**	n.a.	**C (H_2SO_4), for stripping**	n.a.	**pH**	1	**C (H_2SO_4), for stripping**	n.a.	**C (H_2SO_4), for stripping**	n.a.
wash ratio	0.6 t H_2O/t solids	**washing step**	n.a.	**pH**	8	**Purification**		**Unit 1: Evaporation, ˚C**	80	**2. Second solvent extraction**		**2. Crystalization of $MnSO_4$**	
				Filtration and washing	n.a.	**Ion exchange process: lewatit VP OC 1026 resin**	n.a.	**Flash cooling, ˚C**	30	**C (Cyanex 272), disolved in kerosene**	n.a.	No extra data	
						C (Co-Mn OH), addition to precipitate impurities	n.a.	**Centrifugation + washing step[2]**	n.a.	**C (H_2SO_4), for stripping**	n.a.		
						Crystalization				**3. Crystalization of $NiSO_4$ and**			
						H_2SO_4 (dil) (added to the raffinate)	n.a.			No extra data			
						pH	1						
						Unit 1: Evaporation, ˚C	80						
						Flash cooling, ˚C	30						
						Centrifugation + washing step[2]	n.a.						

Table 2.9. Comparison of lithium recovery step between all processes.

Mixed precipitation						Solvent extraction			
Li-cycle		Northvolt		Brunp		Northvolt		Duesenfeld	
Precipitation		Precipitation		Precipitation		Precipitation		Precipitation	
Parameters		Parameters		Parameters		Parameters		Parameters	
Na_2CO_3 solution, 430g/L	1.25 times stoichiometric requirement	**To the Li recovery process (first: precipitation as Li_2CO_3 woth Na_2CO_3; second: conversion to LiOH by addition of KOH/NaOH)**	1. Na_2CO_3: n.a 2. KOH/NaOH: n.a.	n.a.		**To the Li recovery process**	n.a.	**C (Na_2CO_3)**	n.a.
centrifuge wash ratio	1 t H_2O/t cake solid							**T, ˚C**	> 50
T, ˚C	95							**washing (T= 80 - 100 ˚C)**	n.a.
time, min	360								

As can be seen from the tables itself, there's a lack of information in many steps. In those cases, when possible, assumptions will be made for the semi quantitative analysis.

3. Assessment of technologies

In this section, the five above described hydrometallurgical processes (Industrial application) are evaluated. Three of the processes employ mixed precipitation as the method for recovering the CAMs as a mixed cake (i.e., Li-cycle, Northvolt, BRUNP). The other two processes use solvent extraction to recover the CAMs as individual salts or a combination of products consisting of pure salts for some components and mixed cakes for other components (i.e., Northvolt, Duesenfeld).

The five selected processes were different in both the specific process steps that were applied and also in their configuration. Therefore, for the evaluation, the overall process would be broken down into the specific process steps (as described in Table 2.5: .

Table 2.9. Comparison of lithium recovery step between all processes.

Mixed precipitation						**Solvent extraction**			
Li-cycle		**Northvolt**		**Brunp**		**Northvolt**		**Duesenfeld**	
Precipitation		**Precipitation**		**Precipitation**		**Precipitation**		**Precipitation**	
Parameters		**Parameters**		**Parameters**		**Parameters**		**Parameters**	
Na_2CO_3 solution, 430g/L	1.25 times stoichiometric requirement	**To the Li recovery process (first: precipitation as Li_2CO_3 woth Na_2CO_3; second: conversion to LiOH by addition of KOH/NaOH)**	1. Na_2CO_3: n.a 2. KOH/NaOH: n.a.	n.a.		**To the Li recovery process**	n.a.	**C (Na_2CO_3)**	n.a.
centrifuge wash ratio	1 t H_2O/t cake solid							**T, ˚C**	> 50
T, ˚C	95							**washing (T= 80 - 100 ˚C)**	n.a.
time, min	360								

This approach allowed for a separate evaluation of each of the specific process based on the characteristics (e.g. robustness) and on conditions (e.g. operation temperature) of the various processes, using the available data.

In order to objectively and transparently assess the various specific processing steps, a systematic approach was developed that has been applied to the above mentioned technologies. Further below in this report, this approach will be explained followed by a description of the outcome of the assessment.

Finally, hydrometallurgical processes were selected over pyrometallurgical ones because the latter carry disadvantages such as Li losses in the slag, high energy consumption and high CO_2 emissions due to high temperature melting processes.

3.1 Selection of optimal battery recycling steps

A set of criteria for selecting the optimal battery recycling steps was developed , taking into account the available information for each process considered. The selection criteria aim to combine qualitative and quantitative aspects of each process step in a quantitative manner to arrive at a systematic approach with which the optimum recycling step can be selected.

The steps that were considered for the assessment were those with more available information. Furthermore, it was decided to focus only on the final treatment so pre-treatment steps were excluded.

Figure 21 depicts a general scheme of the technologies assessed. The steps that were taken into account for the assessment are highlighted in the coloured boxes.

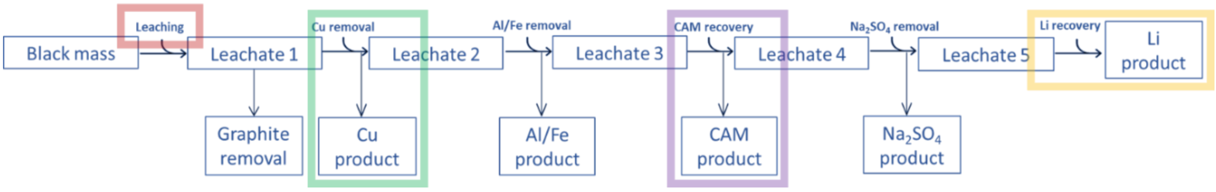


Figure 21: Overview scheme of the different steps involved in the processes (BRUNP process is the only one that starts with the removal of Al prior to the leaching of the black mass, when compared to the other processes).

Each process starts with a leaching step of the black mass. After removal of the graphite from leachate 1, a Cu removal step comes next, giving rise to a Cu free leachate (leachate 2). Afterwards, impurities such as Al and Fe are removed. From the leachate 3, free of impurities, a CAM recovery step follows, in which the CAM is recovered as a cake or metal-salts, depending on the process. From the resulting leachate (leachate 4), Na_2SO_4 is removed. Finally, Li recovery step follows, in which the Li is recovered from the leachate free of CAM and impurities (leachate 5).
The process steps that were selected to be evaluated were (presented in order of importance):

- CAM recovery
- Leaching
- Li recovery
- Cu recovery

3.1.1 Assessment criteria

The criteria for the developed procedure were divided into two categories. The first covered general considerations and pertained to the qualitative and semi-quantitative aspects of each process. In the general category there were four to six considerations (depending of the recycling step) namely:

General considerations

- Versatility of the process: Is the process step applicable to different battery technologies and chemistries?
- Robustness: How well does the process step handle variations in the feedstock composition and conditions?
- Capacity: How much black mass can be processed (i.e., ton/year)?
- Waste stream volume/categories: What is the volume of the waste streams generated and under which waste category can the waste streams be categorized?
- Process complexity: Number of recovery steps. The more process steps and chemicals, the more complex the process becomes.
- Versatility of the products: Are the produced products only suitable for the company's own process or is it suitable for various processes/applications?

The second category covers the quantitative process conditions of each process. The information was mainly retrieved from patents of the specific processes. Some condition criteria are process specific, such as the form of recovered product for the CAM recovery, and may differ for the recycling steps. However, there are also general process conditions similar for all processes. These are listed below along with some overall considerations of desired conditions.

