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Development of Safety Protocols in Aalto University LIB Recycling Laboratory

Master’s Programme in Chemical, Biochemical and Materials Engineering
Major in Sustainable Metals Processing

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Abstract of master's thesis

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Abstract

This thesis studies the development and implementation for suitable laboratory practices for waste LIBs handling and treatment in Aalto University to address concerns regarding the risks associated with LIB components. This thesis is also aimed to be used as reference for researchers working with this hazardous material, particularly but not limited to, the facilities of Aalto University, School of Chemical Engineering.

This thesis provides knowledge about the lithium ion batteries, active materials, electrolytes and electrolyte additives, separator materials and general construction of LIBs. This thesis also provides knowledge about current practices regarding the mechanical separation of waste LIBs, current practices of flotation of black mass from LIBs and challenges regarding the recycling of LIB in a safe manner.

In LIB recycling, there are possible hazards with formation of HF and toxic elements containing dusts. People working with hazardous LIB waste material need sufficient protection against these harmful elements and ways to deal with such hazards.

Keywords LIB, recycling, mechanical separation, flotation of black mass, HF,

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Tiivistelmä

Tämä diplomityö tutkii keinoja kehittää ja implementoida sopivia laboratoriokäytäntöjä käytettyjen litiumioniakkujen siirtelyyn ja käsittelyyn Aalto Yliopistossa ottaen huomioon haasteet liittyen litiumioniakkujen materiaaleihin. Tämä diplomityö on myös tarkoitettu käytettäväksi viitteenä tuktkijoille, jotka työskentelevät vaarallisten litiumioniakkujen materiaalien parissa, erityisesti, mutta ei ainoastaan, Aalto yliopistossa, Kemiantekniikan Korkeakoulussa.

Tämä diplomityö antaa tietoa litiumioniakkuista, niiden aktiivimateriaaleista, elektrolyyteistä ja elektrolyyttien lisäaineista, eristemateriaaleista ja yleisestä rakenteesta. Tämä diplomityö myös antaa tietoa tämänhetkisistä käytetyistä metodeista käytettyjen litiumioniakkujen mekaaniseen eroitteluun ja mustan massan vaahdottamiseen ja haasteisiin, joita esiintyy litiumioniakkujen kierrätyksessä.

Litiumioniakkujen kierrätyksessä mahdollisia vaaroja ovat HF ja myrkyllisiä aineita sisältävissä pölyissä. Työntekijät jotka työskentelevät haitallisen litiumioniakku materiaalin kanssa tarvitsevat riittävän suojan näitä haitallisia aineita vastaan ja keinoja tulla toimeen näiuden haasteiden kanssa.

Avainsanat LIB, kierrätys, mekaaninen prosessointi, mustan massan vaahdotus, HF

Forewords

This thesis was performed with the support of Finland based circular ecosystem of battery metals consortium (BATCircle).

I sincerely thank my supervisor Professor Rodrigo Serna for the interesting and challenging thesis subject and the support he has given me during writing of this thesis. I would like to thank my advisor Michael Saulny, whose positive mentality has been inspiring me during the writing and providing me new approaches on this topic.

Also, I would like to thank all my colleagues in the laboratory of mechanical processing and recycling laboratory and the people in the hydrometallurgical laboratory for support, company and joyful coffee breaks with more or less frozen cakes. Special thanks go to Artemis Kontomichalou for being the model for the guides used in the Aalto LIB recycling laboratory.

Last but not the least I want to thank my family for the great support and encouragement during my studies and especially during the making of this thesis, without you this would not have been possible.

There is a lot of people that have been supporting me during my thesis and you will know that without me mentioning any more names that you were part of it. It has been a privilege to have you being part of my thesis, studies and life, thank you.

List of Symbols and Abbreviations

AAS	Atomic absorption spectrometry
EOL	End of Life
EV	Electric vehicle
FTIR	Fourier transform Infrared Spectroscopy
HEV	Hybrid electric vehicle
HF	Hydrofluorine or hydrofluoric acid
LCO	Lithium Cobolt
LIB	Lithium Ion battery
LI-Ion	Lithium Ion
MIBC	Methyl isobutyl carbinol
MSDS	Material safety data sheet
NMC	Nickel manganese cobolt
PE	Polyethylene
PP	Polypropylene
PPM	Particles per million
PVDF	Polyvinylidene fluoride
RS	Rotary shear
SEI	Solid electron interphase
XRD	X-ray diffraction
XRF	X-ray fluorescence

Table of Contents

1 Introduction

This thesis is part of Finland based circular ecosystem of battery metals consortium (BATCircle), which aims at improving the manufacturing processes of mining industry, metals industry and battery chemicals, and to increase the recycling of lithium-ion batteries.

This thesis has the following structure. In chapter one, the justification of this thesis is done by introducing the current trends of electric vehicle production, combining the resource scarcity to circular economy and how recycling of lithium ion batteries (LIBs) will be in a key role for this. Chapter two explains the physical structure of the lithium ion batteries and the key challenges posed by the recovery of components in the process of lithium ion batteries recycling. Chapter three contains a review of processes used for the lithium ion battery recycling and the focus is on the mechanical pretreatment processes to enrichen or otherwise improve the refining steps in the recycling chain. The fourth chapter includes reviews of research done regarding flotation of black mass, which was intended for the use for flotation of the black mass received in Aalto University. However, as the black mass received was analyzed, various hazardous elements were identified, as described in Chapter five, raising the need to develop safety protocols and adequate facilities for the treatment of LIB waste. Consequently, Chapter six is focusing on the practical work conducted for this thesis, which was the implementation of Aalto LIB recycling laboratory. In the Seventh chapter, conclusions and suggestions for future work are presented.

1.1 Rising trend of electric vehicle production

Recently, the focus of the automotive industry has shifted towards the use of electric vehicles. As the batteries used in electric vehicles reach the end of their lifecycle, they must be recycled for the purpose of reuse of the materials within. This creates an urgent need for efficient recycling of the batteries (especially LIB) used as the power source for electric vehicles. In order to recycle these batteries, some conditions should be met. The battery design has to be sufficiently understood to perform efficient dismantling and recycling. Knowledge on battery chemistry would be beneficial to tailor the mechanical and chemical separation processes. The battery chemistry is more often unknown for the recyclers, since the manufacturing companies protect their product characteristics. To determine suitable recycling processes, one must understand profoundly the battery characteristics after comminution.

In this thesis the focus is on the electric vehicle lithium ion batteries and the individual mechanical separation processes in the beginning stages of recycling of the lithium ion batteries. This thesis also conducts experiments with crushed battery waste to determine LIB characteristics.

1.2 Resource scarcity to circular economy

Electric vehicles (EVs) are a great possibility for reducing carbon emissions caused by the automotive industry. The increasing number of electric vehicles rises a concern of lithium availability in the future. However, this does not seem to be a limiting factor for the companies who produce electric vehicles in the future. Besides only few percent of total costs of a battery comes from mining of the lithium from primary sources (Speirs and Contestabile, 2018). **Figure 1** shows the historical production and the future production estimates for Li. Solely in China, it is estimated to be more than 25 billion units and 500 000 tons of lithium ion batteries going to the waste stream in 2020 (Zeng, Li and Shen, 2015).

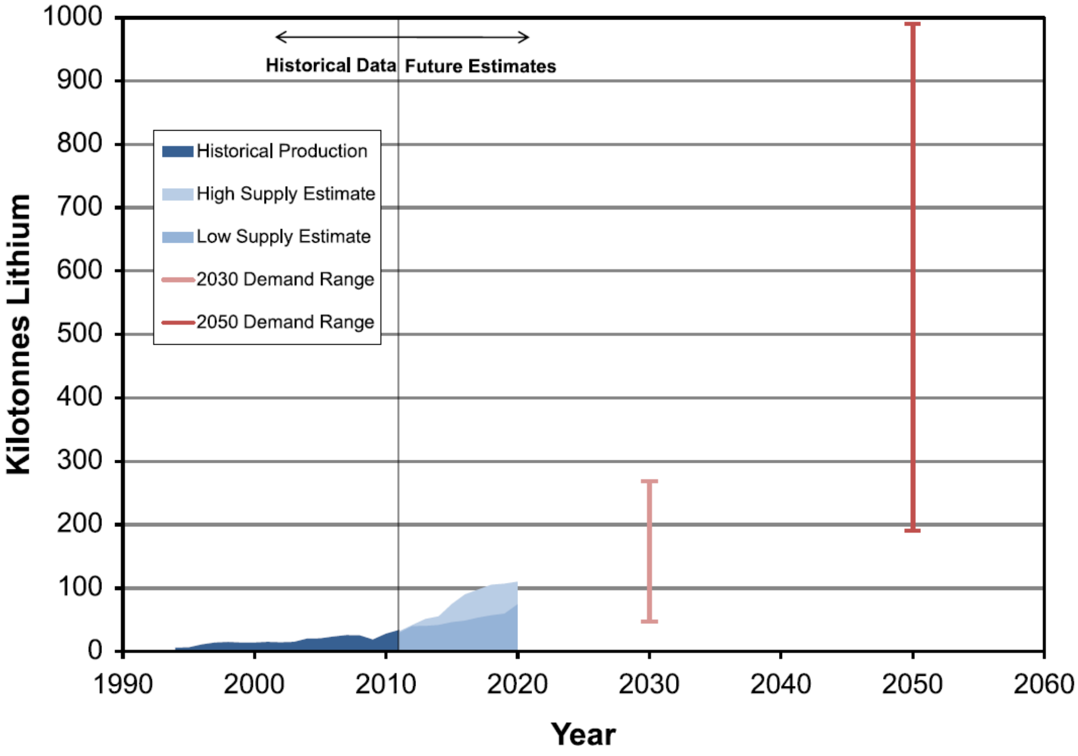


Figure 1 - Lithium historical production, forecast of supply and demand. (Speirs and Contestabile, 2018)

Resource scarcity is a known phenomenon with ores and Li will most likely be following the same principles in the future, as it is known that while extracting these minerals, the grade of the ore mined decreases over time and mining focuses more on the mineral poor ores. When this phenomenon continues, it creates a need for the recycling of lithium to provide a secondary raw material source for the consumer applications. (Henckens *et al.*, 2016)

As the ores become scarcer, it would be beneficial to develop circular economy models around the LIB components. For such development, we need to identify the waste streams for maximising the valuable elements and minimize the losses occurring in the recycling of LIBs. In circular economy, the materials recycled from the discarded product would are ideally of comparable quality as virgin materials, but most likely it will include small traces of impurities. Depending on each specific situation, products made from recycled material can be of same or similar quality as the original product, but it could otherwise still be a lesser grade product sufficient for other uses. The latter case remains nevertheless under the definition of recycling. In optimal scenarios, no additional natural resources are needed for the production of the materials and discarded products are no longer a waste, rather a stream of raw materials needed for new products. Ultimate circularity would be that the entire cycle is closed, with no losses occurring and the products being recycled indefinitely. This is an ideal situation which is not in realistically possible but, provided material cycles can be developed, less virgin material will nevertheless be needed for the production of goods. This creates the need for more efficient recycling methods, with the aim of preventing downgrading of the material as a consequence of recycling (Potting *et al.*, 2017).

1.3 Recycling of Lithium Ion Batteries

The current rate of Li-ion battery recycling is particularly low, as 95% of LIBs worldwide are landfilled once they reach the end of their lifetime (Wang *et al.*, 2016). There is a rising national and global concern regarding the lack of recycling for LIBs. National legislations are being implemented, driving global operators to ensure recycling of LIBs. Solely inside the European Union, the member states are required to collect 45% of used batteries and accumulators by the year 2016 (Directive 2006/66/EC, The European Parliament (2006)). Most of the current plants focusing on the recycling of the lithium ion batteries are based on pyro- and hydrometallurgical processes. Pyrometallurgical processes utilize high temperature smelting to recover valuables and hydrometallurgical processes use chemical leaching for the recovery of materials.(Wang *et al.*, 2016).

Prior to metallurgical processes, various mechanical separation processes are needed to improve the recovery of valuables and reduce unnecessary materials entering the process. The current focus on the end of life (EOL) LIB recycling has been on cobalt recovery since it is the component with has the highest economic value. In case of $LiFePO_4$, copper, nickel and lithium range from 27% to 74% of recoverable valuables of EOL LIBs. While aluminium content ranges generally from 1% to 8% of the total mass of the spent LIBs, there are noticeable energy savings available if it is recovered before the metallurgical processes. Indeed, secondary production of aluminium consumes up to 88% less energy than in the primary production. As seen, the recovery of valuables other than cobalt, can be of economic interest. However, the recycling have to be efficient enough to provide metals that are pure enough for further use (Wang, Gaustad and Babbitt, 2016).

2 Lithium-Ion Batteries

This chapter describes general characteristics of LIBs, including main components and common designs to provide some reference information for the following chapters. LIBs exploit the release of electrons associated with the movement of Li-ions (Li^+) between positive and negative electrode materials (i.e., cathode and anode, respectively) to generate electrical power. When operating the battery, Li^+ alternate between the positive and negative electrode as the battery is cycled. Typically, a primary battery is defined as that which is not intended to be recharged after it has released all its charge and is therefore disposed of after a single use. On the other hand, a secondary battery refers to those that can be recharged after each cycle of discharge, by forcing the movement of ions on the opposite direction than during the discharge cycle. (Linden and Reddy, 2013)

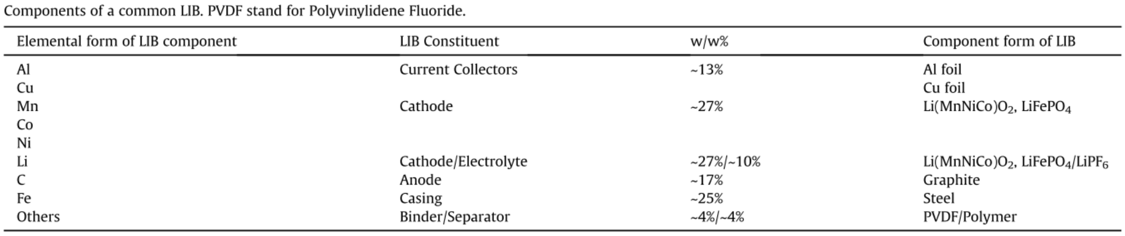
2.1 Active Materials

Cathode material is a most often metal oxide with various compositions available commercially. Table 1 presents the common components of a LIB. The cathode material can be of layered structure, e.g., with lithium cobalt oxide ($LiCoO_2$), or a tunnelled structure, e.g., lithium manganese oxide ($LiMn_2O_4$) deposited on an aluminium current collector. The anode material is typically graphitic carbon with layered structure deposited on a copper current collector. During the charge-discharge process, Li^+ are introduced or removed from the interstitial space between atomic layers of active materials. (Linden and Reddy, 2013)

Most of these batteries utilized LiCoO2 (LCO) as cathode material. LCO has multiple beneficial properties, including a good performance, a relatively simple manufacturing, they are safe, versatile and capable to stand the presence of moisture. Subsequently, designs with other chemistries were introduced, including materials such as: $LiFePO_4$, $LiMn_2O_4$, $Li(NiMnCo)O_2$ and $Li(NiCoAl)O_2$. These materials offer beneficial properties in specific applications than those for which the first generation of LCO was intended. Indeed, under some circumstances, new cathode materials claim a better cycle life, thermal resistance, and higher capacity properties. At this point, it is worth defining cycle life as the number of cycles a secondary battery can last without losing its performance below specified benchmark values. (Linden and Reddy, 2013)

The first commercial LIBs reportedly used coke as their primary negative electrode material in their structure. When graphite materials reached the market, the LIB industry replaced coke by these advanced materials, as they result in higher specific capacity, cycle life and rate capability. Rate capability is defined as the maximum charge or discharge rate of a battery or cell. (Linden and Reddy, 2013).

Table 1 - Components of common LIB (Velázquez Martínez *et al.*, 2019)



Components of a common LIB. PVDF stand for Polyvinylidene Fluoride.

Elemental form of LIB component	LIB Constituent	w/w%	Component form of LIB
Al	Current Collectors	~13%	Al foil
Cu			Cu foil
Mn	Cathode	~27%	Li(MnNiCo)O_2, $LiFePO_4$
Co			
Ni			
Li	Cathode/Electrolyte	~27%/~10%	Li(MnNiCo)O_2, $LiFePO_4$/$LiPF_6$
C	Anode	~17%	Graphite
Fe	Casing	~25%	Steel
Others	Binder/Separator	~4%/~4%	PVDF/Polymer

2.2 Electrolyte

The electrolyte has a major impact on battery properties and performance. The rate capability, cycle life, coulombic efficiency, operation temperature range and safety of LIBs are strongly influenced by the electrolyte. Coulombic efficiency describes the ratio of output charge by battery to input charge and is determined by the internal resistance of a cell. The most common electrolytes consist of dissolved salts, although gels can also be utilized (Wang *et al.*, 2016). Liquid electrolytes contain a lithium salt dissolved in one ore multiple organic solvents; most often carbonates. A gel electrolyte is an ionically conductive material with salt and solvent introduced inside high molecular weight polymer. Gel electrolytes specifically developed for the LIBs are typically films of PVDF-HFP, $LiPF_6$ and carbonate solvent. An alternative method to introduce a gel electrolyte is to use a polymerizable monomer, which is then cross-linked inside the battery, resulting in a solid battery. Gel electrolyte batteries are attractive since they offer a reduced risk of electrolyte leaking (Linden and Reddy, 2013).

Most of the electrolytes in Li^+ cells use $LiPF_6$, since it has high conductivity and good stability. $LiPF_6$ has still some downsides as it is costly, hydroscopic and creates hydrofluoric acid (HF) when in contact with water, making it a potential hazard that needs dry environment during handling. Recent developments in electrolyte chemistry have explored organic salts since they are more stable in the presence of moisture (Linden and Reddy, 2013).

Various LIB electrolyte solvents have been explored, and the trending focus of industry is on carbonates, since they offer excellent stability, good safety characteristics and compatibility with the electrode materials used. Solvents used in commercial LIBs utilize a mixture of three to five different solvents, not including electrolyte additives, which will be discussed in the next chapter. Mixed electrolyte solvents reportedly provide better cell performance, higher conductivity, and a broader temperature range than single solvents. Unfortunately, the use of mixtures also complicates the recycling of LIBs (Linden and Reddy, 2013).

2.3 Electrolyte additives

When aiming to improve LIBs performance and safety, electrolyte additives are one of the most promising research directions. Regarding recycling, electrolyte additives are a rather complex issue, since they are present in small quantities, but they may be highly valuable. This can be attractive regarding the recycling economics, but may result in significantly complex processes in order to be collected (Linden and Reddy, 2013).

Electrolyte additives have various roles depending of its intended purpose in the battery cell. Additives affecting the solid electrode interphase (SEI) should be either reduced (as anode additive) or oxidized (cathode additives) before being introduced into the electrolyte to prevent detrimental changes on the SEI. Safety of the battery can be enhanced with, e.g., flame retardants or redox shuttles additives. (Haregewoin, Wotango and Hwang, 2016). Additives are present in the electrolyte in low quantities (<10%) and are mainly consumed during the SEI formation process, making them even difficult to detect afterwards. Additive formulations are trade secrets, and thus, it is not in the interest of LIB manufacturers to publish details on their electrolyte additives or battery chemistries in general. Consequently, there is a wide gap of public knowledge available on these components. Additives introduced to enhance specific properties may negatively affect others and thus, multiple combinations of additives are used. The combined enhancing properties of additive mixtures result in an overall benefit compared to single additives acting alone. (Haregewoin, Wotango and Hwang, 2016)

2.4 Separator materials

In LIBs, microporous films (16 to 40 μm) are used to electrically insulate the positive and negative electrode from each other and prevent short-circuit. All commercial LIBs currently use microporous polyolefin as their insulator material. This is because polyolefin has excellent mechanical properties, chemical stability and acceptable cost. There has been research using nonwoven materials (Linden and Reddy, 2013), but these materials lack the necessary mechanical strength and their cost is comparatively higher. Currently used microporous polyolefins are polyethylene, polypropylene or their corresponding laminates. As these materials have low melting point, they can be used as the thermal fuse, where the polyolefin melts and shuts down the battery from further damage in case of fire. Upon reaching the melting point of the polymer (e.g., polyethylene (PE) at 135 °C and polypropylene (PP) at 155 °C), the polymer melts with the associated loss of porosity, thus preventing the electron transfer between anode and cathode and preventing the battery from short-circuiting (Linden and Reddy, 2013). For recycling, these separators are removed from the process in order to prevent blockage of sieves or other equipment. This can be done with different mechanical separation methods or by incineration during pyrometallurgical treatment (Huang *et al.*, 2018).

2.5 Construction

There is a wide spectrum of battery designs, as they are produced around the globe by more than 100 manufacturers. The most commonly used geometries for LIBs are classified as: cylindrical, prismatic and “polymer” type. Wound cells, commonly referred as cylindrical or prismatic cells, are the most commonly associated with small cell designs (<4 Ah), while larger prismatic cells have a flat plate or stacked construction. Most commonly used designs for Li^+ cells are two types, flat-mandrel wound pseudo-prismatic design and stacked, true prismatic design. (Linden and Reddy, 2013)

2.5.1 Construction of Wound Li-Ion Cells

The construction of a wound cylindrical and wound prismatic Li-ion cell is shown in Figure 2. As seen, wound cells consist of a positive and negative electrode separated by an insulator layer with a thickness of 16 to 25 µm. The positive electrode is usually made of aluminium foil with active material coating on both sides (foil thickness 10 to 20 µm) with an overall thickness of 100 to 250 µm. Negative electrodes are composed of copper foil (foil thickness 8 to 15 µm) with a coating of graphite as the active material, with a thickness in the range of 100 to 250 µm. The battery casing can also be used as a current terminal. When the casing is used as the negative terminal, it is usually made of nickel plated steel, while Al is used as positive terminal (Linden and Reddy, 2013).

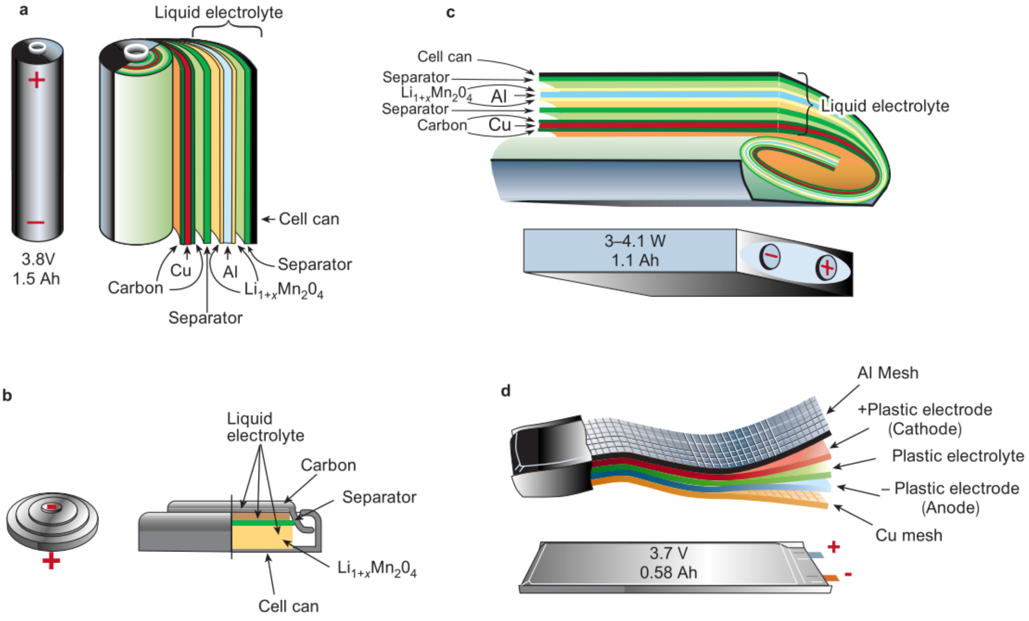


Figure 2 - Main construction types of LIBs: a) wound cylindrical, b) button cell, c) wound prismatic and d) pouch cell (Armand, 2001)

2.5.2 Construction of Stacked Li-Ion Cells

The construction of a stacked prismatic cell is shown in Figure 2. Similar to the wound cells mentioned above, a stacked cell also contains a microporous separator to prevent contact between positive and negative electrodes. Each plate has a tab, from which they are welded as a bundle to the terminals or to the cell case. The cell casing material is commonly Al, Ni-plated steel or stainless steel. The cover usually has one to two terminals, a filling port and a rupture disk and is welded to the casing. There are three constructions for terminal: glass to metal seal and compression type seal (popular in low cost application). Batteries with this type of design find applications where the space of installation is the limiting factor. This is due to the scalability of these cells and that they can be arranged into different shapes. (Linden and Reddy, 2013)

2.5.3 Construction of Polymer or pouch Li-Ion Cells

Pouch LIBs is a category referring to cells whose packaging is made of heat-sealable flexible aluminized plastic. These batteries are constructed using propylene, aluminium foil and propylene tri-layered system, each layer being thermally laminated to each other. The electrolyte addition is performed under vacuum before sealing. Sealing can be done using heat welding or ultrasonic welding. Flat tabs in the figure protrude from the package after sealing. Because the cell is constructed under vacuum, the normal ambient pressure holds the cell firmly packed (Linden and Reddy, 2013).

