Solid state sUlfide Based LI-MEtal batteries for EV applications

Deliverable 6.3 Report on possible recycling path including a flow sheet and mass balance calculation

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Publishable summary

Recycling of batteries is an indispensable step in the life cycle with regard to the circular economy. Batteries contain valuable and critical raw materials such as lithium and cobalt. In view of further increasing demand and prices for raw materials due to expanding electromobility, geopolitical dependencies in the supply of raw materials and legal drivers, the development of new battery systems is not possible without a holistic view that also includes recycling options. Only by means of a closed raw material cycle can the goal of a sustainable energy supply be achieved. Therefore, within the SUBLIME project, a theoretical recycling concept with expected recycling rates is drawn up at an early stage during cell development.

The battery cells developed in SUBLIME differ in their structure from the lithium-ion batteries (LIBs) already available on the market, due to their sulphide solid electrolyte and the metallic lithium anode. This means that previous recycling processes cannot be transferred directly and require adaptations and, in some cases, new process steps.

For the development of a possible process flow chart, a comprehensive literature study was first carried out on existing industrial recycling processes for common LIBs and those currently under development. In this context, the process components thermal and mechanical pre-treatment, hydro- and pyrometallurgy as well as the concept of early-stage lithium recovery were examined more closely.

A theoretical approach of two possible recycling chains is investigated based on this research: a pyrometallurgical and a hydrometallurgical one with thermal treatment. In the pyrometallurgical process, the whole cells are melted at high temperatures of around 1500 °C with addition of slag formers. This leads to a splitting of the more noble elements from the ones with more ignoble character. In the metal phase copper, nickel and cobalt are collected, whereas lithium and aluminium, as well as parts of manganese are enriched in the slag. Since the SUBLIME cells contain a non-negligible amount of phosphorous and copper and nickel show a good solubility, it is expected to be enriched in the alloy. Therefore, a converter step is necessary to remove phosphorous from the metal phase, which can afterwards be feed/sold to already existing metal producing plants. There is only little report on recovery of lithium from the slag. It can be shipped to primary lithium producers. After energy-intensive crushing and milling steps, it can be treated with the concentrated ore for lithium recovery, but low recovery rates of around 50 % are expected.

In comparison, the hydrometallurgical process option is based on an inert shredding step of the batteries for liberation of the single components. Afterwards, a thermal pre-treatment step at around 600 °C is planned to remove the binders on the one hand and deactivate the metallic lithium by CO_2 insertion on the other hand. The metallic lithium will react to lithium carbonate and the bounded lithium in the NMC is also liberated by phase transformations. The removal of binders is quite important for the following process steps of sorting and hydrometallurgical treatment and leads to higher leaching efficiencies.

The thermal pre-treatment is followed by mechanical sorting steps to recover the aluminium and copper foils and the casing of the cell. The separated black mas is feed to an ethanol washing step. Since the solid electrolyte shows good solubility in this solvent, high recovery-yields of around 90 % are expected in this case. The other cell components are not soluble in ethanol and remain in the solid residue. Afterwards the solid residue is feed to the lithium recovery step. Since most of the lithium is previously converted to water soluble lithium carbonate, a water washing step with CO2 insertion to gain higher solubilities is intended. Based on literature research and comparison of the process with other reported recycling chains of batteries with metallic lithium anode, high recovery rates of around 90 % are expected in this step. This leads to an expected overall recycling efficiency of lithium of around 82 %. The other metals from the NMC oxide are insoluble in water, so it is a highly selective process. The NMC oxides can be feed to a common hydrometallurgical process flow, consisting of sulfuric acid leaching and cementation and precipitation steps. Copper and aluminium impurities are removed from the

solution in the first two steps, followed by pH driven precipitation of a Mn, Co, Ni mixed hydroxide salt. Recovery rates of these single metals are predicted to be around 90 %. The salt can be sold to purification plants and new NMC production. Overall, this hydrometallurgical based recycling approach is expected to allow high recycling efficiencies for the single battery components, which can deal with the new EU directive.

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Abbreviations

SYMBOL	SHORTNAME
ASSB	All-solid-state batteries
ESLR	Early-stage lithium recovery
HNBR	Hydrated Poly(acrylonitrile-co- butadiene)
LIBs	Lithium-ion batteries
LPSC	Li_6PS_5Cl
NMC811	LiNi0.8Co0.1Mn0.1O2
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

1 Introduction

The aim of the work package presented in this report is to develop a theoretical recycling concept for the battery cells investigated in SUMBLIME. For a holistic approach and circular economy, recycling is of high interest, as it closes the loop of material supply and is crucial for the sustainability of the battery cells. Due to the new cell chemistry the cells cannot be feed to already existing recycling plants directly. The actual industrially implemented recycling processes are focussing on the recovery of cobalt and nickel [1]. Lithium is not recovered in industrial scale at the moment [2]. But especially lithium is of high importance for the battery production industry and the European Union has classified it as critical raw material [3]. To overcome the environmental issues during primary production and the geopolitical dependence from the lithium mining countries out of Europe, a sufficient recovery is of high importance. For this reason, special regard is attached to lithium recovery in this work package. Of course, all other battery components are to be recovered as well. In comparison to commercial LIBs already used, this approach also regards the recovery of the solid electrolyte for a holistic, economic and ecologic process chain.

Based on the chemical composition of 40 mAh pouch cells provided by Fraunhofer IST and TU Braunschweig, two possible recycling chains are developed theoretically. First, an extensive literature review was conducted on recycling processes for commercial NMC LIBs. Both processes that have already been implemented industrially and approaches that are currently under researched were considered. Section 2.1 gives an overview of the single process steps and summarizes the different recycling routes. The following section 2.2 describes the adaptation of individual recycling steps for the processing of all-solid-state batteries (ASSB). The aim is to find entry points into already existing processes as early as possible. Based on material properties and process step details described in the literature, the behaviour of the SUBLIME cells is derived theoretically. Process windows are determined within the framework of the theoretical possibilities for the individual process steps and intermediate and by-products are defined. Based on thermochemical calculations and literature data, reaction equations are determined as well.

As ASSB recycling is an innovative field of research where not much data is available yet, most of the data shown in this report is derived from studies with liquid electrolyte NMC batteries. Based on similarities and differences in the phase composition of the different battery systems, the behaviour of the SUBLIME material can be derived. The structure of this report is thus divided into the motivation and necessity of battery recycling and the European framework conditions, followed by the presentation of existing recycling routes for LIBs with liquid electrolyte. This knowledge is essential for understanding the recycling of SUBLIME cells. In addition, possible entry points into already established LIB recycling plants can be identified. The report structure includes a detailed description of two possible process routes, 1. Thermal hydrometallurgical and 2. Pyrometallurgical recycling for the SUBLIME cells. Here, explicit study results regarding the individual process steps on liquid electrolyte and metallic lithium cells, as well as knowledge from the manufacturing process of the solid electrolyte and thermochemical data and modelling are used to develop and model the processes.

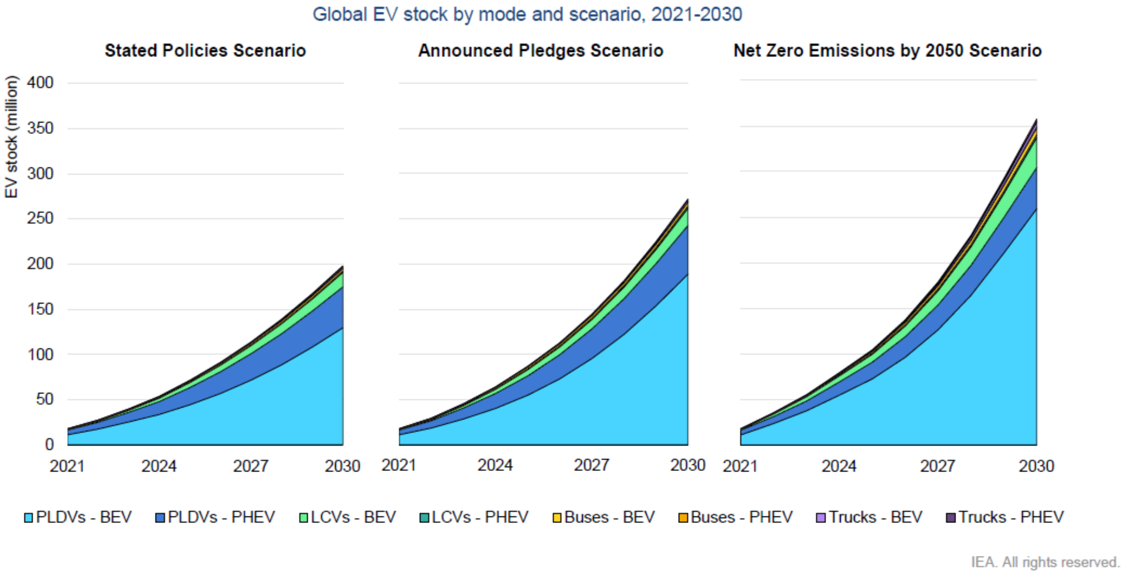
Afterwards, a theoretical mass flow is calculated. This calculation is derived from literature data of different cell systems, synthetic material systems, thermodynamic calculation software and assumptions backed up by experience from previous projects. All this data is summarized in a process flow chart at the end of this report. It represents a part of the input for the LCA to be carried out in following deliverables.

The objectives of the work package were reached; however, it must be considered, that this is a purely theoretical consideration of the recycling possibilities of the SUBLIME cells. This means that quantitative data should be understood as approximations and be validated in follow-up projects. Nevertheless, this report gives a good assumption on the recyclability of the batteries and are the base for further research.
The results of this report can also be useful for the further cell development. For example, the choice of binders plays an important role for the recyclability of the cells and the required effort. This early investigation could help to figure out potential improvements in cell development regarding a design for recycling.

2 Methods and Results

2.1 Literature review on current recycling processes for conventional LIBs

To understand the importance of recycling batteries, it is important to look at the demand and supply situation of both batteries and their raw materials. The expansion of e-mobility is leading to a strong increase in demand for LIBs, as shown in Figure 1.



Notes: PLDVs = passenger light-duty vehicles; BEV = battery electric vehicle; LCVs = light commercial vehicles; PHEV = plug-in hybrid electric vehicle. The figure does not include electric two/three-wheelers. For reference, total road vehicle stock (excluding two/three-wheelers) in 2030 is 2 billion in the Stated Policies Scenario, 2 billion in the Announced Pledges Scenario and 1.8 billion in the Net Zero Emissions by 2050 Scenario.

Figure 1: Trends in EV-sales by different scenarios from 2021 to 2030. [4]

The scenarios shown are also accompanied by an increased demand for battery raw materials. NMC-based cells have been a widely used battery system up to now. The project SUBLIME also uses cells in which NMC and lithium are essential components. Cobalt and lithium have already been classified as critical raw materials by the EU [3]. The security of supply for Europe from primary raw material sources is critical for all three metals nickel, cobalt and lithium. Moreover, phosphorous, which plays an important role in the batteries as well, is a critical element [3], too Only a few countries worldwide have significant deposits for mining. For example, a large part of the cobalt (around 60 %) comes from the Democratic Republic of Congo, where mining takes place under poor safety conditions, corruption, and child labour [5, 6]. In the case of lithium, the main issue is ecological problems in mining. On the one hand, very large quantities of minerals have to be processed, and on the other hand, the extraction process is very water intensive. On average, 1900 t of water are needed to extract 1t of lithium. This is particularly critical because the largest lithium mining areas are located in arid regions of the world, such as Chile. [7, 8]

The nickel supply situation in Europe has been exacerbated by the Ukraine crisis. The dependence on Russia is currently leading to reduced imports.

Against the backdrop of geopolitical dependencies, as well as environmental and social aspects, the recycling of batteries is essential to secure the future supply situation and meet the increasing demand for raw materials for battery production. Figure 2 shows exemplary the forecast of the demand of lithium for 2030 with different models/scenarios. In contrast, the demand of lithium in 2020 was 74,183 t, so in the next 10 years, a multiplication by a factor of 2-7.5 can be expected.

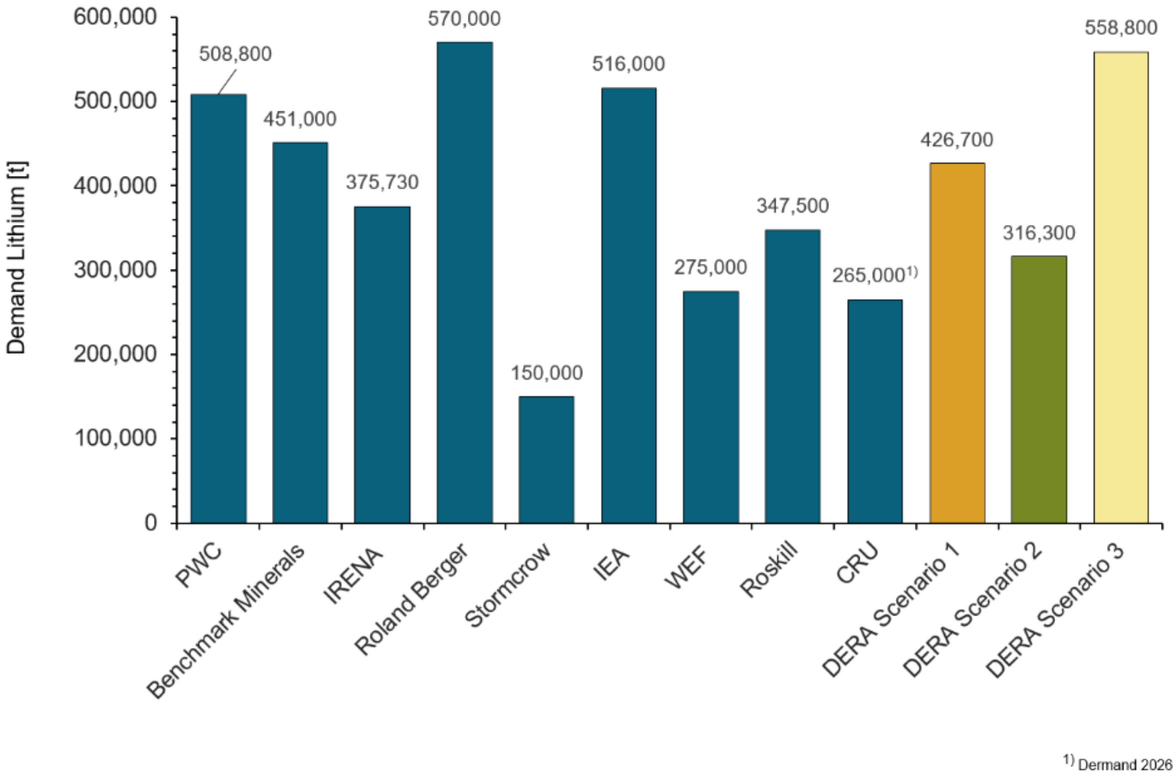


Figure 2: Demand of Lithium – different forecasts for 2030 (status 2022). [9]

In addition to the push factors for battery recycling already mentioned, there are also legal requirements in the EU. Currently, it is the EU Battery Directive 2006/66/EC [10]. This stipulates a mass recycling efficiency of 50%. A new directive is currently being worked out, in which recycling efficiencies are specified for individual battery elements. The medium level of ambition specifies 90% for Co, Ni and Cu and 35% for Li, with an overall recycling efficiency of 65% [11].
All these aspects show the importance of battery recycling and the motivation for the presented work-package. Just with a successful recycling concept, a sustainable battery life cycle can be established. Therefore, considering possible recycling paths already during cell-development is a sensible procedure.