Process conditions

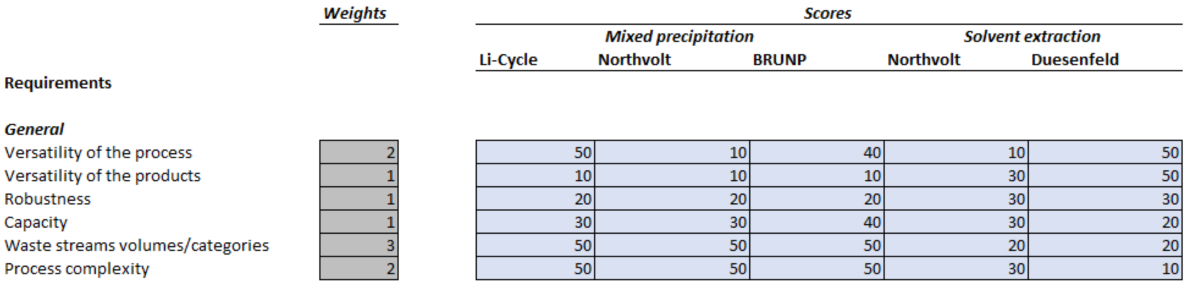
- Temperature: Typically, a lower temperature is desired as energy requirement will be lower.
- pH: pH close to neutral is desired. Extreme pH requires more post-treatment for waste
- streams and could also increase material of construction costs.
- Residence time: Lower residence time is desired as this leads to smaller reaction vessels and
- lower CAPEX.
- Product purity: High product purity is desired.
- Product recovery: High product recovery is desired.

It is important to note that the process steps are related to one another. For example, for higher process temperatures a lower residence time can be used. For some processes it is decided to tolerate higher value (“less favourable”) for one condition in order to minimize that of other conditions. It is thus important to keep in mind when assigning weights to the different criteria that some process conditions are interrelated.

3.1.2 Process assessment procedure

The assessment procedure has been executed in the following way: the processes and criteria were discussed by the project group in the presence of a metallurgical expert. Based on the available data and the expert opinion, criteria were weighed and scored, as described below. In case of missing data, process steps were given scores or not, depending on the impact and importance of that specific process step, also based on the expert opinion. Decisions on weights and scores are further explained in Section 3.2.

The first step for the process assessment was to assign a weight of importance to each criterion. The weights ranged from 1 (low importance) to 3 (high importance), highlighted in grey in Figure 22.
The second step in the assessment was to assign a score for each process for each criterion, depending on the characteristics of the process (highlighted in blue, Figure 22). The score ranged from 10 (very low score, not preferable) to 50 (very high score, highly preferable) in steps of 10, with 30 being neutral. The scores were also assigned relative to one another meaning that the highest score (50) was given to the best value/input and the lowest score (10) to the worst value/input and the rest of the scores were assigned relative to these scores. If no information was available for the process for that specific criterion a value of zero was assigned. An example of the scoring card is given in Figure 22. The process with the highest score would be the most preferable one.



	Weights	*Scores*				
		Mixed precipitation			*Solvent extraction*	
		Li-Cycle	Northvolt	BRUNP	Northvolt	Duesenfeld
Requirements						
General						
Versatility of the process	2	50	10	40	10	50
Versatility of the products	1	10	10	10	30	50
Robustness	1	20	20	20	30	30
Capacity	1	30	30	40	30	20
Waste streams volumes/categories	3	50	50	50	20	20
Process complexity	2	50	50	50	30	10

Figure 22: Example of scoring card for the general category of the CAM recovery step.

Once the weights and scores were assigned, the score was multiplied with the weight of the criterion to give the final score. The scores for each process were summed to give a total absolute score. However, not all information required for each criterion was available for all the processes. Therefore, to avoid a process being penalized for information gaps, a relative score was defined for comparing the processes which accounts for the information gaps. The relative score was defined as the absolute score of the process divided by the maximum score that the process could achieve with the given information. For example, if the information of the process covers four out of five criteria points, the maximum score that the process can achieve was defined as the sum of the weights of those criteria multiplied with 50 (maximum score). The absolute score for the process was then divided by the estimated maximum value to obtain a relative score. The results of the relative scores can be found in Annex A for all process steps.

It is important to note that the weight assigned to the general considerations was the same for each process and recycling step. The information and scores appeared to be comparable, so the final scores for the general consideration for each industrial process remained relatively the same for each recycling step. Only for the CAM recovery step, two additional general criterions were added pertaining to the versatility of the retrieved products and the process complexity.

Once the selection matrix for each process was completed with the available information, the absolute and relative scores were calculated and a comparison was made. From the comparison, the most favourable process step (with the highest score) was selected. The selection matrix for each processing step was filled in during a working session held with the project team and an external expert in the battery recycling field. The results of the working session are given in Section 3.2.

3.2 Results and discussion

3.2.1 General considerations: weights and scores

The general considerations (versatility, robustness, capacity and waste streams) were mainly specific to the overall process and were considered similar for all process steps (see Table 3.1) For the CAM recovery steps, two additional considerations were added for the evaluation, namely complexity of the process and versatility of the products (see Section 3.2.2). The addition of the two considerations follow from significant differences between the separation processes of the technologies.

For general considerations, the assigned weights and scores also remained relatively constant over all process steps, which means that the general score for the different processes remained relatively constant. The only value that changed was the score for the waste volume/category, but the weight remained the same. For this reason the general considerations score for each process is discussed in this section and is applicable to the other sections as well. The results for the general scores are shown in Table 3.1 and the separate scores for all process steps can be found in Annex B.

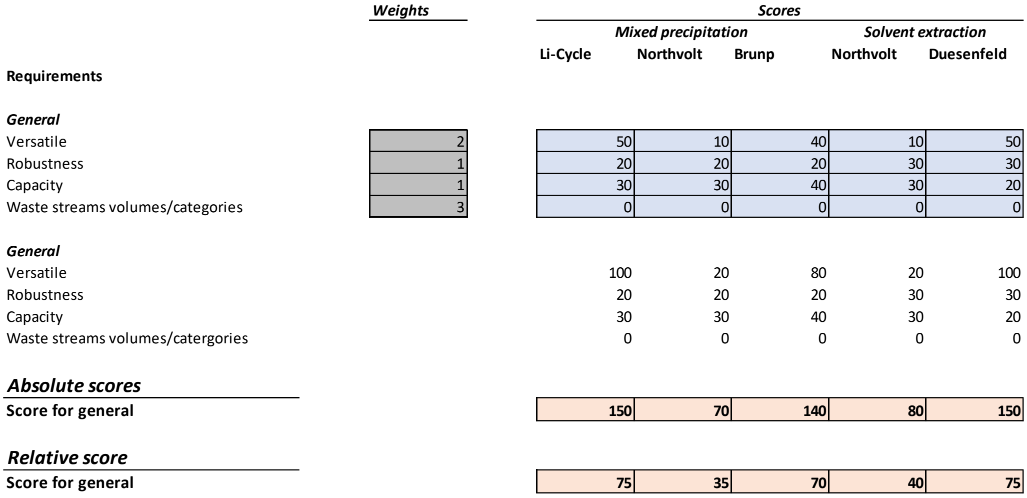
The four general aspects that were considered, were: versatility, robustness, capacity (referring to capacity black mass) and waste streams volume/categories. The highest weight (3) was assigned to the waste volume/category, as the generation of waste streams is the most important consideration, especially with the strict European regulations pertaining to waste volumes and disposal.