3 Current practices on mechanical separation for recycling of waste LIBs

Although there are interesting reviews on the recycling technologies available for end-of-life LIBs (Valio, 2017), this chapter offers a review useful articles specifically related to pretreatment steps for black mass. The efficient separation of black mass may be necessary before the enrichment of its components with froth flotation, which will be dealt in Chapter 4. This chapter also reveals characteristics of the crushed battery material, which were needed for the research conducted for the implementation of Aalto LIB recycling lab, discussed in Chapter 6.

3.1 Wuschke et. al. 2019

Wuche et. al. (2019) presented a study on the processing of mixed spent LIB feed consisting of undetermined EVs, HEVs, and starter batteries. Their focus on this study was to understand the crushing behavior of these batteries. They used low speed axial-gap rotary shear (RS) mill constructed by TU Bergakademie Freiberg. This RS had two sections as presented in Figure 3. Section A has conventional blade discs with narrow gap as rotary shear. The B side is equipped with V-shaped teeth and wide gap. The specific mechanical stress energy obtained for aluminum housing was 0.7 kWh/t and for alloyed steel 3.5 kWh/t and for complete cell 4.5 kWh/t (Wuschke *et al.*, 2019).

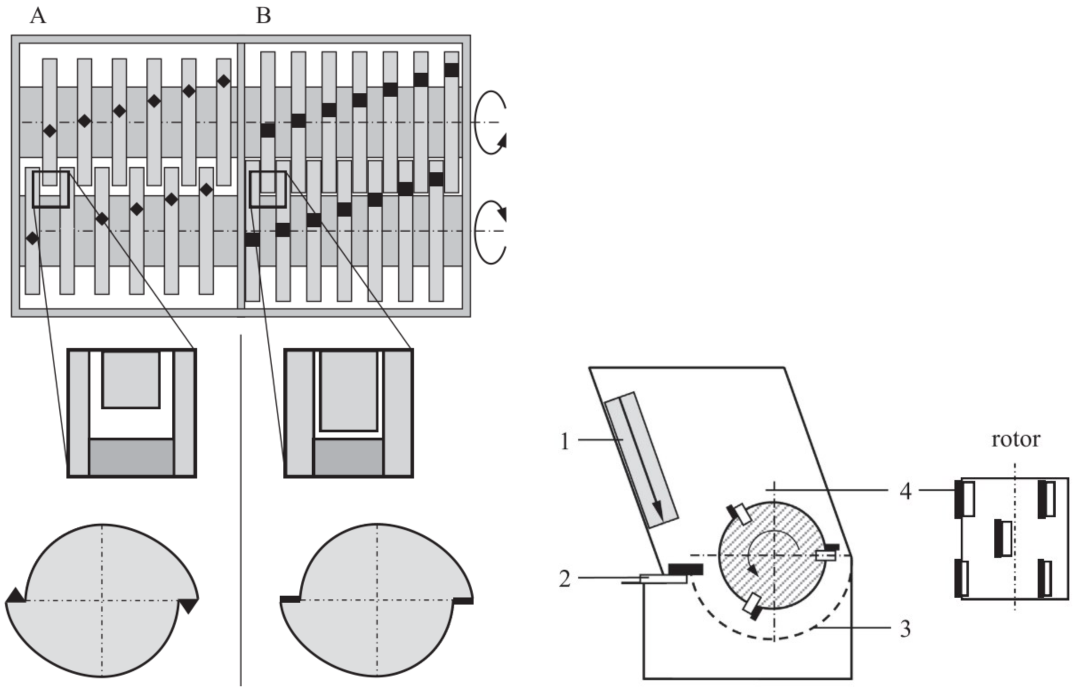


Figure 3 – Low speed axial-gap rotary shear with A and B sides and rotary shear on the right UG300 MS (Wuschke *et al.*, 2019)

After the primary crushing, the secondary crushing proceeded for individual cells and also for manually dismantled casings with a rotary shear mill UG300 MS produced by MeWa/Andritz, Germany. This machine has a radial gap of 6 mm and an operating speed of 6 m/s. Sieve sized used in their experiment after secondary crushing were of 1,2,4,5,8,10,12½, 16 and 20mm.

Volatile solvents are recovered by a vacuum cleaner with activated carbon filter (model DS2from RUWAC, Germany). Afterwards, fine dusts are recovered using the same vacuum by an upstream gas cyclone.

The state of charge affects linearly the temperature of the crushed battery particles as a result of short circuiting. The highest temperature reading was reported 20 s after crushing. Figure 4 shows the temperature increases measured in the experiments by Whuschke et al. (2019).

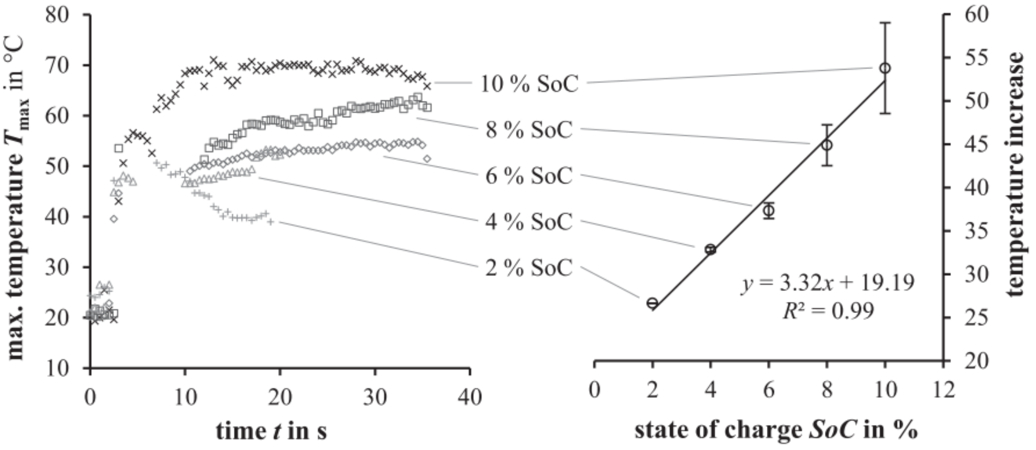


Figure 4 - Temperature increase of crushed Li-ion battery cells with variable SoC. (Wuschke *et al.*, 2019)

In order to understand the characteristics of single cell components, they crushed manually dismantled LIB cells. This crushing provided particle size distributions (Figure 5) for the anode and the cathode foils. Anode foils have more particles (40% to 68%) smaller than 1 mm whereas cathode foils only contained 6% to 25% in this size fraction. Anode foils consist of around 66% of coating by mass and cathode foils contain up to 90% of coating by mass.

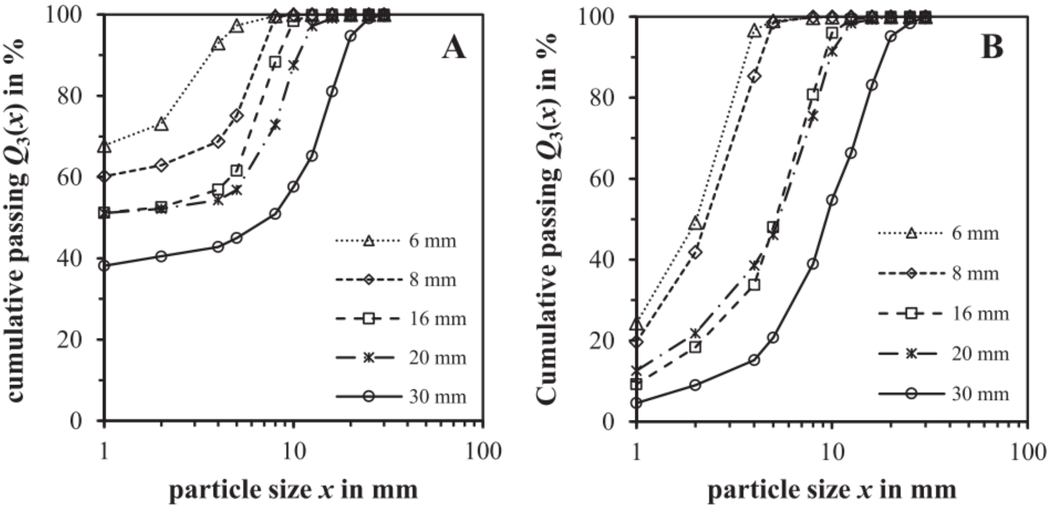


Figure 5 - PSD of electrode foils (A anode, B cathode) after crushing with UG300 with different grid sizes. (Wuschke *et al.*, 2019)

Figure 6 - Adhesive tensile strength distribution density of anode and cathode foils. (Wuschke *et al.*, 2019)Figure 6 shows the tensile strength of the coatings of anode and cathode. Comminution of separator foils with 6 mm grid causes the grid to become blocked of the foils. Heating or cooling would cause the foils to become brittle and ease the crushing, but it also creates extra operational costs.

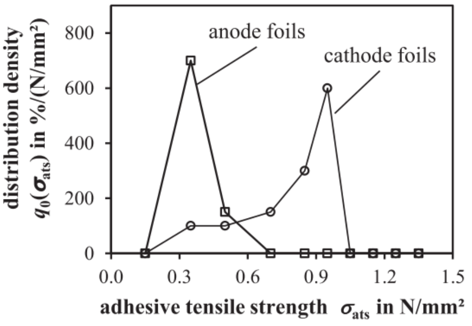


Figure 6 - Adhesive tensile strength distribution density of anode and cathode foils. (Wuschke *et al.*, 2019)

3.2 Diekmann et al. 2016

Diekmann et al., (2016) examined studied end-of-life Panasonic CGR186652CH battery cells to understand crushing, including its associated gas release, and the separation processes of primary air classification, secondary crushing, sieving and secondary air classification. Cells were individually crushed using a six-disc rotor in a converted cutting mill. Crushing was conducted under inert nitrogen atmosphere. Exhaust gases were examined online by Fourier Transform Infrared Spectroscopy (FTIR). The process steps used in this experiment are presented schematically in Figure 7. In the experiment, EV battery modules were used consisting of six prismatic 25 Ah battery cells with NMC and graphite as cathode and anode active materials, respectively, and with an average weight of 4.95 kg (Diekmann *et al.*, 2016)

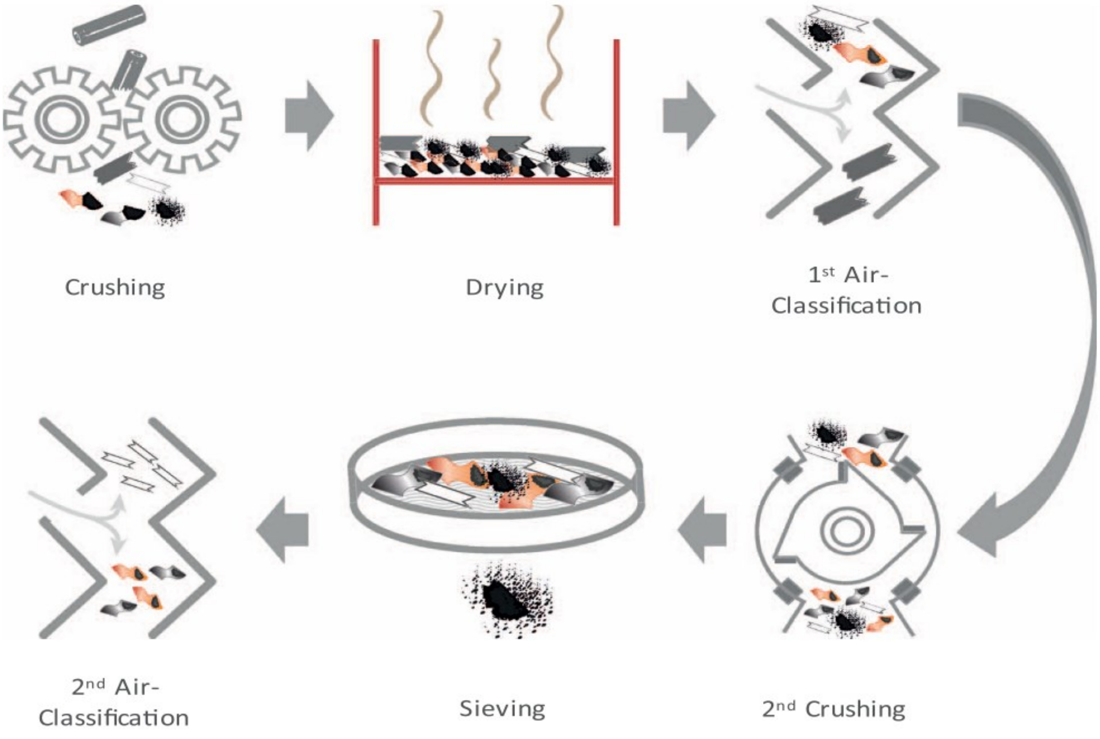


Figure 7 - Process steps used in experimental recycling process with varied second crushing. (Diekmann *et al.*, 2016)

The crushing of battery modules was done using a rotary-shear mill with four shafts and 20 mm discharge screen under nitrogen atmosphere with oxygen concentration of 4%. Electrolyte solvent fumes in the crushing did not reach the lower explosion concentration limits (DMC value 0.2 vol.-%, limit 4.22 vol.-%). Fragments produced by rotary-shear were dried at 105°C for five hours, causing 8.05% mass reduction. Crushing and drying phases produced a cumulative size distribution of different materials shown in Figure 8. The first mechanical separation treatment used in the experiment is air classification, which separates heavy parts based on density, creates two particle populations. This is followed by a cutting mill with a 10 mm discharge screen. To further separate black mass from collector foils and separators, 5 mm mesh was used in the vibration sieve. Using ICP-OES, the black mass components were mostly found in the 20 µm – 6,3 mm size fractions. (Diekmann *et al.*, 2016)

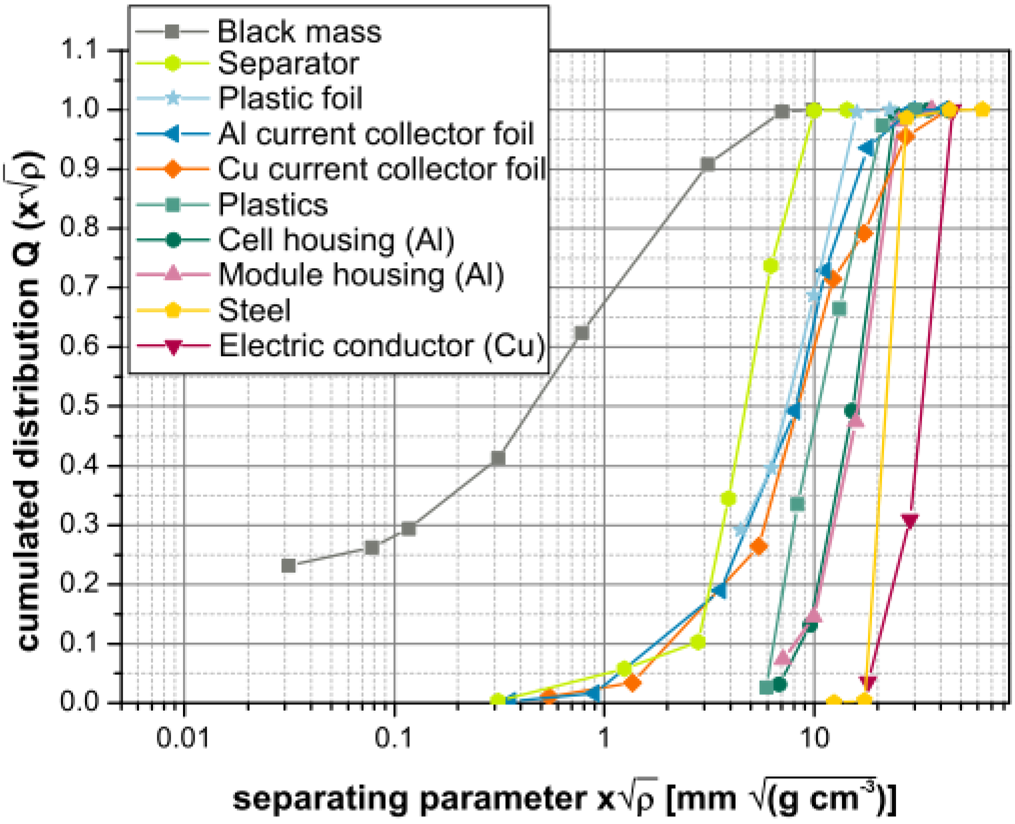


Figure 8 - Cumulative distribution of different materials after crushing and drying. (Diekmann *et al.*, 2016)

The secondary crushing results in an improved liberation of particles, associated to an increased the yield of black mass to 75%, while just barely increased Cu and Al impurities. Secondary crushing also promoted the removal of separator in the air classification process. The general effect of secondary crushing on the separation of black mass is presented in Figure 9. (Diekmann *et al.*, 2016)

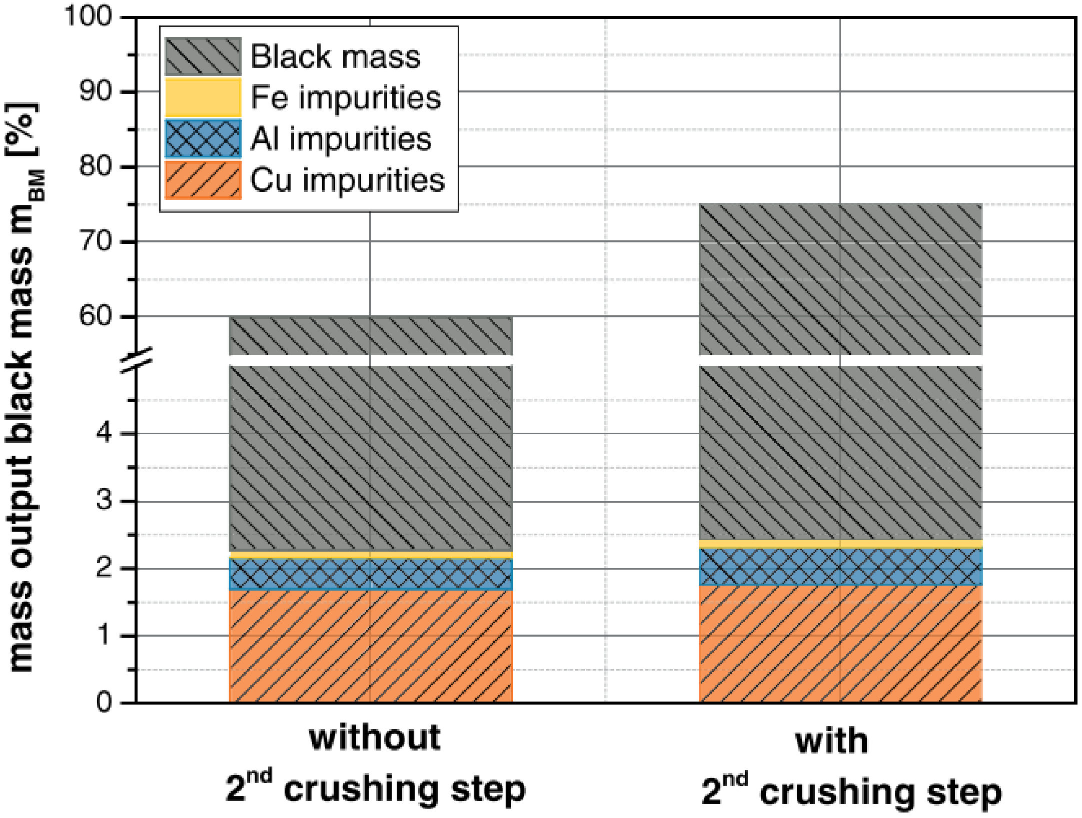


Figure 9 - Yield of black mass and impurities with and without second crushing (Diekmann *et al.*, 2016)

3.3 Xiao et al. 2017

Xiao et al. (2017) proceeded with mechanical separation with spent $LiMn_2O_4$. Prior to mechanical processing, the iron casing was removed manually to prevent damage in the subsequent crushing stages. In the pretreatment phase, these batteries were discharged in 5 wt-% NaCl solution for 24h and then air dried manually. The mechanical pretreatment steps are illustrated in Figure 10.

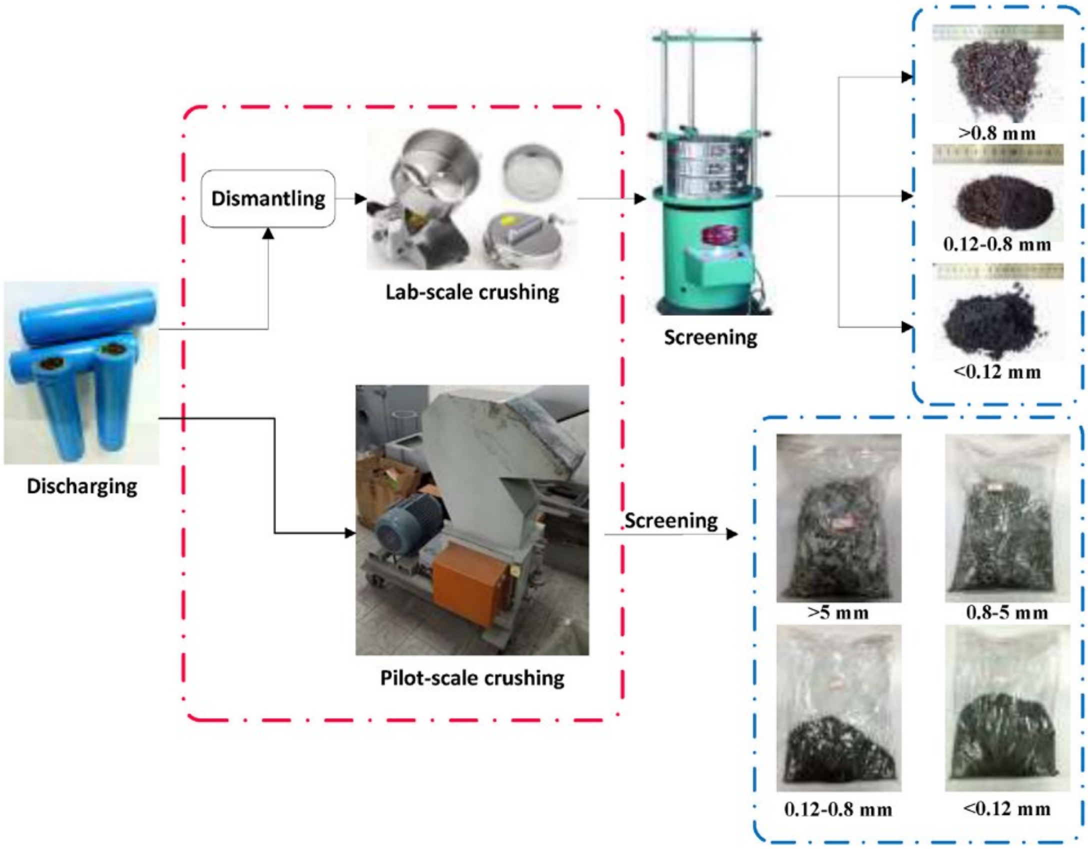


Figure 10 - Schematic illustration of mechanical treatment steps (Xiao, Li and Xu, 2017)

Batteries were crushed for 10 minutes using a crusher and vibrating screen, producing the size distribution in Figure 11. In this study, pilot scale experiments were also conducted, where 100 spent LIBs were treated by a hammer crusher and screened to produce an element distribution as shown in Table 2. This table shows that crushing and screening can effectively separate graphite and manganese from the spent LIBs. The major portion of mixed powders were graphite and lithium manganese with small traces of other elements.

