Master's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Engineering
Department of Energy and Process Engineering

Iman Dorri

# Comparative LCA of Li-ion Battery Cells' Recycling processes

Master's thesis in Circular Economy
Supervisor: Anders Hammer Strømman
Co-supervisor: Lorenzo Usai, Nelson Manjong

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# Abstract

Nowadays, lithium-ion batteries (LIBs) play a crucial role in the electric vehicles industry. Hence, they have been developed dramatically during the last decade worldwide. LIB cell is where the main components of a battery lie within it. Active cathode materials are one of the most important because they contain the most valuable materials of an LIB, such as cobalt, nickel, and manganese. LIBs also contain some hazardous materials, which in the case of leakage, can become a risk to humans and the environment. Therefore, it is important to manage spent LIBs properly. Recycling LIBs is the best solution to recover the valuable materials within LIBs, and also to prevent the risks that LIBs may cause. Pyrometallurgy and hydrometallurgy are the most common methods for recycling LIBs worldwide. Although pyrometallurgy can recycle LIBs independently, it needs a supplementary hydrometallurgical process to extract various materials separately. This study conducted a comparative LCA to assess the environmental impacts of a combined pyro- and hydrometallurgy method with an independent hydrometallurgy method. For this purpose, a comprehensive LCI and transparent model were created for each recycling method based on the thorough literature review carried out in the thesis. The lithium-nickel-manganese-cobalt oxide battery, also known as NMC, was selected as the recycling target of the intended recycling processes.

The LCA results demonstrated that hydrometallurgy is generally associated with higher environmental impacts, mainly due to more chemicals used in its different processes. Production of the chemicals causes high environmental burdens, and it has a significant influence on various environmental impact categories, including ozone depletion potential (ODP), global warming potential (GWP), and terrestrial acidification potential (TAP). Also, the hydrometallurgical process of the pyro- and hydrometallurgy method was the main source of environmental burdens caused by this recycling process. Thus, reducing the chemicals consumption and utilizing more environmentally friendly chemicals can be the most effective solution to reduce the environmental impact of the recycling processes investigated in this study.

**Keywords:**

electric vehicles, LIB, NMC, pyrometallurgy, hydrometallurgy, recycling

***Title**: Comparative LCA of Li-ion Battery Cells' Recycling processes*

## Background

Nowadays, batteries are the most common energy storage system globally, which exist in different types. Of them, the Li-ion battery (LIB) has had the highest rate of growth lately and is predicted to become the most common form of battery shortly. There are different reasons for this significant increase, of which electrification of the vehicle fleet is considered as one of the main ones. Internal combustion engine vehicles are accounted as one of the main culprits and contributors of transport-related GHG emissions and global warming. Therefore, substituting them with battery electric vehicles is crucial to reducing their environmental impacts. Nevertheless, there are serious concerns regarding the exponential growth of LIBs. First of all, the production of LIBs requires the use of various substances, including Cobalt (Co), Nickel (Ni), Lithium (Li), and Aluminium (Al), that supplying them are associated with different environmental burdens. Moreover, some of them are not easily accessible. For instance, Co mining is geographically concentrated in the Democratic Republic of Congo, which is politically unstable. In addition, the life of LIBs is limited and existing batteries in various appliances will become waste in the near future. This issue poses a serious waste management challenge to the environment and society.

Recycling is the best solution to tackle the problems mentioned above regarding LIBs. To this end, there are different recycling methods to recover the materials within LIBs, which are associated with various environmental impacts depending on the recycling process. With this in mind, the student will perform a comparative LCA for recycling processes for LIB cells. The selection of technologies will be performed in dialogue with the supervisors.

**The following tasks are considered:**

1) **Compile the LCIs for the chosen recycling processes**
2) **Conduct the comparative LCAs and compare the results.**
3) **Perform a sensitivity analysis with respect to the ranges of recovered materials**
4) **Discuss the results with previous works done in the same area available in the literature.**

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# Abbreviations

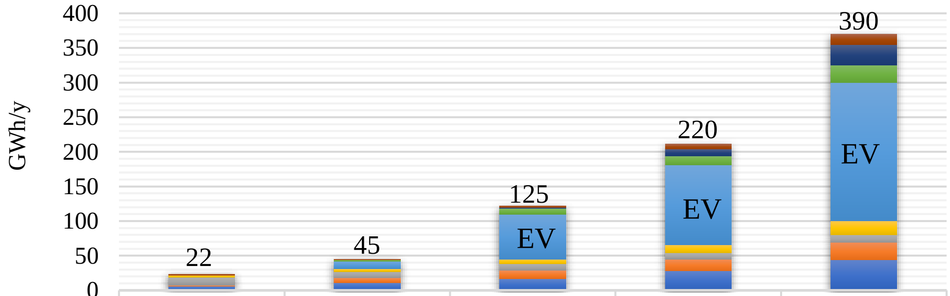
| | |
|---|---|
| BEV | Battery Electric Vehicles |
| BoMs | Bill Of Materials |
| EV | Electric Vehicle |
| EVI | Electric Vehicle Initiatives |
| FDP | Fossil Depletion Potential |
| FEP | Freshwater Eutrophication Potential |
| GWP | Global Warming Potential |
| HTP | Human Toxicity Potential |
| HEV | Hybrid Electric Vehicles |
| LCA | Life Cycle Assessment |
| LCIA | Life Cycle Impact Assessment |
| LCI | Life Cycle Inventory |
| LCO | Lithium Cobalt Oxide |
| LFP | Lithium Iron Phosphate |
| LMO | Lithium Manganese Oxide |
| NMC | Lithium Nickel Manganese Cobalt Oxide |
| LIB | Lithium-Ion Battery |
| NiMH | Nickel–Metal Hydride |
| ODP | Ozone Depletion Potential |
| PC | Personal Computer |
| PHEV | Plug-In Hybrid Electric Vehicle |
| PVDF | Polyvinylidene Fluoride |
| REE | Rare Earth Element |
| SA | Sensitivity analysis |
| SPA | Structural Path Analysis |
| TAP | Terrestrial Acidification Potential |

# 1. Introduction

## 1. 1. Surge of lithium-ion Batteries (LIBs) in recent years

Nowadays batteries are the most important and ubiquitous energy storage systems in the world (Chan & Majid, 2017; Roberts et al., 2018; Velázquez-Martínez et al., 2019). They chemically store the energy and convert it to electricity to supply the energy required to use and work with different types of machinery, devices, and apparatuses such as vehicles, cellphones, and laptops. Batteries are found in different types and chemistries. Among all existing batteries, lithium-ion batteries (LIBs) have had the highest increase and growth rate in recent years globally (Zubi et al., 2018). The global value of LIB's market was US$ 25.6 Billion in 2020, and it has been anticipated to reach US$ 47 Billion by 2025 (Pillot, 2019).

All evidence clearly shows the significant development of LIBs in recent years, and it is anticipated to continue in the future. One of the main reasons for the surge in the LIBs industry has been their comparative advantage over other batteries, including high energy and power density, long lifespan, and environmental friendliness, among other advantages (Beaudet et al., 2020; Lu et al., 2013; Velázquez-Martínez et al., 2019). They have a wide range of applications in different scopes, of which electrification of the vehicle fleet is considered one of the main ones. Internal combustion engine vehicles are accounted as one of the main culprits of transport-related environmental impacts. Substituting them with battery-electric vehicles can have a crucial role in reducing some environmental burdens, especially greenhouse gas emissions contributing to the deterioration of global warming (Usai et al., 2021). In this regard, various plans have been put forward, such as Electric Vehicle Initiatives (EVI), in which LIBs play a crucial role (*Global EV Outlook 2020*, 2020). As shown in Figure 1. electric vehicles (EVs) have had the highest share in the use of LIBs and are considered their main market worldwide.



| | 2010 | 2015 | 2020 | 2025 | 2030 |
|---|---|---|---|---|---|
| ■ Other applications | 1 | 1 | 2 | 7 | 15 |
| ■ Storage in power supply | 0 | 0 | 2 | 10 | 30 |
| ■ PHEV | 0 | 2 | 8 | 13 | 25 |
| ■ EV | 0 | 11 | 65 | 115 | 200 |
| ■ Portable electronics, other | 3 | 4 | 7 | 12 | 20 |
| ■ PC | 12 | 9 | 9 | 9 | 11 |
| ■ Tablets | 1 | 7 | 12 | 17 | 25 |
| ■ Cell phones | 6 | 11 | 17 | 28 | 44 |

**Figure 1. The share of different devices and apparatuses from the LIB global market in GWh/y (Zubi et al., 2018)**

LIBs could revolutionize the transportation sector environmentally by providing a more environmental-friendly energy source compared to fossil fuels. This achievement has caused a reinforcing effect in the surge of LIBs, which many reach their end-of-life phase shortly. Therefore, it is vital to have proper solutions and strategies to manage them.

## 1. 2. The importance of recycling LIBs

The advent of LIBs has strongly influenced the development of consumer electronics and demonstrated a notable potential concerning energy sustainability and carbon emission reduction in the global transport system (Zubi et al., 2018). Nevertheless, the considerable growth of LIBs' production/usage has caused new challenges and systematic problems for the environment and human societies. In this regard, there are numerous problems enumerated for LIBs in the literature. The most common ones could be summarized as follows: environmental impacts of mining and extraction of the materials used in LIBs (Chaves et al., 2021; Kaunda, 2020; Manjong et al., 2021), sustainability issues and long term material supply for LIBs' production (Olivetti et al., 2017; Pinegar & Smith, 2019; Richa et al., 2014; Väyrynen & Salminen, 2012; Yu & Manthiram, 2021), and accumulation of spent LIBs and the risks associated with the release of hazardous materials existing within them (Beaudet et al., 2020; Harper et al., 2019; Winslow et al., 2018; Zeng et al., 2015).

LIBs' recycling is one of the best and most comprehensive solutions that can help tackle the problems mentioned above for the following reasons. To begin with, recycling LIBs can halt the accumulation of LIBs as waste at their end-of-life phase. Also, the materials recovered by recycling can cover some part of the material demand for producing new LIBs. It can reduce the pressure for mining and extraction of precursors used in the LIB industry. Thereby the environmental impacts of mining activities related to LIBs are decreased. In addition to mining activities, producing some materials is associated with high energy demand and environmental burdens, of which many can be obtained through recycling processes. Nickel is a case in point that can be obtained with 75% less energy compared to getting from virgin resources by recycling (European Commission, 2014).

Furthermore, some of the materials existing in LIBs, such as cobalt, are scarce, and they pose a risk to the sustainable supply chain in the LIB industry. Recovering them through recycling LIBs can contribute to the sustainable supply of these materials. In addition to environmental benefits, recycling can cause economic benefits as well. The cost of producing new LIBs can be reduced by using valuable recovered materials, such as lithium, nickel, and cobalt (Nogueira & Margarido, 2012; Remler et al., 2020). The reasons mentioned above are some of the main reasons that illustrate the crucial role of recycling in different sectors of the LIB life cycle.

According to Larouche et al. (Larouche et al., 2020), there are three major approaches concerning LIBs' recycling, which have been demonstrated in Figure 2. The first approach mainly focuses on the materials with high economic value in LIBs, e.g., cobalt, manganese, and nickel. They can be either reused for LIBs' production as the raw material or downcycled in lower-value products. Pyrometallurgy is the typical recycling method utilized to implement the first approach.

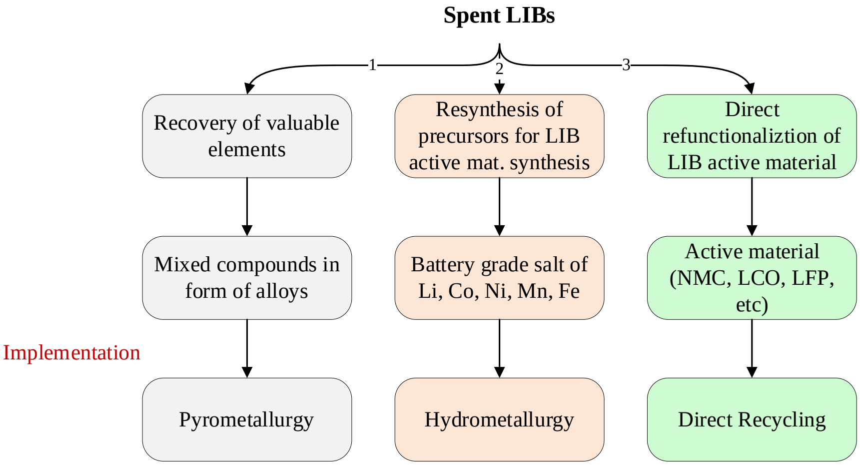


**Figure 2. Main approaches concerning LIBs' recycling introduced by Larouche et al.**

The second approach aims to recover the materials used on LIBs as much as possible with high quality to reuse them in producing new LIBs. Hydrometallurgy is the prevalent method employed to materialize the goal of the second approach. Finally, the goal of the third approach is to regenerate the LIBs' active materials with the least change and modification to be used in producing new LIBs. This approach is in line with a closed-loop material flow paradigm. Direct recycling is the recycling method used to implement this approach. The LIBs' recycling methods mentioned above (pyrometallurgy, hydrometallurgy, and direct recycling) are completely explained in the literature review.

## 1. 3. Problem statement, objectives, and scope of the study

Recycling LIBs is one of the hot topics that has gained a lot of attention in recent years due to the surge of LIBs during the last decade. Although recycling processes are considered a solution for the sustainability and environmental problems stemming from the increase of spent LIBs, they themselves are also associated with environmental burdens. Therefore, it is of high importance to identify and find a solution to resolve them. In recent years, there have been some LCA studies, especially for pyrometallurgy and hydrometallurgy as two of the most common recycling methods, which have addressed these issues. Nevertheless, most studies existing in this regard lack clarity in presenting the recycling processes and their environmental impacts. The main problems of existing LCA studies for LIBs' recycling methods can be summarized as follows:

- Lack of transparency in the flowsheets, diagrams, and models presented in LCA studies of LIBs' recycling processes
- Incomplete LCIs
- Lack of clarity regarding the point of use and application of the materials enumerated in LCIs

The LIBs' recycling processes are usually either too general or are in the form of a black box in LCA studies existing in the literature. There are different reasons for this, of which confidentiality issues is the most important one. Also, some of the LCAs of LIBs' recycling methods are based on lab-scale and simulation-based processes. In such cases, usually, the LCIs are shorter than industrial-scale studies, which leads to different results. Moreover, some industrial-scale LCA studies also do not reveal all the materials in the LCIs due to challenges related to keeping the processes confidential. Last but not least, the role of chemicals used in the process is not clear in the environmental impact categories reported in LCA studies

Accordingly, with regard to the problems and issues mentioned above, the main goals of this research are as follows:

1. To present a transparent and generic model for pyro- and hydrometallurgical and an independent hydrometallurgical recycling methods
2. To present a comprehensive LCI for the aforementioned methods
3. To conduct an LCA for the methods in question based on the presented models and LCIs
4. To make a comparison between intended recycling methods from an environmental impact point of view
5. To compare the environmental impacts of obtaining main metals used in manufacturing LIBs (nickel, cobalt, manganese, lithium) from the recycling methods in question and virgin sources

As stated before, pyrometallurgy, hydrometallurgy, and direct recycling are the main methods for recycling LIBs. Of these, the first two are the ones that are more common and known as technologically mature methods, which have been implemented on a large scale worldwide. Hence, these two were selected as the target recycling methods in this study. Also, since the final products of pyrometallurgy and hydrometallurgy are different, the pyro- and hydrometallurgical process is evaluated to make the comparison more reasonable. The other reason for this is that, usually, a pyrometallurgical process is dependent on a supplementary hydrometallurgical process to extract the target materials from its outputs. Therefore, it is better to study them together. In this study, the focus is just on the recycling processes existing on an industrial scale to get more realistic results. The spent NMC111 LIBs from BEVs are considered in the recycling models presented in this study. The main reason for this selection is that they are among the most common LIBs existing in the EVs market, making them the main target for recycling LIBs from the transportation sector shortly. Also, NMC111 is the target battery in most of the LCA studies existing about recycling LIBs (Mohr et al., 2020). Furthermore, NMC batteries contain more scarce and valuable materials than other LIBs existing in the market. Consequently, they are more appealing targets for recycling.

To reach the goals of this study, first, LIBs, as the main input of recycling processes, are investigated briefly in terms of function and materials content. Then, various LIBs recycling methods are introduced thoroughly. Also, the materials and energy used in the intended recycling processes for the LCA are investigated and analyzed based on the literature review. Accordingly, a generic and transparent model and LCI is created for each recycling process. Finally, the comparative LCA is accomplished based on the LCIs and models presented for the LIBs' recycling methods in question.

# 2. Literature review

## 2. 1. LIBs' structure and materials content in a nutshell

LIBs are a special group of batteries that are similar in terms of having lithium as one of the main elements in their structures. LIBs are divided into different subsidiaries based on their chemistries and structure. They were first manufactured and introduced commercially by SONY in the 1990s, made of $LiCoO_2$ and graphite as cathode and anode, respectively (Nitta et al., 2015). It was the beginning of LIBs' dominance in different scopes and applications, which was mainly because of their unique properties; high energy density, relatively long lifespan, diversity in forms and structure, and the use of less toxic materials in production, to name but a few (Kraytsberg & Ein-Eli, 2012). Generally, the LIBs structure is comprised of five main parts: cathode/positive electrode, anode/negative electrode, electrolyte, separator, and the outer casing (battery outer cover) (Yoshino, 2014), of which electrolyte, cathode, and anode form around 60% of the LIBs' weight (Zeng et al., 2014).

When it comes to recycling LIBs, the cathode is usually the most attractive part. It contains the most valuable and scarce elements of an LIB (Rahman & Afroz, 2017) and forms around 30% of the battery's cell mass (Gaines et al., 2011). Cathodes exist in different chemistries, and the name of different LIBs stems from the name of the materials within active materials used in cathodes. lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$ or NMC), lithium iron phosphate ($LiFePO_4$ or LFP), lithium cobalt oxide ($LiCoO_2$ or LCO), and lithium manganese oxide (LMO) are some of the well-known active materials existing in the market and used broadly in LIBs (Gaines et al., 2011; H.-J. Kim et al., 2020; Winslow et al., 2018). Cathode active materials adhere to a metallic plate known as the current collector, usually made of aluminium, by a polyvinylidene fluoride (PVDF) binder (Brückner et al., 2020; Larouche et al., 2020; Zeng et al., 2014).

The negative electrode or anode has less diversity compared to cathodes. The most common anode's chemical composition is graphite, although it also can be found in other chemistries such as lithium titanate (LTO, Li4Ti5O12) (Brückner et al., 2020; Gaines et al., 2011; Hannan et al., 2018). As with cathode, the material used for the anode is attached to a current collector, usually made of Copper, through a PVDF binder. The electrolyte is a crucial element in LIBs that fills the space between cathode and anode, and is a medium for the movement of lithium between cathode and anode. Depending on the type of battery, the electrolyte can be in a liquid or solid state. The electrolyte used in LIBs usually is made of different chemistries, of which lithium hexafluorophosphate (LiPF6), lithium tetrafluoroborate ($LiBF_4$), and lithium perchlorate ($LiClO_4$) are more common (Aravindan et al., 2011). As considered, some of the materials existing in the electrolyte, such as fluorine, chlorine, and boron, are toxic to humans and the environment. Hence, it is of high importance to manage them properly in the recycling processes to avoid their emission into the environment.

The set of LIB components introduced so far are the ones that have a higher importance in LIBs' recycling processes. These parts are decisive in determining the recycling method and are also recognized as the battery cell. Various devices require a different amount of voltage to work. Accordingly, there might be more than one cell in a LIB. For instance, the LIB used in mobiles and headphones is just one cell. However, larger devices, such as laptops and tablets, possess more than one cell in a LIB. The LIBs used in EVs are much more complicated than the batteries existing in mobiles and laptops, and there are so many cells in a LIB, as many as thousands (*The Composition of EV Batteries*, n.d.). In addition to the cells, EVs' LIBs have other modules, including electronic parts, insulation, and an outer peripheral cover that embraces all the LIB components and integrates its structure. As considered, an LIB might have different segments depending on its application in different devices and apparatuses. This issue can sometimes be confusing in the papers related to the recycling of LIBs.