The versatility of the process received a weight of 2, as it is important that the processes are able to treat a variety of battery chemistries and/or mixtures of the chemistries. For the scoring, the mixed precipitation process of Li-Cycle and the solvent extraction process of Duesenfeld scored the highest (50), due to the variety of battery chemistries it’s claimed to be able to process. BRUNP had a score of 40 and the Northvolt processes (mixed precipitation and solvent extraction) had the lowest scores (10). The robustness and capacity (black mass capacity) both had a weight of 1. The mixed precipitation processes (Li-Cycle, Northvolt, BRUNP) received a score of 20 for the robustness, as the process produces CAM cakes with specific ratios, this also means there cannot be too much variation as this will affect the composition of the CAM cake. The solvent extraction processes received a score of 30, as the end product is an individual salt and not a mixture of products in a certain ratio. It can thus handle some more variations.

For the capacity BRUNP received the highest score (40) as it has the highest capacity, followed by Li-Cycle and Northvolt (30) and then Duesenfeld (20).

From the results it is thus seen that the mixed precipitation process of Li-Cycle and the solvent extraction process of Duesenfeld had the highest scores (absolute and relative). The biggest contribution to the score was the high score for versatility.

Table 3.1: Summary of general score for different battery recycling processes.



	Weights	*Scores*				
		Mixed precipitation			*Solvent extraction*	
		Li-Cycle	**Northvolt**	**Brunp**	**Northvolt**	**Duesenfeld**
Requirements						
General						
Versatile	2	50	10	40	10	50
Robustness	1	20	20	20	30	30
Capacity	1	30	30	40	30	20
Waste streams volumes/categories	3	0	0	0	0	0
General						
Versatile		100	20	80	20	100
Robustness		20	20	20	30	30
Capacity		30	30	40	30	20
Waste streams volumes/catergories		0	0	0	0	0
Absolute scores						
Score for general		**150**	**70**	**140**	**80**	**150**
Relative score						
Score for general		**75**	**35**	**70**	**40**	**75**

3.2.2 CAM recovery

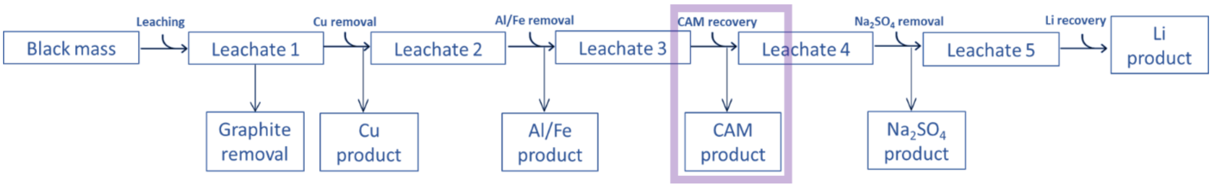


Figure 23: Overview scheme of the different steps involved in the processes (BRUNP process is the only one that starts with the removal of Al prior to the leaching of the black mass, when compared to the other processes).

There are two hydrometallurgical routes by which the CAM material can be retrieved. The first is via mixed precipitation and the second via solvent extraction with subsequent precipitation. After mixed precipitation, a CAM cake (containing all the CAM mostly in the form of a hydroxide cake) is retrieved, while after solvent extraction the individual cathode components can be recovered in the form of pure metal salts. Comparing the processes was challenging due to the difference in products and applications of the products. For mixed precipitation, the retrieved CAM cake consisting of NMC (Ni, Mn and Co) salts is typically regenerated by re-lithiation and re-used for the production of new batteries in a closed-loop system. While for solvent extraction, the individual components, Ni, Mn and Co are retrieved separately as salts and can be used either for the production of new batteries or other applications.

In order to compare processes, the general considerations were expanded to consider the versatility of the product and process complexity. The versatility of the product considers the application range of the product. For mixed precipitation, a low score of 10 was assigned as the CAM cake can only be used in closed-loop systems for the production of new batteries, while for solvent extraction where the end products are individual salts (as for the Duesenfeld process) a high score of 50 was assigned as the products have a broad range of applications. For solvent extraction processes, with an intermediate distribution of products, i.e. both salts and cakes (as the case for the Northvolt - solvent extraction process) a score of 30 was assigned.

Process complexity looks at the number of process steps. The more steps the process has the more complex the process becomes with regards to operation, process control, chemical usage, regeneration etc. Mixed precipitation compared to solvent extraction has fewer steps and was assigned a score of 50. Solvent extraction, where all the components are retrieved as individual salts, received a score of 10 (for process complexity), while solvent extraction, with an intermediate distribution of products, received a score of 30. The scores assigned for the process complexity were the exact opposite of the score for the product versatility, however, the scores did not balance one another as the weights of the two criteria were different. The weight for product versatility was valued as 1, while that of the process complexity was 2. The product versatility received a lower weight due to CAM cake already being seen as a valuable product even with limited applications. Process complexity has an influence of the operability of the process, chemical consumption, energy consumption, waste generation, utility usage etc. and thus it received a higher weight of importance. The relative score results (considers the information gaps) for the five processes are shown in Figure 24.

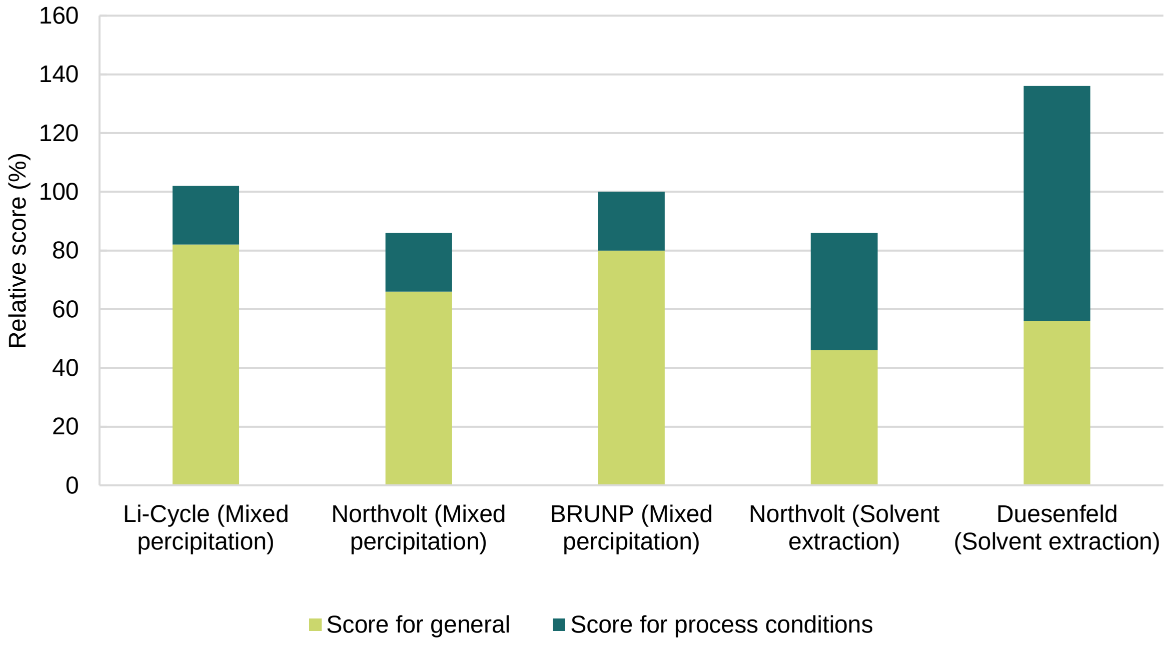


Figure 24: Relative score results for CAM recovery steps.

This graph shows that for general considerations, Li-Cycle had the highest score, while for the process conditions and the total relative score Duesenfeld had the highest score. The reason for Li-Cycle having the highest general score was the high score (50) it received for the categories of process versatility process, waste streams volumes/categories and process complexity all of which had assigned weights of 2 and 3. For the categories versatility of products, robustness and capacity, Li-Cycle had a lower score, however, the assigned weights for these categories were 1 and therefore the effect on the overall score was limited.

