Deliverable 5.1

Comparative Study on Existing LIB Recycling Technologies

Project acronym:	ECO2LIB
Project title:	Ecologically and Economically viable Production and Recycling of Lithium-Ion Batteries
Grant Agreement number:	875514
Coordinator:	Martin Krebs

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 875514.

Funding Scheme: **H2020-LC-BAT-2019-2020 / LC-BAT-2-2019**

Delivery Date from Annex I:	31/12/2020
Start date of the project:	January 1st 2020
Project duration:	48 months

Work package:	5
Lead beneficiary for this deliverable:	ACC
Authors:	Qiaoyan Pan, Reiner Sojka, Laura Billmann

Dissemination level		
PU	**Public**	**x**
CO	**Confidential, only for members of the consortium (including the Commission Services)**	
CI	**Classified**	

Executive Summary

This study provides a comprehensive review of Li-ion battery (LIB) recycling technologies. In the study, we outline and evaluate the current existing industrial LIB recycling processes globally as well as novel lab-scale initiatives.

We briefly introduce the LIB components and their possible reactions during battery handling, in order to substantiate the technical requirements for recycling plant specification and process management. Secondly, we give a brief introduction of LIB recycling technologies and an overview of current LIB recyclers in the world. Thirdly, we further introduce the industrial recyclers, giving more detailed information about the companies, their LIB recycling technologies, treatment capacity, etc. Afterwards, several representative examples of novel lab-scale LIB recycling technologies are described, in order to integrate the latest development. Finally, we evaluate and compare these recycling technologies comprehensively from technical, economic, and environmental performances points of view.

Main conclusions from the study can be drawn as follows:

1) The LIB materials and their reactions generate environmentally hazardous, human-toxic, highly corrosive substances (e.g. HF), as well as explosive gas mixtures, which must be considered to design a safe LIB recycling process.

2) After investigating current industrial available LIB recycling technologies, we can structure them into four different process steps, namely Preparation, Pretreatment (including thermal and mechanical Pretreatment), Pyrometallurgy and Hydrometallurgy, which can be combined in six different possible sequences. What they all have in common is that the material has to undergo the final necessary hydrometallurgical refining, to obtain tradeable products.

3) Currently only two of the combinations, both of which involve thermal Pretreatment and Pyrometallurgy, have proven their technical feasibility and industrial maturity. Economic evaluation shows that these two process routes exhibit overall advantages.

4) In contrast, those process routes without these two steps (e.g. mechanical Pretreatment + Hydrometallurgy) show technical-economic disadvantages, because, for example, the formed corrosive gases increase maintenance cost in Pretreatment step and the highly contaminated intermediate products require additional effort and cost for impurity removal in the final hydrometallurgical refining step, which indicates the reason why they have not been upscaled to mature industrial technologies yet.

5) Many novel lab-scale LIB recycling technologies are being developed in order to increase recycling rate and/or to lower the cost, including a so-called Direct Recycling Process, in which cathode or anode materials are separated, reconditioned and then directly re-used for manufacturing LIB, instead of undergoing pyro- and hydrometallurgy. However, the commercialization feasibility of those lab-scale technologies still needs to be proved. Considering unproved product quality, “Direct Recycling Process” and usage of separated AM for battery material precursor seem to be unrealistic.

List of abbreviations

AM	Active Mass (Powder)
DEC	Di Ethyl Carbonate
DMC	Di Methyl Carbonate
EC	Ethylene Carbonate
EMC	Ethyl Methyl Carbonate
EOL	End of Life
EV	Electric Vehicle
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
ISC	Internal Short Circuit
LCO	Lithium Cobalt Oxide, LiCoO2
LFP	Lithium Iron Phosphate, LiFePO4
LFL	Lower Flammability Limit
LIB	Li-ion Battery
LMO	Lithium Manganese Oxide, LiMn2O4
LTO	Lithium Titanium Oxide, Li4Ti5O12
NCA	Lithium Nickel Cobalt Aluminum oxide, LiNixCoyAlzO2
NMC	Lithium Nickel Manganese Cobalt Oxide, LiNixMnyCozO2
PC	Propylene Carbonate
SEI	Solid-Electrolyte Interphase
SME	Small and Medium-Sized Enterprises
UFL	Upper Flammability Limit

Table of contents

Executive Summary 2

1. Introduction 5

2. Li-ion batteries: structure, material properties and safety-related considerations 5
  - 2.1 Li-ion battery structure and material characteristics 5
  - 2.2 Malfunction and reactions of Li-ion batteries 9
    - 2.2.1 Thermal Runaway: mechanism, causes and influencing factors 9
    - 2.2.2 Toxic gas emissions from Li-ion battery 11

3. General overview of Li-ion recycling technologies and recyclers 14
  - 3.1 General overview of Li-ion recycling technologies 14
    - 3.1.1 Preparation 14
    - 3.1.2 Pretreatment 14
    - 3.1.3 Main treatment: pyrometallurgy (intermediate purification) 14
    - 3.1.4 Main treatment: hydrometallurgy 15
  - 3.2 General overview of current LIB recyclers in the world 17

4. Industrial-scale (>1000t/a) Li-ion battery recycling processors 19
  - 4.1 Processors within EU 19
    - 4.1.1 Umicore (Belgium) *[Pyro + Hydro]* 19
    - 4.1.2 Accurec (Germany) *[Thermal + Mechanical + Pyro + Hydro]* 21
    - 4.1.3 Nickelhütte Aue (Germany) *[Thermal + Pyro + Hydro]* 22
  - 4.2 Processors outside EU 23
    - 4.2.1 SungEel HiTech (South Korea) *[Mechanical + (Thermal +) Hydro]* 23
    - 4.2.2 Kyoei Seiko (Japan) *[Pyro]* 24
    - 4.2.3 Dowa (Japan) *[Thermal + Pyro + Hydro]* 25
    - 4.2.4 Brunp (China) *[Thermal + Mechanical + Hydro]* 25
    - 4.2.5 GEM (China) *[Mechanical + Hydro]* 26
    - 4.2.6 Huayou Cobalt (China) *[Mechanical + Hydro]* 27
    - 4.2.7 Ganzhou Highpower (China) *[Mechanical + Pyro + Hydro]* 27

5. Pilot-scale (<1000 t/a) Li-ion battery recycling processors 28
  - 5.1 Processors within EU 28
    - 5.1.1 SNAM (France) *[Thermal + Pyro + Hydro]* 28
    - 5.1.2 EDI (France) [*Mech (aqueous shred) + unknown]* 28
    - 5.1.3 AkkuSer (Finland) *[Mechanical + unknown]* 29
    - 5.1.4 Redux (Germany) *[Thermal + Mechanical + unknown]* 29
    - 5.1.5 Duesenfeld (Germany) *[Mechanical + Hydro]* 29
    - 5.1.6 Promesa (Germany) *[Mechanical (aqueous shred) + unknown]* 30
    - 5.1.7 TES-AMM (formerly: Recupyl) (France) *[Mechanical (inert gas)]* 30
  - 5.2 Processors outside EU 31
    - 5.2.1 Retriev (US) *[Mechanical (aqueous shred) + Hydro]* 31
    - 5.2.2 Kobar (Korea) *[Mechanical + Hydro]* 31
    - 5.2.3 JX Nippon (Japan) *[Thermal + Mechanical + Hydro]* 32
    - 5.2.4 Telerecycle (China) *[Mechanical + Hydro]* 33
    - 5.2.5 Guanghua (China) *[Mechanical + Hydro]* 34

6. Lab-scale novel Li-ion battery recycling technologies 35
  - 6.1 Mechanical separation and reconditioning for direct reuse (“Direct Recycling”) 35
  - 6.2 Liquid/Supercritical CO_2 for electrolyte extraction 36
  - 6.3 Froth flotation for separating active mass 37
  - 6.4 Electrohydraulic Fragmentation using shock waves 38
  - 6.5 Sulphate roasting of active mass for early stage lithium extraction 39

7. Evaluation of various Li-ion battery recycling processes 41

8. Summary 46

9. References 47

1. Introduction

In recent years, Lithium-ion batteries (LIBs) are undergoing unprecedented development, especially driven by the development of electric vehicles (EVs) and renewable energy technologies. Accordingly, it is foreseeable that the amount of spent lithium-ion batteries will also increase dramatically in the next few years. However, LIB materials are intrinsically environmentally hazardous (e.g. flammable components, hazardous decomposition products) and present a safety risks (e.g. Thermal-Runaway behavior), leading to a serious waste-management challenge. On the other hand, spent batteries also present an opportunity to gain valuable resources as they contain numerous valuable materials, e.g. lithium, nickel and the EU critical raw material Cobalt. Therefore, the recycling of Li-ion batteries has attracted great attention in view of conservation of valuable resources, environmental and ecological impacts.

2. Li-ion batteries: structure, material properties and safety-related considerations

The LIB components and their possible reactions during battery handling are introduced in this chapter, in order to substantiate the technical requirements for recycling plant specification and process management.

2.1 Li-ion battery structure and material characteristics

A lithium-ion battery (LIB) is an advanced type of rechargeable batteries. Inside the batteries, lithium ions move from the negative electrode through an electrolyte to the positive electrode during discharge, and back when charging. Today, the negative electrode of a commercial lithium-ion cell is usually made from graphite. The positive electrode is a lithium metal oxide, for example, $LiCoO_2$ (LCO), $LiNi_xMn_yCo_zO_2$ (NMC), $LiMn_2O_4$ (LMO) or $LiFePO_4$ (LFP), and the electrolyte is a lithium salt (e.g. $LiPF_6$) dissolved in organic solvents (e.g. PC, EC, DMC, DEC). Exemplary cell components and their mass fractions are demonstrated in **Table 1** [1].

Table 1: Exemplary commercial Li-ion battery cell composition[1].

Battery component	Materials	Mass-%
Housing	Steel or Al	20-25
Cathode (positive electrode)	LCO, NMC, NCA, LFP or LMO	25-35
Anode (negative electrode)	Graphite	14-19
Electrolyte	$LiPF_6$ dissolved in PC, EC, DMC or DEC	10-15
Cathode current collector foil	Aluminum	5-7
Anode current collector foil	Copper	5-9
Separator	PP, PE	1-4
Others (additives)	Carbon black, silicon, etc.	Balance

LIB can be constructed as cylindrical, prismatic or pouch cell for the whole range of applications. Exemplary cell constructions are shown in **Figure 1** [2] [3]. Most commercial, cylindrical lithium-ion cell design (18650) are equipped with a positive thermal coefficient (PTC) current limiting switch in the top cap, whose resistance will rise when large current runs through it, to protect the cell from external short circuits [4]. However, for prismatic and pouch cells there is no such short circuit protection device equipped in the cell. Therefore, for those cells, usually additional external devices such as electronic components need to be available for short circuit protection.

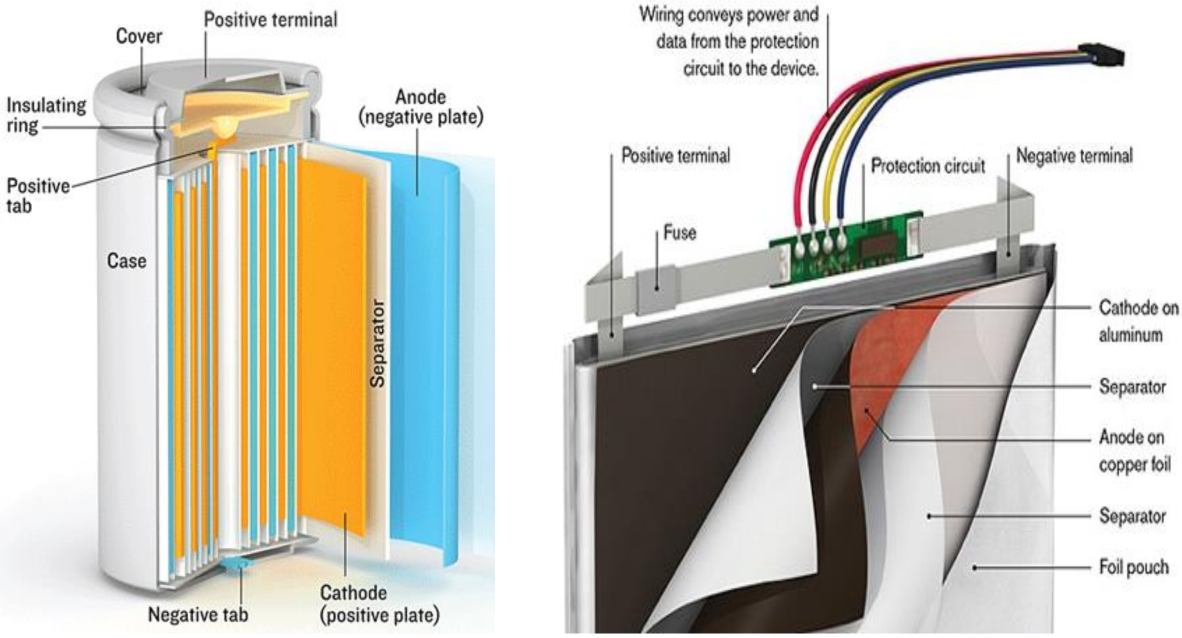

Figure 1: Constructional design of Li-ion cells (left: cylindrical, right: pouch) [2][3].

It is noted that the materials of LIB are more complex than that of previous battery systems (lead acid, NiCd, NiMH, Alkaline, etc.). For example, the electrochemical reactions of anode and cathode material are relatively simple in NiCd or lead batteries, and their water-based electrolyte makes them insensitive to thermal or mechanical abuse. Ingredients could therefore only have a chronic eco- or human-toxic effect. In contrast, LIB contains volatile, flammable organic electrolytes and fine solid particles (graphite and metal oxide), whose leakage or exposure is related to risks of fire and pollution. Environmentally related properties of materials used in commercial LIB are summarized in **Table 2** and flammability limits as well as flash points of LIB electrolytes are summarized in **Table 3**. As seen from the tables, the ingredients can pose various types of hazards, in particular

- Fire and explosion hazard due to high calorific, highly volatile and self-igniting carbonate electrolytes,
- Human toxic effects due to gaseous, sometimes lethal decomposition products (e.g. HF, benzene, etc.) from battery components,
- Carcinogenic effect through release of inhalable particles of Ni/Co/Mn compounds (<10 µm).

Those potential hazards should be considered in handling of waste Li-ion batteries. Additionally, under certain circumstances (e.g. overcharged, external/internal short-circuit, overheat, etc.), a so-called ‘‘thermal runaway’’ behavior can be triggered, releasing rapidly massive heat and toxic off-gases, bringing technical hazards and health risks. This will be discussed in more details in next sub-chapter.

Table 2: Environmentally related properties of materials used in commercial LIB [9].

Material	Properties
Ethylene carbonate (EC, $C_3H_4O_3$) 	• Vapor pressure: 21 Pa (20 °C). • Toxicity and hazard to water: ○ Causes serious eye irritation ○ slightly hazardous to water (German water hazard class: WGK 1[*])
Propylene carbonate (PC, $C_4H_6O_3$) 	• Vapor pressure: 4 Pa (20 °C), 130 Pa (50 °C). • Toxicity and hazard to water: ○ Causes serious eye irritation ○ slightly hazardous to water (German water hazard class: WGK 1)
Dimethyl carbonate (DMC, $C_3H_6O_3$) 	• highly flammable, highly volatile • Vapor pressure: 5300 Pa (20 °C). • Toxicity and hazard to water: ○ irritant effects, nausea, intoxication, unconsciousness, respiratory stop ○ slightly hazardous to water (German water hazard class: WGK 1)
Diethyl carbonate (DEC, $C_5H_{10}O_3$) 	• highly flammable, highly volatile • Vapor pressure: 1100 Pa (20 °C). • Toxicity and hazard to water: ○ low toxicity ○ slightly hazardous to water (German water hazard class: WGK 1)
Ethyl methyl carbonate (EMC, $C_4H_8O_3$) 	• highly flammable, highly volatile • Vapor pressure: 3600 Pa (25 °C). • Toxicity and hazard to water: ○ irritant ○ slightly hazardous to water (German water hazard class: WGK 1)

---

[*] About WGK: The foundation for the classification are scientific tests on the respective substance. […] How the data is to be collected is specified in Regulation (EG) No. 440/2008 on the definition of test methods (with corresponding regulations to amend them). If hazard statements according to Regulation (EC) No. 1272/2008 (CLP Regulation) have been derived for the respective substance from these scientific tests, these hazard statements are assigned corresponding assessment points. The more toxic a substance is, the more points are assigned.
The basic data set consists of the four hazard characteristics:
i. Acute oral or dermal mammalian toxicity
ii. Acute aquatic toxicity
iii. Biodegradability
iv. Bioaccumulation potential" Source https://www.umweltbundesamt.de/wgk-einstufung
There are 3 Classes of these classification system the higher the number the higher the thread to stretches of water and the inside living fauna and flora. For Further information please read Regulation 2000/60/EG, 2006/123/EG, 91/676/EWG.

Lithium hexafluorophosphate (LiPF6) 	• Toxicity and hazard to water: ○ causes severe skin burns and eye damage ○ highly hazardous to water (German water hazard class: WGK 3)
Lithium cobalt dioxide (LiCoO2) 	• At high temperatures, exothermic decomposition reaction with release of oxygen • Toxicity and hazard to water: ○ irritant, hazardous to health ○ Cobalt salts can lead to cardiomyopathy (heart muscle disease) ○ possibly carcinogenic
Lithium-nickel-manganese-cobalt oxide ($LiNi_xCo_yMn_zO_2$) 	• Toxicity and hazard to water: ○ toxic, Co, Ni in the compound ○ Hazard to water: no information
Lithium – Titanate ($Li_4Ti_5O_{12}$) 	• Toxicity and hazard to water: ○ slightly irritating to the respiratory tract ○ Nanocrystals can be toxic due to their small size

Table 3: Lower/Upper Flammability Limit (LFL/UFL) and flash point of Li-ion battery electrolytes.