First, a detailed literature review was carried out on current recycling processes for conventional NMC LIBs. Understanding of already existing process routes and alternatives is crucial for their adoption or the development of new recycling strategies for the innovative SUBLIME cells.
In case of common LIBs, many different process routes and options are existing in industry and further are under research and development. Figure 3 gives an overview on the various recycling paths.

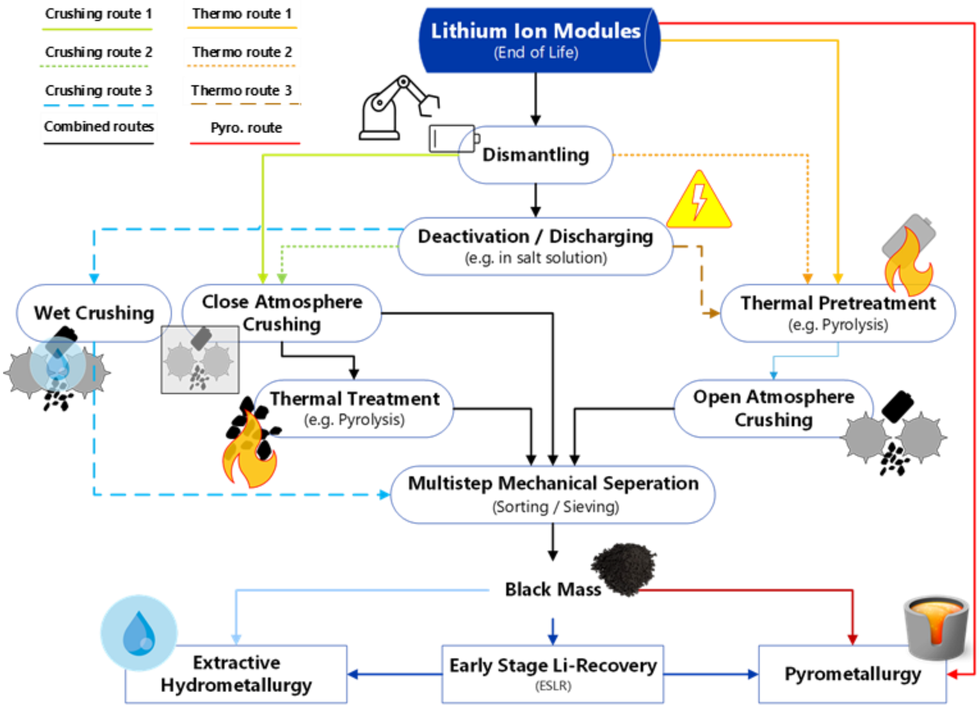


Figure 3: Possible recycling paths of conventional LIBs. [12]

In general, battery recycling can be divided in mechanical, thermal, hydrometallurgical and pyrometallurgical processes steps or modules [2, 12, 13]. In most cases, several of these modules are combined to achieve the highest possible recycling efficiencies. The following sub-sections present the different process modules in general and form the basis for developing a recycling concept for the SUBLIME cells. The following section 2.2 presents the development of the recycling process for SUBLIME cells, also based on detailed literature research for assumption of possible process parameters.

2.1.1 Thermal pre-treatment

Due to the high complexity of LIBs, their recycling is challenging. The organic electrolytes in common cells as well as metallic lithium in new cell generations cause fire and explosion risks. Moreover, the binders hinder the separation of the active material from the collector foils during mechanical separation and can lead to low leaching efficiencies and kinetics in hydrometallurgical process steps. Those challenges can be overcome by thermal treatment of battery cells or shredded battery material. [14–16]. One kind of thermal treatment is the pyrolysis process under inert atmosphere [14].

During pyrolysis, the input material is heated under inert atmosphere like Ar, N_2 or CO_2 [17]. In case of conventional NMC batteries, the temperature is limited by the melting point of aluminium, so the range differs between 300-650 °C [2]. Due to the heating under absence of oxygen, contained organic compounds are cracked and volatized. This leads to the formation of a permanent gas, but also condensates like tar and oil and a solid residue named pyrolysis coke are products of the process. In addition to organics, other volatile components such as halogens can be removed from the material via the exhaust gas [2, 18]. Because of the controlled process conditions and the off-gas treatment, pyrolysis is a safe deactivation process for batteries, especially in case of cells with unknown history or damaged ones. The thermally treated battery material can be transported and processed safe and easily under atmospheric conditions to gain the valuable active mass.

Due to the high organic and halogen amount of the exhaust gas, its treatment is crucial during the process [18]. Common described techniques are post-combustion for the organics and wet or dry scrubbing for the acidic components, followed by activated charcoal filtration. The generated heat from the post-combustion can be used for heating of the furnace in industrial processes. This could make an autothermal process possible [19]. Other options under current research could be condensation of pyrolysis oils for usage in petrochemical applications.

Next to the organic and halogen removal, targeted phase transformations in the solid state are aimed by the pyrolysis process [20]. In case of common NMC battery cells this are metal oxide reductions. This leads to the transformation of the NMC oxides to, e.g., metallic nickel [20]. If the black mass is to be treated hydrometallurgical afterwards, this is beneficial for the leaching efficiency and kinetics of the process [15, 21]. Moreover, the usage of the expensive leaching additive hydrogen peroxide can be reduced [22]. Of special interest are possible phase transformations of the containing lithium as well. In this course, phase transformations to water soluble lithium carbonate are reported. The conversion rate depends on the process parameters, in particular temperature and atmosphere. Temperatures of around 600 °C and CO_2 atmosphere showed the best results in published research. [17, 23–27] Those optimised process conditions in the thermal pre-treatment enable process steps such as early-stage lithium recovery, described in section 2.1.3.

Table 1 summarizes the described benefits of a thermal pre-treatment of batteries regarding the following mechanical and hydrometallurgical process steps.

Table 1: Benefits of thermal pre-treatment regarding mechanical and hydrometallurgical processing.

Mechanical treatment	**Hydrometallurgy**
Removal of electrolyte - No fire risk - Atmospheric shredding possible - Less corrosion Removal of binders - Improved delamination of collector foils - Higher recycling efficiencies	Removal of electrolyte and binders - Higher leaching efficiencies - Better kinetics Removal of haldies (e.g. F) - Improved purities of products and waste water management Phase changes of metal oxides - Less consumption of expensive H_2O_2 during leaching - Better kinetics - Innovative process steps like early-stage lithium recovery possible

2.1.2 Mechanical pre-treatment

The main aim of mechanical treatment steps is the liberation of the valuable active mass and separation of casing and foil material. It can be carried out directly after a deactivation/discharging step or after thermal pre-treatment [2, 12]. The timing determines the requirements that are placed on the mechanical crushing of the battery cells. If a thermal pre-treatment step with removal of the contained organics is carried out first, the fire and explosion risk of common LIBs is eliminated. This enables open atmosphere shredding, e.g. in hammer- or cutting mills. If the batteries should be mechanical processed directly, the shredding has to be carried out under more special conditions like inert atmosphere. Therefore, the batteries can be processed under N_2, CO_2 or Ar [2]. Volatile components from the electrolyte are removed by drying at low temperatures, as reported by Duesenfeld up to 80 °C and/or in a vacuum distillation step [28].

An alternative is wet shredding in water or salty solutions [2]. In this case, the organics and soluble elements like parts of lithium and fluorine will be enriched in the solution [2]. Because of that, process water treatment is an important issue, especially regarding hydrofluoric acid formation.

Next to the described options, also cryogenic shredding is possible [29], but very energy intensive.

Shredding of batteries is followed either by thermal pre-treatment, described in section 2.1.1 or by mechanical separation steps, which are based on the physical properties of the material. These include density, magnetic and electrostatic properties as well as particle size and granulometric properties. Especially for hydrometallurgical treatment, it is very important to separate the individual fractions of casing, current collector foils, plastics as separator foils and black mass as purely as possible. Under current research is the separation of graphite from the black mass fraction as well. To achieve these goals, combinations of various separation techniques are carried out. Examples are magnetic separation especially after reductive thermal treatment to separate magnetic Ni or Co-oxides, eddy

current separation, screening, sieving and shifting to separate collector foils and separator, gravity sorting in flow fields and flotation for graphite recovery. [29]
Crucial for sufficient sorting is the delamination of the collector foils. However, a purely mechanical pre-treatment is difficult due to the organic binders. Prior chemical or thermal treatment to remove the binder is therefore recommended.

2.1.3 Early-stage lithium recovery (ESLR)

Lithium recovery from batteries has so far been insufficiently or not at all implemented in industry. Due to its non-precious character, recovery of lithium is always the last step in the common industrial process routes like pyro or hydrometallurgy. This leads to significant lithium losses over the previous process steps. In case of hydrometallurgical treatment, lithium is lost over the single cementations and precipitations as shown in Figure 4 [30].

Figure 4: Example of lithium distribution in hydrometallurgical recycling after the single cementation and precipitation steps. [30]

On the one hand, this causes decreased lithium recovery rates and on the other hand contaminated intermediate products.
In pyrometallurgy, there are two different strategies for recovering lithium:

1. Enrichment in the slag,
2. Enrichment in the flue dust.

However, exclusive enrichment in only one of the two phases is not possible and cross-contamination also occurs in this case, as presented in Figure 5 [30].

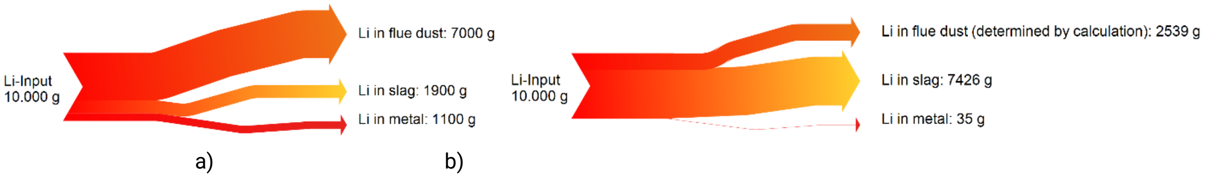


Figure 5: Example of lithium distribution in pyrometallurgical recycling for a) enrichment in flue dust and b) enrichment in slag [30]

Furthermore, the hydrometallurgical recovery of lithium from the two intermediate products requires high effort. The slag must be mechanically pre-treated and afterwards the high amount of material has to be leached or concentrated before, e.g., by flotation. As silicon oxide is a common fluxing agent in pyrometallurgy, the leaching step is complicated by silica gel formation [31].

The issues described provide the motivation for the innovative process step of early-stage lithium recovery. After sufficient thermal and mechanical pre-treatment, the lithium recycling from black mass is performed before entering hydro- or pyrometallurgical recycling steps. Therefore, the lithium is transferred to water-soluble compounds like Li_2CO_3 or LiOH, which are then washed out of the black mass by a water-leaching step. The required phase transformation can be carried out already during thermal pre-treatment under appropriately adapted process conditions. To achieve high leaching efficiencies, the water leaching step can be assisted by CO_2 addition to the solution, either under atmospheric condition or under pressure up to supercritical CO_2 in an autoclave. The CO_2 treatment leads to higher lithium solubility and carbonisation of up to > 90 % leaching efficiency, depending on the black mass/input material. [14, 30, 32]

The described process has many advantages over recycling lithium after the conventional hydrometallurgical or pyrometallurgical treatment [30]:

- Highly selective
- No chemicals needed

- No losses of other valuable battery components
- Flexible, can be implemented in hydro- as well as pyrometallurgical process routes
- Simultaneous halogen, esp. fluorine removal possible
- Near zero waste process possible by water circulation

Due to the high lithium amount in SUBLIME cells, this process step is of special interest for the design and investigation of possible recycling paths.

