LAPPEENRANTA-LAHTI UNIVERSITY OF TECHNOLOGY LUT
School of Engineering Science
Master’s Programme in Chemical Engineering and Water Treatment

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ENHANCED HYDROMETALLURGICAL PROCESS FLOWSHEET FOR RECOVERY OF VALUABLE METALS FROM LI-ION BATTERY WASTE LEACHATES

Examiners: Docent Sami Virolainen

Lic.Sc. (Tech.) Mika Haapalainen

ABSTRACT

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Enhanced hydrometallurgical process flowsheet for recovery of valuable metals from Li-ion battery waste leachates

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Keywords: lithium-ion battery, valuable metal recovery, hydrometallurgy, solvent extraction

The use of Li-ion batteries (LIBs) has increased rapidly over the past years with the increase in the use of electric devices and the growing interest toward electric vehicles. This increase also means that in the following couple of years, there will be a significant amount of waste batteries and efficient recycling methods are needed. The batteries can create significant environmental pollution if they are not properly treated. In addition, LIBs contain valuable metals such as cobalt and nickel making it desirable to recover the metals from them for reuse.

The aim of this Thesis was to provide a hydrometallurgical flowsheet suggestion for the recovery of pure metal solutions applicable to production of battery grade metal products. In the literature part the present hydrometallurgical methods used to recycle LIBs are discussed. Also, fluoride in LIBs and the possible hazards it poses to the recycling are considered. In the experimental part the suggested separation methods and their combinations were studied in practice with laboratory scale batch and continuous separation experiments. The migration of fluoride throughout the suggested recycling process was also monitored.

Based on the results of the experimental part it can be concluded that efficient recovery of valuable metals can be achieved with the suggested process. Copper can be efficiently recovered as pure copper sulfate with solvent extraction and iron can be removed as a hydroxide with precipitation. Manganese and aluminum can be recovered together with solvent extraction, but further optimization is still necessary. If manganese were to be extracted as pure product, aluminum would have to be removed at some other step such as in the pretreatment. The remaining cobalt and nickel can be separated together from lithium with solvent extraction. The produced cobalt and nickel sulfate solution could be utilized in precipitation of precursors in the manufacturing of new batteries. The last solvent extraction of cobalt and nickel was not fully optimized but it showed to be a promising alternative.

TIIVISTELMÄ

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Edistynyt hydrometallurginen prosessi arvokkaiden metallien talteenottamiseen litiumioniakkujäteliuoksesta

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Hakusanat: litiumioniakku, arvometallien talteenotto, hydrometallurgia, neste-nesteuutto

Litiumioniakkujen käyttö on lisääntynyt nopeasti viime vuosina, kun sähkölaitteiden käyttö on lisääntynyt ja kiinnostus sähköajoneuvoja kohtaan on kasvanut. Tämä kasvu tarkoittaa, että tulevina muutamina vuosina syntyy merkittävä määrä käytettyjä akkuja ja niille tarvitaan tehokkaita kierrätysmenetelmiä. Akut voivat aiheuttaa merkittäviä ympäristöhaittoja, jos niitä ei käsitellä asianmukaisesti. Lisäksi akut sisältävät arvokkaita metalleja, kuten kobolttia ja nikkeliä, mikä tekee kierrätyksestä vielä toivottavampaa.

Tämän työn tarkoituksena oli antaa ehdotus hydrometallurgisesta prosessikaaviosta puhtaiden metalliliuosten talteenottamiseen litiumioniakkujäteliuoksesta. Kirjallisuusosassa käsitellään nykyisiä hydrometallurgisia menetelmiä litiumioniakkujen kierrättämiseen. Huomioon on otettu myös akkujen sisältämä fluoridi ja sen tuomat mahdolliset vaarat kierrätykseen. Kokeellisessa osassa ehdotettuja menetelmiä ja niiden yhdistelmiä tutkittiin käytännössä laboratoriomittakaavassa panoskokeilla sekä jatkuvilla erotuskokeilla. Myös fluoridin kulkeutumista ehdotetussa kierrätysprosessissa seurattiin.

Kokeellisesta osuudesta saatujen tulosten perusteella voidaan päätellä, että arvokkaiden metallien tehokas talteenotto voidaan saavuttaa ehdotetulla prosessilla. Kupari voidaan ottaa talteen puhtaana kuparisulfaattina neste-nesteuuton avulla ja rauta voidaan poistaa hydroksidina saostamalla. Mangaani ja alumiini voidaan ottaa talteen yhdessä neste-nesteuuton avulla, mutta lisäoptimointi on edelleen tarpeen. Jos mangaani haluttaisiin saada puhtaana tuotteena, olisi alumiini poistettava jossain muussa vaiheessa, kuten esikäsittelyssä. Jäljellejääneet koboltti ja nikkeli voidaan erottaa yhdessä litiumista neste-nesteuutolla. Tuotettua koboltti- ja nikkelisulfaattiliuosta voitaisiin hyödyntää prekursorien saostamiseen uusien akkujen valmistuksessa. Viimeistä, koboltin ja nikkelin neste-nesteuuttoa ei optimoitu täysin, mutta se osoittautui lupaavaksi vaihtoehdoksi.

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Jasmin Niemi

CONTENTS

ABBREVIATIONS

A/O	Aqueous to organic phase ratio
D2EHPA	Di-(2-ethylhexyl)phosphoric acid
EV	Electric vehicle
HEV	Hybrid electric vehicle
ISE	Ion selective electrode
LCO	Lithium cobalt oxide battery ($LiCoO_2$)
LIB	Lithium-ion battery
LIBWL	Lithium-ion battery waste leachate
LMO	Lithium manganese oxide battery ($LiMn_2O_4$)
LPF	Lithium iron phosphate battery ($LiFePO_4$)
NCA	Lithium nickel cobalt aluminum oxide battery ($LiNiCoAlO_2$)
NMC	Lithium nickel manganese cobalt oxide battery ($LiNiMnCoO_2$)
O/A	Organic to aqueous phase ratio
PHEV	Plug-in hybrid electric vehicle
PVDF	Polyvinylidene fluoride
TBP	Tributyl phosphate
TISAB	Total ionic strength adjustment buffer
TOA	Trioctylamine

1 INTRODUCTION

Li-ion batteries (LIBs) have been extensively utilized in the previous years in different applications including cell phones, laptops, and other electronic devices. LIBs are the preferred choice for portable electronics because of their superior performance, such as high power and energy density, high voltage, long storage life, low self-discharge rate, and wide operating temperature range. The use of LIBs has continued to increase in the recent years owing to the introduction and growth in electric and hybrid electric vehicles. The number of LIBs around the world reached 7.8 billion in 2016, which is a 40 % growth from 2015 when the number of LIBs was 5.6 billion (Y. Zheng et al., 2018). The largest fraction of the total number LIBs sold in 2016 were in portable electronics, with only a small fraction being used in electric and hybrid vehicles. However, when considering the total masses of LIBs used the largest masses are used in electric and hybrid vehicles. The total mass of LIBs used in 2016 was estimated to be 374 000 metric tons. Over 60 % of the total amount was used in electric and hybrid electric vehicles (Winslow et al., 2018). An increase in the demand for LIBs in the following years has also been predicted.

With the increase in production and use of LIBs, there will unavoidably soon be a large quantity of spent batteries because of their limited lifespans. Also, the constant upgrading of electronics leads to more and more spent LIBs. The spent LIBs contain substantial quantities of valuable metals as well as toxic chemicals. The valuable metals include cobalt and lithium. Cobalt is considered to be strategically significant with many uses in industry and military. The use of Co in LIBs is around 25 % of the worldwide requirements of Co and the resources are not very abundant. Also, Li resources are starting to deplete, and it is estimated that with this rate the resources are not enough to meet the demand in the following years (L. Li, Zhang, et al., 2018). Both Co and Li are also on the list of critical materials by the European Commission. The criticality of materials in the assessment is based on the economic importance and supply risk of materials. Co has been on the list since the first assessment was done in 2011, and Li was also added to the list in 2020 (European Commission, 2020).

Even though LIBs can be technically considered to be “green”, they contain many hazardous components that can create pollution if not handled properly. The solvent used in LIBs is flammable and if the batteries come into contact with air or water or are burned, production of toxic gases may occur. Furthermore, Co and Ni, are considered to be carcinogenic, mutagenic, and toxic to human reproduction. With these reasons in mind the main reason for recovering metals from LIBs is to reduce the production of virgin material and to prevent pollution to the environment. It also provides economic benefits and a desirable alternative to being able reuse expensive materials, such as Co, Li and Cu (L. Li, Zhang, et al., 2018).

Because LIBs contain many materials and metals, the recycling of them can be quite complex. Mostly pyrometallurgical processes have been utilized in the recycling and hydrometallurgy has been used to recover metals from the produced alloys. In pyrometallurgy thermal treatment is used to change the chemistry of the materials, whereas hydrometallurgy is dependent on the chemical properties of metals in solution. The hydrometallurgical methods that have been used in the separation and recovery of metals from spent LIBs include leaching, precipitation, and solvent extraction, among others. Hydrometallurgy is preferred in comparison to pyrometallurgy since it can create very high purity products with high recovery rates. Another advantage is that Li can be recovered whereas in pyrometallurgy it is often lost within the slag that is produced (Winslow et al., 2018).

In this Thesis some of the methods used to recycle LIBs are reviewed with a focus on the hydrometallurgical recover of metals from the batteries. The fluoride in LIBs is examined and possible methods to remove it are considered. In the experimental part the recovery of valuable metals from LIB waste leachate was attempted and a possible flowsheet for the recovery is proposed. The target of the experimental part was to separate metals as efficiently as possible to create battery grade purity products. Impurity metals were first separated with solvent extraction and precipitation. The final fractionation of Co, Ni and Li was also done with solvent extraction. Also, the migration of fluoride throughout the suggested process was studied.

2 LITHIUM-ION BATTERIES

2.1 Basic operating principle of Li-ion batteries

The basic operating principle of a rechargeable LIB is shown in Figure 1. Between two electrodes there is an electrolyte which contains a dissociated Li conducting salt. Also, in that location is the separator that isolates the two electrodes. Li ions move between the two electrodes when the battery is charged and discharged. The Li ions are inserted into the active materials of the electrodes. The active materials of the positive electrode (cathode) are often mixed lithium oxides. The negative electrode (anode) active materials are mostly graphite and amorphous carbon compounds (Leuthner, 2018).

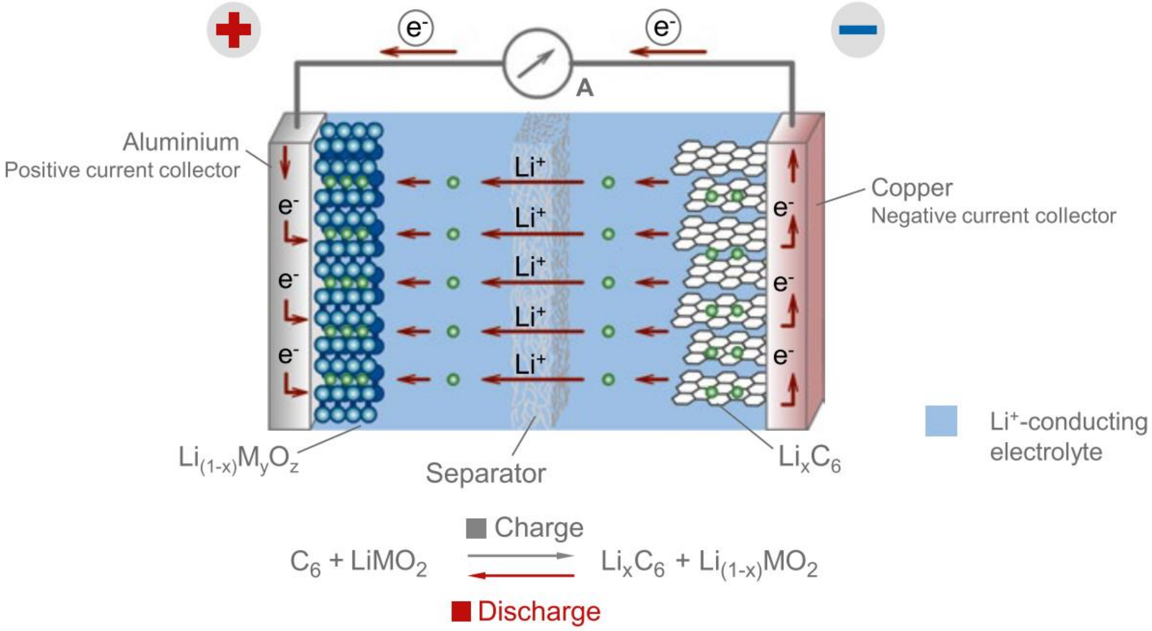

Figure 1. Basic working principle of a LIB. The discharging process is shown (Leuthner, 2018).

As can be seen from Figure 1, the Li ions move through the electrolyte and the separator to the cathode when the battery discharges. Simultaneously, electrons acting as electricity carries move from the anode to the cathode via an outer electrical connection. During charging, the process happens in reverse: Li ions move from the cathode to the anode through the electrolyte and separator (Leuthner, 2018).

2.2 Components of Li-ion batteries

There are usually four basic components in a LIB cell: a cathode, an anode, an electrolyte, and a separator. The cathode consists of an Al current collector sheet which is often assembled into thin layers with a metal oxide. The metal oxide is often called the cathode material. Different compositions of cathode materials give the batteries different properties. The largest amount of valuable metals in LIBs are usually present in the cathode. The anode typically has a Cu current collector sheet that has a coating of graphite as the anode material. An inert binder, such as polyvinylidene fluoride (PVDF), is often used to adhere the electrodes to their respective current collectors. Between the electrodes is the separator which has an electrolyte salt dissolved in an organic solvent. The electrolyte allows for the Li ions to move from one electrode to the other when the battery charges and discharges. The electrodes and the electrolyte are contained within an outer casing, which is usually made from steel, Al, or plastics (Winslow et al., 2018). A mass percent composition of a typical battery system used in electric vehicles (EV) is shown in Figure 2.

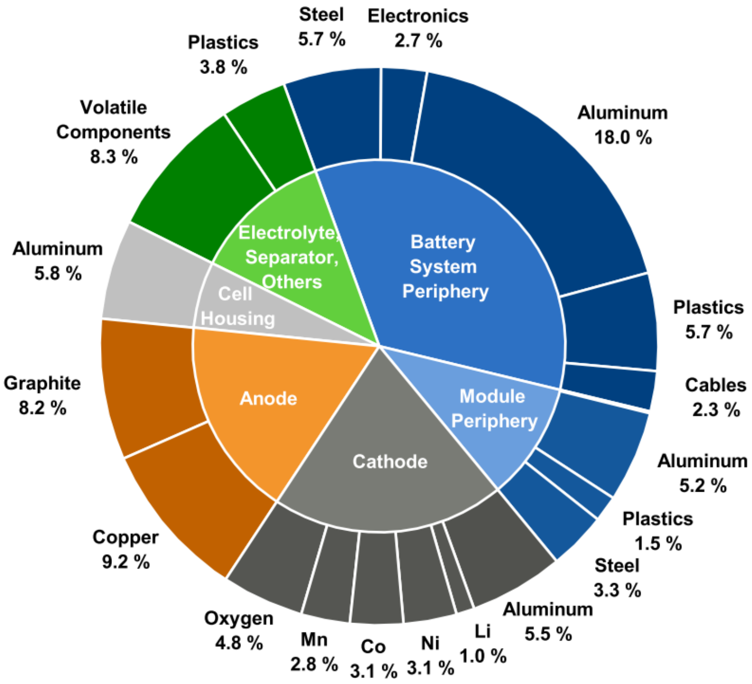

Figure 2. Composition of a typical EV battery system. The cathode material in this case is NMC ($LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$) (Diekmann et al., 2017).

2.2.1 Cathode materials

The current commercial LIBs are named based on the cathode active materials, since that is usually the biggest determinant of the cell properties (Zubi et al., 2018). Common materials used in LIB cathodes are oxides of transition metals that can be oxidized as the Li ions move from the cathode during charging. Also, some lithium metal phosphates can be used as cathode materials (Winslow et al., 2018). The commercially used cathode materials and their chemistries are compiled to Table 1.

Table 1. Commercially used LIB cathode compounds (Winslow et al., 2018).

Compound	Abbreviation	Chemistry
Lithium cobalt oxide	LCO	$LiCoO_2$
Lithium manganese oxide	LMO	$LiMn_2O_4$
Lithium iron phosphate	LFP	$LiFePO_4$
Lithium nickel cobalt aluminum oxide	NCA	$LiNiCoAlO_2$
Lithium nickel manganese cobalt oxide	NMC	$LiNiMnCoO_2$

The LCO battery was the first commercially available LIB in 1991. It is most often used in portable electronics, such as phones, tablets, and laptops, because the battery has a high specific energy (150-190 Wh/kg). The durability of LCO batteries is around 500-1000 full cycles, which means that the calendar life of these batteries is a few years. The drawback of LCO batteries is their poor safety, which is caused by cobalt oxide’s poor thermal stability. There is a possibility for thermal runaway already at 150 °C (Zubi et al., 2018). However, the valuable Co is what makes LCO cathode the most recycled among the other chemistries (Winslow et al., 2018).

The LMO battery was first brought to the markets in 1996. The oxide has a structure of a three-dimensional spinel. This structure results in a better flow of ions on the electrode. The enhanced ion flow in turn leads to a lower internal resistance in the battery, which sequentially leads to a higher specific power. LMO batteries have a longer life cycle than LCO at 1000–1500 cycles, but their energy density is considerably lower at 100-140 Wh/kg. LMO batteries are safer because manganese oxide has a higher thermal stability compared to cobalt oxide. Thermal runaway can occur at approximately 250 °C. Another advantage of LMO is that it does not use Co, but more eco-friendly materials are utilized. The biggest applications of LMO batteries include e-bikes, power tools as well as medical devices (Zubi et al., 2018).

The LFP battery was first brought to markets in 1999. It was considered to be a promising technology because of the high durability, enhanced safety as well as the utilization of abundant materials. Existing LFP batteries have cycle lives of up to 2000 full cycles. There are also estimates for longer lifetimes in the industry. LFP batteries can operate in a wide state of charge window (15-100%), and there is a constant voltage exhibited inside the range which indicates constant performance. These benefits made LFP batteries an attractive option to be used in EV. However, the comparatively low specific energy of 90-140 Wh/kg is a big drawback when comparing to other LIB cathodes. LFP batteries have a minimal role in EV batteries today, but they are more used in e-bikes. Also, there is a lot of potential for use in power supply systems, both off-grid and grid-connected (Zubi et al., 2018).

The NCA battery was first commercialized in 1999. Typically, the cathodes have a mixture of 80 % Ni, 15 % Co and 5 % Al. Thus, the dependence on Co is comparatively small when comparing to LCO batteries. The specific energy of NCA batteries is excellent at 200-250 Wh/kg. They also have a high specific power. The cycle life can be around 1000-1500 complete cycles. The main application of NCA batteries is EV but there are also plans for grid-connected use. Most importantly, NCA batteries are used by Tesla in its EV. Tesla also has big plans for production of LIBs, which can lead to a cost benefit for NCA batteries (Zubi et al., 2018).

The cathode in NMC batteries is $LiNiMnCoO_2$ with different amounts of Ni, Mn and Co. When comparing to NCA batteries, the NMC batteries have a lower specific energy at 140-200 Wh/kg, but the cycle life is longer at 1000-2000 cycles. The quantities of Ni, Mn and Co in the cathode can be altered to impact the characteristics of the battery and they can be used in specialized applications. When the amount of Ni is increased, the specific energy is increased. Increasing the amount of Mn on the other hand causes an increase in specific power. Even though the NMC was initially brought to markets as late as in 2004, it is the dominant battery used in EV and PHEV. The batteries are also used in portable electronics, power tools and medical devices. Grid-connected uses are also in the plans for the NMC batteries (Zubi et al., 2018).

2.2.2 Anode materials

In the anode, graphite is typically used, and it contains hexagonally bonded carbon atoms in sheets. When charged, the Li ions are stored in the sheets of graphite. The battery’s capacity is defined by the amount of Li ions that can be stored in the anode material. Another commonly used anode material is the spinel form of lithium titanate ($Li_4Ti_5O_{12}$), which has the advantage of a longer cycle life when compared to graphite (Heelan et al., 2016). There is also a lot of research made for new technologies to improve anode performance. Some of the latest technologies include carbon nanotubes, tin compounds, and metallic nanoparticles. These new chemistries in the anode would increase the value for recycling the anode as well, since now it is mainly recycled only for the Cu that is present in the current collector sheet (Winslow et al., 2018).

2.2.3 Electrolyte and separator

The electrolyte plays a big part on the performance of LIBs. For example, cycle life, operation temperature and safety of LIBs are primarily defined by the composition of the electrolyte. In the electrolyte a Li salt is dissolved in an organic solvent. The organic solvent is often a combination of alkyl carbonates, which can include ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC). Some electrolyte additives, such as vinylidene carbonate (VC), can also be added to the electrolyte. The additives can help improve the cycle life and safety of LIBs (Heelan et al., 2016).

There are many Li salts that can be used as the electrolyte. The properties of these salts determine how well they transfer the Li ions among the electrodes. Often used salts in LIBs are for example $LiPF_6$, $LiClO_4$, $LiBF_4$, $LiAsF_6$ and others. From these the most used in commercial systems is $LiPF_6$ because of its thermal stability and non-toxicity. Hazardous gases, such as hydrogen fluoride (HF) as well as phosphorous pentafluoride (PF_5), can be released from the electrolyte if it comes into contact with water in the atmosphere (Heelan et al., 2016; Winslow et al., 2018). These hazards and fluoride compounds in LIBs are discussed in more detail in Chapter 4.

The separator prevents the electrodes from being in physical contact with each other and internal short circuiting. Another purpose of the separator is to offer an ionic transfer route for the electrolyte. The most widely used separators in LIBs are porous polyolefin membranes. They are widely used because of the advantages in performance, safety, and cost. The polyolefin can be polyethylene (PE), polypropylene (PP) or a blend of them. A new ceramic separator has also recently been developed and commercialized. The ceramic separator has a better mechanical and thermal stability (Leuthner, 2018).

2.3 Construction of Li-ion batteries

Depending on the intended application of the LIB, a single battery cell can be used, or a number of cells can be connected in series to form modules. Connecting cells in parallel is also possible depending on the capacity which is needed. When connecting numerous modules together, a battery system or pack is formed (Figure 3). These packs are often used in automotive applications where a higher capacity is needed. Again, the number of cells and modules in a pack differs depending on the application of the battery (Pettinger et al., 2018).

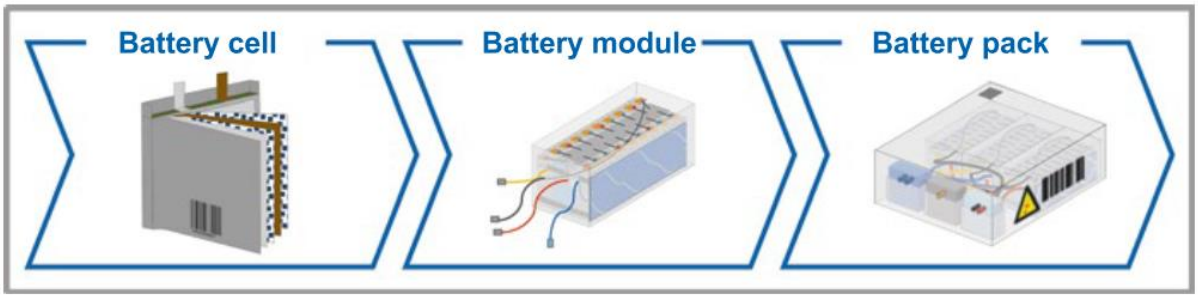

Figure 3. From battery cell to battery pack (Pettinger et al., 2018).

Different types of cells can be used in the battery packs. Some examples of cell types are cylindrical, prismatic and pouch cells (Figure 4).