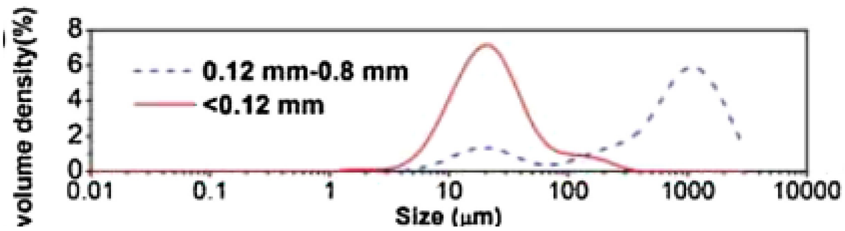


Figure 11 - Size distribution of screened particles. (Xiao, Li and Xu, 2017)

Table 2 - Composition of mixed electrode material produced by mechanical separation. (Xiao, Li and Xu, 2017)

Elements	Li	Mn	Cu	Al	Fe	Co	Ni	C
Content (wt.%)	2.371	37.22	0.2307	0.2276	0.0627	0.0095	0.0062	30.83

3.4 Hanich et al. 2014

Hanich et al. (2014) examined NMC cathode rejects which consisted of 20 μm aluminum foil and its coating layer consisting of NMC, PVDF binder and conducting agents. Their goal was to separate current collectors from the coating with the best possible purity. Electrodes were pre-dried for 10 minutes at 120°C in order to evaporate the volatile fractions from the electrolyte.

In their physio-mechanical separation process, they followed the process presented in Figure 12. First, drying was done for 120 hours at 150°C and calcination at 500-°C for 15 minutes in a muffle oven. Both of these steps were considered as a successful pretreatment steps. The effect of pretreatment can be seen in Figure 13. In the second process step, the material was treated with a cutting mill under a rotor peripheral speed from 1.2 to 10 m/s using a 2 mm trapezoid sieve. Increasing rotation speed improves

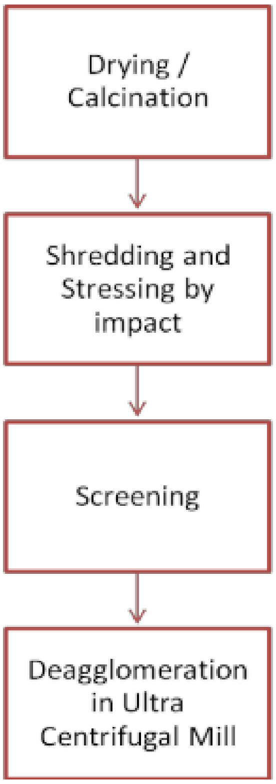


Figure 12 – Physio-mechanical separation process

the fracture behavior inside the mill, reportedly causing an improvement in yields, as presented in Figure 14.

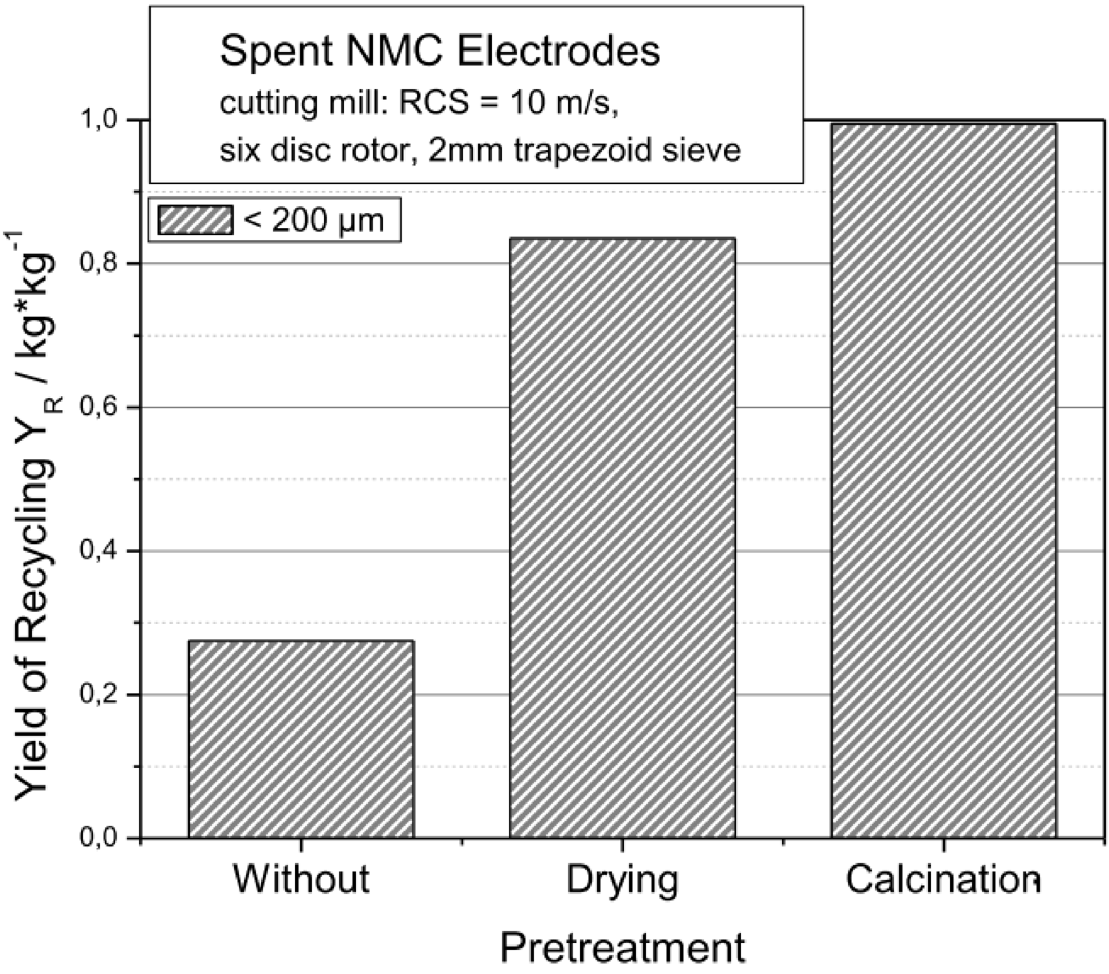


Figure 13 - Influence of thermal pretreatment on the yield (Hanisch *et al.*, 2015)

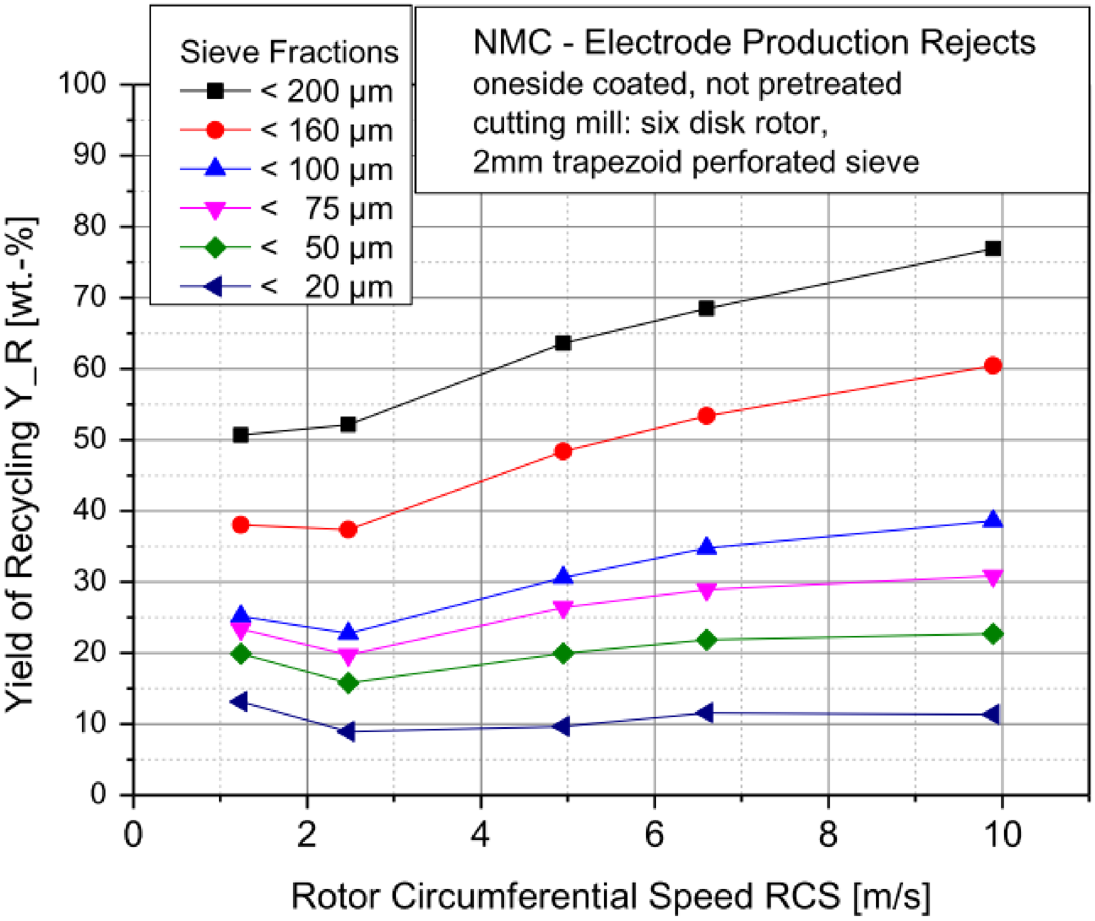
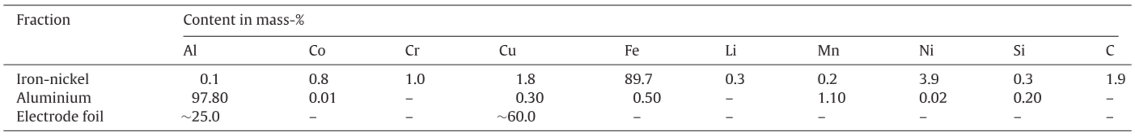


Figure 14 - Influence of the Rotor Circumferential speed on the yield (Hanisch *et al.*, 2015)

3.5 Georgi-Maschler et al. 2012

Georgi-Marcher et al., (2012) focused on the development of a pyrometallurgical process step in an electric arc furnace for the carbo-reductive melting of the fine particles fraction extracted from spent LIBs. The study also includes the characterization and evaluation of all metallic fractions generated by mechanical processing. The experimental material used consisted of three batches of LIB scrap with different manganese content. In the pretreatment phase, the batteries were dismantled, separating the electronic components and plastics. In EV batteries, electronics are needed for control and diagnosis. In the second step, pyrolysis was carried out in a resistance-heated retard furnace at 250°C. According to the authors of such work, pyrolysis discharged the batteries and evaporated volatiles that were collected by a condenser downstream. More of these steps can be found in the ACCUREC processes. If volatiles can be successfully recovered, the recovery percentage of electrolyte can be around 80%. The following processing steps carried out with a secondary mill. Subsequently, classification is carried out in a vibrating screen, while sorting takes place by a drum magnetic separator and an air zig-zag separator. In this manner, the following fractions are obtained: iron-nickel and aluminum fraction from the casings, electrode foil fraction and fines. The elemental composition of said fractions is presented in Table 3. (Georgi-Maschler *et al.*, 2012)

Table 3 - Composition of metal containing fractions. (Georgi-Maschler *et al.*, 2012)



Fraction	Content in mass-%									
	Al	Co	Cr	Cu	Fe	Li	Mn	Ni	Si	C
Iron-nickel	0.1	0.8	1.0	1.8	89.7	0.3	0.2	3.9	0.3	1.9
Aluminium	97.80	0.01	–	0.30	0.50	–	1.10	0.02	0.20	–
Electrode foil	~25.0	–	–	~60.0	–	–	–	–	–	–

3.6 He et al. 2017

He et al. (2017) studied a mix of various consumer electronics, focusing on tartaric acid and H_2O_2 leaching. The flowsheet of their proposed system is seen in Figure 15. The mix of electronics was manually dismantled and discharged by 5% NaCl solution and then dried for 24h at 60°C. Afterwards, ultrasonic cleaning of the removed cathodes was performed using the following settings in the ultrasonic cleaning: solid/liquid ratio of 1/10 g/ml, 70°C, 240W at a frequency 40 kHz and 90 min cleaning time. The cathode material separated by ultrasonic leaning from the aluminum foil was then filtered, screened and dried. The contents of materials obtained by the ultrasonic cleaning are shown in Table 4. The presence of aluminum was attributed to the cathode decomposition by the influence of ultrasonic cleaning. From Figure 16, the dispersive effect of ultrasonic washing appears to be beneficial for the following process steps. After mechanical treatment, the material is processed by leaching for further research. (He *et al.*, 2017)

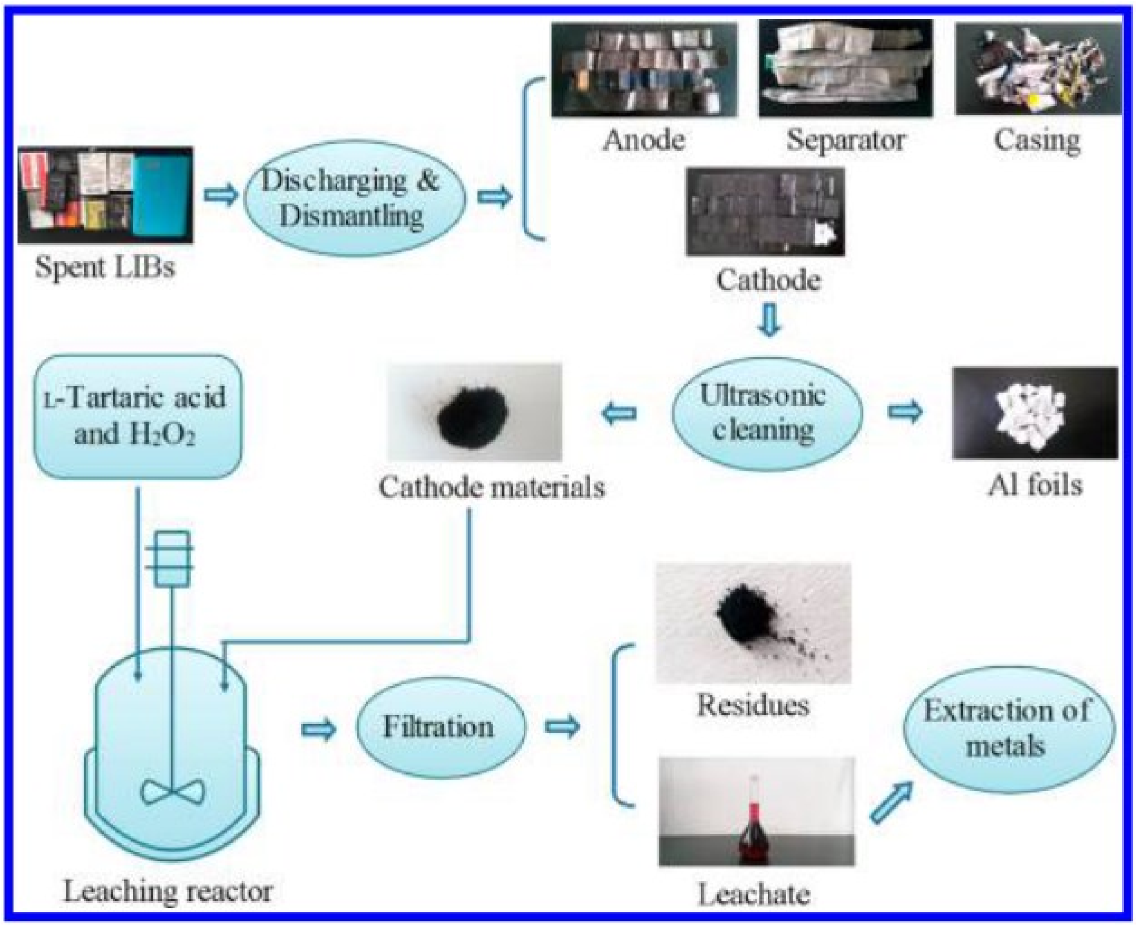


Figure 15 - Flowsheet for the process recycling spent LIBs (He *et al.*, 2017)

Table 4 - Metal content in the cathode materials from ultrasonic washing in spent LIBs. (He *et al.*, 2017)

Element	Li	Ni	Co	Mn	Al
Content (wt%)	6.28	11.85	35.52	8.15	0.11

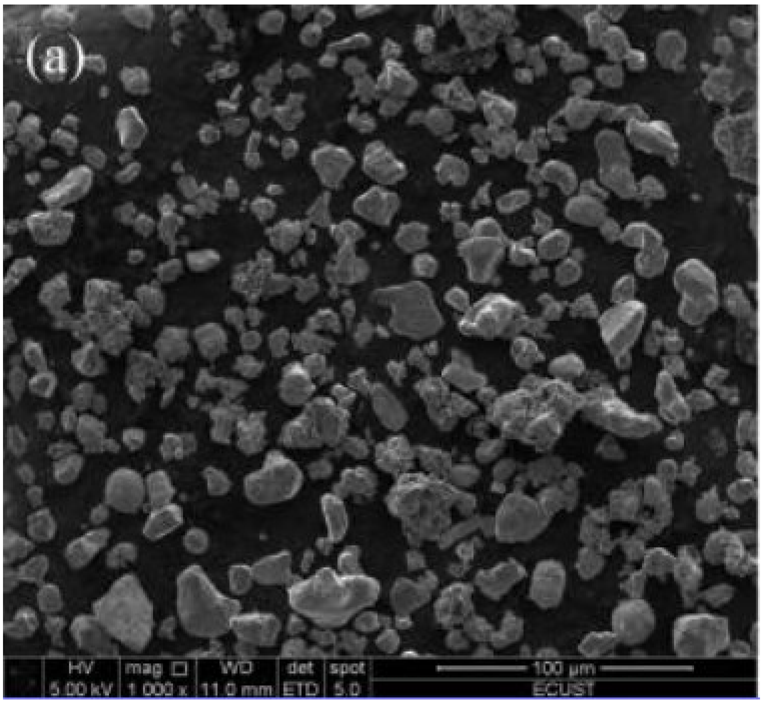


Figure 16 - SEM image of cathode material produced by ultrasonic cleaning. (He *et al.*, 2017)

3.7 Hanisch et al. 2015

Hanisch et al. (2015) studied the separation of current collectors foil and coating using a combination of thermal and mechanical processes. They used batteries with mixed chemistry and thus, a variable range of temperature (i.e., 400-800°C) was used for the evaporation and decomposition of binder material. PVDF binder can be evaporated from the material by using 550°C temperature without interfering with other elements. Results from a thermogravimetric analysis of the electrode components can be seen in Figure 17.

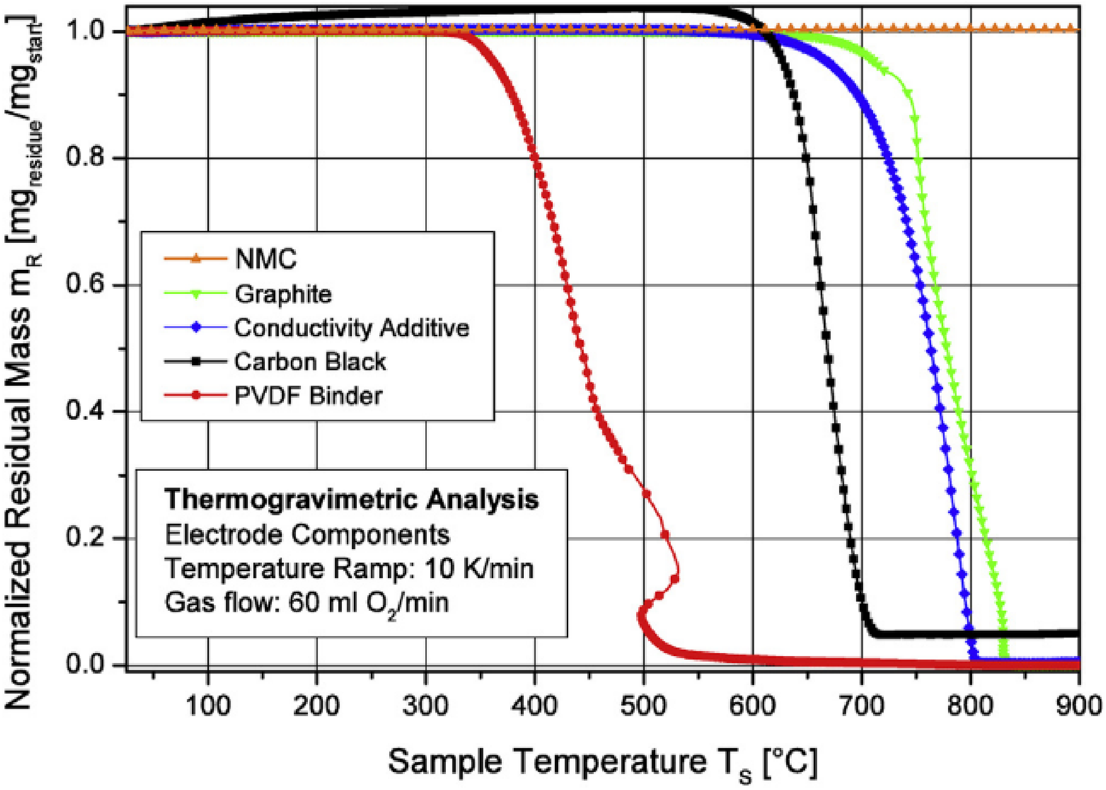


Figure 17 - Thermogravimetric analysis of single electrode components. (Hanisch *et al.*, 2015)

The material used for this research was industrial, untreated $LiCo_{0,33}Ni_{0,33}O_2$ cathode production rejects. These rejects consist of 20 µm aluminum foil and NMC coating, PVDF binder and conducting agents. Comminution was performed using a cutting mill SM 2000 made by Retsch GmbH, Haan, Germany. The cutting mill operated with 9,9 m/s speed and used a 6-disc rotor and trapezoid bottom sieve with 2 mm openings to reduce the maximum product size. After milling, the product was sieved to produced fractions for characterization with atomic absorption spectrometry (AAS). The separation process used was denominated Adhesion Neutralization via Incineration and Impact Liberation (ANVIIL). Sample pieces were calcinated at 500°C for 30, 60, 90 and 120 minutes in air atmosphere. After calcination, an ALPINE air jet sieve was used with an air stream flow of 300 m^3/h. The sieves used for jet have openings down to sizes of 50 µm. The resulted fine fractions were separated with 63 and 200 µm sieves and collected by a cyclone. The resulting fractions of this process can be seen Figure 18. With 90 minutes of calcination time, the most efficient separation was achieved, as longer time did not further increase efficiency.