2.1.4 Hydrometallurgy

The lithium-ion battery black mass can be treated either by hydro- or pyrometallurgy. This section describes the hydrometallurgical process options. As black mass does not really fit in already existing hydrometallurgical metal production routes, and the recovery of the compounds besides Co and Ni is still under research, industrial implementation is still pending. Hereby two general approaches can be divided. The first option aims the production of intermediate mixed salt products which can be feed to existing metal production processes for further refinement. The second process option tends for pure single metal products, which requires more complex treatment. [2, 13, 15, 29]

Both process options start with a leaching step, where black mass is treated with acids, e.g., H_2SO_4 and with elevated temperature. For better leaching efficiencies and kinetics addition of H_2O_2 is recommended. After leaching, the solid residue, mainly consisting of graphite is separated by filtration. Purification and graphitisation of the solid residue are under current research. [2]

In case of the production of intermediate products, the first step after leaching is the Cu-cementation by the addition of iron powder. In the next step, aluminium and iron are removed from the solution by pH-adjustment. Therefore, alkali like NaOH is added until a pH of around 4 is reached. Further pH-adjustments by addition of NaOH lead to precipitation of Co and Ni salts. Because most Co and Ni refiners are not able to cope with high Mn impurities, it is important to keep the co-precipitation of Mn low. The next step is the Mn precipitation, which is nearly completed when a pH of around 10 is reached. The last step in this process flowsheet is the lithium recovery as carbonate. Through addition of Na_2CO_3 and temperature adjustment, the lithium salt is precipitated. [15]

The direct production of high-grade products requires a more complex treatment of the black mass. It is commonly carried out by solvent extraction after the leaching and cementation steps. In mixer-settler plants, the single metals Mn, Co and Ni are recovered by extraction and stripping from organic solvents. Co and Ni can afterwards be precipitated as salts or in metallic form via electrolysis. Figure 6 gives an overview on possible process flows within this framework. [2, 15]

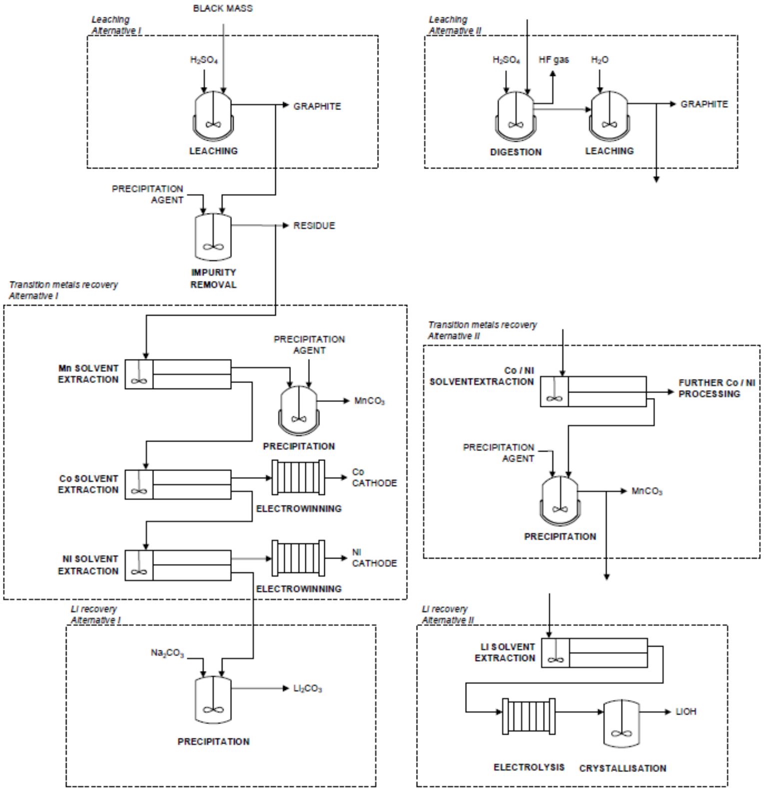


Figure 6: Process flow-chart of hydrometallurgical battery recycling. [2]

In case of common LIBs containing F, the formation of hydrofluoric acid is an important issue. If a thermal pre-treatment is carried out before, a huge amount of fluorine is already removed from the black mass [18]. However, the black mass still contains around 2 wt.-% of fluorine [14], which can lead to corrosion or act as an impurity in the salt products. The behaviour of fluorine and possible ways to deal with it are still under current research.

2.1.5 Pyrometallurgy

Pyrometallurgical battery recycling means the melting of whole modules/cells or of already separated black mass generated from different process options as shown in Figure 3. The material is smelted at high temperatures of around 1450-1600 °C with addition of fluxes [2, 33–36]. They are necessary to form a slag with appropriate liquidus-temperature below 1400 °C. Common fluxes are silicon oxide and lime [35, 36]. They are forming an oxidic slag with the aluminium and lithium (if not removed in the previous process steps) and, if present, iron from the battery material. The slag is used in the construction industry. Recovery of lithium from the slag has not yet been carried out industrially, as no economic process has yet been developed, but is under current research. The noble metals copper, nickel and cobalt are concentrated in an alloy, which can be further treated hydrometallurgical for single metal recovery. Thus, the smelting process is a splitting of noble and less-noble metals. If the material is not thermally pre-treated, the organic is used as an energy source and together with the graphite as reducing agent of the metal oxides. Halides like fluorine are mainly evaporated and enriched in the flue dust. [2, 33–36]

An example in industry for pyrometallurgical battery recycling is the Umicore process [37]. Whole batteries are processed together with coke, SiO_2 and CaO, as well as to be reduced copper slag in a shaft furnace, see Figure 7.

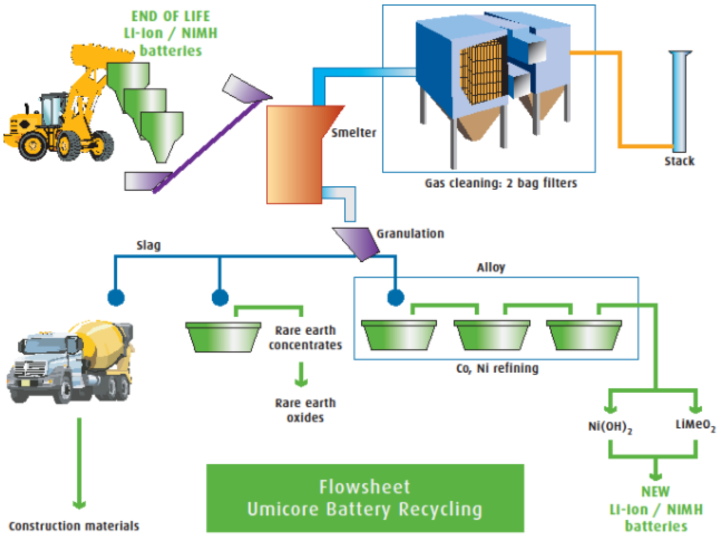


Figure 7: Simplified process flow chart of the Umicore process. [38]

This furnace can be divided in three zones: preheating, pyrolysis and melting and reducing zone. In the preheating zone, the spent batteries are slowly heated to temperatures of up to 300 °C by the gas counterflow that comes from the melting and reduction zone. During this process, the electrolyte evaporates and the slow rise in temperature reduces the risk of explosion. In the pyrolysis zone, the temperature rises to about 700 °C. The organics from the batteries are cracked and volatized. The resulting hot gases are rising through the shaft and are heating the preheating zone. In the melting and reduction zone, preheated and oxygen-enriched air is blown in at the bottom of the furnace. The coke and aluminium react as reducing agents of nickel and cobalt. As described above, the resulting alloy of nickel, cobalt and copper settles from the slag phase and can be further processed to recover the single metals. [2, 29]

The gases produced during the process are carried out upwards via the shaft. This is followed by an exhaust gas cleaning similar to thermal pre-treatment with post-combustion of the organics and a washing step to remove the acidic components. In addition, filtration of the flue dust is necessary. [2]

Alternative to the processing of whole battery cells, the already separated black mass, for example out of the Accurec process can be melted in an electric arc furnace, as described by Georgy-Maschler or Sommerfeld et al. [34–36]. In this case the pre-heating and pyrolysis zone are not necessary anymore, so that the material is directly feed into the melting zone. The principle of splitting an alloy from the slag phase stays the same as described above. But due to the already mainly removed aluminium casings and foils during mechanical processing, less aluminium has to be transferred to a slag phase and therefore also less fluxes are necessary. This leads to a smaller amount of slag per processed batteries and a higher lithium content in the slag (if not already removed by early-stage lithium recovery) [35, 36]. The recovery of lithium from the produced slag is under current research. Another investigated option reported in research is the enrichment of lithium in the flue dust. The enrichment either in slag or in dust is depending on the slag design because its composition is responsible for the solubility of lithium. When the maximum solubility is reached, all further lithium is volatilised. The lithium can then be recovered hydrometallurgical from the flue dust.

2.2 Recycling concept for SUBLIME cells

2.2.1 Characteristics and composition of SUBLIME cells

For the development of a recycling concept for the cells from SUBLIME, which belong to ASSBs (see Figure 8), the differences to conventional NMC battery cells are decisive. Based on these, it can be decided which existing process steps from LIB recycling can be used, which need to be modified and whether completely new steps are necessary. shows the the structure of the ASSB battery cell.

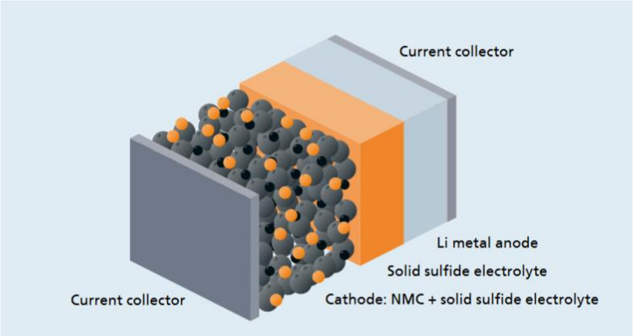


Figure 8: Structure of sulfide based ASSB cell. [39]

Especially the metallic lithium electrode and the solid Li_6PS_5Cl electrolyte place special demands on the recycling process. Their reactions with air and humidity must be avoided due to toxic gas evaluation as well as fire and explosion risk. In the following sections two possible recycling routes are presented which take this into account.

The recycling concept is based on the chemical composition of the monolayer 40 mAh pouch cell. The calculation of cell composition in weight percentages at the cell level was made on the basis of data obtained from the project partners TU Braunschweig and Fraunhofer IST, which included the material and composition of individual layers, their thickness, their mass loading and surface area.

The conception is based on the following chemical composition of the battery:

Table 2: Composition of SUBLIME cell, monolayer, 40 mAh pouch cell, calculated based on data provided by TU Braunschweig and Fraunhofer IST.

Cell component	Material	Amount/cell [wt.-%]
Casing	Aluminium	85.21
Anode foil	Copper	2.08
Anode	Lithium (metal)	0.82
Electrolyte	Li_6PS_5Cl	7.06
Binder (electrolyte + cathode)	HNBR	0.33
Cathode	NMC 811	0.37
Additive Cathode	C65	0.09
Cathode foil	Aluminium	1.04

2.2.2 Recycling Option 1 – Thermal, mechanical and hydrometallurgical treatment

The first developed recycling route is a combination of thermal pre-treatment, shredding and sorting, early-stage lithium recovery and hydrometallurgical treatment.

First, before entering the recycling process, the cells are discharged for safety reasons and energy recovery. This is followed by an inert shredding step, to liberate the single battery components for the further treatment steps. Afterwards the whole cells are thermally pre-treated in a resistance heated batch furnace. This primarily pursues two goals: the removal of the binders and the conversion of the lithium to Li_2CO_3.

Binders should be removed for better delamination of collector foils on the cathode side, as well as better leaching behaviour of NMC in leaching steps later on. The phase transformation of the lithium will facilitate its recovery, as this will enable the ESLR process step described in section 2.1.3 and avoid fire hazards in further handling. Another positive side effect that should be exploited as much as possible during thermal treatment is the reduction of NMC layered oxides. In this way, the leaching kinetics can be improved, and possibly incorporated lithium can also be mobilised for the ESLR process. The achievement of these goals depends on the process conditions.

In the following the single steps of the process are described in more detail.

Disassembly and Shredding

When thinking already in industrial scale, after discharging the batterie packs, the disassembly to module level is carried out. Otherwise, the handling and shredding of the large packs is difficult up to not possible in common sized plants. In addition, peripheral parts such as cables and metal and plastic housings should be separated as early as possible so that they can also be fed into appropriate recycling routes.

Shredding of the batteries is possible for example in a cutting mill. This is necessary to make all components accessible for the further chemical recycling steps. Potential risks during this process emanate from the electrolyte/separator and the metallic lithium. Since metallic lithium causes fire and explosion risks and contact of the Li_6PS_5Cl with atmosphere and moisture leads to decomposition with release of toxic H_2S, the handling of the battery material must be ensured in a dry, inert atmosphere. This procedure does not have to be developed from scratch, as inert gas shredding already exists for conventional NMC batteries. For example, the Düsenfeld company in Germany follows this procedure [2, 28]. After the shredding process, the material has to be carried through inert pipelines or something similar to the furnace of thermal pre-treatment.

Thermal pre-treatment

For the parameter design of the thermal pre-treatment, the behaviour of the individual battery components at elevated temperature and under different atmospheres is considered in the present work. In the case of the binders, the decomposition temperature is of particular importance, as they should be removed from the system via the exhaust gas as completely as possible. For this purpose, Table 3 lists the corresponding data for the possible binders mentioned in Deliverable 4.3.

Table 3: Thermal decomposition of possible binders in SUBLIME cells.

Binder	Decomposition Temperature [°C]	Source
SBS	~475 °C	[40, 41]
SBR	~450 °C	[42]
NBR	~500 °C	[43]
PIB	~400 °C	[44]
PBMA	~450 °C	[45, 46]
PVDF	~500 °C	[47]
HNBR	~ 460 °C	[48]

As HNBR is the most promising binder on the cathode site, its thermal degradation, investigated by TGA analysis is shown in Figure 9. For this study, just the red line showing pure HNBR is interesting. As can be seen in the diagram, the decomposition starts already at around 420 °C and ends by 460 °C with nearly no residual weight [48]. For the thermal pre-treatment process this leads to process temperatures of minimum 500-550 °C to ensure the complete binder decomposition.