For the process conditions only one category was scored which pertained to downstream processing (further treatment) of the products outside the battery limits. This category relates to whether the recovered product is ready for use in either a downstream process or for an end user, or if further treatment of the product is required. Mixed precipitation produces an NMC salt cake that is used for the production of new batteries in a closed-loop system. Once retrieved from the mixed precipitation, the hydroxide cake needs to be washed, regenerated and replenished to ensure that the ratio of NMC is correct for the new batteries, there are thus numerous post-treatment steps required and a low score of 10 was awarded for all mixed precipitation processes. For the solvent extraction process of Northvolt a score of 20 was given as a combination of products are recovered namely $NiSO_4$ salts and a mixed cobalt-manganese sulphate cake. The salts are washed and dried afterwards, while the sulphate cake needs to be further processed in the same manner as the hydroxide cakes. For the Duesenfeld process, salts are recovered and it was assumed that the salts only need washing and drying before being ready for use, which is why it received a score 40. For this reason the Duesenfeld process had the highest score for the process conditions and subsequently the highest relative score for all the processes.

Even though the Duesenfeld process step received the highest score, it does not mean that the process is necessarily most favourable as important factors, such as the product purity, recovery, waste and emissions, and energy consumption were not evaluated in depth given the limited information available. For a complex process such as the solvent extraction step, various reagents (Cyanex 272, kerosene etc.) and stripping mediums are used to recover the individual components which need to be regenerated, recovered and partly discarded as a waste stream. Additionally, the solvent extraction process of Duesenfeld contains three crystallization steps which are energy intensive. Thus if waste emissions and energy consumption, as well as chemicals consumption were considered for the process step, the Duesenfeld solvent extraction step might not be the most favourable choice. This is also dependent on the scores that the other processes would receive. For mixed precipitation, the utility and energy consumption would be less and thus these process steps would receive a better score for these categories.

3.2.3 Leaching

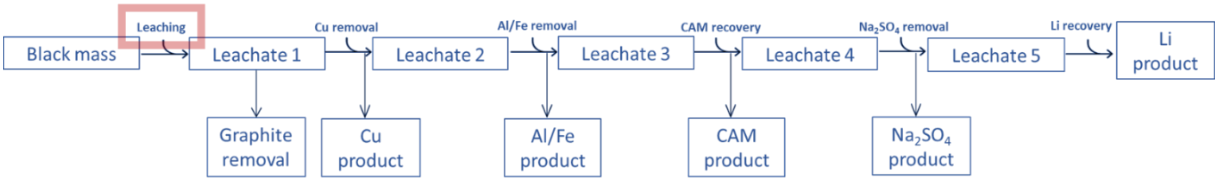


Figure 25: Overview scheme of the different steps involved in the processes (BRUNP process is the only one that starts with the removal of Al prior to the leaching of the black mass, when compared to the other processes).

For the evaluation of the leaching step, only four of the five processes were considered. The Duesenfeld process was omitted as their process has an additional digestion step, prior to the leaching step (see Section 2.4.4), and thus the input stream is not the same as for the other processes which is the black mass. For the process of BRUNP, the aluminium and graphite is removed prior to the leaching step, while for the other processes leaching is the first step. Nevertheless, the BRUNP leaching step was also evaluated. The results of the relative scores are presented in Figure 26.

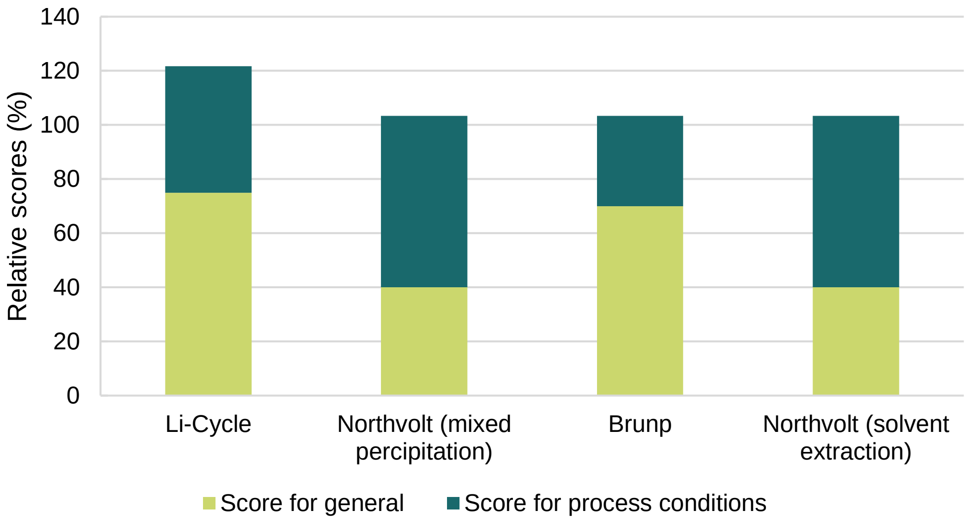


Figure 26: Relative score results for leaching step.

From the results it is seen that Li-Cycle and BRUNP scored the highest in the general considerations, with Li-Cycle having the highest overall score. The two processes of Northvolt scored the lowest and had the same score as the leaching step for both processes (mixed precipitation and solvent extraction). The general considerations were the same as described in Section 3.2.1, where Li-Cycle scored the highest due to versatility of the process. The waste category is also relevant in this process step and should be scored whenever there is available information. No additional general considerations were added as the case with the CAM recovery step.

For, the process conditions, only three conditions could be filled in namely the temperature, solid to liquid (S/L) ratio and the pH. The other categories, leaching efficiency, leaching agent concentrations etc. were left empty due to lack of information. However, these should be taken into account and scored whenever information is available. Residence time was also a process condition, but even though the information was available it was not scored as the residence time is directly related to the leaching temperature. As the leaching temperature increases, the residence time will decrease. Thus the score of the temperature, will be the inverse of the score for the residence time and the scores would cancel each other. For this reason, only temperature was scored as this is also an indication of the energy consumption of the process.

The leaching step of Northvolt (both technologies) had the highest process conditions score, due to the high scores received for the temperature and S/L ratio. The S/L ratio is considered important (assigned weight of 3) as it gives an indication of the consumption of water/chemicals and also indicates the potential energy consumption required to dry the product. The lower the S/L ratio the higher the chemical consumption and energy requirement for drying and thus the lower the assigned score. Northvolt had a higher S/L ratio compared to Li-Cycle and received a score of 40, while Li-Cycle received a score of 20. The S/L ratio was not specified for the BRUNP process. Northvolt and BRUNP received a higher score (30) for the process temperature as it was lower than for Li-Cycle, while the score for the pH was lower, as the pH of these processes was lower.

Same as with the CAM recovery, the high score achieved for Li-Cycle does not necessarily mean that the leaching step of Li-Cycle is the best, because the information was very limited and important factors such as leaching efficiency, energy consumption and emissions were not considered. The leaching efficiency is also dependent on the quality of the black mass entering the system, which in turn is dependent on pre-treatment process which falls out of the scope of the evaluation. For the information available and compared to the information available of the other processes considered, Li-Cycle received a high score.

3.2.4 Lithium and copper recovery

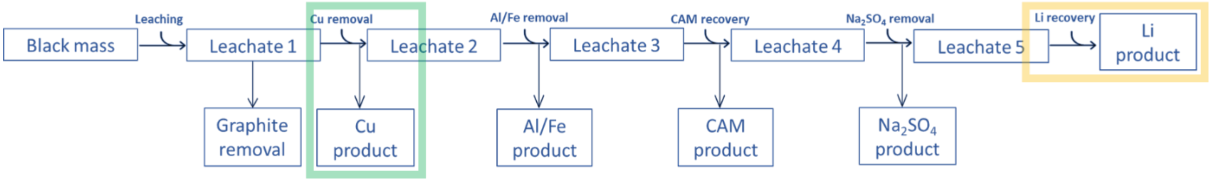


Figure 27: Overview scheme of the different steps involved in the processes (BRUNP process is the only one that starts with the removal of Al prior to the leaching of the black mass, when compared to the other processes).