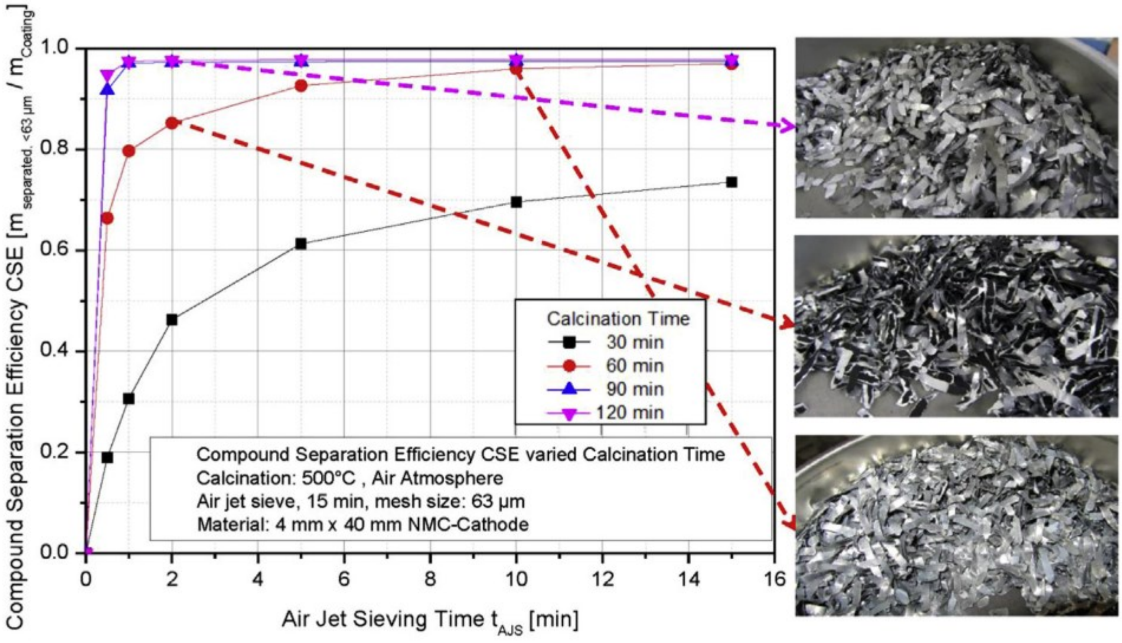


Figure 18 - Compund separation efficiency related to calcination time

From Figure 19 it can also be seen how the adhesion between the foil and the black mass greatly decreased after treatment at 500°C. The ANVIIL process produces a narrower particle size distribution (PSD) compared to the one after crushing, as seen in Figure 20. This can be beneficial when the target particle size must be specific in the following process steps.

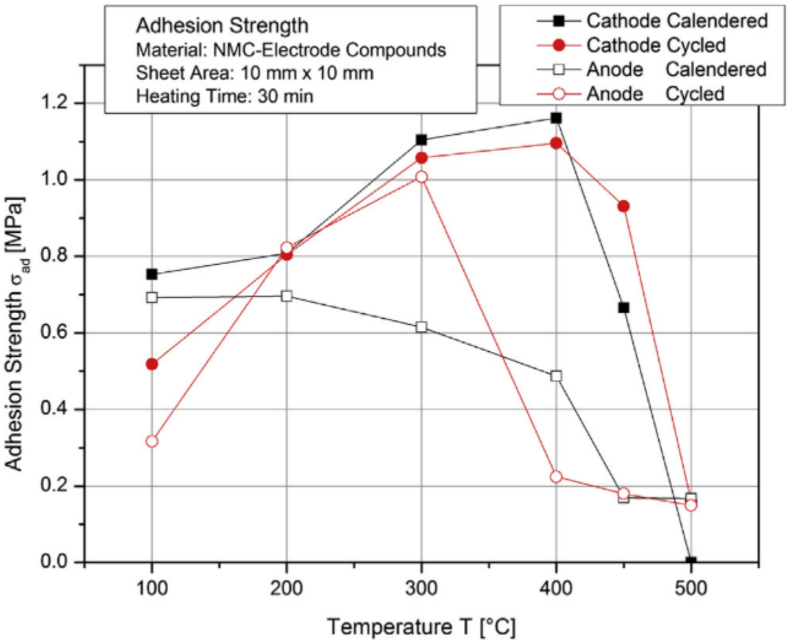


Figure 19 - Adhesion between the foil and the coating after temperature treatment. (Hanisch *et al.*, 2015)

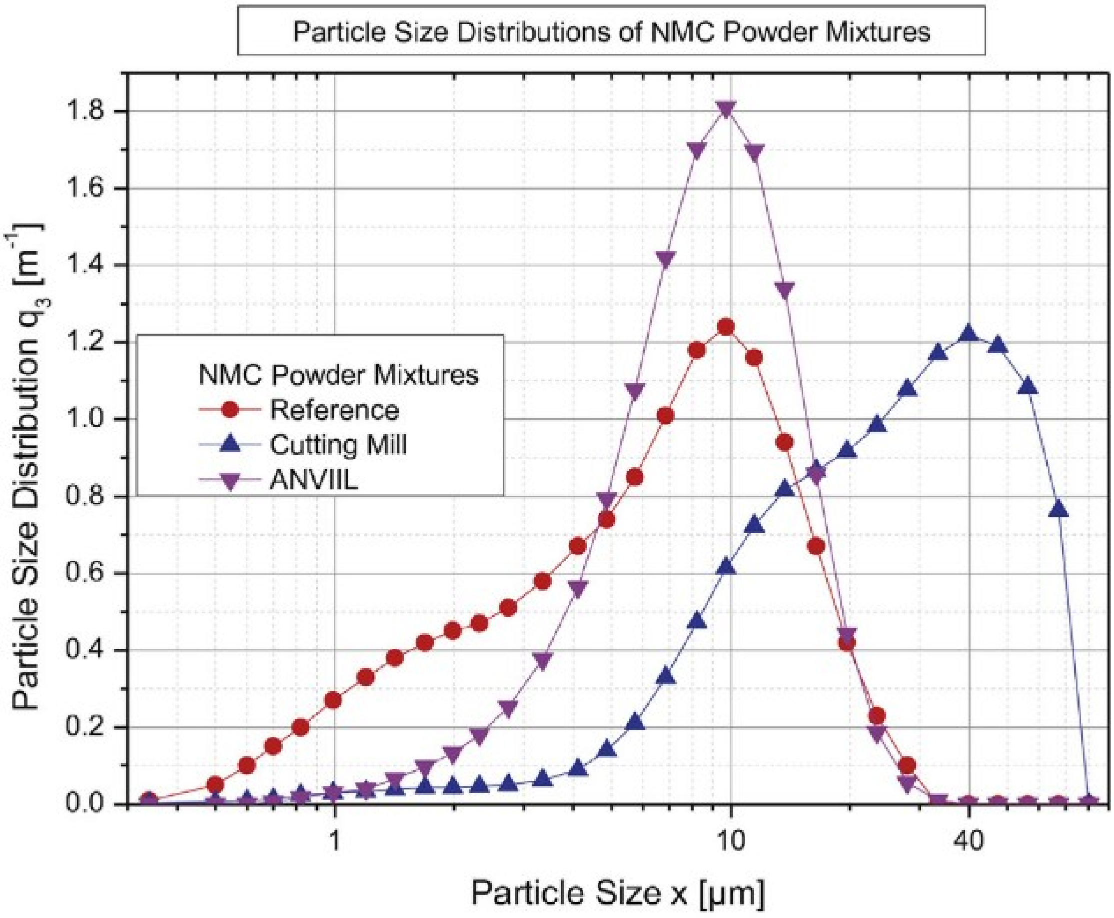


Figure 20 - Particle size distributions of different processing of NMC material. (Hanisch *et al.*, 2015)

3.8 Wang et al. 2016

Wang et al., (2016) studied different battery chemistries from 10 end-of-life laptop battery kits and 49 other cells. Battery chemistries in their study include mixed metal, $LiCoO_2$, $LiFePO_4$ and $LiMn_2O_4$.

First, LIB packets were dismantled to remove the electronics used for the operation of the battery and afterwards, batteries were soaked in liquid nitrogen to discharge the batteries for safe use. After nitrogen immersion, shredding was done with a commercial granulator (i.e. EconoGrind 180/180) to a target size of < 7,5 mm. After shredding, the material was let to evaporate for one week to guarantee complete evaporation of the electrolyte under a fume hood. The product of the shredding was classified using sieves with various opening sizes, as detailed in Figure 21. Sieving was conducted with a Vibration Machine Test System (Molde 7000-10, Lansmont, USA) using 20 minutes sieving time with random vibration mode. The composition of the resulting fractions was analyzed using XRF, although it is worth noting that Li cannot be determined with this technique.

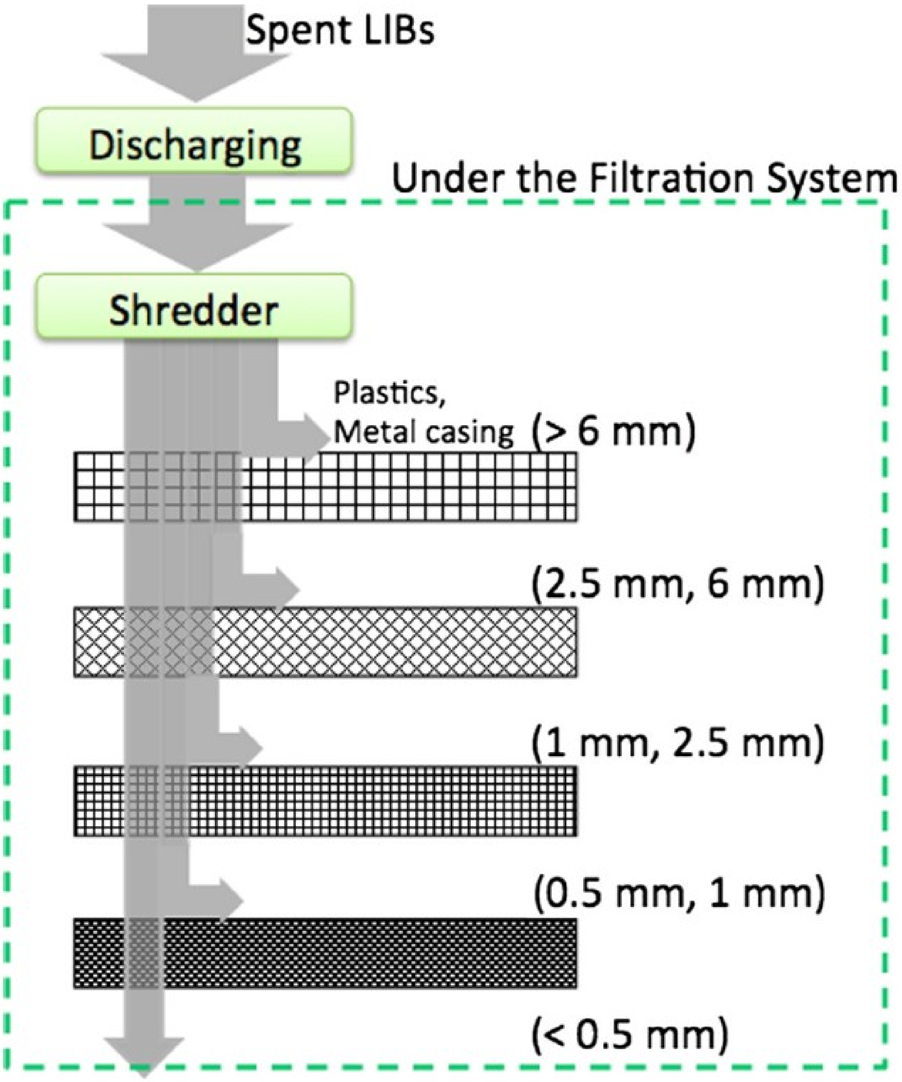


Figure 21 - Flowsheet of preprocesses for LIB recycling. (Wang, Gaustad and Babbitt, 2016)

Shredding of the battery material provided interesting results, where the coarser fractions are mostly casing and plastic separator parts. The 2,5–6,0 and 1–2,5 mm fractions contained evident quantities of copper and the fine black powder dominated the smallest (i.e., <0,5 mm) size fraction. In $LiCoO_2$ batteries, Co reported to the smaller size fractions, representing over 80% of the <0,5mm fraction, 65% of the 0,5-1 mm fraction, around 40% in the 1-2,5 mm fraction and only 20% left in the 2,5-6 mm fraction. No Co was detected in the >6 mm size fraction.

In the case of mixed metal cathode batteries, Mg is present in all fractions except the >6 mm, whereas Ni was detected throughout all fractions although without a clear trend. Cu behaves similarly as in case of $LiCoO_2$ and was mostly found in the fractions between 0,5 and 6 mm.

4 Flotation of black mass from lithium-ion batteries

This Chapter consists of a literature review of work on the field of flotation of black mass from LIBs. The reviewed articles provide important knowledge of this separation process, since flotation of the black mass is a topic that remains largely unexplored. This chapter also compiles the experimental conditions used and can thus be used as reference for future experimental work.

4.1 Yu et al. 2018

Yu et al. (2018) studied flotation as a recycling method to separate and recover $LiCoO_2$ and graphite from spent LIBs. 100 pieces of the same LIB type were used, although their source was not specified. The batteries were discharged in 5 wt-% NaCl solution for 48 hours and air dried for 24h hours. Beforehand, the batteries were dismantled manually to remove the anode and cathode components for further processing. Anodes and cathodes were crushed in an impact crusher. After crushing, the product was sieved and the undercut of 0.074 mm, consisting mostly of $LiCoO_2$ and graphite used as feed for flotation. Measurements of composition were conducted with XRF and XRD and these results indicated $LiCoO_2$ content of 66.75% in the mixed electrode powder.

The equipment used for the grinding flotation were a crushing mill and a laboratory-scale flotation machine. In each experiment, 40 g of mixed electrode material and steel balls were fed to the grinding chamber. The mixture was milled for 2,5, 5, 10, 20 and 30 minutes. After grinding, the products were forwarded to a flotation: pulp solids content of 40 g/l, impeller speed at 1960 rpm and aeration rate of 0.75 l/min. 2000 g/t Methyl isobutyl carbinol (MIBC) and 200 g/t n-dodecane were used as frother and collector, respectively. The flowsheet of the process used in this experiment is presented in Figure 22. According to the authors of this study, grinding increases the hydrophobicity of the graphite. $LiCoO_2$ contents from flotation products were measured with XRD and XRF.

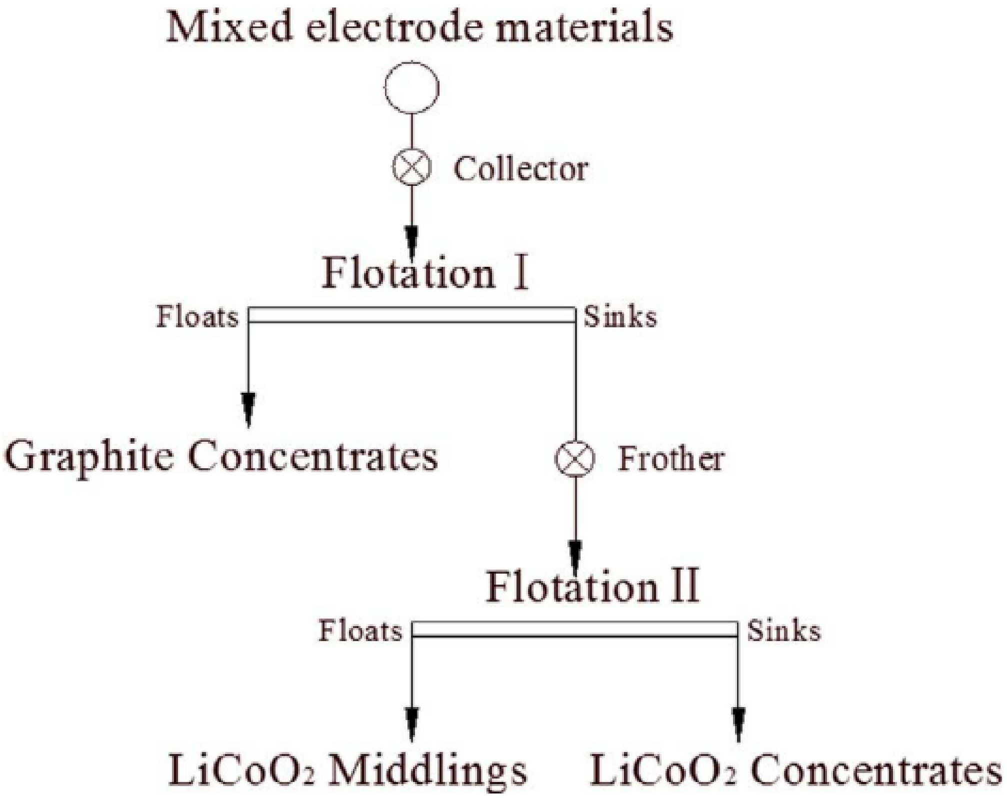


Figure 22 - Flowsheet of the flotation experiments (Yu *et al.*, 2018)

This work also reports interesting results regarding the effect of grinding time on the $LiCoO_2$ separation performance. Figure 22 shows how the grade of $LiCoO_2$ increases at the beginning of the flotation process and then declines at a value of 90% after 20 min. With optimal grinding time of 5 minutes the grade of the flotation concentrate reaches 97.19%. When this short grinding is done, both graphite and graphite with small traces of $LiCoO_2$ enter the foam layer this causes the concentrate at the bottom reach 95% grades. The decrease in the grade of the concentrate is caused because of the excess grinding causes the particle size to decrease and this will cause further agglomeration of the graphite particles on the surface of the $LiCoO_2$ particles. And this causes these graphite particles no longer enter the froth and causes the decrease in grade, but increase in the recovery rate, which can be altered for case specific optimization. Yu et al. (2018)

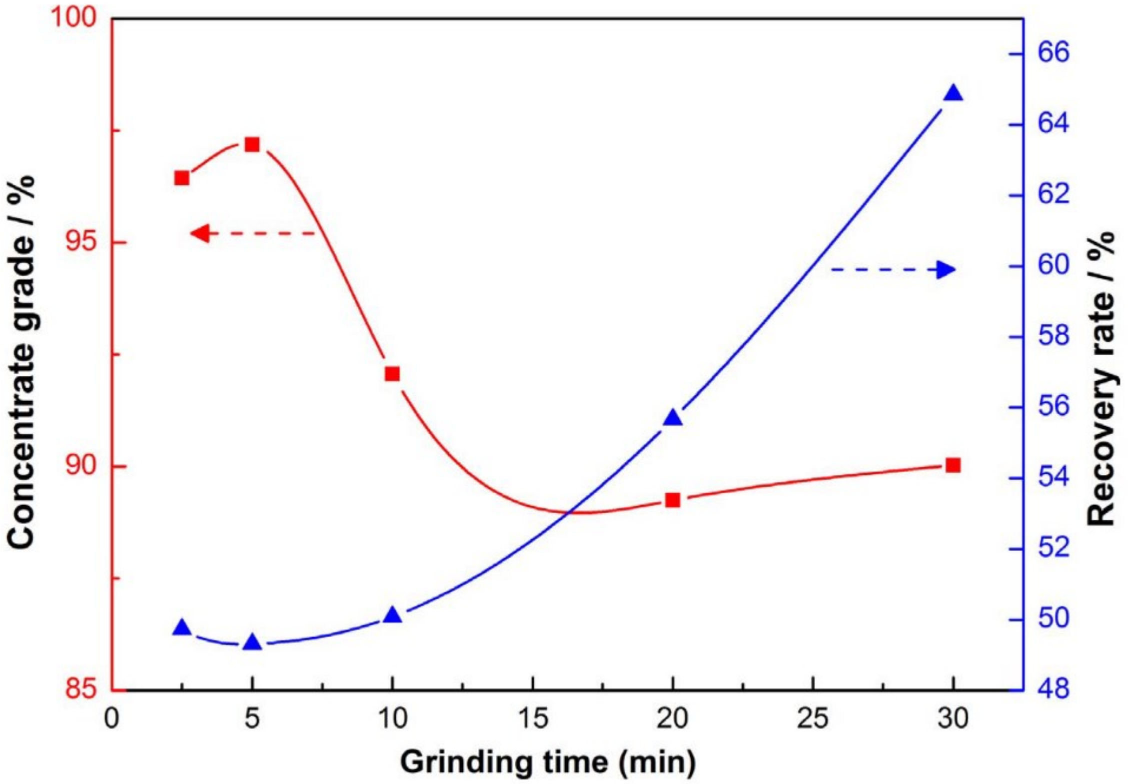


Figure 23 - Flotation results for $LiCoO_2$ concentrate with different grinding times. (Yu *et al.*, 2018)

4.2 Wang et al. 2018

Wang et al. (2018) studied mechanical separation combined with thermal treatment for the recovery of valuable metals and graphite from crushed LIBs. A total of 1 kg of spent LIBs were treated in the study. Experiments started with the discharge of batteries in 5 wt-% NaCl solution for 24 hours and then air dried. Prior to crushing, batteries were manually dismantled to anode and cathode fractions which were subsequently crushed and sieved to form three different samples. -0.25 crushed product from anode was the graphite concentrate, $LiCoO_2$ concentrate was from the cathode and mixed $LiCoO_2$ and graphite concentrate was from both anode and cathode.

Roasting test results were analyzed using Thermogravimetric analysis (TGA) coupled with Fourier-transform infrared spectroscopy (FTIR). Decomposition mass losses and the generated waste air composition were monitored between 25 and 900°C. TGA was performed under the flow of air at 100 ml/min and with a heating rate of 15°C/min. FTIR wavelength range was set from 400 to 4000 cm^{-1}. The roasted surface properties were analyzed by SEM and XPS. A DSA Contact Angle Meter (Kruss, Germany) was used to indicate any wettability changes. For reproducibility, six contact angle measurements for each sample. The temperature considered optimal for roasting was 450 °C for 15 minutes, as these conditions promoted the floatability of graphite. (Wang *et al.*, 2018)

5 Challenges in the recycling of end-of-life lithium-ion batteries containing fluorine components

The following chapter highlights the challenges faced in the research for mechanical separation of LIBs and flotation of black mass. The research carried out in this thesis, provided necessary information about the hazards of waste LIB materials handling, especially black mass, resulting in strategies for risk minimization.

5.1 Evolution of hazardous fluorine components from end-of-life lithium ion batteries

Recycling of end-of-life batteries entails plenty of challenges and one major concern is the formation hydrofluoric acid (HF). Since $LiPF_6$ is a common electrolyte material, this issue is one of the core problems regarding recycling of LIBs. $LiPF_6$ has been shown to thermally decompose according to the following reaction:

$$LiPF_6 \rightarrow LiF\ (s) + PF_5\ (g)$$

LiF is more stable than $LiPF_6$, and has a slight solubility in water ~1,2 g/L. When the battery material mixture is heated beyond 50°C, the possible formation of HF may happen with the presence of hydrogen and atmospheric pressure. LiF forms hydrofluoric acid when it is in contact with water. The presence of water mist in a process has been found to increase the production rate of HF, although not the amount produced (Larsson *et al.*, 2017). In case of fire, the battery waste material containing PVDF binder material may decompose to hydrogen fluoride when reaching 400 °C, as mentioned in Chapter 2.2. Also, there is the possibility of phosphorus pentafluoride (PF_5) and phosphoryl fluoride (POF_3) formation. Fluorine-containing compounds can be also present in the separators and electrode materials i.e. fluorophosphates (Larsson *et al.*, 2017). It should be noted that studying the formation mechanisms of hydrofluoric acid is not within the scope of this thesis, as the focus was more on the implementation of laboratory safety procedures. (Appendix A)

5.2 Pathophysiology of Hydrofluorine

Hydrofluorine and hydrofluoric acid have serious health risks and their handling is one of the key issues regarding recycling of LIBs. The toxicity of hydrofluoric acid is based on its dehydration and corrosive potential on living tissues because of its free hydrogen ions. Also, the fluoride ion F^- presents severe toxicity. F-ions make complexes with bivalent cations present in living organisms, mostly Ca and Mg. Fluorine reacts with the calcium metabolism of the body and causes severe soft and bone tissue damage. HF is a problematic acid, since it is weak acid in dilute solutions, and initial signs of exposure can be nonexistent. For this reason, contact with HF can go unnoticed for long periods of time, enabling deeper penetration of fluorine and causing further damage to tissues. Exposure to concentrations of less than 20% can take even up to 24 hours to generate visible symptoms. Thus, the effect of HF becomes a combination of concentration, time of exposure and the affected surface area. (Bertolini, 1992)

Immediate effects of over 5 ppm exposure of HF in the workspace air causes irritation of eyes and airways, but the symptoms can be delayed. High concentrations cause difficult and painful damages to skin, eyes and mucous membrane. Irritation and redness are easily caused by HF gas. Fumes can cause respiratory corrosion, pulmonary edema and often cardiac arrhythmia. Short exposures for 50 to 250 ppm concentrations are already life threatening (Työterveyslaitos, 2017)

HF corrodes the skin and its deep underlying tissues. This substance binds Ca from the blood serum, causing cardiac arrhythmia. Strong HF (50-70 %) causes serious skin corruption while causing immediate pain on the skin. At the beginning, the skin swells, and redness is severe. After this, white and yellow blisters are formed with intolerable pain. Serious skin exposures to strong hydrofluoric acids have caused deaths with 2-3% skin coverage (400-600 cm^2) within few hours of the exposure. Hydrofluoric acid splashes in the eyes causes irritation and corrosion. This may end up in serious eye corrosion and blindness (Työterveyslaitos, 2017). The effects of diluted HF aqueous solutions begin after few minutes. Solutions with less than 20 % concentrations can take up to a few hours to have noticeable symptoms.