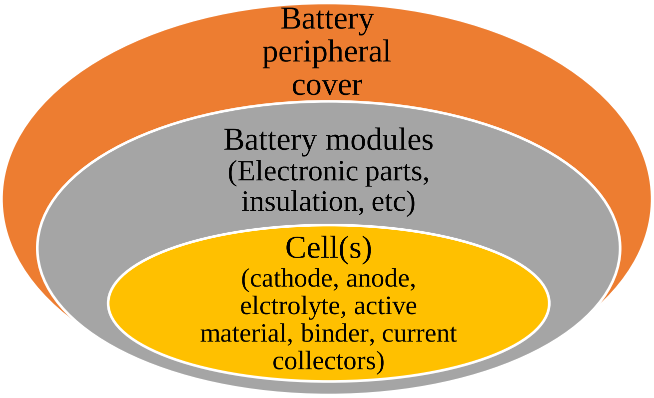


**Figure 3. The modular structure of LIBs in EVs**

Another important point that should be noted regarding LIBs is that depending on the case of use (e.g., vehicles, cellphones, laptops, etc.), different types of an LIB exist. For instance, when it comes to NMC111 as a subset of NMC batteries, the amount and proportion of its constituents vary for different applications. The bill of material (BOM) of some LIBs used in battery electric vehicles (BEV) and hybrid electric vehicles (HEV) have been demonstrated in Table 1. As observed, NMC111 is used in both BEVs and HEVs. However, the amount of active cathode materials is 125.43 kg and 4.89 kg in BEVs and HEVs, respectively. This issue can be another source of confusion if there is no clear mention of the application for the LIB in question.

**Table 1. BoMs for common LIBs used in vehicles, units in kg (Winjobi et al., 2020)**

| | HEV | | | BEV | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **LMO** | **NMC 111** | **LFP** | **LMO** | **NMC 111** | **LFP** | **NMC 532** | **NMC 622** | **NMC 811** | **NCA** |
| Active cathode material | 6.52 | 4.89 | 5.65 | 166.35 | 125.43 | 145.78 | 121.11 | 105.87 | 89.81 | 97.27 |
| Carbon black | 0.14 | 0.1 | 0.12 | 3.47 | 2.61 | 3.04 | 2.52 | 2.21 | 4.99 | 2.03 |
| graphite | 2.22 | 2.5 | 2.9 | 56.19 | 63.67 | 74.44 | 62.07 | 62.52 | 64.6 | 63.87 |
| Binder (PVDF) | 0.18 | 0.23 | 0.18 | 4.61 | 5.96 | 4.56 | 3.79 | 3.48 | 6.31 | 3.33 |
| Copper | 3.57 | 4.08 | 8.55 | 31.02 | 23.17 | 32.9 | 21.97 | 20.25 | 20.06 | 18.67 |
| Aluminum | 1.88 | 2.09 | 4.27 | 17 | 13.13 | 18.5 | 12.38 | 11.5 | 11.45 | 10.7 |
| Electrolyte: LiPF6 | 0.38 | 0.36 | 0.66 | 5.3 | 4.55 | 7.23 | 4.13 | 4.01 | 3.96 | 3.83 |
| Electrolyte: Ethylene Carbonate | 1.05 | 1 | 1.85 | 14.8 | 12.7 | 20.19 | 11.53 | 11.19 | 11.05 | 10.7 |
| Electrolyte: Dimethyl Carbonate | 1.05 | 1 | 1.85 | 14.8 | 12.7 | 20.19 | 11.53 | 11.19 | 11.05 | 10.7 |
| Plastic: Polypropylene | 0.37 | 0.43 | 0.95 | 3.04 | 2.17 | 3.23 | 2.48 | 1.85 | 2.18 | 1.68 |
| Plastic: Polyethylene | 0.09 | 0.1 | 0.23 | 0.68 | 0.47 | 0.72 | 0.56 | 0.4 | 0.48 | 0.36 |
| Plastic: Polyethylene Terephthalate | 0.07 | 0.06 | 0.1 | 0.7 | 0.62 | 0.82 | 0.58 | 0.55 | 0.56 | 0.53 |
| **Subtotal: Cell** | **17.5** | **16.86** | **27.29** | **317.95** | **267.21** | **331.57** | **254.63** | **235.02** | **226.49** | **223.67** |
| **Module components without cell (kg)** | | | | | | | | | | |
| Copper | 0 | 0 | 0 | 0.39 | 0.43 | 0.48 | 0.42 | 0.43 | 0.43 | 0.43 |
| Aluminum | 0.76 | 0.74 | 1.1 | 13.94 | 12.48 | 16.13 | 11.76 | 11.32 | 11.42 | 10.94 |
| Plastic: Polyethylene | 0.01 | 0.01 | 0.01 | 0.13 | 0.13 | 0.13 | 0.13 | 0.13 | 0.13 | 0.13 |
| Insulation | 0 | 0 | 0 | 0.1 | 0.11 | 0.12 | 0.11 | 0.11 | 0.11 | 0.11 |
| Electronic part | 0.21 | 0.21 | 0.21 | 1.12 | 1.12 | 1.12 | 1.12 | 1.12 | 1.12 | 1.12 |
| **Subtotal: Module sans cell** | **0.98** | **0.96** | **1.32** | **15.68** | **14.27** | **17.99** | **13.54** | **13.1** | **13.2** | **12.74** |
| **Pack components without module (kg)** | | | | | | | | | | |
| copper | 0.43 | 0.44 | 0.49 | 0.08 | 0.09 | 0.1 | 0.09 | 0.09 | 0.09 | 0.09 |
| Aluminum | 1.87 | 1.84 | 2.4 | 33.48 | 31.09 | 36.37 | 30.31 | 29.52 | 29.56 | 29 |
| Steel | 0.63 | 0.6 | 0.98 | 2.23 | 1.98 | 2.71 | 1.83 | 1.76 | 1.78 | 1.69 |
| Insulation | 0.21 | 0.22 | 0.25 | 1.06 | 0.99 | 1.16 | 0.97 | 0.94 | 0.94 | 0.93 |
| Coolant | 1.03 | 1.02 | 1.34 | 7.92 | 8.58 | 10.94 | 8.5 | 8.65 | 8.47 | 8.97 |
| Electronic part | 3.72 | 3.74 | 3.82 | 4.36 | 4.43 | 4.5 | 4.22 | 4.22 | 4.22 | 4.23 |
| **Subtotal: Pack without module** | **7.89** | **7.86** | **9.28** | **49.14** | **47.16** | **55.79** | **45.91** | **45.18** | **45.06** | **44.9** |
| **Total: Pack** | **26.37** | **25.68** | **37.89** | **382.77** | **328.64** | **405.35** | **314.09** | **293.3** | **284.75** | **281.31** |

## 2. 2. Pyrometallurgical recycling method (Pyrometallurgy)

Among all LIBs' recycling methods, pyrometallurgy is considered as the oldest and most common method that is commercially used by many companies worldwide (Brückner et al., 2020; Makuza et al., 2021; Sommerville et al., 2021), especially in North American and European countries (Du et al., 2022). Therefore, it is known as a mature and technically-proved technology for recycling LIBs. In pyrometallurgy, the spent LIBs are treated as if they are ores containing valuable materials, and the goal is to extract them (Ekberg & Petranikova, 2015; Gaines et al., 2021). Hence, to some extent, this recycling process is similar to the refinement processes carried out on ores to extract the intended materials. Generally, there are two types of pyrometallurgical processes from a technological point of view: single furnace and two-furnace technology (Cheret & Santen, 2007).

The two-furnace pyrometallurgical process is the first and oldest technology among other LIB recycling methods. The process begins with pyrolyzing the batteries in the first furnace to remove the plastic container and evaporate the electrolyte. The heating of the first furnace is a crucial part of the process, which should be accomplished gradually because rapid heating may lead to the explosion of the batteries due to the high pressure of the evaporated electrolyte within the battery (Cheret & Santen, 2007; Dunn et al., 2014). The combustion process of plastic parts is usually incomplete, and given the presence of halogens from the electrolyte in the process, Dioxin and Furan may be produced. Also, some other toxic materials, such as fluorine and chlorine, are emitted due to burning electrolytes and the binders.

Hence, the system should be equipped with a gas treatment system to prevent the emission of these perilous gases into the environment. After burning the batteries in the first furnace, the output of this unit is cooled down and then transmitted to the second furnace for the final melting phase. Finally, the main product of the system is an alloy containing metallic materials. The main disadvantage of a two-furnace pyrometallurgical recycling plant is its high investment and also operational costs (Cheret & Santen, 2007). Moreover, this method requires two separate furnaces, which consume a high amount of energy. Last but not least, the quality of outputs is lower than other alternatives. Hence, it is not a popular and common recycling method for recycling LIBs.

Single furnace pyrometallurgical recycling was first presented and patented by a Belgian company called "Umicore" in 2007 (Cheret & Santen, 2007). The main goal of this recycling process is to recover and reuse the metals existing in the battery with high economic value, such as cobalt and nickel (Bankole et al., 2013; Lv et al., 2018; Makuza et al., 2021; Velázquez-Martínez et al., 2019). Since LIBs and nickel metal hydride (NiMH) batteries contain a relatively high amount of cobalt and nickel, they are the main target of this recycling method. Nevertheless, pyrometallurgy is also capable of treating other types of batteries, including Alkaline lead batteries. The outline of a pyrometallurgical recycling method has been demonstrated in Figure 4.

As seen in Figure 4. , the inner space of the furnace is divided into three zones: preheating zone (<300 °C), plastic pyrolyzing zone (~700 °C), and metal smelting and reducing zone (1100 – 1500 °C) (Assefi et al., 2020; Beaudet et al., 2020; Harper et al., 2019; Knights & Saloojee, 2015; Sojka et al., 2020). Spent batteries, coke, and slag formers are the main inputs of the process, which are inserted into the preheating zone (Dunn et al., 2014; Rajaeifar et al., 2021; Vezzini, 2014; Zhou et al., 2021). Slag formers are the materials that mainly contain $SiO_2$ and Cao (Brückner et al., 2020; Heulens et al., 2019). They contribute to achieving the spent batteries' valuable contents separately so that they get recycled with higher purity. The most common materials used for this purpose are sand (as Silicon-containing material), Limestone (as Calcium-containing material), and a type of slag that is usually supplied from the steel industry (Cheret & Santen, 2007; Dunn et al., 2014; Rajaeifar et al., 2021).

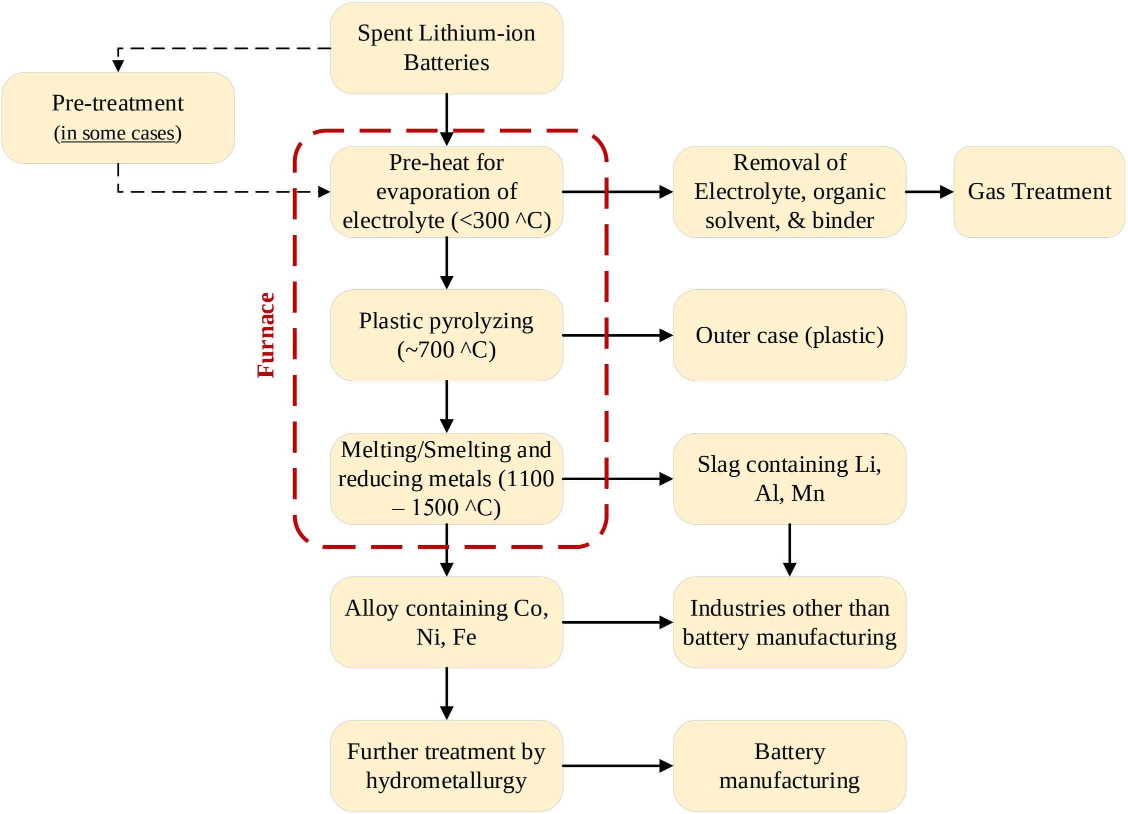


**Figure 4. The outline of the pyrometallurgy recycling method**

The main goal of the preheating zone is to evaporate the electrolyte slowly, which is accomplished in temperatures around 300 °C. Higher temperatures cause rapid evaporation of the electrolyte and could cause the explosion of the LIBs in the furnace. The heat of this zone is mainly provided through the hot gases coming from the other two zones. After eliminating the electrolyte, the heated inputs are transmitted to the plastic pyrolysis zone, where plastic parts are removed. The temperature rises to 700 °C in this part of the system by burning the plastic components. Also aluminium- containing materials can be so effective in this regard because oxidation of aluminium is an exothermic process, which produces a high level of heat (Cheret & Santen, 2007). Finally, the materials go to the last section, entitled the metal smelting and reducing zone, in which the temperature is about 1100 to 1500 °C to melt the metallic contents of input batteries. To reach high temperatures in this phase, oxygen and/or rich-oxygen air is injected into this part of the furnace. Nonetheless, sometimes auxiliary materials, such as CaCl2, NaHSO4, and NH4Cl, are used to increase the temperature enough to melt the metals (Assefi et al., 2020; Gaines et al., 2011).

In the end, the final output comprises some gases, slag, and an alloy, which is accounted as the most important part, containing cobalt, nickel, copper, and iron. These metals can later get recycled separately by further treatments in a hydrometallurgical process. All the other materials existing in the slag, including manganese, lithium, aluminium, and Silsium, are either downcycled in other industries, such as construction, glass, road, and cement, or get squandered as waste in landfills and incinerations (Ekberg & Petranikova, 2015; Georgi-Maschler et al., 2012; Harper et al., 2019; Morawski, 2012; Sommerville et al., 2021; Winslow et al., 2018). In addition to the alloy and slag, some gases are produced through the pyrometallurgy process. These gases might contain hazardous materials like Dioxin and Furan (Cheret & Santen, 2007). Therefore they should be treated before getting released into the environment. Gas treatment is usually accomplished through a plasma torch in a post-combustion process, which heats the gas in the temperature range of 1100 – 1150 °C (Cheret & Santen, 2007; Jin et al., 2022; Saloojee & Lloyd, 2015; Sojka et al., 2020; Vezzini, 2014). Part of the heat of the plasma torch is transmitted to the top of the furnace to prevent accumulation and condensation of evaporated components produced from the different parts of the process in the preheating zone. In the academic literature, pyrometallurgy is dominated by single furnace smelting technology and will thus be the technology investigated in this study.

Pyrometallurgy has some pros and cons that should be taken into account in analyzing them. The main advantage of this recycling process is its capability to recycle a wide range of batteries, particularly LIBs, without the need for any particular pretreatment process (Beaudet et al., 2020; Harper et al., 2019; Thompson et al., 2020). This advantage is especially important in countries with no efficient infrastructure to separate the collected batteries. In the cases where pyrometallurgy and hydrometallurgy are used together, pretreatment might be used before pyrometallurgy to remove some parts of the input batteries. Also, if the goal of recycling is further than just recovering the economically valuable materials, it is important to remove intended parts before inserting the batteries into the furnace. In terms of safety risks, pyrometallurgy is one of the safest ways to manage batteries because there is the least of human contact with hazardous material within batteries, such as electrolyte, and adhesives (Du et al., 2022). Another advantage of the pyrometallurgical recycling process is its maturity and reliability, making it the most common LIBs' recycling method globally. Umicore[1] (Belgium), Tectonic (UK), Intmetco (USA), Accurec (Germany), Dowa (Japan), and SNAM (France) are some of the eminent LIB recycling plants utilizing pyrometallurgy (Knights & Saloojee, 2015; Larouche et al., 2020; Makuza et al., 2021; Rajaeifar et al., 2021; Velázquez-Martínez et al., 2019; Winslow et al., 2018).

Beside the merits accounted for pyrometallurgy above, it has some critical drawbacks that should be considered. First of all, it is an energy-intensive process (Gaines et al., 2021; Morawski, 2012) that is usually supplied by fossil fuels sources, such as coke and natural gas (Cheret & Santen, 2007; Dai et al., 2019; Dunn et al., 2012; Rajaeifar et al., 2021). Furthermore, to make a pyrometallurgy recycling plant economically viable, there should be a significant amount of cobalt and nickel in the input (Harper et al., 2019; Wang et al., 2016). Hence, recycling some batteries that lack these materials is not economically viable through pyrometallurgy, including lithium-iron-Phosphate (LFP) and lithium-manganese-Oxide (LMO) (Gaines, 2018; Hendrickson et al., 2015). Also, the production of hazardous gases is another downside mentioned for pyrometallurgical recycling processes in some sources (Beaudet et al., 2020; Larouche et al., 2020; Wang et al., 2016).

### 2. 2. 1. Analysis of materials and energy in a pyrometallurgical recycling process

As explained earlier, pyrometallurgy is a robust recycling process that can treat and recycle a wide range of LIBs without pretreatment. Some requirements concerning input materials should be fulfilled to make the process more efficient and economically viable, which are elaborated on in the following.

In order to make the recycling process economically viable, there should be enough proportion of cobalt and nickel in the input. Accordingly, as a rule of thumb, at least 30% and preferably 50% of materials' weight in the input of the process should be LIBs containing cobalt and nickel (Cheret & Santen, 2007; Saloojee & Lloyd, 2015). The main source of energy for melting the metals is coke, which should be around 0.33 kg per kg of LIBs in the input (Cheret & Santen, 2007; Ciez & Whitacre, 2019). Burning coke requires supplying enough oxygen to complete the combustion process. According to Heulens et al, the suitable amount of oxygen is 130 $Nm^3$ per ton of LIBs (Heulens et al., 2019), which is supplied through various ways, such as pumping the air or oxygen to the metal smelting zone.

Slag formers are another important input that separates the output materials between alloy and slag. Slag formers are usually consist of three parts of sand, Limestone, and a special type of slag provided from the steel industry. The optimized amount of slag formers are as follows: 0.15 kg of sand per kg of LIBs (Dai et al., 2019; Heulens et al., 2019), 0.3 kg of Limestone per kg of LIBs (Dai et al., 2019; Dunn et

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[1] Umicore has two plants for LIBs recycling in Belgium and Sweden. The recycling plant in Belgium utilize pyrometallurgy and its output is sent for further processing in Sweden by hydrometallurgical process.

al., 2014; Heulens et al., 2019), 0.17 kg of slag from steel industry per kg of LIBs (Cheret & Santen, 2007; Rajaeifar et al., 2021; Saloojee & Lloyd, 2015).

One of the important units of a pyrometallurgy recycling process that is usually neglected in LCA studies is the gas treatment part. Post-combustion is the first part of the gas treatment process, which is done by using one plasma torch, which consumes about 1.3 kWh per kg of LIBs in the input (Heulens et al., 2019). Moreover, also different materials are used in this unit, including Sodium, Calcium, and Zinc containing materials, to separate the hazardous materials emitted during the combustion process in the furnace (e.g., fluorine, chlorine, Halogens, Dioxin, and Furan). In this regard, Calcium hydroxide ($Ca(OH)_2$) is the most common one, which is suggested to be used in the proportion of 0.03 kg per kg of LIBs in the gas treatment unit (Rajaeifar et al., 2021). Finally, water is sprayed on gases to cool it down before releasing it into the environment and also capture some of the coarse materials existing in the gas. The required amount of water is estimated to be around 1 kg per kg of LIBs (Fisher et al., 2006; Hischier et al., 2007; Richa, 2016).