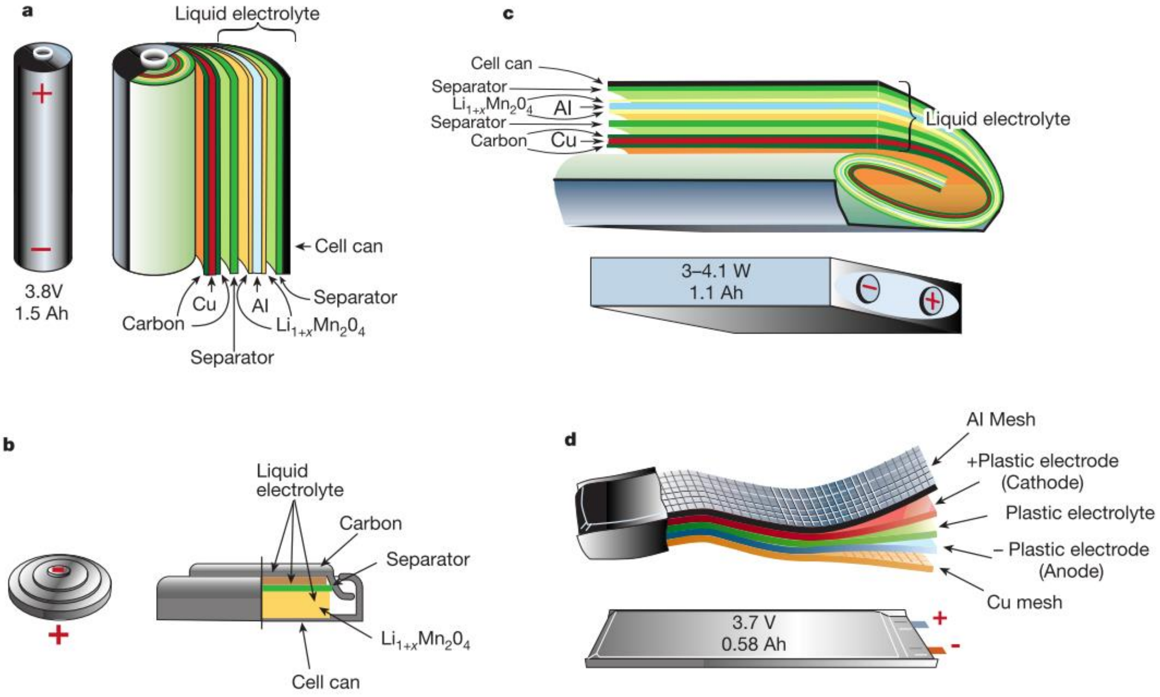

Figure 4. Types of LIB cells: a) wound cylindrical, b) button cell, c) wound prismatic and d) pouch cell, also referred to as a polymer cell (Tarascon & Armand, 2001).

The cylindrical cell has sheet-like electrodes and separators which are on top of one another and rolled up to be packed into a cylinder shape. It is the most used type of battery cells. The advantages of cylindrical cells are their good mechanical stability and toleration of high internal pressure. The disadvantage is low packaging density into packs and modules because of the circular cross-section that cannot utilize the space fully. However, the thermal management of cylindrical cell battery packs can be easier because of the empty space between the cells (Arar, 2020).

Prismatic cells also have sheets of electrodes and separators rolled up but instead of a cylinder they are inside a cubic housing made of metals or hard plastics. The cells can also be put together by stacking in layers instead of jelly rolling. Prismatic cells in battery packs use the available space better due to their box-like shape. But a more challenging thermal management is the result of this (Arar, 2020).

Pouch cells have a flexible foil as the container of the cell. This means that flexible cells that are able to fit into the space of any wanted product are created. The weight of the cell is also reduced as a consequence. The electrodes and separator layers are stacked instead of rolling.

There should be enough space included for the swelling of the cell during the design. The cells can swell with gas during the charging and discharging processes. Because of the soft construction of the pouch cell, a supporting structure is essential. Also, the cell should be kept away from sharp edges (Arar, 2020).

Li-ion cells also need to have a battery management system (BMS) in them to be considered liable and safe to use. The management system is used to track and manage functionality and performance aspects of the LIB. These tracked aspects include voltage, current, state of charge (SOC), state of health (SOH) and temperature. The structure of the system depends a lot on the application of the battery. For example, a portable LED lantern requires a very simple BMS, while more sophisticated systems are needed in aviation applications (Zubi et al., 2018).

2.4 Applications and markets

LIBs can be used in a large variety of applications with the largest use being in portable electronics. Recently, there has been an increase in the demand for LIBs used in road transport. The batteries have also been used in satellites, aviation, and it has a capability to be applied in power supply systems. Other smaller markets for applications include medical devices, self-powered microelectronics, flashlights, radio-controlled toys, and wireless vacuum cleaners, among others (Zubi et al., 2018). Table 2 shows the different applications and markets of LIBs from the past and also future perspectives are presented.

Table 2. Past development and future perspectives in LIB markets presented as GWh/year (Zubi et al., 2018).

	2010	**2015**	**2020**	**2025**	**2030**
Cell phones	6	11	17	28	44
Tablets	1	7	12	17	25
PC	12	9	9	9	11
Portable electronics, other	3	4	7	12	20
Portable electronics, total	**21**	**31**	**45**	**66**	**100**
EV	0	11	65	115	200
PHEV	0	2	8	13	25
HEV	0	0	2	7	15
Road transport, other	0	0	1	2	5
Road transport, total	**0**	**13**	**76**	**137**	**245**
Storage in power supply	0	0	2	10	30
Other applications	1	1	2	7	15
Total	**22**	**45**	**125**	**220**	**390**

The initial and for a long time the main market area for LIBs has been portable electronics (Table 2). From these the biggest market share is on cell phones, tablets, and laptops, while other electronics also include digital cameras, camcorders, video games and toys. The high specific energy and power combined with the low weight make LIBs the favored battery system in these applications. Especially LCO battery types is used in portable electronics because of the specific power and low self-discharge rate. Cell phones usually use only one cell, while for tablets there are often two to three cells connected in parallel. For laptops more cells need to be used and usually they are in series (Zubi et al., 2018).

The need for LIBs is growing with the demand for EV, PHEV and HEV increasing as can be seen from Table 2. It is predicted that the car industry is becoming the main market for LIBs. Other road transport applications of LIBs include electric motorcycles and electric bicycles. The cathode chemistries that are most often used in the car industry are NMC and NCA because they can offer high lifetimes, in addition to the high specific energy. Bigger battery pack that contain modules of battery cells are needed for applications for road transport (Zubi et al., 2018).

3 RECYCLING OF LI-ION BATTERIES

LIBs are not currently recycled as much as other battery types. This is because there is such a variety in the composition of LIBs that makes the recycling processes more complex and difficult. The stream to be recycled often has so many metals in it, that many steps are required to efficiently separate them all. More and more end of life products are to be produced in the following years (Heelan et al., 2016).

LIBs contain many valuable and important materials, which makes recycling desired. For example, the use of Co in LIBs is around 25 % of the worldwide requirements and the Co resources are not very abundant. Li is also starting to become scarcer and since the demand for new batteries is increasing, the needed amount of Li is also increased. Thus, it is important to conserve resources by recovering metals from batteries (L. Li, Zhang, et al., 2018).

From an ecological and health point of view, spent LIBs pose risks as well. Disposing or landfilling of LIBs contains many hazards. Since LIBs include reactive materials, organic and inorganic materials, which can explode, catch fire or otherwise pollute the environment. Also, Co and Ni are considered carcinogenic, mutagenic, and toxic to human reproduction. So, recycling of LIBs prevents these hazards of being released into the environment. Also, reducing the amount of virgin material production can help decrease environmental pollution (L. Li, Zhang, et al., 2018).

Usually, the main objective in recycling LIBs is to recover the Co and Li in them since they are seen as the most precious materials. The treatment methods used in LIB recycling can be divided into physical, and chemical methods. Usually, a combination of both of these unit processes is required for the recycling to be efficient enough. The chemical processes can be further divided into pyrometallurgical and hydrometallurgical processes (Chagnes & Pospiech, 2013; L. Li, Zhang, et al., 2018; Winslow et al., 2018). Pyrometallurgical recycling is briefly described in the next chapter and hydrometallurgical recycling is described in more detail in the following chapters.

In pyrometallurgy thermal treatment is utilized to induce chemical change in the waste, which leads to the production of an alloy. Many of the current industrial recycling processes are similar to smelting. The produced alloy is often further processed with hydrometallurgy to recover and purify the metals. During pyrometallurgical processing, the organic electrolyte and binder are burnt off. This means that hazardous gases are released, and substantial amounts of energy are needed to handle the gases before they can be discharged into the environment. Also, Li and Al are active materials with high reducibility. This means that during the smelting, they are often likely to be oxidized. Their oxides often go into the slag, and they cannot be recovered from the process. All in all, the hydrometallurgical processes are thus thought to be more desirable for LIB recycling (Winslow et al., 2018).

3.1 Hydrometallurgical recycling process

Hydrometallurgy utilizes the chemical properties of metals in aqueous solution in order to separate and recover them. The hydrometallurgical process for LIB recycling can be roughly divided into sections of pretreatment, leaching and recovery of metals from the leachate. During the pretreatment section, the batteries are discharged and dismantled with mechanical processes such as crushing and sieving etc. The pretreatment can also include dissolution and thermal treatment to remove binders and electrolyte from the electrode materials. In leaching, the pretreated electrode materials are leached into solution with a suitable leaching media. For example, inorganic or organic acids, alkali or bacteria solution can be used to leach metals from the cathode active materials. After leaching the metals are recovered from the leachate with processes, such as solvent extraction, ion exchange (Virolainen et al., 2021), chemical precipitation, or electrolytic deposition. The advantages of hydrometallurgical processing of LIBs include high recovery rates of metals with high product purity, lower consumption of energy and reduced gas emissions. The processes can be quite complex however, and the used separation materials can be expensive, making the processes less economical (Yao et al., 2018).

3.1.1 Pretreatment

Having a pretreatment step in the recycling process of LIBs is very important since the composition of LIBs is complicated and in order to separate the metals efficiently, the cathode material should be separated from the other material. Generally, the pretreatment consists of discharging, dismantling, and the separation of the cathode material (Figure 5) (Yao et al., 2018).

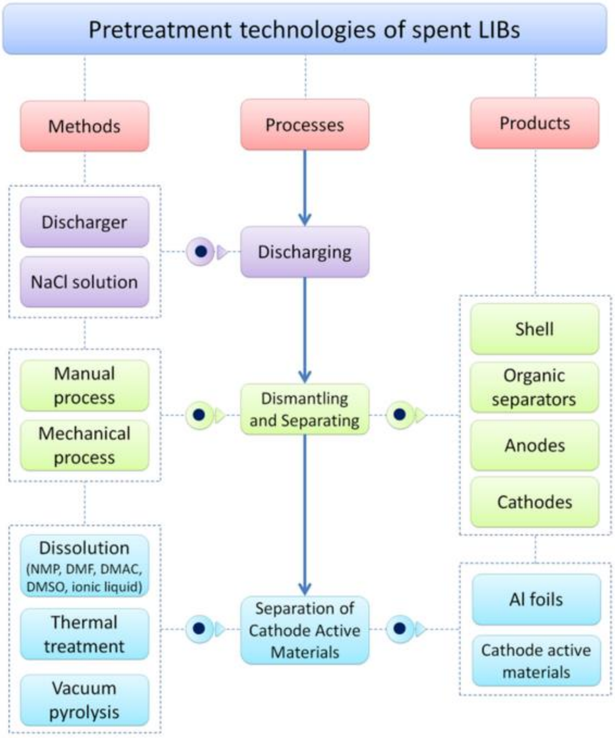

Figure 5. The pretreatment methods that can be used in the recycling of spent LIBs (Yao et al., 2018).

Another important thing to be done before recycling is the sorting of the batteries based on the chemistries used. This makes the overall process more efficient and reduces mixing of metals, which in turn can make the process more economical by decreasing the number of reagents and energy required. This can be a difficult task however, since the outer casing of the battery usually does not indicate what type of chemistry is used in the cathode (Winslow et al., 2018).

At first, the batteries to be recycled should be discharged for safety reasons. The discharging process prevents potential dangers such as self-ignition and short circuiting by discarding the remaining capacity in the battery (Yao et al., 2018). For example, NaCl can be used to discharge LIBs efficiently (L. He et al., 2017).

After discharging, the spent batteries are usually dismantled. The dismantling can be done manually by separating the battery into its different components or by a mechanical treatment.

Since manual dismantling is not very feasible for larger scale operation, the mechanical treatment is preferred. Often used methods for mechanical treatment include crushing, sieving, flotation, gravity separation and magnetic separation (Yao et al., 2018). During crushing there is the potential for explosion and combustion to happen. Thus, during crushing there should be an inert atmosphere and low temperature to prevent these hazards. Also, different gases may be released during crushing, which needs to be taken into consideration (Diekmann et al., 2017).

Sieving is another method used to separate components in batteries. Plastics, separators, and current collecting foils are mainly found in the coarse fraction, with particle sizes over 1 mm. Electrode materials are on the other mainly found in the fine fraction where particle size is less than 1 mm (X. Wang et al., 2016). Crushing and sieving can be utilized in combination to achieve a convenient range of particle sizes of the various components. This has proven to be beneficial in the leaching step as well (L. Li, Zhang, et al., 2018).

Separation by flotation depends on the different wettability of the electrode. The metal oxides in the cathode tend to be hydrophilic and graphite in the anode tends to be hydrophobic. One downside of flotation, however, is that often after crushing, the electrode materials may be covered with a layer of organic compounds from the electrolytes being decomposed. Thus, modifications are required to gain bigger differences in wettability. Gravity separation can be utilized to separate components that have different densities. Magnetic separation, on the other hand, can be utilized to remove magnetic impurities such as Fe (L. Li, Zhang, et al., 2018).

The dissolution process can be used in the separation of the electrode materials from the current collector sheets that they are attached to with binders. The process of dissolution is quite simple and efficient in the separation. A commonly used binder in LIBs is PVDF. Organic solvents, such as NMP (N-methylpyrrolidone), can be used to dissolve the binder since they are both polar and thus can dissolve into each other. Immersing the electrodes into NMP for a certain amount of time at a high temperature results in the electrode active materials being easily detached from the current collectors. The current collectors can also be recovered in their metal forms, which is an advantage. The disadvantages of the dissolution process are that the organic solvents are not able to remove all the impurities. Also, the solvents are expensive, and a single solvent is not capable of dissolving all types of binders, such as PTFE (polytetrafluoroethylene). The solvents can however be reused so that is a plus (Yao et al., 2018).

Thermal treatment as a pretreatment is also quite commonly used to remove organic compounds, binders as well as electrolytes from LIBs and to separate the electrode materials from the current collector sheets (L. Li, Zhang, et al., 2018). One example of using thermal treatment as a pretreatment is that at first spent LIBs are treated at a lower temperature of around 100 °C to separate the material from the current collectors. After this comes calcination at a higher temperature of 500-900 °C to combust carbon and the binder (Lee & Rhee, 2002). Thermal treatments are simple to operate and are suitable for operation at a larger scale. The disadvantages are that toxic gases and smoke emissions are released from the incineration of carbon and binders, and thus extra purification equipment is required. Also, the processes have a high consumption of energy (Yao et al., 2018).

3.1.2 Leaching

Leaching is an essential step in the recovery of valuable metals from used LIBs. Leaching is used to turn metals from solids to soluble forms and leach them into the solution to be recovered in the later steps. In LIB recycling the leaching is usually done as acid leaching, but alkaline leaching can also be used to dissolve Al foils. Most often inorganic acids are used but recently organic acids have gained more interest in academic research. Also, recently research has increased toward bioleaching using bacteria solution as the reagent for leaching. The leaching can also be intensified with different kinds of assisting methods, such as using ultrasound and mechanical processes to enhance the leaching efficiency (L. Li, Zhang, et al., 2018; Yao et al., 2018).

The most used inorganic acids for leaching have been sulfuric acid (Zhu et al., 2012; Kang et al., 2010; R. Zheng et al., 2016; Tang et al., 2014; Meshram et al., 2015; Meshram et al., 2016; L. Chen et al., 2011; Meshram et al., 2016), hydrochloric acid (J. Li et al., 2009; R. C. Wang et al., 2009) and nitric acid (Lee & Rhee, 2003). Very good efficiencies have been achieved with them when leaching LIB wastes. Some research and results for inorganic acids as leaching agents is shown in Table 3.

Table 3. Some research and results with inorganic acids as leaching agents for spent LIB wastes.

Reagents	**Electrode type**	**Temperature (°C)**	**S/L ratio (g/L)**	**Efficiency (%)**	**Ref.**
2 M H_2SO_4 + 2 vol-% H_2O_2	LCO	60	33	Co: 96.3; Li 87.5	(Zhu et al., 2012)
2 M H_2SO_4 + 6 vol-% H_2O_2	LCO	60	100	Co: 98; Li: 97	(Kang, Senanayake, et al., 2010)
4 M HCl	LCO	80	-	Co: 99; Li: 97	(J. Li et al., 2009)
1 M HNO_3 + 1.7 vol-% H_2O_2	LCO	75	10	Co: 99; Li: 99	(Lee & Rhee, 2003)
0.7 M H_3PO_4 + 4 vol-% H_2O_2	LCO	40	50	Co: 99.7; Li: 99.9	(X. Chen et al., 2017)
2.5 M H_2SO_4	LFP	60	100	Li: 97; Fe: 98	(R. Zheng et al., 2016)
4 M H_2SO_4 + 20 vol-% H_2O_2	LTO	80	25	Ti: 98; Li: 97	(Tang et al., 2014)
1 M H_2SO_4	Mix	95	50	Co: 66.2; Li: 93.4; Ni: 96.3; Mn: 50.2	(Meshram et al., 2015b)
1 M H_2SO_4 + 5 wt-% H_2O_2	Mix	95	50	Co: 79.2; Li: 94.5; Ni: 96.4; Mn: 84.6	(Meshram et al., 2016)
4 M H_2SO_4 + 10 vol-% H_2O_2	Mix	85	100	Co: 95; Li: 96	(L. Chen et al., 2011)
1 M H_2SO_4 + 0.78 wt-% $NaHSO_3$	Mix	95	20	Co: 91.6; Li: 96.7; Ni: 96.4; Mn: 87.9	(Meshram et al., 2016)
4 M HCl	Mix	80	20	Co: 99.5; Li: 99.9; Ni: 99.8; Mn: 99.8	(R. C. Wang et al., 2009)

As can be seen from Table 3 most research has been for LCO type batteries, and the focus has been on the leaching of Co and Li. Research for mixtures of different types of battery cathodes have also been gaining more attention. Hydrochloric acid is a very efficient leaching agent but usually H_2SO_4 is preferred since it is more economical, and it does not cause corrosion to process equipment. Also, during leaching with HCl, some Cl_2 is created, which can be an environmental problem. This means that special antisepticising equipment is required, which sequentially increases the costs of the recycling process (Yao et al., 2018).

When sulfuric acid or nitric acid is used for leaching, a reducing agent, such as H_2O_2, $NaHSO_3$ or glucose, is usually present. Having the reducing agent present means that the metals in the active materials can be converted to their divalent states. For example, Co is reduced from Co(III) to Co(II) and Mn is reduced from Mn(IV) to Mn(II). The divalent states of these metals are more soluble in water and thus the leaching efficiency is improved with the addition of the reducing agent. Hydrogen peroxide can also accelerate the leaching process. (Yao et al., 2018) For example, according to Lee & Rhee (2003) having hydrogen peroxide present can increase the leaching efficiency of both Co and Li when comparing to leaching with only nitric acid. When leached with just 1 M HNO_3, the efficiency for Co was 40 % and for Li 75 %. When H_2O_2 was added to the leaching the efficiencies increased to 80 % for both Co and Li (Lee & Rhee, 2003).

Even though inorganic acids have shown high leaching efficiencies of metals from cathode materials from spent LIBs, and over 99 % of Co and Li can be leached in certain circumstances, there are some drawbacks in using them. The biggest disadvantage is that during the leaching process some dangerous gases such as Cl_2, SO_3 and NO_x are likely to be created (L. Sun & Qiu, 2012). This is a risk to the environment and also to human health. This also increases the costs of the process since additional disposal of these gases is needed to be added to the recycling process. Another disadvantage is that the leachates produced in leaching often have a very low pH. Having a low pH makes the following recovery processes more complicated since the solution often needs to be neutralized to be processed more efficiently. For example, if impurities are removed from the solution by chemical precipitation more neutralizing agent is needed. Another disadvantage is that wastewater from the leaching process can contain high concentrations of strong acids and thus it needs to be properly treated to avoid secondary pollution, meaning again an increase in the costs of the whole recycling process (Yao et al., 2018).

Because of the disadvantages related to inorganic acids, in the recent years more interest has been shown towards using organic acids as leaching agent. Organic acids are easier to degrade and recycle. They are also less likely to cause secondary pollution to the environment while at the same time being acidic enough to efficiently leach cathode active materials from spent

LIBs (Yao et al., 2018). Some research and results from using organic acids in leaching is shown in Table 4.

Table 4. Some research and results from using organic acids to leach spent LIBs.

Reagents	Electrode type	Temperature (°C)	S/L ratio (g/L)	Efficiency (%)	Ref.
1.5 M succinic acid + 4 vol-% H_2O_2	LCO	70	15	Co: 100; Li: 96	(L. Li et al., 2015)
1.25 M ascorbic acid	LCO	70	25	Co: 94.8; Li: 98.5	(L. Li et al., 2012)
1.25 M citric acid + 1 vol-% H_2O_2	LCO	90	20	Co: 91; Li: 99	(L. Li et al., 2010)
1.5 M malic acid + 2 vol-% H_2O_2	LCO	90	20	Co:90; Li: 100	(L. Li et al., 2013)
1.5 M aspartic acid + 4 vol-% H_2O_2	LCO	90	10	Co: 60; Li: 60	(L. Li et al., 2013)
1.2 M DL-malic acid + 1.5 vol-% H_2O_2	NMC	80	40	Co: 94.3; Li: 98.9; Ni: 95.1; Mn: 96.4	(C. Sun et al., 2018)
1 M acetic acid + 6 vol-% H_2O_2	NMC	70	20	Co: 97.7; Li: 98.4; Ni: 97.3; Mn: 97.1	(L. Li, Bian, et al., 2018)
2 M maleic acid + 4 vol-% H_2O_2	NMC	70	20	Co: 98.4; Li: 98.3; Ni: 98.1; Mn: 98.1	(L. Li, Bian, et al., 2018)
3.5 M acetic acid + 4 vol-% H_2O_2	NMC	60	40	Co: 93.6; Li: 99.97; Ni: 92.7; Mn: 96.3	(Gao, Song, et al., 2018)
2 M citric acid + 2 vol-% H_2O_2	Mix	80	33	Co: 95; Li: 99; Ni: 97; Mn: 94	(X. Chen & Zhou, 2014)

As can be seen from the Table 4, many different organic acids, such as citric, malic, acetic and succinic acid, have been utilized with good efficiency for metals from both LCO and NMC type batteries. For example L. Li et al. (2013) researched three different organic acids for leaching in their publication. With citric and malic acid, they were able to reach nearly 100 % recovery of Li and over 90 % recovery for Co. However, the efficiency when using aspartic acid was considerably lower at around 60 % recoveries for both Li and Co. The researchers believe that the reason for lower efficiency was because aspartic acid is less acidic than the others and is less soluble in water. Also, the leaching with aspartic acid took a longer time even to achieve 60 % efficiency while a much shorter amount of time was needed for the other acids to achieve better efficiencies (L. Li et al., 2013).

Because organic acids are weak acids, they bring a few drawbacks to the leaching of spent LIBs. Organic acids are unable to completely dissolve cobalt oxides in the cathode materials even when enough of hydrogen peroxide is added as a reducing agent (L. Sun & Qiu, 2012). Also, they are not able to have complete reactions with the cathode material according to the stoichiometric ratio. This is due to the dissociation equilibrium of weak acids. For instance, when LCO type cathodes were leached with citric acid, the best results were able to be seen when the molar ratio between citric acid and LCO is up to 4:1. This is only because of the dissociation equilibrium (Yao et al., 2018).