Electrolyte	Name	Chemical formula	LFL, %vol (in air)	UFL, %vol (in air)	Flash point, °C
EC	Ethylene carbonate	$C_3H_4O_3$	3,6	16,1	143
DMC	Dimethyl carbonate	$C_3H_6O_3$	4,22	12,87	18
EMC	Ethyl methyl carbonate	$C_4H_8O_3$	2	N.A.	23
DEC	Diethyl carbonate	$C_5H_{10}O_3$	1,4	N.A.	33
PC	Propylene carbonate	$C_4H_6O_3$	1,7	21	123
EA	Ethyl acetate	$C_4H_8O_2$	2,2	9	-4
DE	Diethyl ether	$C_4H_{10}O$	2	36	-45
THF	Tetrahydrofuran	C_4H_8O	1,5	12	-17
AN	Acetonitrile	C_2H_3N	3	16	2
DME	Ethylen glycol dimethyl ether	$C_4H_{10}O_2$	1,6	10,4	5
DMSO	Dimethyl sulfoxide	C_2H_6OS	2,6	42	89
g-GBL	g-Butyrolactone	$C_4H_6O_2$	3,6	16	98

2.2 Malfunction and reactions of Li-ion batteries

In order to be able to assess the battery behavior and its effects in recycling activities, it is necessary to take a closer look at the malfunctioning and reactions of LIB. It is irrelevant whether the cell is mechanically or thermally damaged - reactions of the ingredients will occur. In the case of (partially) charged batteries, this happens mainly through the mechanism of a so-called *Thermal Runaway*, but also in discharged batteries relevant reactions take place. In addition, the ingredients inevitably react with the substances in the surrounding environment (e.g. $LiPF_6$ reacts with H_2O).

2.2.1 Thermal Runaway: mechanism, causes and influencing factors

An increasing number of fire incidents during using, storing, or treating LIB are reported and they are attributed to the self-ignition by Thermal Runaway (TR). The TR is self-reinforcing, continuous, exothermic chemical reactions that can be triggered by faults or damage in a LiB, leading to heating and final spontaneous ignition (as shown in **Figure 2** [5]).

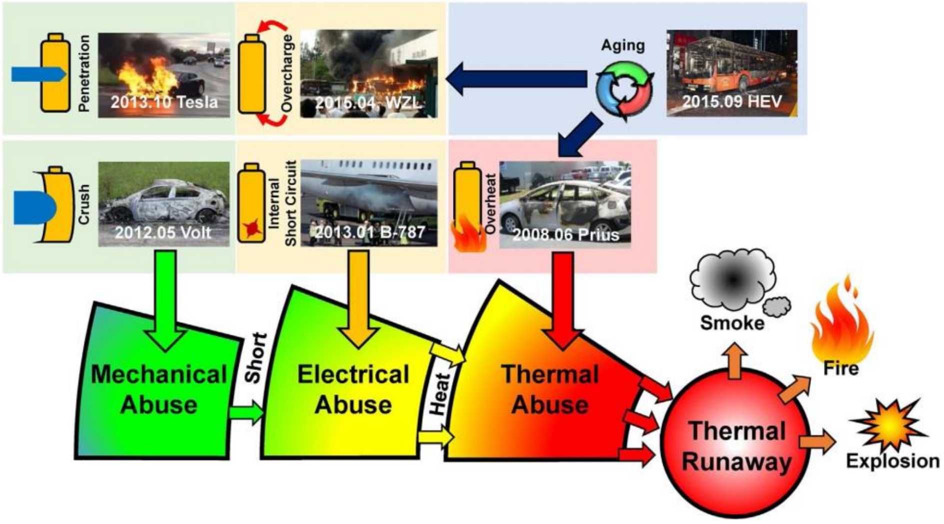

Figure 2: Accidents related with lithium-ion battery failure, and correlated abuse conditions [5].

Figure 3 shows an example of surface temperature development of a LIB (NCM) undergoing Thermal Runaway [6]. The development undergoes several stages, accompanying with numerous temperature-dependent reactions. Once the TR is triggered, the reactions proceed very quickly and cannot be interrupted from the outside and it ends within seconds with a complete destruction of the battery cell. Moreover, the TR of one cell can propagate to the surrounding cells or other materials, leading to “Chain Reaction” and thus escalate the fire. The features of TR are:

1) Reacts very fast (from start to peak, only ca.20 seconds)
2) Releasing massive heat
3) Releasing large volume of toxic gases

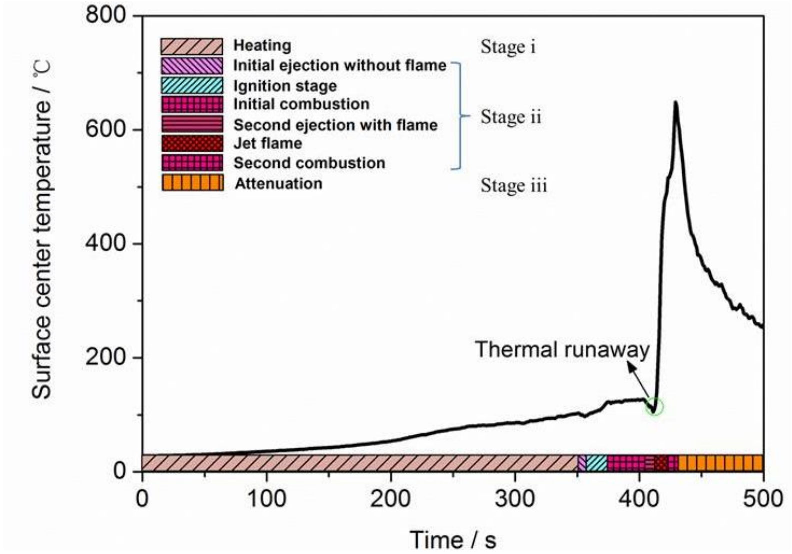

Figure 3: Example of surface temperature evolution at LIB Thermal Runaway [6].

The intrinsic heat source for Li-ion battery's thermal runaway is associated with electrical energy and chemical energy. The electrical energy can be evaluated by the battery rated capacity and the state of charge (SOC) of the battery, while the chemical energy is a material issue (related to decomposition / interaction of materials). In other words, the chemical energy mainly depends on the properties of the substances used in the battery.

A schematic diagram of energy release of Li-ion battery is shown in **Figure 4** [5]. Under various temperatures different reactions of materials occur. More details about the overall reactions can be found in paper [5] and [7]. It is worthy to pay special attention to the decomposition reaction of cathode material (under charged state), which releases O_2 gas and leads to more exothermic reactions (see exemplary reactions below [5]). On one hand, the generated O_2 can react with organic electrolytes (as combustion reaction), releasing massive heat [5]. On the other hand, it is reported in [8], the generated O_2 can also reacts with reductive anode material (LiC_x), contributing to even more heat generation.

$$Li_{0.5}CoO_2 \rightarrow 1/2\ LiCoO_2 + 1/6\ Co_3O_4 + 1/6\ O_2 \tag{1}$$
$$Li_{0.36}Ni_{0.8}Co_{0.15}Al_{0.05}O_2 \rightarrow 0.18\ Li_2O + 0.8\ NiO + 0.05\ Co_3O_4 + 0.025\ Al_2O_3 + 0.372\ O_2 \tag{2}$$
$$Li_{0.35}(NiCoMn)_{1/3}O_2 \rightarrow Li_{0.35}(NiCoMn)_{1/3}O_{2-y} + y/2\ O_2 \tag{3}$$
$$2.5\ O_2 + C_3H_4O_3(EC) \rightarrow 3\ CO_2 + 2\ H_2O \tag{4}$$

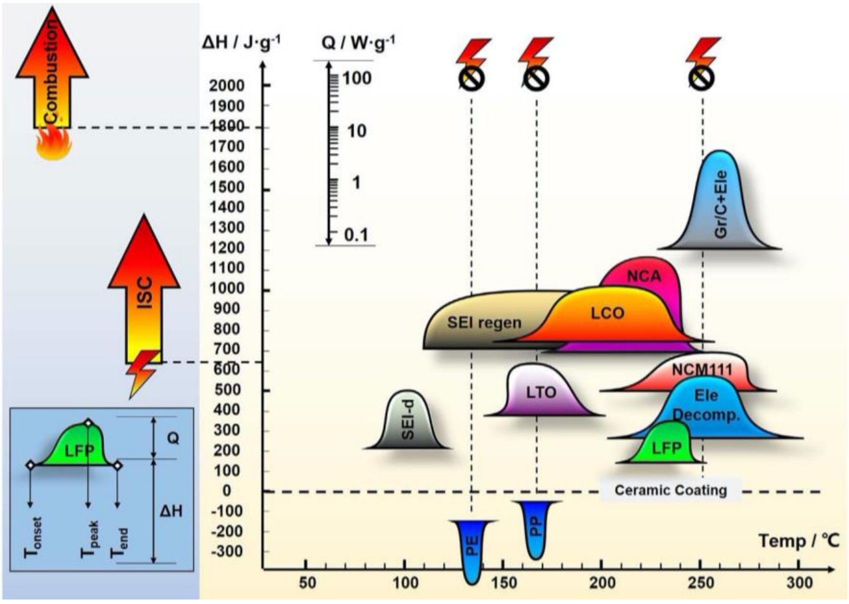

Figure 4: Schematic diagram of the energy release of lithium-ion battery [5].

The thermal runaway of the LIB cell can be attributed to different causes as follows [5][9]:

- External short circuit,
- Overcharge,
- Over-discharge,
- Internal short circuit (due to cell failure or abuses), is the most common feature for all abuse conditions,
- Overheating due to external heating,
- External mechanical damage to the cell (leading to internal short circuit).

The course (reaction kinetics) and the intensity (amount of energy, temperature level) of the TR depends on the following boundary conditions:

- State of Charge (SOC): Most violent at 100% SOC or >100% SOC (overcharge) due to max. electric Energy,
- Ambient temperature,
- Cell chemistry (LCA/LCO/NMC/LMO/LFP): LFP is less reactive,
- Construction of the cell (cell size, electrolyte volume etc.).

The spread of TR of one cell to neighboring cells in the sense of a chain reaction is dependent on the

- type of contact of cells and distance to the neighbouring cell,
- Type of insulation material used between the packed LIB (low thermal diffusivity α [m2/s] material is good for packaging and storage of LIB [10]),
- the type and extent of exposure to hot gases from pressure release or combustion gases after self-ignition.

2.2.2 Toxic gas emissions from Li-ion battery

As a result of the self-destruction of the battery cell, gas mixtures are formed whose composition depends on the battery subtype, state of charge and ambient atmosphere. **Table 4** summarizes the emitted gases from various LIB sub-chemistries, tested under various abuse conditions and various atmospheres [7]. It can be seen that under all different conditions, no matter thermally or mechanically treated, no matter in air or in inert gas (Ar, N_2), unneglectable number of toxic gases is generated. It is important to note that, toxic fluoride gases (e.g. HF and/or POF_3) are generated both in thermal treatment (namely, heating, fire, or combustion) and in mechanical treatment (penetration test) [7] [11]. As a consequence, adequate off-gas cleaning system is not only needed in thermal treatment, but also in mechanical treatment.

The fluoride gases mainly come from the decomposition reaction of electrolyte $LiPF_6$, which is promoted by the presence of water/humidity according to the following reactions [11]:

$$LiPF_6 \rightarrow LiF + PF_5 \quad (5)$$
$$PF_5 + H_2O \rightarrow POF_3 + 2HF \quad (6)$$
$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF \quad (7)$$

Table 4: Summary of emission gases from LIB (adopted from [7]).

References	Material		Test Condition		Off-gas							<u>Test equipment</u>
	Cathode	Type	Method	Atm.	Electrolyte	CO_2	CO	H_2	C_xH_y	HF	Other	
Campion et al. (2004)			Heating			✖				✖	Fluoride	GC-MS, NMR
Ohsaki et al. (2005)	LCO	633,048	Overcharge			✖	✖	✖	✖			GC
Abraham et al. (2006)	NCA	18650	Vent/ Penetration			✖	✖	✖	✖		C_2HF	GC-MS
Onuki et al. (2008)	NCA	Pouch	Heating	Ar		✖	✖	✖	✖			GC/AED
Ribière et al. (2012)	LMO	Pouch	Combustion	Air		✖	✖		✖	✖	HCN, NO_x, SO_x, HCl	FTIR, FDI, paramagnetic analyzer
Wang et al. (2012)	LCO	n. a.	TR			✖		✖	✖	✖	C_2H_5F	FTIR, GC-MS, NMR
Chanson (2013)	Li-ion	n. a.	TR			✖	✖	✖	✖	✖		n. a.
Ponchaut et al. (2014)	LCO	Pouch	TR	Ar		✖	✖	✖	✖			GC-MS
Larsson et al. (2014b)	LFP	Pouch	Propane fire	Air		✖				✖	POF_3	FTIR
	LCO	633, 048	Overcharge			✖	✖	✖				GC
Golubkov et al. (2015)	NMC, LFP	18650	Heating	Ar		✖	✖		✖			GC
Lecocq et al. (2016)	LFP	Pouch	Combustion	Air			✖	✖			SO_2	NDIR, FTIR, FID
Sun et al. (2016)	Li-ion	Both	Combustion	Air		✖	✖	✖	✖	✖	SO_2, COS, $C_xH_yN_z$, C_5H_9NO	GC-MS, IC
Kwade et al. (2016)	NCM	Pouch	Penetration	N2	✖	✖	✖		✖	✖		FTIR
	NCM	18650	Penetration	N2	✖	✖	✖		✖	✖		
	NCA	18650	Penetration	N2	✖	✖	✖		✖	✖		
Nedjalkow et al. (2016)	NMC	Pouch	Penetration	Air	✖	✖	✖		✖	✖	ClO_2, SO_2, Acrolein, COS	GC-MS, QMS, QEPAS, IC
Warner (2017)	n. a.		Heating	Air		✖			✖	✖	HCl, HCN, SO, H_2S	FTIR
Diaz et al. (2019) [7] & Bartosinski, et al (2017) [12]	LCO, NCM, LFP	18650 and pouch	Pyrolysis, combustion, penetration	Air or N2	✖		✖			✖	Accrolein (C_3H_4O), COF2, HCl	FTIR, IC

Those emitted gases are harmful not only to the equipment (due to corrosion effect) but also to humans if inhaled. The toxicological evaluation of most important resulting gases is demonstrated in **Table 5** in detail [13]. Special attention must be drawn to the danger of acid gases, especially HF. If inadequate measures are taken to clean/control the emitted gases during mechanical treatment of Li-ion batteries, these toxic gases could be inhaled by workers accidentally, causing serious damage or, in worst case, even fatal consequence.

Table 5: Toxicological evaluation of gases released from LIB [13].

Reaction product	Properties according to GHS
Benzene ($C6H6$) 	H225 H304 H315 H319 H340 H350 H372 H412 Single lethal dose of benzene for humans: 125 mg/kg (= 10 ml/70 kg)
Styrenics ($C8H8$) 	H226, H315, H319, H332, H372, H361d Ingestion: LC50, for rats: 5000 mg/kg, in mice: 316 mg/kg
Hydrofluoric acid (HF) 	H300, H310, H330, H314, H318 lethal dose: 20 mg/kg body weight. (A ton of LIB cells can release 1.0 - 6.6 kg HF, according to Accurec's off-gas measurement and calculation [12])
Hydrochloric acid (HCl) 	H300, H310, H330, H314, H318 30-min LC50, in rats: 4700 ppm, in mice: 2600 ppm
Carbon monoxide (CO) 	H220, H331, H372, H360d 30-min LC50, in humans: 3000 ppm

But not only the emission of gases can cause enormous problems. The energy release, for example, up to 22,000 MJ/t in the case of standard household LiB packs, is also often underestimated in process control and in the event of fire.

In conclusion, it can be said that in all parts of the reverse chain, i.e. the intermediate storage, collection and recycling process, significant material and environmental risks arise from spontaneous combustion, chain reactions and the possible release of eco- and human-toxic gases, regardless of the SOC of the battery. Therefore, great attention has to be paid considering safety and emission issues during storage and recycling of LIB.

3. General overview of Li-ion recycling technologies and recyclers

3.1 General overview of Li-ion recycling technologies

The processing of complex waste such as a Li-ion battery requires a multi-stage process chain. With the growing demands on the variety and quality of the output products, the number of treatment stages increases proportionally. Conversely, a simple, undifferentiated treatment (e.g. direct melting) would produce an equally undifferentiated, mixed product with a high number of elements at low level evaluation.

If one tries to categorize and schematize the Li-ion battery recyclers with their applied techniques, this can be illustrated with the simplified flowchart in **Figure 5.** They can be divided into

- Optional **preparation** before recycling, including sorting, disassembly, discharging, etc.
- Multi-step **pretreatment** in dedicated battery recycling plants, these are companies specializing in battery pretreatment, commonly medium-sized companies,
- Multi-step **main processing** in (mostly) non-dedicated battery recycling plants.

3.1.1 Preparation

Upstream preparation processes are not directly assigned to the recycling process because they are not directly involved in the recovery of the ingredients and do not change the condition or composition of the LIB cell. Classically, this includes the dismantling of large stationary or automotive battery packs to cell or module size or sorting by subtype, separation of plastic housings (common household power packs) and/or discharging.

3.1.2 Pretreatment

Different from the preparation processes, the components are chemically and/or physically changed during the Pretreatment of Li-ion cells. It only serves the goal of separating or changing the battery ingredients to such an extent that they can be fed into existing, large-scale industrial routes. While in the 2000s a negligible amount of end-of-life LIB (EOL-LIB) was still untreated and heavily diluted in industrial routes, today its volume in the EU (> 10.000 t/a) can no longer be disposed of in this way without disruptive effects. If left untreated on this large scale, they would cause operational disruptions, e.g. in converters or smelters by:

- Fire and explosion events in feeding systems (TR),
- Input of impurities due to incorrect sorting (Pb, Cd, Hg etc.) and
- Gas explosions in smelters due to spontaneous evaporation and reaction of organic components (especially volatile electrolytes) and/or water components.

A pretreatment can be merely mechanical or thermal treatment, or a combination of both.

3.1.3 Main treatment: pyrometallurgy (intermediate purification)

Following pretreatment, the battery residues should be subjected to a pyrometallurgical intermediate purification in order to be able to supply them to a hydrometallurgical final refining process. This pyrometallurgy serves to remove unwanted or process disturbing components and to convert the target components into a uniform intermediate product. In particular, it can compensate the fluctuations in the composition of the feedstock, to which hydrometallurgical processes are extremely sensitive. Battery components such as fluorine, graphite, phosphorus etc. are also technically disturbing in hydrometallurgy. However, they can be slagged or used in the pyrometallurgical step (e.g. graphite used as a reducing agent) and thus removed. It also makes economic sense here to slag low-value, non-precious metals such as iron, manganese or aluminium residues, which would cause high material and energy costs through dissolving, precipitation, and filtering in the hydrometallurgy.