Concerning the outputs of the pyrometallurgy recycling process, it is possible to estimate them based on studies and experiments done in this regard and also analysis of the existing materials within the LIBs in the input. Alloy is the main product of the process that is a mix of cobalt, nickel, iron, and Copper. The amount of these metals within the alloy depends on the proportion of LIBs and slag formers in the input. Cheret and Santen reported some examples of material distribution between alloy and slag, which one of them has been demonstrated in Table 2. as an example (Cheret & Santen, 2007). As observed, 92.8% of copper, 99% of nickel, 64.5% of iron, and 94% of cobalt end up in the alloy, and the rest of the materials (including the whole amount of Calcium, aluminium, Silicium, and lithium) go either into slag or dust. Also, the carbon content of the materials in the input is converted to $CO_2$. To calculate the amount of $CO_2$, it is crucial to have a complete understanding of the batteries' bill of materials (BoMs) existing in the process. In this regard, Dunn et al. presented an approximation of the carbon content for different segments existing in LIBs, to which a part of carbon dioxide in the output of the process can be calculated (Dunn et al., 2014). Slag contains valuable materials such as lithium, aluminium, and sometimes manganese (Cheret & Santen, 2007; Ciez & Whitacre, 2019; Zhou et al., 2021). Although it is possible to recover them, it is not economically viable, and hence usually, they are used as aggregate in concrete (Rajaeifar et al., 2021). Plastic parts, biner, electrolyte, and most of the other parts containing organic materials go to the gas treatment part and end up in the dust or wastewater. A summary of the explanations above has been presented in Table 3.

**Table 2. An example of materials distribution between slag and alloy in a pyrometallurgical process (Cheret & Santen, 2007)**

| | | mass (kg) | composition (wt. %) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **Cu** | **Ni** | **Fe** | **Al** | **CaO** | **Sio2** | **Al2O3** | **Li2O** | **Co** | **Others** |
| **Input** | **Limestone** | 100 | | | | | 60 | | | | | |
| | **sand** | 110 | | | | | | 100 | | | | |
| | **Li-ion batteries** | 1200 | 7 | 2.5 | 35 | 5 | 0 | 0 | | 1 | 14 | 35.5 |
| | **Coke** | 400 | | | | | | | | | | |
| | **Slag (from the steel industry)** | 200 | | | 1 | | 38.7 | 34 | 11 | | 0 | 15.3 |
| **Output** | **Slag** | 679 | 0.9 | 0 | 22.1 | - | 20.2 | 26.2 | 22.8 | 1.8 | 1.5 | 4.5 |
| | **Alloy** | 538 | 14.5 | 5.6 | 50.6 | | | | | | 29.4 | |

| | | Recovery % (materials fate) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Component** | **Fraction (wt%)** | **Cu** | **Ni** | **Fe** | **CaO** | **SiO2** | **Al2O3** | **Li2O** | **Co** |
| **Slag** | 44.2 | 7.2 | 1 | 35.5 | 100 | 100 | 100 | 100 | 6 |
| **Alloy** | 55.8 | 92.8 | 99 | 64.5 | | | | | 94 |

**Table 3. Summary of the requirements regarding the input and output materials in a pyrometallurgical recycling process for LIBs**

| | Material /energy | Amount | Refrence |
|---|---|---|---|
| **Inputs** | LIBs | 30% (minimum)<br>50% (preferably) | (Cheret & Santen, 2007; Dunn et al., 2012; Kwade & Diekmann, 2018; Saloojee & Lloyd, 2015) |
| | sand | 0.15 kg/ kg LIBs | (Dai et al., 2019; Heulens et al., 2019) |
| | Limestone | 0.3kg /kg LIBs | (Dai et al., 2019; Heulens et al., 2019) |
| | Slag | 0.17 kg / kg LIBs (***steel industry slag***) | (Cheret & Santen, 2007; Rajaeifar et al., 2021; Saloojee & Lloyd, 2015) |
| | Coke | 0.33 kg/kg LIBs | (Cheret & Santen, 2007; Ciez & Whitacre, 2019; Zhou et al., 2021) |
| | $O_2$ | 130 $Nm^3$/1 ton LIBs | (Cheret & Santen, 2007; Heulens et al., 2019) |
| | Electricity (Plasma) | 4.68 MJ /kg LIBs | (Dai et al., 2019) |
| | | 1.3 MWh per ton LIBs | (Heulens et al., 2019) |
| | $Ca(OH)_2$ | 30 kg per ton of LIBs in input for gas treatment | (Rajaeifar et al., 2021) |
| | water | 1 kg per kg LIBs | (Fisher et al., 2006; Hischier et al., 2007; Richa, 2016) |
| **Outputs** | Alloy | An example presented in Table 2. | (Cheret & Santen, 2007; Ciez & Whitacre, 2019) |
| | Slag | An example presented in Table 2. | (Cheret & Santen, 2007; Ciez & Whitacre, 2019; Zhou et al., 2021) |
| | $CO_2$ | Mainly depends on the LIB and coke in the input | (Dunn et al., 2014; Winjobi et al., 2020) |

## 2. 3. Hydrometallurgical recycling method (Hydrometallurgy)

Hydrometallurgy is the most common process for recycling LIBs in some countries, such as China, and is known as a mature and reliable solution for recovering materials used in LIBs worldwide (Du et al., 2022; Jiang et al., 2022). In a hydrometallurgical recycling process, as with pyrometallurgy, the LIB is viewed as if it is an ore. However, the goal of recycling is not just limited to the valuable materials, and it goes for recovering materials within LIBs as much as possible. Therefore, it matches more to a circular economy paradigm than pyrometallurgy. Hydrometallurgy is a collection of chemical and physical processes that can be divided into three main stages: pretreatment to remove the impurities, leaching, and purification and recovering the material (Brückner et al., 2020; Ekberg & Petranikova, 2015). An overview of hydrometallurgy has been illustrated in Figure 5.

Unlike pyrometallurgy, pretreatment is crucial in hydrometallurgy because the chemical process for recovering the materials is usually designed for extracting specific types of materials (Larouche et al., 2020; S. E. Sloop, 2016). Some hydrometallurgy processes have been designed for recycling LIBs and NiMH batteries together, although they are mainly on a lab-scale (Liu et al., 2019). Generally, pretreatment includes chemical, physical, and thermal processes (H. S. Kim & Shin, Eun Jung, 2013), which depending on the process, sometimes just some of them are used for pretreatment. In the case of having EVs' spent LIBs from, the first part of pretreatment is removing the cover of the battery pack. Then the batteries are discharged, and their modules are disaggregated to obtain their cells separately. After that, the cells are usually shredded into small pieces to segregate different parts of LIBs, including electrolytes, and positive and negative electrodes. In this phase, the metallic scraps, such as aluminium, iron, and copper are transmitted for reuse in other industries and the cathode active materials are sent to the leaching process in the form of powder. In some cases, graphite is separated from the electrode powders to get recycled (Du et al., 2022). Although, it usually is extracted from the leaching process as a by-product (Neumann et al., 2022). Other parts, such as electrolytes containing hazardous materials, are burnt in furnaces and then disposed safely (Du et al., 2022; Neumann et al., 2022). It is worth mentioning that usually, the input of the hydrometallurgical process comes from a pyrometallurgical recycling plant. As explained in the previous section, the main output of a pyrometallurgy recycling plant is an alloy, containing the target material, including cobalt and nickel, which should get separated by a hydrometallurgical process.

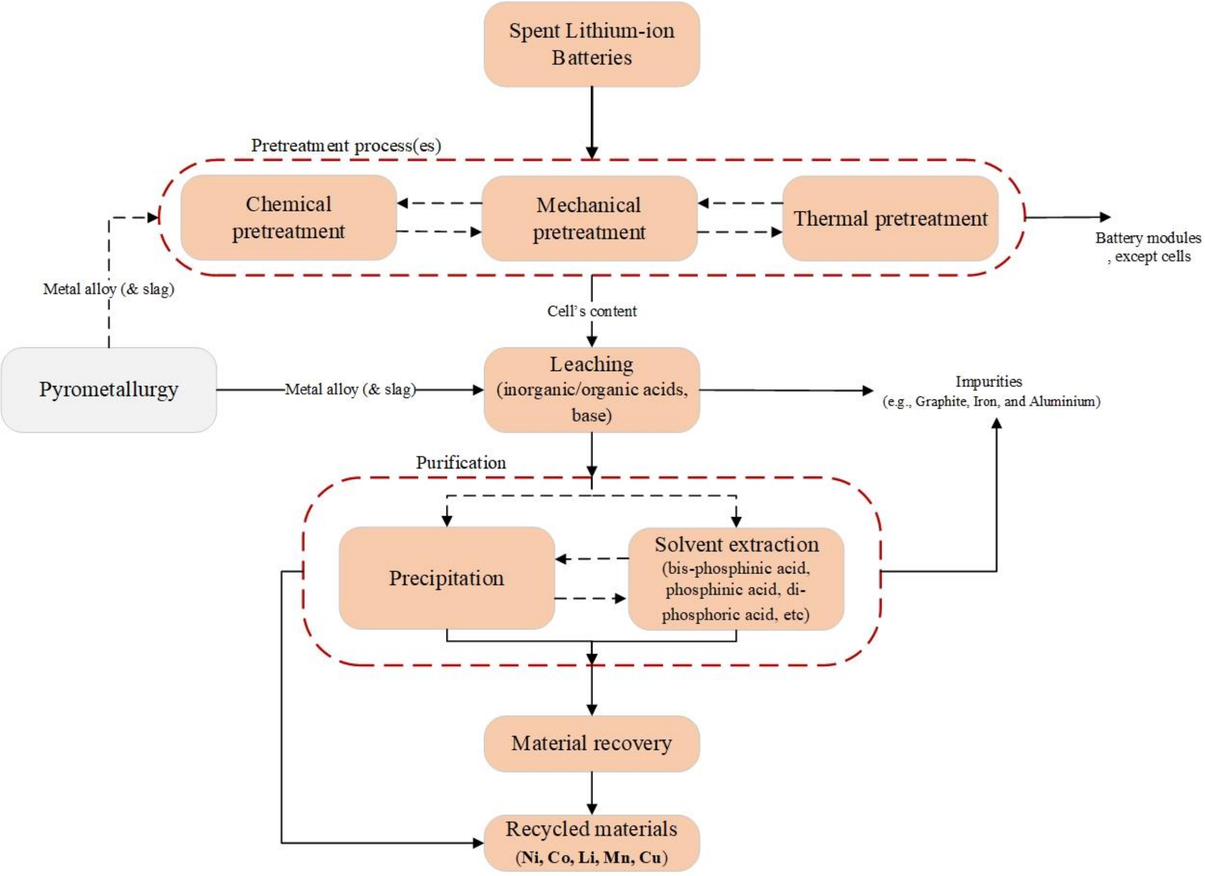

**Figure 5. An outline of the hydrometallurgical process**

Leaching is the first part of the chemical recovery in a hydrometallurgical process after pretreatment. The input of the leaching process is mainly the active cathode materials with some other elements that have not been removed completely in the pretreatment (Sommerville et al., 2021). In the leaching process, all of the inputs are mixed with water and acids to dissolve the inputs in a solution. Since organic compounds and graphite are not dissolved in the solution, they are removed from the rest of the materials by precipitation (Liu et al., 2019; Rinne et al., 2021). Different types of acids can be used in the leaching phase, including organic and inorganic acids, such as $H_2SO_4$, $H_2O_2$, HCl, and $C_6Hs_7$ (Ekberg & Petranikova, 2015; Zeng et al., 2014). Of these, $H_2SO_4$ (sulfuric acid) and $H_2O_2$ (hydrogen peroxide) are more common than others in the leaching process (Larouche et al., 2020). In addition to the type of acids used in the leaching phase, other factors such as temperature and leaching time affect the efficiency of the material recovery as well (Nogueira & Margarido, 2012).

After leaching, all the materials are extracted from the solution by changing the pH of the solution through different types of chemicals such as kerosene, P204, P507, sodium hydroxide (NaOH) (Du et al., 2022; Ma et al., 2022; Quan et al., 2022). Typically, manganese is the first product of the process that is obtained through a solvent extraction process, and then nickel, cobalt, and lithium are the next products of the recycling process (Neumann et al., 2022). It is worth mentioning that some elements such as iron, aluminium, and copper can reduce the efficiency and quality of the products (Ekberg & Petranikova, 2015). Hence, it is important to eliminate them before extracting the aforementioned elements.

Hydrometallurgy has gained a lot of attention in recent years due to specific reasons. First of all, it makes it possible to recover most of the materials existing within LIBs, including lithium, cobalt, manganese, nickel, copper, aluminium, and graphite (Gaines et al., 2021; Larouche et al., 2020; Sommerville et al., 2021; Thompson et al., 2020). As regarded, many of these materials are squandered in pyrometallurgical recycling processes, and it is not possible to reuse them in new LIBs. The second reason for the popularity of hydrometallurgy is its lower energy consumption than pyrometallurgy (Hendrickson et al., 2015; Zheng et al., 2018), which reduces environmental impacts stemming from the consumption of different types of fuels. Moreover, the quality of hydrometallurgy products is relatively higher than other recycling processes, which makes it a reliable solution for LIBs' material recovery (Larouche et al., 2020). Also, it is worth mentioning that hydrometallurgical recycling processes are capable of recycling LIBs with a low or even no amount of valuable materials (e.g., cobalt and nickel), such as LFP and LCO, while it is not economically viable to recycle them through the pyrometallurgical recycling process (Gaines, 2018).

Nonetheless, hydrometallurgy has some downsides that should be considered beside the advantages stated above. Firstly, the hydrometallurgical recycling processes are designed for specific types of batteries, and the impurities (materials other than the target materials for recycling) in the inputs materials can reduce the quality and rate of material recovery (Beaudet et al., 2020; Morawski, 2012). Hence, it is required to have a thorough pretreatment process before that. It should be noted that although a hydrometallurgical process can be utilized for recycling more than one type of LIBs, the efficiency of the recycling process is usually higher for the cases with just one type of spent LIBs in the input (Larouche et al., 2020). Moreover, the water consumption is relatively high in this method, converted to polluted wastewater with a high amount of chemicals. Therefore, there is a need for a wastewater recycling unit before releasing it into the environment. Last but not least, hydrometallurgy is known as a complicated recycling method in which many chemicals are used in its different phases. It should be noted that producing and using chemicals is associated with high environmental burdens. Nonetheless, despite the drawbacks mentioned above for hydrometallurgy, its advantages outweigh the disadvantages, and many companies in the world utilize it for recycling LIBs. Recupyl in France, GEM and Brunp in China, and Toxco in the US are some known companies in this regard (Knights & Saloojee, 2015; Sojka et al., 2020).

### 2. 3. 1. An overview on the materials and energy consumption in hydrometallurgy

Different chemicals are involved in a hydrometallurgical process depending on the input materials and process design. Accordingly, different recycling processes and chemicals can be used to recycle the same type of LIBs. The amount and type of materials existing in the literature are so diverse in this regard, for which there are specific reasons. First of all, the boundary of the systems studied in this regard is different. For instance, the primary treatment and dilution of the wastewater have been taken into account in some studies (Rinne et al., 2021), although it is not the case for most papers. Another reason that can be stated is that different recycling processes have different products. That is, depending on the type of chemicals used in the recycling, the chemical structure of the products containing the intended elements (e.g., cobalt, nickel, lithium, manganese, etc.) is different. Moreover, the efficiency of hydrometallurgical processes is different, although it is usually minor and negligible in most cases. Larouche et al. have done a comprehensive literature review in this regard and reported various parameters, including types of recycled LIBs, leach feed and acid concentration, leaching time, and recovery rates in the supplementary materials of their paper (Larouche et al., 2020). In this part, the materials (chemicals) and energy consumption have been investigated for recycling spent LIBs from EVs sector. In Table 4, some papers' life cycle inventory (LCI) has presented, of which cases number three (Mohr et al.) to five (Du et al.) are related to recycling spent NMC batteries; nonetheless, the type and amount of chemicals used in these processes are different. Papers in Table 4. are discussed briefly in the following.

**Table 4. An overview on the materials and energy used in different hydrometallurgical processes for recycling spent EVs' LIBs**

| **No.** | **1** | | **2** | | **3** | | **4** | | **5** | | **6** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **References** | **(Rinne et al., 2021)** | | **(Quan et al., 2022)** | | **(Mohr et al., 2020)** | | **(Jiang et al., 2022)** | | **(Du et al., 2022)** | | **(Dai et al., 2019)** | |
| **Type(s) of battery** | **LIBs + NiMH** | | **NMC battery** | | **NMC battery** | | **NMC battery** | | **NMC battery** | | **Not determined (n.d.)** | |
| **Scale of recycling** | **Lab-scale** | | **Industrial-scale** | | **Industrial-scale** | | **Industrial-scale** | | **Industrial-scale** | | **-** | |
| **Parameter** | **Amount** | **Unit** | **Amount** | **Unit** | **Amount** | **Unit** | **Amount** | **Unit** | **Amount** | **Unit** | **Amount** | **Unit** |
| **Spent battery** | 1 | kg | 1 | kg | 1 | kg | 1 | kg | 3.34 | kg | 1 | kg |
| **H2SO4 (98%)** | 3.15 | kg | 1.1 | kg | 0.796 | kg | 0.912 | kg | 3.94 | kg | 1.08 | kg |
| **HCl (30%)** | - | - | 0.04 | kg | | | 0.259 | kg | 0.338 | kg | 0.012 | kg |
| **NaOH (30%)** | 2.1 | kg | 1.87 | kg | 0.191 | kg | 0.654 | kg | 4.21 | kg | 0.561 | kg |
| **Na2CO3** | | | 0.021 | kg | 0.478 | kg | 0.0224 | kg | | | 0.02 | kg |
| **Ammonia (28%)** | | | 0.112 | kg | | | | | 0.00024 | | | |
| **P507 extractant** | | | 0.0002 | kg | | | 0.0000647 | kg | 0.000238 | kg | | |
| **P204 extractant** | | | | | | | | | 0.00024 | kg | | |
| **kerosene** | | | 0.00489 | kg | | | 0.000324 | kg | 0.00143 | kg | | |
| **H2O2** | | | 0.366 | kg | | | | | 2.04 | kg | 0.366 | kg |
| **Water** | 18.22 | kg | 14 | kg | n.d. | - | 6.47 | kg | 23.3 | kg | 3.79 | kg |
| **Li2CO3** | | | 0.121 | Kg | | | | | | | | |
| **Electricity** | 0.29 | kWh | 0.28 | kWh | 1.37 | kWh | 0.254 | kWh | | | 0.035 | kWh |
| **Natural gas** | | | 2.33 | m3 | | | 0.785 | MJ | 0.00702 | $m^3$ | | |
| **Oxygen Liquid** | | | | | 0.0956 | kg | | | 2.66 | kg | | |
| **Activated carbon filter** | | | | | 0.0648 | kg | | | | | | |
| **Inert gas (nitrogen, liquid)** | | | | | 1 | lit | | | | | | |
| **NaClO3** | | | | | | | 0.000141 | kg | | | | |
| **Steam** | | | | | | | 1.91 | MJ | | | | |
| **NaCl** (sodium chloride) | | | | | | | 0.00735 | kg | 0.0867 | kg | | |
| **Na2SO4** | 0.26 | kg | | | | | | | 0.000837 | kg | | |
| **KMnO4** | 0.05 | kg | | | | | | | | | | |
| **Na3PO4** | 0.11 | kg | | | | | | | | | | |
| **iron powder** | | | | | | | | | 0.00763 | kg | | |
| **CaO** | | | | | | | | | 0.0521 | kg | | |
| **NaF (sodium fluoride)** | | | | | | | | | 0.323 | kg | | |

The first paper in Table 4. (Rinne et al., 2021) is a study on the LCA of a proven hydrometallurgical recycling process for recycling mixed LIB and NiMH waste. The hydrometallurgical process was modeled based on a particular hydrometallurgical process proposed by Liu et al., in which NiMH batteries play the role of reductant for LIBs (Liu et al., 2019), to reduce the consumption of some chemicals such as $H_2O_2$. The modeling is mainly based on chemical reactions and stoichiometric relationships. This approach leads to the precise calculation of material/chemicals required for the process. However, since the reaction efficiency can be different in real situations, more materials may be needed in practice. The water consumption in this study is more than in other studies, which is mainly due to including the wastewater neutralization process in the boundary of the system studied in this research.

The second paper (Quan et al., 2022) is a comprehensive comparative LCA for two of the most common LIBs used in EVs, NMC and LFP. The study covers the whole life cycle of the batteries, from mining and refining in the battery production phase to recycling. The data presented in Table 4. are related to the recycling of NMC batteries. The LCA of the recycling phase has been done for two scenarios for each battery; pyrometallurgy and hydrometallurgy for NMC and hydrometallurgy and direct recycling for LFP. As explained earlier, LFP is not recycled through pyrometallurgy due to the lack of economic justification. The data used for the recycling phase has been gained from a battery recycling company in Guandong province in China.

The third paper (Mohr et al., 2020) aims to make generic models for hydrometallurgy and pyrometallurgy as benchmarks to compare the environmental impacts of an advanced hydrometallurgical process with them. The data in Table 4 are related to the materials and energy used in the advanced hydrometallurgical process gained from a recycling company. Also, the environmental impacts of recycling different LIBs have been compared to see which ones are associated with higher environmental benefits. One of the interesting points in this paper is the presentation of mean values for some of the environmental impact categories for pyrometallurgy and hydrometallurgy that are based on the literature review they have done in this regard. These values can be used as a basis to evaluate the result of other LCA existing for recycling LIBs.