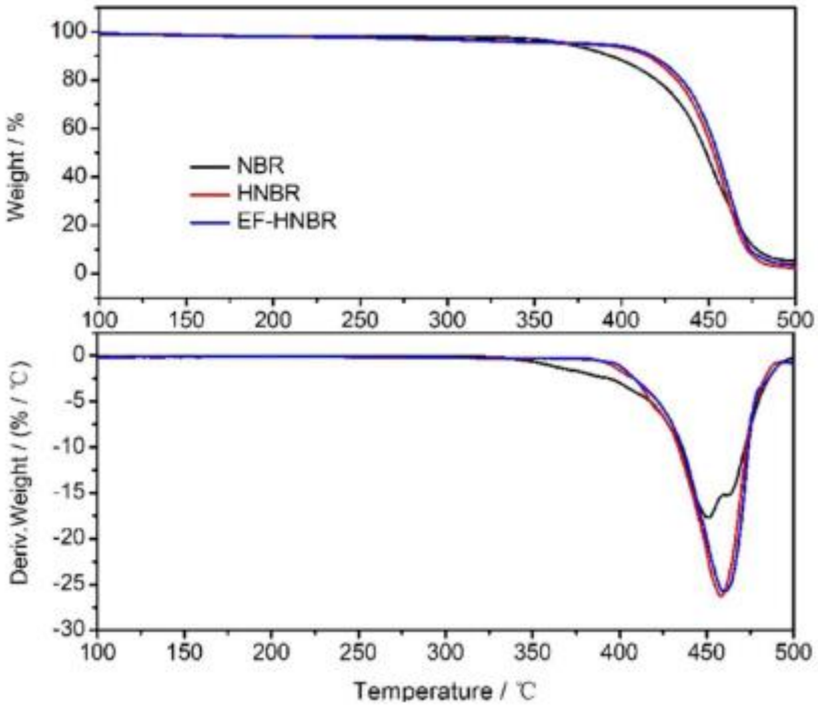


Figure 9: TGA analysis of HNBR binder. [48]

The transformation of the metallic lithium to Li_2CO_3 is carried out by inserting CO_2 as process gas in the furnace over the whole process. Similar trials have been carried out by Schwich et al. for lithium-sulphur batteries [17]. As shown by thermochemical FactSage calculations in Figure 10, the transformation of metallic lithium to Li_2CO_3 with a CO_2 gas in thermochemical equilibrium is completely on the product side. It can be assumed that increased temperatures contribute to better conversion and kinetics in the real process.

Regarding the following chemical recycling steps, the deactivation of metallic lithium is crucial. Therefore, the shredding process is to be carried out under CO_2 atmosphere. Metallic lithium is very reactive, so even at room temperature (25 °C) the reaction between Li and CO_2

$$2Li + CO_2 \rightarrow Li_2CO_3 + CO$$

is spontaneous and exothermic, with [49]

$$\Delta G^0 = -480.47\ kJ$$
$$\Delta H^0 = -539.52\ kJ$$

This will result in heating of the material and the furnace and makes the process therefore less energy intensive.

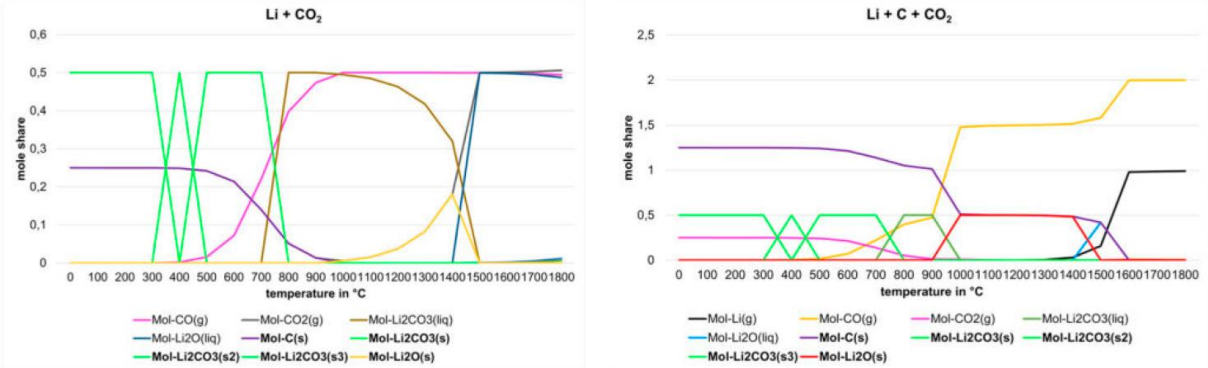


Figure 10: Thermochemical FactSage simulation of reaction products of lithium with CO_2 and C between 0 and 1800 °C carried out by Schwich et al. [17]

Due to the complete conversion of the lithium, the low melting point of 180.5 °C is unproblematic for thermal treatment, since the melting point of lithium carbonate is 723 °C. The presence of carbon, for example from the binder decomposition or from the carbon black, has no negative influence on the desired reaction in the interesting temperature range of up to 600 °C as well.

The behaviour of the cathode material during thermal treatment has already been studied by some researchers in the context of conventional NMC lithium-ion batteries [20, 50–52]. Organic decomposition and the presence of solid carbon such as carbon black and metallic aluminium at elevated temperatures lead to reducing conditions during the process. Thus, with increasing temperatures, there is a gradual reduction of the mixed oxides. XRD analyses by Balachandran et al. [53], given in Figure 11 show these changes with process temperature for conventional LIBs.

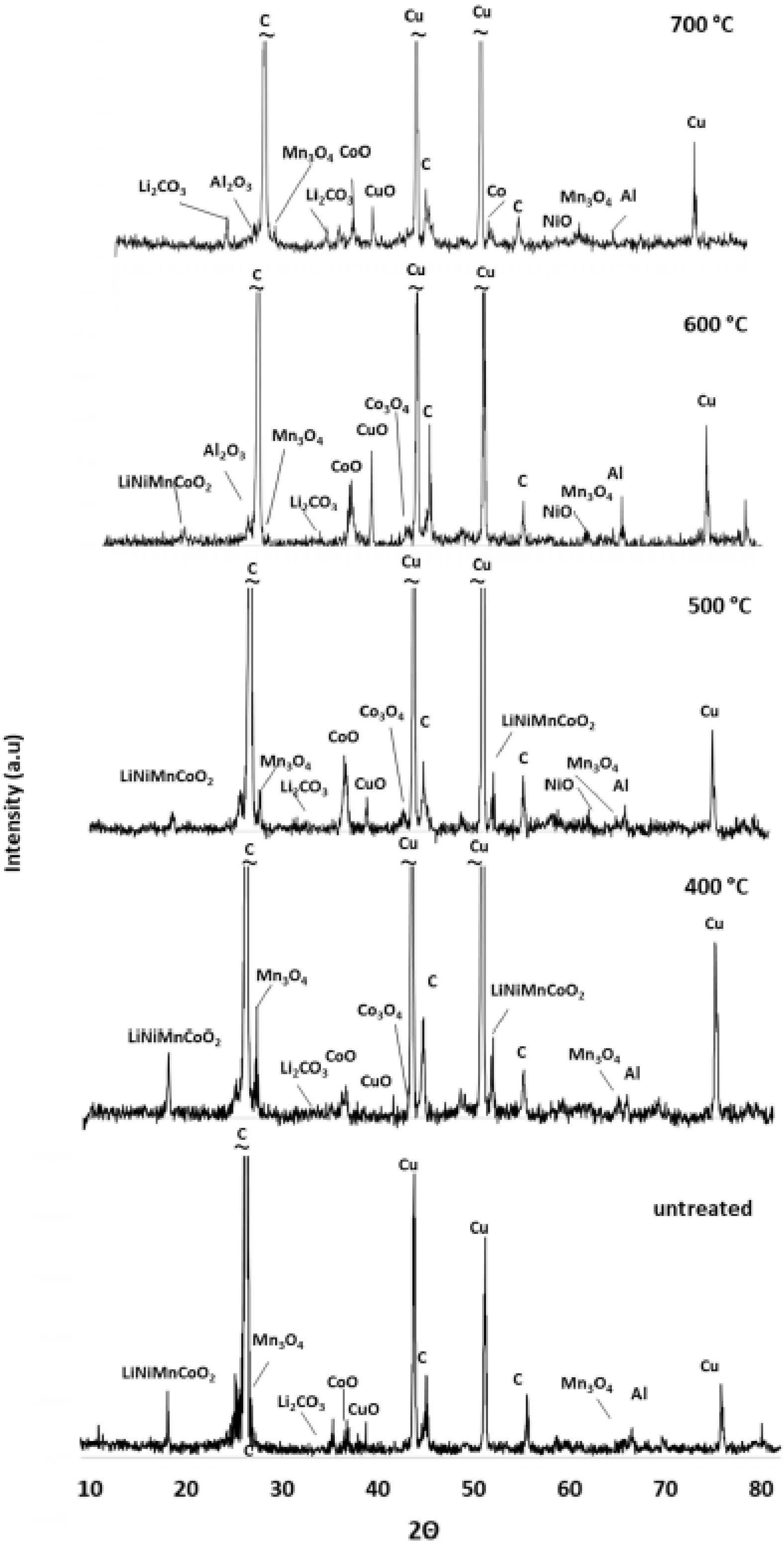


Figure 11: XRD Analysis of common LIBs NMC black mass after pyrolysis at different temperatures. [53]

Based on this experience, it can be assumed that reduction reactions will also occur in the SUBLIME cells at the minimum necessary temperatures for binder decomposition of 500-550 °C. However, a major difference is the significantly lower organic content of the SUBLIME cells, so that a smaller amount of reducing gases is expected. Although the solid-solid reaction with aluminium is also possible, it will proceed more slowly than the solid-gas reaction and is therefore time-dependent.

Since no thermochemical data are available for the thermal degradation of the electrolyte and possible reactions with the other cell components and the gas atmosphere, no FactSage simulation can be carried out in this respect. But since the electrolyte is produced in a sinter process at 550 °C [54, 55], it is assumed, that no decomposition during the thermal pre-treatment takes place. As the process takes place at elevated temperature and under inert atmosphere, external humidity contact with the electrolyte can be avoided. Nevertheless, a certain level of emissions is always to be expected, as water could be a reaction product from the binder decomposition. This makes adequate exhaust gas cleaning indispensable. For the organic compounds a post combustion is recommended. The removal of possibly evolved H_2S can be carried out either by a wet scrubbing, for example with a copper sulphate solution or by filtration with activated carbon. A combination of all three cleaning steps would be the safest solution and ensures compliance with maximum emission values. It is also a common industrial set-up for pyrolysis plants.

Mechanical separation

After the shredding and thermal treatment, a shifting and sieving step is necessary, to separate the copper and aluminium foils and the casing from the other materials. The separation is crucial for the highest possible recovery of the active materials. Residues adhering to the films cannot be recovered without an extremely high effort. The foil fractions can be fed into the conventional pyrometallurgical copper and aluminium recycling plants.

Depending on the nature of the active materials, a grinding step is necessary for further digestion. Before the active materials are fed to the leaching steps, they should be as fine-grained as possible for high reactivity. But the necessity will have to be investigated experimentally.

For common LIB cells, Zhang et al. reported a delamination efficiency of the current collector foils of 98 %, in case a thermal treatment is carried out beforehand, to remove the binders [16].

Ethanol washing of electrolyte

The electrolyte of the SUBLIME cells is also to be recycled for the most holistic recycling possible. This would also be an advantage over conventional LIBs, from which the electrolyte can currently only be thermally used.

Since the electrolyte is soluble in polar organic solvents such as ethanol, a leaching process is a suitable option for recovery [56]. From the manufacturing process, it is known that the electrolyte can be dissolved in ethanol to form a solution of at least 10%. Figure 12 shows tests carried out by Ruhl et al. [57], where the solubility of Li_6PS_5Cl in different solvents was investigated. From the investigated solvents just ethanol and methanol are able to chemically dissolve the electrolyte.

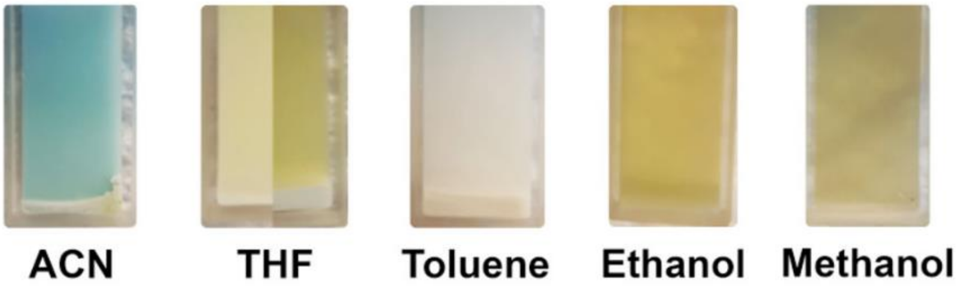


Figure 12: Cuvettes with different solvents and 10 wt.-% Li6PS5Cl. [57]

Since the lithium has already been converted to lithium carbonate, no reaction will occur at this point. The NMC is also insoluble in ethanol, so this is a selective recovery step. Since a special requirement for the electrolyte is also its separator property, it is of high importance that there is no carbon in it. Since carbon is also insoluble in ethanol, this is not a problem. Accordingly, solid-liquid separation is important after the ethanol leaching step, in which even the smallest particles must be filtered off.

Electrolyte recovery can be implemented as conventional stirred leaching. The solid-to-liquid ratio of shredded battery mass and ethanol must be evaluated in trials. Since a solution with 10% LPSC is used for the battery manufacturing process, the appropriate amount of ethanol should be used based on the LPSC content in the battery mass.

Sulphur losses may have occurred during usage and the preliminary recycling steps, so that a sulphur carrier such as Li_2S may have to be added again for remanufacturing. This can be evaluated, for example, via the conductivity of the solution and/or chemical element analysis.
After leaching, the electrolyte is crystallized by evaporating the ethanol at 180 °C. Subsequently, the electrolyte can be regenerated analogous to the description in previous deliverables, either by grinding in a ball mill or by a sintering process at 550 °C [54, 55, 58].

Water washing of lithium-carbonate (CO_2 assisted?)

The concept of early-stage lithium recovery is already known from investigations of common LIB cells and is reported as well for lithium-sulphur cells. Since lithium carbonate has a solubility in water of 13.3 g/l at 20 °C whereas the NMC oxides and metals are insoluble, a selective washing is possible. Balachandran et al. investigated the lithium recovery from pyrolyzed black mass of conventional LIB cells depending on thermal treatment temperature. The resulting leaching efficiencies are shown in Figure 13.