3.1.4 Main treatment: hydrometallurgy

The highly complex hydrometallurgical refining step usually consists of an autoclave, (chlorine) acid leaching of the intermediate product from pyrometallurgical treatment, precipitation and filtering of non-noble metals or undesirable elements, followed by solvent extraction and nickel electrowinning, ion exchange and cobalt electrowinning. Further roasting, dissolving, precipitation, filtering, and electro-extraction processes take place in parallel and sequentially on side routes to extract copper and other by-metals such as lead, precious metals, etc.

An economic recovery of the most important LIB valuable components, which so far and certainly in the medium term still concentrate on Co/Ni/Cu, is therefore only possible after a detailed pretreatment and pyrometallurgical intermediate purification in order to finally return them as products into the economic cycle.

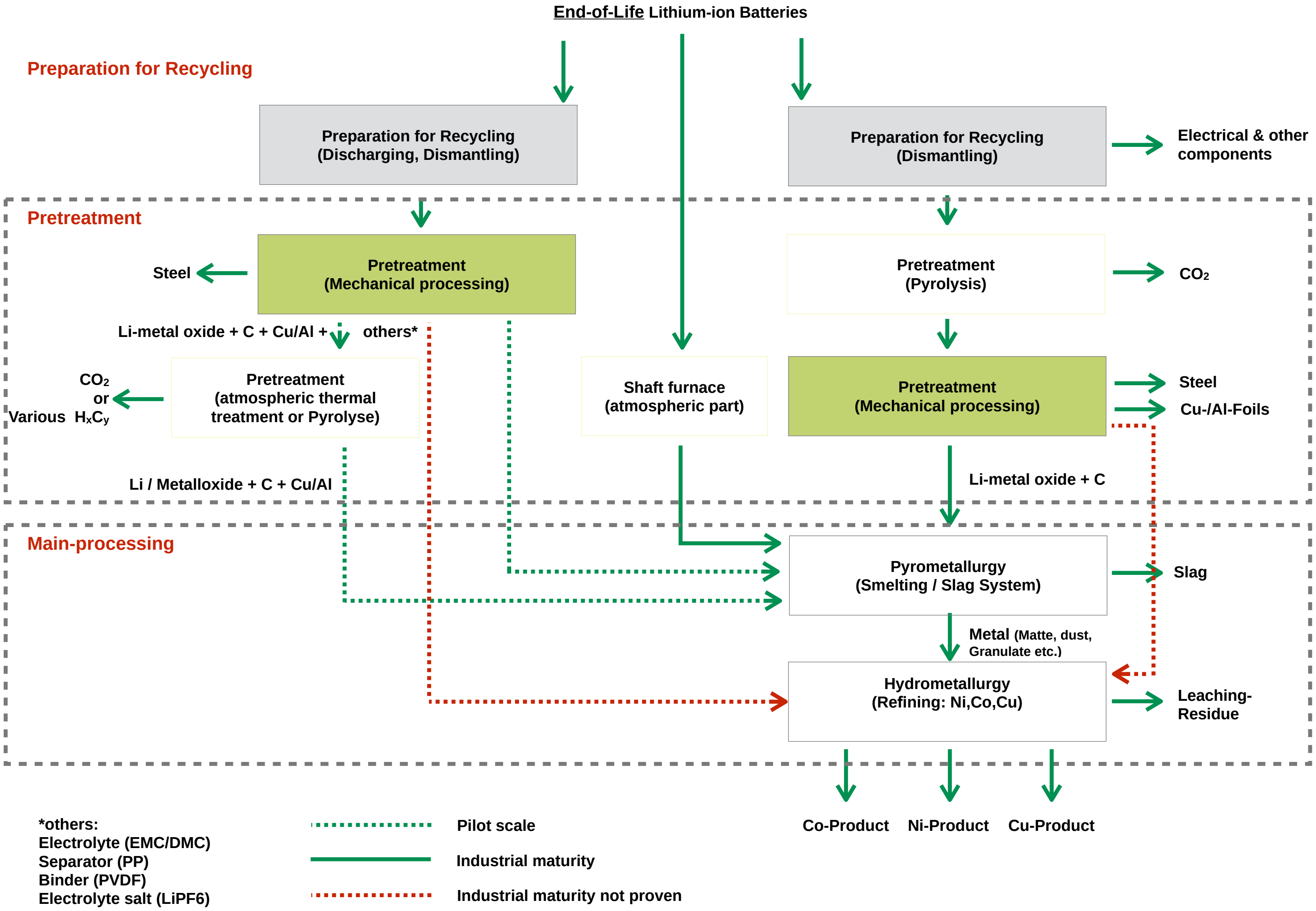

Figure 5: Overview about schematized Li-ion batteries recycling routes.

3.2 General overview of current LIB recyclers in the world

In **Table 6**, an overview of current LIB recyclers in the world is given. It is noted that we introduce the main players on the market, but not all world-wide companies are listed. Especially for the market outside EU, accessible information is limited. Therefore, some companies outside EU could be missing in the list. Also, in recent years many companies announced to start LIB recycling business, but by now (2020) they have not started pilot or industrial operation yet (i.e. still under planning or under construction). Those companies are also not listed.

We categorize the recyclers into three different scales according to their current treatment capacity:

- Industrial scale: > 1000 t/a
- Pilot scale: < 1000 t/a (e.g. a few hundred tons/a)
- Lab-scale: small-scale trials (some grams or kilograms), or sometimes pilot-scale trials (some hundred kilograms or more) but not commercialized yet.

Table 6: Current worldwide LIB recycling companies and their recycling technologies

Scale	Inside EU		Info. reliability*
Industrial scale (>1000 t/a)	Umicore (BE)	**Pyro + Hydro**	(Green: Detailed info. confirmed by various sources)
	Accurec (DE)	**Thermal + Mech + Pyro + Hydro**	🟩
	Nickelhütte Aue (DE)	**Thermal + Pyro + Hydro**	🟩
Pilot scale (<1000 t/a)	SNAM (FR)	**Thermal + Pyro + Hydro**	(Red: limited info. available, only source from the company)
	EDI (FR)	**Mech** (aqueous shred + unknown)	🟥
	TES-AMM (formerly Recupyl) (FR)	**Mech** (inert gas)	🟥
	AkkuSer (FI)	**Mech** + unknown	(Orange: Further info. available, but still limited)
	Duesenfeld (DE)	**Mech** + Hydro	🟧
	Promesa (DE)	**Mech** (aqueous shred) + unknown	🟥
	Redux (DE)	**Thermal + Mech** + unknown	🟩
Lab scale	Erlos (DE)	Mech + reconditioning (direct recycling)	🟥
	Outside EU*		
Industrial scale (>1000 t/a) Lab scale	SungEel (KR)	**Mech +** (thermal +) **Hydro**	🟩
	Kyoei Seiko (JP)	**Pyro**	🟩
	Dowa (JP)	**Thermal + Pyro + Hydro**	🟩
	Brunp (CN)	**Thermal + Mech + Hydro**	🟧
	GEM (CN)	**Mech + Hydro**	🟧
	Huayou Cobalt (CN)	**Mech + Hydro**	🟧
	Ganzhou Highpower (CN)	**Mech + Pyro + Hydro**	🟧
Pilot scale (<1000 t/a)	Retriev (US)	**Mech** (aqueous) + Hydro	🟥
	Kobar (KR)	**Mech+ Hydro**	🟥
	JX Nippon (JP)	**Thermal + Mech + Hydro**	🟥
	Telerecycle (CN)	**Mech + Hydro**	🟥
	Guanghua (CN)	Mech + **Hydro**	🟥

** Notes:*

- Thermal: Thermal pretreatment. Mech: Mechanical treatment. Pyro: Pyrometallurgy. Hydro: Hydrometallurgy.

- The process steps do not represent necessarily the inhouse operation in the company. Operations could be conducted by external partners.

*- *Info. of Asian recyclers are limited/not easily accessed. Their capacities are estimated by the authors. There could be more production scrap rather than End-of-Life batteries as input material. Additionally, their processes were mostly built in recent years, although they are large in scale, the technical maturity may have not been proved. Their choice of technologies may also be affected by local policies, besides technical and economic considerations (For example, the company could choose mechanical pre-treatment instead of thermal-pretreatment due to limited permit of incinerator operation).*

More information about the recyclers and their recycling technologies will be described in following chapters.

4. Industrial-scale (>1000t/a) Li-ion battery recycling processors

This chapter will demonstrate the industrial-scale (>1000 t/a) LIB recycling processors within EU and outside EU, including the company background, LIB recycling capacity, technologies, etc.

4.1 Processors within EU

4.1.1 Umicore (Belgium) *[Pyro + Hydro]*

Umicore N.V. is a multinational material processing group headquartered in Brussels, Belgium. It has relatively wide business divisions, including Energy Materials, Performance Materials, Catalysis, and Recycling. In 2011, a battery recycling pilot plant has been tested in Hofers, Sweden and later was upscaled and installed in Hoboken, Belgium (known as subsidiary Umicore Battery Recycling H.Q.). A permitted capacity of 7000 t/a for Li-ion batteries has been announced in the Hoboken plant [14]. The current treatment capacity is unknown.

The Umicore process is mainly composed of smelting (in shaft furnace) and subsequent hydrometallurgical treatment steps (see flowchart in **Figure 6**) [15]. Li-ion and NiMH batteries and production scraps are fed directly without significant preparation treatment into the smelter. Preparation is limited to large sized industrial batteries, which are first dismantled to small size (e.g. cell level). Besides batteries, additives such as coke, sand and limestone (slag formers) are fed into the smelting furnace.

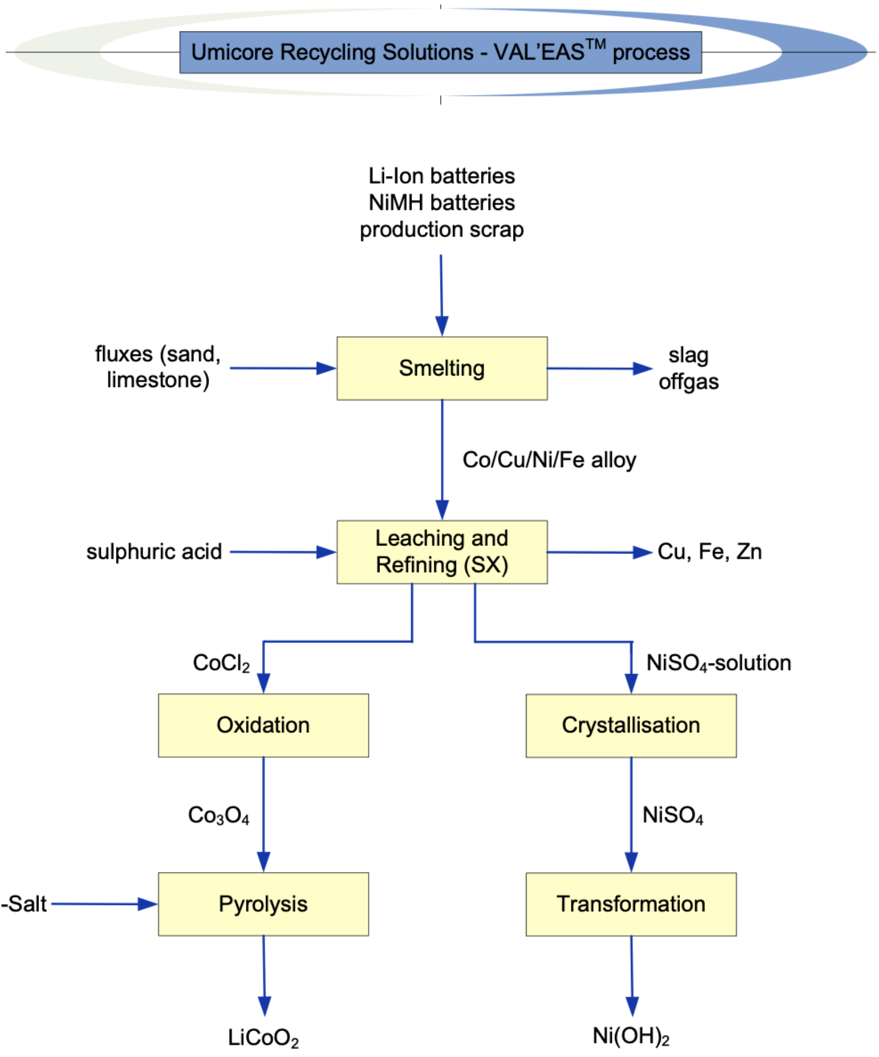

Figure 6: Li-ion & NiMH battery recycling process published by Umicore [15].

More details about the smelting process in the shaft furnace can be schematically shown in **Figure 7** [16]. Based on the reactions occurring as a result of the gradual temperature increase in the process, the smelter can be divided into three zones: 1) upper zone (<300°C), where electrolytes are evaporated, 2) middle zone (700°C), where plastics are pyrolyzed and 3) bottom zone (1200-1450°C), where smelting and reduction happen [16] [17].

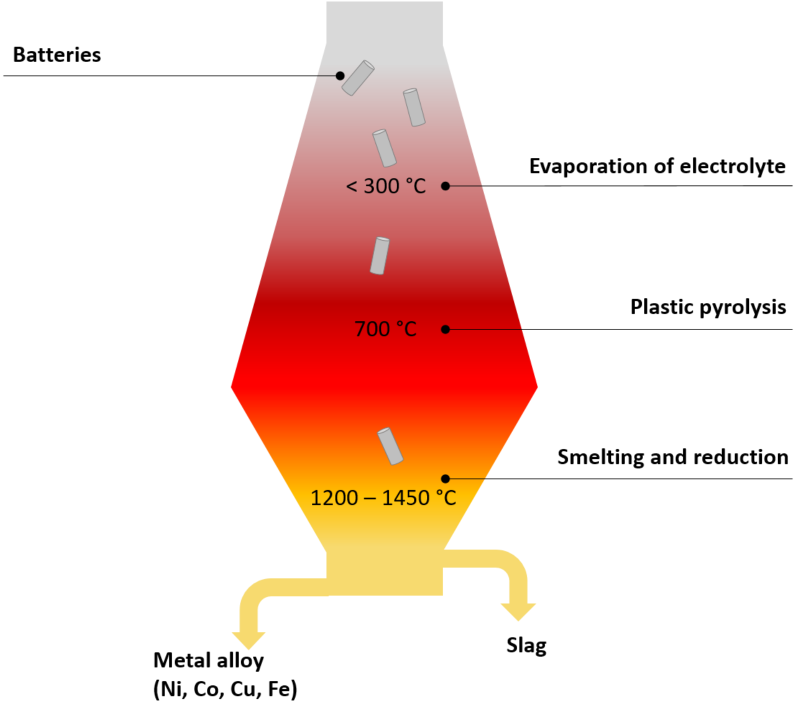

Figure 7: Schematic diagram of Umicore's shaft furnace [16].

The organics (electrolyte solvents and plastic housings) and graphite, which account for appr. 25-50 wt% (depending on battery packs' construction) of batteries, are used as combustible compounds and reducing agent for metal oxides. It is said that the energy released during these reduction reactions provides sufficient energy to heat up the smelter.

It is said a gas cleaning system ("UHT technology") has been installed, in order to fully decompose the organic compounds and ensure that no harmful dioxins or volatile organic compounds (VOC's) are produced [14]. Fluorine is captured in the flue dust.

To summarize, the smelter generates following output fractions [14]:

- **Metal alloy:** Containing Co, Ni, Cu, Fe, which can be forwarded to the downstream hydro-metallurgical process for recovery of Co, Ni and Cu. It is noted that since hydrometallurgical process requires fine particle as input material (especially in leaching step), the alloy shall be granulated before forwarding them into leaching step in hydrometallurgical process.
- **Slag:** Containing Al, Li, Mn, which can be used in the construction industry or further processed for metal recovery. The slag from Li-ion batteries is said to be integrated in Li-recovery flowsheets through a cooperation with external partners.
- **Cleaned gas:** Off-gas is cleaned by UHT technology. The flue dust resulting from cleaning system, which contains the halogens (mainly F), is landfilled.

4.1.2 Accurec (Germany) *[Thermal + Mechanical + Pyro + Hydro]*

Accurec Recycling GmbH, founded in 1995, is a dedicated battery recycling company based in Germany for all kind of modern rechargeable batteries. Concerning Li-ion batteries, both portable and industrial applications, including automotive batteries, can be recycled at Accurec. In 2016, Accurec opened a new Li-ion dedicated recycling center in Krefeld, Germany. In 2019, Accurec has reached treatment capacity of 3000 t/a of Li-ion batteries.

Following above-mentioned categories, Accurec recycles Li-ion batteries through thermal pretreatment and mechanical separation (see **Figure 8**). Before this, batteries are prepared, including sorting, disassembly and discharging (depending on needs). Afterwards, Accurec employs thermal treatment (in rotary kiln, currently via external service) to crack and pyrolyze the organic components. The temperature in this rotary kiln treatment is limited to 600°C, to avoid oxidization of certain unnoble metals like Al. The off-gas is cleaned by afterburner, quenching system and the excess energy from incineration of organic components is transformed to high pressure steam and used in industrial processes. Thereafter, the pyrolyzed battery cells are screened, crushed and classified/sorted by Accurec's inhouse multi-step mechanical separation plant. Output products include steel fraction, Cu/Al fraction and Co- and Ni-rich electrode powder. The steel fraction and Cu/Al fraction can be delivered to corresponding metal smelting facilities for metal recovery, while the CoNi concentrate can be forwarded to pyrometallurgy and subsequent hydrometallurgy plants for final recovery of Co- and Ni-salts or -metals.

With course of technology development, Accurec is currently developing new technics, which will be installed until 03/2021 at the company's Li-ion battery recycling center in Krefeld. Besides nickel, cobalt and copper, the recovery of lithium and graphite are targeted in a future step.