Initially, four process steps would be evaluated, however, during the working session it was decided to not evaluate the Li recovery and Cu recovery steps. Sufficient information with regard to the general considerations was available, however, the information regarding the process conditions was very limited.

For the Cu recovery, similar technologies were used in both the processes of Northvolt and Li-Cycle. There Cu was recovered via electrowinning. For BRUNP, crystallization was used, while for Duesenfeld the Cu was precipitated using Fe(II)-salt. Crystallization is known to be an energy intensive process, however, without information on the exact energy consumption, product recovery and purity for all processes a selection cannot be made.

Same as for Cu recovery, the technologies for the recovery of Li were similar for three of the five processes. For the processes of Li-Cycle, Duesenfeld and the mixed precipitation process of Northvolt, precipitation with Na_2CO_3 was done to recover $Li_2CO_3(s)$. For the Northvolt process, an extra crystallization step was also specified, which could be applicable to the other processes as well. The Li recovery step for BRUNP was not specified, while for the solvent extraction process of Northvolt it was stated that the streams coming from the solvent extraction of the CAM and Ni recovery were sent to the Li recovery plant without further specifications.

3.2.5 Optimum process steps

From the evaluation it is seen that versatility of the process with respect to both feedstock and products was a highly valued characteristic. For the general considerations, the processes able to treat a wide variety of batteries, had the highest scores, while for the CAM recovery the process with the most versatile product had the highest score. From the assessment results it follows that an optimal battery recycling process would adopt the leaching step of Li-Cycle (mixed precipitation) and the CAM recovery step of Duesenfeld namely the solvent extraction process.

3.3 Limitations of this approach

During the assessment of the hydrometallurgical processes, it became clear that the available information was very limited to only certain process conditions and general qualitative information. When comparing different processes it is important to consider factors such as energy consumption, environmental aspects, including waste generation and emissions as well as the economics of the process. The information should also be presented in a standardized way to be able to have a fair comparison between the different steps. Evaluating a process solely based on direct process conditions is not ideal. However, due to the limited data available it was the only feasible approach.

With the above described procedure, a selection could be made; however, it is important to be aware of the limitations of this procedure. This procedure only considers the information available for the selection procedure and will only give the best process step for the processes evaluated, thus not the best process steps globally known. The process steps were evaluated individually, as defined in the scope of the original proposal. The selected steps might thus not be readily compatible, without intermediate steps to ensure that the output stream of the previous step has the desired process conditions for the subsequent process step. Integration of the different steps can be challenging as these processes are typically designed and engineered as a collective process and not as interchangeable steps that can be easily switched with another. With the robustness criterion in the general considerations it was attempted to consider the integration of the steps, however with the limited process information it is challenging to quantify. With information from literature it would be possible to do a comparison between the processes, but this would be more a comparison of technologies rather than a comparison of the individual industrial process steps. Therefore, additional information from literature might still not be sufficient to make a fair comparison between the different processes.

3.4 Further considerations for future assessment

On a broader scope when comparing processes, removal of impurities such as F, Cu and Na_2SO_4 needs to be considered as it affects the product purity at the end. The fluoride should be removed early in the process to avoid contamination of the end products as fluoride is considered a highly dangerous contaminant.

A very important consideration is also the pre-treatment process implemented before the hydrometallurgical process, to retrieve the black mass. For the processes evaluated in the above sections there were similarities between many of the process steps, however, the differences between these industrial processes, lies with the pre-treatment steps. For example, Li-Cycle implements water shredding (50:1 Liquid to Solid ratio), which is very water intensive. By performing this pre-treatment step, the downstream processing parameters become more favourable and when evaluating the process steps individually this process step would then be selected as the best. This is however, not a fair manner of comparing as the favourable downstream step (e.g. leaching) requires the water intensive shredding step to have these conditions. Another example is the pre-digestion step implemented by Duesenfeld for the safe removal of F from the black mass. The resulting solution from the digestion (done in a concentrated H_2SO_4 solution), is then sent to the leaching unit, where the conditions are mild compared to the other industrials steps. By only evaluating the leaching step it can appear to be the best process to use, however, what is then not considered, is the required pre-digestion step which could make it less favourable to implement.

Going a step further (not just looking at the pre-treatment combined with the leaching step) is to consider the process as a whole, thus including the separation and recovery of the CAMs. For example when evaluating the chemical consumption it is important to look at the absolute pH shifts of all processes, as these are indicative of how much chemicals need to be added to adjust the pH. In Figure 28 and 29, an example is given of the absolute pH shifts for the CAM recovery for Northvolt mixed precipitation and Northvolt solvent extraction.

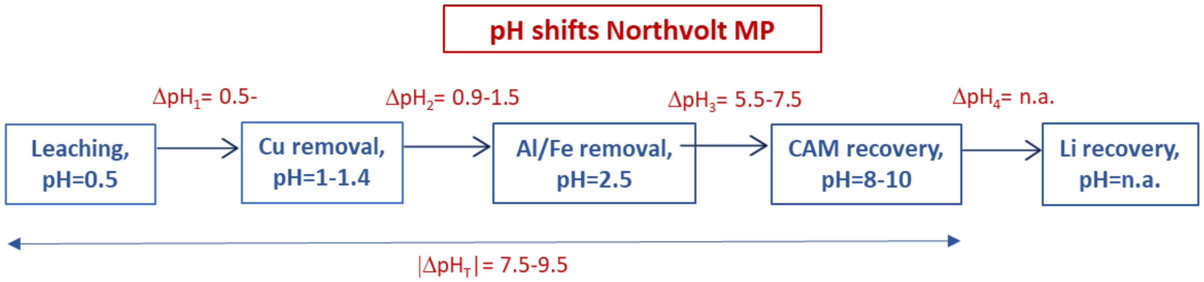


Figure 28: pH shifts for the Northvolt mixed precipitation (MP) recycling process. ΔpH_T is the pH shift from the leaching to the final product: CAM-OH cake.

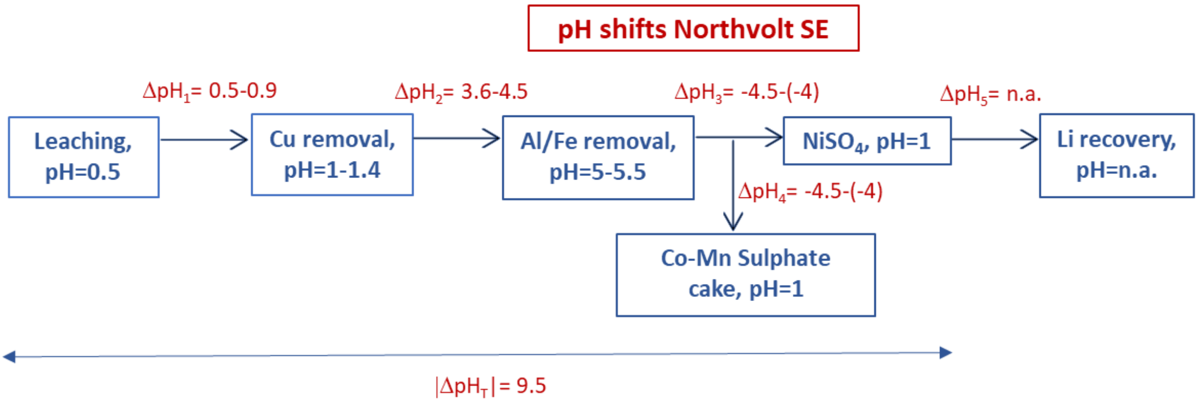


Figure 29: pH shifts for the Northvolt solvent extraction (SE) recycling process. $|\Delta pH_T|$ is the absolute pH shift from the leaching to the final products: CAM-SO_4 cake and $NiSO_4$.