When considering application of organic acids as a leaching agent for spent LIBs in industrial scale, there are some problems that may arise. In general, organic acids cost more than inorganic acids, which would raise the costs of the recycling. Another thing is that the kinetics of leaching for organic acids is typically slower than the speed for inorganic acids. Also, the solid to liquid ratio in leaching is often lower for organic acids than it is for inorganic acids. This means that the capacity for treating cathode materials per unit volume of organic acid is a lot less than the capacity of inorganic acid (Gao, Liu, et al., 2018). All these reasons combined mean that having organic acids as the leaching agent in industrial scale may not yet be efficient, even though there would be way less environmental pollution when compared to inorganic acids (Yao et al., 2018).

In the recent years, bioleaching has also gained a lot of interest as a possible technology for leaching spent LIBs. It is an appealing choice for leaching as it is more environmentally friendly, has lower cost and the industrial application is less demanding than with inorganic and organic acids. Previously, bioleaching has been mainly utilized in treating for example low-grade ores, spent catalysts, and fly ash (Yao et al., 2018).

Even though bioleaching is a very attractive choice for leaching, it still has some issues that need to be considered. The kinetics of bioleaching is quite slow which limits the chances for use in industrial scale. Also, the required microbes are quite laborious to develop effectively. These reasons mean that long treatment periods are needed to achieve efficient leaching even when catalysts are used. Another drawback of bioleaching is that it is capable of producing only low concentration solutions of metals. Having high concentrations of metals in the solution is considered to be toxic for the microbes. Having low concentrations of metals in the produced leachate on the other hand increases the difficulty in the following steps of the process. Thus, even though bioleaching might be very attractive in relation to the environment it may not be efficient enough when considering the whole recycling process. But bioleaching is still quite a new technology and more research is expected to be released in the future years possibly making the technology more profitable (Yao et al., 2018).

In all the leaching methods described above the purpose is that hydrogen ions interact with the cathode materials in acidic conditions. But another leaching method can also be used in alkaline environment. In this the hydroxide ions interact with the metals in the cathode materials. Most often NaOH is used for selective leaching of Al. This is possible because Al is an amphoteric metal which is capable of dissolving in both acidic and alkaline solution, whereas the other metals present in cathode materials, Co, Ni, and Mn, are insoluble in alkaline solution (Hu et al., 2013). Thus, alkaline leaching can be utilized before acid leaching to separate the Al from the material. This would make the downstream of the recycling process simpler since there would be one less metal to separate from the others. For example, Ferreira et al. (2009) found that up to 60 % of Al could be leached when using different concentrations of NaOH as leaching agent. The leaching efficiency of Al increased with the increase in NaOH concentration. Basically, no Co was leached in any experiment, but the leaching of Li was also dependent on the concentration of NaOH. When 15 wt-% NaOH was used, 58 % of Al could be leached and 12 % of Li was also leached. Since no Co was leached, they were able to conclude that NaOH does offer great selectivity for Al over Co (Ferreira et al., 2009).

Another commonly utilized alkaline leaching agent is ammonia. H. Ku et al. (2016) studied the leaching of LIB metals from cathode materials with ammonia, ammonium carbonate and ammonium sulfite. They were able to conclude that during the leaching, ammonium carbonate acts as a buffer for the pH and keeps the pH of the solution constant. Ammonium sulfite on the other hand can act as a reductant and reduce the oxidation states of Co and Ni to lower more soluble oxidation states. The divalent cations of Cu, Ni and Co can form a complex ion with ammonia, which can lead to an enhancement in the leaching rate. With the optimal conditions in leaching the researchers were able to completely leach both Co and Cu from the cathode active materials. Mn and Al were barely leached at all and some of Ni could be leached (H. Ku et al., 2016).

3.1.3 Recovery of valuable metals from leachate

After leaching, the metals from LIBs, such as Li, Co, Ni, Mn, Cu, Al, and Fe, are dissolved in the leachate. There are many methods that can be used to separate and recover these metals from the leachate. Some of these methods are solvent extraction, chemical precipitation, electrochemical deposition, and ion exchange. Since the leaching solution can be very complex with a lot of different metals, usually a combination of two or more methods are needed for efficient separation (Lv et al., 2018; Yao et al., 2018).

Chemical precipitation is often utilized in the separation of metals from LIBs. Precipitation depends on the distinct solubilities of the precipitation products. Most used precipitation chemicals are for example sodium hydroxide, oxalic acid, ammonium oxalate, and sodium carbonate. These precipitants can all react with Co and Li to create insoluble precipitates of $Co(OH)_2$ (Pegoretti et al., 2017), CoC_2O_4 (Nan et al., 2005; L. Sun & Qiu, 2012; Zhu et al., 2012), and Li_2CO_3 (Nan et al., 2005; Zhu et al., 2012). Precipitation can also be used to separate impurities, such as Fe, Cu, and Al, from LIB waste leachates (L. Chen et al., 2011; Joo, Shin, Oh, Wang, Senanayake, et al., 2016). Precipitation is depends on the varying solubilities of the compounds at specific pH values and temperature, which thus need to be carefully monitored during operation (L. Li, Zhang, et al., 2018). One example of metals precipitation by sodium hydroxide and sodium carbonate is shown Figure 6.

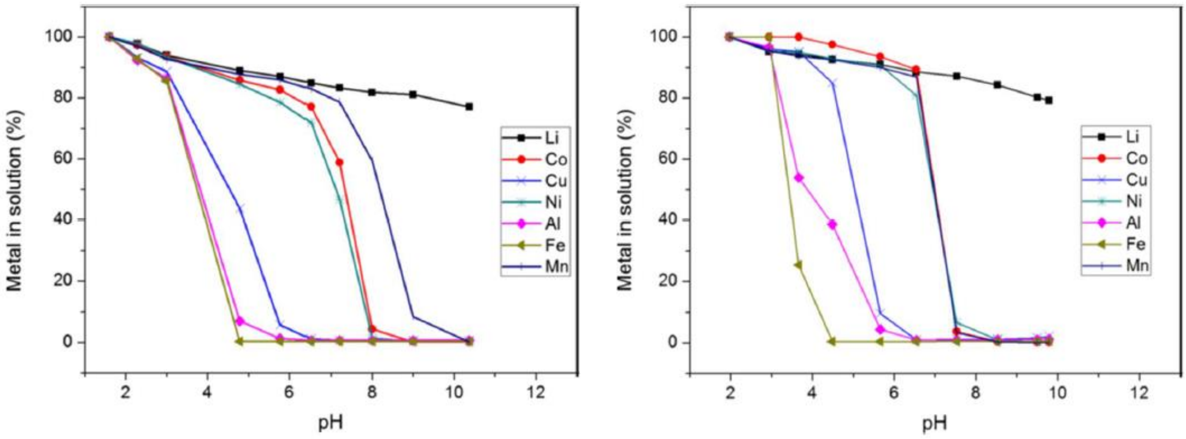

Figure 6. Precipitation of metals with NaOH (left) and Na_2CO_3 (right) at a temperature of 40 °C (H. Wang & Friedrich, 2015).

As can be seen from the Figure 6 when using NaOH and Na_2CO_3 to precipitate metals, the selectivities for impurity metals are not very good. It seems that there will inevitably be some substantial losses of valuable metals if Fe, Al, and Cu would be removed completely with precipitation by NaOH.

Since the LIB leachates are often so complex and many metals are present, more than one precipitation step is usually required to separate valuable metals. For example, in their research H. Wang & Friedrich (2015) suggested a process with multiple precipitation steps.. In their suggestion Fe and Al are removed first with precipitation by alkali at a pH of 3.5-4. Afterwards, cathode materials, Co, Ni, and Mn, are co-precipitated with either sodium hydroxide or sodium carbonate by increasing the pH to 10. Lastly, Li was also crystallized with the addition of sodium carbonate to form lithium carbonate (H. Wang & Friedrich, 2015).

Another example of a recycling process with multiple precipitation steps was studied by X. Chen et al. (2016). They studied the separation of Mn, Ni, Co and Li from a leachate solution with multiple precipitation steps. First, Mn is precipitated as manganese oxides (MnO_2 or Mn_2O_3) with the addition of a potassium permanganate (0.5 M $KMnO_4$) solution. Afterwards, Ni, Co and Li were recovered step by step as their precipitates. Ni was recovered by dimethylglyoxime (0.2 M DMG, $C_4H_8N_2O_2$) as $Ni(C_4H_6N_2O_2)_2$, Co was recovered by oxalic acid (0.5 M $H_2C_2O_4$) as $CoC_2O_4 \cdot 2H_2O$, and Li was recovered by phosphoric acid (0.5 M H_3PO_4) as Li_3PO_4. All the metals could be recovered with a high efficiency and a high purity. The recovery rate for Ni was 98.5 %, for Co 96.8 % and for Li 92.7 %. The obtained products had purities of 99.3 % for Ni, 98.9 % for Co and 99.5 % for Li (X. Chen et al., 2016).

Usually, Li in the leach solution is precipitated as Li_2CO_3 by adding saturated sodium carbonate to the solution. Before precipitation, the leachate needs to be concentrated because Li_2CO_3 is slightly soluble in water and the concentration of Li in the leachate can be low. Also, the solubility of Li_2CO_3 is inversely proportional to temperature. Thus, the precipitation is often done at a high temperature in order to precipitate as much as possible of Li_2CO_3. Because of these reasons there is an increase in the energy intake of the process (Yao et al., 2018).

Direct coprecipitation of battery precursors is often used to decrease the amount of needed precipitation steps (Gratz et al., 2014; L. P. He et al., 2018; Zhang et al., 2018). In co-precipitation, the concentrations of Ni, Mn and Co are altered to wanted values and the metals are precipitated together. Again, sodium hydroxide, sodium carbonate or oxalic acid can be used to create precipitants in the forms $Ni_xCo_yMn_{1-x-y}(OH)_2$, $Ni_xCo_yMn_{1-x-y}CO_3$ or $Ni_xCo_yMn_{1-x-y}C_2O_4$, respectively. The precipitants can then be reacted with lithium carbonate at a certain stoichiometric ratio to form cathode materials in the form of $LiNi_xCo_yMn_{1-x-y}O_2$ (Gratz et al., 2014).

All in all, chemical precipitation is quite widely utilized in LIB recycling because the requirements for equipment are low, the operation is simple, and the costs are low. Some of the used precipitation methods are compiled to Figure 7. The key factors that need to be considered in precipitation are choice of fitting precipitants and finding the ideal settings where precipitate dissolution and possible losses of valuable metals are prevented (L. Li, Zhang, et al., 2018).

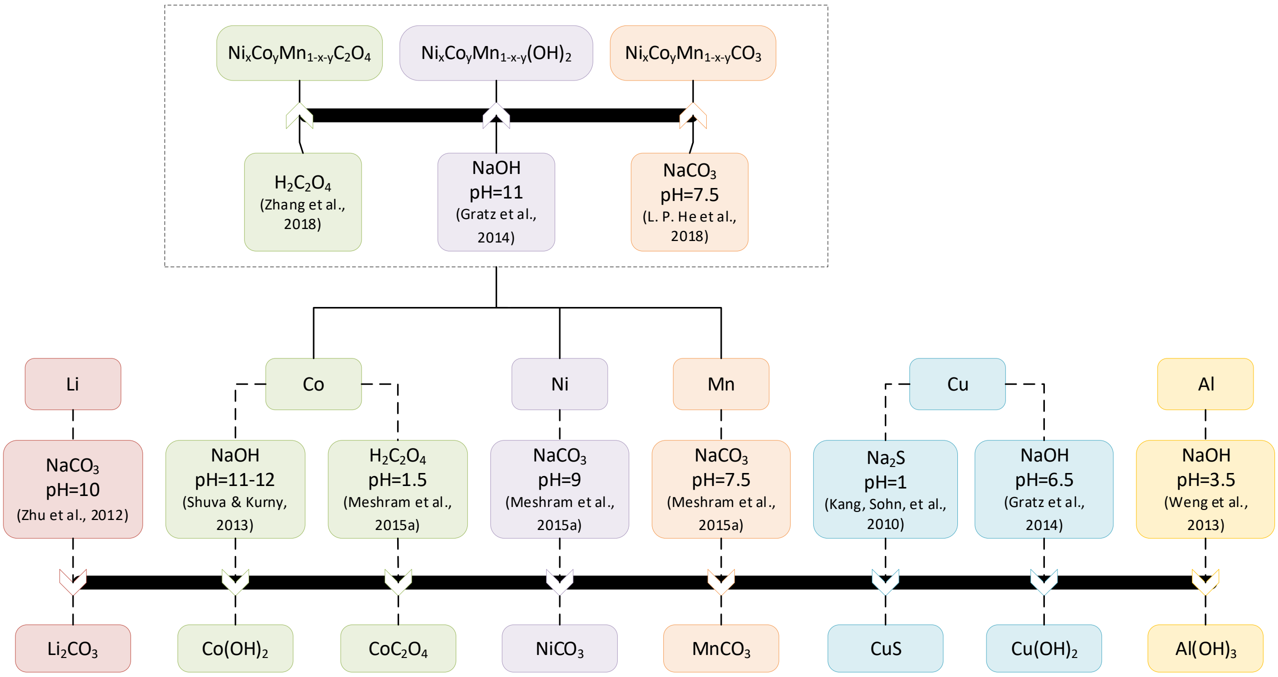

Figure 7. Some precipitation methods used in the recycling of LIBs (Yao et al., 2018; Zhang et al., 2018; L. P. He et al., 2018; Zhu et al., 2012; Shuva & Kurny, 2013; Meshram et al., 2015a; Kang, Sohn, et al., 2010; Gratz et al., 2014; Weng et al., 2013)

Solvent extraction has been extensively utilized in different hydrometallurgical processes. It is an efficient way to separate valuable metals because the extractants have a high selectivity for different metal ions. Metal ions are extracted from an aqueous phase into organic phase though reversible chemical reactions. The metals form organic-soluble complexes with the extractant. The extractant usually has a low solubility in water and it is often diluted in a kerosene-based hydrocarbon solvent due to the viscosity of the extractant. During mixing, one of the phases (aqueous or organic) is dispersed within the other one. This creates a big surface area, and the metal compounds can move to the other phase over the surface area (Kislik, 2012).

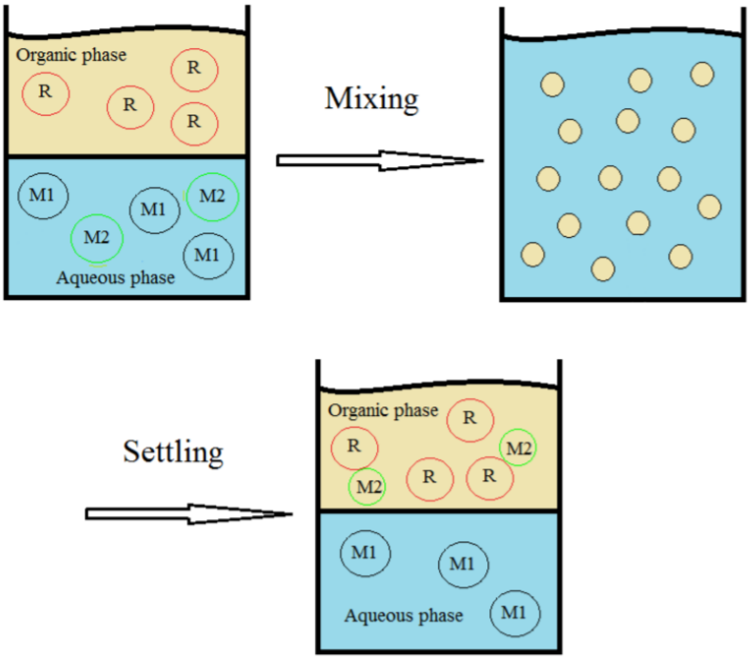

Figure 8. The basic principle of solvent extraction. R symbolizes the reagent and M1 and M2 represent different metals (Virolainen, 2013).

Solvent extraction reagents can be divided based on their extraction mechanisms into three categories, compound forming, ion associating and solvating extractants. Compound forming extractants include acidic and/or chelating extractant and the mechanism for extraction is cation exchange. Ion associating extractants include amine extractants, which can extract ion pairs and anionic species through anion exchange. Solvating extractants include oxygen or phosphorus containing extractants, which make metal complexes or inorganic molecules more soluble to the organic phase (Kislik, 2012). The typical reaction for acidic and chelating (compound forming) extractants is shown in Equation 1 (Virolainen, 2013).

$$\mathrm{M^{n+}} + \mathrm{n}\overline{\mathrm{HA}} \rightleftarrows \overline{\mathrm{MA_n}} + \mathrm{nH^+}, \quad (1)$$

Where $\mathrm{M^{n+}}$ metal cation with charge n+

$\overline{\mathrm{HA}}$ extractant

$\overline{\mathrm{MA_n}}$ metal complex of extractant.

The most used extractants in LIB recycling include acidic extractants such as di(2-ethylhexyl) phosphoric acid (D2EHPA), bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), trioctylamine (TOA), neodecanoic acid (Versatic 10), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A). Hydroxyoxime reagents can also be used, like 2-hydroxy-5-nonylacetophenone oxime (LIX84-I) and 5-nonyl-2-hydroxy-benzaldoxime (Acorga M5640). These are usually used to separate particular metals from the leachate leaving Li into the aqueous solution (L. Li, Zhang, et al., 2018; Yao et al., 2018).

The solvent extraction circuit typically includes extraction, scrubbing, and stripping steps. In the extraction or loading step, the metals are extracted from the aqueous phase into the organic phase with the extractant. The loaded extractant can then be scrubbed with for example the target metal salt to get the possibly co-extracted impurities removed. The raffinate from scrubbing can be recycled back to the extraction and combined with the aqueous feed. After scrubbing, the scrubbed organic is stripped usually with some acid. The loaded target metals are transferred back from the organic phase to the aqueous phase and recovered this way. The stripped organic phase can then be recycled back to the extraction. Some other regeneration or washing way be needed before the extractant is used again (Kislik, 2012). Some research into using solvent extraction in LIB recycling is summarized in Table 5.

Table 5. Some research and results about using solvent extraction in the recycling of LIBs.

Extractant	Solution composition (g/L)	Extraction	Scrubbing	Stripping	Ref.
D2EHPA	Co: 0.18; Ni: 0.01; Mn: 5.3; Li: 1.2	20 vol-% D2EHPA, 70-75 % saponified, pH 5, A/O 1, Mn: 97%	-	0.1 M H_2SO_4, A/O 1	(X. Chen, Zhou, et al., 2015)
Mextral 5640H	Ni: 4.3; Co: 7.2; Mn: 5.7; Li: 1.5; Cu: 1.8	10 vol-% Mextral 5640H, pH 1.94, A/O 2, Cu: 100 %	-	0.2 M H_2SO_4, A/O 1	(X. Chen, Xu, et al., 2015)
Ni loaded Mextral 272P	Ni: 4.3; Co: 7.2; Mn: 0.045; Li: 1.5	20 vol-% Mextral 272P, pH 4.5, A/O 1, Co: 97.8 %	5 g/L Na_2CO_3, A/O 1, 10 min, Li: 100 %	0.1 M H_2SO_4, A/O 1, 5 min, Co: 99 %	(X. Chen, Xu, et al., 2015)
Co-D2EHPA	Co: 6.4; Ni: 0.089; Mn: 6.3; Li: 1.6	15 vol-% Co-D2EHPA, pH 3.5, O/A 1, Mn: 97.1 %	5 w/v oxalic acid, Co: 100%	0.1 M H_2SO_4, A/O 0.5, Mn: 99 %	(X. Chen, Chen, et al., 2015)
P507	Co: 20; Ni: 0.5; Li: 2.5	25 wt-% P507, initial pH 3.5, O/A 1.5, Co: 95 %, <5 % Ni and Li	-	3 M H_2SO_4, O/A 4	(L. Chen et al., 2011)
Cyanex 272	Co: 13.8; Ni: 0.015; Mn: 0.011; Li: 2.04	0.4 M Cyanex 272, 50 % saponified, pH 5.5-6.0, A/O 1, 95-98 % Co, 1 % Ni	-	2 M H_2SO_4, O/A 11.7	(Kang, Senanayake, et al., 2010)
LIX 84-I + Versatic 10	Co: 7.9; Ni: 7.6; Mn: 7.6; Li: 3.2	0.23 M LIX 84-I + 1.41 M Versatic 10, pH 5, O/A 1, 93% Ni	-	3 M H_2SO_4	(Joo, Shin, Oh, Wang, Senanayake, et al., 2016)
D2EHPA + Versatic 10	Co: 11.4; Ni: 12.2; Mn: 11.7; Li: 5.3	0.43 M D2EHPA + 0.7 M Versatic 10, pH 4.5, O/A 1, Mn: 98.33 %, Co: 4.11 %, Ni: 1.06 %, Li: 0.25 %	0.1 M EDTA, O/A 4	0.5 M H_2SO_4, O/A 2	(Joo, Shin, Oh, Wang, & Shin, 2016)
PC-88A	Co: 25.1; Ni: 2.5; Li: 6.2	0.56 M PC-88A, 60 % saponified, O/A 3, pH 4.5	2.0 g/L $CoSO_4$, pH 4.75, O/A 2	0.2 M H_2SO_4, O/A 1	(Nguyen et al., 2014)
Cyanex 272 + TOA	Co: 14; Ni: 0.5; Li: 2.8	1 M Cyanex 272 + 5 vol-% TOA, pH 6.8-7.1, A/O 0.77, 99.9 % pure Li_2SO_4 raffinate	0.3 g/L $NiSO_4$, pH 6.5, O/A 1.5	0.025 M H_2SO_4, pH 5-6, O/A 1.5, 99.6 % pure Co in org. phase, 99.7 % pure Ni in aq. phase	(Virolainen et al., 2017)

Even though, using a single extractant is more common, there has also been some research where a mixture of extractants is utilized to improve the separation of valuable metals. For example, Pranolo et al. (2010) used a blend of 2 vol-% Acorga M5640 and 7 vol-% Ionquest 801 in impurity removal of synthetic LIB waste solution. They tried to separate impurities of Cu, Fe, and Al from the solution, which contained 16.9 g/L Co, 3.8 g/L Li, 0.6 g/L Fe, 0.15 g/L Ni, 0.7 g/L Al and 0.4 g/L Cu. During extraction they observed a considerable shift in the pH isotherm for Cu when Acorga M5640 was added to Ionquest 801. At the same little or no effect was noticed with the isotherms for Fe and Al. Thus, they suggested that Ionquest 801 was the extractant while Acorga M5640 creates a synergism in the extraction of Cu. With this synergistic extraction they were able to extract basically all the Fe, Cu, and Al from the solution leaving only Co, Ni, and Li into the raffinate. After the impurity removal, Co was extracted with 15 vol-% Cyanex 272. The Ni and Li that remaimed in the raffinate could be separated with an anion exchange resin such as Dowex M4195 (Pranolo et al., 2010).

In addition to the synergistic effect, also the antagonist effect of extractants has been researched to improve the separation of valuable metals from LIB wastes. For example, Joo, Shin, Oh, Wang, & Shin (2016) studied the extraction of Mn from Co, Ni, and Li with the use of a blend of Versatic 10 and D2EHPA. Adding Versatic 10 provided an antagonist effect. The loading capacity of D2EHPA was decreased for Co and Mn and the extraction of Co to D2EHPA was disrupted. Thus, increasing the concentration of Versatic 10 in the system decreased the distribution coefficient of both Co and Mn. Simultaneously, the separation factor value of Mn over Co increased from 14.3 to 33.97. As a result, 98.3 % Mn could be extracted with only 4.11 % Co, 1.06 % Ni, and 0.25 % Li co-extraction. The co-extracted impurities of Co, Ni and Li could be efficiently scrubbed from the loaded extractant using 0.1 M EDTA solution with a phase ratio O/A of 4. The stripping was done with 0.5 M H_2SO_4 with a phase ratio O/A of 2 and 99.8 % of Mn could be stripped from the loaded and scrubbed extractant with a very a high purity (Joo, Shin, Oh, Wang, & Shin, 2016).