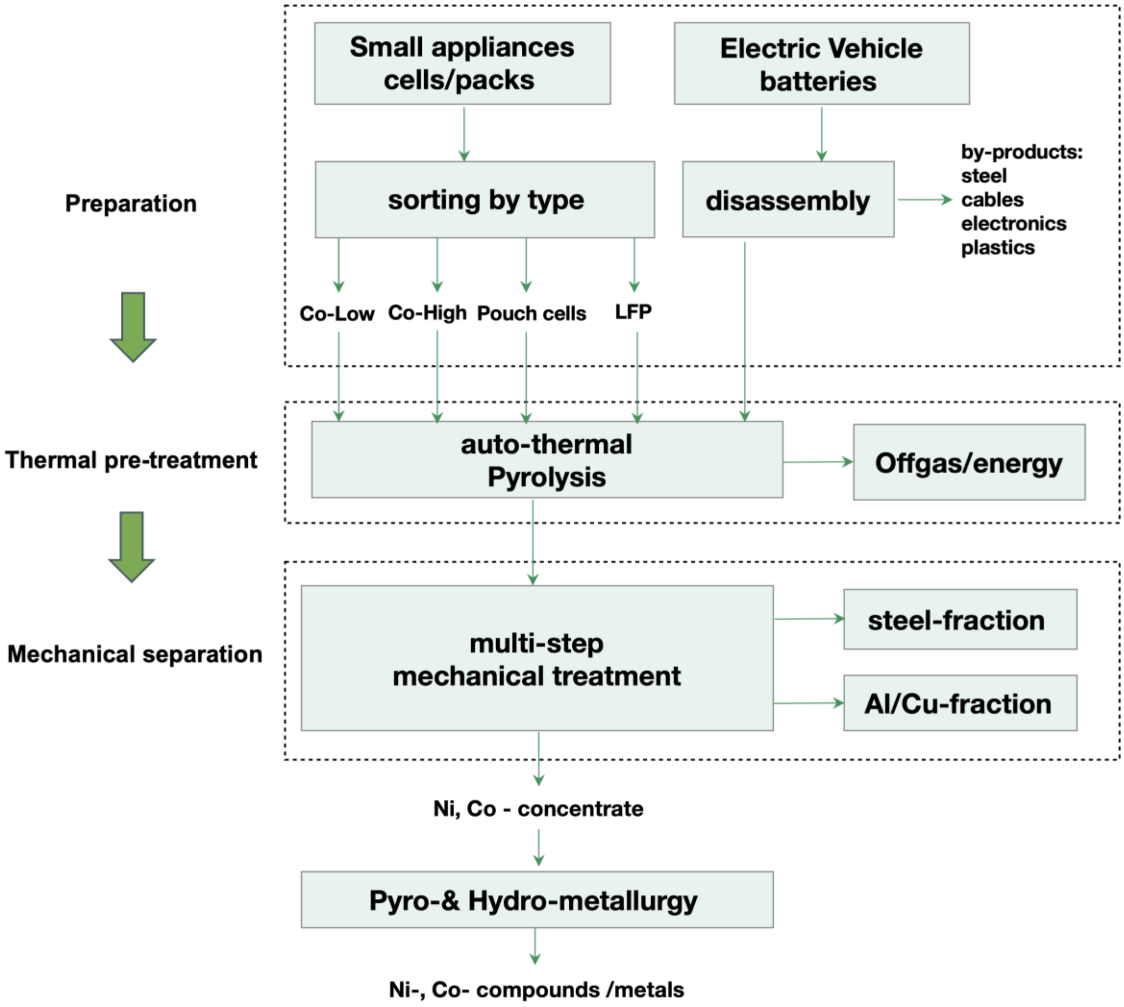

Figure 8: Current Li-ion batteries recycling process at Accurec (2020).

4.1.3 Nickelhütte Aue (Germany) *[Thermal + Pyro + Hydro]*

Nickelhütte Aue GmbH (NHA), founded in 1635 in Aue, Germany, is known as pyrometallurgical works and recycling company. NHA is specialized in the recycling of waste materials containing non-ferrous metals. The facility is especially interested in Nickel, Copper, Cobalt, Vanadium, Molybdenum and precious metal containing spent catalysts from chemical and pharmaceutical industries but also from petrochemical industries and from hydrogenation processes of oils and fats. But they are also able to treat other kinds of residues like ashes, dusts, grindings, liquids and slurries as long as they contain one or a combination of the above-named metals [18].

Since 2011, NHA started to get involved in recycling of Li-ion batteries [18]. The recycling process applied is mainly composed of thermal pre-treatment, pyrometallurgy and subsequent hydrometallurgy. The flowchart of Nickelhütte Aue's battery recycling process is shown in **Figure 9** [19]. In the pyro-treatment step, the batteries can be melted in a short drum furnace (batch-wise furnace), producing NiCoCu-Matte. The company also partly uses a rotary kiln as an alternative to thermally pretreat the batteries. More detailed information about the final hydrometallurgy treatment is currently not available. The process capacity is said to be 7000 t/a by using thermal rotary kiln pre-treatment.

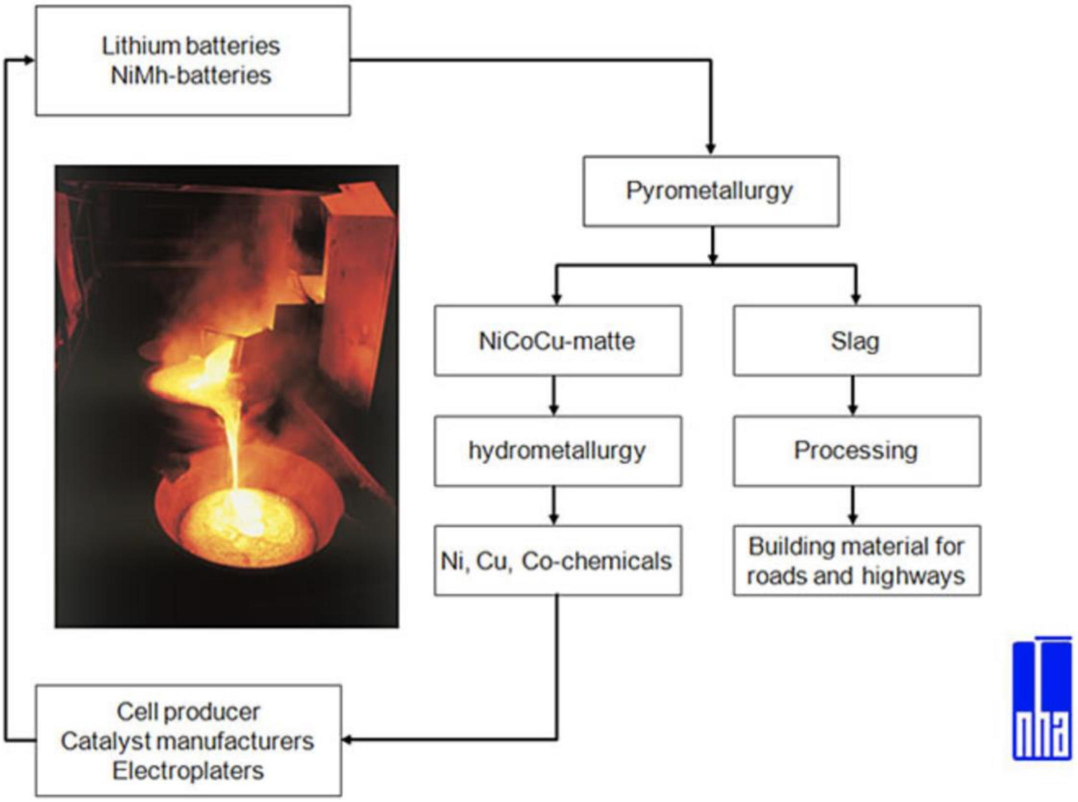

Figure 9: Li-ion & NiMH batteries recycling process published by Nickelhütte Aue [19].

4.2 Processors outside EU

4.2.1 SungEel HiTech (South Korea) *[Mechanical + (Thermal +) Hydro]*

SungEel Hi-Tech Co., Ltd, headquartered in Korea, Gunsan City, is a resource recycling company established in 2000 to recover precious metals and valuable metals from industrial wastes [20]. In 2017, the corporate split into Sungeel Hi-Tech (SHT) and Sungeel Hi-Metal. While Sungeel Hi-Metal focuses more on treatment of electronic industrial waste and petrochemical industry waste, Sungeel Hi-Tech focuses on Li-ion battery recycling [20] [21]. Today, SungEel Hi-Tech recycles over 8,000 tons of spent LIBs and scraps annually [22].

The LIB recycling process of SHT consists mainly mechanical pretreatment and hydrometallurgical process. The Li-ion batteries (mainly production scraps) are grinded into water, to avoid fire. Subsequently, the grinded material is separated mechanically into a) ferrous metal fraction, which is forwarded to ferrous metal processing plant, b) Cu, Al foils, which is forwarded to non-ferrous metal processing plant and c) battery active mass, which is forwarded to inhouse hydro-process (leaching, precipitation, etc.) for final recovery of metal-salts.

The process is said to recover lithium phosphate [23] possibly, but not yet confirmed. According to [24], in 2018, SHA has produced 1,000 tons of cobalt, 720 tons of manganese, 720 tons of nickel and 1,000 tons of lithium (lithium carbonate equivalent).

In 2020, SHT announced to bring a new hydro system at its headquarters factory in Gunsan online [24]. This will triple the site’s capacity to 24,000 tons per year of LIB. SungEel also have bases outside Korea. In 2018, SungEel HiTech and Metallica Commodities Corp. LLC (MCC, headquartered in US) announced the establishment of a joint venture, SMCC, in New York, US. It is announced that the joint venture will initially recycle over 3,000 tons of spent lithium-ion batteries annually [22]. This joint venture facility in New York is due to start up in 2020 [24].

From the permit [25], the process of the joint venture facility in New York includes main steps as: 1) drying/heating in rotary dryer (T<600°C), 2) grinding and 3) hydrometallurgical process. Therefore, a thermal pretreatment step is introduced in the process.

4.2.2 Kyoei Seiko (Japan) *[Pyro]*

Kyoei Seiko is a Japanese steel manufacturer, who also collects and treats industrial and medical wastes. The subsidiary Kyoei Industrial Co. Ltd. utilizes its electric arc furnace technology to treat EOL Li-ion batteries and other wastes [26].

The recycling flowchart can be seen in **Figure 10.**

Li-ion batteries are charged in electric arc furnace (EAF) together with other solid wastes. After melting in EAF, the molten metal is further treated via steelmaking technologies of the parent company to produce steel. The generated slag can be used for road construction. More details about the process are not available.

It is noted that direct charging of high Li-ion batteries into EAF may cause safety risk because the explosion of cells could make the molten metal splashing out. Therefore, the ratio of Li-ion batteries in the mixture must be controlled below a small-scale level.

The recovery rate of Ni, Co, Cu is not known or not verifiable for battery feedstock due to co-processing with other wastes. Additionally, we can speculate that light metals like Al and Li are lost in slag.

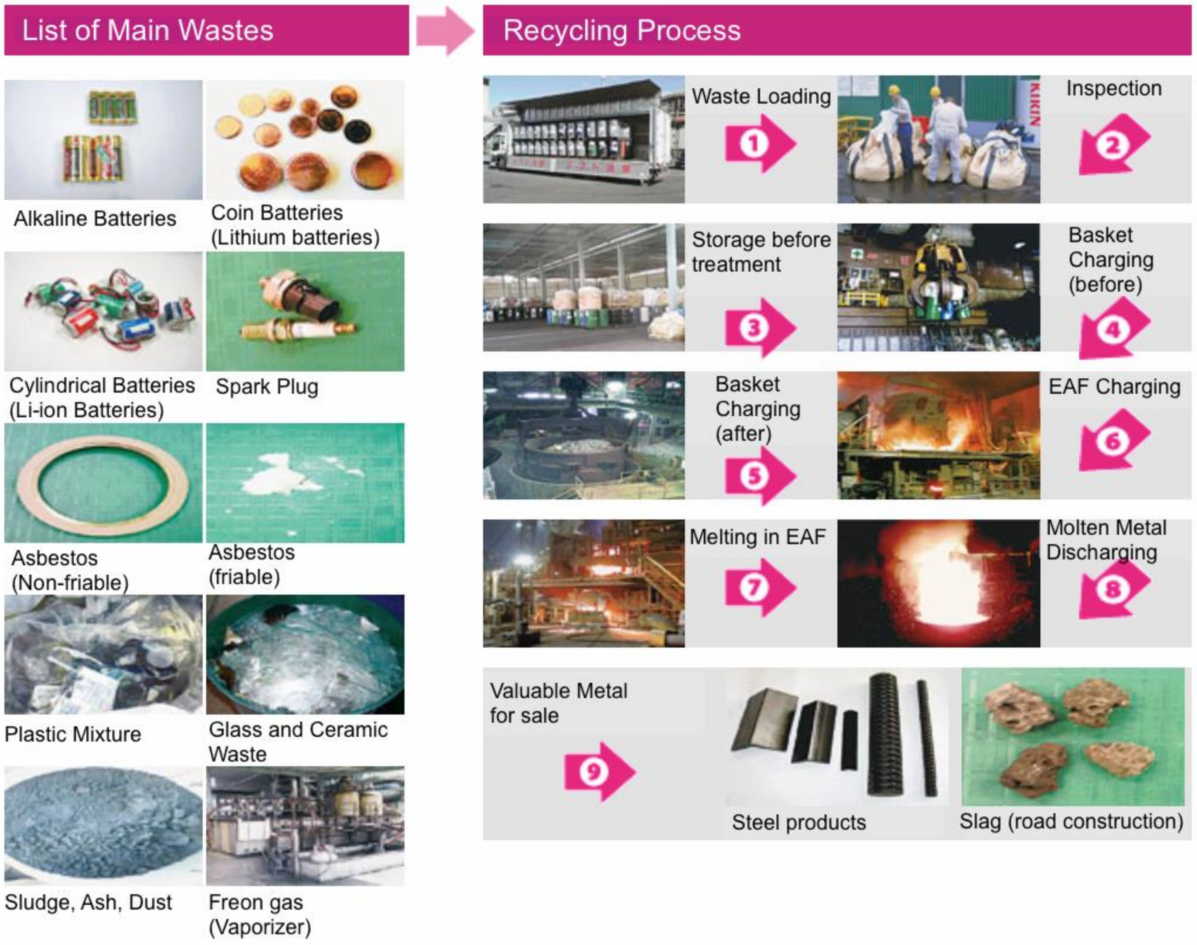

Figure 10: Flow chart of waste (including Li-ion batteries) recycling process published by Kyoei Seiko [26].

4.2.3 Dowa (Japan) *[Thermal + Pyro + Hydro]*

Dowa Holdings Co., Ltd., a Japanese company founded in 1884, has relatively wide business divisions, including environmental management & recycling, nonferrous metals, electronic materials, metal processing, and heat treatment. In November 2010, Dowa announced, that its subsidiary, Dowa Eco-System Co., has commercialized its lithium-ion battery recycling business at its existing facilities. EOL Li-ion batteries as well as scraps generated from the battery manufacturing process will be recycled [27].

Utilizing existing facilities such as Dowa's industrial waste intermediate treatment plants, each year over 1000 tons of used lithium-ion batteries can be received and treated [27]. The main treatment steps include dismantling (of packs/modules), thermal pretreatment (roasting), pyro- and hydro-metallurgical processing.

The thermal pretreatment is performed in a rotary kiln. Afterwards, the pyrolyzed materials are sent to Dowa smelter. In the final step, the materials are recovered via Dowa hydro-process, which has run over many years to extract metals such as copper and gold from wastes including electronics [28][29]. High-purity cobalt is also reported to be produced. More information about the recycling technologies is not available.

The recovery rate of Ni, Co, Cu is unknown, but can be compared with existing industrial processes, according to Schema in **Figure 5.**

4.2.4 Brunp (China) *[Thermal + Mechanical + Hydro]*

Brunp Recycling Technology Co. Ltd. was founded in 2005 in Fushan, China [30]. The main business segments include recycling of spent batteries and cars. Brunp has facilities in Guangdong and Hunan provinces. From 2013 to 2015, LIB manufacture CATL continuously acquired Brunp's stock (to 69.02%) [31] and Brunp became a subsidiary of CATL. It is reported in 2018 that Brunp's annual waste battery (including LIB and other batteries) treatment capacity exceeded 30,000 tons [32]. Therefore, it can be considered that Brunp treats mostly LIB waste materials from production scrap. However, the exact ratio between EOL Li-ion batteries and production scrap and other waste is unknown. Brunp reports an annual production of 10,000 tons of nickel cobalt manganese hydroxide.

Brunp's Li-ion battery recycling process mainly include discharging, thermal pretreatment, mechanical treatment and hydrometallurgy [33]. The company's hydrometallurgical treatment is based in the facility in the Hunan province. The hydrometallurgical process includes acid/basic leaching, solvent extraction, crystallization, etc. [30] A photo of an acid-leaching workshop from Brunp is shown in the **Figure 11** below. The company described the LIB recycling technologies in several patents [34][35][36], however, it is unknown which technology is actually installed in production.

Main final products from Brunp battery recycling process are Ni-Mn-Co hydroxide, cobalt sulfate, nickel sulfate, cobalt chloride, etc., which are classical products resulted from hydrometallurgical process. It is speculated that the recycling rate of Ni, Mn, Co is high, due to high recovery rate in hydrometallurgical process. But the recycling rate of lithium is unknown.

Figure 11: Acid-leaching workshop published by Brunp [30].

4.2.5 GEM (China) *[Mechanical + Hydro]*

GEM Ltd. (Green Eco-Manufacturer Hi-tech Co., Ltd) is a recycling company founded in 2001 in Shenzhen, China. GEM processes “Urban Mines”, including electronic wastes, battery wastes, discarded cars, Nickel / Cobalt / Tungsten metal scraps, etc. From nickel / cobalt metal scraps and spent Li-ion batteries, GEM separates Co and Ni by hydrometallurgical process and then synthesizes the Co-/Ni-salts or producing ultrafine Co-/Ni-powder. GEM has a designed annual production capacity of 5000 tons of NCM and NCA ternary precursor material. The company shows its recycling process as in **Figure 12** [37].