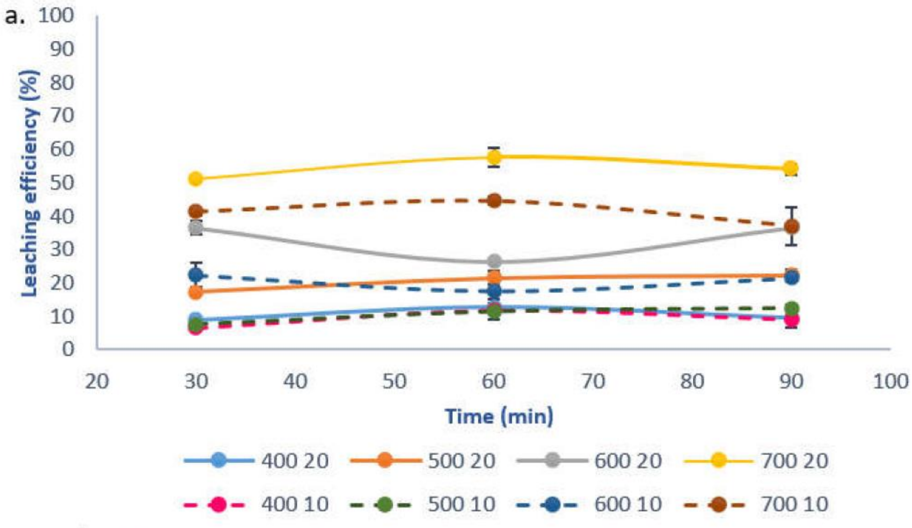


Figure 13: Leaching efficiency of lithium from pyrolyzed NMC black mass depending on pyrolysis temperature, pyrolysis time and liquid to solid ratio (20:1 and 10:1 ml/g). [53]

High temperatures up to the melting point of aluminium are favourable for higher leaching efficiencies, due to the decomposition and reduction reactions of the NMC oxides presented in Figure 11. In comparison an incineration process shows very low leaching efficiencies around 20 % for lithium. This underlines the importance of reductive conditions in the thermal treatment process. For the mobilisation of the lithium from the NMC oxide, an optimised thermal treatment is necessary. In addition, the liquid-to-solid ratio has an influence on lithium recovery. In the example shown, an excess of water at an L/S of 20:1 is advantageous. Thus, in the case of used, thermally pre-treated NMC cells and mixed black mass of NMC and graphite, lithium yields of 60 to around 70 % have been achieved in the literature so far [17, 53]. Here, thermal treatment under CO_2 atmosphere seems to offer advantages over inert treatment [17]. However, this has not yet been investigated in depth. So far, it is also unclear in which compounds the non-leachable lithium is present; this is the subject of further research. Other studies that examined pure NMC cathode material with the addition of carbon carriers such as carbon or graphite without further battery components even showed yields of up to 98.9 % [26]. In real mixed black mass and with material already used and aged in cells, however, lower yields as observed with Balachandran are to be expected due to reactions with other cell components. For the consideration of the SUBLIME cells, a recovery of 60 % of the lithium bound in the NMC can thus be conservatively assumed in case of thermally treated material.

The metallic lithium was converted to carbonate in the previous process steps by reaction with CO_2. Similar studies are available for lithium sulphur batteries by Schwich et al. [17]. Here, battery cells that also contain metallic lithium were thermally pre-treated under different atmospheres with the aim of complete reaction to carbonate. Afterwards a CO_2 assisted water leaching step was carried out: The

black mass is stirred in water. Additionally, CO_2 gas is bubbled in the solution. The formation of carboxylic acid and resulting lithium hydrogen carbonate leads to improved solubility of lithium. Normally, the solubility of lithium carbonate decreases with increasing water temperature, but in the case of CO_2 introduction, higher solubilities are observed with temperature. Accordingly, in the study by Schwich et al. experiments were carried out at a medium temperature of 60 °C in addition to room temperature. The best results were obtained for a material thermally pre-treated under CO_2 and Ar with an s/l = 1:80, temperature of 60 °C and a leaching time of 120 min with CO_2 introduction at 2.5 L/min. The amount of sample and water used per test is not given [17].
After water leaching, the water was evaporated so that the lithium salt is recovered as a solid. Yields of up to 95 % were achieved [17]. Since these are also cells with metallic lithium in the presence of sulphur in the system, similar results can be inferred for the anode of the SUBLIME cells.
In addition to the elemental lithium yield, Schwich et al. [17] characterised the lithium product in terms of phase composition using XRD. The product consists mainly of lithium carbonate. Li_2SO_4 can be detected as an additional component. The purity of the lithium product is given as 94.35 % [17]. Of course, the purity of the lithium salt cannot be determined exactly without experimental validation when recovering from SUBLIME cells, but these values serve as an order of magnitude. It must be noted that this is a different cell system.

In an industrial process, water consumption is of high interest. The lithium is precipitated by temperature rising and evaporation of water. This water vapor can of course be recovered, condensed, and circulated for leaching of the next material batch. Because of the solubility decrease with rising temperature also partial precipitation of the lithium salt with temperature rising without complete boiling could be possible. The resulting depleted lithium solution can be used for the next leaching step as well until saturation is reached. In this way, a complete water cycle and a process without the use of chemicals but with CO_2 capturing can be realized. As one can never calculate with 100 % recovery yields, it has to be considered, that parts of the electrolyte that were not dissolved in the previous process step during ethanol leaching could enter the water washing step, too. For this reason, the off gas, consisting of CO_2 and possibly H_2S must be washed with e.g., a copper solution, where the sulphur can be captured in a sulfidic copper phase, or filtered by active coke. This will avoid harmful gas emissions.

Hydrometallurgy of NMC residue
The resulting solid residue from the water leaching step, the so-called black mass is treated hydrometallurgical in this approach. As process sheet, the process flowchart carried out by Wang and Friedrich [59], shown in Figure 14 is adopted for the SUBLIME cells.

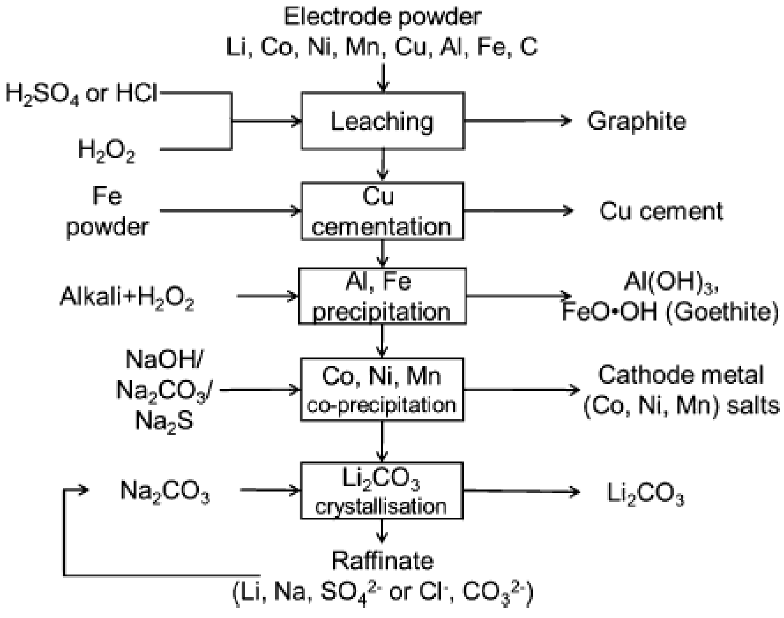


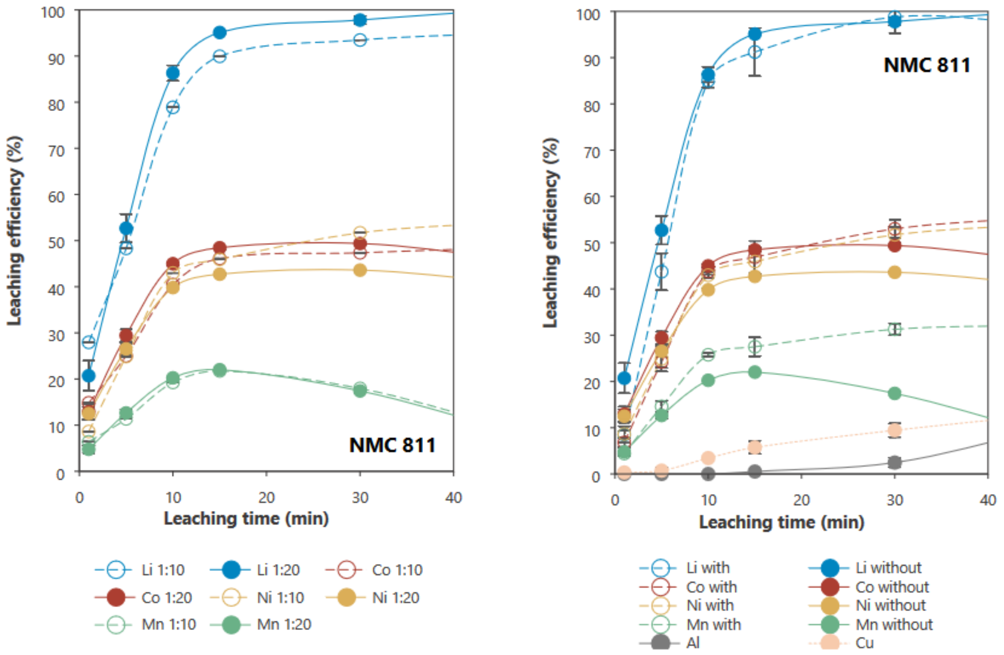
Figure 14: Hydrometallurgical Process, developed by Wang and Friedrich. [59]

The first step carried out, is the leaching of the NMC residue. There are already many studies dealing with the leaching of NMC black mass from common LIBs in literature. Until now, leaching with mineral acids like H_2SO_4, HCl and HNO_3 show the best leachabilities and are investigated for a wide range of cathode materials and process parameters [15]. For this reason, the hydrometallurgical process for SUBLIME cells will be based on sulfuric acid leaching in this investigation. Since the cells are based on a sulfidic system, H_2SO_4 don't bring any new elements in the process. The following equation gives the chemical reaction of the leaching of NMC811 with H_2SO_4:

$$40LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2(s) + 60H_2SO_4(aq) \rightarrow 32NiSO_4(aq) + 4MnSO_4(aq) + 4CoSO_4(aq) + 20Li_2SO_4(aq) + 60H_2O(l) + 5O_2(g)$$ [60]

In many studies, the reducing agent H2O2 is added during leaching to reduce Co3+ to Co2+ and Mn4+ to Mn2+. But a sufficient thermal treatment can lead to less needed H2O2 because of partial reduction of the NMC oxides as presented above.

To gain high leaching efficiencies of the single metals, acid concentration, addition of reducing agent, temperature and leaching time and solid to liquid ratio are the most important process parameters. Variations of this parameters were studied for example by Viceli et al. [61] for pure NMC811. Figure 15 presents the investigation of different process parameters. The first diagram gives the influence of the s/l ratio. As expected, higher liquid amount results in better leaching efficiencies, but in this case, the difference between 1:10 and 1:20 are not very high. Another important aspect is the presence of Al and Cu, because due to the shredding process, the NMC black mass will still contain amounts of these elements. In case of Mn, the presence of the two metals is advantageous, because they can also work as reducing agents. But significantly higher leaching efficiencies are reached when H_2O_2 is added to the solution. For best leaching efficiencies, a multistage addition is preferred against a onetime addition at the beginning of the process. The addition leads to higher leaching efficiencies of close to 100 %, except of Mn with a leaching efficiency of around 88 %. Moreover, the kinetics are very high; the elements are completely leached after ~ 15 min and Mn after ~ 60 min. The last diagram (4) shows the adoption of the parameters (50 °C, 2M H_2SO_4, s/l = 1:20 g/ml, 3%v/v H_2O_2 (59% w/w)) for a real spent of life battery black mass, but with NMC 111. All elements expect of Al can be leached with an efficiency of close to 100 %.



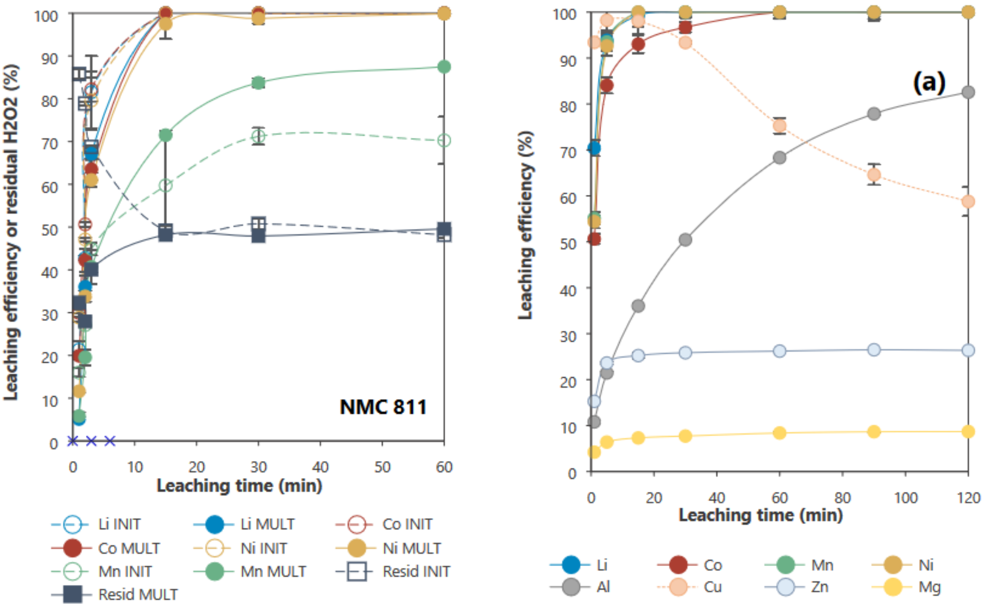


Figure 15: Leaching efficiency of the single metals from pure NMC811 with 2M H_2SO_4 at (1) different s/l ratios, (2) with and without the presence of Al and Cu, (3) with initial and multistage addition of H_2O_2 and (4) for real end of life black mass from NMC111 cells. [61]

Further studies have investigated mostly LCO and NMC 111 battery systems. To classify the results obtained in the individual studies, it is important to take the difference in cell chemistry into account on the one hand, but also to know the pre-treatment of the material on the other.