The fourth (Jiang et al., 2022) and fifth (Du et al., 2022) papers in Table 4 are two of the last studies related to LCA of LIBs' recycling published at the time of writing this thesis. Jiang et al. investigated the environmental impacts of producing new LFP and NMC111 traction[2] batteries through materials recycled by a hydrometallurgical process and compared the results with the case of producing the same batteries with virgin raw materials. The LCI presented in their study is based on data gathered from some LIBs' recycling plants in China and the estimation of experts who collaborated with them in this study. Du et al. paper was specifically focused on just recycling NMC111 LIBs by a hydrometallurgical recycling process. However, the production of active cathode materials has also been included in this study. The LCI of this study comes from one of the world-leading companies in the scope of recycling batteries (including LIBs) located in Hubei and Jiangxi provinces, China. Compared to similar studies related to recycling LIBs, the list of materials and energy presented in this study seems to be more comprehensive, encompassing all the materials and energy required in recycling LIBs by a hydrometallurgical process. Nevertheless, there is not much detail regarding the processes used in the intended hydrometallurgical process.

Finally, the data presented in column six (Table 4) is based on a generic model prepared by Dai et al. at Argonne National Laboratory (Dai et al., 2019). Argonne is one of the most important research centers in the Energy sector located in the US, and part of its activities is focused on recycling LIBs (*Recycling | Argonne National Laboratory*, n.d.). A well-known model existing for the environmental assessment of LIBs' production and recycling is GREET. This model and its database were made and developed by

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[2] Traction battery is another name for the batteries used in vehicles.

Argonne group, which has been currently used in many studies. Nonetheless, the data presented in this model is abstract with a high level of approximation.

Although having a comprehensive list of materials and energy used in a recycling process is necessary to determine its environmental impacts, it does not give a clear notion of the process. It is helpful and illuminating to determine the units and sections of a recycling process in which various materials and energy are used in different parts. Therefore, the point of use of the chemicals in Table 4 has been illustrated in Table 5, which is based on the review done on hydrometallurgical processes elaborated in the literature. It is worth mentioning that some chemicals may be used in more than one part of the system, such as HCl, kerosene, and NaOH.

**Table 5. The application and point of use of chemicals presented in Table 4 regarding hydrometallurgical recycling processes**

| Chemical | Application/Possible point of use(s) | Reference |
|---|---|---|
| $H_2SO_4$ | Leaching | (Du et al., 2022; Larouche et al., 2020; Ma et al., 2022; Mohr et al., 2020; Rinne et al., 2021) |
| HCl | Leaching – Solvent extraction – stripping (cobalt extraction) | (Doaming, 2020; Dunn et al., 2014; Larouche et al., 2020; Ma et al., 2022, 2022) |
| NaOH | Leaching – iron removal - Precipitation | (Doaming, 2020; Dunn et al., 2014; Larouche et al., 2020) |
| P507 | Solvent extraction<br>(Li, Ni, Co extraction) | (Ma et al., 2022) |
| P204 | Solvent extraction<br>(Li, Ni, Co extraction) | (Doaming, 2020; Ma et al., 2022) |
| kerosene | Solvent extraction<br>(Li, Ni, Co extraction) | (Doaming, 2020; Ma et al., 2022) |
| $H_2O_2$ | Leaching | (Larouche et al., 2020; Liu et al., 2019; Ma et al., 2022) |
| Water | Leaching – wastewater neutralization | (Dai et al., 2019; Doaming, 2020; Dunn et al., 2012; Ma et al., 2022; Rinne et al., 2021) |
| $Li_2CO_3$ | Sintering - Firing | (Dunn et al., 2014) |
| $NaClO_3$ | Leaching | (TANG et al., 2020) |
| $Na_2SO_4$ | REEs[3] recovery - Leaching | (Du et al., 2022; Rinne et al., 2021) |
| $KMnO_4$ | Mn recovery | (Rinne et al., 2021) |
| $Na_3PO_4$ | Li recovery | (Rinne et al., 2021) |
| iron powder | copper removal - extraction | (Doaming, 2020) |
| CaO | Pretreatment | (Du et al., 2022) |
| NaF | Solvent extraction | (Rosales et al., 2019) |

As observed, different chemicals can be used in the leaching phase (e.g., HCl, $H_2SO_4$, $H_2O_2$, and NaOH), which depends on the type of the process. P507[4], P204[5], and kerosene are the chemicals that are usually consumed for solvent extraction, which is for extracting lithium, nickel, and cobalt. Other chemicals (except the ones mentioned above) appear less than other chemicals in the LCI of LCA studies for hydrometallurgical recycling of LIBs.

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[3] Rare Earth Elements.

[4] 2-ethylhexyl phosphoric acid-2-ethylhexyl ester

[5] Dioctyl Phosphate

## 2. 4. Direct recycling

Direct recycling is the most current method of recycling LIBs, which has a different approach concerning LIBs. The main aim of this recycling method is to recover the active cathode materials without any change in their morphological state and breaking their crystal structure (Gaines et al., 2021; Pinegar & Smith, 2019). Thereby, the extracted active materials can be used directly in manufacturing new LIBs. It is worth mentioning that in addition to cathode active materials, all the other parts of a LIB can be recycled through direct recycling, including electrolyte, biner and current collectors, which are wasted in other recycling methods. Generally, a direct recycling process can be divided to four main stages: preparation and processing of Spent LIBs, separation process, product upcycling, and recycled material quality investigation (Gaines et al., 2021), which has been demonstrated in Figure 6. However, it should be noted that the main goal of direct recycling is the extraction of the active materials, and hence, sometimes, all of the phases illustrated in Figure 6 are not accomplished.

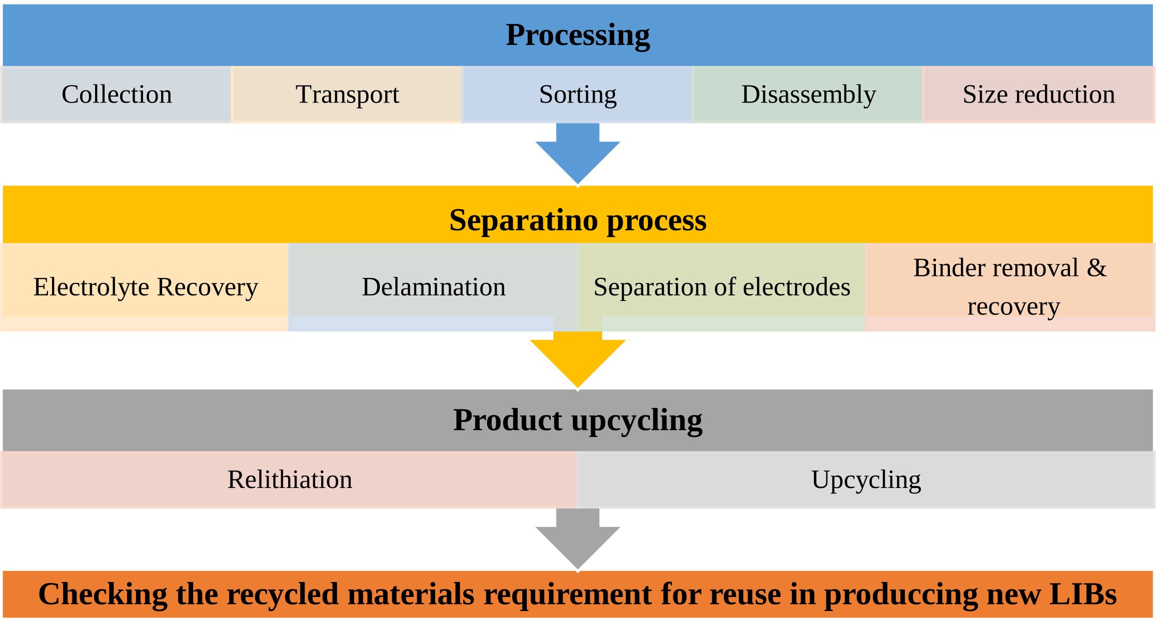

**Figure 6. The various phases of a direct recycling process**

The recovery process in direct recycling is designed for a specific type of battery. Therefore, it is important to have the LIBs sorted after collecting them. Afterward, LIBs are shredded through hammermills and/or shredders in small pieces around 0.6 mm to facilitate the separation of LIBs' different segments (Larouche et al., 2020). If the electrolyte is supposed to get recycled, it should be detached from the particles in this stage. Otherwise, it will be disintegrated in the next chemical processes, and it is not possible to recycle it anymore. Water washing, solvent extraction, and thermal drying are among the common methods utilized in this regard (S. Sloop et al., 2020; Spangenberger & Gillard, 2021a).

Delamination is the process of separating active materials attached to current collectors. For this purpose, it is important to get rid of the binder, which can be done through burning the binder, disaggregation of binders, or removing it by a chemical based on Ethylene Glycol (Bai et al., 2020; Larouche et al., 2020). The first two methods are simpler, although the binder is no longer recoverable. After the delamination process, aluminium and copper are segregated from the rest materials and can be used for making new current collectors.

After delamination, a mix of electrodes is obtained, which should get separated from each other. Froth floatation is the method usually used to this end, which works based on the hydrophilicity of cathode and anode active materials (Spangenberger & Gillard, 2021b). As stated before, graphite is the most common material used as the anode, which is hydrophobic in the presence of ambient air (Rathnayake et al., 2017). Now by having the active cathode materials, the relithiation process is carried out. As the function of LIBs described earlier, lithium moves between anode and cathode in the charging and discharging process of the battery, and it continues during its lifetime. However, gradually some lithiums remain in the graphite structure and do not commute between electrods. Therefore, the amount of lithium in cathode active materials decreases, and in the case of using them in new LIBs, at first lost lithiums should be replaced by new lithiums. This process is called relithiation, and can be done through various methods, such as chemical, thermal, hydrothermal, and redox mediator (Gaines et al., 2021; Spangenberger & Gillard, 2021a). The final phase of direct recycling is the evaluation of recovered materials, especially active cathode materials, to make sure they meet some specific qualitative requirements to be used in new LIBs.

Direct recycling has been one of the promising solutions to reach a circular economy paradigm in LIB industry. It has the potential to make it possible to recycle all of a LIB's components, regardless of its constituents. Moreover, the recycling process is more environmentally friendly, with fewer environmental impacts (Gaines, 2018). Nevertheless, it is still not a mature recycling process and has been implemented in a few projects globally. Despite all the merits, there are some serious challenges concerning direct recycling. First of all, the recycling process depends on the quality of LIBs in the input. That is, if the active materials within LIB have been damaged in the use phase, they are not recovered through direct recycling because they cannot be used directly in new LIBs anymore. Furthermore, direct recycling is complicated and requires a high level of knowledge and technology, which is not accessible everywhere (Larouche et al., 2020). Last but not least, the development and change in the LIB industry is occurring so fast, and the chemistry and structure of manufactured LIBs are going through different changes. Hence, there is a risk that recovered LIBs may not be usable in LIBs that are produced in the future (Gaines et al., 2021). These drawbacks are some of the main reasons that this recycling method has not been widely implemented worldwide. Therefore, due to the limited use of this recycling method and shortage of existing data, it was not investigated in this study.

## 2. 5. A review on the LIBs' recycling LCA studies

LIBs' Recycling has been developed significantly in recent years as a solution to tackle environmental and sustainability problems brought up due to the surge of LIBs. It requires the consumption of various materials, chemicals, and energy, which itself is associated with environmental impacts. LCA Studies on recycling LIBs may address one or both of the following issues: the environmental impacts of recycling processes and/or the environmental benefits of recycling materials within LIBs. Investigation of existing LCA studies on LIBs' recycling should be carried out with regard to their type and application. The LCA studies presented in the following are related to recycling LIBs from electric vehicles.

Rajaeifar et al. did a comparative study on recycling spent LIBs from EVs by pyrometallurgy (Rajaeifar et al., 2021). Their study investigated the three scenarios for recycling NMC111: recycling through a pyrometallurgical process with the direct current plasma technology with (Sc-1) and without pretreatment (Sc-2), and a conventional pyrometallurgical recycling process with a high-temperature furnace (Sc-3). The results of this study showed that the pyrometallurgical process with plasma technology is generally associated with lower global warming potential (GWP) compared to conventional pyrometallurgy. Also, pretreatment could reduce the GWP. This study took one ton of NMC111 as the functional unit, and the analysis was done based on two perspectives, closed-loop recycling and open-loop recycling. The former implies the reuse of materials for manufacturing new LIBs. However, the latter assumes the use of recycled materials in other industries. Accordingly, GWP was calculated -1200 (CO2-eq), -2080 (CO2-eq), and -770 (CO2-eq) for Sc-1, Sc-2, and Sc-3 respectively for the closed-loop recycling approach. The results of GWP for the open-loop recycling were 1100 (CO2-eq), -290 (CO2-eq), and 1410 (CO2-eq), in the same order of methods mentioned above. It is worth mentioning that the negative values are due to considering the environmental credits for the recycled materials. It has explained in the method section.

Quan et al accomplished a comparative cradle-to-cradle LCA for the NMC and LFP batteries (Quan et al., 2022). Concerning the recycling of NMC, two methods of pyrometallurgy and hydrometallurgy were investigated based on the LCIs obtained from the related industries in China. The functional unit of the LCA was a 1 kWh battery pack. The results showed that recycling made less environmental impacts compared to the other phases (production, first use, repurposing, second use, and recycling) of the intended LIBs' life cycle in most of the impact categories, including GWP, ozone depletion potential (ODP), eutrophication potential (EP), and acidification potential (AP). The study also concluded that the environmental benefit of recycling NMC through hydrometallurgy is higher than recycling it by pyrometallurgy. Gaines et al analyzed environmentally three existing methods of recycling LIBS, namely pyrometallurgy, hydrometallurgy, and direct recycling, concerning the recycling of NMC111 (Gaines et al., 2021). Their findings demonstrated the superiority of direct recycling over other recycling methods. Pyrometallurgy had less water consumption, $SO_2$ emission, and energy consumption compared to hydrometallurgy. However, the GWP calculated for pyrometallurgy and hydrometallurgy were close.

Mohr et al. conducted an LCA for different LIBs' recycling methods based on a review of existing studies in the literature (Mohr et al., 2020). They parametrized pyrometallurgical and hydrometallurgical recycling processes for recycling different types of LIBs, such as LFP, NMC, and NCA, and took 1 kg treated cells as the functional unit. Their study aimed to investigate the potential of LIBs' recycling in reducing battery production environmental impacts. According to this study's result, LIB type has a crucial role in this regard, and the most benefit is gained by utilizing the hydrometallurgical recycling of NMC111. It is mainly due to the recovery of cobalt and nickel. Moreover, based on the literature review accomplished in this study, the range of net GWP was -0.8 to -2.2 kg $CO_2$ per kg of NMC111 recycled through hydrometallurgy. The intended range for recycled NMC111 by pyrometallurgy was around +1.2 to -3.2 kg $CO_2$ for each kg of recycled battery.

In another study, Jiang et al. studied the environmental impacts of recycling LFP and NMC111 through a hydrometallurgical process and reusing the recycled material to produce new LIBs in China (Jiang et al., 2022). This study concluded that although the use of recovered material could generally reduce the environmental impacts of manufacturing new LIBs, the potential for reducing GWP was not considerable. This was mainly because of the efficiency of recycling processes and the electricity consumption in producing new LIBs in China. The last study presented here is a study by Du et al about the LCA of recycling NMC111 by a hydrometallurgical recycling process (Du et al., 2022). This study investigated the environmental impacts of all processes involved in a hydrometallurgical process, comprising spent battery collection, pretreatment, leaching and extraction, precursor production, and ternary cathode material production. As regarded, the processes related to the production of active cathode materials were also included in this study. The LCA was divided into different parts in this study, i.e., the environmental impacts of each part of the recycling process were calculated separately. The results illustrated that a significant share of environmental impacts in various impact categories was related to leaching and extraction phases in recycling. Pretreatment, precursor production, and spent battery collection were the next parts of recycling with the main role in environmental impacts.

# 3. Method

The main aim of this study was to perform a comparative LCA of a combined pyro- and hydrometallurgy method with an independent hydrometallurgy method for recycling LIBs. First each option was modeled to get the process flow diagrams. A flow diagram is a systemic model consisting of unit processes and flows of materials and energy used in the intended process/technology. Based on the definition by ISO14040, a unit process is the smallest part of the model, and energy and materials flow among them (ISO, 2006). Hence, there was a need to compile a comprehensive LCI consisting of all materials and energy consumed in the system. All the components within the boundary of the intended model are part of the system called the foreground. The remaining materials, energy, and activities beyond the foreground are called background flows. After compiling the LCI, inventory data pertaining to the materials and energy used in processes were identified in the Ecoinvent 3.7 database (Moreno Ruiz et al., 2020). Finally, the calculation of environmental impacts was accomplished through Arda 1.7, a Matlab-based LCA software developed by an industrial ecology research group at NTNU (Majeau-Bettez & Strømman, 2016).

## 3. 1. Functional unit

Spent NMC111, obtained from BEVs, was selected as the target battery in the recycling processes for the following LCA. Accordingly, the functional unit is 1 kg of spent NMC111 recycled through each method, which is one of the inputs to the intended processes. The material content of the intended battery was presented in detail in Table 1.

## 3. 2. Modeling the pyro- and hydrometallurgical recycling process

The pyro- and hydrometallurgical recycling model comprises a pyrometallurgical process and a supplementary hydrometallurgical process to extract the intended materials. The pyrometallurgical process was modeled based on the Umicore pyrometallurgical process patented by Cheret and Santen (Cheret & Santen, 2007), which is the most common process used in the existing LCA studies on recycling LIBs by pyrometallurgy method. The supplementary hydrometallurgical process just encompasses the necessary unit processes of a hydrometallurgy model needed to separate the elements in the alloy obtained from the pyrometallurgical process. This part of the model is based on the process suggested by Dunn et al (Dunn et al., 2012). Material and energy flows are also crucial to completing the model and they were added accordingly based on the literature review presented in Table 3.

### 3. 2. 1. Assumptions and limitations in pyro- and hydrometallurgical recycling model

The efficiency of LIBs' recycling processes are different case by case and depends on the recycling conditions, including the quality of input materials and the precision of process operation. The efficiency in the recycling processes investigated in this study are defined as the amount of target material recovered through the process in question. The target material in the pyro- and hydrometallurgical recycling process are cobalt and nickel. Hence, its efficiency in recycling is the percentage of the recovered cobalt and nickel from NMC111. The efficiency of the pyrometallurgical part assumed 94% and 99% for cobalt and nickel, respectively, which was based on the cobalt and nickel content of the alloy obtained from the pyrometallurgical process. The detail of alloy content was presented in Table 2. The study uses the values for the alloy content presented in Table 2 from Cheret and Santen (Cheret and Santen, 2007) because the quantity and quality of the input materials in both studies were similar. Concerning the hydrometallurgical part of recycling, the efficiency was assumed to be 100%. The reason behind this assumption is that generally, the efficiency and quality of a hydrometallurgical process for cobalt and nickel is high, especially if there is just one type of LIB in the input. The efficiency of hydrometallurgical recycling processes was investigated thoroughly in previous work by Dorri (Dorri, 2021).

The final products of LIBs' recycling processes are not in the form of pure elements, and depending on the chemicals and unit processes, target elements are combined with other compounds. In this study, the target elementary materials within the final products are the sole materials considered in the analysis of the environmental benefits of intended recycling processes. For instance, the target materials in the pyro- and hydrometallurgical recycling process are cobalt and nickel. The environmental benefits resulting from their recovery and subsequent use as a substitute to virgin raw materials in required industries was investigated for some environmental impact categories.

In addition to products, wastewater and $CO_2$ are other outputs of the system. $CO_2$ is considered a stressor and direct emission of the recycling process. Wastewater is a mix of water and all the contaminants stemming from the materials within LIBs and from materials used in different parts of the system. It is worth mentioning that no pretreatment was assumed for the process, and both processes involved in the LIBs' recycling are at the same location and there is no need for transportation between them.

## 3. 3. Modeling the hydrometallurgical recycling process

The diversity of hydrometallurgical recycling processes is more than pyrometallurgy. Even in the case of having the same type of LIBs in the input, different processes can be utilized in the hydrometallurgical process to recycle them. Hence, it is possible to present different models for a hydrometallurgical recycling process for recycling NMC111 batteries, and each one has different unit processes, chemicals, and energy requirements. In this study, the following criteria were taken into account to model a hydrometallurgy system based on the information and data available in the literature: completeness of available LCI, the scale of recycling process (industrial scale), and access to up-to-date process and data.