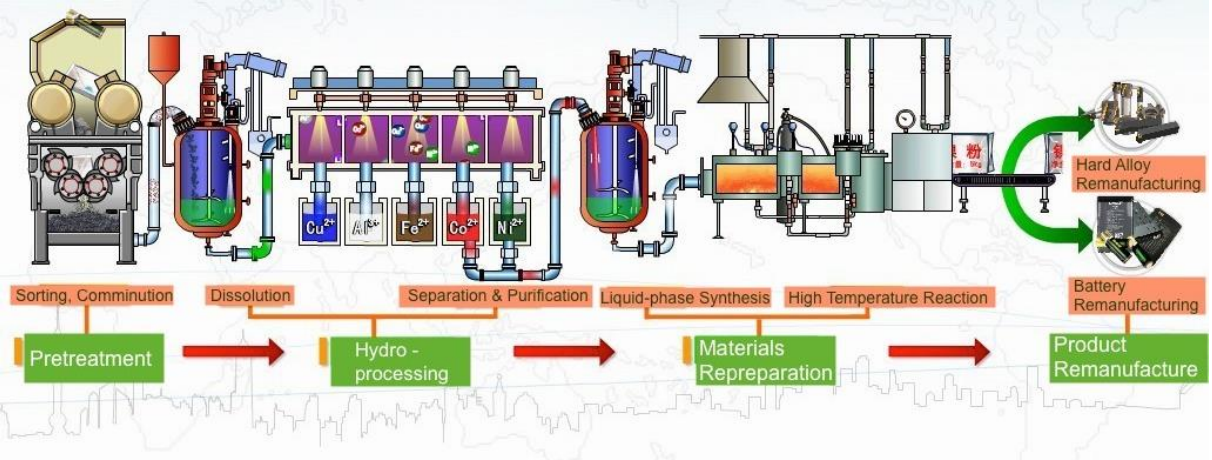

Figure 12: Flow chart of Ni/Co waste and Li-ion battery recycling process published by GEM [37].

As shown in the figure, spent Li-ion batteries, together with Ni/Co containing wastes, are primarily comminuted. After the mechanical separation, the comminuted Ni/Co containing material is sent to hydrometallurgical treatment. The material is dissolved into solution and then metal ions such as Cu^{2+}, Al^{3+}, Fe^{2+}, Co^{2+} and Ni^{2+} are separated into various solutions. The obtained Co/Ni-containing solutions are subsequently processed through liquid phase synthesis and high temperature treatment to produce Co/Ni-salts for battery production. As mentioned before, the company also announced producing ultrafine metal powders from waste Li-ion batteries. According to patents of the company [38][39][40][41], ultrafine Co/Ni-products may be produced by atomizing-hydrolysis method, ball milling + H_2 reduction method, or airflow crushing technology. The ultrafine metal powders can be used in hard alloy production.

In a patent [42], mechanical pretreatment of sorting and comminution of spent Li-ion batteries is described in more details. However, the risk evaluation during mechanical separation is not available due to lack of information. Also, information about the removal of other impurities such as electrolyte, PVDF binder is insufficient.

As the Co/Ni-products are produced from the mixed materials of batteries and other metal wastes, the specific recycling number of batteries is not known. Nevertheless, from the battery collection scheme of GEM it is known that around 11,000 t/a of mixed spent batteries are collected [37]. Assuming 20% of them are LIB, one can estimate that the treatment of LIB is about 2000 t/a.

4.2.6 Huayou Cobalt (China) *[Mechanical + Hydro]*

Huayou Cobalt Co., Ltd, founded in 2002 in Zhejiang, China, is primarily a supplier of cobalt. Huayou said to aim at achieving a closed-loop industrial chain, and its business sectors include mining (of Co, Ni), cathode material precursor and cathode material production and recycling. Its 100% own subsidiary Huayou Recycling Technology Co. (Huayou Recycling), founded in March 2017 in Zhejiang, focuses on LIB recycling [43].

Regarding the recycling technology, Huayou Recycling’s dedicated production line for LIB, which started to put into operation in 2018, contains processing steps such as battery pack/module (automatic) dismantling, cell crushing, material classification and hydrometallurgical treatment [32]. The existing hydrometallurgical process for Co/Ni-primary production (from ores) in the parent company (Huayou Cobalt) can be applied/adapted for the hydro-processing of waste Li-ion battery materials.

It is announced that the production plant has an annual treatment capacity of 65,000 tons batteries (packs) [44]. However, data of current capacity is not available.

4.2.7 Ganzhou Highpower (China) *[Mechanical + Pyro + Hydro]*

Highpower International Inc., founded in 2001 in Guangdong province, China, is an integrated “clean energy” supplier. The main businesses include R&D, manufacturing and sales of Ni-MH and Li-ion rechargeable batteries as well as energy storage systems. In 2012, the company built a plant in Ganzhou City, Jiangxi province, entering battery and electronic waste recycling business [45]. In 2016, Ganzhou Highpower announced to establish a production plant with treatment capacity of 10,000t/a for waste (NiMH & Li-ion) batteries and production scraps [46]. The current treatment capacity is unknown. Besides recycling, the company reported also involving in echelon utilization of used EV batteries.

Regarding the LIB recycling technologies, it is described by the company that it utilizes physical deconstruction (mechanical treatment), pyrometallurgical and finally hydrometallurgical process [47]. More details are not available.

5. Pilot-scale (<1000 t/a) Li-ion battery recycling processors

This chapter will elaborate the pilot-scale (<1000 t/a) LIB recycling processors within EU and outside EU, including the companies backgrounds, LIB recycling capacity, technologies, etc. The processors can be large enterprise or SME, non-dedicated or dedicated battery recyclers. They are categorized as pilot-scale processor because their current LIB recycling capacity is still relatively small (a few hundred or max. 1000 t/a).

5.1 Processors within EU

5.1.1 SNAM (France) *[Thermal + Pyro + Hydro]*

SNAM (Societe Nouvelle d'Affinage des Metaux) is a dedicated battery recycling company founded in 1977 in Lyon, French. The Floridienne group shared its capital since 1996. The main activities are recycling of Nickel-Cadmium, Nickel-Metal-Hydride, Lithium-Ion and Alkaline batteries. Especially, over many years the company has recycled Nickel-Cadmium batteries through pyrolysis, distillation and refining treatments. In 2000, the company announced starting the treatment of the first tonnages of Li-ion batteries [48].

For Li-ion batteries, the company is using its NiCd pyrolysis technic for thermal pretreatment [49]. In the pyrolysis step, sorted Li-ion batteries are heated so that their constituent organics are decomposed and incinerated in an afterburner. The remaining battery metals are subsequently sent to non-dedicated primary metallurgy processors, to recover Co, Ni, and Cu.

The recycling efficiency can be estimated to be similar according to their schematized route in **Figure 5**.

5.1.2 EDI (France) *[Mech (aqueous shred) + unknown]*

EDI (Euro Dieuze Industrie) is a dedicated battery recycling company, as a subsidiary of Veolia SA, located near the Metz-Nancy industrial corridor in French. The company is specialized in four types of batteries: Alkaline, zinc carbon, primary and secondary lithium batteries [50]. It announced a treatment capacity of 5,000-6,000 tons of used batteries and portable accumulators [51].

EDI battery treatment course is divided into several steps: sorting, shredding, mechanical separation [50]. In the first step, the mixed used batteries are sorted manually. Lithium-containing batteries are shredded in a specially designed process with water flow in order to catch the electrolyte solvents and reduce TR incidents. Subsequently, the crushed batteries go through a vibrating sieve in order to separate the electrode active mass powder and all other materials. Then the iron part is separated by an electromagnetic conveyor belt and finally the last part sorts the paper and plastic from the nonferrous materials on an eddy current disk. In this mechanical treatment process, the final destination of evaporating electrolyte and conducting salts is not clearly described.

Four products result from mechanical separation: electrode active mass powder, iron scraps, papers with plastics, and nonferrous metals. Iron scraps are further recycled through existing iron metallurgy. Papers and plastics are sent to incineration and energetic valorization. The electrode active mass powder is said to be further treated to recover cobalt and copper via pyrometallurgical process [52].

Current implementation status of the pilot plan is not available.

5.1.3 AkkuSer (Finland) *[Mechanical + unknown]*

AkkuSer Ltd. is a dedicated battery recycler founded in 2006 in Nivala, Finland [53]. AkkuSer treats Alkaline, NiMH, and Li-ion batteries with a so-called "Dry- technology", a mechanical treatment process, which described in more details in the next paragraph.

The Dry-Technology was described by AkkuSer in several Patents [54][55]. In the process, spent batteries undergo two-stages crushing. During the first crushing process, a cyclonic air separator removes all the electrolyte and reaction gases, including hydrogen and oxygen, accumulated within the crusher. The gases are subsequently cleaned by filters. In second crushing process, the crusher reduces the battery pieces to 0-6 mm. All the gases and dust are removed/collected in a second air mover. The resulting powder passes through a magnetic separator and extracts iron flakes. The output iron flakes are reclaimed by smelting, while the metal concentrate powder is delivered as raw material to pyrometallurgical metal refineries.

Impact of generated toxic gases are not clearly described. Technically, highly volatile electrolytes and generated HF/HCl cannot be segregated just by described technologies before emitted to environment.

5.1.4 Redux (Germany) *[Thermal + Mechanical + unknown]*

Redux Recycling GmbH is a dedicated battery recycler, founded in 1997 in Dietzenbach, Germany [56]. Redux offers battery recycling services from sorting to recovery of various systems (NiMH, Alkaline, Li-ion). In June 2018, Saubermacher and Redux announced to open a new recycling plant in Bremerhaven for Li-ion batteries [57]. The shredding system is capable of processing all types of pre-pyrolysed lithium-ion battery and is said to provide an annual treatment capacity of 10,000 tons.

Regarding the Redux's Li-ion treatment process, as described in [57] it contains four steps:

1) Discharging,
2) Disassembly,
3) Thermal treatment (by external service, in rotary kiln) and
4) Mechanical processing (in-house).

The output products include steel, aluminum, copper, plastic (from disassembly) and active mass (in an unknown segregation degree). Final treatment destination of Co/Ni containing active mass is unknown.

5.1.5 Duesenfeld (Germany) *[Mechanical + Hydro]*

The Duesenfeld GmbH, started operation in June 2018 in Wendeburg, Germany. The recycling facility has been specialized in the mechanical treatment of Li-Ion batteries without thermal deactivation. Currently, acceptance of batteries for recycling is stopped, due to technical problems (status 06/2020).

Duesenfeld's recycling process is published in **Figure 13** [58]. After discharging and disassembly to cell or module level, the spent batteries are mechanically comminuted by crushing in inert atmosphere. The electrolyte is announced to be evaporated, condensed and collected. The remaining crushed material mix then undergoes further mechanical separation. Apart from the recovered electrolyte, Duesenfeld's output fractions after mechanical processing are iron parts, an aluminium-copper fraction, active mass powder, and additionally plastic parts from housing and separator foils. This process is announcing to recover electrolyte instead of being lost in a thermal pretreatment. Neither a proof of quality of recycled electrolytes has been verified, nor how to re-use it. Also, the information about how to solve the problem of HF-corrosion of machines is not clearly described. Additionally, the machines are not explosion-proof, which poses safety risk.

After mechanical separation, it is reported that the active mass powder can be forwarded to hydrometallurgical treatment to recover lithium, nickel, cobalt, manganese and graphite. It is noted that the hydro-process has not installed, and it is only proven in lab-scale tests.

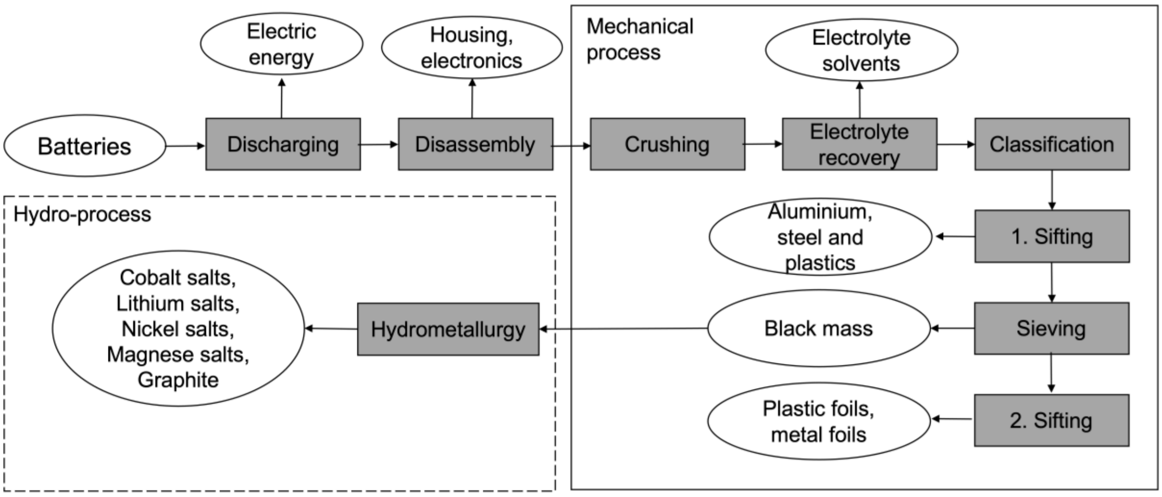

Figure 13: Mechanical recycling process published by Duesenfeld [58].

5.1.6 Promesa (Germany) *[Mechanical (aqueous shred) + unknown]*

PROMESA GmbH & Co. KG, headquartered in Hettstedt, Germany, was founded in 2016 specifically for the treatment and recycling of lithium battery systems. It is a subsidiary of VVG (Verwertungs- und Vertriebsgesellschaft), which was founded in 1991 in Germany and specializes in the disposal of industrial wastes. Promesa mechanically treats lithium-ion batteries, ranging from small household to large EV battery packs [59] [60]. The large battery systems are dismantled prior to special treatment areas.

Regarding the recycling technology, a special feature of their mechanical treatment is that the batteries are shredded under aqueous solution, by which the safety can be obviously improved. More details about the processing are not available. It appears that the generated acids and electrolytes are ending in aqueous solution without known further destination.

Subsequent mechanical process separates the materials into different fractions. It is reported that Co/Ni-containing materials are recovered in a subsequent hydrometallurgical process [61].

The current annual treatment capacity is unknown but estimated to be at low pilot scale.

5.1.7 TES-AMM (formerly: Recupyl) (France) *[Mechanical (inert gas)]*

Recupyl is a dedicated battery recycling company founded in 1993 in the area of Grenoble, France. Recupyl recycles batteries including alkaline, zinc-carbon and lithium-ion batteries, via mechanical separation technology. At Grenoble plant, a pilot test with capacity of several hundreds of tons per year was installed [62]. Since 2007, Recupyl has sold several patent licenses [63] or set joint ventures. In 2019, Recupyl went bankrupt, so that certain subsidiaries became independent (Recupyl Poland) or have been passed to other companies, e.g. TES-AMM, an international electronics waste recycler based in Singapore [64].

Recupyl's mechanical separation process after discharging consists of

1) Shredding of Li-ion batteries in inert gas atmosphere (N_2),
2) Grinding by pin mill and
3) Sieving of materials to fractions of plastics, Al, Cu, Steel and Active Mass powder.

Their capacity is not available but expected to be low. The active mass generated needs to be pre-refined by pyrometallurgy before submitting to hydrometallurgical process.

5.2 Processors outside EU

5.2.1 Retriev (US) *[Mechanical (aqueous shred) + Hydro]*

Retriev Technologies (formerly "Toxco Inc."), headquartered in Lancaster, is a battery recycling company founded in 1990s in U.S.A [65]. Retriev provides recycling technologies for Lead acid, NiCd & NiMH, Li-ion, Li-primary and alkaline batteries. In 2009, Retriev was awarded 9.5 million dollars from US Department of Energy to build a new plant in Lancaster, Ohio to support US lithium-containing battery recycling, especially hybrid and electric vehicle batteries.

For both Li-primary and Li-ion batteries, Retriev applies mechanical pretreatment. Initially, the Retriev Li-battery recycling process was designed to treat primary lithium metal batteries, mainly from military applications, in the early 1990s [66], in which cryogenic cooling with liquid nitrogen is applied for safety consideration [65].

Retriev's Li-ion recycling process mainly consists of following steps [65]:

1) Manual disassembly (of large format batteries),
2) Crushing under aqueous solution, producing three types of materials: metal solids, metal-enriched liquid, and plastic fluff.
3) Further treatment (off-site): The metal solids, containing various amounts of copper, aluminum, and cobalt (depending on the type of Li-Ion battery processed), can be further treated to recover the metals for new products. The metal-enriched liquid is solidified using filtering technology and is sent off-site for further metal purification.

In patent US 8616475 (B1) [67] in 2013, Retriev (Toxco) demonstrated a newly developed Li-ion recycling process, including main steps of crushing, screening, filtration, froth flotation of carbon, filtration and thermally re-generation of LIB cathode material. The company announced to commercialize the described process. However, the current status does not show an implementation into operation.

5.2.2 Kobar (Korea) *[Mechanical + Hydro]*

Kobar Ltd, located in Seoul, Korea, is a specialized recycling company for rechargeable batteries such as NiCd, NiMH and Li-ion batteries. For recycling of NiCd and NiMH batteries, Kobar applies mechanical crushing and subsequent pyrometallurgical processes, producing Fe-Ni-alloys and Cd-metal. For recycling of Li-ion batteries, information from the company's web page shows that crushing, screening and hydrometallurgical processing are applied, as seen in **Figure 14** [68] [69]. Cobalt-containing powders are the main product from recycling of Li-ion batteries.

Very little details of the treatment are not published. One can see from the flowchart that after sulfuric acid leaching, two fractions are generated: a) cobalt oxalate, which probably produced by precipitation with ammonium oxalate; b) a filtrate containing Li, Fe, Al and Cu. However, the post treatment of the filtrate is unclear.

It is reported that the recycling capacity of Kobar is 1,200 t/a for NiCd and NiMH batteries, and 900 t/a for Li-ion batteries [68].

Figure 14: Flowchart of Li-ion battery recycling process published by Kobar [68].

5.2.3 JX Nippon (Japan) *[Thermal + Mechanical + Hydro]*

JX Nippon Mining & Metals Corporation is a large international company based in Japan, 100% owned by JXTG Holdings, Inc. The businesses mainly involve non-ferrous metals mining, processing and manufacturing. In 2010, the company launched a commercial feasibility trial of lithium-ion battery recycling technology at their Tsuruga Plant. It is reported that in 2019 it has achieved operation using recycled materials only, mostly end-of-life lithium-ion batteries [70]. Some 600 tons of end-of-life lithium-ion batteries, collected from smartphones and personal computers, are processed annually, recovering at least 100 tons of cobalt. In addition, it has recovered lithium in the form of lithium carbonate.