5.3 Treatment of hydrofluoric acid burns

The treatment for HF exposures is to remove contaminated clothing and rinse the contaminated area with plenty of water. The time used for flushing should be shortened to 5 minutes if calcium gluconate gel is present. In this case, time is not lost before the crucial step of binding the fluoride ions using 2.5 % calcium gluconate gel. Massaging the gel into the tissue increases the absorption of the gel, thus improving the binding of the fluorine ions. When using the gel, the user should be aware of exothermal behavior of the neutralization process, which can cause burns to the patient (Bertolini, 1992). This is especially for the case of treating fingers. Severe exposure may need multiple applications of the gel and supervision of medical personnel. When moving the patient to medical care, cover the affected area with the gel and then with a bandage. (Appendix A)

When swallowed, milk, chewable calcium carbonate tablets or milk of magnesia can be given, if the patient is still conscious. In the case of inhalation, the person should be moved to an open area with plenty of fresh air and, in the case where the patient is not breathing, artificial respiration is necessary. Artificial oxygen can be given if it is present (see Appendix A) (Työterveyslaitos, 2017).

In all kinds of exposures, the monitoring of the patient is necessary, in serious exposure immediate medical attention is needed. (Appendix A)

5.4 Safety procedures when working with HF-containing materials

HF can be distinguished by its smell when its concentration in air is greater than 0.04 – 0.13 ppm. HF has a strong and irritating smell. HF can decompose when stored, creating flammable hydrogen gas, but in it is not flammable itself (Työterveyslaitos, 2017).

HF is rather reactive with different materials, since it corrodes glass, leather and several other different metals. When reacting with metals, HF forms flammable hydrogen gas. When HF reacts with water, it forms toxic and corrosive fumes and in strong concentrations, its exothermic reaction creates a spatter hazard. Corrosion levels upon human contact can be classified as shown in Table 5. Following levels have been adopted for animal testing. (Työterveyslaitos, 2017)

Table 5 - Hydrofluoric acid exposure limits (Työterveyslaitos, 2017)

Hydrofluoric Acid Exposure Limits			
Level of exposure	Concentration (**c**)	Exposure (**t**)	Observated time (t_obs)
Skin corrosion class 1A Strong skin corrosion and damage to eyes (H314)	**c** ≥ 7 %	**t** ≤ 3 min	t_ obs ≤ 1 h
Skin corrosion class 1B Strong skin corrosion and damage to eyes (H314)	1 % ≤ **c** < 7 %	3 mins < **t** ≤ 1 h	t_ obs ≤ 14 days
Eye irritation 2 Strong eye irritation (H319)	0,1 % ≤ c < 1 %	1 h < **t** ≤ 4 h	t_ obs ≤ 14 days

For the safe working in workspace, 1.8 ppm / 8 hours (skin) and 3 ppm / 15 min (skin) are the threshold levels of HF in air (Appendix A). Fluoride from HF accumulates into the bones and ligaments, potentially causing weak bones and chronic fluorosis (stiffness in the joints). Fluorine is disposed from the bone tissues really slowly, having an estimated half time between 8 and 20 years (European Commission, 2001).Continuous exposure to small dosages of HF possibly causes stinging in the eyes and on the facial skin and also irritation in nasal mucosa. (Työterveyslaitos, 2017)

Gaseous hydrofluorine reacts with the moisture forming hydrofluoric acid, which descends to the surfaces of the room. In general, there is a possibility for HF accumulation on the surfaces if the cleaning of the working space is not sufficient.

5.5 Other hazardous factors in LIB waste

Spent LIB black mass contains various other hazards in addition to the formation HF acid. Main concerns of elements present in the spent LIB in addition to fluorine are from toxicity of cobalt, copper, nickel, thallium and silver. (Zeng, Li and Liu, 2015 and Appendix 1). Based on the practical research done in the Aalto University Mechanical Processing and Recycling laboratory, black mass is composed of fine particles, as presented in Figure 24. This fine particle size enables the possibility of black mass powder to be carried into the respiratory system of the laboratory workers. This is a concern that should be addressed as presented in the MSDS in Appendix 1.

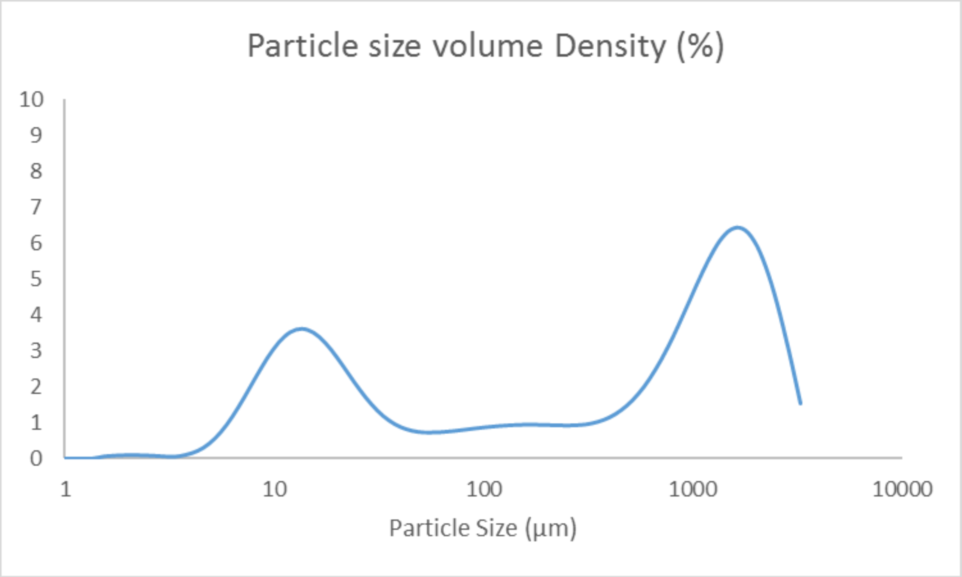


Figure 24 - Black mass particle size distribution

In addition to the hazards associated with HF formation and fine powders, there is a third concern, which is caused by the electrostatic behavior of this black mass. Workers have been noticing complications when trying to handle the black mass in the laboratory, for example during transportation from one container to another. This behavior could come as a surprise for new unexperienced workers and this can be decreased by using non electrostatic materials in the laboratory and educating workers on these hazards. (Appendix 1)

6 Development and implementation of safety protocols

This Chapter contains the steps followed to implement suitable laboratory practices for waste LIBs handling and treatment in Aalto university. These protocols were necessary to address concerns regarding the risks of associated with LIB components described in the previous Chapters. It is worth noting that LIBs recycling research in Aalto is carried out using real, crushed, lithium ion batteries waste. This Chapter is also aimed to be used as reference for researchers working with this hazardous material, particularly but not limited to, the facilities of Aalto University, School of Chemical Engineering.

6.1 Development of laboratory practices

This thesis work was produced as part of a larger research project in which it is intended to mechanically separate crushed, spent, LIB wasted received from Dusenfeld Gmbh. The waste LIB sample received consists mostly of black mass (i.e., anode and cathode materials, with traces of separator and casing materials). Accompanying black mass was its corresponding material safety data sheet (MSDS), which can be found in the Appendix 1 of this thesis. This document revealed the presence of fluorine ion containing compounds, which caused major concerns about health and environmental safety. In collaboration with professors and technical staff of Aalto University School of Chemical Engineering, it was decided to develop strict safety procedures and laboratory work protocols for the handling and experimentation with waste LIBs. As will be further described in this Chapter, due to the characteristics of LIB black mass, it was clear that ordinary personal laboratory safety gear was not enough. Also, the need for a separate, isolated area for safe operations was evident, to avoid contamination of other working areas and have a higher degree of control in case of accidental spills or release of hazardous components. It is worth noting that these safety measures resulted in a unique laboratory in Finland, with the strictest safety measures for LIB handling.

6.2 Implementation of safety procedures in Aalto University LIB Laboratory

The following safety procedures have been established for safe operations in Aalto LIB lab. A dedicated room was reserved for the experimentation with LIB waste. The chosen laboratory space was selected because it counted with a split layout. In this way, the entrance area works as a dressing room and storage of safety gear, while the experimental equipment remains isolated in the backroom.

6.2.1 Laboratory practices

The entrance area of the LIB lab was dedicated as the low-risk side, to store all necessary safety gear and as dressing room to prevent direct exposure of workers to the waste LIB. Inside this low risk side of the laboratory, presented in Figure 25, one finds a dedicated storage space for: i) gasmasks, motors and filters; ii) outer and inner nitrile gloves in various sizes; iii) disposable overalls (more information below 6.2.2 Personnel protection); iv) personal safety boots; v) tacky mats for the collection of dust particles; vi) containers for low risk waste; and vii) calcium gluconate gel. Cleaning procedures include changing the tacky mat as needed. It is the responsibility of each worker to clean the surfaces after their work with alcohol, e.g., ethanol or propanol. Disposal of waste in appropriate manner. After conducting laboratory experiments the HF gas detector/alarm has to be turned off and plugged in for recharging. Door has to be closed all the time. Specific safety regulations are applied to this laboratory and all safety consumables and concerns are to be followed to Safety committee of School of chemical engineering. Research plan & risk evaluation has to be proofed by this safety committee in addition to be approved by the supervisor.

Figure 25 – LIB Recycling Laboratory low risk side

Special safety procedures should be followed in the high-risk side of the LIB lab (Figure 26) due to the challenging material used for the experiments. The high-risk area contains fume hoods with individual filtered ventilation. All experimental equipment is placed inside these fume hoods. For mechanical separation experiments, there is flotation cell dedicated solely for the flotation of black mass. In addition, the LIB-lab counts with a sieving machine with grinding vessels. Tacky mats are placed throughout the floor to catch dust particles. There are containers dedicated to high risk waste. Calcium gluconate gel can also be found in the high-risk side of the laboratory.

Cleaning protocols are established for work on the LIB lab, including regular change of tacky mats. The expiration date of all chemicals should be checked on a regular basis and expired materials disposed accordingly. Working alone in this room is not allowed when conducting experiments. In addition, personal equipment e.g. mobile phones are not allowed in the lab. The laboratory doors must be closed all the time. The laboratory has an emergency exit leading to the roof, where fire ladders/escape is. Specific safety regulations are applied to this laboratory and all protective equipment and safety materials are monitored by the Safety committee of the School of Chemical Engineering. A research plan containing risk evaluation must be approved by the academic supervisor of each researcher and the aforementioned safety committee.

Prior to every experiment, the worker must make sure that the fume hoods are functional e.g. using a paper towel. The working area should be visually inspected to determine whether it is sufficiently clean to conduct experiments. Cleaning the working space surfaces with alcohol (e.g., ethanol or propanol) should be carried out immediately after the daily programmed experiments and is the responsibility of each researcher. Disposal of waste should be carried out into the appropriate containers. The LIB-lab also contains absorption chemicals and absorption cloths which are to be changed after each use. The laboratory also counts with HF gas detector/alarm with portable pump hose for checking the possible HF gas formation from a safe distance.

Figure 26 - LIB Recycling laboratory high risk side

6.2.2 Personnel protection

The following sequence for dressing up with special personnel protection has been implemented in the Aalto LIB laboratory (presented in Figure 27):

1. Nitrile gloves, to be used as under gloves this is to ensure safety when undressing the clothes.
2. Acid resistant safety boots with anti-slippery and electrostatic discharging properties.
3. Ansell Microchem 4000/3000 overalls.

4. 4. motorized gas mask with 2 FFP3 class activated carbon filters. Attach the motor to the gas mask and then turn it on before wearing the mask, then wear the face mask and check the sleeve will cover your neck.
5. Outer, long sleeved gloves with acid resistant properties. Gloves should be tightened to the overalls with glove connectors. If this is not available, adhesive duct tape can be used.
6. HF gas detector/alarm attached to the chest pocket.

Figure 27 - LIB recycling lab protection manual

7 Conclusions and suggestions

The proper handling of spent LIB for recycling is a rather challenging and complex task with the presently available technology. This complexity is caused because of the varying battery constructions, battery chemistries and hazardous and toxic elements inside the battery. When the recycling of LIBs is considered, the safety concerns addressed in this thesis should be considered thoroughly, especially focusing on the possible hydrofluoric acid formation. This becomes particularly problematic when the LIB waste is part of a mixed stream of different chemistries, where hazardous fluorine components will likely be introduced.

Hydrofluoric acid has serious health hazard having both acute toxicity and a cumulative nature. This requires tight safety measures to prevent its contact with operating personnel and workplace contamination.

Regarding the processing of LIB black mass, the literature provides some solutions to the challenge of black mass flotation, where the hydrophobicity of graphite is prevented by the organic layer. Roasting has been reported to have a positive effect (Wang *et al.*, 2018) enabling the separation of graphite with flotation, an approach that demands further study. Roasting may also be used as a cleaning process for the volatiles inside the black mass.

This thesis is reports the first efforts to deal with the hazardous LIB waste in Aalto University. This work was compiled with the objective to be used as a future reference for any experimental campaign where LIB waste is handled, especially with the hazardous elements containing LIBs.

Any future experimental work in Aalto's LIB-lab will use the outcome and safety protocols detailed in this thesis. It should be also kept in mind that this is a first approach at setting safety guidelines for experimental work with waste LIBs and consequently, as further knowledge on the subject matter is gathered, the need for more strict safety may become evident. Nevertheless, the present thesis is aimed as a starting point for good laboratory practices with waste LIBs, since they were largely missing in Aalto University and several other research institutes.

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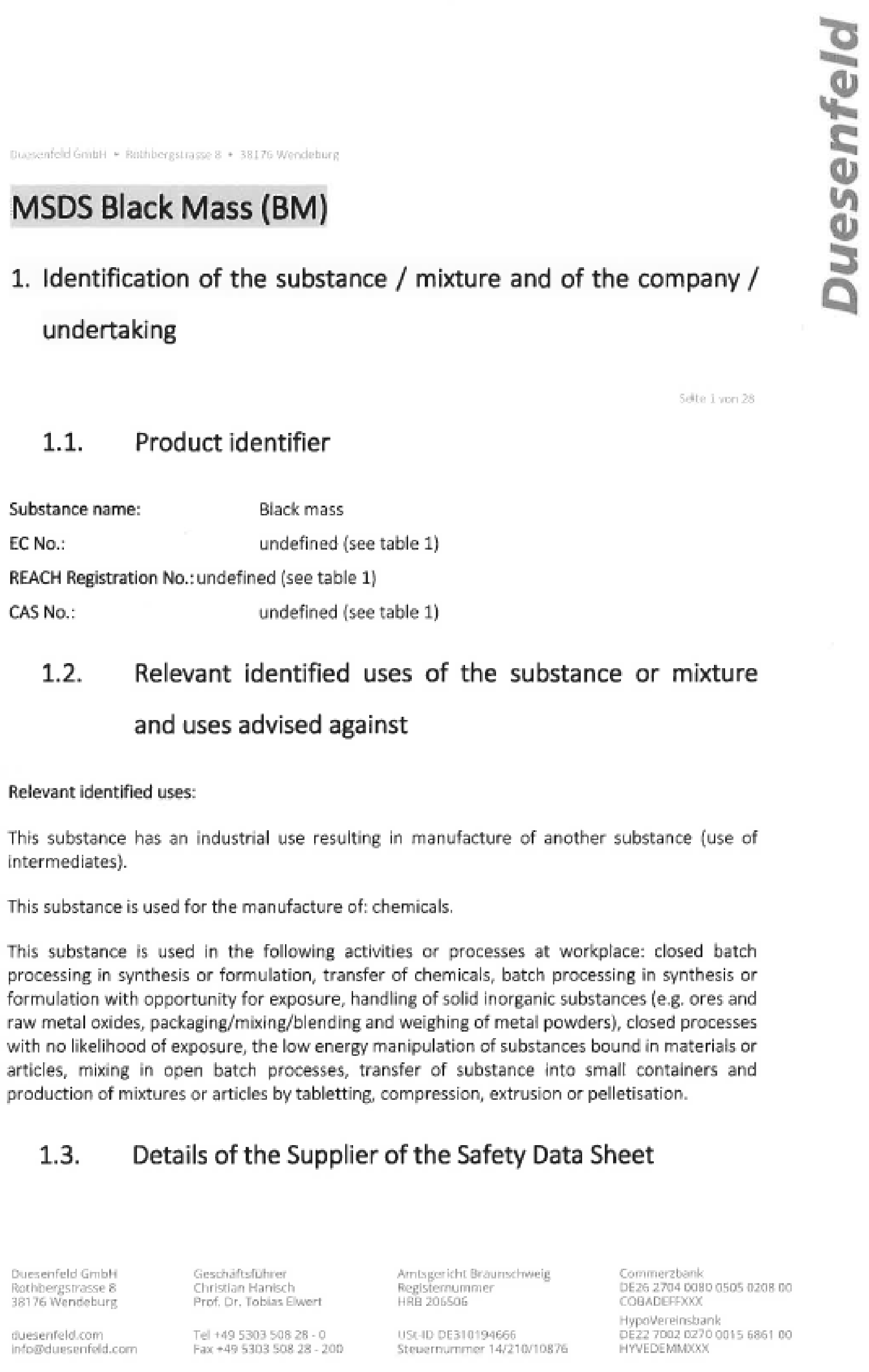
Appendices

Appendix A: Black Mass MSDS



Duesenfeld

Duesenfeld GmbH • Rothbergstrasse 8 • 38176 Wendeburg

MSDS Black Mass (BM)

1. Identification of the substance / mixture and of the company / undertaking

1.1. Product identifier

Substance name: Black mass
EC No.: undefined (see table 1)
REACH Registration No.: undefined (see table 1)
CAS No.: undefined (see table 1)

1.2. Relevant identified uses of the substance or mixture and uses advised against

Relevant identified uses:

This substance has an industrial use resulting in manufacture of another substance (use of intermediates).

This substance is used for the manufacture of: chemicals.

This substance is used in the following activities or processes at workplace: closed batch processing in synthesis or formulation, transfer of chemicals, batch processing in synthesis or formulation with opportunity for exposure, handling of solid inorganic substances (e.g. ores and raw metal oxides, packaging/mixing/blending and weighing of metal powders), closed processes with no likelihood of exposure, the low energy manipulation of substances bound in materials or articles, mixing in open batch processes, transfer of substance into small containers and production of mixtures or articles by tabletting, compression, extrusion or pelletisation.

1.3. Details of the Supplier of the Safety Data Sheet

Duesenfeld GmbH
Rothbergstrasse 8
38176 Wendeburg

duesenfeld.com
info@duesenfeld.com

Geschäftsführer
Christian Hanisch
Prof. Dr. Tobias Elwert

Tel +49 5303 508 28 - 0
Fax +49 5303 508 28 - 200

Amtsgericht Braunschweig
Registernummer
HRB 206506

USt-ID DE310194666
Steuernummer 14/210/10876

Commerzbank
DE26 2704 0080 0505 0208 00
COBADEFFXXX
HypoVereinsbank
DE22 7002 0270 0015 6861 00
HYVEDEMMXXX

Supplier:	Duesenfeld GmbH
Street / P.O. Box:	Rothbergstraße 8
Postcode / City:	38176 Wendeburg
Country:	Germany
Telephone (Telefax):	+49 (0) 5303 508 280
E-mail (competent person):	info@duesenfeld.com
National contact:	info@duesenfeld.com

1.4. Emergency Telephone Number

Please contact	x
Opening hours:	24 hours, 365 days a year
Other comments:	Languages of the phone service are: German, English

2. Hazards identification

2.1. Classification of the substance or mixture

Labelled according to regulation (EG) No. 1272/2008

- Substances and mixtures corrosive to metals (category 1), H290
- Acute toxicity, oral (category 3), H301
- Acute toxicity, dermal (category 3), H311
- Skin Corrosion / Irritation (category 2), H315
- Skin Sensitisation (category 1), H317
- Serious Eye Damage (category 1), H318
- Acute toxicity, inhalation (category 3), H331
- Respiratory Sensitisation (category 1), H334
- Carcinogenicity, inhalation (category 1A), H350i
- Carcinogenicity (Category 2), H351
- Reproductive Toxicity (category 2), H361
- Specific target organ – toxicity – repeated exposition (category 1), especially bone and teeth, H372
- Hazardous to the aquatic environment – chronic, H412

Full text of these hazard indication can be found in chapter 16.

2.2. Label elements

Please note: the substance is not fully investigated yet.

Identification following regulation (EG) No. 1272/2008

Pictogramm

Danger

Labelling in accordance with EC directives Danger symbol and danger designation:

$LiCoO_2$, $LiNiO_2$, $LiPF_6$

Desciption(s) of danger:

H290	May be corrosive to metals
H301	Poisonous when swallowed
H302	Harmful if swallowed
H311	Toxic in contact with skin
H315	Causes skin irritation
H317	May cause an allergic skin reaction.
H318	Causes serious eye damage
H331	Toxic if inhaled
H332	Harmful if inhaled
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled
H350i	Can cause cancer when inhaled
H351	Suspected of causing cancer
H361	Suspected of damaging fertility or the unborn child
H372	Causes damage to organs through prolonged or repeated exposure. Especially Bones and teeth when inhaled

H412	Harmful to aquatic life with long-lasting effects
H413	May cause long-lasting harmful effects to aquatic life

Measurements for precaution

P201	Obtain instructions before use.
P260	Do not inhale dust / fume / gas / fog / steam / aerosol.
P261	Avoid breathing dust/fume/gas/mist/vapours/spray.
P264	Wash skin thoroughly after handling.
P280	Wear protective gloves, clothing and eye protection plus face protection.
P281	Use personal protective equipment as required.
P301 + P330 + P331 + P310	If swallowed: Rinse out mouth. Do not induce vomiting. Immediately call a poison centre or doctor/physician.
P302 + P352	IF ON SKIN: Wash with plenty of water
P303 + P361 + P353	If in contact with skin or hair: Immediately remove all contaminated clothing. Rinse or shower skin with water.
P304 + P340 + P310	If inhalated: Get the person affected into fresh air and ensure unrestricted breathing. Immediately. Immediately call a poison centre or doctor/physician.
P305 + P351 + P338	If in contact with the eye: Flush carefully with water for several minutes. Remove possibly existing contact lenses if possible. Continue flushing.
P308 + P313	In case of exposure or if affected: obtain medical advice or medical help.
P 405	Store locked up.
P501	Dispose of contents/container according to regional and/or national laws

Other Information None,

Only for industrial application.