Solvent extraction can produce high purity metals with a high efficiency. It is also often done at room temperature or near and a short time is needed for the reactions to occur. The disadvantages of solvent extraction are that the process can be quite complex to operate, and the solvents used can have high costs. Thus, in the future there should be more research into cheaper solvents and to the efficient recycling the solvents in the process (L. Li, Zhang, et al., 2018).

3.2 Industrial recycling

The main methods for industrial recycling of LIBs used include pyrometallurgy, hydrometallurgy, and a combination of the two. Typically, the recycling process includes sorting, classification, mechanical treatment, pyro- or hydrometallurgical treatment and waste disposal. The recycling companies often collaborate with recycling companies to ensure sufficient recycling amounts (L. Li, Zhang, et al., 2018). Some of the industrial processes used to recycle LIBs are summarized in Table 6.

Table 6. Summary of some of the current industrial scale LIB recycling processes (Heelan et al., 2016; Lv et al., 2018; Sonoc et al., 2015; Winslow et al., 2018).

Company/ process	**Location(s)**	**Annual capacity (tons)**	**Description**
Umicore (VAL'EAS)	Belgium/ Sweden	7000	Pyrometallurgical smelting produces a slag and an alloy of Co, Ni, Co, and Fe. Alloy processed with hydrometallurgy to recover Co and other metals. Li lost in slag
Retriev technologies (Toxco Inc.)	Canada/ USA	3500	Mechanical processes to reduce size and separate material into fractions. Hydrometallurgy to recover Li and Co
Sony-Sumitomo	Japan	150	Calcination at 1000 °C to burn plastics and organic solvent. Residue processed with hydrometallurgy to recover Co. Li lost in fly ash and not recovered.
ReCupyl (Valibat)	France	110	Mechanical process to reduce size and separate into different fractions. Cu, Al, and plastics removed with physical process. Li and Co recovered with hydrometallurgy.
Accurec	Germany	4000	Mechanical treatment and vacuum pyrolysis to remove plastics, electrolyte, and solvent. Further mechanical treatment to remove Al, Cu, and steel. Pyrometallurgical smelting to produce an alloy of Co and Mn. Li ends up in slag, which can be processed with hydrometallurgy to recover Li_2CO_3
Batrec	Switzerland	1000	Mechanical process to reduce size in inert atmosphere. Material then processed with leaching and solvent extraction.
OnTo (Eco-Bat Process)	USA	-	Discharging before dismantling. Further processing with CO_2 in the form of supercritical fluid.
Inmetco	USA	6000	Pyrometallurgical process to produce an alloy of Co, Ni, and Fe. Graphite and organic material consumed and used as reducing agents. A slag also produced containing unrecoverable Li.
AEA	UK	-	Mechanical process to reduce size. Acetonitrile and NMP used to remove electrolyte, solvent, and binder. Li and Co leached from the cathode by electrolyzing the cathode material in LiOH, which results in CoO_2 and additional LiOH
Glencore plc. (formerly Xstrata)	Canada/ USA	7000	Combined pyrometallurgical/hydrometallurgical process to recover Co, Ni, and Cu. Other materials are either consumed as reducing agents or slagged.
SNAM	France	300	Series of mechanical and pyrometallurgical steps to produce a ferro Co alloy and ferro Ni alloy.
AkkuSer Ltd.	Finland	4000	Two-phase crushing line followed by magnetic and other separation methods. Scrap delivered to smelting plants and leaching.

4 FLUORIDE IN LI-ION BATTERIES

Fluoride is usually present in LIBs in the electrolyte and in the binder. It needs to be considered in the recycling of LIBs, since it is hazardous itself and it can produce toxic compounds during the recycling. In many recycling processes the fluoride containing components are removed before leaching so that the remaining process steps are safer.

In the electrolyte fluoride is present in the Li salt. The most common used is Li hexafluorophosphate ($LiPF_6$). It can react with water to create the highly corrosive and toxic hydrogen fluoride according to Equation 2. Other toxic products can also be created during the decomposition of $LiPF_6$, such as phosphorous pentafluoride (PF_5) and phosphor oxyfluoride (POF_3) (Nowak & Winter, 2017).

$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2\ HF \tag{2}$$

The binder that is often used is polyvinyl fluoride (PVDF). It can also easily decompose to HF especially at higher temperatures.

4.1 Safety considerations

Gaseous hydrogen fluoride and aqueous hydrofluoric acid are toxic and corrosive even in small concentrations. Direct effects of low concentrations cause irritation in the eyes and airways. The symptoms of exposure to HF can be however delayed. If the concentrations are high, HF can cause damages to the skin, eyes, and mucous membranes. In gaseous phase HF can cause irritation and redness as well as respiratory corrosion (Työterveyslaitos, 2017).

HF can react with many materials, and it can corrode glass, leather, and other metals. Thus, it is important to consider what kind of vessels are used when there might be HF present. HF itself is not flammable but when it reacts with other materials it can create flammable hydrogen gas. It can also react with moisture in the air to form hydrofluoric acid which falls to the surfaces of the room. There is a possibility that it can accumulate on surfaces if not cleaned properly (Työterveyslaitos, 2017).

Proper safety measurements need to be taken when working with LIBs that contain fluoride and HF as well as other hazardous components. The working area needs to be isolated so that other areas do not get contaminated. The working area needs to have fume hoods and proper ventilation. Working surfaces need to be cleaned with alcohol after working. Personal protection equipment needed include nitrile gloves under long sleeved acid resistant gloves, safety boots, overalls, motorized gas mask, and HF gas detector/alarm (Nissi, 2019).

4.2 Fluoride in LIB recycling

In many LIB recycling processes there is usually a pretreatment step that removes the electrolyte and separates the electrodes from all the other materials. This makes the treatment of cathode active materials more efficient and there is no need for a separate fluoride removal step. The pretreatment step can include for example some sort of thermal treatment or crushing and sieving. The electrolyte is usually not recovered but combusted or disposed of (Diekmann et al., 2017).

One example of a LIB recycling process that removes the fluoride components before leaching is the LithoRec process. The pretreatment steps in the LithoRec process include discharging, disassembly, crushing, drying and mechanical separation processes. The crushing step in the process must be done under inert atmosphere since the flammable electrolyte components are still present. The released gases from the crushing can be cleaned with activated carbon (Diekmann et al., 2017).

After the crushing is the drying step, in which the remaining electrolyte components are removed. The organic solvents of the electrolyte are vaporized under decreased pressure and temperatures around 100 to 140 °C. The solvents can be recovered after the vaporization by a thermal post-combustion process which regains the thermal energy. The electrolyte salt $LiPF_6$ also decomposes during the drying and creates HF gas. A gas scrubber is thus needed to handle the toxic gas. Removing the electrolyte makes the rest of the process safer since there is no HF generation and the flammable solvents have been removed (Diekmann et al., 2017).

Other methods to remove fluoride containing components include using organic solvents to dissolve PVDF binders and extraction of the electrolyte with sub- or supercritical CO_2. During the CO_2 extraction, the electrolyte components can also be recovered, which is a big advantage since the conducting salt is very expensive (Nowak & Winter, 2017).

If the fluoride, however, is not removed with the pretreatment and it ends up being leached, hydrofluoric acid is created because of the acidity of the leaching solution. In addition, the fluoride can cause corrosion of equipment and it can act as a complexing agent for Al and Fe. The chemical behavior of Al and Fe can thus be altered. There is little research about how fluoride behaves in the hydrometallurgical LIB recycling processes. It is suggested that the fluoride should be removed in the beginning of the process to avoid further health and safety risks. A good method of removal would likely be precipitation as CaF_2. However, the precipitation is highly dependent on pH and the reaction only happens to a certain degree when pH is below 7 (Figure 9). In addition, it expected that gypsum is also precipitated, and another cation impurity is added to the already complex solution. Another alternative to manage fluoride could be to selectively wash the black mass in alkaline conditions before leaching. The removal of halogens by selective washing is in industrial practice and it might be suitable in the case of fluoride as well (Brückner et al., 2020).

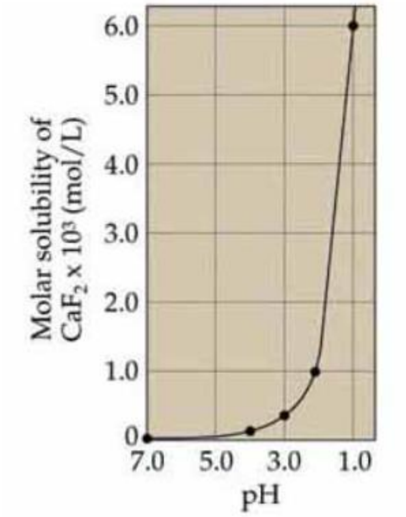

Figure 9. The molar solubility of calcium fluoride as a function of pH.

4.3 Possible fluoride removal methods from LIB leachates

The traditional method for removing fluoride from water is precipitation with lime. The fluoride reacts with the calcium to form fluorite (CaF_2). The precipitate can then be removed from the water with filtration or coagulation and clarification. However, the precipitation with lime can only reduce the fluoride concentration to 10-20 mg/l, which means that more treatment is still needed if the water is intended for drinking water (Bhatnagar et al., 2011; Shen et al., 2003).

For example, Ezzeddine et al. (2015) studied the precipitation of fluoride with calcium hydroxide (lime) and calcium carbonate (limestone). They were able to remove over 95 % of fluoride from aluminum fluoride manufacturing wastewaters, which contained up to 5 g/L of fluoride. They concluded that precipitation with limestone needs a higher molar ratio of calcium to fluoride to be able to precipitate as much as when using lime. They also suggested that the precipitated solid CaF_2 could be reused in the manufacturing of HF. The precipitated solids were mainly CaF_2 with small amounts of silica, and they are acceptable in the manufacturing of HF in small quantities (Ezzeddine et al., 2015).

There has also been a lot of research for fluoride adsorption with different types of adsorbents (Bhatnagar et al., 2011). For example, Ku & Chiou (2002) studied the adsorption of fluoride by alumina. According to them, the adsorption of fluoride is dependent on the binding between fluoride species and the active sites on the surface of the adsorbent. Some of the Al from the alumina may be dissolved and some Al-F complexes can be formed. In acidic and neutral solutions various Al-F complexes are dominant (Figure 10). They concluded that the optimum operating pH was in the range 5-7. Also, in acidic and neutral solutions, the presence of sulfate ion was proved to be interfering for the adsorption (Y. Ku & Chiou, 2002).

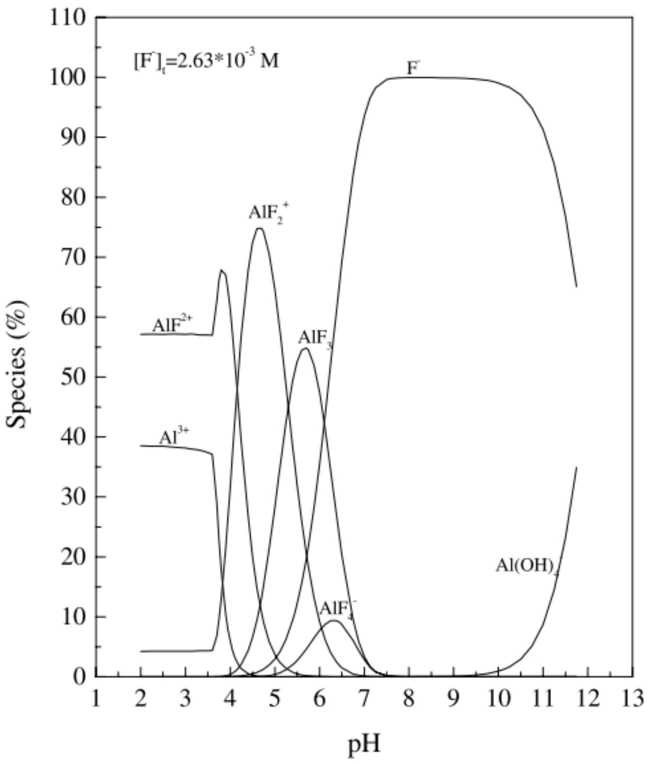

Figure 10. Species distribution of fluoride in aqueous solution in the presence of 0.004 M Al ion as a function of pH (Y. Ku & Chiou, 2002).

If fluoride were to be removed with precipitation as CaF_2, the pH of the solution would have to be increased quite a lot. In the beginning the typical LIB leachates have quite a low pH and the increase in pH might lead to losses in valuable metals. Also, if calcium were to be added to the solution, there would be another impurity cation in the already complex solution and the process might become even more complex. But since it is not exactly known how fluoride behaves in possible further processing of leachates it is also important to study the effects it may have.

In conclusion, it would be easiest to remove the fluoride before leaching in the pretreatment steps. Fluoride reacts quite easily with humidity and air to create HF gas. So most likely most of the fluoride could be removed as gas by some sort of thermal treatment. There would need to be gas scrubbers to deal with the gases, but the removal would be easier than having to deal with the possibility of hydrofluoric acid formation and corrosion of equipment in addition to there being more health and safety risks.

5 MATERIALS AND METHODS

The aim of the experimental part is to demonstrate in practice the separation of metals from a synthetic leachate that resembles actual leach solutions of LIB wastes. The metals are separated with of solvent extraction and precipitation unit processes. The goal is to create a techno-economically efficient and realistic flowsheet that could be used in the future in the planning of a LIB waste recycling plant. The starting point for the experiments is shown in Figure 11 as a simplified flowsheet of the process. From there, the process is started to be optimized with the experiments described below.

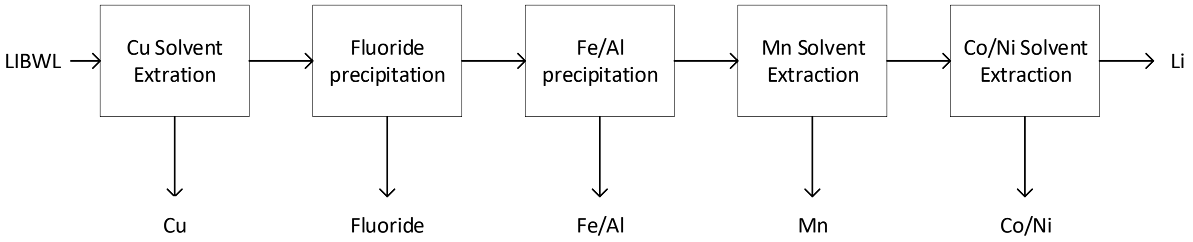

Figure 11. Simplified process flowsheet used as the starting point in the experiments.

At first, solvent extraction is used to remove Cu from the solution. Then, fluoride is possibly precipitated out with calcium hydroxide. After that, Fe and preferably Al are precipitated with sodium hydroxide. If Al cannot be totally separated with precipitation, it will be separated in the next stage together with Mn. Solvent extraction is again used for Mn and possible Al separation. In the final stage, Co and Ni are separated together with solvent extraction, leaving pure Li into the raffinate. The obtained Co and Ni solution could be used as a precursor in the manufacturing of Li-ion battery cathodes.

5.1 Materials

The feed solution used in the experiments was a synthetic solution resembling actual leach solutions of LIB wastes. The synthetic solution was prepared by Metso Outotec at their research center in Pori and it was used throughout the experiments. The composition of the solution is presented in Table 7.

Table 7. Composition of the synthetic Li ion battery waste leachate solution used in the experiments. The concentrations were measured at LUT.

Compound	Concentration, mg/L
F^-	530
Li	5070
Mg	127
Al	2250
Mn	8330
Fe	554
Co	7610
Ni	24900
Cu	1630

The used extractants are presented in Table 8. They were all diluted to the wanted concentration by kerosene (Exxsol D80, ExxonMobil Chemical).

Table 8. The extractants used in the experiments.

Extractant	Chemistry	Purity	Manufacturer/supplier
Acorga M5640	5-Nonyl-2-hydroxy-benzaldoxime	30-60 %	Cytec
Cyanex 272	Bis(2,2,4 trimethylpentyl)phosphinic acid	88 %	Cytec
D2EHPA	Di-(2-ethylhexyl)phosphoric acid		Sigma-Aldrich
TOA	Trioctylamine	98 %	Sigma-Aldrich
TBP	Tributyl phosphate	97 %	Sigma-Aldrich
Versatic Acid 10	Neodecanoic acid		

Other chemicals used included sodium hydroxide (Merck, pro analysi), sulfuric acid (Merck, 95-97 %), hydrochloric acid (VWR Chemicals, 35 %), calcium hydroxide (Merck, pro analysi), and sodium acetate (Merck, pro analysi).

5.2 Equipment

Batch experiments were done in jacketed glass reactors. For initial experiments, the reactor used was 1 L in size. For larger batch experiments with precipitation the reactor size was 3 L. The temperature of the reactor was adjusted with a Lauda Eco Silver heating thermostat.

Continuous counter-current solvent extraction experiments were done in MSU-0.5 laboratory scale pilot unit provided by MEAB Metalextraktion AB, Sweden. The pilot has a similar geometry than industrial mixer-settlers (Figure 12). The units are self-contained mixer-settler units, and they can be arranged in wanted configurations. The active mixer volume is 0.12 L, and the settler volume is 0.48 L. The units have a thermal insulation, but the temperature of the units has to be controlled by heating the feed solutions. The pumps used in the feeding of the solutions to the unit were ProMinent gamma/XL pumps.

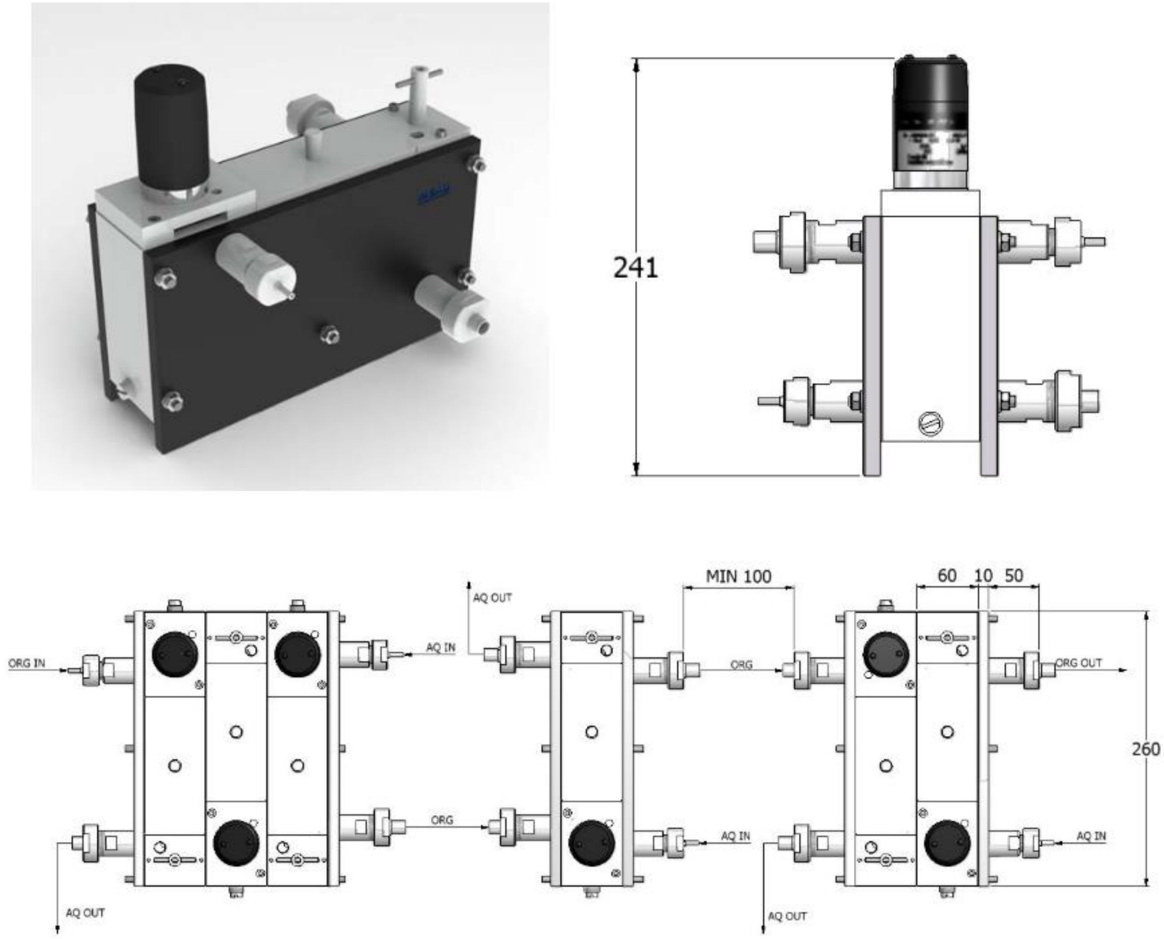

Figure 12. The schematic of the mixer-settler unit used in continuous counter-current solvent extraction experiments (MEAB, 2010).

5.3 Analyses

Metal concentrations from samples were measured with ICP-MS (Agilent 7900). Metals from organic samples were first backextracted to aqueous phase with 5 M hydrochloric acid at a phase ratio of A/O = 20. Samples were first diluted with pure water and then with a matrix acid solution which contained 1 % HCl (35-37 %) and 1 % HNO_3 (67-69 %). Solid samples from precipitation were first washed with pure water, dried, dissolved into sulfuric acid and then analyzed with ICP-MS.

Fluoride concentrations in samples were measured with Sentek Fluoride combination Ion Selective Electrode (ISE). The samples and standards were diluted with 15 % sodium acetate to buffer the pH of the samples to 4-5. This was necessary since some of the samples might be very acidic and in acidic conditions the fluoride is often complexed with hydrogen as hydrofluoric acid, which the ISE cannot detect. So, buffering the pH a bit higher decomplexes the fluoride into free fluoride ions, which the ISE can detect. Total ionic strength adjustment buffer (TISAB) was also added to all standards and samples. The TISAB also preferably complexes Fe and Al in samples that might be complexed with fluoride and interfering with the measurement. Some fluoride concentrations were measured by Metso Outotec at their Research Center in Pori.

5.4 Conducting the experiments

Brief descriptions of the experiments are provided in the following chapters. Since the experiment parameters were quite different for the different steps in the process, more details on them are given with the results in Chapter 6.

In precipitation experiments a certain amount of solution was put into a jacketed glass reactor and stirring was applied. The temperature during the experiments was 50 C and it was adjusted by circulating water in the jacket of the reactor. The pH of the solution was adjusted with the addition of 5 M NaOH. The amount of NaOH was recorded and the addition was taken into consideration in the final results by data treatment if needed. Samples were taken at different pH values so that the pH value was stable for 15 minutes before taking the sample.

The continuous counter-current solvent extraction runs were performed with the MEAB mixer-settlers mentioned above. The phase ratio and residence time in the mixer were adjusted by adjusting the flowrates of the aqueous and organic feeds. The pH and temperature in mixers of the cascade were measured online. Sometimes the pH needed to be adjusted and then NaOH was fed into the mixer with a syringe pump. The temperature of the cascade could be only adjusted by heating the feeds of the flows and some heat loss in the cascade was detected so that there was a temperature gradient in the cascade. Samples were taken from the outlets of the equipment at certain time intervals.

The solvent extraction pH isotherms were conducted in a 1 L glass jacketed reactor at a temperature of 25 °C. The phase ratio in the isotherms was O/A = 2:1. The aqueous and organic phases were added to the reactor and stirring was applied. The pH of the dispersion was adjusted with the addition of 5 M NaOH. Samples were taken from the dispersion at different pH values.

The solvent extraction loading isotherm was also conducted in a 1 L glass reactor at a temperature of 25 °C. The phase ratio of the system was changed by adding a certain amount of fresh organic to the mixture. After addition, the pH of the dispersion was adjusted to the wanted value by adding 5 M NaOH. After pH adjustment some fresh organic might have been added to adjust the phase ratio to the correct value. After the pH and phase ratio were adjusted, the solution was equilibrated for 15 minutes. The stirring was stopped, and the phases were let to separate. Samples were taken from both phases separately.