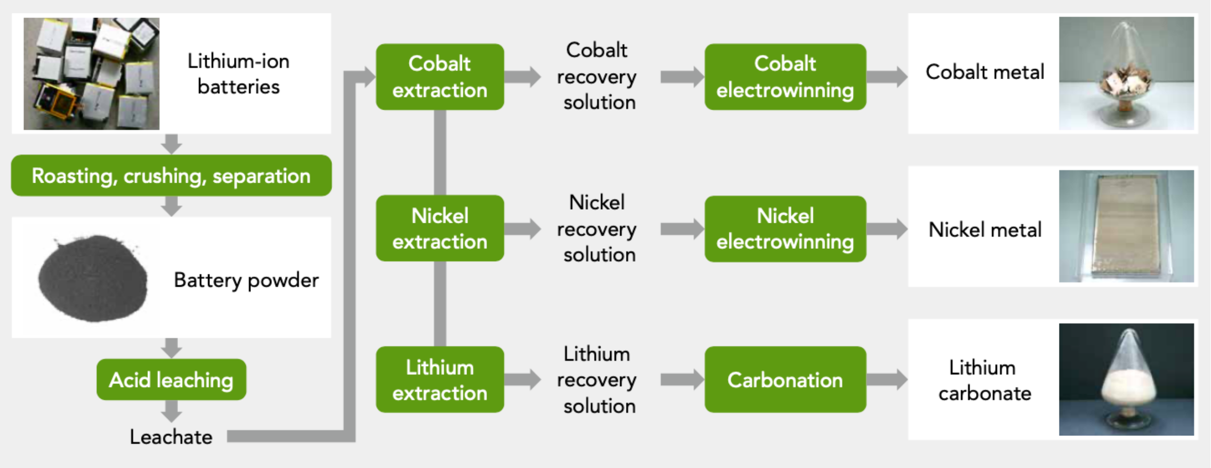

Figure 15: Flow chart of Li-ion battery recycling process published by JX Nippon Tsuruga [70].

The process of Li-ion battery recycling at JX Nippon Tsuruga is illustrated in **Figure 15**. To recover valuable metals such as cobalt, nickel, and lithium, end-of-life lithium-ion batteries are incinerated (roasted) and the battery electrolyte and other organic matter are removed, destroying the functioning as batteries. Next, crushing and separation are performed, and “battery powder” containing valuable metals in concentrated form is extracted. The powder is dissolved in acid, resulting in a solution containing the valuable metals. Subsequently, solvent extraction (SX) is then used to separate and recover the target metals [70]. More details of the process are not available.

In addition, the company claimed to pursue closed-loop recycling, by exploring technology for extraction of Co/Ni-sulfate of a quality that will enable the raw materials extracted from lithium-ion batteries to be used again as lithium-ion battery materials. To conduct tests of their stable mass production, verification equipment is being built in Hitachi City, Ibaraki Prefecture, and was expected to go into operation in fall 2019 [70]. Current status of implementation is not available. The treatment capacity is expected to be low.

5.2.4 Telerecycle (China) *[Mechanical + Hydro]*

Tele Battery Recycling Co., Ltd., founded in Shenzhen, China in 2007, is a small-medium size dedicated battery recycling company. Telerecycle has a R&D center in Shenzhen and a production base in Shangrao. The annual treatment capacity of Shangrao plant is 3000 tons of waste batteries (including Li-ion and other batteries) [71]. The current treatment capacity of merely Li-ion battery is unknown.

The company also build a battery collecting platform, which has 32,130 collecting stores/points and collects over 3 t/d of waste batteries. The data is expected to expand and to achieve 20 t/d in 2019 [71]. The current capacity is not available yet.

In addition, to recycle EV Li-ion batteries, the company has developed automatic disassembly line for automotive Li-ion battery packs [72].

Regarding recycling technologies, Telerecycle recycles spent Li-ion batteries via mechanical separation and hydrometallurgy [73]. Main products include Co-sulfate and lithium carbonate. More details about the process are unfortunately not available.

5.2.5 Guanghua (China) *[Mechanical + Hydro]*

Guangdong Guanghua Sci-Tech Co., Ltd., founded in 1980 in Guangdong province, China, is a specialty chemicals service provider. The main products include high-performance electronic chemicals, chemical reagents and “new energy” materials [74].

With the knowledge and experience in hydro-treatment of electronic chemicals, Guanghua started to enter Li-ion battery waste recycling in recent years. In September 2018, Chinese Ministry of Industry and Information Technology announced a list of first five Chinese companies that comply with the “Specifications for Comprehensive Utilization of Used and Scrapped New Energy Vehicle (NEV) Batteries” [75]. Guanghua was in the list (rest four: Hauyou Cobalt, Ganzhou Highpower, GEM, Brunp).

Regarding the LIB recycling process, Guanghua reported to apply mechanical pretreatment and hydrometallurgy [76]. The hydrometallurgy plant is based in the Gaolangang factory, while the Fushan factory focuses on the second-life utilization and pretreatment of used EV battery packs, including battery evaluation, refurbishment, disassembly. etc. The mechanical separation of battery materials could be done by external process. After mechanical pretreatment, the resulting active metals (Co, Ni, Mn) containing material goes back to Gaolangang factory for hydrometallurgical treatment. More details of the treatment technologies are not available. It is reported in April 2019 that a production line with capacity of 10,000 t/a of used EV battery packs has been built [77]. However, the current treatment capacity is unknown.

6. Lab-scale novel Li-ion battery recycling technologies

This chapter will give examples of lab-scale LIB recycling (sub-) treatment technologies. Because there are too many related literatures, only several selected examples are described here. They can be developed by enterprises, research organizations or universities.

6.1 Mechanical separation and reconditioning for direct reuse ("Direct Recycling")

A so-called "direct recycling" process, in which cathode or anode materials are separated (by mechanical separation), reconditioned and then directly re-used for manufacturing LIB [78], has also attracted many people's attention.

The ERLOS GmbH, a recycler of plastic waste (especially from the automotive sector), founded in 2002 and headquartered in Zwickau, Germany [79], pursues this direct recycling strategy in recent years for recycling of LIB. The main recycling steps include mechanical separation of electrodes, followed by washing, filtering and drying (see **Figure 16**).

More details about the process are described as follows [16]:

1) After discharge (surplus of energy used within the company), the battery packs are dismantled completely to battery cell level mainly by hand.

2) Subsequently, the pouch cells enter an encapsulated chamber flooded with inert gas to prevent fire or explosion where the pouch are automatically opened and separated into anodes and cathodes by the help of robots. This automation is a further safety measure in contrast to manual processing. The electrolyte vapor is collected by an exhaust system with an activated carbon filter that has to be exchanged regularly. Beside the electrodes, the separator foils are collected for plastic recycling or for thermal usage in incineration plants.

3) The cathode and anode electrodes are treated separately in the following washing process. The cathode is treated with water and/or sodium hydrogen carbonate solution at 20-30°C and with a maximum of 90 bar air pressure to separate the aluminum foil and the coating (active mass containing nickel, manganese, cobalt and carbon).

4) The liquid fraction containing the cathode materials is filtered, pressed, washed and dried in a gas oven, obtaining marketable recycled cathode materials that can be used partially for the production of new cells. However, the recycled cathode materials need to be mixed with primary cathode materials. All collected aluminum foils from the cathode are sent to an independent metal recycler.

5) The anode is treated in the same way, separating and recovering the copper foil and the graphite active mass. However, the recycled graphite material is not used for battery anodes, but for other purposes. All collected copper foils from the anode are dried and sold for third party recycling.

6) Because the washing water contains parts of the electrolyte and other contaminants it is treated and cleaned in a sewage treatment plant.

According to the company, this kind of recycling technique is applicable to pouch and prismatic cells, but less suitable for cylindrical cells. Additionally, direct recycling could struggle to accommodate feedstocks of unknown or poorly characterized provenance and cross contamination while processing, and there will be commercial reluctance to re-use material if product quality is affected. Therefore, it might be more meaningful for treatment of production scrap or a pure type material rather than battery mixtures. Moreover, the product quality still needs to be proven.

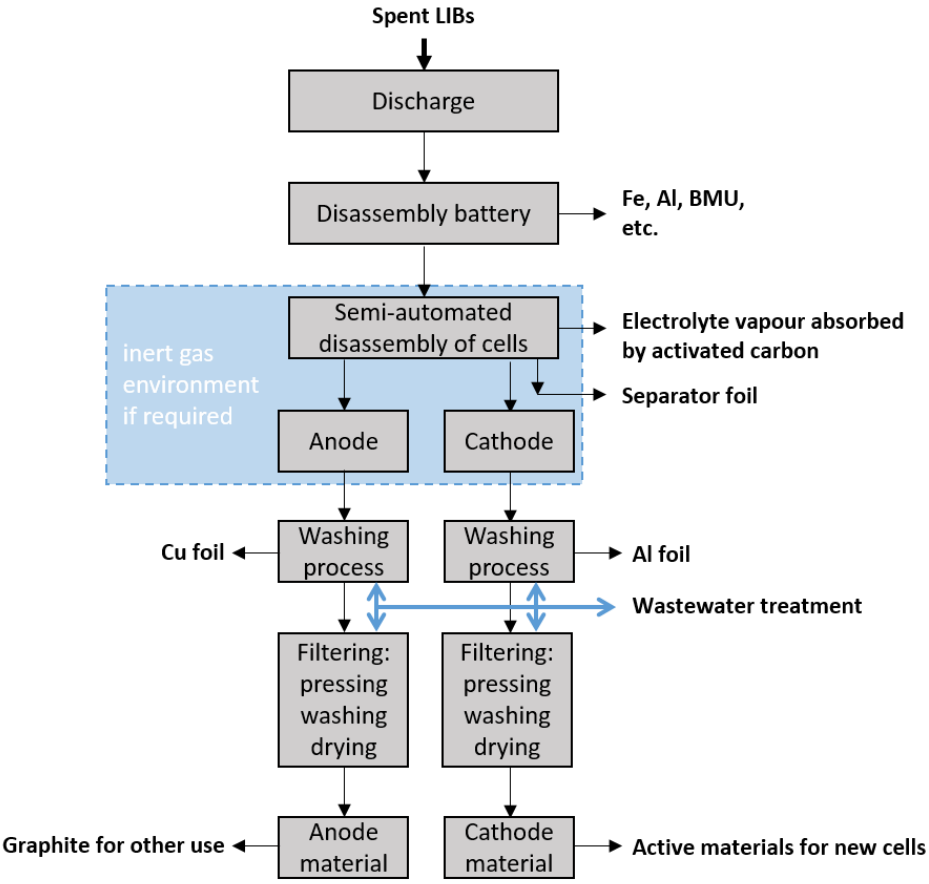

Figure 16: Direct recycling process including mechanical separation and reconditioning applied by Erlos [16].

6.2 Liquid/Supercritical CO_2 for electrolyte extraction

Steven E. Sloop et al. described a method of removing electrolytes by using supercritical fluid in a patent (US 7.198.865 B2) in 2007 [80].

In 2015, M. Grützke et al. from MEET Battery Research Center of University of Muenster also published a study of extraction of electrolytes with liquid and supercritical CO_2 [81] in scope of LithoRec II project. It reported that linear carbonates like DMC and EMC, respectively, were better extracted with liquid CO_2, whereas the cyclic carbonate EC was recovered in higher amounts with supercritical CO_2. The best recovery rate of electrolytes reported by this paper is 89.1±3.4 wt%.

In 2020, S. Sloop, et al. published a direct recycling case study [82], in which electrolytes are extracted with CO_2. The process is demonstrated in **Figure 17**. It is also a so-called direct recycling process. In this study, the recycled materials are re-built in battery cell for testing. It is reported that the final products demonstrated useful capability in the first full cells made from direct recycled cathodes and anodes. Nevertheless, as explained before, the direct recycling process could struggle to accommodate feedstocks of unknown or poorly characterized provenance, and there could be commercial reluctance to re-use material considering its questionable product quality.

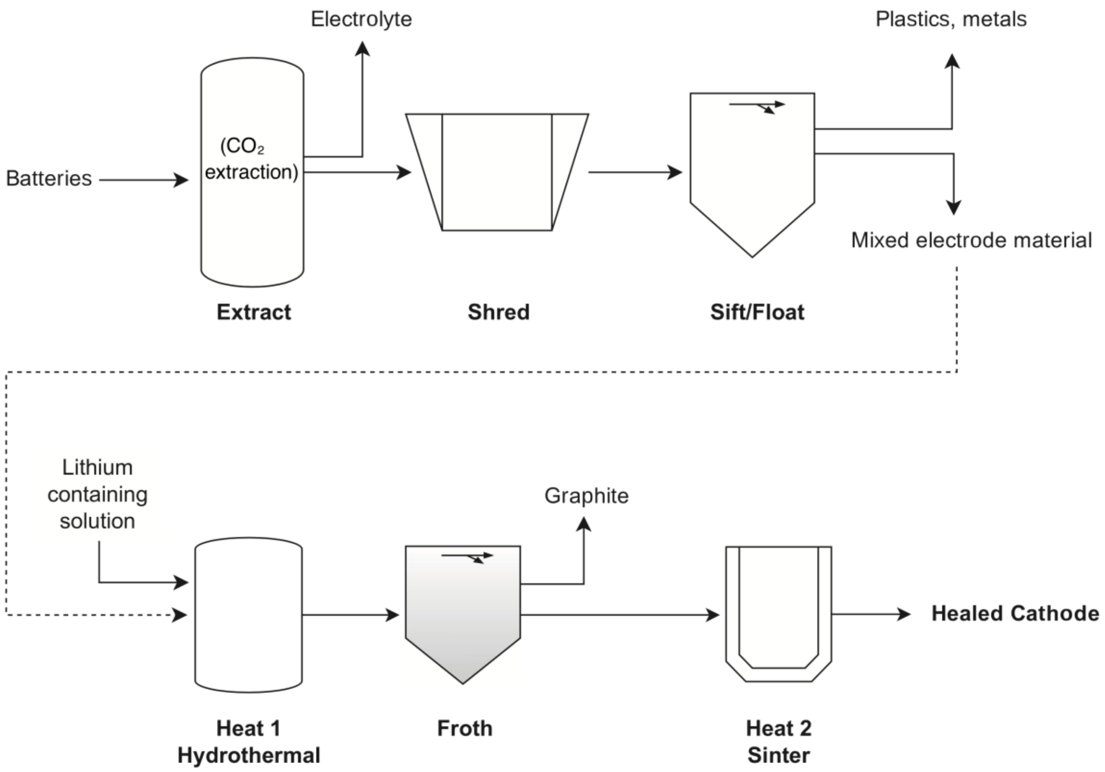

Figure 17: Direct recycling process with extraction of electrolyte with CO_2 [82].

6.3 Froth flotation for separating active mass

Froth flotation is a technology for selectively separating hydrophobic materials from hydrophilic. It has been used in mining industry for long time. In Li-ion batteries, anode material, commonly graphite, is naturally hydrophobic, while cathode material such as $LiCoO_2$ is hydrophilic. Therefore, researchers try to use froth flotation to separate these two materials.

Zhan et al. [83] demonstrated an experimental work of separating anode and cathode material (fine powder after mechanical separation) using froth flotation (see **Figure 18**). It was reported that over 90% of anode materials were floated in froth layers, while 10–30% of cathode materials were floated. In terms of purity of graphite particles, froth concentrates contain 16% and 22% of active cathode materials at 60 µm and 18 µm grinding sizes, respectively. A further upgrading of the purity of graphite materials in the froth products is believed to be difficult. As a result, the authors concluded that the froth flotation is not applicable to produce high purity graphite material. Nevertheless, the purity of output cathode material is higher than the output anode material. Detailed purity of cathode is unfortunately not reported. The authors pointed out the purity of cathode material might vary with the feed samples and grinding conditions, which brings concern for re-using the recycled cathode material in new cells.

The technology is still under development and still needs to prove its viability. Nevertheless, it provides alternative solution for separation of electrode materials and increases the concentration of valuable cathode metals (e.g. Co, Ni) and thus increases the value of active mass powder.

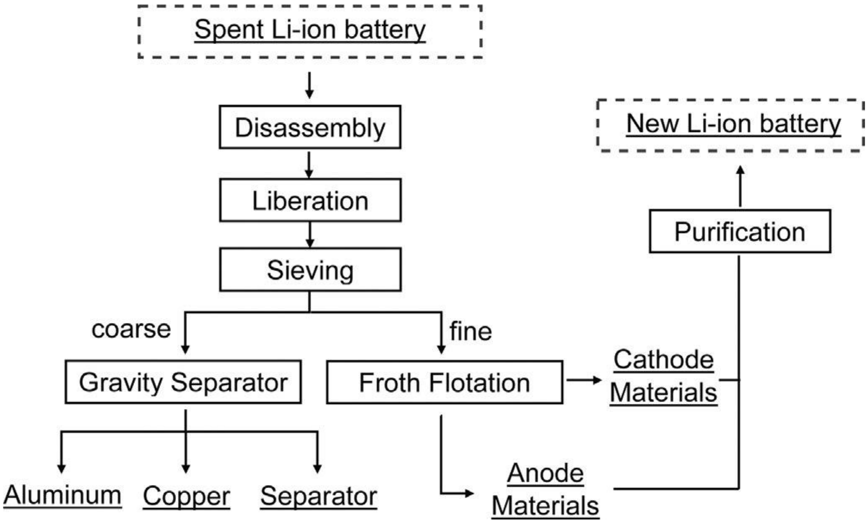

Figure 18: Recycling process with froth flotation separation of active mass [83].

6.4 Electrohydraulic Fragmentation using shock waves

An innovative treatment technology, electrohydraulic fragmentation using shock waves, was developed within a research project, namely NEW-BAT project in 2016-2019 by Fraunhofer Project Group for Materials Recycling and Resource Strategies (IWKS) and several partners [84].

The innovative core of the recycling process is the electro-hydraulic fragmentation using shock waves. The material is introduced into a liquid medium, such as water or other liquids. The shock waves are generated by an electrical discharge. The shock waves hit the materials uniformly. This makes it possible to split the composites at the material boundaries in a non-contact manner and thus achieve a simple and gentle separation of the components [84] [85]. Schematic diagram of the electrohydraulic fragmentation is shown in **Figure 19** [86].

The processing flowchart is shown in **Figure 20** [16]. First of all, the batteries are discharged and then disassembled to cell level. In the following electro-hydraulic fragmentation step, the cells are opened up and their components are separated by mechanical shockwaves in a fluid medium (e.g. water).

In a subsequent step, the mixed components are separated mechanically (similar to previously described classical mechanical separation), obtaining similar fractions as those resulting from currently applied mechanical treatments: mixed active mass, plastic parts and separator, metal foils, and cell housing. The active mass has still to undergo further treatment such as hydrometallurgy or separation into anode and cathode materials and refurbishing (direct recycling).

However, current processing volumes are still on lab scale and aspects such as energy efficiency and economic feasibility can thus not be assessed yet. The energy efficiency is expected to be low due to high energy consumption.