2.3. Other hazards

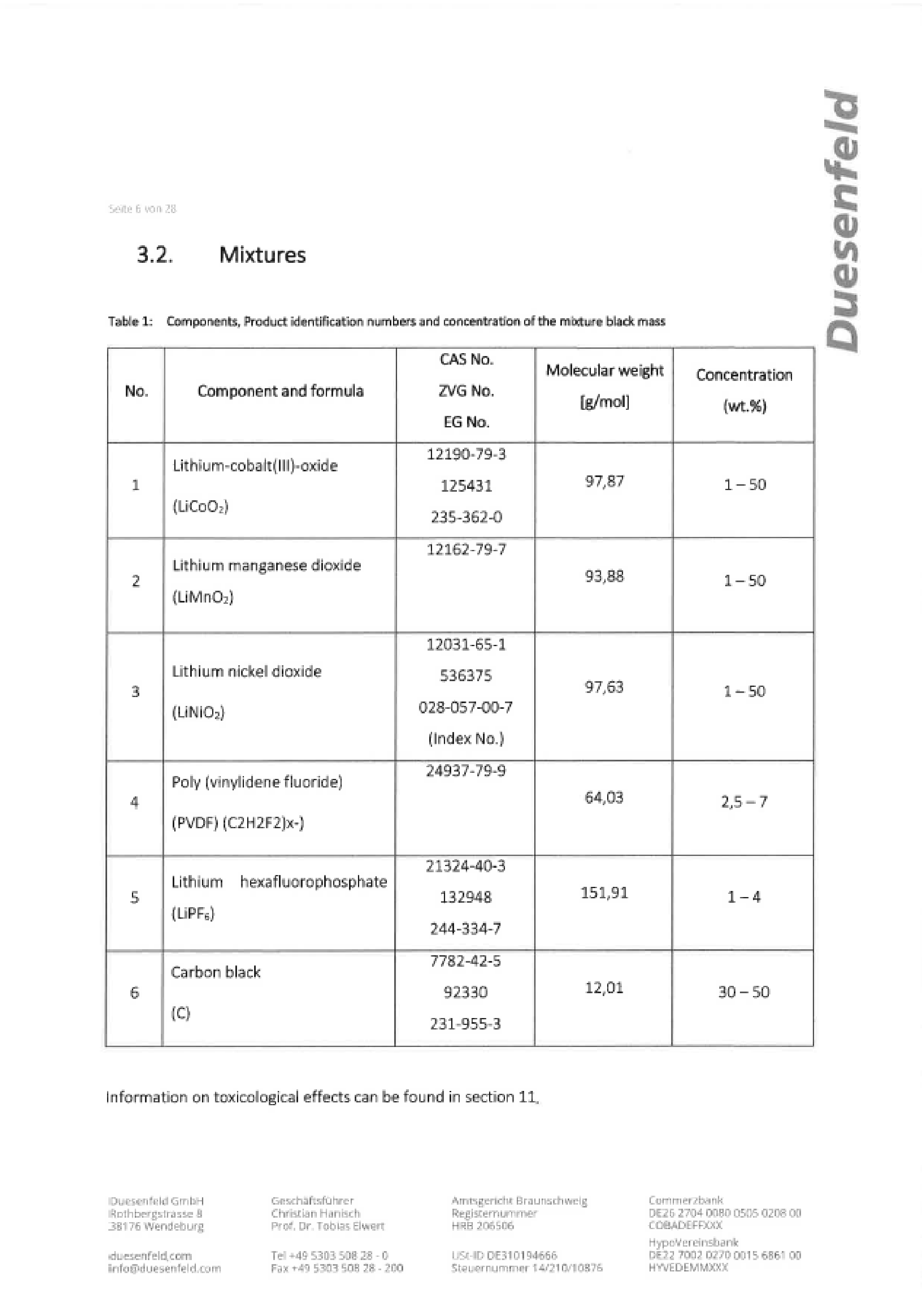
This mixture does not contain any components in concentrations above 0,1 % that are either listed as persistent, bioaccumulateable, toxic or very persistent and very bioaccumulatable.

Do not heat above 85 °C. Otherwise: Heavy release of hydrofluoric acid.

3. Composition / information on ingredients

3.1. Substances

All substances are listed in table 1 (see below).

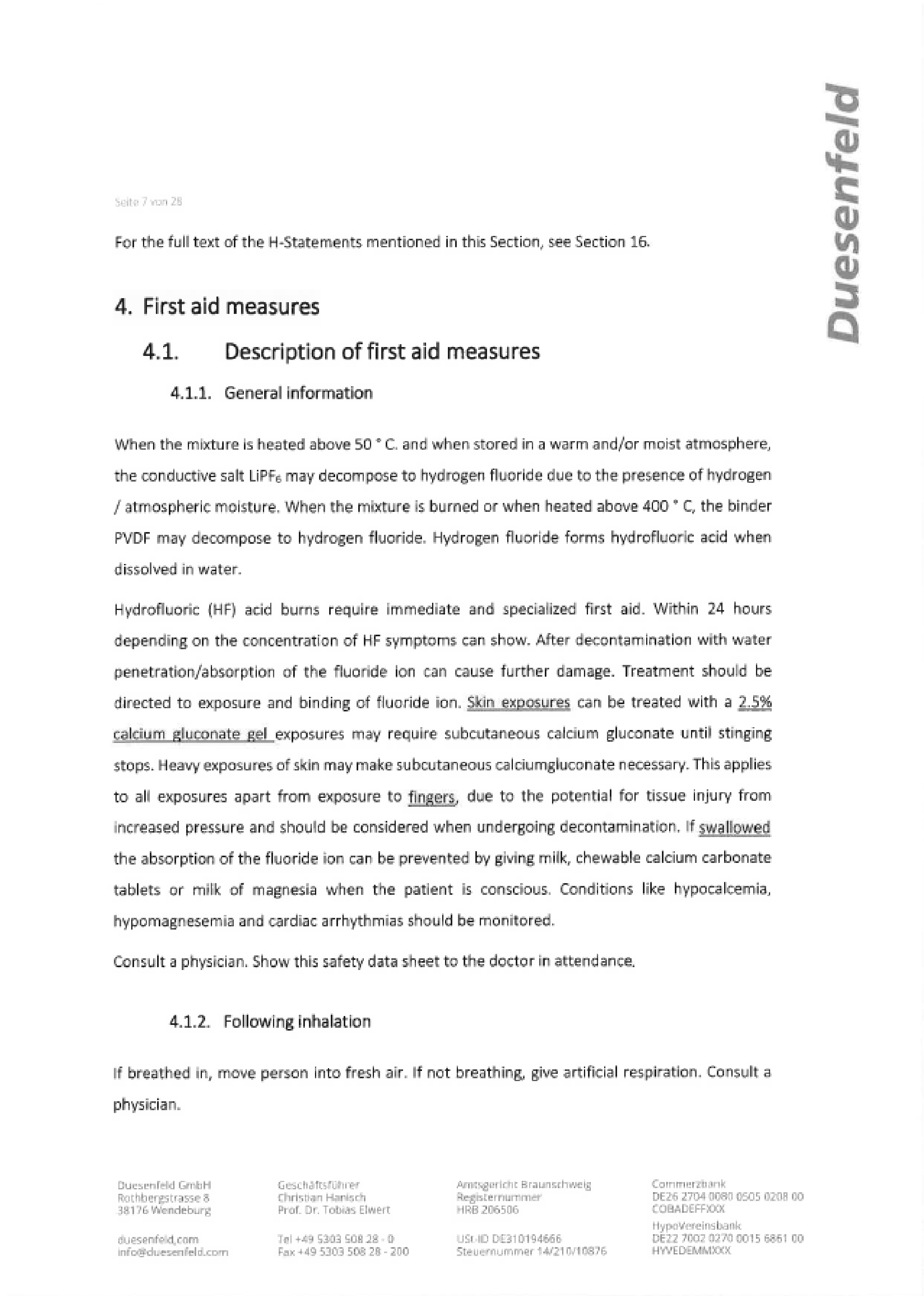


3.2. Mixtures

Table 1: Components, Product identification numbers and concentration of the mixture black mass

No.	Component and formula	CAS No. ZVG No. EG No.	Molecular weight [g/mol]	Concentration (wt.%)
1	Lithium-cobalt(III)-oxide ($LiCoO_2$)	12190-79-3 125431 235-362-0	97,87	1 – 50
2	Lithium manganese dioxide ($LiMnO_2$)	12162-79-7	93,88	1 – 50
3	Lithium nickel dioxide ($LiNiO_2$)	12031-65-1 536375 028-057-00-7 (Index No.)	97,63	1 – 50
4	Poly (vinylidene fluoride) (PVDF) (C2H2F2)x-)	24937-79-9	64,03	2,5 – 7
5	Lithium hexafluorophosphate ($LiPF_6$)	21324-40-3 132948 244-334-7	151,91	1 – 4
6	Carbon black (C)	7782-42-5 92330 231-955-3	12,01	30 – 50

Information on toxicological effects can be found in section 11.



For the full text of the H-Statements mentioned in this Section, see Section 16.

4. First aid measures

4.1. Description of first aid measures

4.1.1. General information

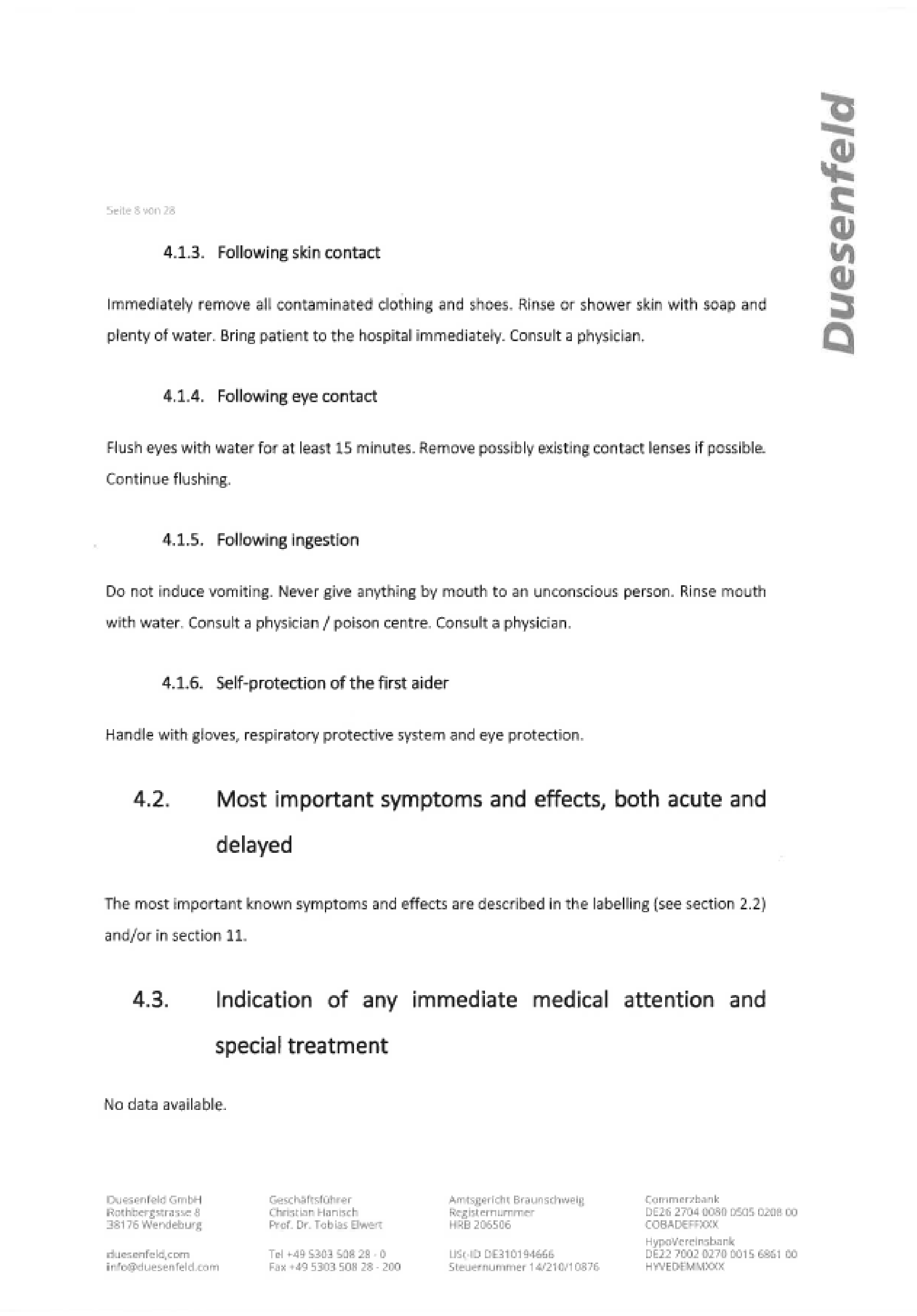
When the mixture is heated above 50 ° C. and when stored in a warm and/or moist atmosphere, the conductive salt $LiPF_6$ may decompose to hydrogen fluoride due to the presence of hydrogen / atmospheric moisture. When the mixture is burned or when heated above 400 ° C, the binder PVDF may decompose to hydrogen fluoride. Hydrogen fluoride forms hydrofluoric acid when dissolved in water.

Hydrofluoric (HF) acid burns require immediate and specialized first aid. Within 24 hours depending on the concentration of HF symptoms can show. After decontamination with water penetration/absorption of the fluoride ion can cause further damage. Treatment should be directed to exposure and binding of fluoride ion. Skin exposures can be treated with a 2.5% calcium gluconate gel exposures may require subcutaneous calcium gluconate until stinging stops. Heavy exposures of skin may make subcutaneous calciumgluconate necessary. This applies to all exposures apart from exposure to fingers, due to the potential for tissue injury from increased pressure and should be considered when undergoing decontamination. If swallowed the absorption of the fluoride ion can be prevented by giving milk, chewable calcium carbonate tablets or milk of magnesia when the patient is conscious. Conditions like hypocalcemia, hypomagnesemia and cardiac arrhythmias should be monitored.

Consult a physician. Show this safety data sheet to the doctor in attendance.

4.1.2. Following inhalation

If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.



4.1.3. Following skin contact

Immediately remove all contaminated clothing and shoes. Rinse or shower skin with soap and plenty of water. Bring patient to the hospital immediately. Consult a physician.

4.1.4. Following eye contact

Flush eyes with water for at least 15 minutes. Remove possibly existing contact lenses if possible. Continue flushing.

4.1.5. Following ingestion

Do not induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician / poison centre. Consult a physician.

4.1.6. Self-protection of the first aider

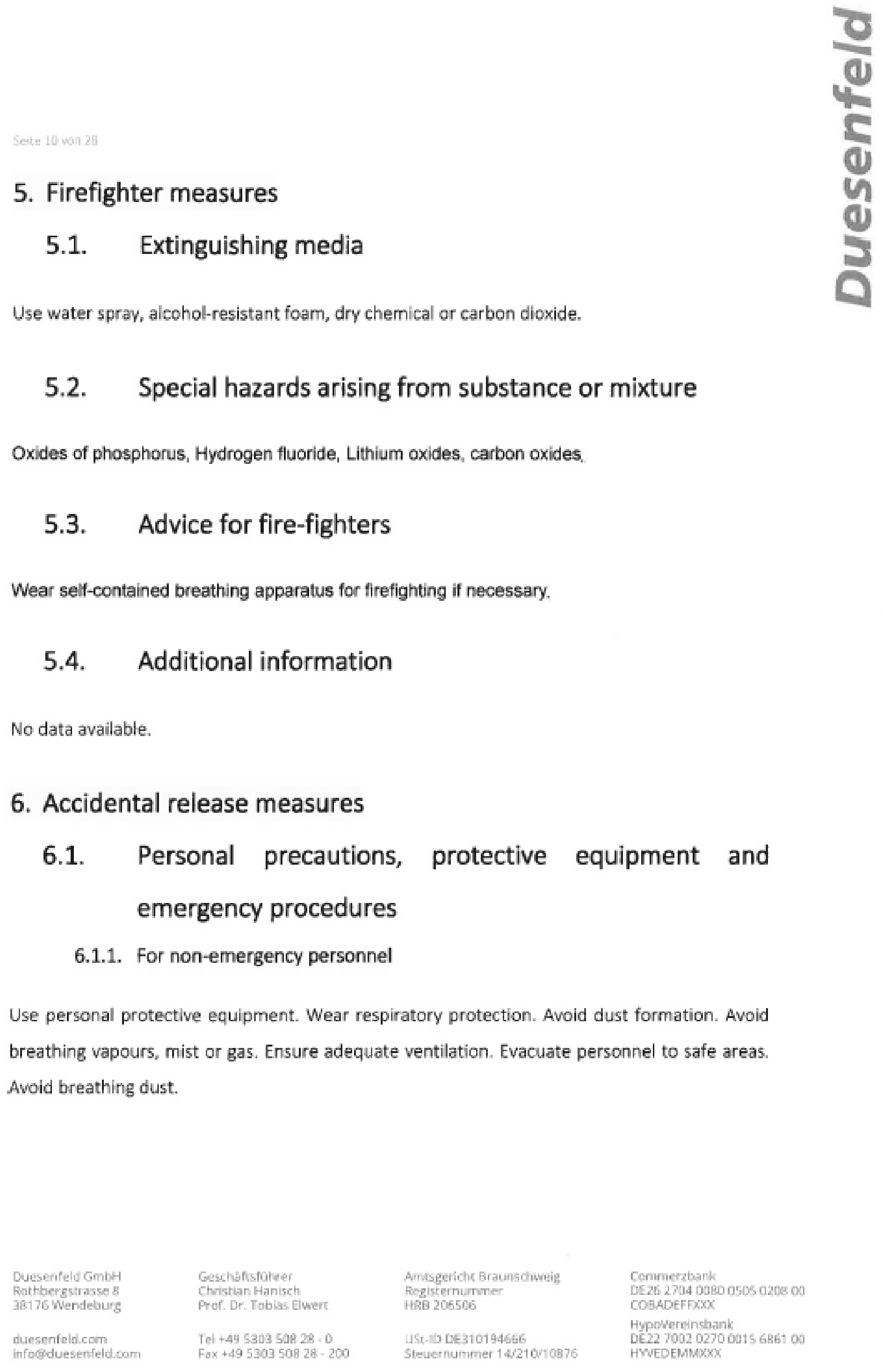
Handle with gloves, respiratory protective system and eye protection.

4.2. Most important symptoms and effects, both acute and delayed

The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11.

4.3. Indication of any immediate medical attention and special treatment

No data available.



5. Firefighter measures

5.1. Extinguishing media

Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

5.2. Special hazards arising from substance or mixture

Oxides of phosphorus, Hydrogen fluoride, Lithium oxides, carbon oxides.

5.3. Advice for fire-fighters

Wear self-contained breathing apparatus for firefighting if necessary.

5.4. Additional information

No data available.

6. Accidental release measures

6.1. Personal precautions, protective equipment and emergency procedures

6.1.1. For non-emergency personnel

Use personal protective equipment. Wear respiratory protection. Avoid dust formation. Avoid breathing vapours, mist or gas. Ensure adequate ventilation. Evacuate personnel to safe areas. Avoid breathing dust.

6.1.2. For emergency responders

For personal protection see section 8.

6.2. Environmental precautions

Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

6.3. Methods and material for containment and cleaning up

Pick up and arrange disposal without creating dust. Sweep up and shovel. Keep in suitable, closed containers for disposal. Do not use water for removal (Danger of the formation of HF).

Small amounts (up to 0,5 kg): Use ethanol and a paper towel to remove the mass.

Big amounts (more than 0,5 kg): Use industrial vacuum cleaner with with appropriate filters (e.g. H14) if applicable, otherwise sweep up and shovel the mass into a closed container for disposal.

6.4. Reference to other sections

Protective measures: see section 7 and 8

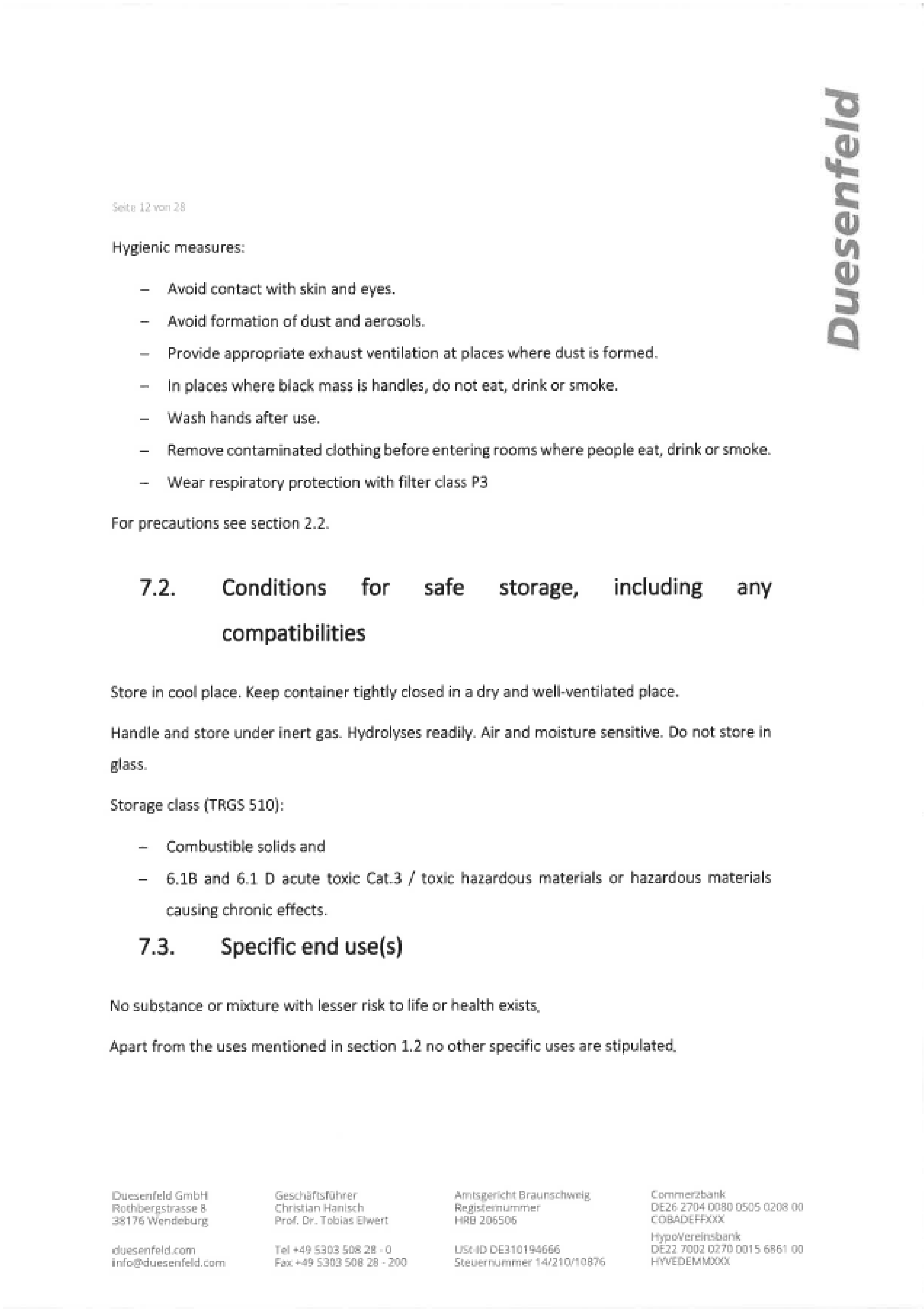
Disposal: see section 13

7. Handling and storage

7.1. Precautions for safe handling

Do not leave containers with black mass stand open.

Get instructions before use.



Hygienic measures:

- Avoid contact with skin and eyes.
- Avoid formation of dust and aerosols.
- Provide appropriate exhaust ventilation at places where dust is formed.
- In places where black mass is handles, do not eat, drink or smoke.
- Wash hands after use.
- Remove contaminated clothing before entering rooms where people eat, drink or smoke.
- Wear respiratory protection with filter class P3

For precautions see section 2.2.