Upon comparing the pH shifts of the different processes, it could be stated the mixed precipitation process, has the highest chemical consumption as it has the largest pH shift. The pH gradually increased with each step, and indicates that a lot of basic solution had to be added throughout the process to increase the pH. The pH shifts for the mixed precipitation processes were similar to that of the solvent extraction processes, however, the information is limited. What is also important to mention is that pH shift is not the only of the chemical consumption, for processes such as solvent extraction the chemical consumption is also high due to the use of solvents and stripping agents. Evaluating the pH shift does, however, illustrate the reason why the process should be evaluated as a whole instead of individual steps.

4. Conclusions and recommendations

Based on scientific and publicly available literature, a literature survey was performed on recycling processes for metals from black mass from end-of-life lithium batteries. From this survey, it was decided to focus on hydrometallurgical processes over pyrometallurgical processes, because the former are considered to have advantages over the latter with respect to recovery of lithium (i.e., losses in the slag), energy use and concerns over health and environmental impact.

Next, an overview was made of hydrometallurgical processes that are under development by various companies and institutes. From this inventory, a selection was made of five processes that have reached already a high technology readiness level, consisting of both mixed precipitation processes and solvent extraction processes. Four of these processes are under development for implementation in Europe, by Northvolt (2x), Duesenfeld, and Li-Cycle and one in China by BRUNP that was included for purpose of comparison.

To assess these selected processes a semi-quantitative approach was developed. This approach combines quantitative data (e.g. process conditions like temperatures, and process performance figures like recovery rates and purities) and qualitative information (advantages and disadvantages) in a semi-quantitative manner to make an inventory of the different specific process steps in the various recycling processes. This approach was challenging as detailed information on industrially developed process steps is rather limited and mainly available in the form of patents which are not always completely and accurately describing the actual process.

With the developed approach, four critical process steps were assessed, namely 1) CAM recovery, 2) leaching, 3) Cu recovery and 4) Li recovery, for the five selected recycling processes. For the CAM recovery step and for the leaching step, the available data was sufficiently complete to obtain a score with this method, however for the Cu recovery and Li recovery steps, the available data was insufficiently detailed and the processes of the different companies were too similar to reach a conclusion.

For the general considerations, the conclusion was that the mixed precipitation process of Northvolt and the solvent extraction process of Duesenfeld were the best processes mainly due to the versatility of the processes for different battery chemistries. With regards to the CAM recovery step, it was concluded that the Duesenfeld solvent extraction step was the best. This was mainly due to the high score Duesenfeld received for the process conditions. The CAM is retrieved as individual salts which require minimum further treatment, which led to it receiving a high score. For the leaching step the Li-Cycle process step received the highest score of the four processes evaluated. This was mainly due to the high score received for the general considerations, as the process conditions score was lower compared to the other process due to the high operating temperature. The Li and Cu recovery step could not be scored due to lack of information, which meant that no process conditions could be scored. From the results of the assessment, the ideal process would start with the leaching step of Li-Cycle (for mix precipitation) and apply the solvent extraction step of Duesenfeld for the recovery of CAM. In general is can be concluded that processes with versatility in both feedstock and products are most valued for the battery recycling, according to the developed assessment method and limited information available.

4.1 Recommendations

The following recommendations are made for the improvement of the assessment method for the evaluation of future technologies:

- Conduct interviews with experts at the industrial parties that develop and design the recycling processes (out-of-scope for this project) to gain sufficient information on aspects such as emission, energy consumption, utility consumption, economics, process efficiency, and product recovery and purity.
- Include considerations such as the hydrogen fluoride (HF) removal, waste disposal of sodium sulphate (Na_2SO_4) and pre-treatment. These process steps also play an important role yield and quality of the CAM.
- Instead of separating the process into steps and evaluating each step separately, consider the business case of the integrated process as well, taking into account feedstock and product streams, product composition and value. Additionally estimate the costs of the major cost contributors like waste treatment (especially salt waste), energy consumption and losses of process chemicals that have to be replenished.