Accordingly, process number five, presented in Table 4, was selected as the base for modeling the hydrometallurgical recycling process, which was based on the study done by Du et al on a leading LIBs' recycling plant in Jiangxi province in China (Du et al., 2022). This study met all the intended criteria mentioned above. Firstly, the data was related to a real industrial case in China, a pioneer country in utilizing hydrometallurgical processes for recycling LIBs. Moreover, the study in question is one of the last studies published at the time of doing this master thesis with updated data. Also, the LCI presented for this case is more complete than other similar studies, which makes the result of LCA more reliable with less uncertainty. Nevertheless, the description of the hydrometallurgical process is abstract, and there is no flow diagram in detail. Hence, it is not specified which unit processes exist in the recycling process. To resolve this issue, a study was done on hydrometallurgical processes in the literature, and the unit processes were identified based on the chemicals existing in the LCI of the intended study. The results were presented in Table 5. Thereby, the final model was made based on the LCI obtained from the study mentioned above and the unit processes identified based on them in the literature.

### 3. 3. 1. Assumptions and limitations in the hydrometallurgical recycling model

As mentioned earlier, one of the main advantages of hydrometallurgy is the high efficiency of the recycling process and the quality of its products, especially if the process is designed for one type of LIB. Also, it should be noted that depending on the LIB(s) in the input and the processes utilized in a hydrometallurgical process, different materials can be recovered from LIBs. Based on the thorough literature review accomplished by Larouuche et al in 2020, in cases in which NMC111 was the only input of a hydrometallurgical recycling process, the main products are cobalt, nickel, lithium, and manganese, with efficiencies of more than 95% (Larouche et al., 2020). Accordingly, in this study, the main hydrometallurgical recycling process products for spent NMC111 were assumed to be cobalt, nickel, lithium, and manganese with 100% recovery rate. Besides products, some stressors and wastewater are also part of the system's outputs. Stressors were determined based on the explanation presented in the study by Du et al (Du et al., 2022), and all the other materials were assumed to end up in the wastewater. P204 and P507 are two common extractants used in hydrometallurgical processes in trivial amounts (P204, P507 = 7.18E-05, 7.12E-05). They were not available in the databases used in this thesis. Also, no related information was found in the literature in this regard. Therefore, they were assumed zero out of necessity.

### 3. 3. 2. Electricity consumption in the hydrometallurgical process

Various phases of a hydrometallurgical recycling process occur in reactors, thickeners, and filters, which require electricity to work. The electricity consumption is different case by case and should be measured for each case separately. In this study, the electricity requirement was calculated based on the electricity consumption model presented by Rinne et al (Rinne et al., 2021), who worked on an experimental hydrometallurgical recycling process. Accordingly, the electricity consumption was estimated in this study as follows: 3.33 kWh per ton of batteries for the leaching unit, 125.7 kWh per ton of manganese precipitated p204 solvent extraction unit, 242.29 kWh per ton of lithium and 60.62 kWh per ton of nickel in P507 solvent extraction, and finally, 225.29 kWh per ton of cobalt in the stripping unit.

## 3. 4. Life cycle impact assessment (LCIA)

This study adopted the ReCiPe 2016 approach (Huijbregts et al., 2017) to determine and assess the environmental impacts of recycling 1 kg NMC111. The main reason for this selection is that this method is more up-to-date than other methods, such as CML 2001. Also, many studies related to this subject had used it for the final LCIA based on the literature review done for this thesis. Among different midpoint impact categories existing in ReCiPe 2016 Global Warming Potential (GWP), Freshwater Eutrophication Potential (FEP), Human Toxicity Potential (HTP), Terrestrial Acidification Potential (TAP), Fossil Depletion Potential (FDP), and Ozone Depletion Potential (ODP) were used to illustrate the environmental impacts of each process.

## 3. 5. Methodological considerations in the calculation of environmental impacts

The environmental impacts of a recycling process can be calculated based on different methods and perspectives, of which two methods are the "simple cut-off" and "cut-off plus credit". Both were utilized in this thesis. The simple cut-off method just uses materials and energy consumed in the recycling process to measure the environmental impacts. However, the cut-off plus credit method also considers the avoided manufacturing of materials and products replaced by recycling (Ekvall et al., 2020). That is, the environmental impacts of the avoided production process due to the recycled materials should be subtracted from the environmental impacts calculated based on the simple cut-off method. While the first method does not give any environmental credit to the recycled material, the second encourages recycling by subtracting the avoided environmental impacts due to the reduced demand for virgin resources to the final environmental footprint of the recycling process.

Each of the methods described above gives different insights into the recycling methods investigated in this study. Therefore, applying both methods can help better grasp the environmental impacts of recycling processes and the benefits they can bring about. Hence, both were used in this study to evaluate LIBs' recycling processes from different perspectives.

## 3. 6. Considerations in comparing the environmental impacts of obtaining materials from LIBs vs. virgin sources

Five types of comparison were made in this study to investigate the environmental performance of obtaining materials from spent LIBs versus virgin sources. It should be noted that the materials recovered from hydrometallurgy are assumed to be cobalt, nickel, manganese, and lithium. However, in pyrometallurgy, recycled material implies just cobalt and nickel. Hence, the mass of these materials was taken into account as products' weight in analyses where it was needed.

The first comparison was between the environmental impacts of getting the materials from a pyrometallurgy recycling process versus producing the same amount through virgin sources. This comparison was accomplished from two aspects: products individually and the sum of all products together. The same evaluation was done for the materials recycled by hydrometallurgy and virgin materials. Finally, a comparison was made between the environmental impacts of getting 1 kg product from pyrometallurgy and hydrometallurgy.

In cases where the comparison of environmental impacts is related to materials individually, the total environmental impacts of the intended recycling process should be divided between products reasonably. This action is called allocation, which can be done through various methods. This was done based on the allocation by mass approach in this study. That is, the environmental impacts were distributed among products based on their weight. As a rule of thumb, chemicals and energy consumption correlate with the quantity and proportion of the materials recovered in a recycling process. Consequently, more environmental impacts were attributed to the material/products with higher weight. It is worth mentioning that there was no need to do the allocation in cases where the comparison was based on products in accumulated form.

## 3. 7. The basis of LCA mathematical calculations in Arda

Arda does the LCA mathematical calculations based on an input-output analysis approach. The explanation of LCA calculation through Arda is provided in the following based on Strømman (Strømman, 2010). The calculation of environmental impacts is accomplished based on the unit processes and materials and energy required to fulfill the functional unit. To this end, all the materials and energy consumed in unit processes should be connected to the functional unit. This process is done by forming specific vectors and matrices.

"A" matrix is called the requirements matrix. Its components represent the materials and energy of unit processes required to produce per unit output of processes existing in the foreground. Its components are in the general format of $a_{ij}$, which is the required output flow from process *i* to process *j* per unit production in process j. This matrix also demonstrates the connections between foreground (*f*) and background (*b*) processes with *ff*, *fb*, *bf*, and *bb* indices. Equation (1) demonstrates matrix A. As observed, matrix A is a square matrix.

$$A = \begin{bmatrix} a_{11} & \cdots & a_{1n} \\ \vdots & \ddots & \vdots \\ a_{n1} & \cdots & a_{nn} \end{bmatrix} = \begin{bmatrix} A_{ff} & A_{fb} \\ A_{bf} & A_{bb} \end{bmatrix} \qquad (1)$$

The second matrix is the matrix "Y" which expresses the external demand of each process, including the functional unit. The Y matrix is in the form of a vector.

$$Y = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix} \qquad (2)$$

"X" matrix is the output matrix and represents the output of different units in the system. X matrix covers the external demand and other demands that are related to fulfilling the external demand. It is a vector matrix illustrated in Equation (3).

$$X = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} \qquad (3)$$

The matrices introduced above are related to each other through Equation (4). However, it also can be demonstrated as Equation (5), in which L is called the Leontief inverse and is equal to $(I - A)^{-1}$.

$$X = AX + Y \quad (4) \quad , \quad (I - A)X = Y \rightarrow X = LY \quad (5)$$

*L* relates the total production to per unit demand in matrix Y. *I* is a square identity matrix the same size as the X matrix. So far, all flows of materials and energy between different processes have been determined. The goal of the calculations is to determine the environmental impacts of the system in question. Hence, the stressors associated with all used materials and energy should be applied to them, which is carried out through the "S" matrix, which is the stressor intensity matrix.

$$S = \begin{bmatrix} s_{str1\,pro1} & \cdots & s_{str\,1\,prom} \\ \vdots & \ddots & \vdots \\ s_{strn\,pro\,1} & \cdots & s_{str\,m\,pron} \end{bmatrix} \quad (6)$$

Each column in the S matrix is related to a process in the system, and its indices represent the amounts of stressors stemming from them. The total amount of emitted stressors is calculated based on Equation (7).

$$e = SX \quad (7)$$

"e" is a vector in which the value of each row shows the amount of a specific stressor. However, it does not demonstrate the origin of each stressor. To specify the stressors emitted from each process, X matrix should be diagonalized, i.e., its components lay in the matrix diagonal, and its other components are zero. The diagonalized matrix is shown as $\hat{X}$, and the emission matrix is E.

$$\hat{X} = \begin{bmatrix} x_1 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & x_n \end{bmatrix} \quad , \quad E = S\hat{X} \qquad (8)$$

The next phase is to convert the emissions/stressors to environmental impacts. It is accomplished through characterization factors, which are in the format of a matrix called the C matrix. The intended impacts are calculated based on Equation (9).

$$d = Ce \quad (9)$$

"d" matrix is a vector that just shows the environmental impacts. However, the role of different processes is not specified in the calculated environmental impacts. Equation (10) is used to determine the contribution of each process to the calculated environmental impacts. Each column of $D_{pro}$ is related to a process in which rows express the contribution of that process to different environmental impact categories.

$$D_{pro} = CE \quad (10) \quad , \quad D_{pro} = \begin{bmatrix} d_{imp1\,pro1} & \cdots & d_{imp1\,pro\,m} \\ \vdots & \ddots & \vdots \\ d_{imp\,n\,pro1} & \cdots & d_{imp\,n\,pro\,n} \end{bmatrix}$$

Finally, Equation (11) is utilized to investigate how each stressor affects the environmental impacts. The difference between $D_{str}$ and $D_{pro}$ is that the columns in $D_{str}$ represent the stressors and the rows show the contribution of stressors to the environmental impacts.

$$D_{str} = C\hat{e} \quad (11) \quad , \quad D_{str} = \begin{bmatrix} d_{imp1\,str1} & \cdots & d_{imp1\,str\,m} \\ \vdots & \ddots & \vdots \\ d_{imp\,n\,str1} & \cdots & d_{imp\,n\,str\,n} \end{bmatrix}$$

# 4. Inventory modeling

The flow diagrams of methods in question for LIBs' recycling and their corresponding LCI were prepared based on the literature review done for this study. The summary of material and energy requirements for the pyro- and hydrometallurgical process is presented in Table 3. The intended data for the hydrometallurgical process is shown in Tables 4 and 5. There are the foreground data and all the activities and processes beyond them are related to the background. The study assumed that the location of the recycling plants is in Europe. Accordingly, the average European (RER) data were used for the background processes related to chemicals and materials production and energy supply from Ecoinvent 3.7. In cases that the intended item was not available, the global (GLO) data was used instead.

## 4. 1. Pyro- and hydrometallurgical recycling process model and LCI

The generic model of a pyro- and hydrometallurgical recycling process has been illustrated in Figure 7. It was made based on the information presented in the literature review. As observed, the spent batteries enter the furnace with coke and slag formers to be heated in different phases. The outputs of this part of the system are an alloy, slag, and gases containing hazardous compounds and materials, such as fluorine, chlorine, and Halogens. The gas stream is sent to the gas treatment chamber, and the alloy is transferred to the supplementary recycling processes in the hydrometallurgy plant. Slag is usually sent for waste disposal in landfills, although it can also be used as concrete aggregate. The hydrometallurgical plant is responsible for separating materials within alloy to obtain the desired products of the whole process, namely cobalt and nickel.

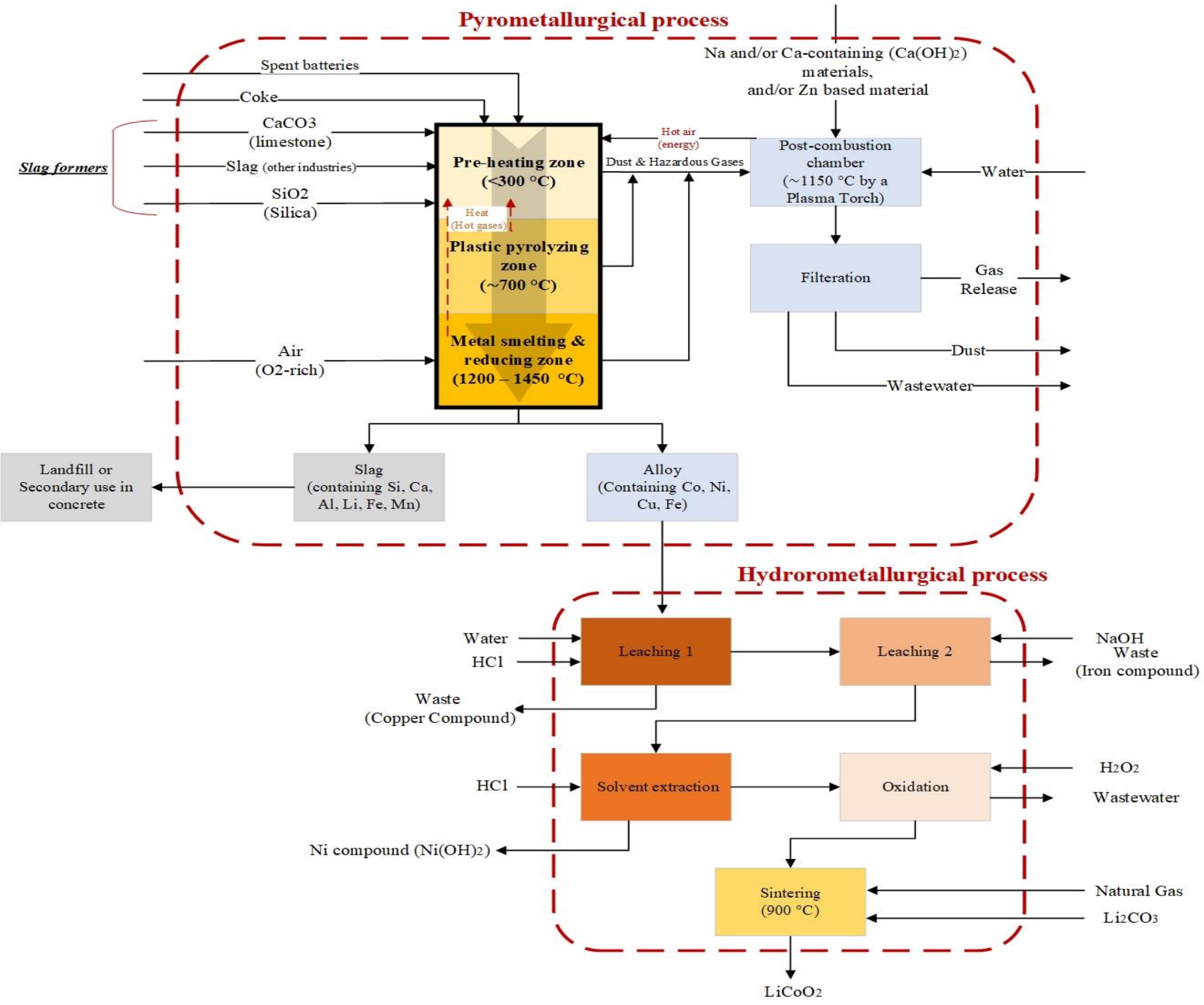

**Figure 7. Pyro- and hydrometallurgy model**

As shown in Figure 7, various materials are used in different parts of a pyro- and hydrometallurgy recycling process, which have been presented in Table 6. The amounts of materials and energy in the table are required to recycle 1 kg of NMC111 and recover nickel and cobalt, calculated based on the requirements mentioned in Table 3.

**Table 6. LCI of presented pyro- and hydrometallurgy model for recycling 1 kg NMC111**

| **Unit** | | **Material/energy** | | **Amount** | **unit** |
|---|---|---|---|---|---|
| **Inputs** | Pre-heating zone | Spent LIBs (NMC111) | | 1.00E+00 | kg |
| | | Coke | | 3.30E-01 | kg |
| | | Slag formers | sand (silica) | 1.50E-01 | kg |
| | | | limestone | 3.00E-02 | kg |
| | | | slag from steel industry | 1.70E-01 | kg |
| | Metal smelting & reduction zone + gas treatment | $O_2$ | | 1.30E+00 | m3 |
| | | water | | 3.00E-02 | kg |
| | | Electricity | | 9.10E+00 | kWh |
| | | $Ca(OH)_2$ | | 2.10E-01 | kg |
| | Leaching 1 + Leaching 2 + Solvent extraction | water | | 6.00E-02 | kg |
| | | HCl | | 1.87E+00 | kg |
| | | Electricity | | 8.00E-02 | kWh |
| | | NaOH | | 5.00E-02 | kg |
| | Oxidation | $H_2O_2$ | | 4.76E+00 | kg |
| | Sintering | $Li2CO_3$ | | 7.70E-01 | kg |
| | | Heat | | 1.00E+00 | MJ |
| **output** | Metal smelting & reduction zone + gas treatment | Slag | | 7.90E-01 | kg |
| | | Wastewater from Pyro | | 3.80E-01 | kg |
| | | CO2 | | 7.00E-02 | kg |
| | | Dust | | 1.00E-02 | kg |
| | Leaching 1 | copper compound | | 1.20E-01 | kg |
| | Leaching 2 | iron compound | | 1.01E+01 | kg |
| | Solvent extraction | **nickel compound** | | 1.20E-01 | kg |
| | Oxidation | Wastewater from Hydro | | 1.30E+00 | kg |
| | Sintering | **cobalt compound** | | 3.00E-02 | kg |

Pre-heating zone, metal smelting, reduction zone, and gas treatment are the parts of the pyrometallurgy plant. The rest, including leaching, solvent extraction, oxidation, and sintering, are unit processes in the hydrometallurgical recycling process. Nickel and cobalt compounds are the products of the system, shown in red, and are in the forms of $Ni(OH)_2$ and $LiCoO_2$, respectively. The pyrometallurgical process requires more energy supplied by electricity and coke. However, most of the chemicals are used in the unit processes related to hydrometallurgy.

## 4. 2. Hydrometallurgical recycling process model and LCI

The hydrometallurgical recycling process investigated in this study has been presented in Figure 8. The recycling process starts with the pretreatment unit, in which the active cathode materials are separated in the form of a powder. It mainly contains cobalt, nickel, lithium, and manganese; however, some impurities, including Copper, aluminium, iron, and graphite, also exist in it. The powder is transmitted to a reactor for the leaching phase, which is usually the most chemical-intensive part of recycling in a hydrometallurgical process. All the other outputs of pretreatment are either wasted or sent for reuse in other industries, such as scrap metal and plastics.