7.2. Conditions for safe storage, including any compatibilities

Store in cool place. Keep container tightly closed in a dry and well-ventilated place.

Handle and store under inert gas. Hydrolyses readily. Air and moisture sensitive. Do not store in glass.

Storage class (TRGS 510):

- Combustible solids and
- 6.1B and 6.1 D acute toxic Cat.3 / toxic hazardous materials or hazardous materials causing chronic effects.

7.3. Specific end use(s)

No substance or mixture with lesser risk to life or health exists.

Apart from the uses mentioned in section 1.2 no other specific uses are stipulated.

8. Exposure controls / personal protection

8.1. Control parameters

Components with workplace control parameters.

Lithium nickel dioxide and lithium manganese dioxide:

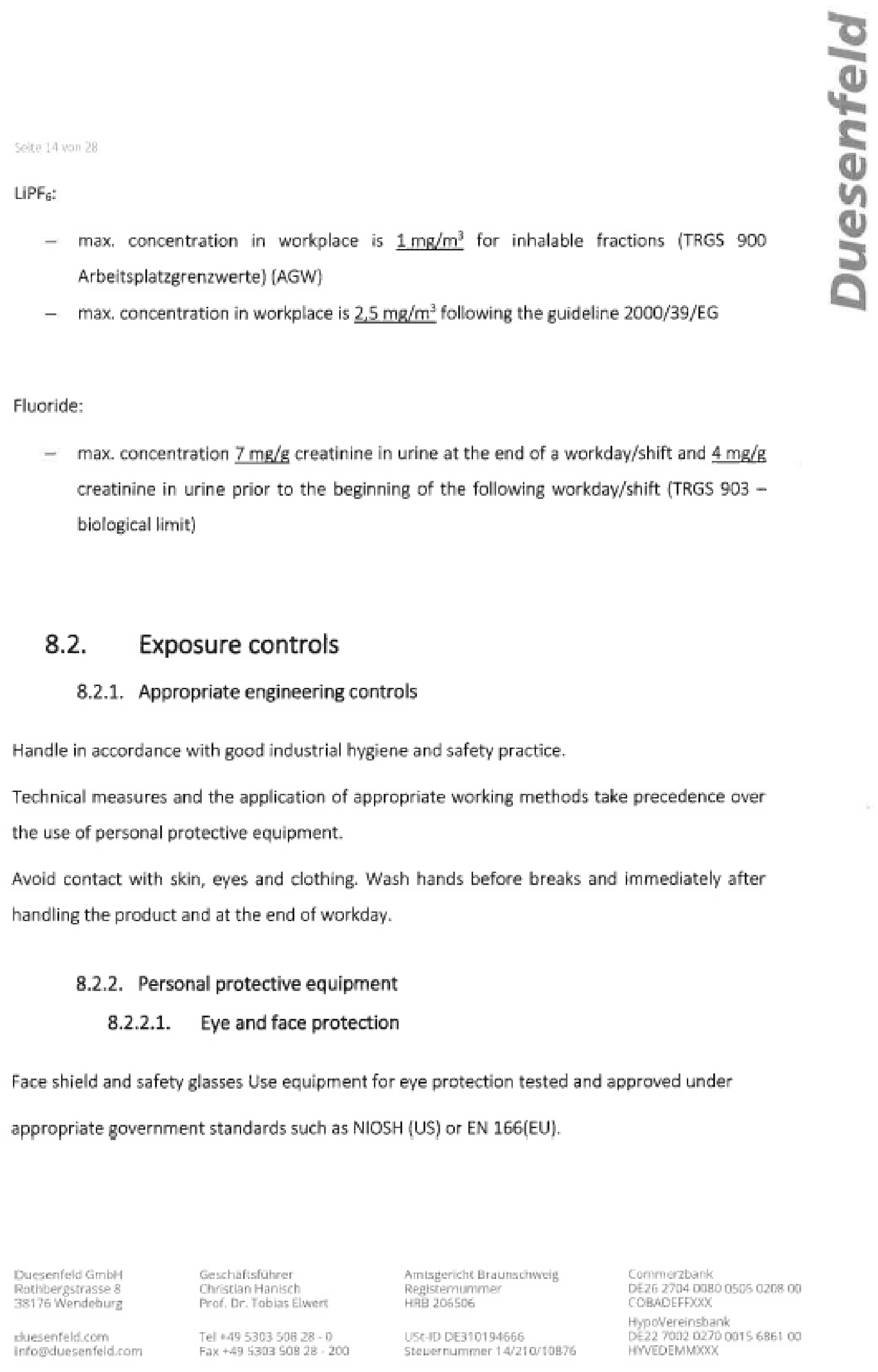
- max. concentration in workplace is 0,2 mg/m3 for inhalable fractions (TRGS 900 Arbeitsplatzgrenzwerte) (AGW). Foetal damage is not to be expected when respecting the limits for workplace exposure.

Lithium manganese dioxide:

- max. concentration in workplace is 0,02 mg/m^3 for alveolar fractions (TRGS 900 Arbeitsplatzgrenzwerte) (AGW). Foetal damage is not to be expected when respecting the limits for workplace exposure.
- max. concentration in workplace is 0,2 mg/m3 for inhalable fractions (TWA). Richtlinie (EU) 2017/164 der Kommission zur Festlegung einer vierten Liste von Arbeitsplatz-Richtgrenzwerten in Durchführung der Richtlinie 98/24/EG des Rates und zur Änderung der Richtlinien 91/322/EWG, 2000/39/EG und 2009/161/EU der Kommission)
- max. concentration in workplace is 0,05 mg/m3 for alveolar fractions (TWA). Richtlinie (EU) 2017/164 der Kommission zur Festlegung einer vierten Liste von Arbeitsplatz-Richtgrenzwerten in Durchführung der Richtlinie 98/24/EG des Rates und zur Änderung der Richtlinien 91/322/EWG, 2000/39/EG und 2009/161/EU der Kommission)

Graphite:

- average value for maximal dust concentration is 1,25 mg/m^3 (TRGS 900 – Arbeitsplatzgrenzwerte)



LiPF$_6$:

- max. concentration in workplace is 1 mg/m^3 for inhalable fractions (TRGS 900 Arbeitsplatzgrenzwerte) (AGW)
- max. concentration in workplace is 2,5 mg/m^3 following the guideline 2000/39/EG

Fluoride:

- max. concentration 7 mg/g creatinine in urine at the end of a workday/shift and 4 mg/g creatinine in urine prior to the beginning of the following workday/shift (TRGS 903 – biological limit)

8.2. Exposure controls

8.2.1. Appropriate engineering controls

Handle in accordance with good industrial hygiene and safety practice.

Technical measures and the application of appropriate working methods take precedence over the use of personal protective equipment.

Avoid contact with skin, eyes and clothing. Wash hands before breaks and immediately after handling the product and at the end of workday.

8.2.2. Personal protective equipment

8.2.2.1. Eye and face protection

Face shield and safety glasses Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

8.2.2.2. Skin protection

Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices.

Wash and dry hands.

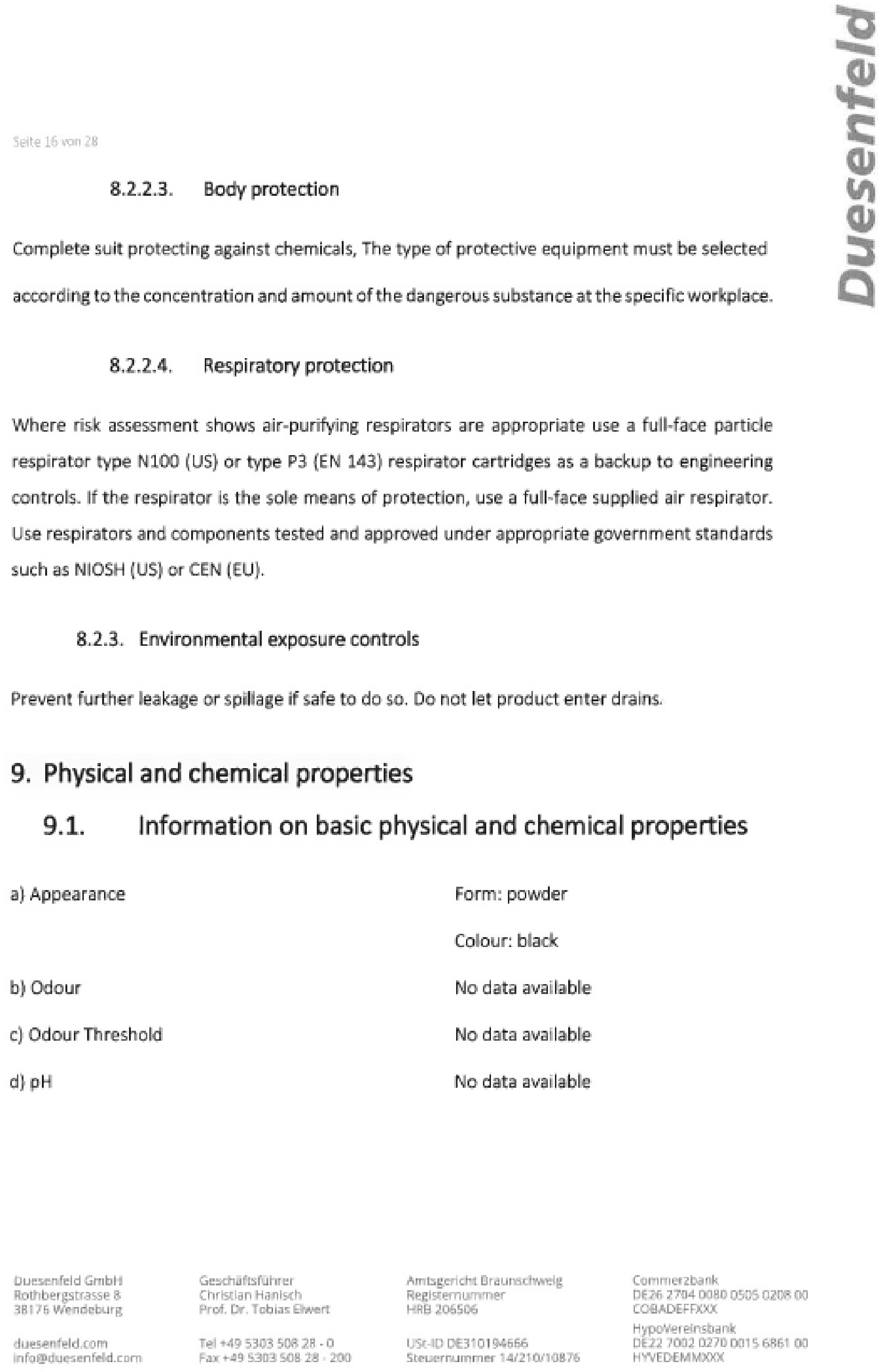
The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and the standard EN 374 derived from it.

Full contact
Material: Nitrile rubber
Minimum layer thickness: 0,11 mm
Break through time: 480 min
Material tested:Dermatril® (KCL 740 / Aldrich Z677272, Size M)

Splash contact
Material: Nitrile rubber
Minimum layer thickness: 0,11 mm
Break through time: 480 min
Material tested:Dermatril® (KCL 740 / Aldrich Z677272, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)6659 87300, e-mail sales@kcl.de, test method: EN374

If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the CE approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist and safety officer familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.



8.2.2.3. Body protection

Complete suit protecting against chemicals, The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

8.2.2.4. Respiratory protection

Where risk assessment shows air-purifying respirators are appropriate use a full-face particle respirator type N100 (US) or type P3 (EN 143) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

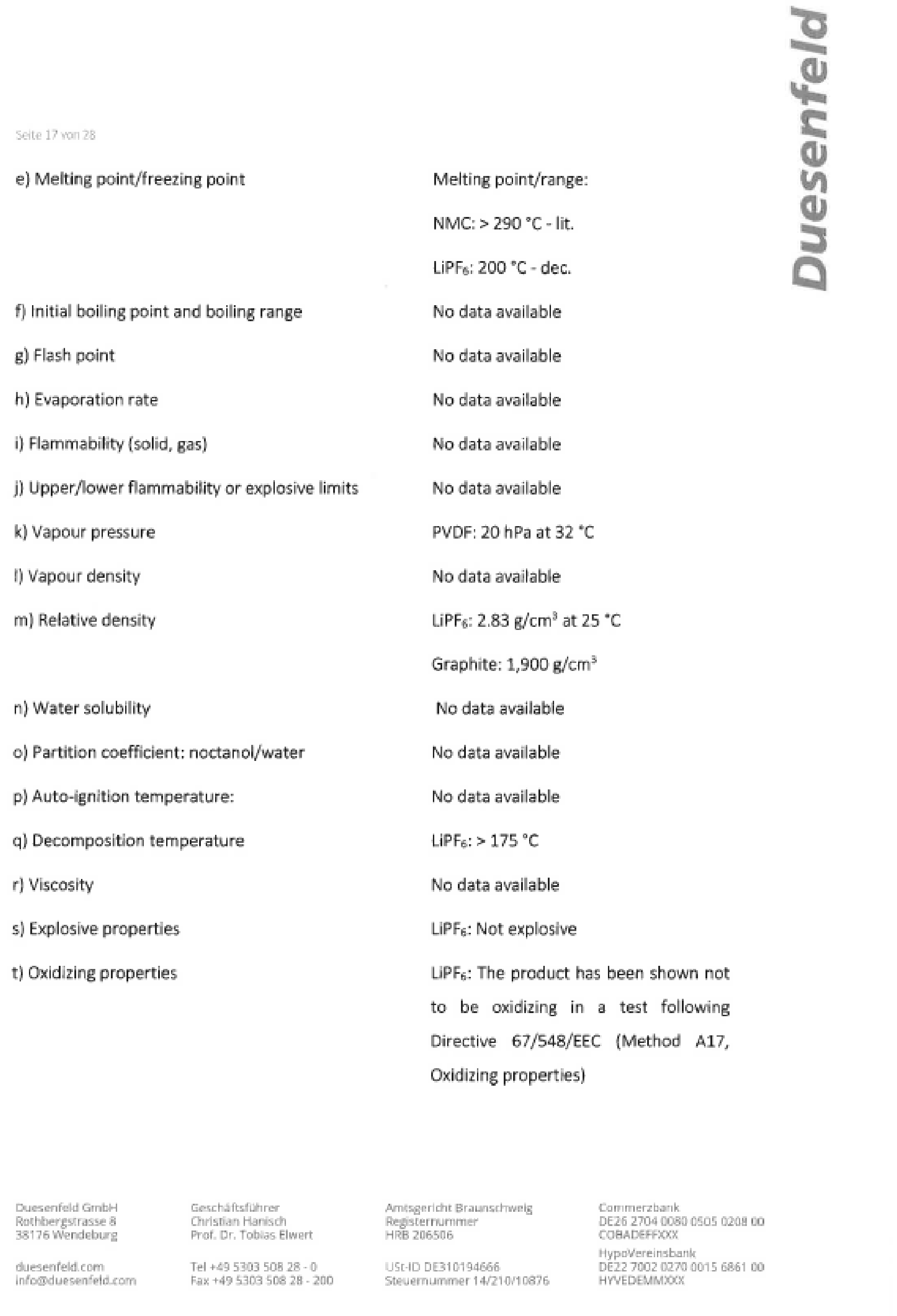
8.2.3. Environmental exposure controls

Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

9. Physical and chemical properties

9.1. Information on basic physical and chemical properties

a) Appearance	Form: powder
	Colour: black
b) Odour	No data available
c) Odour Threshold	No data available
d) pH	No data available



e) Melting point/freezing point	Melting point/range: NMC: > 290 °C - lit. $LiPF_6$: 200 °C - dec.
f) Initial boiling point and boiling range	No data available
g) Flash point	No data available
h) Evaporation rate	No data available
i) Flammability (solid, gas)	No data available
j) Upper/lower flammability or explosive limits	No data available
k) Vapour pressure	PVDF: 20 hPa at 32 °C
l) Vapour density	No data available
m) Relative density	$LiPF_6$: 2.83 g/cm^3 at 25 °C Graphite: 1,900 g/cm^3
n) Water solubility	No data available
o) Partition coefficient: noctanol/water	No data available
p) Auto-ignition temperature:	No data available
q) Decomposition temperature	$LiPF_6$: > 175 °C
r) Viscosity	No data available
s) Explosive properties	$LiPF_6$: Not explosive
t) Oxidizing properties	$LiPF_6$: The product has been shown not to be oxidizing in a test following Directive 67/548/EEC (Method A17, Oxidizing properties)

9.2. Other information

Substance has a corrosive effect on metals.

10. Stability and reactivity

10.1. Reactivity

No data available

10.2. Chemical stability

Stable under recommended storage conditions.

10.3. Possibility of hazardous reactions

No data available

10.4. Conditions to avoid

Exposure to moisture

Reacts dangerously with glass.

10.5. Incompatible materials

Strong oxidizing agents, Strong acid for glass. Metal container for storage.

10.6. Hazardous decomposition products

Hazardous decomposition products formed under fire conditions. - Nickel/nickel oxides, Lithium oxides, Cobalt/cobalt oxides, Manganese/manganese oxides, Oxides of phosphorous, Hydrogen fluoride

Other decomposition products - No data available

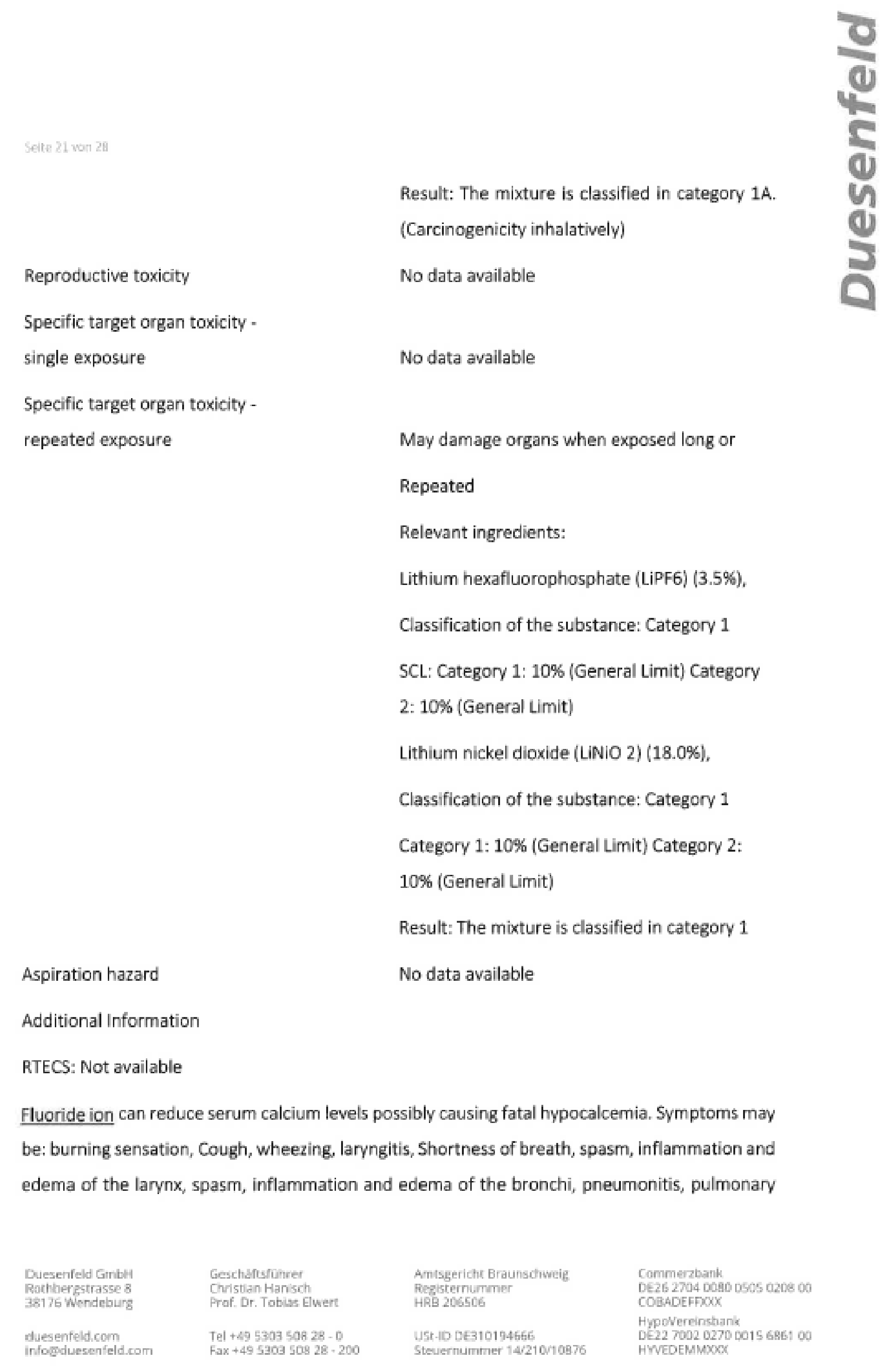
In the event of fire: see section 5

11. Toxicological information

11.1. Information on toxicological effects

Acute toxicity	Ingredients that may contribute to acute oral toxicity: Lithium hexafluorophosphate (LiPF6) (3.5%), LD 50 (oral): ATE 100 mg / kg Calculated estimated acute oral toxicity ATE (mix): 2857 mg / kg
Skin corrosion/irritation	Relevant ingredients: Lithium hexafluorophosphate (LiPF6) (3.5%) additive, Classification of the substance: Category 1C SCL: Category 1C: 5% (General Limit) Category 2: 10% (General Limit) Result: The mixture is classified in category 2.
Serious eye damage/eye irritation	No data available

Respiratory or skin sensitisation/	LiPF$_6$: in vivo assay - Mouse(Lithium hexafluorophosphate) Result: Does not cause skin sensitisation. (OECD Test Guideline 429) Relevant ingredients: Lithium cobalt (III) oxide (LiCoO 2) (18.0%), Classification of the substance: Category 1B SCL: Category 1B: 1% (General Limit) Lithium nickel dioxide (LiNiO 2) (18.0%), Classification of the substance: Category 1 Category 1: 1% (General Limit) Result: The mixture is classified in category 1.
Germ cell mutagenicity	LiPF$_6$: Ames test(Lithium hexafluorophosphate) S. typhimurium Result: negative No data available for rest
Carcinogenicity	Lithium cobalt (III) oxide (LiCoO 2) (18.0%), Classification of the substance: category 2 SCL: Category 2: 1% (General Limit) Lithium nickel dioxide (LiNiO 2) (18.0%), Classification of the substance: Category 1A Category 1A: 0.1% (General Limit) Result: The mixture is classified in category 2. (Carcinogenicity)



	Result: The mixture is classified in category 1A. (Carcinogenicity inhalatively)
Reproductive toxicity	No data available
Specific target organ toxicity - single exposure	No data available
Specific target organ toxicity - repeated exposure	May damage organs when exposed long or Repeated Relevant ingredients: Lithium hexafluorophosphate ($LiPF_6$) (3.5%), Classification of the substance: Category 1 SCL: Category 1: 10% (General Limit) Category 2: 10% (General Limit) Lithium nickel dioxide ($LiNiO_2$) (18.0%), Classification of the substance: Category 1 Category 1: 10% (General Limit) Category 2: 10% (General Limit) Result: The mixture is classified in category 1
Aspiration hazard	No data available