The extraction efficiency of different metals at certain points was calculated from the analysis results gotten from ICP with equation 3.

$$E_i = \frac{c_{\mathrm{i,feed}} - c_{\mathrm{i,aq}}}{c_{\mathrm{i,feed}}} = \frac{c_{\mathrm{i,org}} \cdot O/A}{c_{\mathrm{i,feed}}} \tag{3}$$

Where	E_{i}	extraction efficiency of metal i
	$c_{\mathrm{i,feed}}$	concentration of metal i in the feed
	$c_{\mathrm{i,aq}}$	concentration of metal i in the aqueous phase at a certain point
	$c_{\mathrm{i,org}}$	concentration of metal i in the organic phase at a certain point
	O/A	organic to aqueous phase ratio.

Usually, the efficiency was calculated from the aqueous (i.e., the raffinate) but if the loading was quite small, it was sometimes seen to be more reliable to calculate the efficiency from the concentration in the loaded organic.

6 RESULTS AND DISCUSSION

6.1 Solvent extraction of copper

First, Cu was removed from the LIBWL with solvent extraction. In a previous research project by Metso Outotec and LUT University it has been shown that Cu can be easily removed from LIBWL with continuous counter-current solvent extraction using a hydroxyoxime extractant Acorga M5640. The solvent extraction can be done in acidic pH, which is beneficial since there is no need for pH adjustment during the extraction.

In the solvent extraction cascade, there were two loading and two stripping stages. The organic extractant was 30 vol-% Acorga M5640 in Exxsol D80 and the stripping solution was 2 M sulfuric acid. The runs were done at room temperature and the residence time was 6 minutes. The phase ratio O/A during the runs was 0.5:1 for loading and 1:1 for stripping. The stripped organic was recycled back to the loading step during operation.

The concentrations of different metals during Cu extraction are shown in Table 9 and the extraction efficiencies during extraction are shown in Figure 13.

Table 9. The concentrations (in mg/L) of different metals in different phases during Cu extraction with 30 vol-% Acorga M5460. The phase ratio during loading was O/A = 0.5 and the residence time was 6 min. Phase ratio in stripping was O/A = 1.

	Feed	**Raffinate**	**Stripping product**	**Stripped organic**
Li	5240	4830	< 2.07	< 2.07
Mg	134	127	< 1.17	< 1.17
Al	2470	2280	3.73	2.46
Mn	8120	7760	< 1.94	< 1.94
Fe	544	525	10.0	3.13
Co	7340	6820	0.71	< 0.10
Ni	25300	23700	2.25	< 0.91
Cu	1540	44.0	2700	89.9

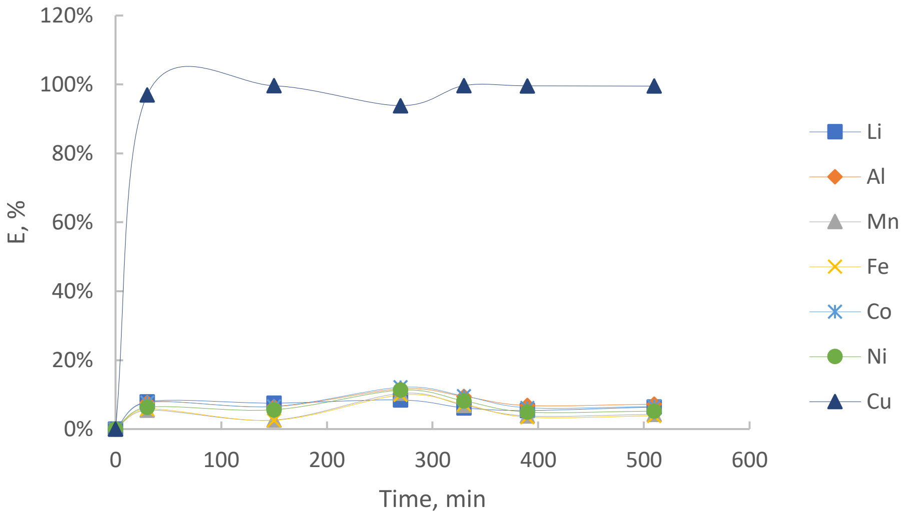

Figure 13. The extraction efficiency of metals during solvent extraction with Acorga M5640. The phase ratio during loading was O/A = 0.5 and the residence time was 6 min.

The extraction of Cu was efficient leaving less than 44 mg/L of Cu into the raffinate yielding 97.3 % extraction efficiency. The stripping of the loaded organic was also efficient, and the purity of the stripping product was 99.4 % pure copper sulfate with 2700 mg/L Cu in it. Some Fe (10 mg/L) was also extracted and stripped to the stripping product, but the purity of the solution was still around 99.4 % Cu.

However, some Cu was still left into the stripped organic. As the organic was recycled back into the loading step, the amount of Cu in the stripped organic accumulated slightly. This is quite normal in industrial solvent extraction and usually it is not even the purpose to strip the organic completely since it can still remove enough Cu from the feed solution. Some of the co-extracted Fe was also left into the stripped organic but it did not affect the extraction efficiency in regard to Cu.

6.2 Fluoride precipitation

The precipitation of fluoride was attempted after Cu removal. Fluoride precipitation experiments were conducted in glass reactors with the addition of calcium hydroxide. The amount of added $Ca(OH)_2$ was calculated from stoichiometry so that only enough calcium would be added for all the fluoride to react into CaF_2. The pH of the solution was then adjusted with 5 M NaOH to see if fluoride is removed from the solution and at what pH the removal happens.

The temperature of the experiment was 50 °C since precipitation is usually more efficient at higher temperatures. To 1 L of solution, around 1 g of $Ca(OH)_2$ was added. The solution was stirred for one hour so that all the calcium would have enough time to react with the fluoride. After that NaOH was incrementally added until the pH of the solution was higher than five. Samples were taken after each incremental pH adjustment and before taking a sample it was waited until the pH value was stable. The concentrations of fluoride and calcium during the experiment are shown in Figure 14.

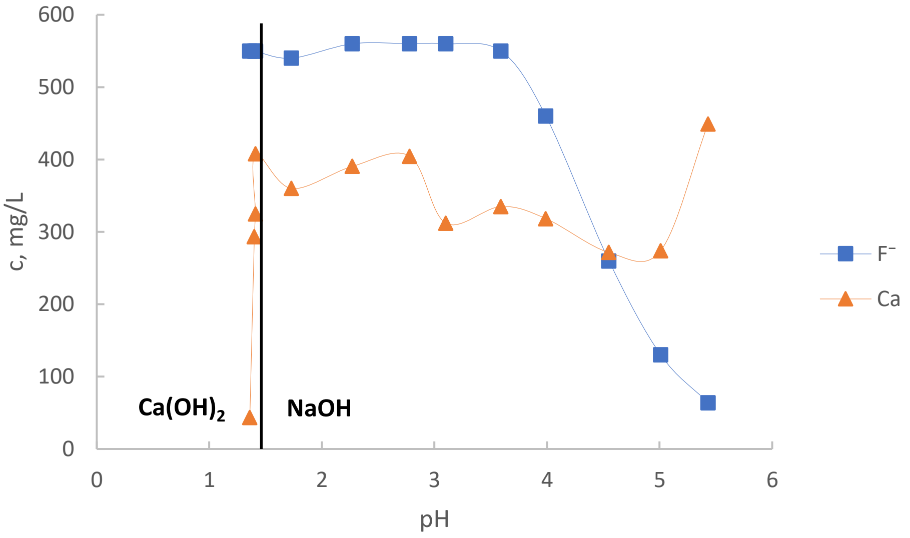

Figure 14. The equilibrium concentrations of fluoride and calcium as a function of pH when $Ca(OH)_2$ and NaOH were added.

From the Figure 14 it can be seen that the fluoride concentration does decrease but the decrease only starts at around pH 4. At the same time, the calcium concentration does not follow a similar pattern. This might indicate that the fluoride does not necessarily precipitate as CaF_2.

Some equilibrium calculations were done with HSC Chemistry to study the possibilities of precipitating fluoride. The concentrations of metals in the calculations were the same as the concentrations in the used synthetic LIB waste leachate. The calculations were done by varying concentrations of $Ca(OH)_2$ and NaOH independently in the solution chemistry. When $Ca(OH)_2$ was added, CaF_2 was the main fluoride compound when pH reached 3 (Figure 15).

So, the calculations suggest that the precipitation should occur in the conditions of the experiment. However, in the calculations the pH is increased completely with the addition of $Ca(OH)_2$. Since in the done experiment only a stoichiometric amount of $Ca(OH)_2$ was added it might not be enough to start precipitating fluoride.

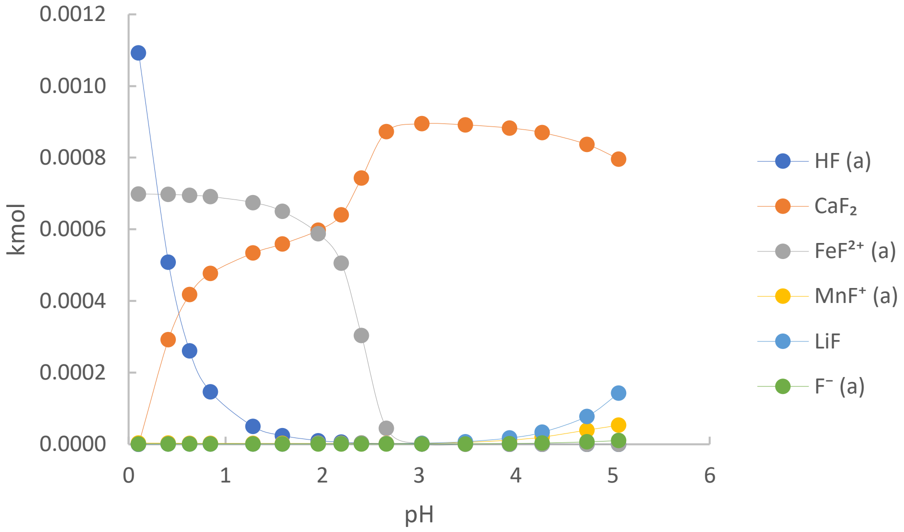

Figure 15. Equilibrium amounts of fluoride compounds when $Ca(OH)_2$ was added. The equilibrium calculations were done with HSC Chemistry. The beginning concentrations of metals were the same as in the solution which was used in the experiments.

The equilibrium concentrations of metals in solution were also studied with the addition of only NaOH (Figure 16). According to the calculations, it seems that fluoride might precipitate with just the addition of NaOH as a complex of Na and Al (Na_3AlF_6) when pH is increased. It is difficult to say whether the precipitation could actually happen as a complex or whether the fluoride actually precipitated as CaF_2 as was it was planned. The precipitate should be analyzed and characterized further to be able to make decisions on it. However, in this Thesis the solids were only analyzed for their metal contents by dissolving the solids.

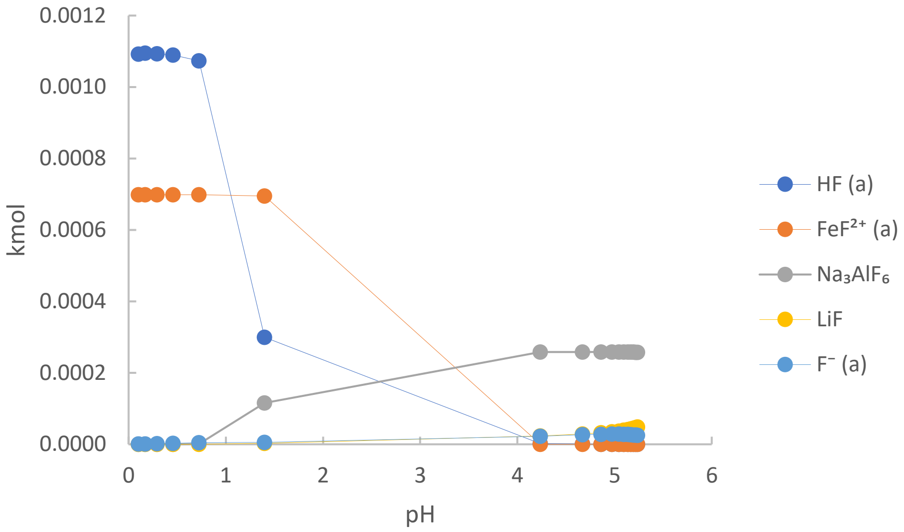

Figure 16. Equilibrium amounts of fluoride compounds when NaOH was added. The equilibrium calculations were conducted with HSC Chemistry. The beginning concentrations of metals were the same as in the solution which was used in the experiment.

From this experiment it can be concluded that it is not reasonable to remove fluoride at this stage of the process, since it would require such a high pH so that the losses of valuable metals would be significant (Figure 17). At pH 5, 74.2 % of fluoride was precipitated but at the same time 23.8 % of Co, 25.8 % of Ni and 18.0 % of Li were also precipitated. Because of this, it was decided that fluoride removal would not be researched more at this point but that it would be monitored what happens to fluoride during the rest of the process. The precipitation should however be studied more as it could be a possible method for fluoride removal. Most likely the stoichiometric amount of $Ca(OH)_2$ added was not enough for the reaction to occur. Adding more of the $Ca(OH)_2$ could help with the precipitation. At the same time, precipitation of gypsum might also occur because of the sulfate media of the solution.

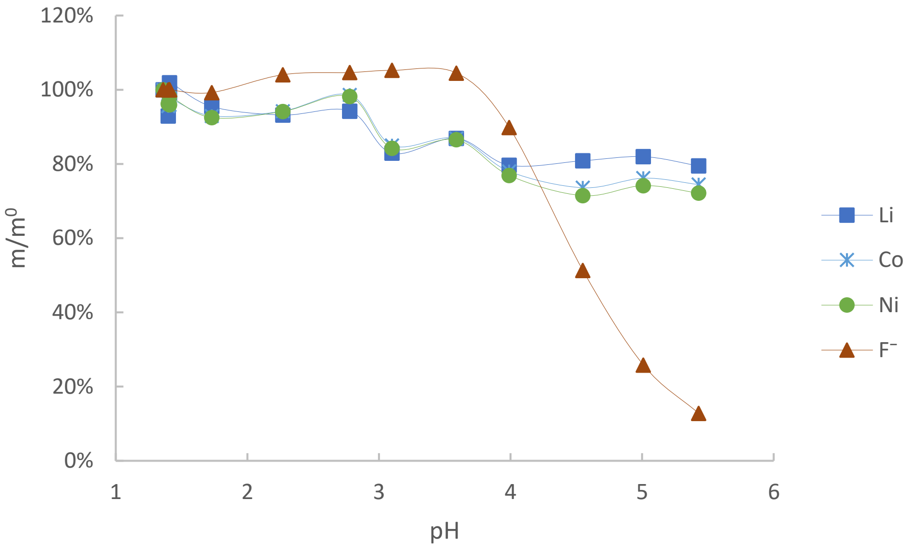

Figure 17. The precipitation of Co, Ni, Li, and fluoride as a function of pH with NaOH addition.

6.3 Precipitation of LIB metals with NaOH

Other precipitation experiments to examine the removal of Fe and Al were conducted in glass reactors. The pH was adjusted with NaOH so that Fe and Al would precipitate as hydroxides. At first, the precipitation was attempted at smaller scale in a 1 L reactor and 5 M NaOH was added. The pH was adjusted all the way to above 5 to see at what pH the metals in LIBWL precipitate. The temperature during this experiment was 50 °C.

During the experiment, the most precipitate was formed between pH 3 and 4. Also, at around 3.5 the pH increased very slowly even though NaOH was added all the time. This indicates that at that point the hydroxide added was mostly used by the formation of metal hydroxides and thus the pH was not able to increase as much. The results of this experiment can be seen in Figure 18.

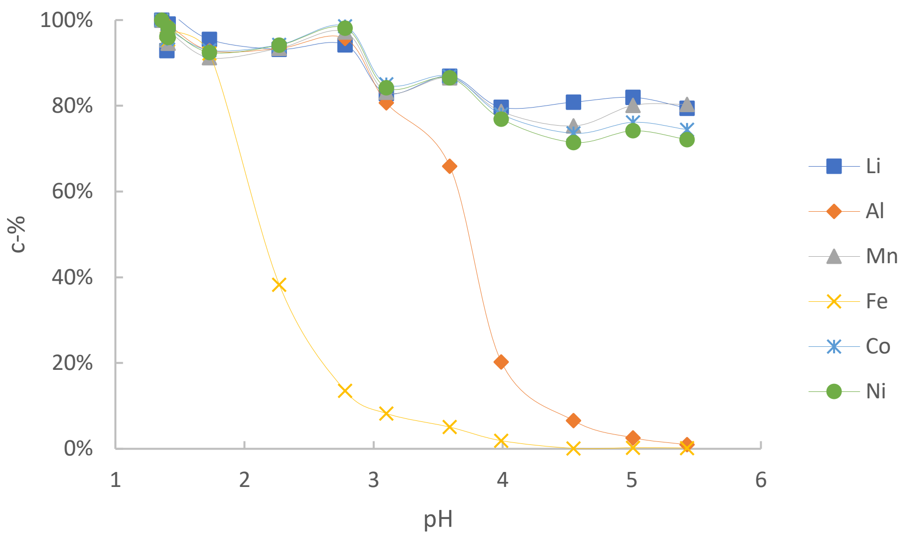

Figure 18. The precipitation of metals as the function of pH when 5 M NaOH is added.

From the Figure 18 it can be seen that Fe already starts precipitating after pH 2. Al, however, only starts precipitating after pH 3. If Al should be removed completely by precipitation, the pH would need to be increased up to 5 and at the same time there would be significant losses of Co, Ni and Li.

The precipitation results when NaOH was used are quite similar to the results presented by H. Wang & Friedrich (2015) in the sense that first Fe precipitates, followed by Al, and afterwards the valuable metals (Figure 6). However, according to them the precipitation of Fe and Al happens after pH 4. In this case Fe is already precipitated before pH 3. The temperature in their experiment was 40 °C whereas in this experiment it was 50 °C. The difference in temperature already explains some of the differences since usually the precipitation occurs faster at higher temperatures. According to H. Wang & Friedrich (2015) at a pH of 5.8, already 21.4 % of Ni, 17.3 % of Co and 14.1 % of Mn were precipitated. In this case when the pH was 5.43, 27.9 % of Ni, 25.6 % of Co and 19.7 % of Mn were precipitated. The differences in the results are most likely caused by the different compositions of the used solutions and the temperature. However, the results are quite in line with each other when taking these things in to consideration.

A few solid samples from this experiment were also analyzed in terms of composition. The solid samples were first washed with pure water, dried in an oven, and then dissolved into 2

M sulfuric acid. The mass fractions of metals in precipitates at different pH values are shown in Figure 19.

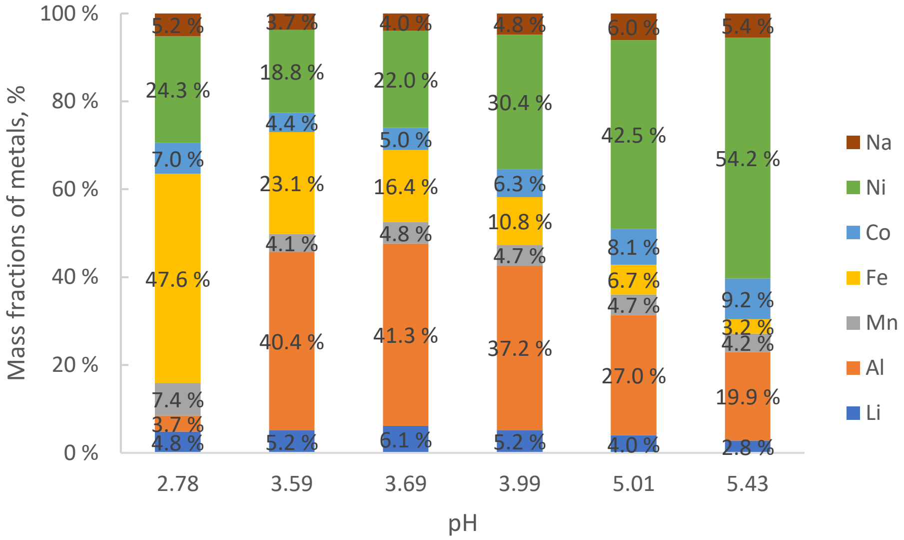

Figure 19. Mass fractions of metals in precipitates at different pH values.

As can be seen from the Figure 19, when the pH was 2.78, the largest fraction of the precipitate was Fe at 47.6 %. When the pH was increased to 3.69 the fraction of Fe was decreased, and the fraction of Al increased to 41.4 %. When the pH was further increased to 5.43, the fraction of Ni in the precipitate increases to be the largest fraction at 54.2 %. This is in line with the results obtained from the solution analysis in Figure 18. After Fe is precipitated, Al starts to precipitate and then the other valuable metals.

Fe can be successfully removed with precipitation but for complete Al removal to be achieved there would be significant Co losses. Thus, Al removal was decided to be removed in the following step with Mn. Based on the results in Figure 18 it was decided that a suitable pH value for Fe precipitation is 2.8 since at that point most of the Fe has already precipitated but the Co losses are not yet too big. Thus, a larger portion of the solution with Cu removed was treated so that the pH was increased to 2.8. The larger batch precipitations of Fe were done in 3 L jacketed glass reactors at a temperature of 50 °C. The results of one of the batch experiments is shown in Figure 20. The precipitation is efficient leaving 59.7 mg/L of Fe in the solution.

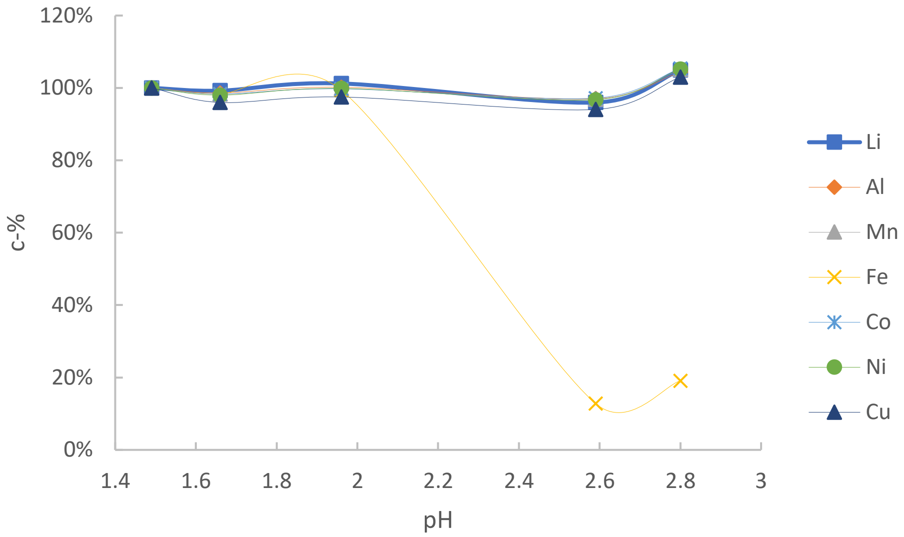

Figure 20. The precipitation of metals when the pH is increased with 5 M NaOH at a temperature of 50 °C.

After increasing the pH to the wanted value, the solution was filtered. However, it was noticed that filtration of iron hydroxide was quite difficult. A lot of the precipitate would go through the filter since the particles are so small. Some particles from previous experiments were then added to ongoing precipitation procedures so that the particles would start growing on the existing particles. This seemed to make the particles bigger, but the precipitate would still go through the filter. The separation of the solids was thus done by letting the precipitate sediment to the bottom and then pumping the clear liquid from the top into a new container. This proved to be the easiest solution for the separation of solids. When considering the continuous operation of the precipitation, the separation of solids is much easier. In continuous operation it is easier to recycle the solids and thus increase the particle size so that filtering is easier. On the other hand, also sedimentation is a possibility if filtering proves to be too impractical.

6.4 Solvent extraction of manganese and aluminum

Removal of Mn and Al were done with solvent extraction using 30 vol-% D2EHPA as extractant. Continuous counter-current solvent extraction runs were done with varying phase ratios, number of stages and pH values. The stripping of the loaded organic was done with 2 M sulfuric acid. The pH adjustment was done with 5 M NaOH, which was injected into two mixers by syringe pumps. The temperature in all the experiments was increased slightly from room temperature. The adjustment was done by heating the feed solutions. Temperatures of the experiments were around 30 °C. A summary of the parameters during different runs with D2EHPA and the extraction efficiencies for Mn, Al, and Co are shown in Table 10. The results of the runs are discussed in more detail below.