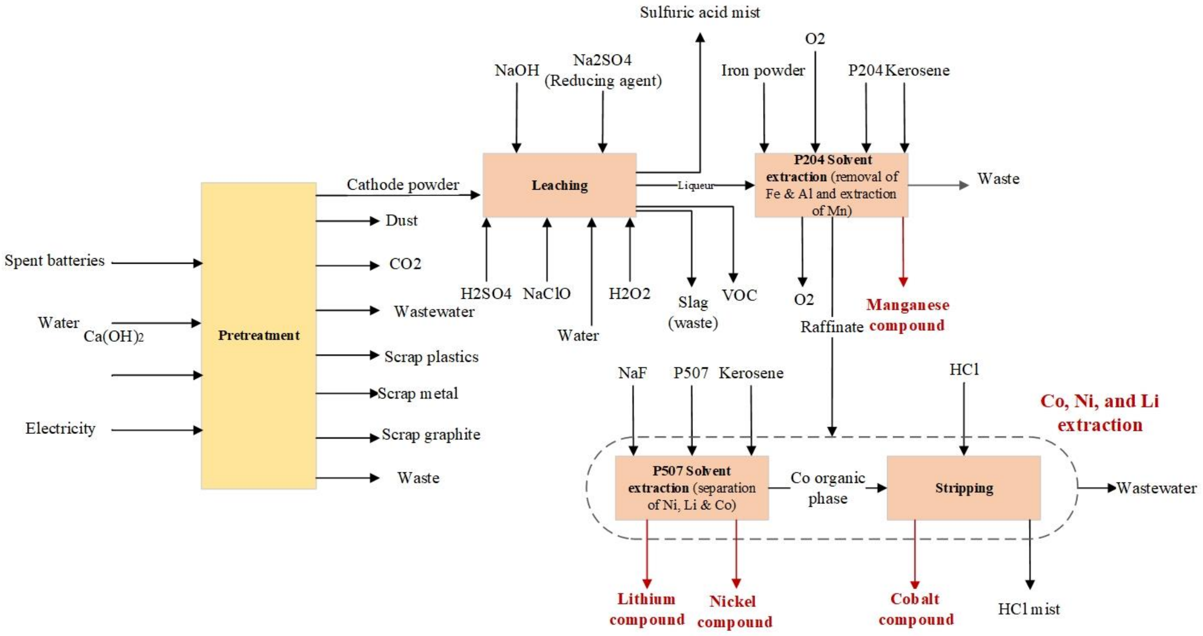

**Figure 8. Hydrometallurgy model investigated in this study**

Water, sulfuric acid, hydrogen peroxide, and reducing agents (such as sodium sulfate and sodium hydroxide) are also added to the leaching reactor to dissolve all the inputs in a solution and to remove the impurities existing in the input, such as the particles from graphite and current collectors. The acids are reactive, and a minor portion is evaporated from the leaching process. After leaching, the organic impurities are separated, and a stream of liquor is transmitted to the first solvent extraction unit. In this phase, kerosene and P204 extractant are used to remove the metallic impurities, such as iron and manganese. The rest of materials are sent for the next extraction process for the separation of other intended materials. Extraction of cobalt, nickel, and lithium occurs through the next solvent extraction unit and stripping phase, which were incorporated into one sector in the modeling for the sake of simplifying the analysis of environmental impacts. P507 is another extractant used to separate cobalt from the solution, which is later extracted in a stripping process.

One of the outputs of the last phase of hydrometallurgy is wastewater containing the chemicals used in the different phases of the recycling process. It is extremely polluted and should be treated properly before releasing into the environment. A complete list of materials and energy used in the hydrometallurgical process has been presented in Table 7.

**Table 7. LCI of presented hydrometallurgy model for recycling 1 kg NMC111**

| **Unit** | | **Material/energy** | **Amount** | **Unit** |
|---|---|---|---|---|
| **Input** | Pretreatment | spent batteries | 1.00E+00 | kg |
| | | water | 6.60E-02 | kg |
| | | $Ca(OH)_2$ | 1.56E-02 | kg |
| | | electricity | 2.59E+00 | kWh |
| | Leaching | water | 6.97E+00 | kg |
| | | sodium hydroxide (NaOH) | 1.26E+00 | kg |
| | | sodium sulfade ($Na_2SO_4$) | 2.51E-04 | kg |
| | | sulfuric Acid ($H_2SO_4$) | 1.18E+00 | kg |
| | | sodium hypochlorite ( NaClO) | 2.60E-02 | kg |
| | | electricity | 1.42E-03 | kWh |
| | | hydrogen peroxide ($H_2O_2$) | 6.12E-01 | kg |
| | P204 solvent extraction | iron powder | 2.29E-03 | kg |
| | | Liquid oxygen | 7.99E-01 | kg |
| | | P204 | 7.18E-05 | kg |
| | | electricity | 3.46E-03 | kWh |
| | | kerosene | 4.28E-04 | kg |
| | Co, Ni, and Li extraction unit | sodium fluoride (NaF) | 9.69E-02 | kg |
| | | kerosene | 4.28E-04 | kg |
| | | P507 | 7.12E-05 | kg |
| | | electricity | 2.03E-02 | kWh |
| | | Hydrochloric acid (HCl) | 1.01E-01 | kg |
| **Output** | Pretreatment | Dust | 3.60E-05 | kg |
| | | $CO_2$ | 4.23E-03 | kg |
| | | wastwater | 1.08E+01 | kg |
| | | scrap plastics | 2.10E-01 | kg |
| | | scrap metal | 1.92E-01 | kg |
| | | slag (waste) | 2.70E-02 | kg |
| | | scrap graphite | 1.43E-01 | kg |
| | Leaching | sulfuric acid mist | 9.80E-07 | kg |
| | | slag (waste) | 1.75E-01 | kg |
| | | VOCs | 7.14E-05 | kg |
| | P204 solvent extraction | $O_2$ | 2.88E-01 | kg |
| | | Mn cmopound | 2.75E-02 | kg |
| | | Scrap metal (Fe, Al, Cu) | 5.87E-02 | kg |
| | Co, Ni, and Li extraction unit | HCl mist | 3.68E-05 | kg |
| | | wastwater | 1.08E+01 | kg |
| | | NCM precursors | 1.82E-01 | kg |

# 5. Results

In this part, the results of LCA are presented from different perspectives because they can together give a better reflection and image of the intended recycling methods to compare them properly. As explained in the method chapter, the environmental impacts were calculated based on two approaches: the simple cut-off and cut-off plus credit. The simple cut-off method just considers the materials and energy used in the recycling processes to calculate the environmental impacts. On the other hand, the cut-off plus credit method, in addition to the materials and energy, also takes into account the avoided manufacturing of materials and products replaced by recycling. While the first approach focuses on the environmental impacts of materials and energy consumption in recycling processes, the second approach also considers the environmental benefits caused by recovered materials. After the presentation of environmental impacts for different categories, the role of various processes is investigated to illustrate the main sources of environmental burdens in each recycling process. Finally, a comparison is made between the environmental impacts of recycling materials from NMC111 and producing the same amount through virgin resources.

## 5. 1. Environmental impacts based on simple cut-off approach

The results of LCA conducted for pyro- and hydrometallurgy and hydrometallurgy recycling methods are presented for several impact categories from ReCiPe 2016. They include climate change (GWP), freshwater eutrophication potential (FEP), human toxicity potential (HTP), terrestrial acidification potential (TAP), fuel depletion potential (FDP), and ozone depletion potential (ODP). The results of LCA in this part are based on the simple cut-off approach described in the method section.

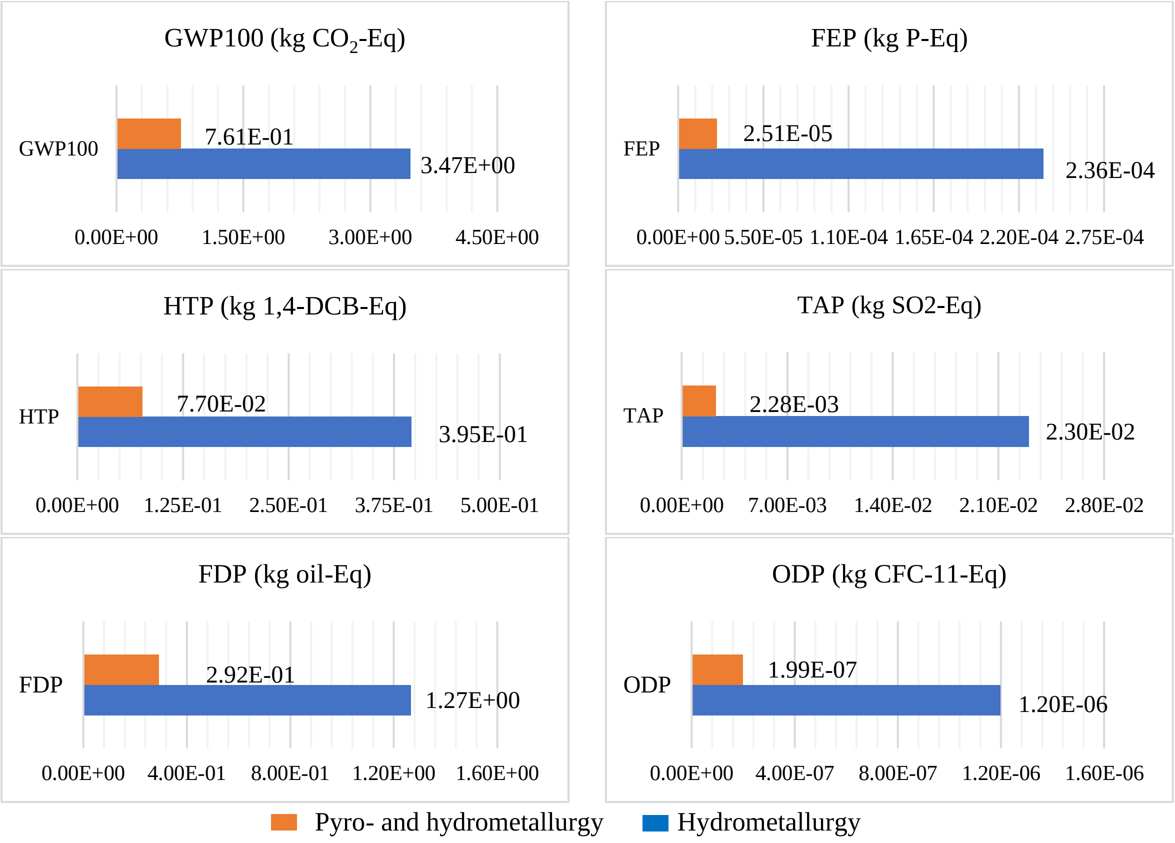

**Figure 9. Environmental impacts based on ReCiPe 2016 for the investigated LIBs' recycling methods**

Pyro- and hydrometallurgy method had a better performance in all impact categories presented above. It shows the environmental advantages of this method over hydrometallurgy for management and recycling spent NMC111. Most of the impact categories demonstrated in Figure 9 are in different orders of magnitude. Therefore, it makes more sense to investigate the options' differences for each impact category based on their ratio. Their main difference is in the TAP impact category, where the value for the hydrometallurgy option is more than ten times that of the other option. And their least divergence is related to the FDP impact category, in which the impact of hydrometallurgy is 4.35 times of pyro- and hydrometallurgy.

Higher environmental impacts of hydrometallurgy method in different impacts categories mainly stem from the chemicals, including hydrogen peroxide and acid sulfuric, and background processes related to producing them. Hence, a significant part of hydrometallurgy's environmental burden are indirect and not from the process itself. The hydrometallurgical part of the pyro- and hydrometallurgy method requires less chemical consumption because its input compound contains materials that are easier to separate. Also, there are no impurities in its input, such as graphite and electrolyte, as they are completely burnt in the pyrometallurgical process phase.

### 5. 1. 2. Contribution analysis

The contribution analysis aims to determine the extent to which different parts of the system affect the environmental impacts calculated in an LCA. The contribution analysis of pyro- and hydrometallurgy method is presented in Figure 10. Leaching and solvent extraction have a dominant role in all the impact categories. It implies that the hydrometallurgical part of the recycling causes more environmental impacts than the pyrometallurgical process. It is mainly due to the chemicals used in these phases. A more detailed explanation is given in the discussion section. The main part of the pyro- and hydrometallurgy direct emission is related to the carbon dioxide emission from the metal smelting and reduction zone in the pyrometallurgical process. Nevertheless, it has a minor effect on various environmental impact categories.

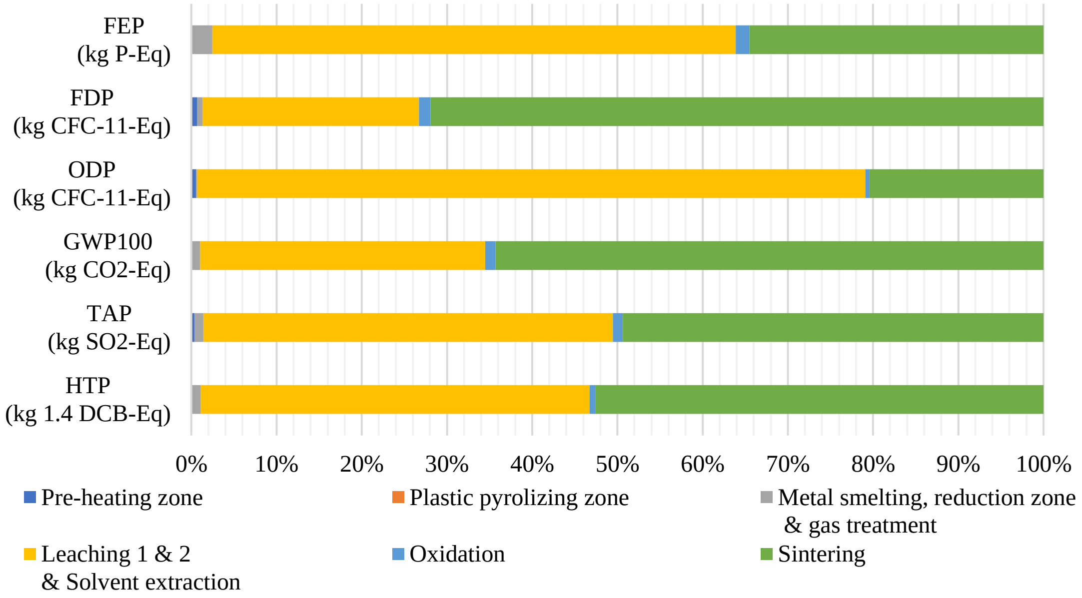

**Figure 10. Contribution analysis for the impact categories investigated for pyro- and hydrometallurgy**

The contribution analysis of the hydrometallurgy method is demonstrated in Figure 11. Leaching is also the main contributor to all the environmental impacts investigated for the hydrometallurgical process. Solvent extraction, stripping, and pretreatment are the next unit processes effective in the environmental impacts categories studied in this study. It is worth mentioning that the main direct emission of the hydrometallurgy method is the wastewater produced due to mixing water with various chemicals. Nonetheless, the direct emissions of the hydrometallurgical process are trivial compared to its indirect emissions.

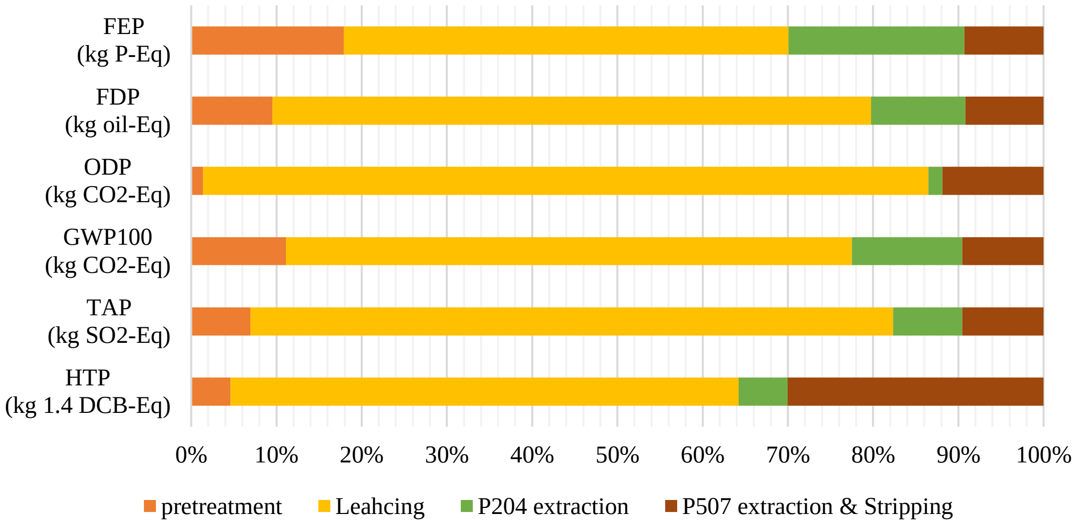

**Figure 11. Contribution analysis for the impact categories investigated for hydrometallurgy**

## 5. 2. Environmental impacts based on cut-off plus credit approach

The result of calculating environmental impacts based on the cut-off plus credit approach are in Figure 12. The values are negative for most of the environmental impact categories. This is because of giving environmental credit to the products of recycling processes. That is, the environmental impacts of avoided production processes (due to recycled materials) were subtracted from the environmental impacts presented before based on the simple cut-off approach. In this case, the difference between the results of the hydrometallurgy recycling method are closer to the pyro- and hydrometallurgy, and it also had a better performance in HTP and TAP categories. This is mainly because of the capability of hydrometallurgy to recover more materials than the pyro- and hydrometallurgy method. Nevertheless, pyro- and hydrometallurgy has better performance in most environmental impact categories.

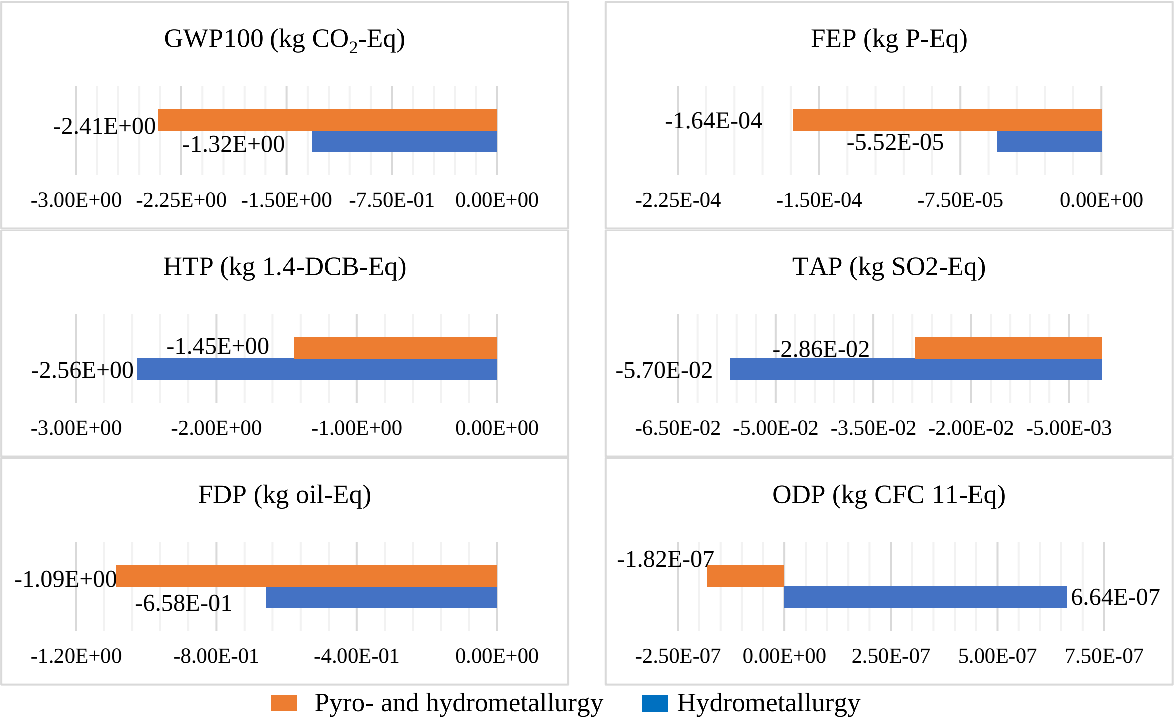

**Figure 12. Environmental impacts based on ReCiPe 2016 for the investigated LIBs' recycling methods with considering environmental credit for recycling products**

## 5. 3. Comparative environmental evaluation of obtaining products through recycling NMC111 vs. virgin resources

In this part, a comparison is made between the environmental impacts of obtaining the materials through recycling NMC111 versus producing the same amount from virgin resources. For this purpose, the environmental impacts of recycled materials are determined through allocation by mass. It is worth mentioning that the environmental impacts were calculated based on the simple cut-off approach used for the following set of comparisons. The recycling process investigated in this thesis can have different products coming from different parts of the LIB. The focus of this study is on the materials recovered from the LIB's cells.

### 5. 3. 1. Pyro- and hydrometallurgy vs. Virgin resources

The products of the pyro- and hydrometallurgy recycling method are 72 g cobalt and 75.5 g nickel per kg of spent NMC111, which have been specified based on the recovery efficiency assumed in this study. The environmental burdens of recycling them were calculated based on dividing the environmental impacts by their mass (allocation by mass). Accordingly, the results of the intended comparison are presented in Figure 13 for two impact categories of GWP and ODP. It should be noted that the values in Figure 13 are based on the mass of material recycled per kg of NMC111.

The results show that recovering cobalt through recycling NMC111 resulted in less environmental impacts for both categories if otherwise produced from virgin resources. However, it is not the case for nickel. Although its production is more environmentally friendly through recycling NMC111 from the GWP point of view, the emission of its production would be less in the case of producing it from the virgin resources based on the ODP category. The main reason of the significant comparative advantage of obtaining cobalt through recycling NMC is that producing cobalt through virgin resources is associated with high environmental burdens.  However, producing nickel through virgin resources causes less environmental impact compared to cobalt.