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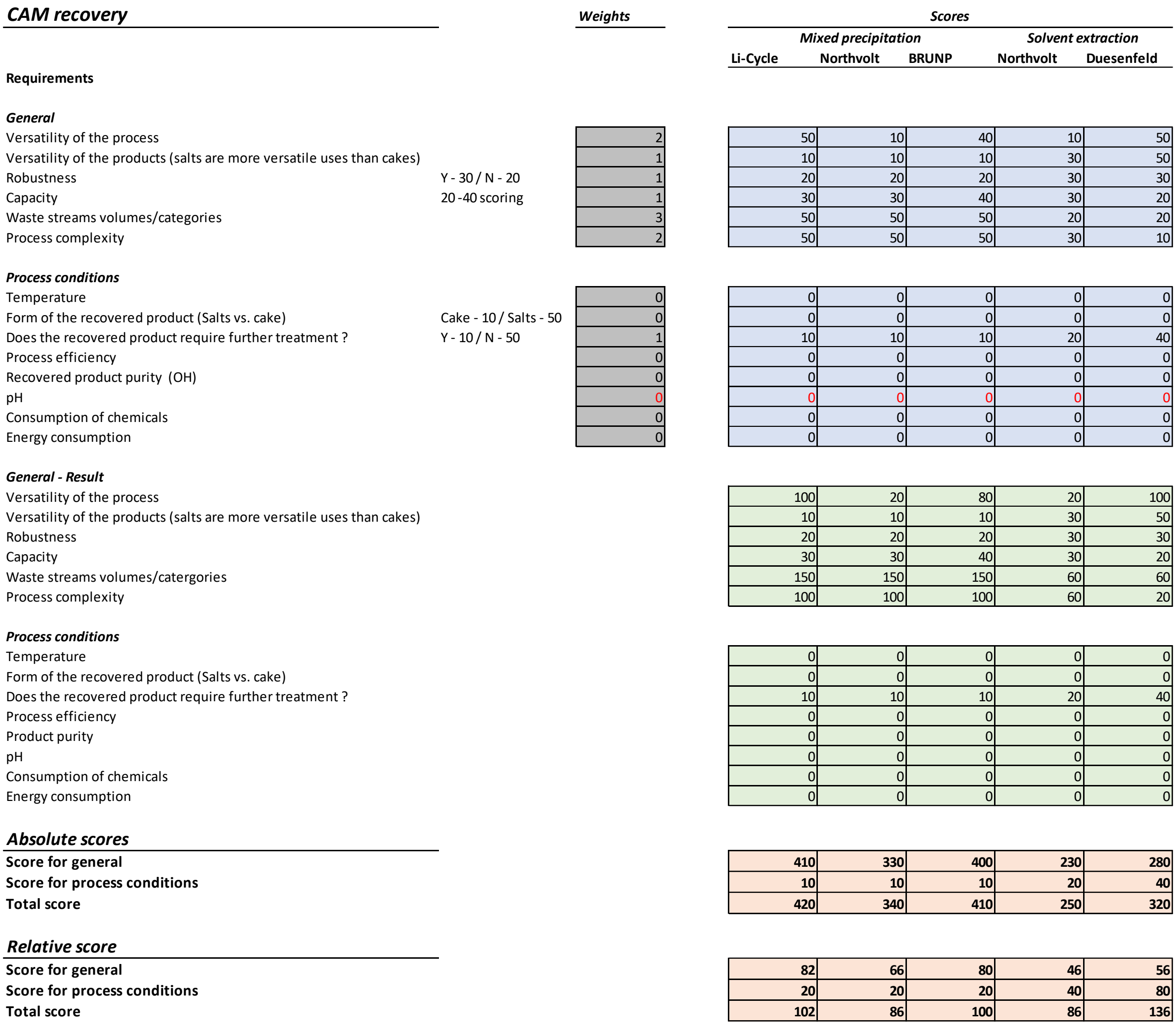
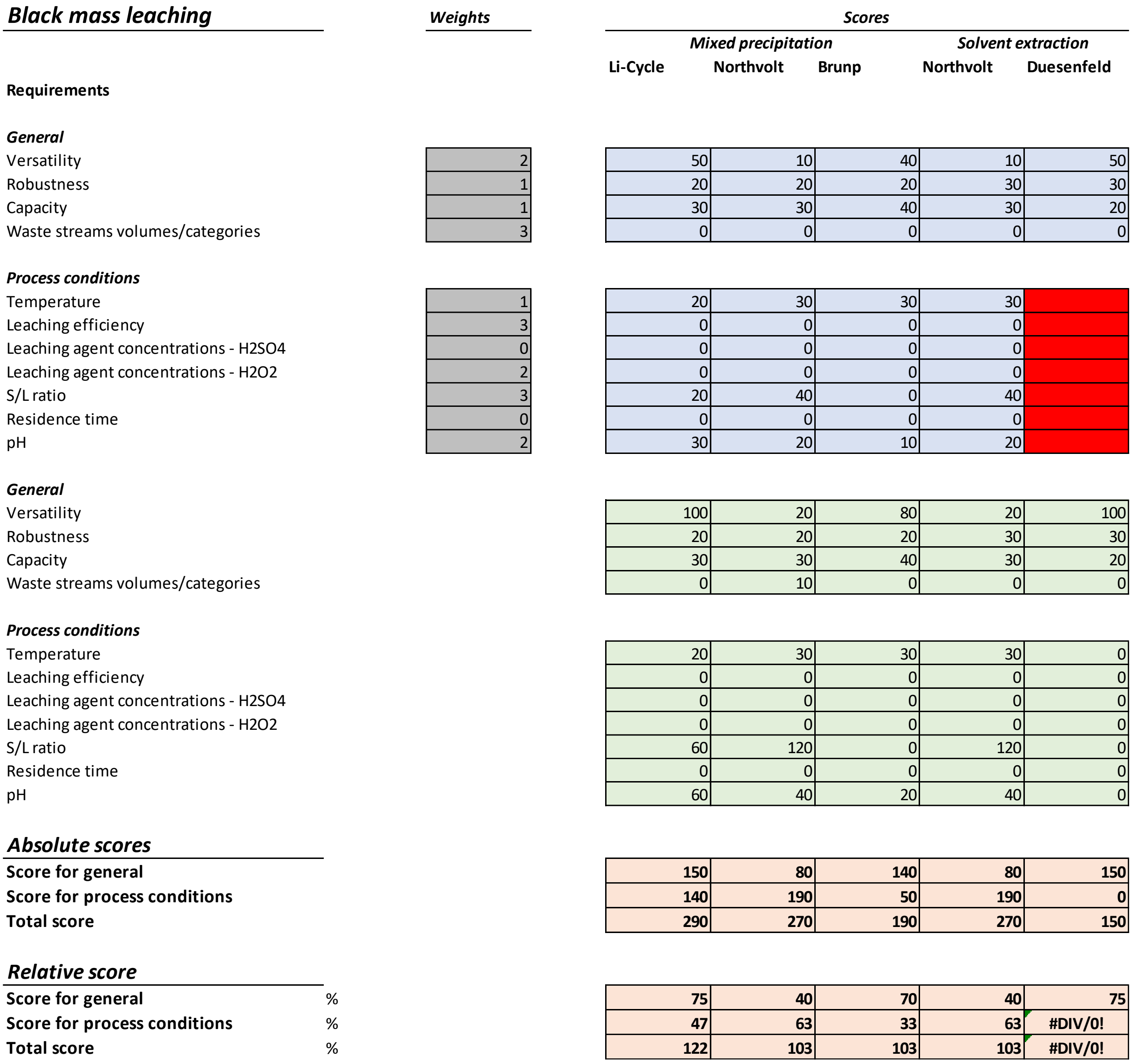
Annex A

Results of the process assessments. For each process, the results are shown separately: the values in the blue cells are the scores, the values in the green cells are the scores multiplied by the weight of the consideration and the values in the orange cells show the total scores, absolute and relative total scores.

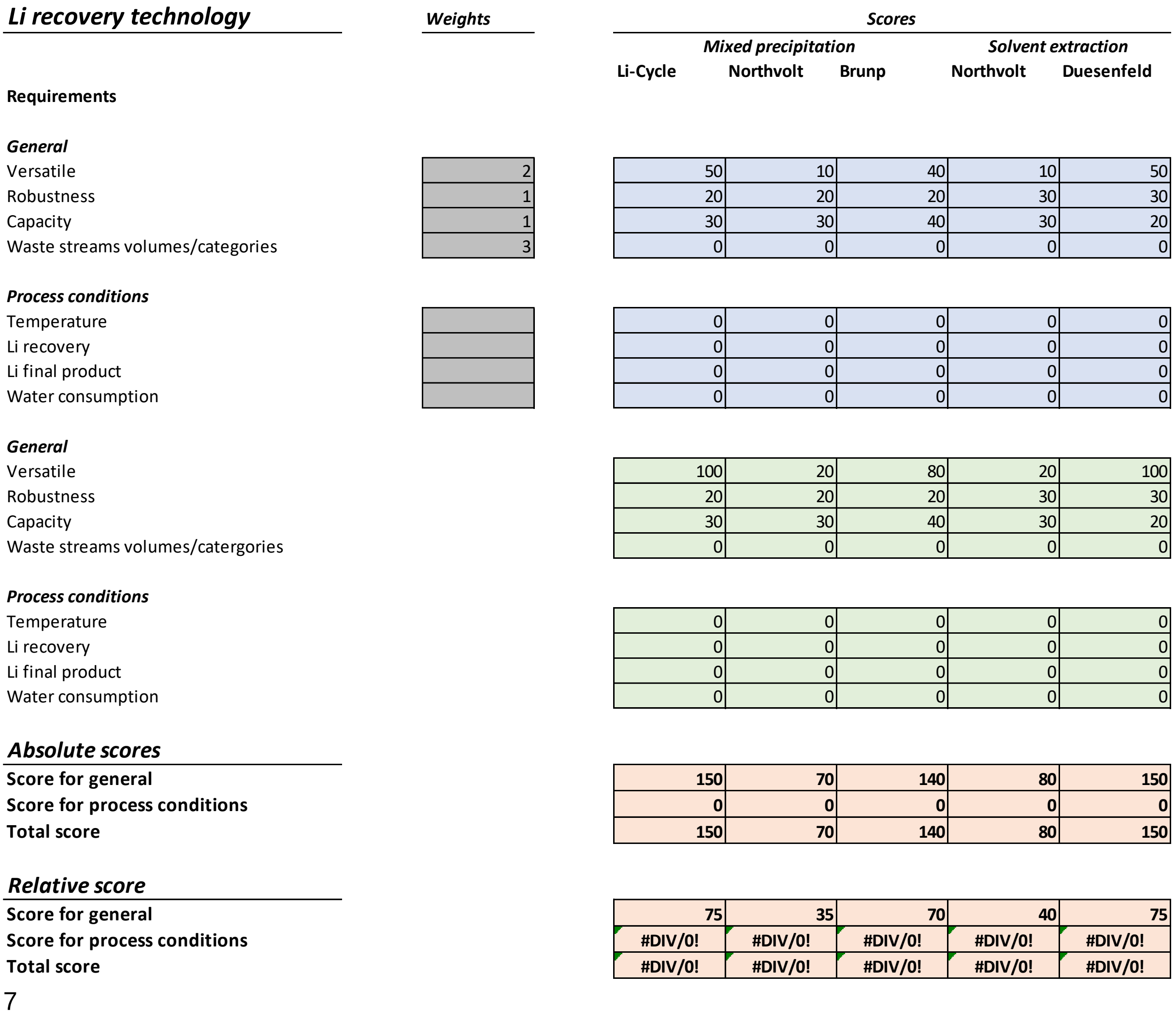
Note: in those cases in which data is lacking, a zero is assigned. Whenever the formula for relative scores divides over zero, an error arises.