Table 10. Summary of the conditions in different solvent extraction runs with 30 vol-% D2EHPA and the extraction efficiencies for Mn, Al and Co. The residence time in mixer in all runs was 6 minutes.

Run number	**Stages in loading**	**O/A in loading**	**Target pH in loading**	**Stages in stripping**	**O/A in stripping**	**E, % Mn**	**E, % Al**	**E, % Co**
1	3	1	2.5	2	2	80.5	78.9	1.67
2	3	1.5	2.5	2	1	92.3	79.4	2.08
3	5	1.5	2.5	3	1	86.1	82.6	0.63
4	5	1.5	3	3	1	100	98.3	8.60

For the first experiment in continuous counter-current extraction, there were three stages in loading and two stages in stripping. The target pH was 2.5 and the pH adjustment was done to the first and third loading stages, counted from the organic phase inlet. The phase ratio in the loading was O/A = 1 and in the stripping, it was O/A = 2. The residence time in the mixer was 6 minutes. The concentrations of metals in different phases during Run #1 are shown in Table 11 and the extraction efficiencies of metals during the run are shown in Figure 21.

Table 11. The concentrations (in mg/L) of metals in different phases during Run #1 with 30 vol-% D2EHPA. The pH during the run was 2.0-2.5 and the temperature was 25-36 °C.

	Feed	**Raffinate**	**Loaded organic**	**Stripping product**	**Stripped organic**
Li	4370	3710	46.6	95.6	< 5.04
Al	1890	398	1100	86.4	1130
Mn	6890	1340	4110	8470	13.2
Fe	94.9	4.82	113	10.7	105
Co	6380	5330	106	186	13.9
Ni	22200	18900	80.5	129	18.6
Cu	35.9	16.2	10.2	19.6	< 0.55

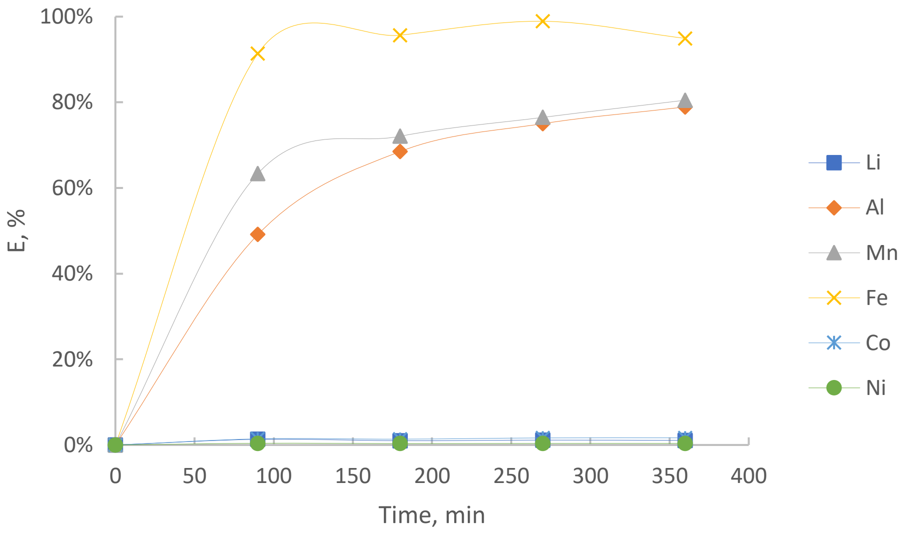

Figure 21. Extraction efficiencies during Run #1 with 30 vol-% D2EHPA as extractant. In the loading, there were 3 stages with O/A = 1. The pH during the run was 2.0-2.5 and the temperature was 25-36 °C.

As it can be seen from the Figure 21, the highest extraction efficiency for Mn was 80.5 % and for Al 78.9 %. This means that still over 1340 mg/L of Mn and over 398 mg/L of Al were left into the raffinate. The concentrations of both of them were still too high in the raffinate. The losses for Co, Ni and Li were 1.67 %, 0.36 % and 1.07 %, respectively, when calculated from the concentrations in the loaded organic phase.

During stripping basically all the Mn was stripped from the loaded organic and there was 8470 mg/L of Mn in the stripping product. Al, however, did not strip as easily from the loaded organic. The Al concentration in the stripping product was 86.4 mg/L while in the stripped organic it was 1130 mg/L. This means that the purity of the stripping product was 94.1 % of Mn. The difficult stripping of Al was quite unexpected. However, the reason for the inefficient stripping is likely the slow mass transfer of Al (Mashimo et al., 1997). Most of the Fe that was extracted during loading was also left into the stripped organic, but this was expected as it is known that Fe can be difficult to strip from loaded D2EHPA with H_2SO_4 (Peng et al., 2020).

The pH values and temperatures during the run fluctuated a little (Figure 22). The values behaved quite similarly in all the runs. All the pH and temperature data from D2EHPA runs is shown in Appendix I. The highest pH value, which was often the closest to the target value, was often in the mixer where aqueous phase was pumped into. Usually, it would be preferable to have a higher pH in the mixer where the organic phase was pumped to. The temperature was usually the highest also in the mixer, where aqueous phase was pumped to. This was because the temperatures had to be controlled by heating the feeds of the streams. Since the extractant was diluted in kerosene it was heated cautiously because of the low flash point of kerosene. Thus, the heat did not transfer as well into the equipment when compared to the aqueous phase.

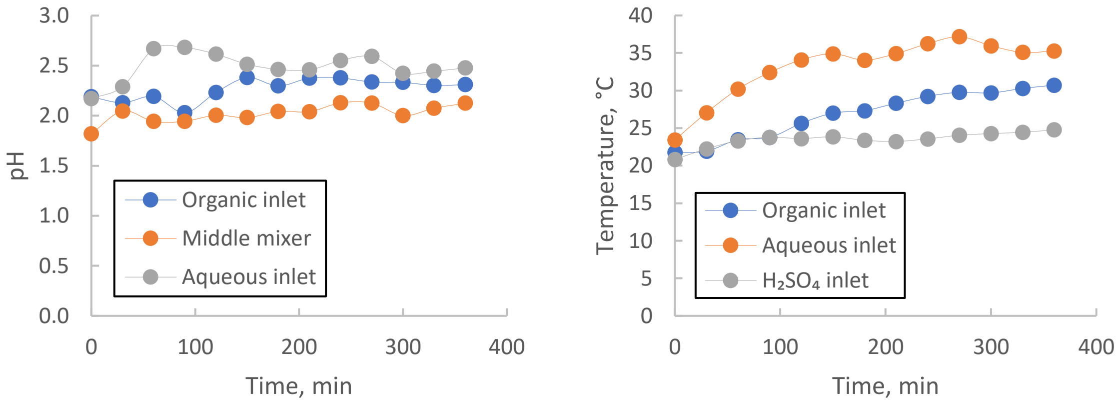

Figure 22. The measured pH values and temperatures during Run #1 with D2EHPA. The sample points are an average of the values measured at a certain time. All the measurements were from different mixers in loading and stripping.

Based on the first experiment it was decided to increase the phase ratio in loading to O/A = 1.5 and decrease the phase ratio in the stripping to O/A = 1. This way in the loading there would be more organic, and the extraction efficiencies should increase. The stripping phase ratio was changed so that more of the Al would be stripped from the loaded organic. All the other parameters were kept the same as in the first run, so target pH was 2.5 and residence time in mixer 6 minutes. The concentrations of metals in different phases during the second run are shown in Table 12 and the extraction efficiencies are shown in Figure 23.

Table 12. The concentrations (in mg/L) of metals in different phases during Run #2 with D2EHPA. The pH during the run was 2.0-2.6 and the temperature was 25-30 °C.

	Feed	**Raffinate**	**Loaded organic**	**Stripping product**	**Stripped organic**
Li	4460	3340	67.1	69.2	< 2.70
Al	2170	447	662	91.2	517
Mn	7690	589	4270	3370	5.51
Fe	132	< 1.84	114	< 1.84	133
Co	6760	5040	93.9	93.0	1.36
Ni	23500	18400	81.1	143	2.22
Cu	39.4	13.9	10.8	7.31	0.52

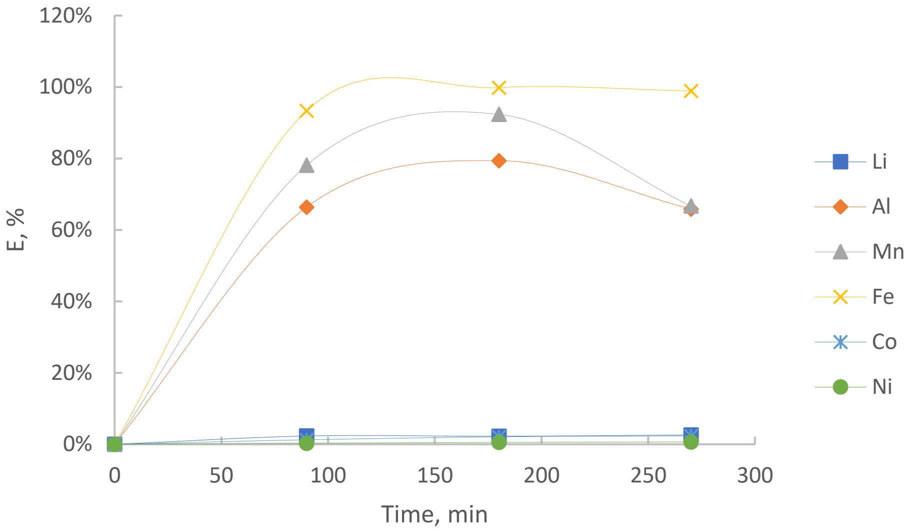

Figure 23. Extraction efficiencies during Run #2 with 30 vol-% D2EHPA. O/A in loading was 1.5 with three stages. The pH during the run was 2.0-2.6 and the temperature was 25-30 °C.

As can be seen from the figure, the extraction efficiency for Mn was slightly better with the increased phase ratio at 92.3 % extracted. For Al, the best efficiency was 79.4 % which was similar than with the lower phase ratio. In the raffinate there was still over 589 mg/L of Mn and 447 mg/L of Al. These concentrations were not yet low enough. The losses for Co, Ni and Li were around 2.08 %, 0.52 % and 2.26 %, respectively, when calculated from the loaded organic phase concentrations.

During the stripping basically almost all the Mn was stripped from the loaded D2EHPA and the concentration in the stripping product was 3370 mg/L. The concentration of Al in the stripping product was 91.2 mg/L, meaning that the purity of the solution was 89.3 % for Mn. Again, all of the Al did not strip from the loaded organic. This time the concentrations of Al in the stripped organic were even higher than in the first run at over 517 mg/L. Again, 133 mg/L of Fe was also left into the stripped organic. In this run the stripped organic was not recycled back into the loading step so it cannot be concluded yet if these amounts of Al and Fe interfere with the loading.

Based on the second run, it was decided to increase the number of stages both in loading and in stripping. The used configuration was decided to be five stages in loading and three stages in stripping. All the other parameters were kept as the same as in the Run #2: O/A in loading was 1.5, O/A in stripping was 1, target pH was 2.5 and residence time in mixer was 6 minutes. The concentrations of metals in different phases during the third run with D2EHPA are shown in Table 13 and the extraction efficiencies of the third run are shown in Figure 24.

Table 13. The concentrations (in mg/L) of metals in different phases during Run #3 with D2EHPA. The pH during the run was 2.2-2.7 and the temperature was 25-35 °C.

	Feed	**Raffinate**	**Loaded organic**	**Stripping product**	**Stripped organic**
Li	4610	3820	29.9	32.6	< 1.43
Mg	105	82.7	< 3.19	< 3.19	< 3.19
Al	2050	469	455	237	446
Mn	7190	2010	2600	2450	0.59
Fe	30.1	< 1.48	230	< 1.48	189
Co	6440	5860	25.6	26.1	0.36
Ni	22100	20600	12.1	18.6	< 3.42
Cu	12.6	9.69	1.29	0.56	< 0.23

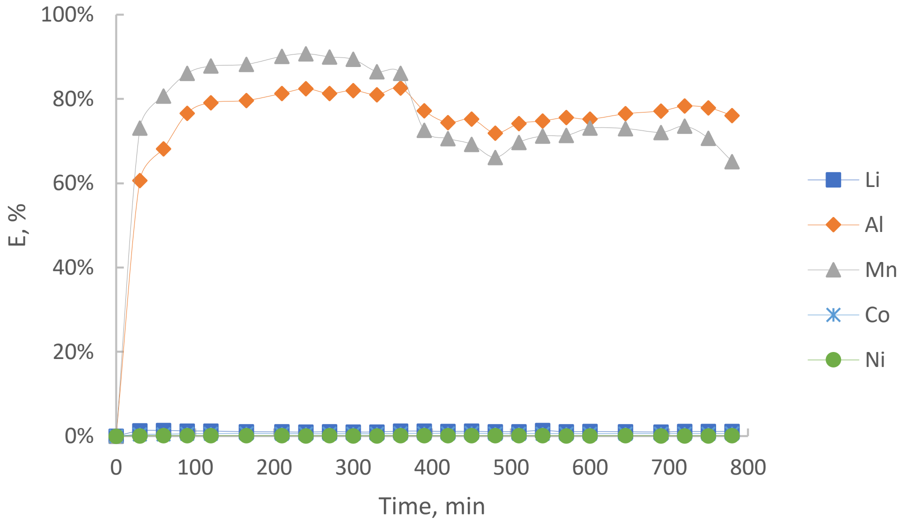

Figure 24. Extraction efficiencies during Run #3 with 30 vol-% D2EHPA. There were 5 stages in loading with O/A 1.5. The pH during the run was 2.2-2.7 and the temperature was 25-35 °C.

As can be seen from the Figure 24, the extraction efficiencies for Mn and Al were at best 90.7 % and 82.5 %, respectively. After a while, the efficiencies however dropped to 72.1 % for Mn and 77.2 % for Al. The stripped organic was recycled during this run, but the recycling only started at around 500 minutes into the run. The drop in efficiencies can be seen already at 400 minutes so the recycling probably was not the cause for the drop. Most likely the D2EHPA is just not capable of loading all the needed Mn and Al at the operating pH of 2.5.

During the stripping, the Mn was again stripped fine, but the Al was not. The concentration of Al in the stripped organic was up to 1390 mg/L but towards the end of the run the concentration dropped to over 400 mg/L. Also, up to 260 mg/L of Fe was again in the stripped organic but the concentration remained in the same area and the recycling of the organic back to the loading did not cause an accumulation of Fe into it.

Since it was concluded that the D2EHPA just may not be capable of loading all the Mn and Al in pH 2.5, it was decided to try the extraction at a higher pH of 3. Higher Co losses are expected but since Mn and Al free solution was needed for the next stage of the process it was decided to be done anyway. The solution used in the Run #4 (Table 10) was the raffinate from the three runs before to ensure that the Mn and Al removal would definitively be enough for downstream processing. Five stages in loading with O/A = 1.5 and three stages in stripping with O/A = 1 were used. The residence time in the mixer was 6 minutes and the target pH was 3. The concentrations of metals in different phases during the fourth run are shown in Table 14 and the extraction efficiencies of the fourth run are shown in Figure 25.

Table 14. The concentrations (in mg/L) of metals in different phases during Run #4 with D2EHPA. The feed was the combined raffinate from previous D2EHPA runs. The pH during the run was 2.5-3.2 and the temperature was 25-35 °C.

	Feed	**Raffinate**	**Loaded organic**	**Stripping product**	**Stripped organic**
Li	4160	3190	115	108	< 1.43
Mg	99.0	44.0	31.0	29.6	< 3.19
Al	854	14.8	1870	330	1590
Mn	2360	< 0.89	1470	1410	< 0.89
Fe	12.6	6.54	272	5.25	276
Co	6190	5020	355	324	< 0.25
Ni	21500	18800	197	192	< 3.42
Cu	10.2	< 0.23	16.2	14.6	< 0.23

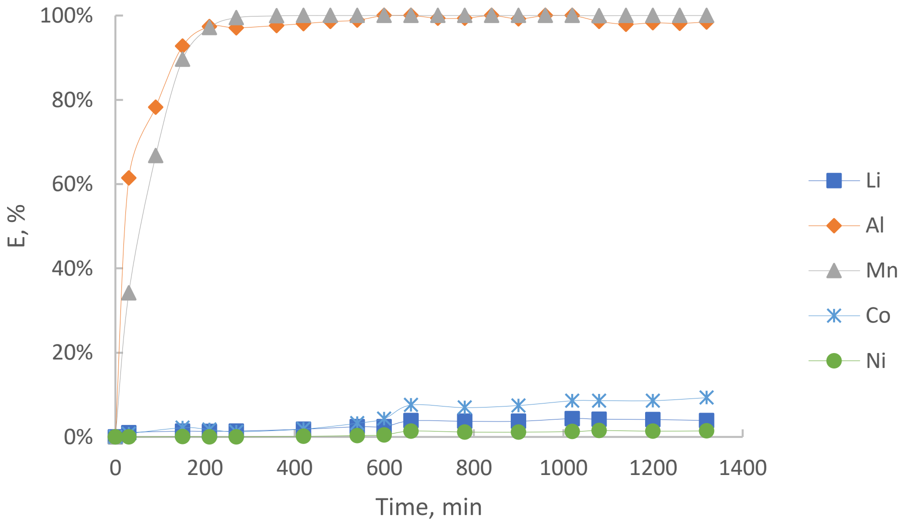

Figure 25. Extraction efficiencies during Run #4 with 30 vol-% D2EHPA. There were five stages in loading with O/A = 1.5. The pH during the run was 2.5-3.2 and the temperature was 25-35 °C. The used feed was the collected raffinate from previous D2EHPA runs.

As can be seen from the Figure 25, the extraction efficiency for Mn was almost 100 % and for Al it was 98.3 %. The concentration of Mn in the raffinate was below detection limit and the concentration of Al was 14.8 mg/L. The co-extraction of valuable metals was higher, which was expected. The Co, Ni and Li losses were 8.60 %, 1.38 % and 4.13 %, respectively. The losses could be avoided with the addition of a scrubbing stage. In the scrubbing stage for example $MnSO_4$ could be used as a scrubbing agent to kick out the co-extracted Co and Li and minimize their losses. The scrubbed solvent would then continue to the stripping stage and the scrub raffinate would be recycled back into the feed of the loading stage.

During stripping, Al was again not stripped properly leaving 1590 mg/L to the stripped organic and only around 330 mg/L was stripped into the stripping product. The stripped organic was again recycled back into the loading step, but the amount of Al in the stripped organic did not seem to accumulate. For example, Peng et al. (2020) discovered that stripping of Al and Fe from loaded D2EHPA was difficult. They concluded that even when the concentration of H_2SO_4 was increased to 2 M, the stripping of Al remains at around 40 % when O/A = 1. Increasing the time of the extraction did not increase the stripping efficiency either. Thus, stronger stripping agents such as HCl would be needed for complete stripping of Al.

Since in Run #4, raffinate from previous D2EHPA runs was used, it cannot be concluded that whether the solvent extraction would be efficient enough when using pH value 3 with higher Mn and Al concentrations. Most probably having the pH higher at 3 would be sufficient in removing Mn and Al to below 100 mg/L level even when starting with higher concentrations. Since already at pH 2.5 the extraction efficiencies for both metals were around 80 % at best, increasing the pH would most likely cause the efficiency to be even better. This would need to be tested in future research. Also, since the Co and Li co-extraction were quite high at the higher pH, a scrubbing stage with for example $MnSO_4$ would be needed in the process.

6.5 Solvent extraction of cobalt and nickel

Usually in the LIB recycling processes in the last steps, Co is first extracted and then Ni is extracted leaving Li in the raffinate. In this Thesis it was decided to try extracting both Co and Ni at the same time. The stripping product would contain only Co and Ni and this solution could be used for precursor precipitation in the production of new cathode materials for LIBs.

Virolainen et al. (2017) did a research where they investigated the chance that Co and Ni would be extracted together but then they would be selectively stripped from the loaded organic. It was decided to have their publication as a starting point in the planning for the extraction, with the exception that the metals be stripped together at the same time.

6.5.1. Continuous counter-current extraction with Cyanex 272

At first, continuous counter-current extraction was attempted based on a publication by Virolainen et al. (2017). As the extractant was 1 M Cyanex 272 with 5 vol-% TOA as a phase modifier. The extractant was preneutralized with 5 M NaOH at a phase ratio of O/A = 10 so that the extractant was in one phase. In the loading step there was three stages with an O/A of 1.5 and the target pH was 6.8-7.1. The residence time in the mixer was 6 minutes and the stripping of the loaded organic was done with 0.5 M H_2SO_4. In the stripping there were two stages with an O/A of 1.5.

After some time into the run, gelling was observed in the organic phase. At first it seemed that just a little bit of the gel was forming, and the run was continued while trying to remove the gel. Soon, however, the whole organic phase in the reactor turned to gel and the run was stopped. A picture of the gel in the loading step is shown in Figure 26.

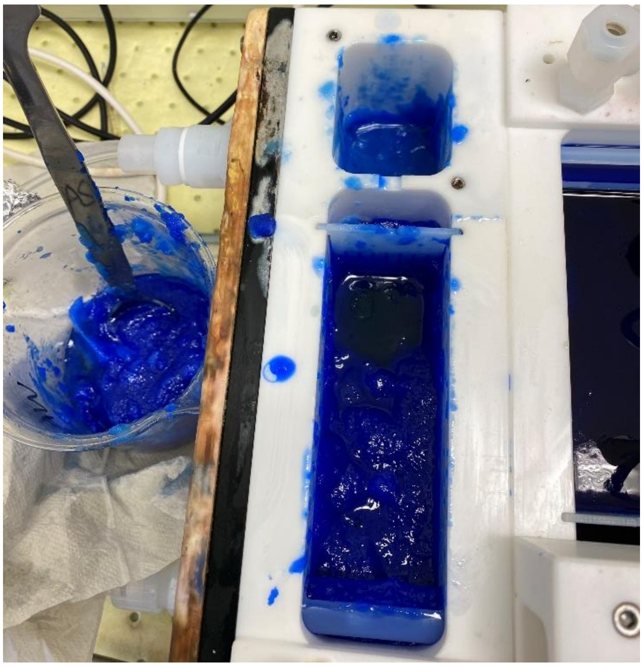

Figure 26. Gel formed during the extraction of Co and Ni when Cyanex 272 was used as extractant. The phase ratio was O/A = 1.5 and the pH was around 7.

The formed gel was solid in nature and running the extraction with that kind of gel is not possible. For resolving the problem, the extractant was diluted with kerosene to 0.67 M and the phase ratio of the extraction was also increased to O/A = 2. The gelling problem was not resolved with these measures and the gel formed again. This time the gel was observed in all the settlers of the loading stage. In the first stage, where the extractant is fed, the gel seemed a bit different and not as dark as in the others. The gelling during this run is shown in Figure 27.

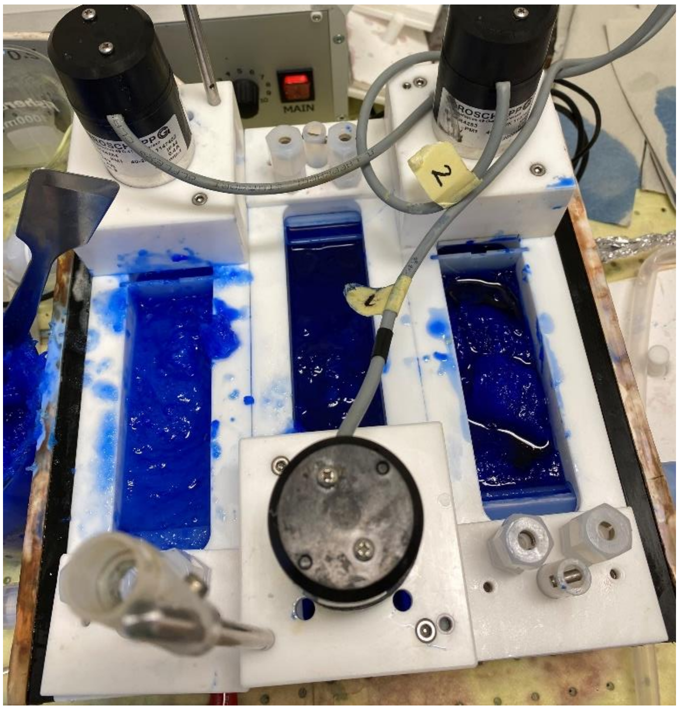

Figure 27. Gel formed during extraction with more 0.67 M Cyanex 272. The O/A in the loading was 2 and the pH was around 7.