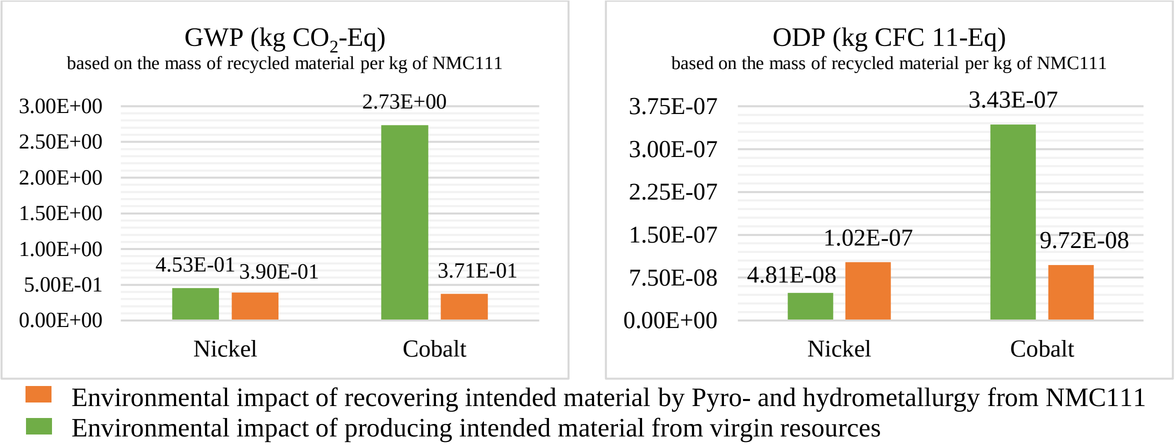

**Figure 13. Comparison of the environmental impact of obtaining nickel and cobalt (recycling vs. virgin resources)**

An alternative method for conducting the intended comparison is by comparing the environmental impacts of total products in accumulated form. The advantage of this comparison is that there is no need to determine each product's environmental impacts individually. Thus, the allocation method used to specify the share of environmental impacts of recycling each material from the total environmental impacts in the previous comparison is of no use in this comparison. The results of the comparison based on the whole products in question are presented in Figure 15. As observed, the environmental impacts of total products of pyro- and hydrometallurgy (nickel & cobalt) are much less than producing them through virgin resources. The largest reduction of environmental impacts is related to terrestrial acidification potential.

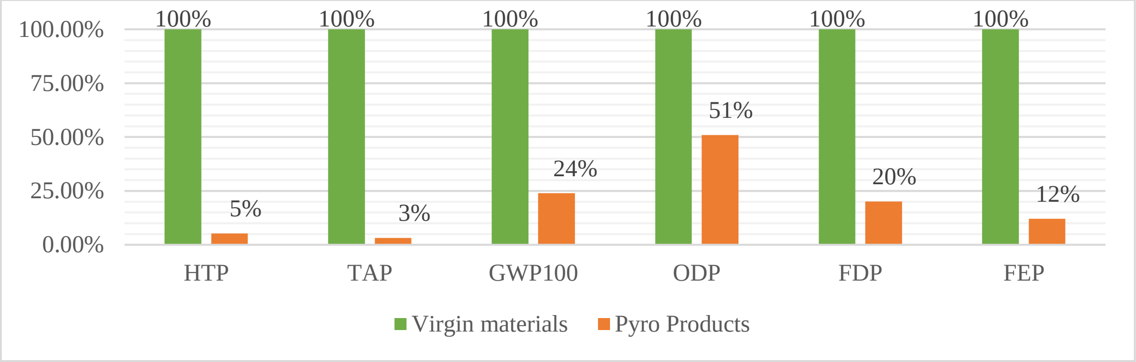

**Figure 14. Comparative environmental evaluation of total products obtained through pyro- and hydrometallurgy vs. producing the same amount of products through virgin materials/resources**

## 5. 3. 2. Hydrometallurgy vs. virgin resources

The environmental evaluation comparison is made for the hydrometallurgy recycling method in this part. Hydrometallurgy is capable of recycling more materials than the pyro- and hydrometallurgy method. Products of hydrometallurgy are 77.4 g cobalt, 77.1 g nickel, 27.6 g lithium, and 27.5 g manganese per kg of spent NMC111 in this study. The results have been illustrated in Figure 15. As considered, the results are not the same for different products and environmental impacts categories. Regarding the GWP impact category, cobalt and lithium showed less environmental burden in the case of producing them through recycling NMC111 by hydrometallurgy. Producing manganese and nickel using virgin resources was more environmentally friendly based on both investigated environmental impact categories. The allocation by mass approach was used to determine the environmental impacts of individual products.

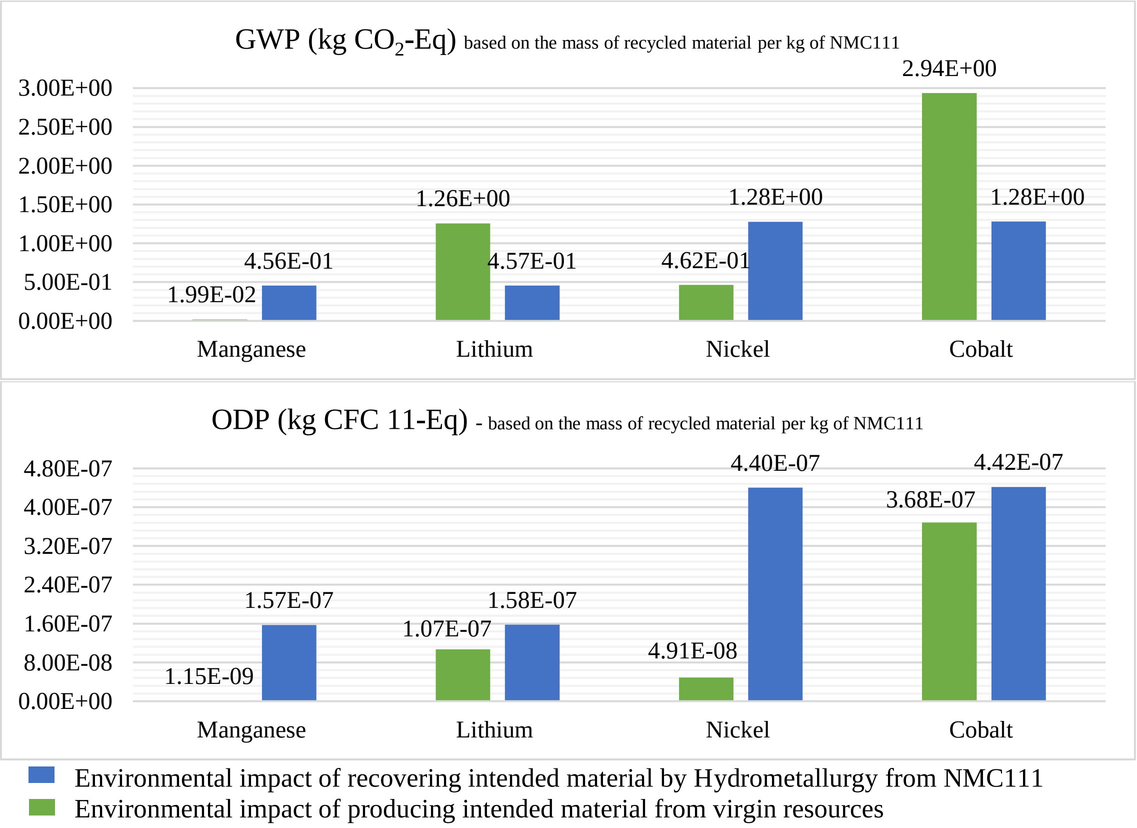

**Figure 15. The comparison of environmental impact of obtaining nickel, cobalt, manganese, and lithium**

Another evaluation was carried out based on the total products accumulated to avoid allocation, as with the investigation done for the pyro- and hydrometallurgy method. The result of the intended evaluation is presented in Figure 16. The results of all impact categories except ODP show that in the case of recycling NMC111 by hydrometallurgy, getting the intended materials is associated with less environmental impacts. Hydrometallurgy has a high potential for deterioration of ozone depletion, which the reason is elaborated on in the discussion section.

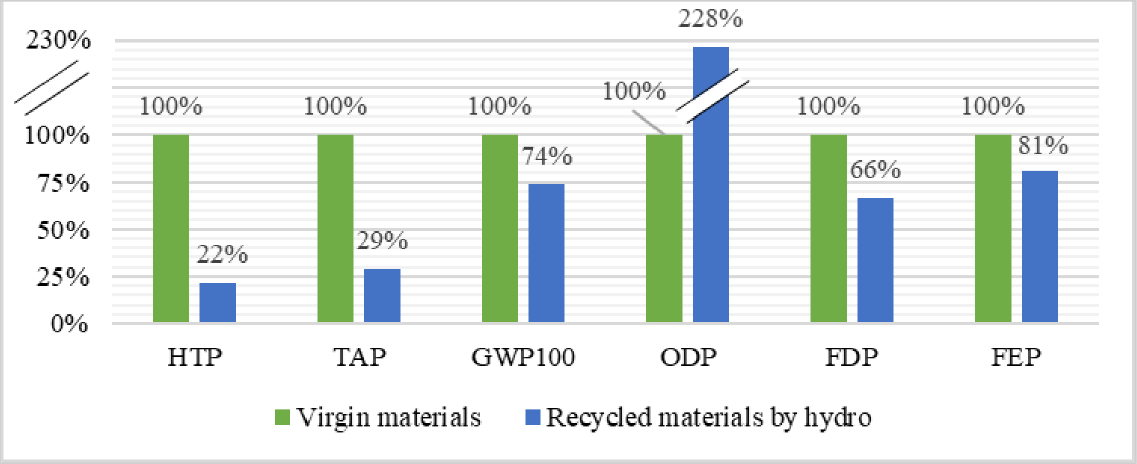

**Figure 16. Comparative environmental evaluation of total products obtained through hydrometallurgy vs. producing the same amount of products through virgin materials/resources**

# 6. Discussion

## 6. 1. Main contributors to the impact categories investigated in this study

One of the main applications of LCA is to inform about the environmental impacts of various activities and services by unfolding their adverse effects. (Ekvall et al., 2020). It also exposes the main factors causing various environmental impacts. Thus, by knowing them, we can reduce or eliminate their negative impacts. However, we also need to know what processes or supply chains lead to those polluting factors. This part investigates the main contributors and the processes related to them. The main contributors to the impact categories investigated in this study for the intended LIBs' recycling methods are presented in Table 8.

In the pyro- and hydrometallurgy method, most of the main contributors to impact categories are related to the sintering unit. It is in line with the results presented in Figure 10 concerning the role of sintering in the environmental burdens of this recycling process. Concerning the impact categories of GWP and ODP, heat production by natural gas and chlor-alkali electrolysis, by far, are the dominant contributors, respectively. Therefore, GWP and ODP can be reduced by mitigating these two factors. However, it is not that straightforward to determine how other impact categories can be reduced because the share of their main contributors is close to the share of other contributors.

Attention to this point is useful in the sense that in impact categories in which the share of the main contributor is low, there are many factors that should be modified to reduce the environmental burden of the impact category in question. While if the share of the main contributor is significantly higher than the rest of the factors, it is possible to reduce the value of the intended impact category substantially just by mitigating the main contributor. In other words, the solution for reducing the environmental impact categories that have a single dominant contributor is more straightforward. Consequently, improving the environmental performance of pyro- and hydrometallurgy is more challenging in TAP, FDP, and FEP impact categories, because many factors should be changed to reduce them.

Concerning the hydrometallurgy recycling method, the most influential factors related to different impact categories are related to the leaching process, except HTP, which solvent extraction and stripping are its main contributor. As mentioned before, leaching is the most chemical-intensive process. Chemicals consumption is associated with much indirect emissions, most of which stem from their production phases. The main contributors to TAP and ODP impact categories are sulfuric acid production and chlor-alkali electrolysis, which are the dominant pollution factors. Chlor-alkali electrolysis is the process used in the production of sodium hydroxide. Therefore, reducing sulfuric acid and sodium hydroxide can significantly reduce TAP and ODP impact categories, respectively. However, the share of main contributors in other impacts categories is not much higher than other factors. Hence, improving them requires more changes and modifications.

Among different chemicals used in the hydrometallurgical process, hydrogen peroxide causes more environmental burdens, which mainly stem from its production phase. It is the main contributor to GWP, FDP, and FEP impact categories. Thus, reducing its consumption can significantly reduce the environmental impacts of the hydrometallurgy process. In this regard, Rinne et al put forward a novel hydrometallurgical process in which NiMH and LIBs are recycled together. NiMH batteries have the role of reductant for LIBs; thereby, the need for hydrogen peroxide is reduced significantly. Nevertheless, this method just has been tested on a lab scale.

Consequently, it can be concluded that the main reason for higher environmental impacts in the hydrometallurgy process is due to the emission stemming from the production phase of the chemicals used in its different unit processes, especially the leaching process. Although it is hard to determine the role of various products in the environmental impacts of the hydrometallurgy method, most of the environmental burdens of the pyro- and hydrometallurgy method can be attributed to cobalt recovery.

**Table 8. The main contributors to the impact categories investigated for the pyro- and hydrometallurgical process**

| Recycling method | Impact category | Main contributor | Relative contribution (%) | Unit processes related to the contributor |
|---|---|---|---|---|
| **Pyro- and hydrometallurgy** | HTP | treatment of decarbonizing waste | 23% | **Sintering** → market for lithium carbonate → lithium carbonate production → market for decarbonising waste → **treatment of decarbonising waste** |
| | TAP | soda production | 7% | **Sintering** → market for lithium carbonate → lithium carbonate production → market for soda ash → **soda production** |
| | GWP | heat production by natural gas | 39% | **Sintering** → **heat production by natural gas** |
| | ODP | chlor-alkali electrolysis | 44% | **Leaching 1 & 2 + Solvent extraction** → sodium hydroxide → **chlor-alkali electrolysis** |
| | FDP | natural gas production | 7% | **Sintering** → **heat production by natural gas** |
| | FEP | soda production | 6% | **Sintering** → market for lithium carbonate → lithium carbonate production → market for soda ash → **soda production** |
| **Hydrometallurgy** | HTP | hydrochloric acid production | 10% | **P507 extraction & Stripping** → market for hydrochloric acid → **hydrochloric acid production** |
| | TAP | sulfuric acid production | 25% | **Leaching** → market for sulfuric acid → **sulfuric acid production** |
| | GWP | heat production by natural gas | 3% | **Leaching** → hydrogen peroxide production → steam production, in chemical industry → steam production, in chemical industry → **heat production by natural gas** |
| | ODP | chlor-alkali electrolysis | 48% | **Leaching** → sodium hydroxide → **chlor-alkali electrolysis** |
| | FDP | hydrogen cracking | 5% | **Leaching** → hydrogen peroxide production → hydrogen peroxide production → **hydrogen cracking** |
| | FEP | hydrogen peroxide production | 1% | **Leaching** → hydrogen peroxide production |

## 6. 2. Comparison with previous studies

GWP is the most common impact category investigated in LCA studies, which is usually calculated based on the cut-off plus credit method. Therefore, among different impact categories, GWP was selected as a criterion to compare the result of this research with other studies in the literature. The comparison between the result of this study and some previous studies are presented in Table 9. It is worth mentioning that all the studies are related to recycling NMC111.

**Table 9. Comparison of GWP results between this and previous studies**

| **Reference** | **LCIA method** | **GWP (kg $CO_2$-eq)** | |
|---|---|---|---|
| | | **Pyro- and hydrometallurgy** | **Hydrometallurgy** |
| This study | ReCiPe 2016 | -2.41 | -1.32 |
| (Buchert & Sutter, 2015) | CML | - | -1.84 |
| (Buchert & Sutter, 2016a) | CML | -2.84 | - |
| (Buchert & Sutter, 2016b) | CML | - | -2.75 |
| (Ciez & Whitacre, 2019) | GREET | - | -0.93 |
| (Mohr et al., 2020) | - | [-2.9, 1.2] | [-0.8, -2.2] |
| (Rajaeifar et al., 2021) | - | -2.10 | - |
| (Jiang et al., 2022) | IPCC | - | -2.70 |

The results related to the study by Mohr et al are the range of values concerning the GWP of recycling NMC obtained based on their literature review. There are various reasons for the discrepancy in the results of different studies. Recycling processes with the same names can utilize different processes to recycle LIBs. Thus, used chemicals and energy consumption vary in different cases. Furthermore, depending on the geographical location of the case studies, the background data differ in various studies. For instance, the chemicals used in a hydrometallurgy plant in China are produced with different environmental impacts than the same type of chemicals used in a similar LIBs recycling plant in Europe. Last but not least, the LCIA method also affects the results because not only are there different characterization factors in different methods, but usually, the characterization factors may change for a method in different years. As observed in Table 9, the studies are related to different years, and they applied different LCIA methods, including CML, GREET, and IPCC. Despite the diversity in the results of LCA studies for different LIBs’ recycling methods, most are in a distinct range. The results obtained from this thesis also lay in that range, which implies the validity of the results and the efficacy of generic models and their LCIs presented in this research.

## 6. 3. Sensitivity analysis

Sensitivity analysis (SA) investigates the uncertainties for model inputs to see how they affect the output or results gotten from a model (Saltelli, 2002). This study assumed particular recovery efficiencies for the LIBs’ recycling methods, which were based on the literature review. Generally, the materials recovery rate of recycling processes varies case by case. Therefore, it is the main source of uncertainty in the models of recycling processes analyzed in this thesis. The efficiency of recycling processes affects the mass of recycled materials. Consequently, it also has an effect on the environmental impacts calculated in this study. The efficiency of the hydrometallurgical recycling processes was assumed to be 100% for all of the target materials in the combined pyro- and hydrometallurgy method and the independent hydrometallurgy method. The recovery efficiency was taken 94% for cobalt and 99% for nickel in the pyrometallurgical process. This study utilizes SA to ensure that the uncertainties related to the recyclings’ efficiencies do not affect the results of comparisons made in the previous chapter.

In the previous chapter, the first set of comparisons was between the environmental impacts of two intended recycling processes based on the simple cut-off approach. The results showed a better environmental performance for the pyro- and hydrometallurgy method. The SA was done based on 10% less efficiency for the pyro- and hydrometallurgy method. However, the efficiency of the hydrometallurgy method was assumed to be fixed at 100%. Nevertheless, the results of the comparison remained consistent, and pyro- and hydrometallurgy still had a decisive superiority in all the impact categories. Also, the same results were achieved after accomplishing the SA for the set of comparisons of the cut-off plus credit approach results, which confirmed the results presented in the previous chapter.

One of the important comparisons made for the result of LCA was between the environmental impacts of obtaining the intended materials through recycling NMC111 versus producing the same amount from virgin resources. This comparison was made for both intended recycling processes. However, just the result of the comparison between total products of hydrometallurgy and the same amount of products produced through virgin resources were investigated by SA in this thesis. Because the results of the other comparison vividly showed that the environmental impacts of manufacturing the products of the pyro- and hydrometallurgy process through virgin resources are significantly higher than getting them through recycling (Figure14). But it was not the case regarding the products of the hydrometallurgy process, and the comparison results were close for GWP, FDP, and FEP impact categories (Figure 16). Hence the focus of SA was just on these impact categories.

In the case of a reduction in the recycling efficiency rate of the hydrometallurgy method, the comparative advantage of obtaining the materials (nickel, cobalt, manganese, and lithium) decreases compared to producing them through virgin resources. Because although the amount of materials and energy consumption do not change in the recycling process, less products are achieved. Thus, while the environmental impacts of recovering intended products were assumed to be fixed for the hydrometallurgy in the sensitivity analysis (dark blue bars in Figure 17), the amount of materials production through virgin resources was reduced. The influence of material reduction on the total environmental impacts of their production through virgin sources was investigated individually. First, it was carried out by reducing their amount by 10%, separately. Then, the same investigation was accomplished based on reducing all of them by 10% (black bar). The results of this SA are presented in Figure 17.

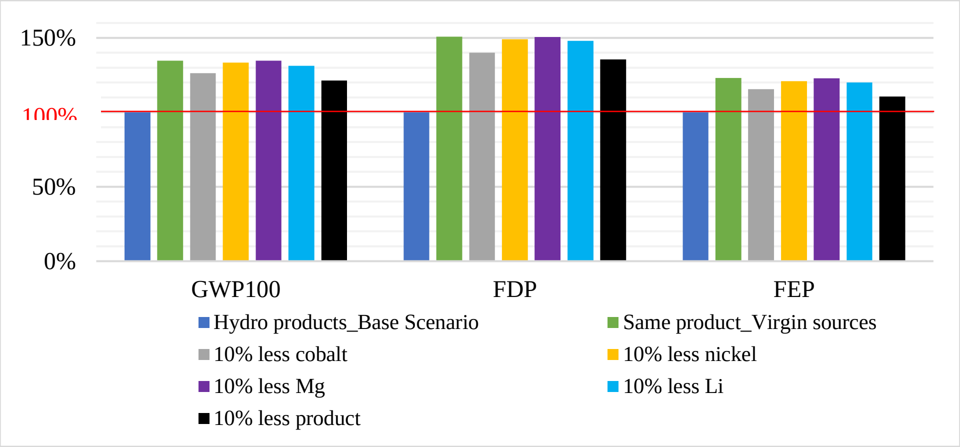

**Figure 17. The result of sensitivity analysis on the result of comparison for the total products obtained through hydrometallurgy vs. producing the same amount of products through virgin materials/resources**

The results illustrated that producing cobalt through virgin resources has a higher environmental impact than other materials. Also, it showed that the 10% reduction of hydrometallurgy recovery rate did not affect the result of the comparison for the total products obtained through hydrometallurgy and producing the same amount of products through virgin resources.