Additional Information

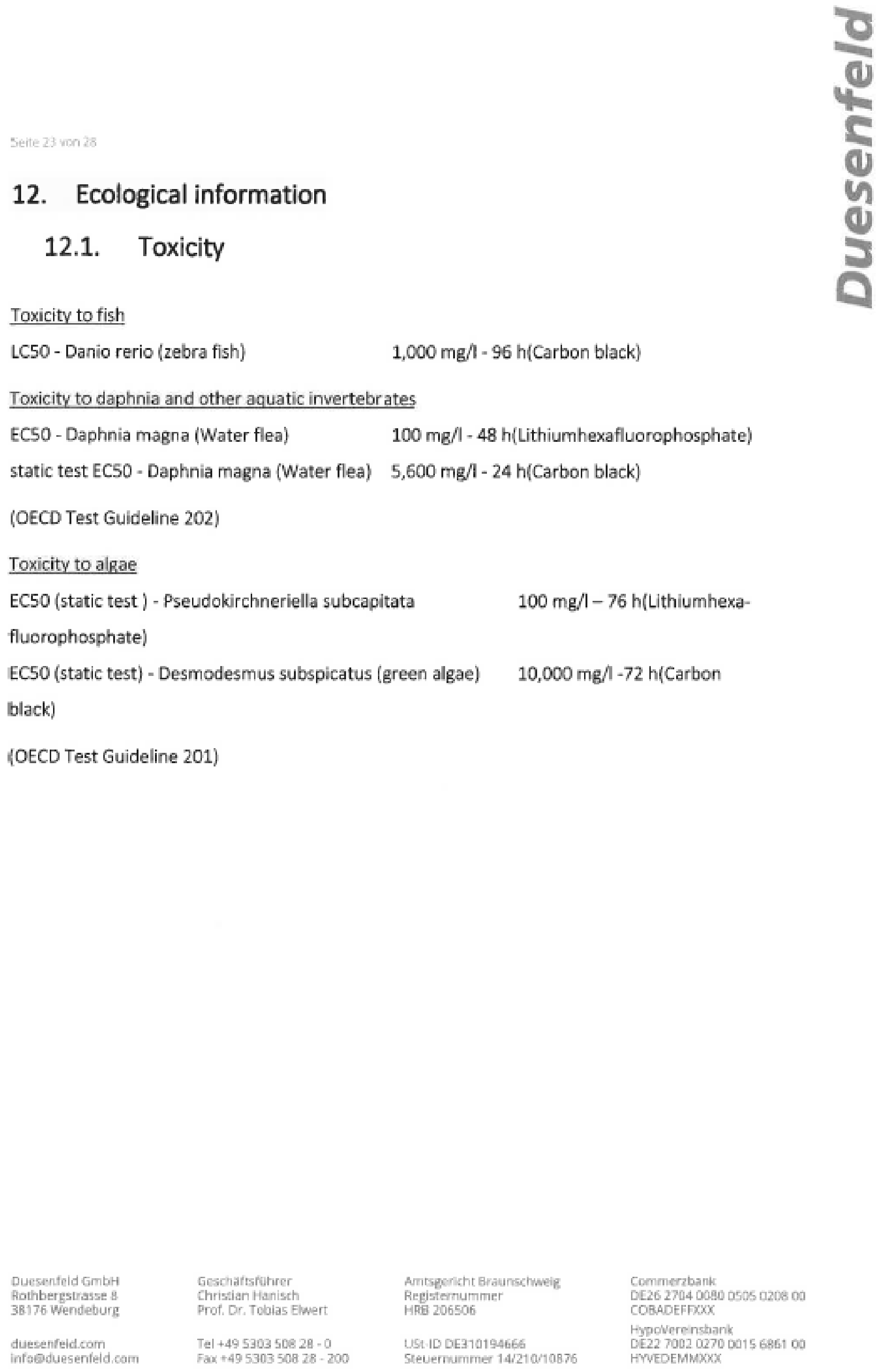
RTECS: Not available

Fluoride ion can reduce serum calcium levels possibly causing fatal hypocalcemia. Symptoms may be: burning sensation, Cough, wheezing, laryngitis, Shortness of breath, spasm, inflammation and edema of the larynx, spasm, inflammation and edema of the bronchi, pneumonitis, pulmonary edema. Material is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes, and skin. To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.(Lithium hexafluorophosphate)

Large doses of lithium ion have caused dizziness and prostration, and can cause kidney damage if sodium intake is limited. Dehydration, weight loss, dermatological effects, and thyroid disturbances have been reported. Central nervous system effects that include slurred speech, blurred vision, sensory loss, ataxia, and convulsions may occur. Diarrhea, vomiting, and neuromuscular effects such as tremor, clonus, and hyperactive reflexes may occur as a result of repeated exposure to lithium ion.

Similar effects to Lithiumcarbonate: Some evidence of adverse effects on sexual function and fertility, and/or on development, based on animal experiments. Lithium and its compounds are possible teratogens by analogy to lithium ca positive animal teratogenic data.(Lithium carbonate) Effects on or via lactation(Lithium carbonate) Overexposure may cause reproductive disorder(s) based on tests with laboratory animals.(Lithiumcarbonate).

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated., Men exposed to manganese dusts showed a decrease in fertility. Chronic manganese poisoning primarily involves the central nervous system. Early symptoms include languor, sleepiness and weakness in the legs. A stolid mask-like appearance of the face, emotional disturbances such as uncontrollable laughter and a spastic gait with tendency to fall in walking are findings in more advanced cases. High incidence of pneumonia has been found in workers exposed to the dust or fume of some manganese compounds., Large doses of lithium ion have caused dizziness and prostration, and can cause kidney damage if sodium intake is limited. Dehydration, weight loss, dermatological effects, and thyroid disturbances have been reported. Central nervous system effects that include slurred speech, blurred vision, sensory loss, ataxia, and convulsions may occur. Diarrhea, vomiting, and neuromuscular effects such as tremor, clonus, and hyperactive reflexes may occur as a result of repeated exposure to lithium ion.



12. Ecological information

12.1. Toxicity

Toxicity to fish

LC50 - Danio rerio (zebra fish)	1,000 mg/l - 96 h(Carbon black)

Toxicity to daphnia and other aquatic invertebrates

EC50 - Daphnia magna (Water flea)	100 mg/l - 48 h(Lithiumhexafluorophosphate)
static test EC50 - Daphnia magna (Water flea)	5,600 mg/l - 24 h(Carbon black)

(OECD Test Guideline 202)

Toxicity to algae

EC50 (static test) - Pseudokirchneriella subcapitata	100 mg/l – 76 h(Lithiumhexafluorophosphate)
EC50 (static test) - Desmodesmus subspicatus (green algae)	10,000 mg/l -72 h(Carbon black)

(OECD Test Guideline 201)

Toxicity to bacteria

Respiration inhibition EC50 - Sludge Treatment 1,000 mg/l - 3 h(Lithiumhexafluorophosphate)

(OECD Test Guideline 209)

12.2. Persistence and degradability

No data available

12.3. Bioaccumulative potential

No data available

12.4. Mobility in soil

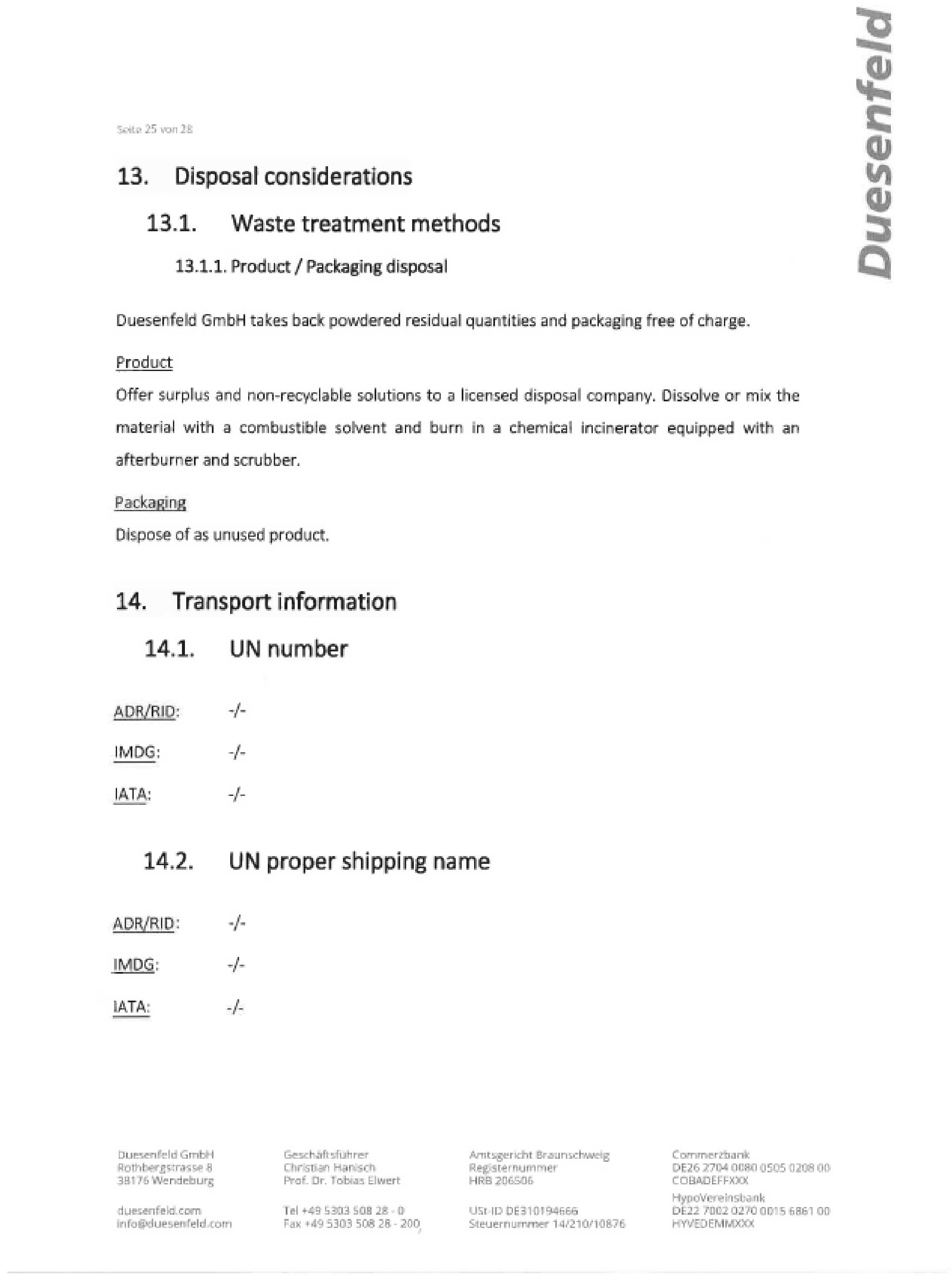
No data available

12.5. Results of PBT and vPvB assessment

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

12.6. Other adverse effects

No data available



13. Disposal considerations

13.1. Waste treatment methods

13.1.1. Product / Packaging disposal

Duesenfeld GmbH takes back powdered residual quantities and packaging free of charge.

Product

Offer surplus and non-recyclable solutions to a licensed disposal company. Dissolve or mix the material with a combustible solvent and burn in a chemical incinerator equipped with an afterburner and scrubber.

Packaging

Dispose of as unused product.

14. Transport information

14.1. UN number

ADR/RID: -/-

IMDG: -/-

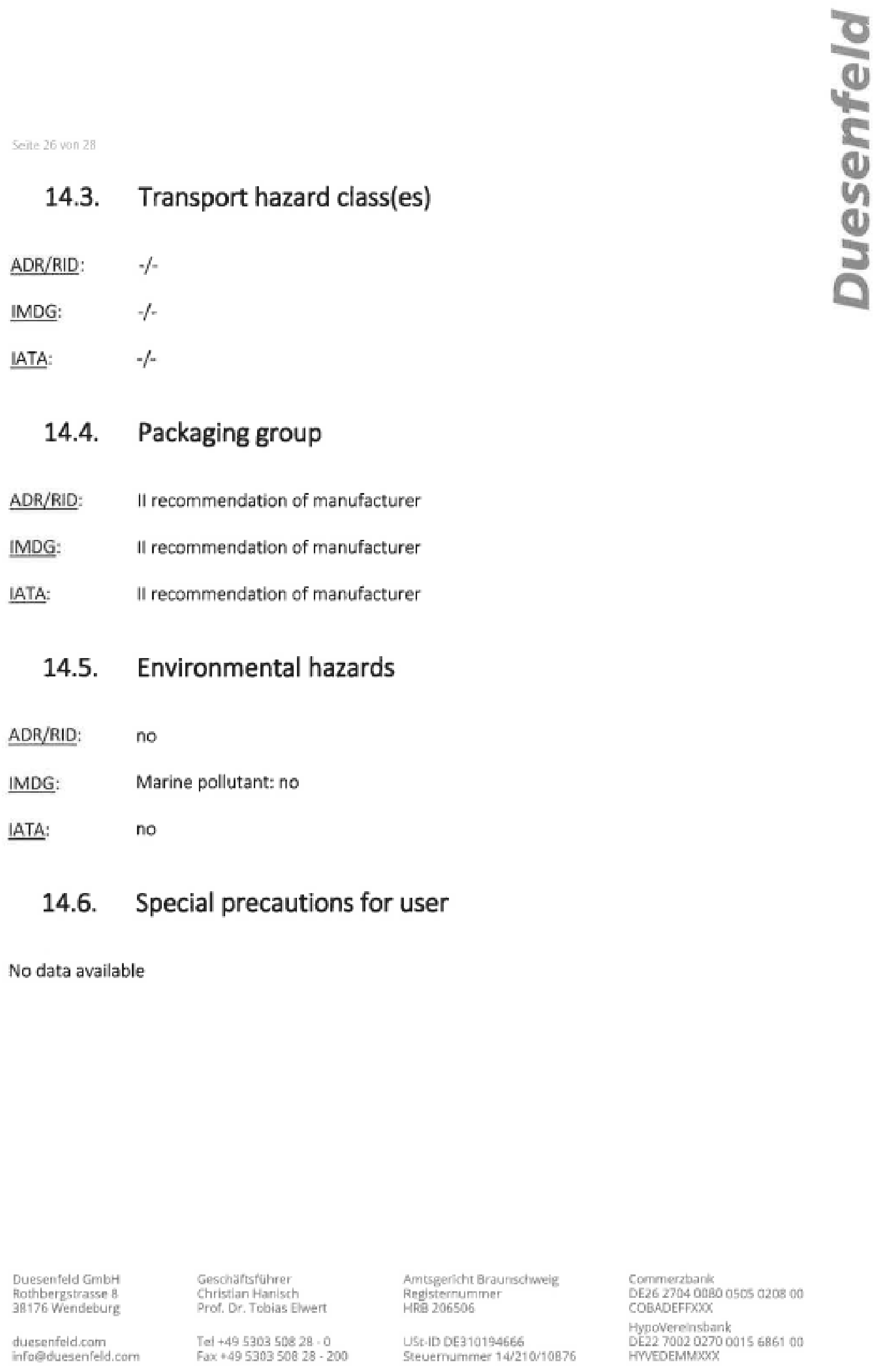
IATA: -/-

14.2. UN proper shipping name

ADR/RID: -/-

IMDG: -/-

IATA: -/-



14.3. Transport hazard class(es)

ADR/RID: -/-

IMDG: -/-

IATA: -/-

14.4. Packaging group

ADR/RID: II recommendation of manufacturer

IMDG: II recommendation of manufacturer

IATA: II recommendation of manufacturer

14.5. Environmental hazards

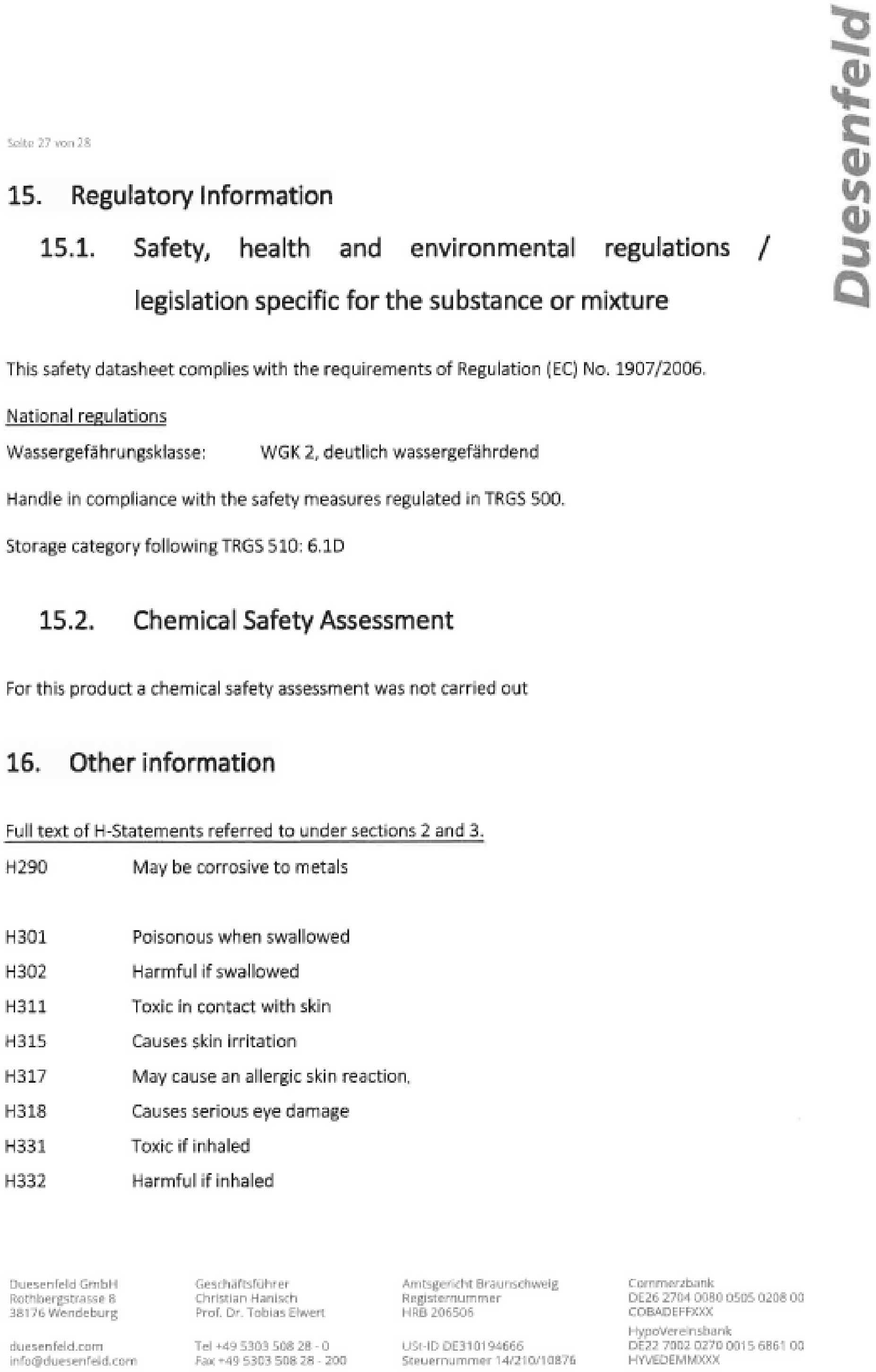
ADR/RID: no

IMDG: Marine pollutant: no

IATA: no

14.6. Special precautions for user

No data available



15. Regulatory Information

15.1. Safety, health and environmental regulations / legislation specific for the substance or mixture

This safety datasheet complies with the requirements of Regulation (EC) No. 1907/2006.

National regulations

Wassergefährungsklasse: WGK 2, deutlich wassergefährdend

Handle in compliance with the safety measures regulated in TRGS 500.

Storage category following TRGS 510: 6.1D

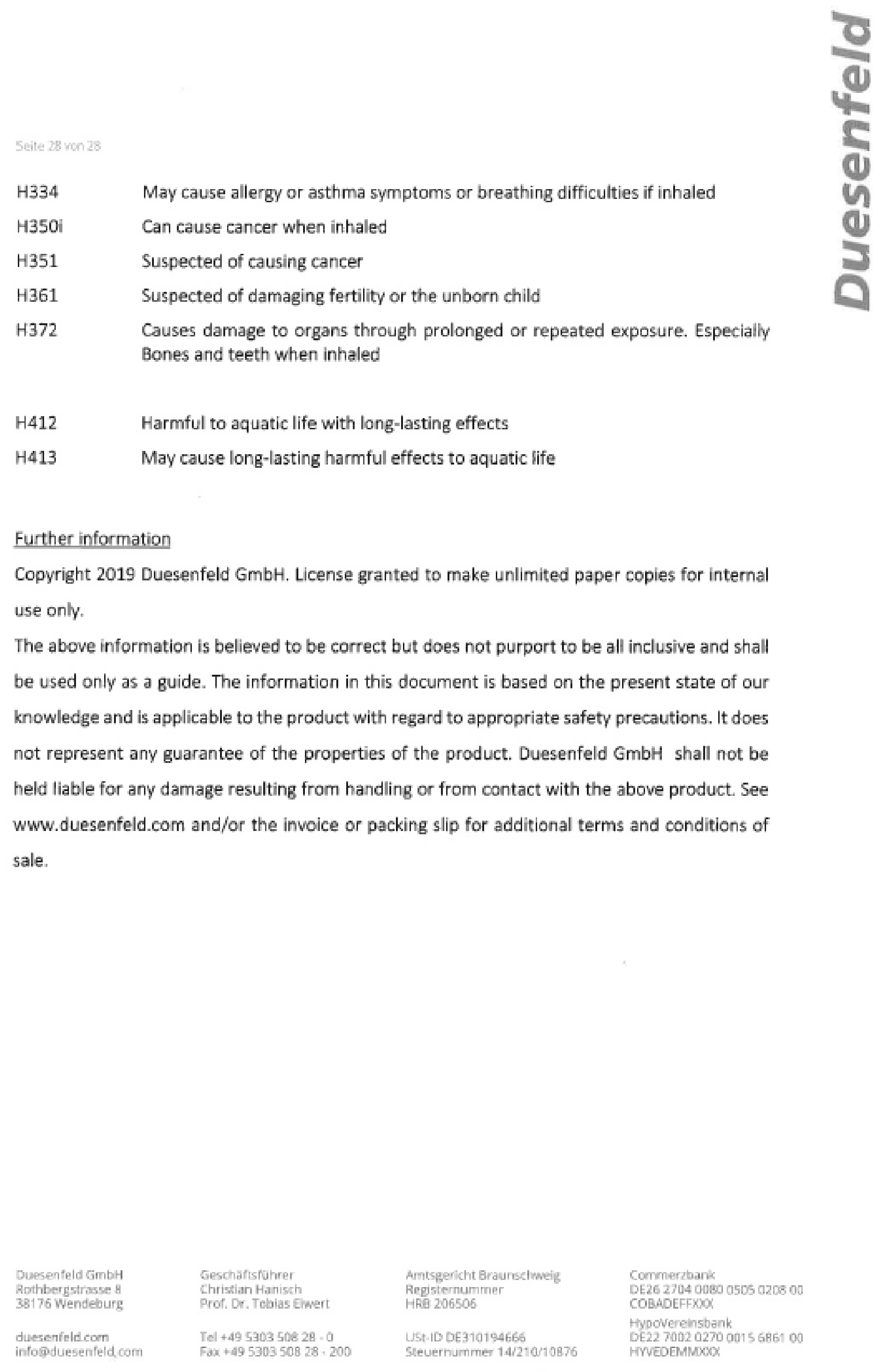
15.2. Chemical Safety Assessment

For this product a chemical safety assessment was not carried out

16. Other information

Full text of H-Statements referred to under sections 2 and 3.

H290	May be corrosive to metals
H301	Poisonous when swallowed
H302	Harmful if swallowed
H311	Toxic in contact with skin
H315	Causes skin irritation
H317	May cause an allergic skin reaction.
H318	Causes serious eye damage
H331	Toxic if inhaled
H332	Harmful if inhaled



H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled
H350i	Can cause cancer when inhaled
H351	Suspected of causing cancer
H361	Suspected of damaging fertility or the unborn child
H372	Causes damage to organs through prolonged or repeated exposure. Especially Bones and teeth when inhaled
H412	Harmful to aquatic life with long-lasting effects
H413	May cause long-lasting harmful effects to aquatic life

Further information

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Duesenfeld GmbH shall not be held liable for any damage resulting from handling or from contact with the above product. See www.duesenfeld.com and/or the invoice or packing slip for additional terms and conditions of sale.