The gelling was most likely caused by the high concentration of Ni in the feed solution. When comparing to the research by Virolainen et al. (2017), the biggest difference is the concentration of Ni. In their research the concentration of Ni was 0.48 g/L, while the concentration in this Thesis was over 20 g/L. Also, since Cyanex 272 is mostly used for the extraction of Co, it most likely was not capable of extracting such a high concentration of both Co and Ni.

Some other extractants were also considered since now Co and Ni are extracted together, and there is no need for a high selectivity between the two. It was decided to compare the selectivities of some extractants with pH isotherms to possibly find a more suitable option for the process.

6.5.2 Comparison of selectivities of different reagents by pH isotherms

The pH isotherms for Co and Ni extraction were done in a 1 L thermostated glass reactor. The pH was adjusted by adding 5 M NaOH into the system while mixing. The phase ratio for the experiments was O/A = 2 and the temperature was 25 °C. The extractants chosen for the experiments were 1 M Cyanex 272 with 5 vol-% TBP as phase modifier (Figure 28), 30 vol-% Acorga M5640 (Figure 29), and 40 vol-% Versatic 10 (Figure 30). Samples were taken at different pH values during the experiments and the system was equilibrated for 15 minutes before taking a sample.

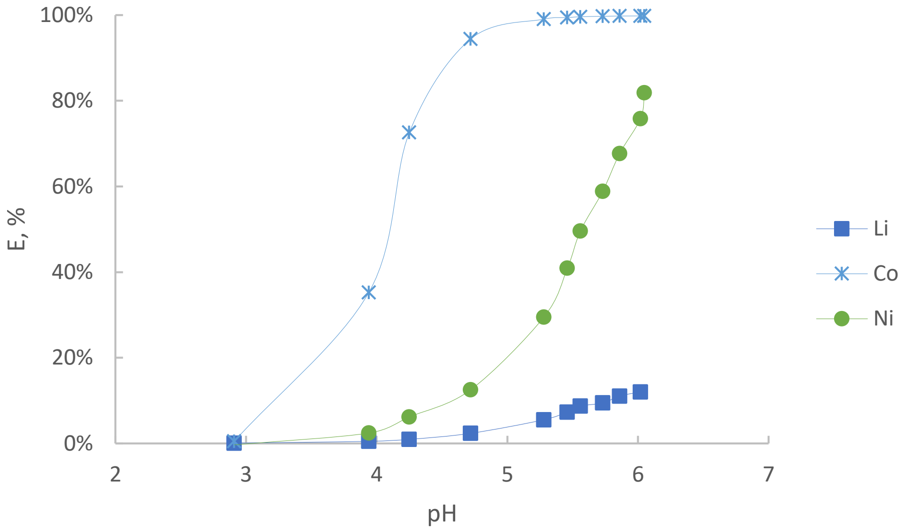

Figure 28. The pH isotherm of 1 M Cyanex 272 with 5 vol-% TBP. O/A was 2 and temperature was 25 °C. The pH was adjusted with the addition of 5 M NaOH.

As can be seen from the Figure 28, with Cyanex 272 Co was already extracted at pH 5. When the pH was 6, 99.8 % of Co, 81.9 % of Ni and 12.0 % of Li was extracted. The gelling of the organic phase was not observed during the experiment. However, after taking the samples the organic phase was gelled in the last two samples. The gelling did not happen rapidly. The last sample, where the pH was 6.05, gelled after a day, and the seconds to last sample, where pH was 6.02, gelled after a few days. Since the gelling happened, and the amount of Ni extracted was not very good, it was concluded that Cyanex 272 would not the best option for the extraction in this case. Also, at the same time the co-extraction of Li was quite high, which would mean that a scrubbing stage would be needed to avoid getting too much Li into the precursor, and on the other hand to maintain a high yield of Li.

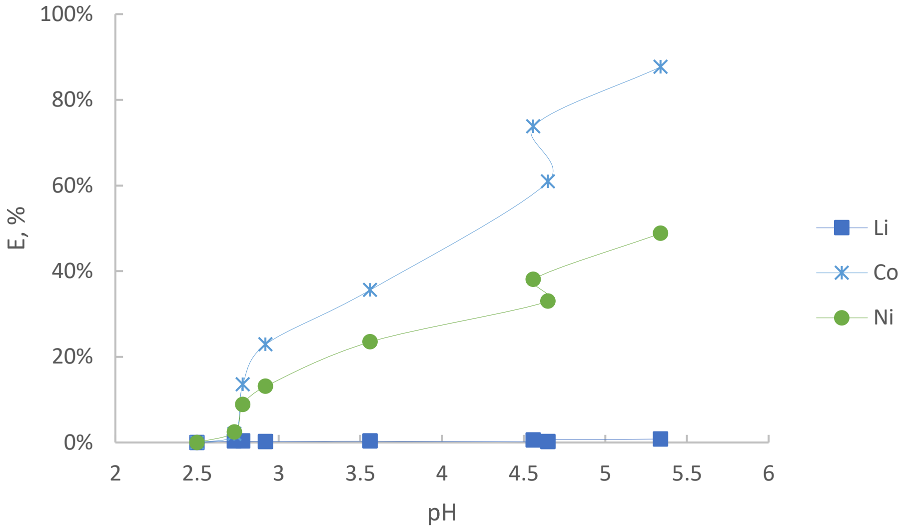

Figure 29. The pH isotherm for 30 vol-% Acorga M5640. O/A was 2 and the temperature was 25 °C. The pH adjustment was done with the addition of 5 M NaOH.

As can be seen from the Figure 29, when using Acorga M5640, decent efficiency was achieved for Co. When the pH was 5.3, the extraction efficiency for Co was 87.7 %. At the same time the extraction efficiency for Ni was only 48.8 %. Less than 1 % of Li was co-extracted throughout the experiment. The pH adjustment in the experiment with Acorga was a bit difficult. Even a little drop of NaOH would increase the pH by a lot, but then the pH would start to drop at slow rate. Even after waiting 15 minutes for the system to equilibrate, the pH was still slightly dropping. Afterwards, it was realized that hydroxyoxime extractants are quite easily saponified when in contact with NaOH. The sodium salt of the hydroxyoxime is soluble in water and it might explain why the pH adjustment was so difficult. If Acorga would be used in this extraction, the pH control should be done with a different chemical such as ammonia.

Another problem with using a hydroxyoxime for the extraction of Co and Ni is the complexation of Co. Co is extracted in to the hydroxyoxime as Co(II) but it then oxides into Co(III). Stripping this Co(III) from the hydroxyoxime is quite difficult with the usual sulfuric acid. Even when backextracting the loaded organic samples with 5 M HCl before analyzing with ICP, all of the Co was not stripped. The measured concentrations in the loaded organic samples were significantly lower than what they should have been according to the mass balance of the system. Poor stripping efficiency would cause evident problems in the solvent extraction circuit. The Co would start to accumulate in the organic phase and the extraction efficiency might be affected. Due to these reasons, it was decided that Acorga M5640 would not be investigated further for the extraction of Co and Ni.

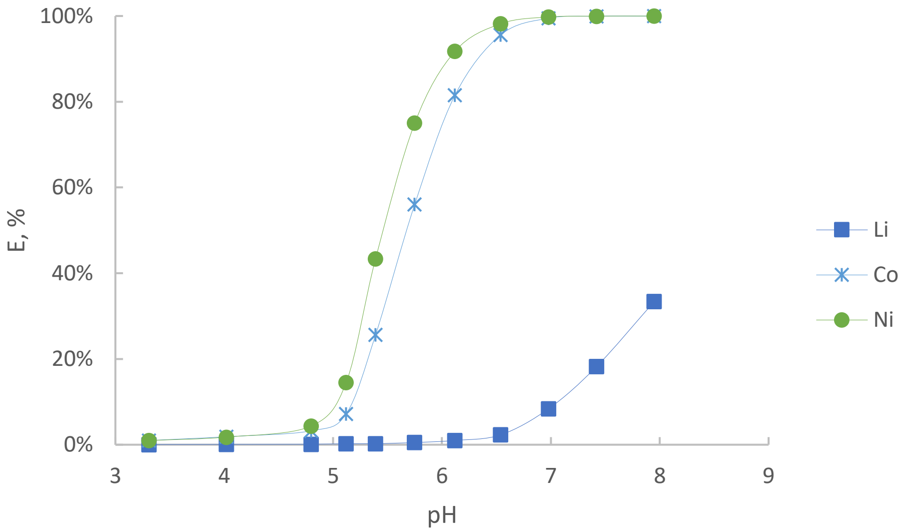

Figure 30. pH isotherm for 40 vol-% Versatic 10. 5 M NaOH was used for the pH adjustment.

As can be seen from the Figure 30, when using Versatic 10 as extractant, both Co and Ni were efficiently extracted. At a pH of 6.5, the extraction efficiency for Co was 95.6 % and for Ni 98.2 %. At that point the co-extraction of Li was 2.32 %. There is practically no selectivity between Co and Ni but since the idea is to co-extract them at the same time, the selectivity is not needed. Only the selectivity towards Li is important at this point. During the experiment, no gelling was observed, and no samples were gelled either. This would suggest that Versatic 10 is capable of loading all the Ni and Co in the feed solution. The phase separation in some of the samples took some time but it should not be a problem in continuous operation. The disadvantage of using Versatic 10 as the extractant is that it is quite soluble in water. The solubility is often higher at higher pH values. This would mean that extractant losses would occur during operation, which would increase the costs of the process. It was however decided that Versatic 10 would be investigated further for the Co and Ni extraction and more experiments such as a loading isotherm would be done to determine what would be the best conditions for continuous counter-current experiments.

6.5.3 Loading isotherm for Versatic 10

The loading isotherm was conducted for 40 vol-% Versatic 10 in a 1 L reactor at different phase ratios. The pH of the experiment was 6.5, which was decided based on the pH isotherm. The pH was adjusted with 5 M NaOH. The phase ratio was changed by adding a certain amount of fresh extractant into the reactor. Then the pH was adjusted and a some more of the extractant was added so that the phase ratio would stay the same as wanted. After pH adjustment the solution was equilibrated for 15 minutes before taking a sample. After equilibration, the phases were left to separate for 10 minutes, and samples were taken from both phases. The phase ratio was changed from O/A = 0.2 to O/A = 3.

During the experiment, no gelling was observed. However, when the mixing was stopped, the extractant started to gel a little bit when the phase ratio was lower than 1. The gelling was not as bad as it was with Cyanex 272, but a small amount of gel could be seen near the phase boundary on the organic samples. The organic samples could still be analyzed so it did not matter that much as the phase ratio in actual operation would most likely not be below 1 anyway. Some precipitate also appeared when the phase ratio was below 1. This may have been because there was so little of the extractant and it was not capable of extracting such concentrations, but the pH was still increased all the way up to 6.5. Thus, the NaOH could have reacted with Ni and Co to create hydroxides. The loading isotherms for Co and Ni are shown in Figure 31.

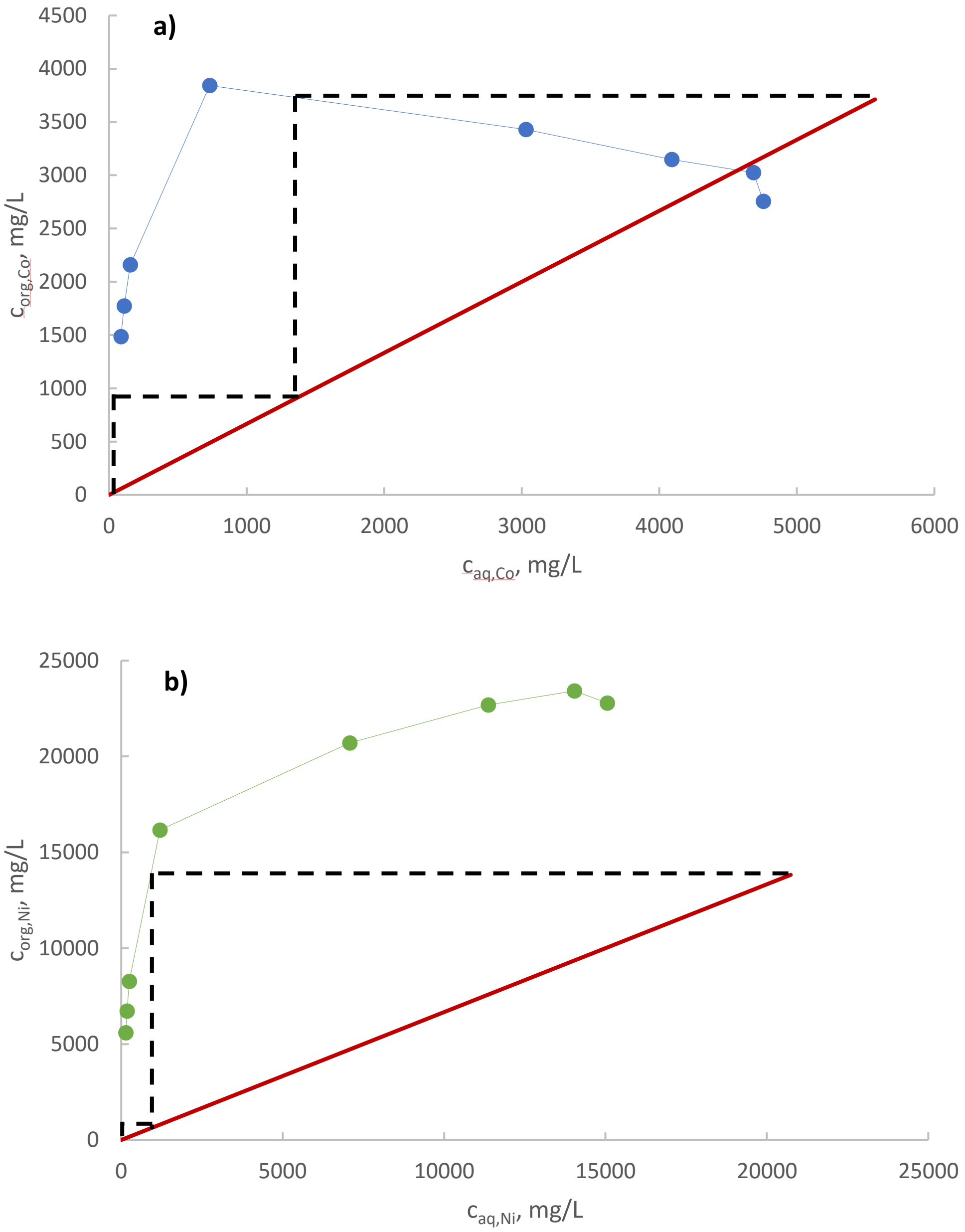

Figure 31. The loading isotherms of a) Co and b) Ni with 40 vol-% Versatic 10 at a pH of 6.5. The dashed black lines indicate McCabe-Thiele analysis. For the operating line O/A = 1.5.

From the Figure 31 it can be seen that the isotherm for Co had a maximum, when the concentration in the organic phase was 3.9 g/L. This is most likely caused by the competition of more Ni being extracted. It can also be seen that Versatic 10 was capable of loading quite a large concentration of Ni (over 22 g/L). This indicates that there should be no problems with the extraction capability of Versatic 10, at least regarding Ni. With a phase ratio of 2, the extraction efficiency for Co was 97.3 % and for Ni 98.8 %. At the same time, 3.51 % of Li was also co-extracted. When the phase ratio was increased, the extraction efficiencies were also increased. The highest co-extraction of Li was 6.11 % when the phase ratio was 3.

McCabe-Thiele analysis was done for both Co and Ni to determine the needed stages and amount of organic phase in continuous counter-current operation. The analysis is shown in the Figure 31 with dashed black lines. For the operating line in the analysis phase ratio O/A = 1.5 was used. If the phase ratio would be 1, the operating line would cross with cobalt's isotherm and the extraction may not work at all. From the figures it can be seen that for both Co and Ni 2 stages should be enough to achieve efficient extraction at a pH of 6.5.

6.5.4 Continuous counter-current extraction with Versatic 10

Based on the pH isotherm and loading isotherm, continuous counter-current extraction was designed. For the loading there were two stages, and the pH was 6.5. The phase ratio in the loading step was changed between the three experiments. The residence time in the mixer was 6 minutes. For the stripping of the loaded organic, there were two stages, and 2 M sulfuric acid was used with a phase ratio of 2. The temperature in the first run was room temperature but for the other two runs the temperature was slightly increased to around 30 °C. The different runs with Versatic 10 are summarized in Table 15 with the extraction efficiencies for Co, Ni, and Li as well as measured pH and temperature values. The results of the runs are discussed in more detail below. The measured pH values and temperatures of the runs with Versatic 10 are shown in Appendix II.

Table 15. The different runs with 40 vol-% Versatic 10. The number of stages in loading was two, the target pH was 6.5 and the residence time in the mixer was 6 minutes. The extraction efficiencies for Co, Ni, and Li as well as actual pH values and temperatures are given also.

Run number	**O/A**	**E, % Co**	**E, % Ni**	**E, % Li**	**pH**	**Temperature, °C**
1	1.5	83.2	76.8	1.58	6.1-7.2	Room temp.
2	2	82.4	63.8	1.03	6.1-6.9	23-33
3	2.5	86.1	74.2	1.93	6.1-6.9	23-31

Since the wanted pH was high and the extractant is acidic, preneutralization was needed. Preliminary batch experiments were done in order to determine if the system could be left in one phase after adding the neutralizing agent. With 10 M NaOH it seemed that one phase could be achieved but such high concentration of NaOH was not wanted to be used. With 5 M NaOH at different phase ratios it did not seem that one phase could be achieved. It was thus decided that the degree of neutralization would be 50 % calculated from the stoichiometry of the neutralization reaction. The required amount of 5 M NaOH was added to the extractant, and the solution was mixed. After mixing the phases were separated and the organic phase was used in the extraction runs. During the preneutralization it could be seen that the Versatic 10 does dissolve quite a bit to the aqueous phase. This could be seen from the increased amount of aqueous phase when comparing to the beginning of the neutralization.

In the first run the phase ratio in the loading was 1.5. Some crud (Figure 32) was observed all throughout the run. It seemed that the crud was on the boundary of the phases but in the aqueous phase. The run was continued with attempting to remove the crud at the same time. However, more crud was formed almost constantly.

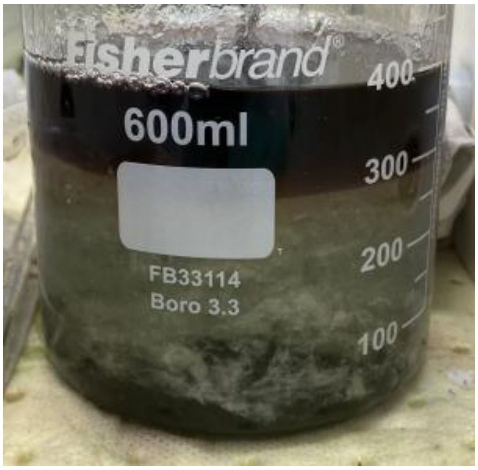

Figure 32. Some of the crud removed from the solvent extraction equipment during the first run with 40 vol-% Versatic 10.

As can be seen from the Figure 32, the crud is mainly at the boundary of the phases but on the aqueous side. Quite a lot the crud was removed during the run and the results may be affected by the removal of the crud. Also, the pH in the mixers during the run was quite difficult to control. The pH fluctuated a lot and sometimes it was needed to feed NaOH into the mixers and sometimes sulfuric acid. The formation of the crud most likely influenced the pH fluctuation. The concentrations of metals in different phases during the first run are shown in Table 16 and the extraction efficiencies are shown in Figure 33.

Table 16. The concentrations (in mg/L) of metals in different phases during the first run with Versatic 10 when O/A was 1.5. The pH during the run was 6.1-7.2 and temperature was room temperature.

	Feed	**Raffinate**	**Loaded organic**	**Stripping product**	**Stripped organic**
Li	3640	3090	38.2	48.4	< 1.31
Mg	66.3	41.8	4.03	5.41	1.67
Al	62.1	7.68	14.0	19.8	7.22
Mn	190	23.8	47.9	75.7	14.1
Fe	1.01	< 0.90	< 0.90	< 0.90	< 0.90
Co	5480	920	1280	2410	24.7
Ni	20400	4740	3370	7010	157
Cu	1.04	< 0.11	0.73	1.08	0.25

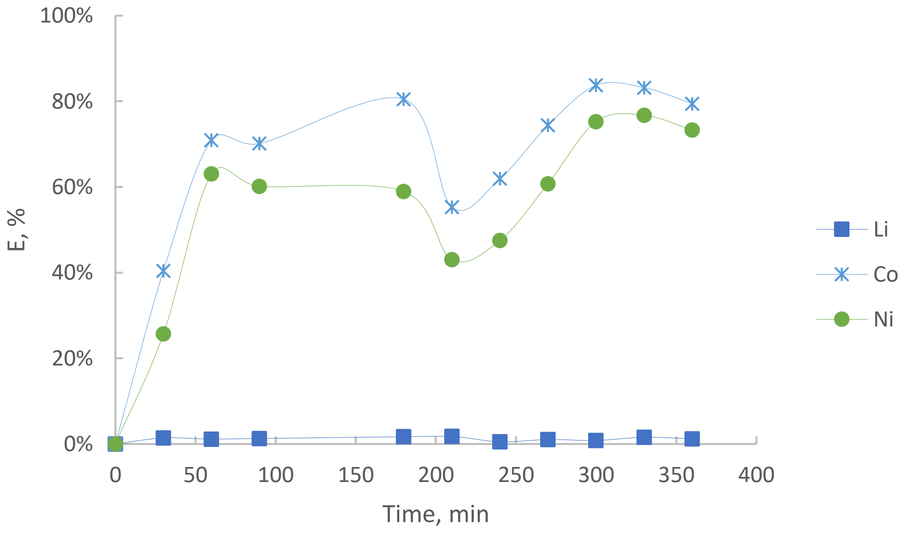

Figure 33. The extraction efficiencies for Co, Ni, and Li during the first run with 40 vol-% Versatic 10. The phase ratio during loading was 1.5. The pH during the run was 6.1-7.2 and temperature was room temperature.

As can be seen from the Figure 33 the Co and Ni extraction efficiencies were not very good. At the best, the extraction for Co was 83.2 % and for Ni it was 76.8 %. This means that 920 mg/L of Co and 4740 mg/L Ni was still left into the raffinate. Not much of Li was extracted which is good. However, the raffinate should be pure Li but as so much of both Co and Ni are left into it, the extraction is not efficient enough.

The stripping of the loaded organic was quite efficient, and most of the Co and Ni were stripped into the stripping product. In the stripping product there was 2410 mg/L of Co and 7010 mg/L of Ni. Over 150 mg/L of Ni was left into the stripped organic. The stripped organic was not recycled during the run so it cannot be said whether or not the Ni might start to accumulate into it.

For the second run, the phase ratio was increased to 2 to increase the Co and Ni yields and to avoid crud formation. The concentrations of metals in different phases during the second run are shown in Table 17 and the extraction efficiencies are shown in Figure 34.

Table 17. The concentrations (in mg/L) of metals in different phases during the second run with Versatic 10 when the O/A was 2. The pH during the run was 6.1-6.9 and temperature was 23-33 °C.