## 6. 4. Analysis of investigated recycling processes from the circular economy perspective

The results of the calculated environmental impacts demonstrated that recycling NMC111 by a combined pyro- and hydrometallurgy method is associated with less environmental impacts compared to an independent hydrometallurgy method. On the other hand, hydrometallurgy can recover more materials from LIBs. Therefore, hydrometallurgy is a better solution for managing and recycling the spent LIBs from a circular economy point of view. Although the focus of this study was mainly on the main elements in active cathode materials of NMC111 cells, more parts can be recycled through hydrometallurgy, including some plastic parts and metallic components. Using these parts in new LIBs depends on their quality after recycling. In the case of recovering the materials with lower qualities, they get downcycled and end up in other industries.

Another point that should be noted regarding the recycling processes investigated in this thesis is that both are incapable of recovering parts of LIBs' cells, such as electrolyte and binder. Also, graphite is usually wasted, or just part of it can be recycled. Electrolyte, binder, and graphite totally form 37% of an NMC111 cell mass in the LIB. Thereby, in the best-case scenario, at least 37% of a LIB's cell mass is wasted through the recycling processes investigated in this study. It is worth mentioning that an NMC111 cell constitutes less than 40% of the LIB in a BEV. Consequently, pyro- and hydrometallurgy method and independent hydrometallurgy method have a limited effect on decreasing environmental impacts of a LIB life cycle. Hence, reaching a circular economy paradigm requires improving the recycling methods. As explained in the literature review, direct recycling could be better solution to reach a circular economy paradigm in LIB industry. Nonetheless, it also has serious limitations which slowed its development worldwide.

# 7. Conclusion

This study conducted a comparative LCA for a combined pyro- and hydrometallurgy method and an independent hydrometallurgy method. The environmental impacts of each option were calculated based on simple cut-off and cut-off plus credit approaches for the GWP, FEP, HTP, TAP, FDP, and ODP impact categories. The results illustrate a better performance of Pyro- and hydrometallurgy in all of the impact categories calculated based on the simple cut-off approach. However, the results derived based on the cut-off plus credit approach show a less divergence between the values of environmental impact categories for the intended recycling methods, and hydrometallurgy has a better performance in HTP and TAP impact categories, which is due to its capability to recover more materials.

Hydrometallurgy generally has higher environmental impacts because of using more chemicals in its various processes. According to the results, chemicals are the main contributors to the environmental impact categories investigated in this study. The environmental burdens of producing chemicals used in the hydrometallurgy method are high. Thus, the hydrometallurgical process and, more specifically leaching process has the highest environmental impacts in both studied recycling methods. Reducing or modification of chemicals consumption can decrease their environmental impacts significantly. Sodium hydroxide and lithium carbonate are the main contributors to the environmental impact categories calculated for the combined pyro- and hydrometallurgy processes. Concerning the independent hydrometallurgy recycling method, hydrogen peroxide and acid sulfuric are the main culprits of its high environmental impacts, and reducing or substituting them with other chemicals can significantly improve the environmental performance of the hydrometallurgical process. Hydrometallurgy can recover more materials than a combined pyro- and hydrometallurgy method. Hence, it is a more suitable method for recycling LIBs from the circular economy point of view. The recycling processes investigated in this study can recover various materials from an NMC111 cell. Of those, recovering cobalt has the highest environmental benefits because producing it has higher environmental impacts than producing nickel, manganese, and lithium.

The models and LCIs of the investigated recycling methods were created based on the literature review done in this thesis. Concerning each option, it was tried to collect the data from industrial cases and include all materials and energy used in their foreground. The chemicals involved in a hydrometallurgical process have high diversity, and each of them can affect the LCA results. The LCIs presented in the literature are usually limited and simplified due to various reasons, including confidentiality issues. The results of environmental impact categories in this study were relatively higher than similar studies, which was mainly due to the comprehensive LCI collected in the thesis.

In the end, it can be concluded that depending on the goal of LIBs' recycling, different recycling methods should be used. If the goal is to manage the spent LIBs with low environmental impacts, pyro- and hydrometallurgy is a better method. However, if the goal is to move toward a circular economy paradigm and recover more materials from LIBs, an independent hydrometallurgy method could be a more suitable option.

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# Appendix

## A) The simplified models

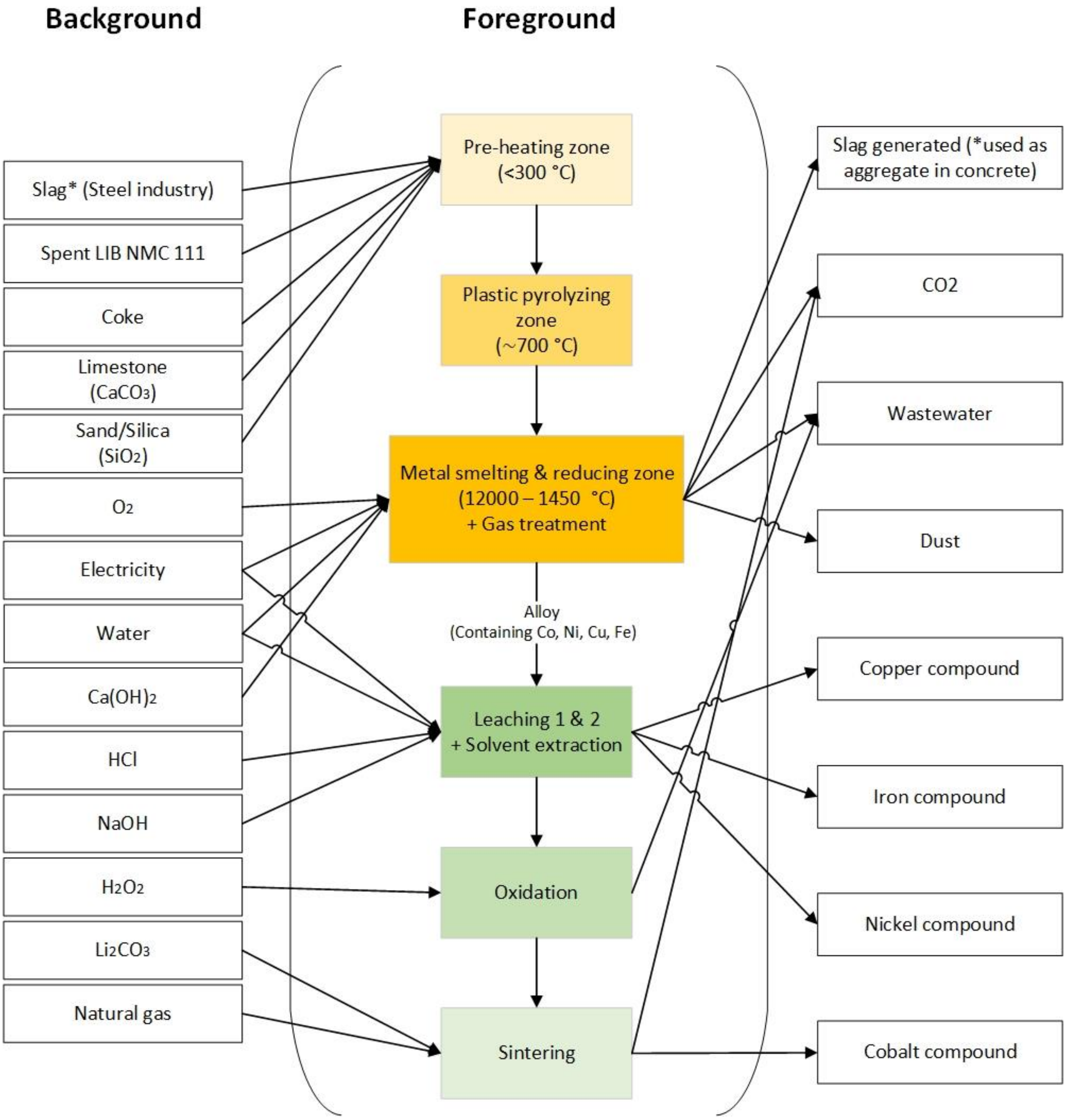


**Figure A1. The simplified model for the pyro- and hydrometallurgical process to form Arda Matrix**

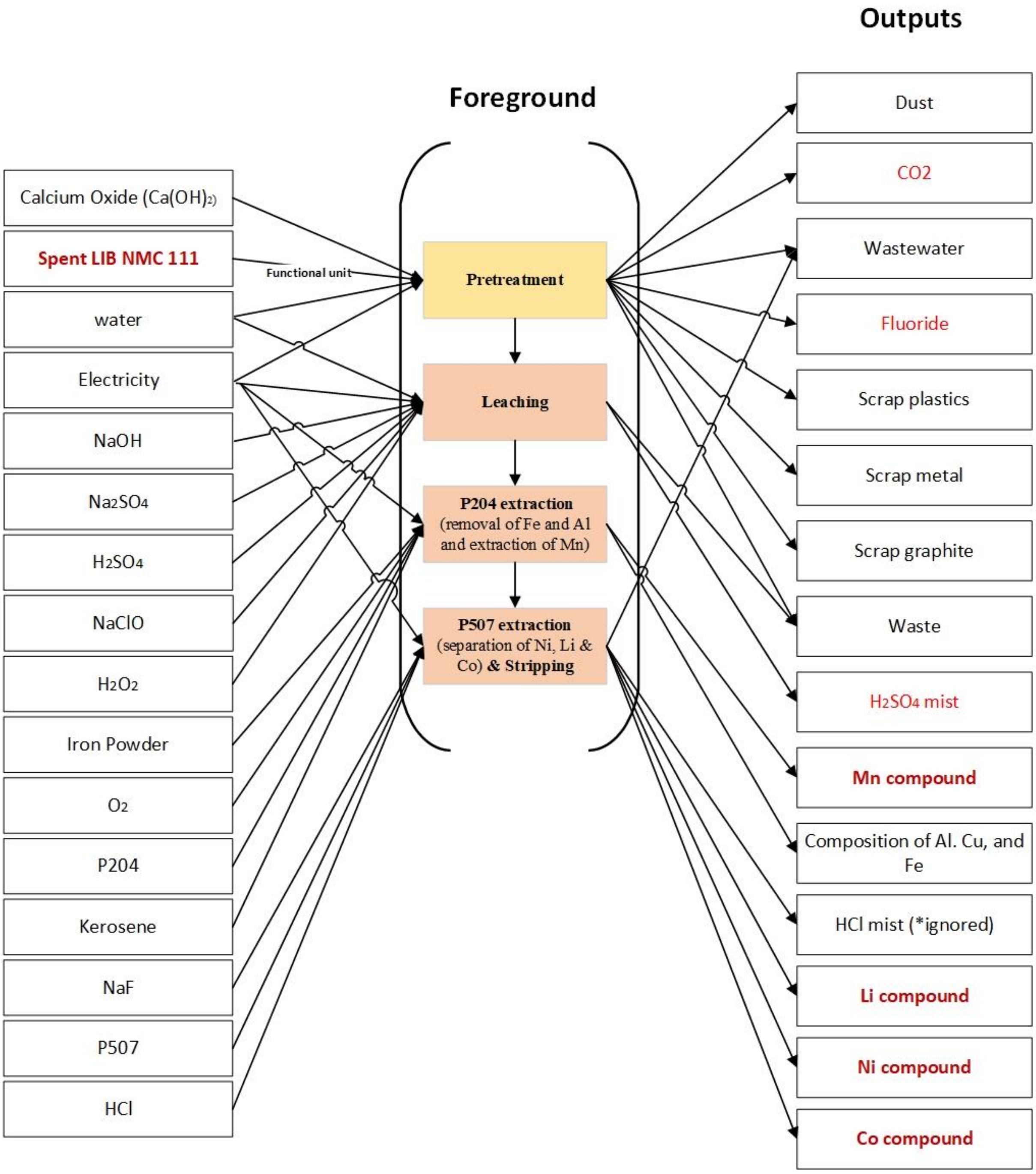


**Figure A2. The simplified model for the hydrometallurgical process to form Arda Matrix**

## B) The background process used from Ecoinvent 3.7

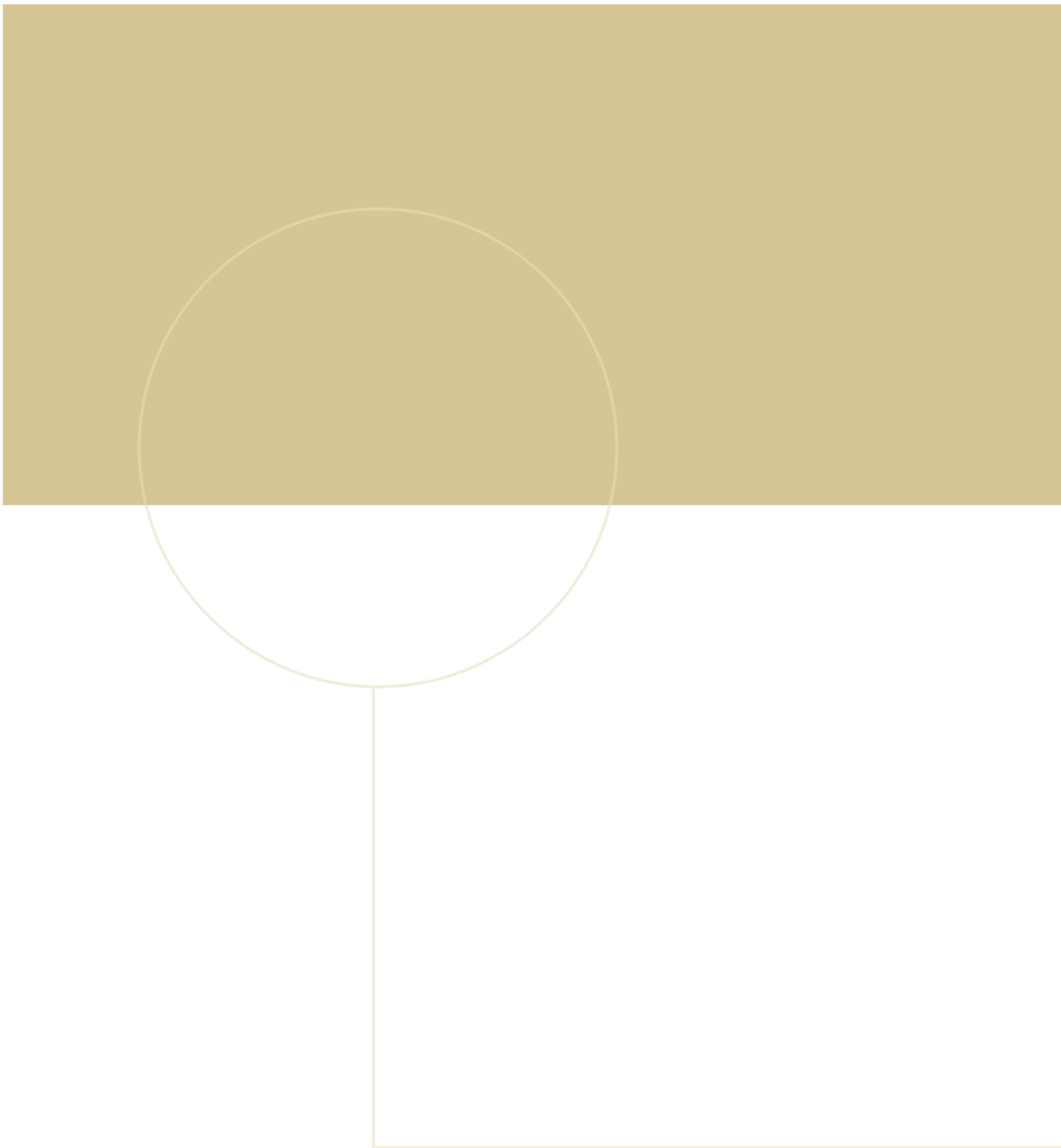
**Table B1. The background process used for the pyro- and hydrometallurgy method**

| Operational Unit | | Material/energy | | Background process from Ecoinvent 3.7 |
|---|---|---|---|---|
| Inputs | Pre-heating zone | Spent LIBs (NMC111) | | - |
| | | Coke | | market for coke |
| | | Slag formers | Sand (silica) | silica sand production |
| | | | limestone | market for limestone, unprocessed |
| | | | slag from steel industry | market for electric arc furnace slag |
| | Metal smelting & reduction zone + gas treatment | O2 | | market for oxygen, liquid |
| | | water | | market group for tap water |
| | | Electricity | | market group for electricity, high voltage-RER |
| | | Ca(OH)2 | | market for Lime |
| | Leaching 1 + Leaching 2 + Solvent extraction | water | | market group for tap water |
| | | HCl | | hydrochloric acid production, from the reaction of hydrogen with chlorine |
| | | Electricity | | market group for electricity, high voltage-RER |
| | | NaOH | | sodium hydroxide production |
| | Oxidation | H2O2 | | hydrogen peroxide production, product in 50% solution state |
| | Sintering | Li2CO3 | | market for lithium carbonate |
| | | Natural gas | | market group for heat, district or industrial, natural gas |
| output | Metal smelting & reduction zone + gas treatment | Slag | | treatment of basic oxygen furnace waste, residual material landfill |
| | | Wastewater from pyro | | market for wastewater, average |
| | | CO2 | | Carbon dioxide, fossil/air/unspecified/kg |
| | | Dust | | treatment of electric arc furnace dust, residual material landfill |
| | Leaching 1 | Copper compound | | copper mine operation and beneficiation, sulfide ore |
| | Leaching 2 | Iron compound | | iron ore beneficiation |
| | Solvent extraction | Nickel compound | | nickel sulfate production |
| | Oxidation | Wastewater from Hydro | | market for wastewater, average |
| | Sintering | CO2 | | Carbon dioxide, fossil/air/unspecified/kg |
| | | Co compound | | cobalt production |

**Table B2. The background process used for the pyro- and hydrometallurgy method**

| Unit | | Material/energy | Background process from Ecoinvent 3.7 |
|---|---|---|---|
| **Input** | Pretreatment | spent batteries | - |
| | | water | market group for tap water |
| | | $Ca(OH)_2$ | market for Lime |
| | | electricity | market group for electricity, high voltage-RER |
| | Leaching | water | market group for tap water |
| | | NaOH | sodium hydroxide production |
| | | Na2SO4 | sodium sulfate production, from natural sources |
| | | H2SO4 | market for sulfuric acid |
| | | NaClO | sodium chloride production, powder |
| | | electricity | market group for electricity, high voltage-RER |
| | | H2O2 | hydrogen peroxide production, product in 50% solution state |
| | P204 solvent extraction | Iron powder | market for iron pellet |
| | | Liquid oxygen | market for oxygen, liquid |
| | | P204 | - |
| | | electricity | market group for electricity, high voltage-RER |
| | | Kerosene | market for kerosene |
| | Co, Ni, and Li extraction unit | NaF | sodium fluoride production |
| | | Kerosene | market for kerosene |
| | | P507 | - |
| | | electricity | market group for electricity, high voltage-RER |
| | | HCl | hydrochloric acid production, from the reaction of hydrogen with chlorine |
| **Output** | Pretreatment | Dust | market for filter dust |
| | | CO2 (stressor) | Carbon dioxide, fossil/air/unspecified/kg |
| | | wastewater | market for wastewater, average |
| | | scrap plastics | market for waste plastic, consumer electronics, sorted |
| | | scrap metal | market for metal part of electronics scrap, in copper, anode |
| | | waste | market for inert waste |

| | | | |
|---|---|---|---|
| | Leaching | Sulfuric acid mist (stressor) | Sulfuric acid/air/unspecified/kg |
| | | waste | market for inert waste |
| | | VOCs (stressor) | NMVOC, non-methane volatile organic compounds, unspecified origin/air/unspecified/kg |
| | P204 solvent extraction | O2 | - |
| | | Mn cmopound | manganese sulfate production |
| | | Scrap metal | market for scrap aluminium |
| | Co, Ni, and Li extraction unit | HCl mist (stressor) | Hydrochloric acid/water/unspecified/kg |
| | | wastwater | market for wastewater, average |
| | | Lithium compound | market for lithium |
| | | Nickel compound | nickel sulfate production |
| | | Cobalt compound | cobalt production |



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