The investigation of Wang describes the H_2SO_4 leaching of mainly NCO battery active mass after thermal treatment with addition of H_2O_2. Recommended results from this study are a s/l = 100 g/L, a leaching temperature of 80 °C, H_2O_2 concentration of 50 g/L, 2 M H_2SO_4 and retention time of 2 h [59]. The achieved leaching efficiencies are summarized in Table 4.

Table 4: Leaching efficiencies achieved by different researchers.

Material	Leaching	Cu	Al	Ni	Co	Mn	Source
Mainly NCO but with Mn	2M H_2SO_4, 100 g/l, 80 °C, 2h, 50g/l H2O2	>99.9 %	99 %	98.6 %	>99.9 %	98 %	Wang [59]
NMC	1.2M H_2SO_4, 100 g/l, 85 °C, 3h, 2.5M H2O2	97 %	100 %	90 %	95 %	95 %	Pagnanelli[62]
NMC, roasted with carbon black at 550 °C	4M H_2SO_4, 100 g/l, 90 °C, 30 min			99.56 %	99.87 %	99.9 %	Liu et al.[22]
NMC with lignite, roastet at 350 °C	H_2SO_4 (1.15 eq), 285 g/l, 55 °C, 2.5 h			98 %	96 %	98 %	Zhang et al.[63]

Other researchers reached similar results such as Pagnanelli et al. [62], who gained just slightly lower leaching efficiencies for the NMC metals, but without thermal treatment of the material. In comparison Liu et al. [22] and Zhang et al. [63] carried out a reductive thermal pre-treatment on NMC material, and therefore didn't used any H_2SO_4 but gained high leaching efficiencies as well.

Thus, for the NMC residue from the SUBLIME cells to be used in leaching, reasonable leaching conditions can be theoretically derived from the literature. Because the material is thermally pre-treated under reducing conditions, the partly decomposition and reduction of the NMC is predicted, as described above. Therefore, no, or just small amounts of H_2O_2 will be necessary to reach high leaching efficiencies in H_2SO_4. For the first investigation a 2 M H_2SO_4 can be chosen, with a leaching time of 60 min and a temperature of around 60 °C, what is a bit more conservative in comparison with the leaching conditions reported for pure NMC 811. The s/l is calculated based on the NMC content of the black mass fraction. Since the reported data from Table 4 originates from common cells, the NMC content in the black mass is lower due to graphite content. In the case of SUBLIME cells, there are just small amounts of pyrolysis coke, residues of lithium and electrolyte from the previous leaching steps and small copper and aluminium particles from the collector foils resulting from the shredding process.

After leaching, the remaining solid residue, which will mainly consist of pyrolysis coke is filtrated. It may be usable in pyrometallurgical processes as reducing agent. It is not expected that it could fulfil requirements for new carbon products.

The filtrate is afterwards treated for single metal recovery. In this approach the precipitation of mixed salts is chosen. It is based on different solubility of the metals in dependence of pH value and temperature. An example for the relevant battery components is shown in Figure 16.

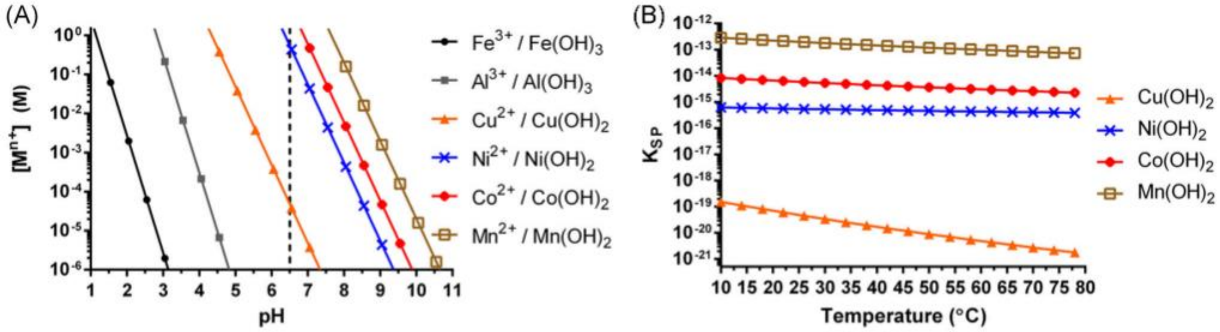


Figure 16: Example of single metal solubility in aqueous solution in dependence of (A) pH value and (B) temperature. [64]

The NMC metals are very close to each other, so selective precipitation and recovery via this method is not possible. But aluminium and copper can be removed from the solution in the first steps.

The first step is the copper removal from the solution via cementation. Iron powder is added, so that the copper ions are reduced, and metallic copper is formed. Wang and Friedrich [59] carried out this process step at 60 °C because the cementation process is faster at higher temperatures. But iron solubility in the solution is rising with temperature, what is not favoured since it has to be removed in the next step. Therefore 60 °C are a good compromise between sufficient kinetics and possibly low iron solubility in the solution in the process of Wang and Friedrich [59]. The next step is the precipitation of aluminium and iron by pH adjustment. The metals are precipitated as hydroxides by adding NaOH until a pH level of around 4.8. Afterwards the solid precipitation product is removed from the solution by filtration. It has to be taken into account, that the exact process parameters are dependent on the single metal contents in the solution. For aluminium and copper, this depends mostly on the mechanical treatment and separation steps. The concentrations of both metals should be as low as possible in the black mass fraction, so the best precipitation results could be achieved. Moreover, adjustment of the pH level has to be carried out carefully, to prevent co-precipitation of Co, Ni and Mn. However, literature studies indicate slight losses of around 3-5 % [59] of the NMC metals during the aluminium and iron removal.

After the removal of copper, iron and aluminium from the solution, the co-precipitation of cobalt, nickel and manganese hydroxide is carried out by further pH adjustment with NaOH to around 10.5, as shown in the following equations [65]:

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$$
$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$$
$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2$$

The recovery rates in this process step are around 99 %. Afterwards, the mixed salt is removed from the solution by filtration and can be sold to already existing metal plants as an intermediate product for production of single and high purity metal salts. The direct recovery of NMC from the mixed salt is an option as well, probably with adjustment of stoichiometry of the single metals and of course lithiation, as reported by Ma et al [65].

Possibly remaining lithium content in the solution can be recovered by adding Na_2CO_3 and temperature adjustment to around 90 °C, so that Li_2CO_3 can be precipitated as well [59].

Process water treatment is an issue in common LIBs recycling as well, so also in this case, no concrete solution can be presented so far.

2.2.3 Flow-Chart and Mass Balance Calculation for Recycling Option 1

Based on the described process in 2.2.2, a flow chart is established. With reported data of recovery rates and leaching efficiencies in literature from common LIBs (described above), as well as thermochemical simulation where possible, a mass balance of the single elements is carried out. For this calculation, many assumptions and simplifications had to be made. The real recycling efficiencies can of course just be figured out by real experiments, which are not part of this project. Therefore, the given results serve as a first estimation and approximation of the recyclability of the SUBLIME cells.

The full mass balance calculation can be seen in Appendix B. Here the amounts of all elements are given for the single intermediate products, as well as the assumed recycling efficiencies over all process steps.

For the evaluation of the process provided and the recyclability of the SUBLIME cells, the overall recycling efficiency is the most important value for each element. The results are given in Table 5.

Table 5: Elemental recycling efficiencies for process option 1.

Element	Recycling Efficiency [%]	EU directive 2025
Ni	90.3	90
Co	91.2	90
Mn	91.2	
Li (salt+electrolyte)	81.9	35
Li_6PS_5Cl	88.2	
Cu (Foil+Powder)	99.6	90
Al Casing	99.5	
Al Foils	no Recovery, because until now, no sufficient separation from Cu foils possible	
Al (all)	98.3	

The recycling efficiencies reached can deal with the new EU directive. Especially for lithium quite high recycling efficiencies are predicted in comparison to already existing industrial recycling routes for common LIBs. The overall battery recycling efficiency is around 96 %. But it has to be assumed, that the calculation is based on the monolayer pouch cell. For this cell, the aluminium casing content is extremely high. This distorts the recycling efficiency to very high values since the recovery of the casing is one of the easiest parts in recycling.

The whole process with its products is summarized in Figure 17.

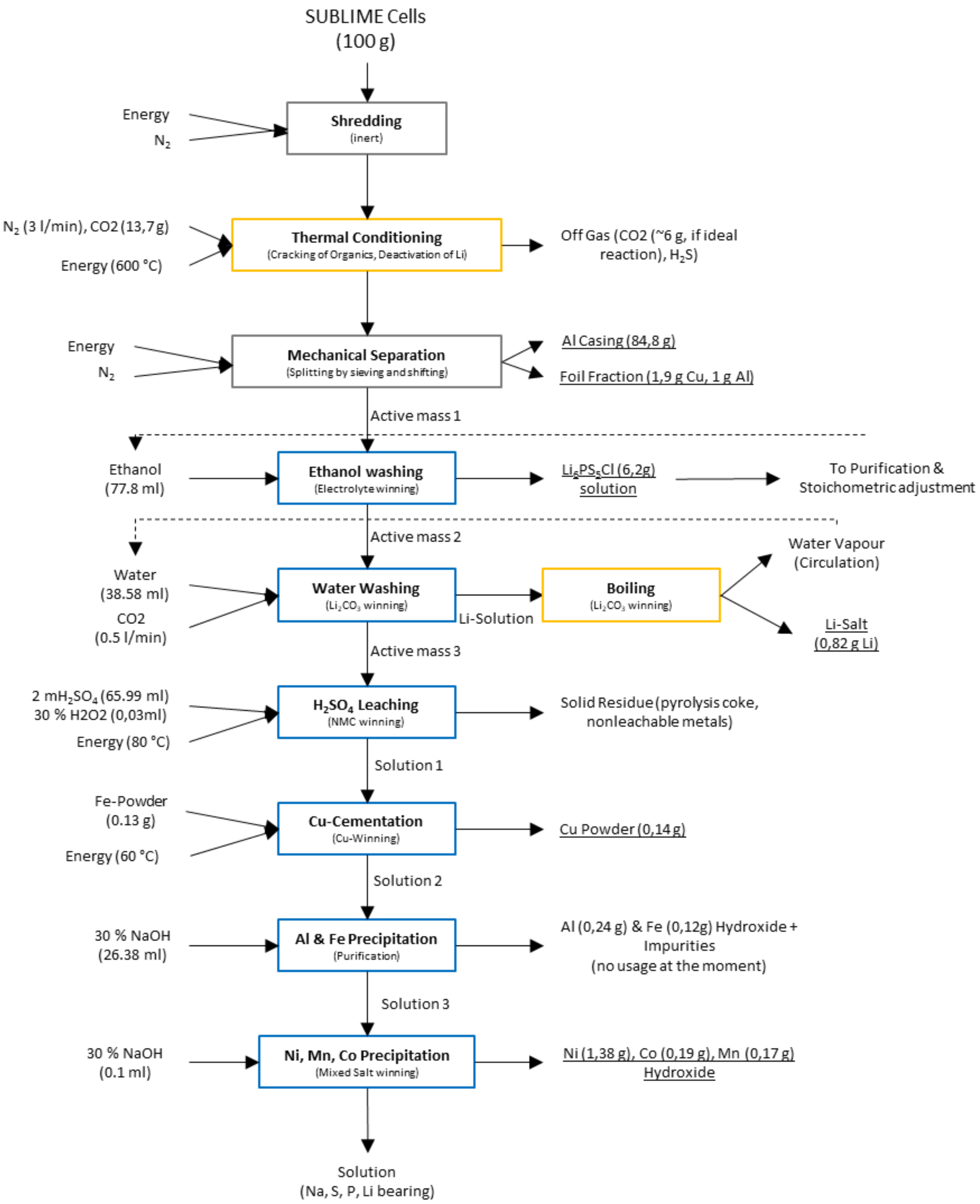


Figure 17: Process flow chart recycling option 1.

The sellable and usable product fractions are indicated by underlined text. The aluminium casing fraction should be a very pour metal, and therefore it can be easily recycled in common aluminium smelters. The foil fraction consists mainly of the copper and aluminium foils but will also contain some impurities from the active mass fractions and the electrolyte (see Appendix). Currently, no separation process for the copper and aluminium foils is reported in large scale. Therefore, the foil fraction will be feed to copper smelters, where the aluminium content is lost in the slag. One other product is the recycled solid electrolyte Li_6PS_5Cl. It is recovered in an ethanol solution. Although it is not known yet in what stoichiometric composition it can be recovered, it must be assumed that degradation processes during cell use can take place as well as during thermal treatment occur. For this reason, it will probably be necessary to adjust the stoichiometry and purify the product at the electrolyte manufacturer. The recovery of the electrolyte is based on the most uncertain assumptions, as there have been no experimental implementations to date, and thermodynamic calculations are also not possible due to a lack of data. Therefore, some assumptions were made here based on the knowledge from the manufacturing process. It can be produced by a sinter process at 500 °C, so it is assumed, that the thermal treatment will nearly not affect its structure. But no TGA DTA data was available and no information on possible reactions with other cell components are given. If future experiments would show the degradation of the electrolyte, a more complex process sheet with recovery of electrolyte directly after crushing could be possible. But in this case, separation or transformation of lithium has to be ensured as well, otherwise the metallic lithium would react with the ethanol.

The solid residue after the leaching step cannot be seen as a product fraction, as its composition is not clear. It is expected to consist mainly of pyrolysis coke as well as small amounts of undissolved metallic cell components. Dependent on its carbon contend it could be a possible feed to pyrometallurgical processes as reducing agent.

After leaching, different precipitation products are recovered. The first is a very pure Cu-powder, which can be feed to copper smelters. The second one is an Al and Fe hydroxide, without field of application. It is expected that most of the halides like S, P and Cl will be precipitated as well in this process step. Therefore, the solid product is to be deposited. In further research, it should be paid special attention to low aluminium contents in the black mass fraction to keep this fraction as small as possible.

The last, and a very valuable product is the mixed Ni, Co, Mn hydroxide. This salt can be sold to metal producers, where the single metals are recovered via solvent extraction and, if desired electrolysis. Before, the relatively high Al content has to be removed, e.g., by treatment with NaOH. This points out the importance for a highest possible separation efficiency in the mechanical treatment steps. Dependent on the purity, the resulting salt, it may also act as input material for the direct synthesis of new NMC material. But this cannot be evaluated in this study.