CAM recovery		***Weights***	***Scores***				
				Mixed precipitation		***Solvent extraction***	
			Li-Cycle	**Northvolt**	**BRUNP**	**Northvolt**	**Duesenfeld**
Requirements							
General							
Versatility of the process		2	50	10	40	10	50
Versatility of the products (salts are more versatile uses than cakes)		1	10	10	10	30	50
Robustness	Y - 30 / N - 20	1	20	20	20	30	30
Capacity	20 -40 scoring	1	30	30	40	30	20
Waste streams volumes/categories		3	50	50	50	20	20
Process complexity		2	50	50	50	30	10
Process conditions							
Temperature		0	0	0	0	0	0
Form of the recovered product (Salts vs. cake)	Cake - 10 / Salts - 50	0	0	0	0	0	0
Does the recovered product require further treatment ?	Y - 10 / N - 50	1	10	10	10	20	40
Process efficiency		0	0	0	0	0	0
Recovered product purity (OH)		0	0	0	0	0	0
pH		0	0	0	0	0	0
Consumption of chemicals		0	0	0	0	0	0
Energy consumption		0	0	0	0	0	0
General - Result							
Versatility of the process			100	20	80	20	100
Versatility of the products (salts are more versatile uses than cakes)			10	10	10	30	50
Robustness			20	20	20	30	30
Capacity			30	30	40	30	20
Waste streams volumes/catergories			150	150	150	60	60
Process complexity			100	100	100	60	20
Process conditions							
Temperature			0	0	0	0	0
Form of the recovered product (Salts vs. cake)			0	0	0	0	0
Does the recovered product require further treatment ?			10	10	10	20	40
Process efficiency			0	0	0	0	0
Product purity			0	0	0	0	0
pH			0	0	0	0	0
Consumption of chemicals			0	0	0	0	0
Energy consumption			0	0	0	0	0
Absolute scores							
Score for general			**410**	**330**	**400**	**230**	**280**
Score for process conditions			**10**	**10**	**10**	**20**	**40**
Total score			**420**	**340**	**410**	**250**	**320**
Relative score							
Score for general			**82**	**66**	**80**	**46**	**56**
Score for process conditions			**20**	**20**	**20**	**40**	**80**
Total score			**102**	**86**	**100**	**86**	**136**



Black mass leaching		***Weights***	***Scores***				
			Mixed precipitation			***Solvent extraction***	
			Li-Cycle	**Northvolt**	**Brunp**	**Northvolt**	**Duesenfeld**
Requirements							
General							
Versatility		2	50	10	40	10	50
Robustness		1	20	20	20	30	30
Capacity		1	30	30	40	30	20
Waste streams volumes/categories		3	0	0	0	0	0
Process conditions							
Temperature		1	20	30	30	30	🟥
Leaching efficiency		3	0	0	0	0	🟥
Leaching agent concentrations - H2SO4		0	0	0	0	0	🟥
Leaching agent concentrations - H2O2		2	0	0	0	0	🟥
S/L ratio		3	20	40	0	40	🟥
Residence time		0	0	0	0	0	🟥
pH		2	30	20	10	20	🟥
General							
Versatility			100	20	80	20	100
Robustness			20	20	20	30	30
Capacity			30	30	40	30	20
Waste streams volumes/categories			0	10	0	0	0
Process conditions							
Temperature			20	30	30	30	0
Leaching efficiency			0	0	0	0	0
Leaching agent concentrations - H2SO4			0	0	0	0	0
Leaching agent concentrations - H2O2			0	0	0	0	0
S/L ratio			60	120	0	120	0
Residence time			0	0	0	0	0
pH			60	40	20	40	0
Absolute scores							
Score for general			**150**	**80**	**140**	**80**	**150**
Score for process conditions			**140**	**190**	**50**	**190**	**0**
Total score			**290**	**270**	**190**	**270**	**150**
Relative score							
Score for general	%		**75**	**40**	**70**	**40**	**75**
Score for process conditions	%		**47**	**63**	**33**	**63**	**#DIV/0!**
Total score	%		**122**	**103**	**103**	**103**	**#DIV/0!**



Li recovery technology

	Weights	*Scores*				
		Mixed precipitation			*Solvent extraction*	
		Li-Cycle	**Northvolt**	**Brunp**	**Northvolt**	**Duesenfeld**
Requirements						
General						
Versatile	2	50	10	40	10	50
Robustness	1	20	20	20	30	30
Capacity	1	30	30	40	30	20
Waste streams volumes/categories	3	0	0	0	0	0
Process conditions						
Temperature		0	0	0	0	0
Li recovery		0	0	0	0	0
Li final product		0	0	0	0	0
Water consumption		0	0	0	0	0
General						
Versatile		100	20	80	20	100
Robustness		20	20	20	30	30
Capacity		30	30	40	30	20
Waste streams volumes/catergories		0	0	0	0	0
Process conditions						
Temperature		0	0	0	0	0
Li recovery		0	0	0	0	0
Li final product		0	0	0	0	0
Water consumption		0	0	0	0	0
Absolute scores						
Score for general		**150**	**70**	**140**	**80**	**150**
Score for process conditions		**0**	**0**	**0**	**0**	**0**
Total score		**150**	**70**	**140**	**80**	**150**
Relative score						
Score for general		**75**	**35**	**70**	**40**	**75**
Score for process conditions		**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**
Total score		**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**

7

Cu recovery

	Weighs	*Scores*				
		Mixed precipitation			*Solvent extraction*	
		Li-Cycle	**Northvolt**	**Brunp**	**Northvolt**	**Duesenfeld**
Requirements						
General						
Versatility	2	50	10	40	10	50
Robustness	1	20	20	20	30	30
Capacity	1	30	30	40	30	20
Waste streams volumes/categories	3	0	0	0	0	0
Process conditions						
Temperature		0	0	0	0	0
Cu extraction efficiency		0	0	0	0	0
pH		0	0	0	0	0
Extraction agent concentration (LIX? + kerosene)		0	0	0	0	0
Stripping agent concentration (H2SO4)		0	0	0	0	0
Cu (s) recovery		0	0	0	0	0
Energy consumption of Cu(s) recovery step		0	0	0	0	0
General						
Versatility		100	20	80	20	100
Robustness		20	20	20	30	30
Capacity		30	30	40	30	20
Waste streams volumes/catergories		0	0	0	0	0
Process conditions						
Temperature		0	0	0	0	0
Cu extraction efficiency		0	0	0	0	0
pH		0	0	0	0	0
Extraction agent concentration (LIX? + kerosene)		0	0	0	0	0
Stripping agent concentration (H2SO4)		0	0	0	0	0
Cu (s) recovery		0	0	0	0	0
Energy consumption of Cu(s) recovery step		0	0	0	0	0

Absolute scores

Score for general	**150**	**70**	**140**	**80**	**150**
Score for process conditions	**0**	**0**	**0**	**0**	**0**
Total score	**150**	**70**	**140**	**80**	**150**

Relative score

Score for general	**75**	**35**	**70**	**40**	**75**
Score for process conditions	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**
Total score	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**