It is also noted that the battery should be deeply discharged before treated by electro-hydraulic fragmentation for safety reasons (to avoid Thermal-Runaway of Li-ion batteries). However, this deeply discharging consumes currently relatively large effort and time in industry. Therefore, this method could be more suitable to treat shredded/crushed materials instead of non-deactivated cells considering safety aspect.

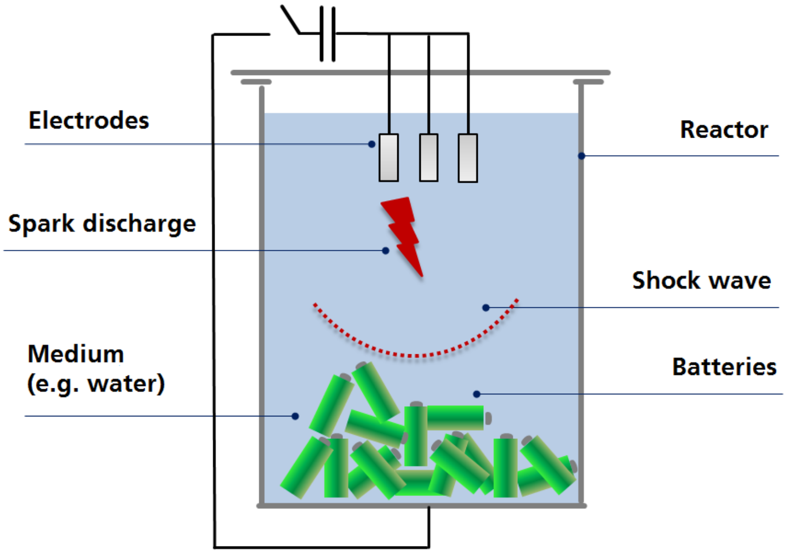

Figure 19: Electrohydraulic Fragmentation of Li-ion battery material (by Fraunhofer IWKS).

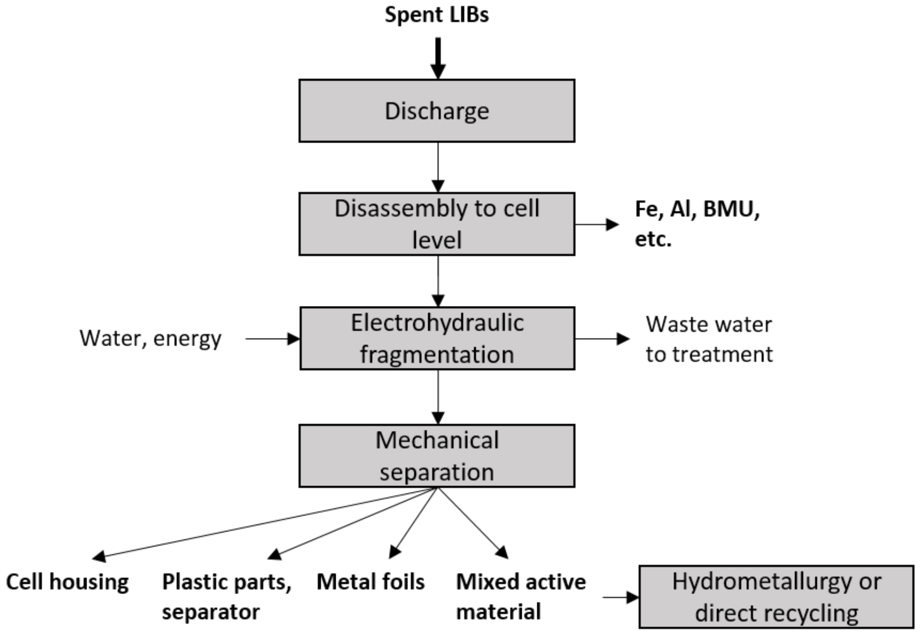

Figure 20: Recycling flowchart with electrohydraulic fragmentation by shock waves [16].

6.5 Sulphate roasting of active mass for early-stage lithium extraction

In 2013, University TU Bergakademie Freiberg developed lithium extraction technologies within a German project called “Hybrid Lithium Extraction” (German: “Hybride Lithiumgewinnung”), in which lithium is targeted to be extracted from Zinnwaldite mineral as well as from spent Li-ion batteries. In the project, one of the Li-extraction routes is to utilize sulphate roasting treatment to facilitate the separation of lithium from other metals such as Co and Ni (see **Figure 21** [87]). It is reported that by roasting with $KHSO_4$, the lithium in pyrolyzed Li-ion material can be transferred to water-soluble phase (Li_2SO_4) and then it is able to be separated from other metals by water leaching and eventually recovered as Li_2CO_3 [87] [88].

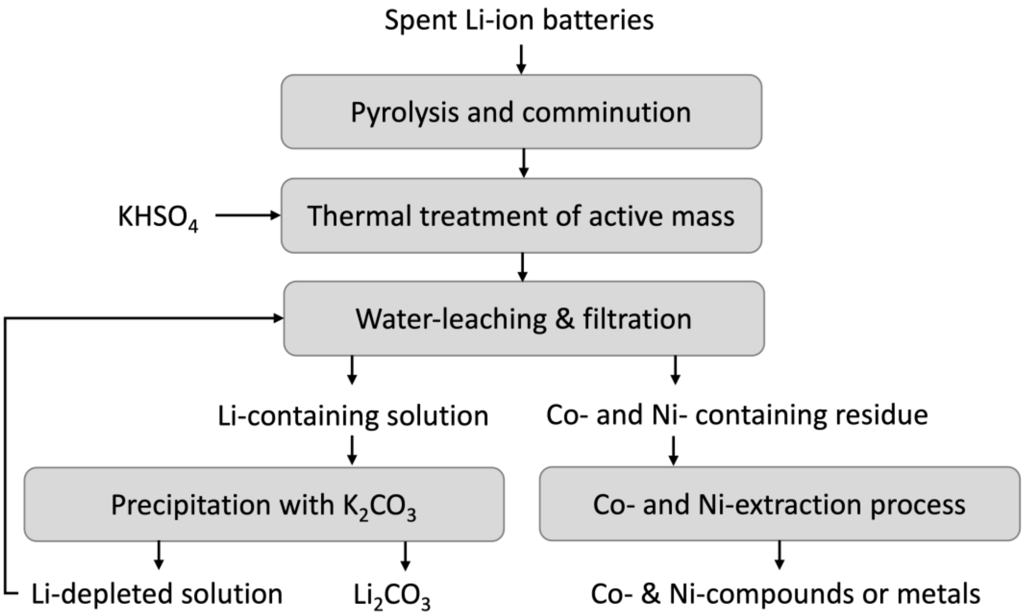

Figure 21: Flowchart of lithium extraction process with sulphate roasting (based on [87]).

In 2020, two papers [89] [90] also reported the idea of selective extraction of lithium by sulfate-roasting treatment. In the study, further investigations regarding treatment conditions (temperature, time, etc.), reaction mechanism and product characterization have been made. It is reported that in sulfation roasting, the metals in NCM cathode powder are selectively converted into water-soluble lithium sulfate (Li_2SO_4) and water-insoluble oxides (NiCoMn-oxide) via following reaction [89]:

$$2LiNi_xCo_yMn_zO_2 + H_2SO_4 = Li_2SO_4 + 2Ni_xCo_yMn_zO_a + H_2O + (3-2a)/2\ O_2 \qquad (8)$$

The process provides alternative to extract lithium from early stage. It is still in lab-scale and further investigation/optimization (e.g. effect of different roasting additives, evaluation of the conversion efficiency of different metals) should be investigated. Also, further study regarding energy efficiency, economic feasibility, environmental impact, etc. should be made in the future.

7. Evaluation of various Li-ion battery recycling processes

According to EU-legislation, a recycling process is complete when, at the end of the process chain, a specified, tradable end product has been produced outside the waste regime. In the present business area, this means predominantly products after hydrometallurgical refining, in the form of a Ni/Co/Cu metal, sulphate or carbonate depending on the process. Since all industrial available processes available today must pass through this hydrometallurgical and upstream pyrometallurgical main treatment, the technical and economic comparison of processes is essentially limited to the pretreatment step. A comparison of various processing routes is summarized in **Table 7.**

The preparation steps (e.g. dismantling and discharging) are not shown in Table 7. However, they also have great impact on the whole recycling processes. A chosen procedure can only generate a long-term advantage if a large electric mobile battery does not necessarily have to be **dismantled** manually before the first treatment step. The designs and strategies of car manufacturers are very different and range from structured modular construction to non-repairable disposable batteries. As a consequence, in the future there will be batteries that can be disassembled by robotics as well as those that cannot be dismantled, i.e. those that are strongly bonded/glued. The technical pretreatment plants must therefore be set up for the expected different dimensions and designs in the long term.

The same applies to the **discharge** step, which could be a bottle neck of a recycling process (as far as discharging is applied in the process). This upstream sub-step is technically demanding, because theoretically the manufacturer would have to decode the access to the BMS (battery management system) in order to diagnose and unlock the high voltage port. However, since EOL batteries are mainly electro-technically defective, the only way to open the battery with high voltage trained personnel and to avoid the safety installations is to use the primary voltage terminals for ohmic discharge. This discharging process is time-, space- and personnel-intensive as well as logistically complex, whereby the feeding of residual charge into a power grid means a subordinate revenue. Using conservative forecasts (e.g. about 250,000 EOL battery units in 2030 in the EU), the feasibility of the upstream discharge step appears unrealistic and thus has restrictive implications for the spread of various recycling routes discussed below.

After 15 years of international research and development efforts, it is striking, based on **Figure 5** and **Table 7,** that only those process combinations **(Route 4 and 6),** which integrate the steps of pyrolysis of the battery cell with subsequent pyrometallurgical pre-cleaning, have achieved industrial relevance. This is mainly due to the fact that in these two steps, impurities and unwanted battery components (e.g. organic solvents) are removed for the final refining in hydrometallurgy. Without removal, these impurities would cause problems and hinder the extraction of the target metals Co, Ni, Cu (see **Table 8**).

Table 7 Comparison of the current pilot and industrial LIB recycling routes from technical and economic points of view.

Process flow combination	**1**	**2**	**3**	**4**	**5**	**6**
pre - processing #1	**Mechanical processing**	**Mechanical processing**	**Mechanical processing**	**Pyrolyse LiB Cells**	**Pyrolyse LiB Cells**	**Pyrolyse LiB Cells**
pre - processing #2		**Pyrolyse Active Mass**	**Pyrolyse Active Mass**		**Mechanical processing**	**Mechanical processing**
main-processing #1			**Pyrometallurgy**	**Pyrometallurgy**		**Pyrometallurgy**
main-processing #2	**Hydrometallurgy**	**Hydrometallurgy**	**Hydrometallurgy**	**Hydrometallurgy**	**Hydrometallurgy**	**Hydrometallurgy**
Technical maturity of the process	Laboratory scale, not industrially proven	Pilot plant scale, not industrially implemented	Pilot plant scale, not industrially implemented	Industrial scale, > 5000 t/a	Laboratory scale, not industrially proven	Industrial scale, > 3000 t/a
Necessity of disassembly	if necessary	if necessary	if necessary	no	no	no
Necessity of discharging	yes	yes	yes	no	no	no
Sensitivity to input contaminants	high	high	low	low	high	low
Controllability of emissions and process safety	low during shredding process	low during shredding process	low during shredding process	regulated afterburner chamber	regulated afterburner chamber	regulated afterburner chamber
Losses of Ni,Co, Cu through cross-contamination in intermediate products	high: ~40-60%	high: ~40-60%	high: ~40-60%	probably low	probably low	low: ~<5 %
Recycling efficiency (according to EU/493/2012)	<< 50%	<< 50%	<< 50%	< 50%	< 50%	> 50%
Recovered metals	Ni, Co, Cu, Fe	Ni, Co, Cu, Fe	Ni, Co, Cu, Fe	Ni, Co, Cu	Ni, Co, Cu, Fe	Ni, Co, Cu, Fe
Total product value recovered	low, due to high losses of AM metals	low, due to high losses of AM metals	low, due to high losses of AM metals	good	optimized	optimized
Process additives (chemicals, activated carbon, N2, etc.)						
comparative energy consumption (including energy recovery)						
Other operating costs (wear, maintenance, personnel, etc.)						
Capex pre-processing per capacity (t/a) and technical usage time (a)						
Bottleneck / hurdle for scalability (for pre-processing only)	Control of explosive atmosphere/HF through whole process Organic / HF-rich AM can hardly be used in hydro	Control of explosive atmosphere Limited use of graphite-rich AM in hydro	Control of explosive atmosphere Economic efficiency (highest costs, low yield)	only as large plant with minimum capacity: >50,000 t/a	Control of explosive atmosphere Limited use of graphite-rich AM in hydro	good modular scalability

Table 8: Possible impurities and their consequences for hydrometallurgical refining.

Accompanying material	Problem formation in hydrometallurgy	Troubleshooting
Electrolyte (e.g. EMC, DMC)	Formation of organochlorine compounds, toxic gases, increased acid consumption, costs for pre-wash required	Evaporation/decomposition by thermal pretreatment
PVDF (Adhesive; 100% in AM)	Insoluble in acids and remains in the filter cake, increase of disposal costs	Decomposition by thermal pretreatment
$LiPF_6$ (conducting salt; 100% in AM)	HF-gas formation, fast corrosive destruction to the equipment. LiF formation, therefore, Li depletion in aqueous and metal-containing phase	Decomposition by thermal pretreatment
Mn	Increased operating costs due to necessary precipitation and disposal, as well as cross-contamination in Fe and Al fraction, more difficult recycling opportunity	Slagging Pyrometallurgy
Al and Fe	Increased operating costs due to necessary precipitation and disposal as waste. Al reduces filtering efficiency.	Slagging Pyrometallurgy
Plastic residues (separator, sleeve, cable covers, etc.)	Additional filter expenditure; disposal costs for incineration	Decomposition by thermal pretreatment
Graphite (100% in AM)	Foam formation with an impact on the plant construction and cost of process additives	Reducing agent Pyrometallurgy
Lithium Iron Phosphate (100% in AM)	Formation of stable phosphates of target metals (Co, Ni), environmental hazardous wastewater with phosphates, corrosion due to gas formation, HF favoritism, basic safety concerns, filtration problems	Slagging Pyrometallurgy
Silicon (LiB Gen. Si Anode)	Gel formation, increased filtration efforts and disposal cost of waste	Slagging Pyrometallurgy

The pre-cleaning effect of **pyrometallurgy** also increases the process robustness, as impurities such as Cd, Pb, K, Zn, La etc. from the missorting of other battery systems or electronic components will be practically contained in the mass production process. If iron and aluminum from housings have not or only partly been removed beforehand by mechanical steps, they will be slagged here as well. This diminishes the recycling efficiency (RE) and overall makes it harder to reach the quota of 50 % given in the Battery directive (2006/66/EC). In order to achieve this minimum percentage of RE for LiB, however, the abundant graphite must also be used. For example, it can be used as a substitute for reducing agents in pyrometallurgy, which is permitted according to EU/493/2012, or via material recovery, which has not yet been proven on an industrial scale.

Pyrolysis as a pretreatment step has several functions: On the one hand, it is intended to completely remove organic matter which is undesired in hydrometallurgy. The organics can be oxidized in a controlled manner in state-of-the-art afterburning plants and/or even used as secondary fuel (energy recovery) in associated plants. On the other hand, it should liberalize the active mass with their target metals, which are permanently bonded to the cathode by the PVDF. If this adhesive bond is not thermally decomposed, it will be difficult to separate the active mass from the electrode foil. Purely mechanical stress cannot loosen this bond, resulting in considerable loss of target metal through cross-contamination. After purely separation by mechanical pretreatment, the cathode foils including AM are found in many output fractions, so that the dissipative AM losses increase up to 40 to 60 % [91] and limit the economic efficiency of the process (as the valuable Co, Ni are in AM fraction). With regard to process safety, pyrolysis also has the advantage of controlled removal of flammable and explosive gas mixtures from electrolytes and decomposition products. It also guarantees a targeted neutralization of the hydrofluoric acid formed. If, on the other hand, LiB are mechanically broken down in the first step, the equipment components (feed, shredder, discharge, intermediate buffering, storage, etc.) have to be, but are usually not explosion-proof and cold. The HF gas, which is spontaneously generated in contact with any available moisture to HF-acid, condenses in the system segments and destroys them corrosively within a very short time. Moreover, highly volatile electrolytes form explosive gas mixtures with atmospheric oxygen and can be self-ignited, as a partial residual energy of the cells can never be completely avoided and short-circuiting potentially occurs. In addition, some smaller plants active in Europe using this mechanical pretreatment could not conclusively show the fate of the evaporated electrolytes.

The **overall economic efficiency** of recycling processes is determined by their cost composition, i.e. capital, general operating and personnel costs, versus revenue composition according to the quantity and quality of the metals recovered.

The necessary **investments and thus capital costs** of the two pretreatment and two main treatment steps increase exponentially in the following order of ranking:

mechanical treatment → pyrolysis → pyrometallurgy → hydrometallurgy.

Following this order, the complexity of the technologies is increasing considerably, so that the scaling of the plants must be increased in order to operate economically. To date, due to the economic advantage of scaling, the intermediate product active mass obtained from the pretreatment from EOL batteries is mostly fed into these large industrial metallurgy plants, which process mostly primary and secondary raw materials with a suitable mixing ratio of secondary feedstock on a scale of 50,000 to 300,000 t/a.

The **maintenance costs** per ton of treated LIB are inversely proportional to the capital costs, especially in the case of mechanical pretreatment **(Route 1, 2 and 3),** since the unavoidable hydrofluoric acid produced there not only increases the maintenance and occupational safety costs, but also leads to a rapid total loss of equipment components and reduces depreciation times to a few years.

The additional primary **energy consumption** via the pyrometallurgical **Routes 3, 4 and 6** incorporating the pyrometallurgical step is seen as a disadvantage. However, these additional costs are compensated by the decreased operating costs in the hydrometallurgical step. If the active mass obtained by shredding and classifying is not pre-cleaned by pyrolysis and/or pyrometallurgy, as in **Routes 1, 2 and 3**, the hydrometallurgical effort would have to be significantly increased. It has to mentioned here that this has not been proven in large scale, but prognoses of additional chemical consumption, gas formation precautions, additional precipitation stages and disposal costs have been mentioned by experts. In addition, there is a **cost**-intensive consumption of activated carbon in the mechanical pre-treatment process, which is used to absorb the evaporated electrolytes from off-gas to meet requirements of emission standards. As a result, in the **Routes 1, 2 and 3**, besides the costs of dismantling and discharging, the additional maintenance and replacement requirements, smaller scaling and poorer expandability of the plants, as well as the significantly higher personnel costs and off-gas cleaning cost have an unfavorable effect on overall profitability.