The presented data shows, that the elaborated recycling process led to highly valuable products and high recycling efficiencies, which can deal with the expected new EU directive in theory.

2.2.4 Recycling Option 2 – Pyrometallurgical treatment

Another approach to recycle the SUBLIME battery cells is the pyrometallurgical melting process. The cells will be directly melted with slag forming elements. This procedure can be understood as a splitting operation of the more noble metals cobalt, nickel, and copper from the less noble elements like lithium, aluminium and manganese. In case of common LIBs, the enrichment of lithium in the flue dust as well as in the slag phase was already investigated. In this approach, for the SUBLIME cells, the enrichment in the slag phase is targeted, so that the slag can be feed as a mineral intermediate product into the primary lithium winning process from ores. To bring aluminium and lithium into the slag phase, fluxes are necessary. The most important aspects by adjusting the flux addition are

- the melting point of the slag phase
- high lithium solubility
- low copper, cobalt, and nickel solubility
- propriate viscosity.

Common already reported fluxes for battery recycling are SiO_2 and CaO [33, 35, 36]. Due to the significant difference in cell chemistry of the SUBLIME cells, especially because of the presence of sulphur, reported metal recovery rates from common LIBs cannot be transferred easily. Therefore, thermodynamic calculations with FactSage are carried out for the given cell system. The amounts of CaO and SiO_2 addition were varied, until completely liquid phases were reached. For this calculation a simplification was assumed: because the provided data for cell composition is just for a small monolayer pouch cell, the amount of aluminium with ~85 % is extremely high per cell. This would lead to extremely high amounts of additives for slag formation and a quite low lithium concentration in the slag. Therefore, the calculations are based on a lower aluminium amount from the foils plus residues from the casing removal, which results in an assumed aluminium content of around 14 % for the Input of the calculations. As process temperature 1 500 °C are set, as a similar range is reported from literature [35, 36] and a high liquidus temperature of the resulting nickel containing alloy is estimated.

For this report, individual computation results are not presented because of the large amount of raw data involved. The best results were gained with an addition of 2 g CaO and 3 g SiO_2 per 100 g (minus casing) SUBLIME cell. Here, all phases were liquid and a high slagging of lithium of around 90 % is reached. The rest of the lithium will be carried out via the flue dust as LiCl. Moreover, slagging of the other valuable metals is quite low, so that around 99 % of Co, Cu, Ni can be enriched in the metal phases. Manganese is spread over the metal and slag phases, because of its more ignoble character. Phosphorous is assumed to accumulate in the metal phase, since copper and nickel have a high P solubility around 15 % [66]. The results are summarized for all relevant elements in Table 6.

Table 6: Element distribution in the metal, slag and gas phase [49].

Input		**Metal phase 1+2**			**Slag**		**Gas**	
	Mass [g]	Mass [g]	Mass [g]	Recovery [%]	Mass [g]	Recovery [%]	Mass [g]	Recovery [%]
Li	2.163	0.0127		0.59	1.96	90.61	0.182	8.41
P	0.815	0.771	0.0012	94.80			0.0356	4.37
S	4.217				4.18	99.12	0.002	0.05
Cl	0.932						0.92	98.68
Ni	1.549	1.54	0.0029	99.61				
Co	0.200	0.117	0.0824	99.70	0.00015	0.08		
Mn	0.182	0.1298	0.0023	72.67	0.04778	26.28		
Al	2.000			0.00	1.949	97.45		
Cu	2.079	2.04	0.025	99.32	0.031	1.49		
CaO	2.000				1.98	99.00		
SiO_2	3.000				2.97	99.00		

It has to be considered, that the presented results are for an ideal equilibrium state. In a real process, for example higher lithium losses via the off gas has to be assumed, but concrete values cannot be given in this theoretical approach. The comparison with literature shows lithium yields either in slag or in flue dust from around 60 to 82 % [35, 36]. For example, Sommerfeld et al. produced a slag with 7.4 wt.-% lithium and a lithium slagging yield of 82.4 % in a SiO_2-Al_2O_3-Li_2O slag system. Due to the comparable high lithium content in the SUBLIME cells, higher lithium concentrations in the slag can be achieved in this case.

For lithium recovery, the slag phase has to be mechanically and chemically treated. From discussion with experts from industry it is known, that from common lithium bearing slags from LIB recycling, a recovery rate of around 50-60 % can be assumed under industrial conditions. Therefore, the slags are shipped to primary lithium producers, e.g., to Australia. Here the slags are milled to small grain sizes. This process will be highly energy intensive. Afterwards the slag is feed to the primary, hydrometallurgical lithium winning process from ores. Since the slag contains around 13 % lithium, a previous concentration is not necessary. Because the composition of the produced slag is not equal to the few ones described in research, no more details of suitable leaching conditions can be given. For concrete leaching conditions, the phase composition of the crystallized slag is important. On the one hand, this is dependent of the chemical composition, but on the other hand, it is also depending on cooling conditions. This would have to be estimated experimentally.

The produced metal phase contains a high P amount of around 14 %. To overcome problems in the already existing industrial hydrometallurgical metal producing plants as described in section 2.1.4, the phosphorous can be removed by a converting step. Therefore, the produced, liquid alloy is fed in a converter, where oxygen is injected into the melt. The phosphorous is removed as P_2O_5 and collected in a slag phase. But high metal losses to the slag, which will require further treatment are to be expected, as shown by the thermochemical modelling in Figure 18 [49]. Here, an exemplary converter process is modeled with 2 g SiO_2 und 2 g CaO as additional slag formers. This leads to an overall maximum metal recovery until this step of 98 % Ni, 97 % Cu, 87 % Co and 72 % Mn. But higher losses have to be assumed in real experiments.

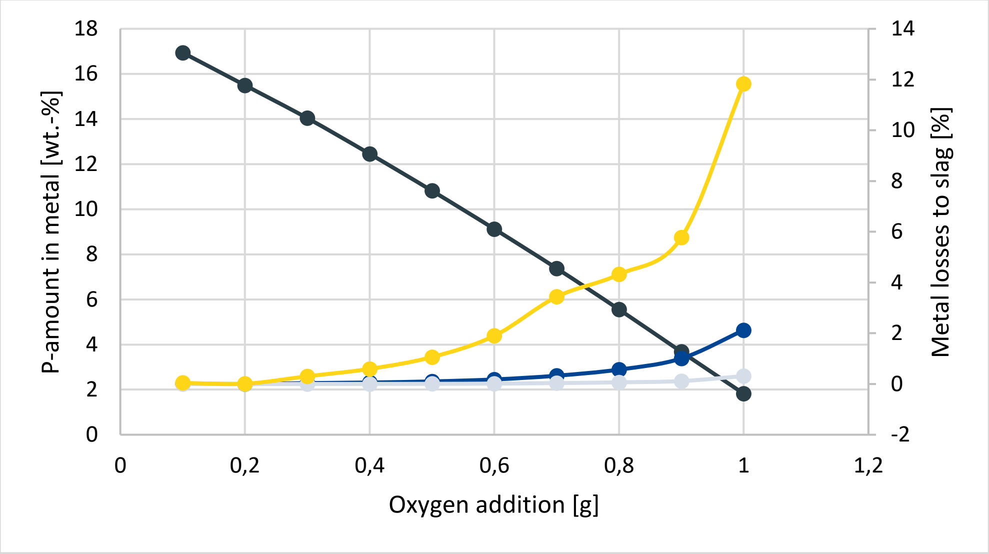


Figure 18: Metal losses during phosphorous removal.

Afterwards, the alloy can be sold to already existing metal extractors. Here, the single metals Mn, Cu, Ni and Co can be recovered for example as metal salts by solvent extraction.
The slag produced may be a possible feedstock for fertilizer production.

All high temperature steps require a sufficient off gas cleaning and dust separation. During melting, a part of the lithium is carried out as LiCl. When lowering the temperature of the off gas, it will be condensed and collected in the flue dust. So, a filter and scrubber system is necessary, to recover on the one hand the flue dust, from which lithium can theoretically also be recycled, and remove possible other halide containing off gas components like SO_2 or H_2S.

The resulting flow chart for this process option is shown in Figure 19.

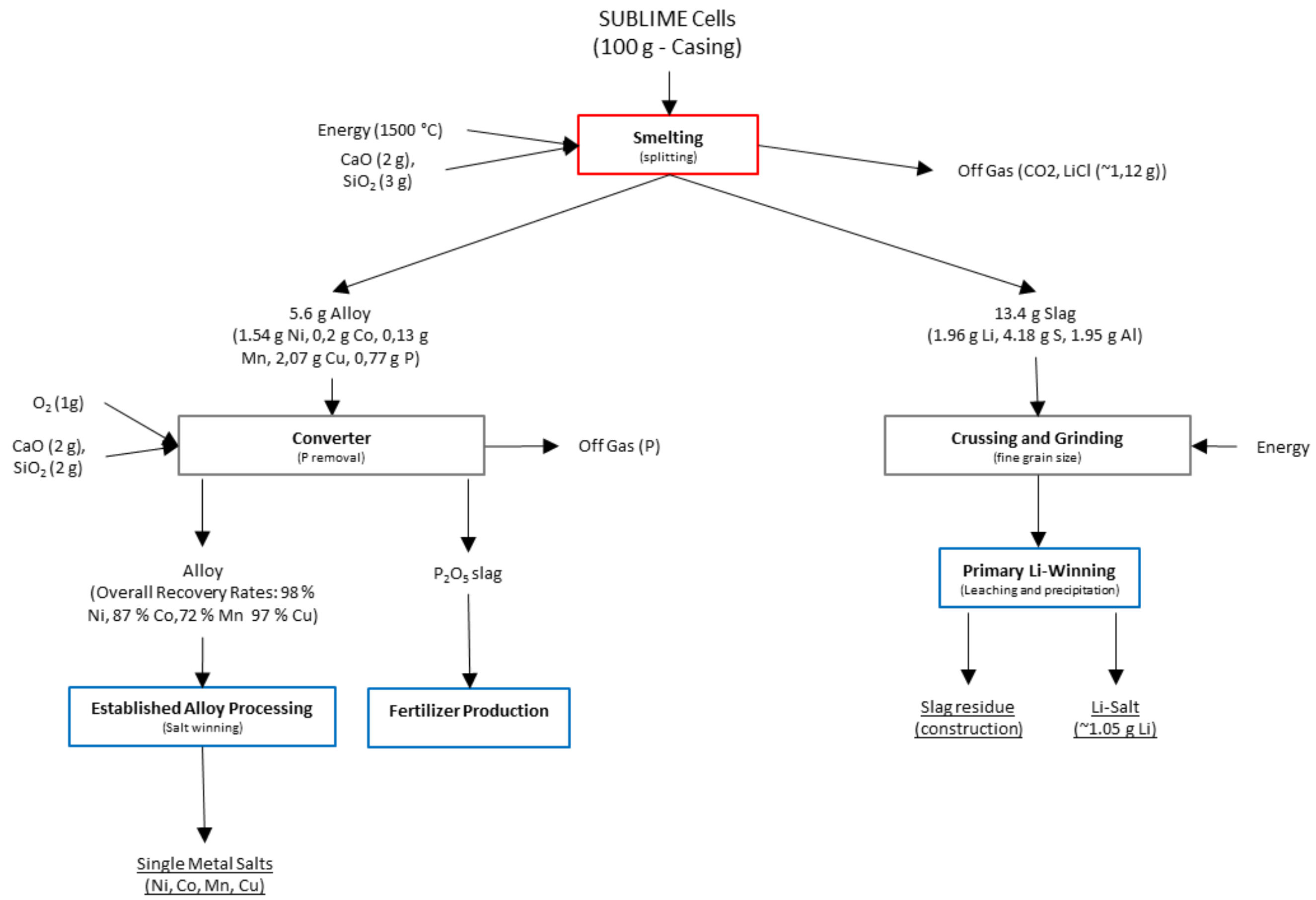


Figure 19: Process flow chart recycling option 2.

Drawbacks of this recycling chain in comparison to the presented option 1 are the loss of the solid electrolyte. Just single elements like lithium are recoverable. Sulphur will be lost in the slag and phosphorous will be downcycled to fertilizer. Moreover, aluminum and around 26 % of manganese are lost in the slag and not recovered. The lithium recovery from the slag is energy and chemical intensive. The recovery of the valuable metals copper, nickel and cobalt in an alloy is possible with high recovery yields, but the necessary converter step to remove phosphorous from the metal will lead to metal losses and is an additional process step.

3 Discussion and Conclusions

Based on detailed literature review, two possible recycling chains for SUBLIME cells have been carried out. Therefore, already existing/applied process steps from LIBs recycling are adapted, and some new process steps are added to get to high recovery yields of the single battery elements. The first approach starts with discharged battery cells which are feed to a shredding process and a thermal treatment for metallic lithium deactivation and binder removal afterwards. The casing and foils can then be separated from the black mass fraction and the electrolyte is recovered in an ethanol washing step. The recovery of the expensive electrolyte is a huge advantage of this process route, since it can be reused for fabrication of new cells after purification and stoichiometric adjustment. In comparison, in the second, pyrometallurgical process route, the electrolyte cannot be recovered. During the melting process, it gets dissolved in the melt and the single elements are spread over all occurring phases (metal, slag, gas). Also, aluminium is lost in the pyrometallurgical process in the slag phase and not recovered.

The lithium recovery is also a crucial point in the recycling of SUBLIME cells. The cells contain a huge amount of lithium, and its recovery has a high relevance, especially since the element was classified as critical raw material by the European Union. The first recycling approach is based on the concept of early-stage lithium recovery, where the lithium is recovered in a water washing step, assisted by CO_2 insertion. Benefits of this concept are no need for chemical usage and a high selectivity of the process. So based on experiences from literature, high recovery-yields of around 90 % for lithium are expected. The recovery of lithium from the pyrometallurgical step is on the other hand more energy and chemical intensive. Although a high enrichment yield of lithium in the slag of around 90 % can be expected, this slag must then be shipped to primary lithium producers, where it must be crushed and milled in an energy-intensive process and then further processed in the primary lithium extraction process. Estimated lithium recovery rates here are only around 50-60 % for the processing of the slag.