On the other hand, as the **revenue** comes from the recovery of Co, Ni and Cu, additionally recovered materials in Routes 1/2/3/5/6 such as aluminum or steel, regardless of their various qualities due to different processing technologies, do not represent an economically decisive factor. Only the recovery rate of the three targeted metals determines this economic contribution, so that the high losses due to cross-contaminations in the mechanical pretreatment led to significant disadvantages. In the business area of household LiB, the leverage of the recoverable value with an average significantly higher cobalt content is so big that the process selection of routes 1/2/3 is uneconomical due to the dissipative losses of typical targeted metals in the process. In addition, the revenues from lithium and graphite extraction have so far not contributed to profits in any of the existing pilot-scale or industrial recycling plants and have only been proven at best on a laboratory scale.

8. Summary

In summary, the present study shows that a variety of chemical-physical reactions occur during the pretreatment of batteries, both in the uncharged and partially charged states. These reactions always produce environmentally hazardous, human-toxic, highly corrosive, process-relevant substances, as well as explosive gas mixtures, which must be handled safely in LIB pretreatment process.

In general, current recycling processes for EOL Li-ion batteries can be divided into four different process steps, namely Preparation, Pretreatment, Pyrometallurgy and Hydrometallurgy, which can be combined in six different possible sequences. Currently only two of these (**Route 4 and 6** in **Table 7**) have proven their technical feasibility and industrial maturity and compete with each other after implementation in commercial enterprises. Both of them involve the sub-steps of pyrolysis and pyrometallurgy, which only appear to be disadvantageous considering their higher energy requirement. In fact, however, an active mass obtained from only mechanical pretreatment cannot be refined directly into the end product in a hydrometallurgy process. Without the pre-cleaning in the two thermal stages, its impurity content and high load of organics and fluorides would lead to uneconomically high additional operating costs in hydrometallurgy. In addition, the widely varying composition of the battery active masses (LCO, NMC, LMO, LFP, NCA, etc.) requires thermal selection and homogenization for the input material of hydrometallurgy. This minimizes the operating costs of the entire process route with relatively low losses of targeted metals (Co, Ni, Cu) and also has a positive effect on the ecological balance, since the production and use of additional operating materials, as in other process routes, is not necessary.

A further improvement or variation of the possible process steps, in particular with the aim of additional recycling products (Li, Graphite), energy savings or lower losses, is to be technically aimed at in the future. It is noted that only when the quantity of active mass generated has increased (due to market development) to a certain extent, the installation of an overall process chain (including hydrometallurgy) specifically designed for EOL-battery sector becomes economically feasible.

Several novel lab-scale LIB recycling technologies have been presented, including a so-called Direct Recycling Process, in which cathode or anode materials are separated, reconditioned and then directly re-used for manufacturing LIB, instead of undergoing pyro- and hydro-metallurgy. However, the commercialization feasibility of those lab-scale (sub-) processes still needs to be proved. In this context, “Direct Recycling Process” and usage of separated AM for battery material precursor seem to be unrealistic considering unproved product quality.

9. References

[1] T. Georgi-Maschler, B. Friedrich, R. Weyhe, et al., Development of a recycling process for Li-ion batteries, J. Power Sources 207(2012) 173-182

[2] Chris Hillseth Enterprises: Lithium-Ion Battery Manufacturing. Available by URL: http://chrishillsethenterprises.com/battery/about-lithium-ion-battery-manufacturing/.

[3] Bullis, K.: Lithium-Ion Battery. MIT Technology Review, Sustainable Energy, 19. Juni 2012. Available by URL: https://www.technologyreview.com/s/428155/ lithium-ion-battery/.

[4] E. Darcy, F. Davies J. Jeevarajan, P. Cowles, Lithium-Ion Cell PTC Limitations and Solutions for High Voltage Battery Applications, Available by URL: https://www.electrochem.org/dl/ma/203/pdfs/0189.pdf

[5] X. Feng, M. Ouyang, X.Liu, et al., Thermal runaway mechanism of lithium ion battery for electric vehicles: A review, Energy Storage Materials 10 (2018) 246–267

[6] Z.Wang, H.Yang, Y. Li, et al, Thermal runaway and fire behaviors of large-scale lithium ion batteries with different heating methods, J. Hazardous Materials 379 (2019) 120730.

[7] F. Diaz, Y. Wang, R. Weyhe, B. Friedrich, Gas generation measurement and evaluation during mechanical processing and thermal treatment of spent Li-ion batteries, Waste Management 84 (2019) 102–111.

[8] Liu et al., Thermal Runaway of Lithium-Ion Batteries without Internal Short Circuit, Joule (2018), https://doi.org/ 10.1016/j.joule.2018.06.015

[9] Kunkelmann, J.: Brandschutzforschung der Bundesländer, Berichte: Untersuchung des Brandverhaltens von Lithium-Ionen- und Lithium-Metall-Batterien in verschiedenen Anwendungen und Ableitung einsatzaktischer Empfehlungen Karlsruhe: Karlsruher Institut für Technologie (KIT), 2015, pp.18-28.

[10] Q. Pan, R. Weyhe, A. Melber, I. Klavina, B. Friedrich, Investigation on packaging materials for safe transport of spent Li-ion batteries, 19th International Congress for Battery Recycling (ICBR), Sept. 2014, Hamburg, Germany, DOI: 10.13140/RG.2.1.1607.8320

[11] F. Larsson, P. Andersson, P. Blomqvist, B. Mellander, Toxic fluoride gas emissions from lithium-ion battery fires, www.nature.com/scientificreports, DOI:10.1038/s41598-017-09784-z

[12] M. Bartosinski, R.Weyhe, Processing of Spent Li-ion Batteries: Environmental Challenges, 22nd International Congress for Battery Recycling (ICBR), Sept. 2017, Lisbon, Portugal

[13] European Chemical agency: Homepage. available by URL: https:// echa.europa.eu/de/home, accessed in May 2020.

[14] Umicore: our recycling process, available by URL: https://csm.umicore.com/en/battery-recycling/our-recycling-process/, accessed in August 2020.

[15] Jan Tytgat, Li-ion and NiMH battery recycling at Umicore: strategic choices, 2015.

[16] M. Mohr, M. Weil, J. Peters, Z. Wang, Recycling of Lithiun-ion Batteries, Encyclopedia of Electrochemistry: Batteries, 2020, DOI: 10.1002/9783527610426.bard110009

[17] C. Vadenbo, Prospective Environmental Assessment of Lithium Recovery in Battery Recycling. ETH IED-NSSI. ETH Zürich, Zürich, 2009

[18] ICBR 2018 Brochure, Nickelhütte Aue introduction, available by URL: http://www.dolav.de/media/2131039/ICBR_2018_Broschüre.pdf, Accessed in May 2020

[19] Nickelhütte Aue GmbH, “Battery recycling.” Available by URL: https://nickelhuette.com/index.asp?katid=30&seite=30050200&bodystart=1, Accessed in May 2020

[20] SungEel HiMetal, Available by URL: http://www.sungeel.com/page/history.php, Accessed in May 2020

[21] SungEel HiTec, Available by URL: http://www.sungeelht.com/business.php, Accessed in May 2020

[22] https://www.smccrecycling.com/2018/04/05/metallica-commodities-corp-and-sungeel-hitech-announce-joint-venture-to-redefine-north-american-metals-recycling-and-energy-markets/

[23] Chen et al., Recycling End-of-Life Electric Vehicle Lithium-Ion Batteries, Joule (2019), https://doi.org/10.1016/ j.joule.2019.09.014

[24] South China Morning Post, SungEel HiTech leads the way in eco-friendly recycling of lithium-ion batteries, 19.04.2020, available by URL: https://www.scmp.com/country-reports/country-reports/topics/south-korea-business-report-2020/article/3079850/sungeel

[25] Permit to Sungeel MCC Americas LLC, available by URL: https://www.dec.ny.gov/dardata/boss/afs/permits/703460021800001_r0.pdf

[26] Available by URL: http://www.kyoeisangyo-ltd.co.jp/recycle/recycle.html, May, 2015 (in Japanese)

[27] Available by URL: http://www.dowa.co.jp/en/ir/pdf/news2010/release101109_e.pdf, 9 November 2010

[28] Available by URL: http://www.dowa-eco.co.jp/EAK/, May 2015 (in Japanese)

[29] Available by URL: http://www.dowa-eco.co.jp/business/recycle/metal_recycle/, May 2015 (in Japanese)

[30] Available by URL: http://brunp2005.battery.com.cn (in Chinese)

[31] Available by URL: http://www.qd-dcw.com/article/7_5369.html, 04.09.2019 (in Chinese)

[32] Available by URL: https://www.nengapp.com/news/detail/2355441, 23.02.2019 (in Chinese)

[33]http://www.csrc.gov.cn/pub/zjhpublic/G00306202/201803/P020180312532112650675.pdf, page 114, 2018 (in Chinese)

[34] C. Li, H. Tang, G. Huang, Method for recovering and recycling waste lithium ion battery cathode material, CN Patent No. 101555030 A, 2009

[35] C. Xu, C. Li, G. Haung, Method for recovering and preparing lithium cobaltate from waste lithium ion cell, CN Patent No. 101383442 B, 2011

[36] R. Chen, et al., Method for preparing battery-grade lithium carbonate from recycled lithium ion battery material, CN Patent No. 104241724 A, 2014

[37] Available by URL: http://en.gem.com.cn/index.php/chanyejieshao/, accessed in May 2020.

[38] K. Xu, et al., Equipment for producing ultra-fine cobalt powder with cycle technology, CN Patent No. CN286331Y, 2007

[39] S. Liu, K. Xu, Superfine cobalt powder and its manufacturing technology, CN Patent No.10054674C, 2009

[40] S. Liu, K. Xu, Method of production of ultrafine cobalt alloy powder, CN Patent No. 102000830 B, 2012

[41] T. Su, et al., Preparation method for cobalt carbonate and ultrafine cobalt powder, CN Patent No. 102910686 A, 2013

[42] K. Xu, Method of controlling fragmentation and recovery of waste battery and system thereof, CN Patent No. 100514745 C, 2009

[43] Available by URL: https://www.gg-lb.com/art-35433.html, 29.11.2018 (in Chinese)

[44] Available by URL: https://m.energytrend.cn/news/20190918-75771.html, 18.09.2019 (in Chinese)

[45] Highpower website, available by URL: https://www.highpowertech.com/about-us.html, accessed in June 2020

[46] Available by URL: http://li-b.cn/post/36223.html (in Chinese), 24.06.2016.

[47] Available by URL: https://www.highpowertech.com/products-recycling, accessed in June 2020

[48] Available by URL: http://www.snam.com, accessed in May 2020.

[49] Available by URL: http://ec.europa.eu/environment/ecoap/about-eco-innovation/good- practices/france/504_en.htm, May 2010

[50] Available by URL: https://elibama.files.wordpress.com/2013/01/euro_dieuze_industrie.pdf, January 2013

[51] Available by URL: https://www.planet.veolia.com/en/recycling-electric-car-batteries-renault, Accessed in May 2020

[52] Available by URL: http://www.recycleforcumbria.org/elibrary/Content/Internet/534/5978/6149/4058413237.pdf, May 2015

[53] Available by URL: https://www.akkuser.fi/en/company/, Accessed in May 2020

[54] J. Pudas, A. Erkkila, J. Viljamaa, Battery recycling method, WO Patent No. 2011113860, 2011

[55] Available by URL: http://ec.europa.eu/environment/archives/ecoinnovation2011/2nd_forum/presentations/Session%2 02/case%20studies/jarmo_pudas_akkuser.pdf, 2011

[56] Redux website, available by URL: https://www.redux-recycling.com/en/our-company/corporate-history/, accessed in June 2020.

[57] Saubermacher AG, “Press information: Saubermacher opens new high-tech recycling plant for lithium-ion batteries,” 05 June 2018. Available by URL: https://www.redux-recycling.com/wp-content/uploads/2018/06/PressRelease_Saubermacher-Redux-LithiumIonenBatterieRecycling_EN-1.pdf

[58] Tobias Elwert, Julia Frank (2020), Auf dem Weg zu einem geschlossenen Stoffkreislauf für Lithium-Ionen-Batterien (English: Towards a Closed Loop for lithium-ion batteries), in Olaf Holm, et al (Eds.), Recycling und Sekundär-Rohstoffe, Band 13, (pp. 524-530), Neuruppin, Thomé-Kozmiensky.

[59] Available by URL: https://www.vvg.eu/en/material-flows/lithium-batteries, accessed in May 2020

[60] Promesa website, available by URL: http://www.promesa-tec.de, accessed in June 2020

[61] Available by URL: https://www.golem.de/news/batterierecycling-viel-zu-wertvoll-zum-wegwerfen-1905-140943-2.html, accessed in May 2020

[62] Recupyl website, available by URL: http://www.recupyl.com/118-industrial-sites.html, accessed in May 2020

[63] F. Tedjar, J-C. Foudraz, Method for the mixed recycling of lithium-based anode batteries and cells, US Patent No. 20070196725, 2007

[64] Available by URL: https://www.tes-amm.com/tes-to-acquire-assets-of-recupyl-sas-2/, 29.10.2019

[65] Retriev website, available by URL: https://www.retrievtech.com/recycling-technology, accessed in May 2020

[66] G. Pistoia, J.-P. Wiaux, S.P. Wolsky, Used Battery Collection and Recycling, Industrial Chemistry Library, 10 (2001) 263-293

[67] W. Novis Smith, et al., Recovery of lithium ion batteries, US Patent No. 8616475 (B1), 31 Dec. 2013

[68] Available by URL: http://www.kobar.co.kr/?module=Default&action=English, May 2015

[69] Kim, H., Jang, Y., Hwang, Y. et al. End-of-life batteries management and material flow analysis in South Korea. Front. Environ. Sci. Eng. 12, 3 (2018). https://doi.org/10.1007/s11783-018-1019-x

[70] JX Nippon Mining & Metals Corporation Sustainability Report 2019, available by URL: https://www.nmm.jx-group.co.jp/english/sustainabilityreport/pdf/report2019_e_full.pdf, Accessed in May 2020

[71] Available by URL: https://gg-lb.com/asdisp2-65b095fb-35079-.html, 06.11.2018 (in Chinese)

[72] Available by URL: http://m.cbea.com/dianchihuishou/201903/114323.html, 25.03.2019 (in Chinese)

[73] L. Li, Current situation of recycling and reusing for spent batteries in China, US-China Electric Vehicles and Battery Technology Workshop, Illinois, USA, 4-5 August 2011

[74] Guanghua Sci-Tech website, https://www.ghtech.com/EAbout/about.html, accessed June 2020

[75] List of enterprises that meet the " Specifications for Comprehensive Utilization of Used and Scrapped New Energy Vehicle (NEV) Batteries " (the first list), Chinese Ministry of Industry and

Information Technology, 05.09.2018, http://www.miit.gov.cn/n1146295/n1652858/n1652930/n4509607/c6365599/content.html (in Chinese), accessed in June 2020

[76] Comprehensive Utilization of Traction Batteries, Guanghua Sci-Tech, 11.09.2018, https://www.ghtech.com/Eapplication/recovery_100000000297454.html, accessed in June 2020

[77] Sina News, available by URL: https://finance.sina.cn/intercept.d.html/?chname=finance&times=1 (in Chinese), 19.04.2019

[78] Harper, G., Sommerville, R., Kendrick, E. et al. Recycling lithium-ion batteries from electric vehicles. Nature 575, 75–86 (2019).

[79] ERLOS website, available by URL: https://www.weckpluspoller.de/erlos-recycling, accessed in June 2020

[80] S. E. Sloop, System and method for removing an electrolyte from an energy storage and/or conversion device using a supercritical fluid, Patent No.: US 7.198.865 B2, 2007.

[81] M. Grützke, X. Mönninghoff, F. Horsthemke, et al, Extraction of lithium-ion battery electrolytes with liquid and supercritical carbon dioxide and additional solvents, RSC Adv. 5 (2015) 43209-43217.

[82] S. Sloop, L. Crandon, M.Allen, et al, A direct recycling case study from a lithium-ion battery recall, Sustainable Materials and Technologies 25 (2020) e00152.

[83] Zhan, R., Oldenburg, Z., and Pan, L. (2018). Recovery of active cathode mate- rials from lithium-ion batteries using froth flotation. Sustain. Mater. Technol. 17: e00062.

[84] https://www.r4-innovation.de/de/new-bat.html, accessed in June 2020.

[85] https://www.isc.fraunhofer.de/en/press-and-media/press-releases/efficient-recycling-of-lithium-ion-batteries-launch-of-research-project-new-bat.html, accessed in June 2020.

[86] https://www.iwks.fraunhofer.de/en/competencies/Separation-and-Sorting-Technologies/Physical-Separation-and-Sorting-Technologies/Electrohydraulic-Fragmentation-EHF.html, accessed in June 2020.

[87] TU Freiberg, Abschlussbericht zum Vorhaben “Hybride Lithiumgewinnung“, August 2013, Available by URL: https://tu-freiberg.de/sites/default/files/media/mvtat-12348/pdf/Abschlussberichte/bmbf_03wkp18a_hybride-lithiumgewinnung.pdf.

[88] https://tu-freiberg.de/en/presse/new-process-patented-for-lithium-extraction-from-primary-and-secondary-resources, accessed in June 2020.

[89] J. Lin, L. Li, E. Fan, et al, Conversion Mechanisms of Selective Extraction of Lithium from Spent Lithium-Ion Batteries by Sulfation Roasting, ACS Applied Materials & Interfaces 2020 12 (16), 18482-18489, DOI: 10.1021/acsami.0c00420

[90] W. Lv, Z. Wang, X. Zheng, et al, Selective Recovery of Lithium from Spent Lithium-ion Batteries by Coupling Advanced Oxidation Processes (AOPs) and Chemical Leaching Processes, ACS Sustainable Chemistry & Engineering 2020 8 (13), 5165-5174, DOI: 10.1021/acssuschemeng.9b07515

[91] Wuschke, L. et al.: Zur Zerkleinerung von Li-Ion Traktionsbatterien (shredding Li-Ion traction batteries). Seminar: ProcessNet Zerkleinern & Klassieren (Process Net shredding and classifying), Technische Universität Bergakademie Freiberg, 2015.