Recovery of copper, nickel and cobalt with high recycling efficiencies is possible in both recycling approaches. The first one is based on a sulphuric acid leaching with following cementation and purification step. Afterwards a mixed manganese, cobalt and nickel hydroxide salt is precipitated by pH adjustment. This mixed salt can be sold to specialized purification plants, where new NMC material can be produced. It is estimated that this process route can fulfil the new EU requirements with recycling efficiencies > 90 %. In case of pyrometallurgical recycling, an alloy is produced. But in this case, just 72 % of the manganese are collected in this phase. Due to its ignoble character, a huge part is lost in the slag phase. One other problem, comparative to common LIBs, is the phosphorus content of the metal. Because of the high phosphorous solubility of copper and nickel, the alloy contains around 17 % phosphorous. To prevent problems in the alloy purification and be able to sell it to already existing metal and metal salt producing plants, the phosphorous is removed in a converter process by injecting oxygen/oxygen enriched air, so it is transferred to a slag phase. The possibility of recovering fertilizer from it is to be investigated. During the converter process, metal losses to the slag phase have to be assumed. Afterwards, the metal can be sold to hydrometallurgical treatment plants, similar to the produced metal salts from the first process option. This description makes clear, that the pyrometallurgical approach has a higher energy consumption, because two process steps have to be carried out at high temperatures of around 1500 °C. Afterwards, the treatment is quite similar to the first recycling approach, so the effort seems higher for the second one.

When taking all these comparisons into account, the first recycling approach described in this report is a more holistic and less energy intensive one for the SUBLIME cells. Therefore, it is recommended to follow the first process flow chart in possible follow-up projects. Of course, it should be noted that this is a purely theoretical report. The presented contents would have to be validated experimentally in the future.

4 Risk register

Risk No.	What is the risk	Probability of risk occurrence[1]	Effect of risk[2]	Solutions to overcome the risk
WP6.3.1	**Fire and explosion risk** - The solid LPSC electrolyte and the metallic lithium electrode place special demands on the recycling process. Their reactions with air and humidity are bearing a risk due to toxic gas evaluation as well as fire and explosion risk.	1	1	The shredding and thermal pre-treatment of the battery cells under inert atmoshere are indispensable.
WP6.3.2	**Toxic gas formation -** Since the thermal pre-treatment takes place at elevated temperature and under inert atmosphere, external humidity contact with the solid sulfide electrolyte can be avoided. Nevertheless, a certain level of emissions is always to be expected, as water could be a reaction product from the binder decomposition.	1	1	The adequate exhaust gas cleaning is necessary. The removal of possibly evolved H_2S can be carried out either by a wet scrubbing, for example with a copper sulfate solution or by filtration with activated carbon. For the organic compounds a post combustion is recommended.
WP6.3.3	**Low efficiency of solid electrolyte recovery** - The recovery of the solid electrolyte is based on the most uncertain assumptions, as there have been no experimental implementations to date, and thermodynamic calculations are also not possible due to a lack of data	1	2	The degradation processes of LPSC during cell use as well as during thermal treatment needs to be further investigated to collect reliable data.

Table 7: Risk Register

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[1] Probability risk will occur: 1 = high, 2 = medium, 3 = low

[2] Effect when risk occurs: 1 = high, 2 = medium, 3 = low

5 Acknowledgement

The author(s) would like to thank the partners in the project for their valuable comments on previous drafts and for performing the review.

Project partners

#	PARTICIPANT SHORT NAME	PARTNER ORGANISATION NAME	COUNTRY
1	FEV	FEV Europe GmbH	Germany
2	ABEE	AVESTA BATTERY & ENERGY ENGINEERING	Belgium
3	CICE	CENTRO DE INVESTIGACION COOPERATIVA DE ENERGIAS ALTERNATIVAS FUNDACION, CIC ENERGIGUNE FUNDAZIOA	Spain
4	FORD	FORD OTOMOTIV SANAYI ANONIM SIRKETI	Turkey
5	CRF	CENTRO RICERCHE FIAT SCPA	Italy
6	AIT	AIT AUSTRIAN INSTITUTE OF TECHNOLOGY GMBH	Austria
7	MIM	MIMI TECH GMBH	Germany
8	POL	POLITECNICO DI TORINO	Italy
9	SAFT	SAFT	France
10	SOL	RHODIA OPERATIONS	France
11	TNO	NEDERLANDSE ORGANISATIE VOOR TOEGEPAST NATUURWETENSCHAPPELIJK ONDERZOEK TNO	Netherlands
12	Fraunhofer	FRAUNHOFER GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V.	Germany
13	CEA	COMMISSARIAT A L ENERGIE ATOMIQUE ET AUX ENERGIES ALTERNATIVES	France
14	UMC	Umicore	Belgium
15	UNR	Uniresearch BV	Netherlands

Table 8: Project Partners

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6 Appendix A – Quality Assurance

The following questions should be answered by all reviewers (WP Leader, peer reviewer 1, peer reviewer 2 and the technical coordinator) as part of the Quality Assurance Procedure. Questions answered with NO should be motivated. The author will then make an updated version of the Deliverable. When all reviewers have answered all questions with YES, only then the Deliverable can be submitted to the EC. NOTE: For public documents this Quality Assurance part will be removed before publication.

Question	**WP Leader**	**Peer reviewer 1**	**Peer reviewer 2**	**Technical Coordinator**
	Rémi Vincent (CEA)	Alexander Tesfaye (UMICORE)	David Echasserieau (SAFT)	Jens Ewald (FEV)
1. Do you accept this deliverable as it is?	Yes	Yes	Yes	Yes
2. Is the deliverable completely ready (or are any changes required)?	Yes	Yes	Yes	Yes
3. Does this deliverable correspond to the DoW?	Yes	Yes	Yes	Yes
4. Is the Deliverable in line with the SUBLIME objectives?	Yes	Yes	Yes	Yes
a. WP Objectives?	Yes	Yes	Yes	Yes
b. Task Objectives?	Yes	Yes	Yes	Yes
5. Is the technical quality sufficient?	Yes	Yes	Yes	Yes

7 Appendix B – Mass Balance Calculation Recycling Option 1

Composition Components		
Component	**weigt [g]**	**Amount of Cell [%]**
Li6PS5Cl	0,438	7,059
NMC	0,209	3,366
HNBR	0,020	0,325
Carbon black	0,006	0,095
Al metal	0,065	1,044
Li metal	0,051	0,820
Cu metal	0,129	2,079
Al casing	5,288	85,211
Sum	**6,205416016**	

Composition Elements		
Component	**weigt [g]**	**Amount of Cell [%]**
Li	0,134	2,163
P	0,051	0,815
S	0,262	4,217
Cl	0,058	0,932
Ni	0,096	1,549
Co	0,013	0,211
Mn	0,011	0,182
Al	5,352	86,255
Cu	0,129	2,079
O	0,073	1,177

Thermal Treatment		
Input/100g Battery	**Weigt [g]**	**inkl. Safety factor**
Shredder	100	
Carbon	2,52	5,04
CO2	6,85	13,7
Energie for heating to 600 °C		
Process example:		
Heating under N2	300 °C/h	
1h holding under CO2	600 °C	
Cooling under N2	furnace off	

Casing				Resulting Foil Fraction		Resulting active mass 1	
Element	**Amount [g]**	**Recovery Yield [%]**	**Element**	**Amount [g]**	**Recovery Yield [%]**	**Amount [g]**	**Recovery Yield [%]**
Al	84,78	99,5	**Cu**	1,934	93	0,146	7
			Al ges	0,971	93	0,499	7
			Ni	0,031	2	1,518	98
			Co	0,004	2	0,207	98
			Mn	0,004	2	0,178	98
			Li	0,021	2	0,804	98
			Li6PS5Cl	0,141	2	6,918	98

Ethanol Washing (10 wt.-% mixture)		
Input:	Black mass from pr	13,74
	Ethanol [ml]	77,83

	Resulting Solution		Restulting active mass 2	
Element	**Amount [g]**	**Recovery Yield [%]**	**Amount [g]**	**Recovery Yield [%]**
Cu			0,146	100
Al ges			0,499	100
Ni			1,518	100
Co			0,207	100
Mn			0,178	100
Li			0,804	100
Li6PS5Cl	6,226	90 (Assumption)	0,692	10

Water Washing

Input		
Black Mass from Ethanol washing [g]	7,516	
Water (20% overstoichomertic) [ml]	38,585	Schwich et al. + 20%
CO2 [l/min]	0,500	Assumption
Time [min]	30,000	
theor. Li2CO3 in blackmass [g]	4,277	
solubility Li2CO3 in H2O [g/L]	13,300	

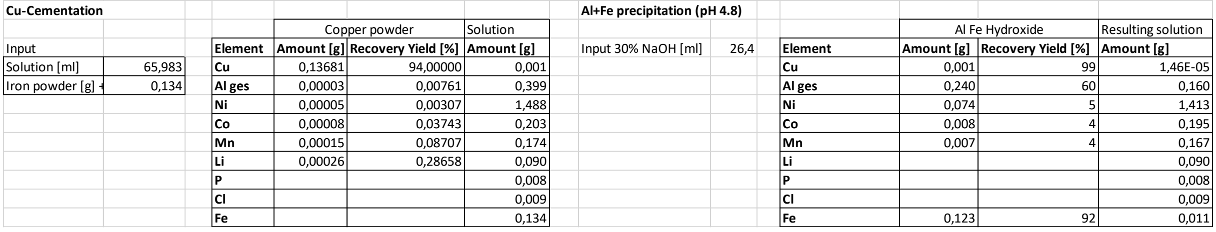
	Resulting Li Product	
Element	**Amount [g]**	**Recovery Yield [%]**
Li2CO3 from met.	3,630	90
Li2CO3 from NMC	0,146	60
Li von Li2CO3	0,709	
Li2S	0,107	90
Al Impurity		nearly no --> CO2 bubbli
Li3PO4	0,269	90
LiCl	0,098	90
Li ges.	0,806	90
Summe	4,103	
Off Gas		
H2S	0,079	90
H2O consumption due to H2S [g]		0,186

	Restulting active mass 3	
Element	**Amount [g]**	**Recovery Yield [%]**
Cu	0,146	100
Al ges	0,499	100
Ni	1,518	100
Co	0,207	100
Mn	0,178	100
Li	0,080	10
Li6PS5Cl	0,069	10

H2SO4 Leaching

Input		
Blackmass from Water washing		
2M H2SO4 [ml]	65,98	based on Vicell
H2O2 [ml] 30%	0,03	
Energy to reach 80 °C		

	Input	Resulting solution		Resulting Filtercake 1	
Element	**Amount [g]**	**Amount [g]**	**Recc**	**Amount [g]**	**Recovery Yield [%]**
Cu	0,146	0,138	95	0,0073	5
Al ges	0,499	0,399	80	0,0998	20
Ni	1,518	1,488	98	0,0304	2
Co	0,207	0,203	98	0,0041	2
Mn	0,178	0,175	98	0,0036	2
Li	0,091	0,090	99	0,0009	1
P	0,008	0,008	99	0,0001	1
S	0,041	0,041	99	0,0004	1
Cl	0,009	0,009	99	0,0001	1



Cu-Cementation

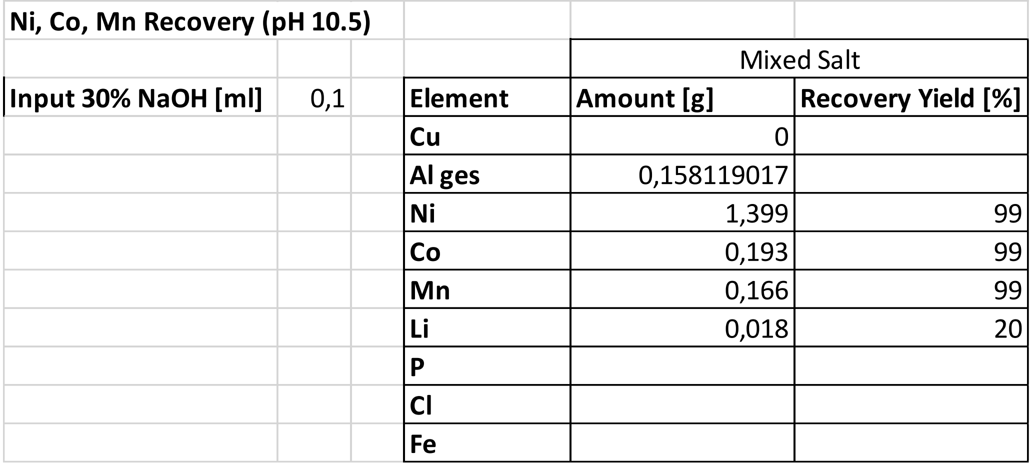
Input	
Solution [ml]	65,983
Iron powder [g]	0,134

	Copper powder		Solution
Element	**Amount [g]**	**Recovery Yield [%]**	**Amount [g]**
Cu	0,13681	94,00000	0,001
Al ges	0,00003	0,00761	0,399
Ni	0,00005	0,00307	1,488
Co	0,00008	0,03743	0,203
Mn	0,00015	0,08707	0,174
Li	0,00026	0,28658	0,090
P			0,008
Cl			0,009
Fe			0,134

Al+Fe precipitation (pH 4.8)

Input 30% NaOH [ml] 26,4

	Al Fe Hydroxide		Resulting solution
Element	**Amount [g]**	**Recovery Yield [%]**	**Amount [g]**
Cu	0,001	99	1,46E-05
Al ges	0,240	60	0,160
Ni	0,074	5	1,413
Co	0,008	4	0,195
Mn	0,007	4	0,167
Li			0,090
P			0,008
Cl			0,009
Fe	0,123	92	0,011



Ni, Co, Mn Recovery (pH 10.5)

Input 30% NaOH [ml] 0,1

	Mixed Salt	
Element	**Amount [g]**	**Recovery Yield [%]**
Cu	0	
Al ges	0,158119017	
Ni	1,399	99
Co	0,193	99
Mn	0,166	99
Li	0,018	20
P		
Cl		
Fe		

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