	Feed	**Raffinate**	**Loaded organic**	**Stripping product**	**Stripped organic**
Li	3640	3550	18.7	41.4	< 1.31
Mg	66.3	64.6	1.54	3.41	< 0.79
Al	62.1	6.50	12.7	16.2	5.17
Mn	190	19.4	64.9	95.8	11.9
Fe	1.01	< 0.90	< 0.90	< 0.90	< 0.90
Co	5480	965	1570	2720	23.8
Ni	20400	7370	4590	8140	95.6
Cu	1.04	0.11	0.53	0.52	< 0.11

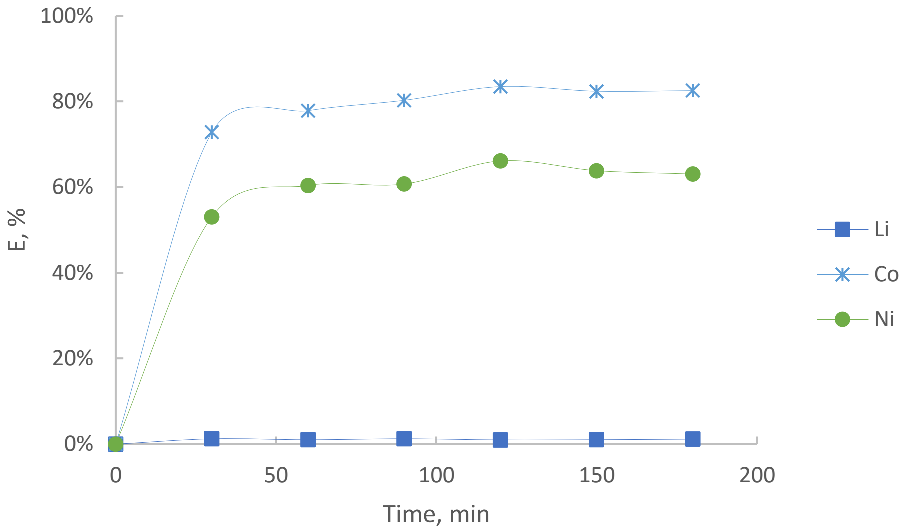

Figure 34. Extraction efficiencies of Co, Ni and Li during the second run with 40 vol-% Versatic 10. The phase ratio was 2. The pH during the run was 6.1-6.9 and temperature was 23-33 °C.

As can be seen from the figure, the efficiencies did not improve a lot compared to the first run. At best, the extraction efficiency for Co was 83.5 % and for Ni it was 66.1 %. This means that 905 mg/L of Co and 6910 mg/L of Ni were still left into the raffinate. Again, this means that the purity of the Li in the raffinate is not sufficient. Not much of Li was co-extracted again, 1.2 % at most.

The stripping of the loaded organic was again efficient. Over 2700 mg/L of Co and over 8100 mg/L of Ni was stripped into the stripping product. Not as much Ni was left into the stripped organic as was left in the first run. Almost a 100 mg/L of Ni was in the stripped organic.

The crud problem was not solved either during this run. There was still crud forming but it seemed that the amount was a little less when compared to the first run. During the second run the pH stayed more stable than in the first run. Some NaOH was needed to be fed into the reactor to keep the pH around 6.5-7.

For the third run the phase ratio was again increased, now to 2.5. The concentrations of metals in different phases during the third run are shown in Table 18 and the extraction efficiencies are shown in Figure 35.

Table 18. The concentrations (in mg/L) of metals in different phases during the third run with Versatic 10 when the O/A was 2.5. The pH during the run was 6.1-6.9 and the temperature was 23-31 °C.

	Feed	**Raffinate**	**Loaded organic**	**Stripping product**	**Stripped organic**
Li	3640	3330	28.0	47.8	< 1.31
Mg	66.3	55.8	2.27	3.81	< 0.79
Al	62.1	8.35	11.2	12.5	4.29
Mn	190	17.2	47.3	75.3	7.82
Fe	1.01	< 0.90	< 0.90	< 0.90	< 0.90
Co	5480	762	1210	2380	18.9
Ni	20400	5270	3910	7250	70.4
Cu	1.04	< 0.11	0.68	1.41	< 0.11

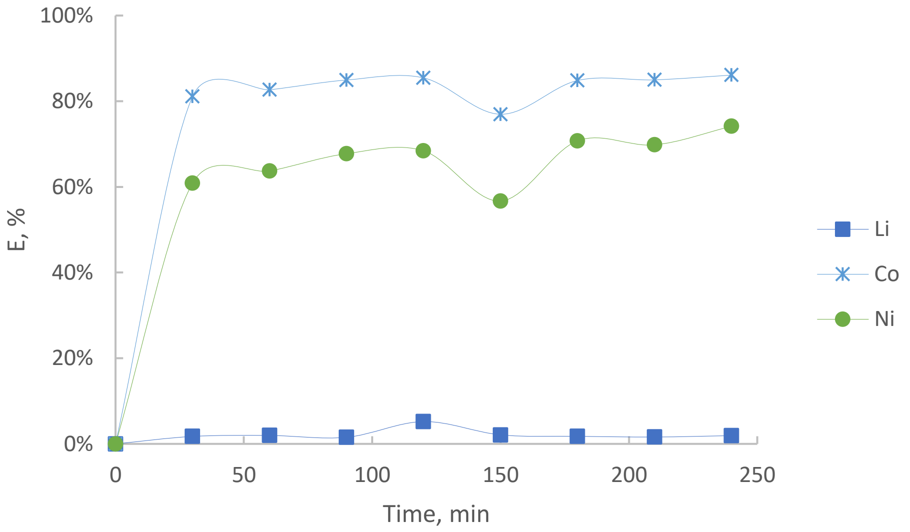

Figure 35. Extraction efficiencies of Co, Ni, and Li during the third run with 40 vol-% Versatic 10. The phase ratio was 2.5. The pH during the run was 6.1-6.9 and the temperature was 23-31 °C.

The extraction efficiencies for Co and Ni were slightly increased comparing to the other two runs, which can be seen from the Figure 35. At best, the extraction efficiency for Co was 86.1 % and for Ni it was 74.1 %. This means that 760 mg/L of Co and 5270 mg/L of Ni are left into the raffinate. The amount of Li that was co-extracted also increased slightly but it was 2.10 % at most.

The stripping of the loaded organic was again efficient. Over 2380 mg/L of Co and 7250 mg/L of Ni was stripped into the stripping product. Some Ni was again left into the stripped organic, but it was around the same amount as in the second run, so around 100 mg/L.

The crud problem was again not resolved, and it seemed that more of crud was formed than in the second run. This time however, the pH was even more stable, and no NaOH was needed to be fed into the reactor.

The formation of the crud in all the runs may have been caused by the NaOH that was used to preneutralize the extractant. It may be that there is spatial and temporal formation of some precipitate, and the crud just keeps forming since the more of NaOH is constantly fed into the reactor. The crud problem might be solved by doing the pH control in some other way. For example, the preneutralization could be done with a more diluted NaOH or with a completely different neutralizing agent such as ammonia. The pH control could also be done by simply feeding the NaOH into the mixer during the extraction.

The low extraction efficiencies could be increased by increasing the number of stages in loading as well as increasing the pH and temperature. For example, having three stages in the loading with a pH closer to 7, and a temperature of 40 °C would most likely increase the extraction efficiencies to a higher level. Most likely the cause for the low efficiencies is not that Versatic 10 is not capable of loading more of the metals, since in the batch experiments it was shown that a lot more could be loaded into the extractant. Having a higher pH would most likely allow for more of the metals to be loaded. Having a higher pH might cause the co-extraction of Li to be also increased. In that case there might be the need to add a scrubbing stage into the process. The loaded organic could be scrubbed with for example $NiSO_4$ to kick out the co-extracted Li from the organic. The scrub raffinate could then be recycled back into the feed of the loading.

6.6 Migration of fluoride in the suggested process

Since the fluoride precipitation experiments after the Cu removal were not effective, it was decided to just follow the concentrations during the whole process to see what happens to the fluoride in the different stages.

During the solvent extraction of Cu, the fluoride is left into the raffinate. Around 530 mg/L of fluoride is in the LIBWL feed that is fed into the Cu removal step. In the raffinate of the Cu solvent extraction around 520 mg/L of fluoride is measured. In the loaded organic and stripping product less than 10 mg/L is measured. It can thus be concluded that the fluoride is not affected by the Cu solvent extraction.

During the precipitation of Fe, the fluoride is again not affected. Its concentration may be slightly diluted by the addition of the NaOH into the solution but almost all of it remains in the solution.

When it comes to the solvent extraction of Mn and Al by D2EHPA, fluoride migrates to the organic phase. The concentrations of fluoride in different streams during different D2EHPA runs are presented in Table 19.

Table 19. The concentrations of fluoride in different streams during runs with 30 vol-% D2EHPA. The conditions of the runs are shown in Table 10.

Stream	**F^-, mg/L D2EHPA run #1**	**F^-, mg/L D2EHPA run #3**	**F^-, mg/L D2EHPA run #4**
Feed	470	470	350
Raffinate	300	340	40
Loaded organic	130	150	260
Stripping product	30	15	50
Stripped organic	120	100	200

As can be seen from the Table 19, the amount of fluoride was decreased in the raffinate in all the runs when compared to the feed. During Run #4 with D2EHPA, the concentration of fluoride in the raffinate dropped to below 50 mg/L, so almost all of it was removed. The fluoride could be detected in the organic phase which proved that the fluoride was actually extracted and not removed some other way. It seemed that fluoride is not easily stripped from the organic phase. This would mean that the fluoride would start to accumulate into the organic phase and that could be a huge safety risk.

The fluoride might be forming a complex with Al in the solution, and it might be extracted with Al into the D2EHPA. Fluoride is known to complex with Al and Fe (Brückner et al., 2020), but the concentration of Fe is decreased during precipitation and almost no Fe is left in the solution when it is fed into the solvent extraction with D2EHPA. This indicates that fluoride rather forms the complex with Al. There is more Al in the solution when compared to Fe in the first place, which might be the reason.

HSC Chemistry was used to study the chemical equilibrium of the solution used in the experiments in order to find out what types of complexes fluoride forms in the solution. For the equilibrium calculations, the measured concentrations of metals in the actual used synthetic LIB waste leachate were converted to kilomoles since the software uses kilomoles. The pH was varied to see the different complexes of fluoride in different pH values. The amounts of different fluoride compounds that the software calculates as a function of pH are shown in Figure 36.

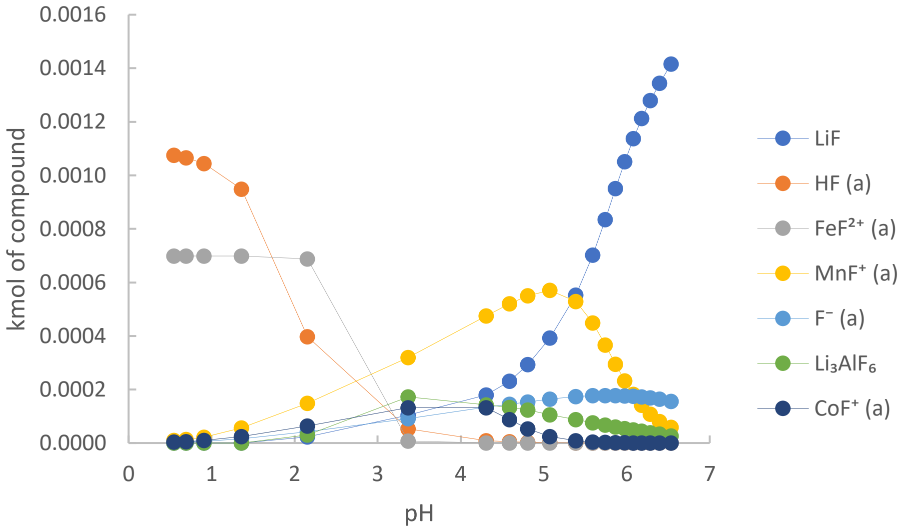

Figure 36. Different fluoride compounds as a function of pH, when calculated with HSC Chemistry. The starting amounts of metals in the calculation were the same as in the synthetic LIB waste leachate used in the experiments. The temperature was 25 °C.

As can be seen from the Figure 36, when the pH is 1-2, the largest amount of fluoride is as aqueous solution of HF. The second largest is a complex ion of iron and fluoride. No Al complexes were shown among the largest fractions of compounds. This was considered to be quite strange, since the concentration of Al in the solution is much higher than that of Fe. It was thought to be more reasonable for fluoride to complex with Al for this reason.

Some diagrams of the equilibrium were also drawn with KTH Medusa software. Again, the actual concentrations of the used solution were used. However, since the solution contains so many metals, the software was not able to calculate with them all. So, it was decided to just use the concentrations of Al, Fe, and fluoride. The other metals were added one by one to see if they make a difference to the diagrams. The other metals did not affect the diagrams when considering fluoride compounds, and it was concluded that mostly Al and Fe affect fluoride in the solution. The fractions of fluoride compounds as a function of pH when drawn with Medusa are shown in Figure 37.

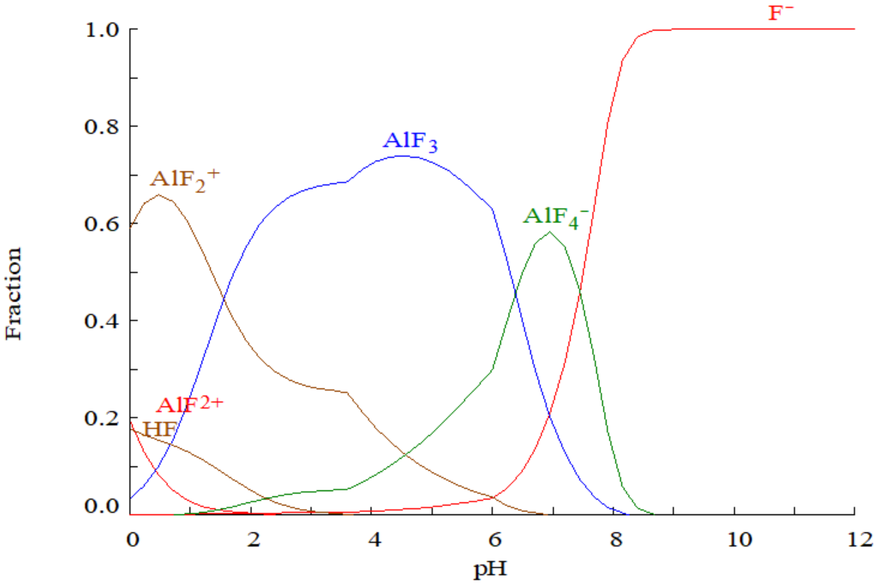

Figure 37. The fractions of fluoride compounds as function of pH when drawn on Medusa. The beginning concentrations of metals were the same as in the actual solution used in the experiments.

As can be seen from the Figure 37, the fluoride was mostly complexed with Al when the calculations were done with Medusa. The fraction of HF was much lower with Medusa than it was with HSC. The Fe complex of fluoride that was present in HSC simulations was not present in Medusa calculations. Based on these differing results from different software it is quite difficult to conclude which would be more reliable. Of course, the results are not completely comparable because of differences in calculations and ways of showing results but since they seem to differ so greatly it is difficult to say.

As was mentioned above, it would seem more likely that fluoride complexes with Al because of the much higher concentration of Al in the solution when compared to Fe. Also, the fluoride concentration is decreased significantly during solvent extraction with D2EHPA when Al also decreases, which moreover indicates that Al complexation. As when Fe was removed the fluoride concentration was not changed much. Another thing that would also emphasize that fluoride rather complexes with Al is the poor stripping from the D2EHPA of both of them. Al can have slower kinetics when it comes to extraction but the similarities of the behavior between fluoride and Al are very large. It might be that as some of the Al and fluoride are extracted as a complex, which is not easily removed from the loaded organic. These results emphasize that it would be best if the fluoride be removed before the other metals are separated from the leachate. Or, at least before solvent extraction with D2EHPA.

During Co and Ni extraction, there was only around 50 mg/L of fluoride in the feed solution. After the extraction, around 30 mg/L is left into the raffinate. In the loaded organic there is only less than 10 mg/L of fluoride, so a significant share is extracted into the Versatic. Also, in the stripping product, there is less than 10 mg/L of fluoride. It seems that a significant amount of fluoride is extracted into Versatic 10 but with such low concentrations near the detection limit of the electrode, it is difficult to say for sure.

6.7 Suggested flowsheet

Based on the experiments above, a flowsheet with main operating parameters is suggested for a process to recover valuable metals from LIB waste leachates (Figure 38).

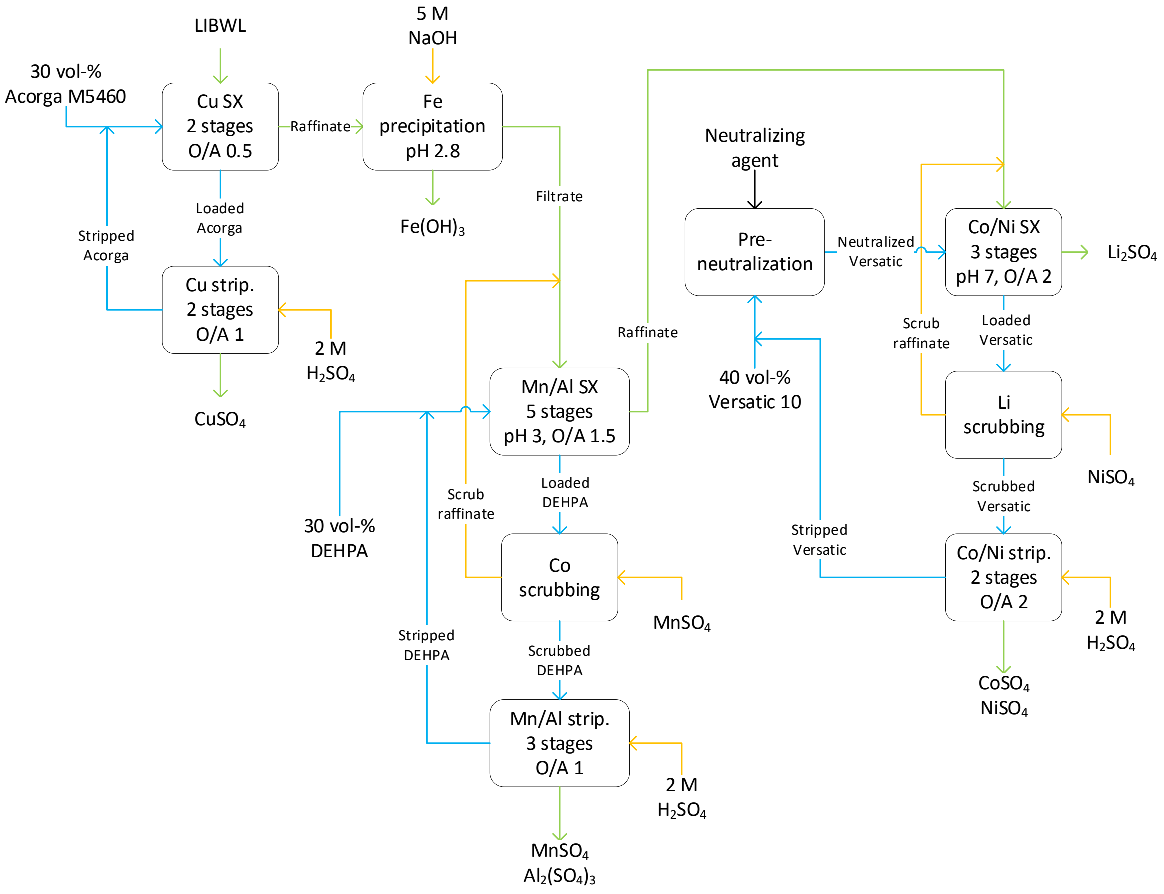

Figure 38. Suggested flowsheet for the recovery of valuable metals from LIB waste leachates.

At first, the LIBWL was fed into Cu solvent extraction, where pure copper sulfate was obtained from the stripping of the loaded extractant. Only less than 50 mg/L of Cu was left in the raffinate in two stages with phase ratio of 0.5. Over 99 % pure Cu was recovered into the stripping product when stripping the loaded organic with sulfuric acid at a phase ratio of 1. The concentration of Cu in the stripping product was around 2700 mg/L. The concentration in the stripping product could maybe be increased by increasing the phase ratio to 2, for example. The sulfuric acid would most likely be capable of stripping the loaded organic efficiently even if less of it was available. Some Cu might be left into the stripped organic but most likely it would not affect the extraction too much.

The other metals that are left into the raffinate go forward into precipitation where Fe is separated. NaOH is added to the solution so that the pH increases to around 3 and Fe precipitates as iron hydroxide. Less than 50 mg/L of Fe was left into the filtrate when pH was

2.8. The obtained solids are filtered and the filtrate with the other metals goes forward into another solvent extraction.

During the second solvent extraction circuit, Mn and possibly Al is separated. If Mn were to be wanted as a pure product, it would be suggested that the Al be removed at some other stage of the process like in the pretreatment step for example. Also since the stripping of Al is not very efficient with sulfuric acid it would be beneficial. The pH of the solvent extraction should be 3, so that efficient Mn removal is ensured. The higher pH means that there will be Co losses during the process and thus a scrubbing stage for Co is required. The scrubbing could be done with $MnSO_4$ and if pure Mn would be produced from the stripping, it could be utilized in the scrubbing.

The raffinate from the D2EHPA extraction circuit, consisting of only Co, Ni, and Li, is fed into the final stage of the process. In the final stage, Co and Ni are extracted together with Versatic 10 and pure Li is left into the raffinate. After the extraction, there needs to be a scrubbing stage to get the co-extracted Li back from the loaded organic. The scrubbing could be done with for example $NiSO_4$ and the raffinate from the scrubbing could be recycled back into the extraction. The scrubbed extractant would then be stripped and Co/Ni sulfate would be obtained as the stripping product. The stripping product can be utilized to precipitate precursors for LIB cathode materials.

It is suggested that the fluoride containing parts of the LIBs are removed before the leaching. This can be done in the pretreatment stages that are not covered in the suggested process flowsheet (Figure 38) and it is often done. Since the fluoride in acidic conditions can be in the form of hydrofluoric acid, it would mean that the equipment materials would need to be carefully considered and the hazards of the process are increased. Also, as it was seen, the fluoride can create problems in the recovery process itself. It was noticed that the fluoride is extracted with the Al in during solvent extraction with D2EHPA. Also, the fluoride is not stripped from the loaded extractant, and it would most likely start to accumulate into the extractant and start to create even more problems.

7 CONCLUSIONS

In this Thesis the separation and recovery of valuable metals from Li-ion battery waste leachate with hydrometallurgical methods was studied. At first, the overall recycling methods that have been used in LIB recycling were discussed with the focus being on different hydrometallurgical methods. Also, the fluoride in LIBs was discussed.

In the experimental part, the goal was to study the separation in practice and recover metals from spent LIB leachate with different methods. At first Cu was successfully recovered as copper sulfate through a solvent extraction circuit.

Fluoride precipitation was attempted with the addition of a stoichiometric amount of lime in the solution. The fluoride concentration started to decrease around pH 4 but at the same time the concentrations of valuable metals started to decrease also. The concentration of calcium in the solution did not behave similarly to the fluoride and thus it was thought that maybe the fluoride precipitates as something else and not as CaF_2. Most likely the stoichiometric amount of added NaOH is not enough for the fluoride to react into CaF_2. The fluoride precipitation might be more successful if more of calcium were to be added into the solution. However, at the same time some gypsum is also expected to precipitate. With the high losses of valuable metals, it is concluded that the fluoride precipitation is not feasible at this point.

With the precipitation experiment it was noted that Fe could be easily removed by increasing the pH to almost 3. It was hoped that some Al could also be removed by precipitation. However, the Al only started to properly precipitate after around pH 4. Then, the valuable metal losses were again too high and thus it was decided that the Al be removed together with Mn through solvent extraction.

When Mn and Al were removed with solvent extraction it was seen that the extractant used was most likely not capable of loading such high concentrations as were present in the solution at a pH of 2.5. Increasing the pH to 3.0 also increased the extraction efficiency. However, when the pH is that high, the Co losses are increased as well. Thus, a scrubbing stage should be added to scrub the co-extracted Co from the loaded organic before stripping. There still most likely needs to be quite a few stages since Al has a slow mass transfer. Another option might be to increase the residence time in the mixer. Another thing to consider is if pure Mn is wanted as a product. If Al could be selectively removed in the pretreatment there would be a chance to recover pure $MnSO_4$, which might be utilized in the scrubbing of Co as well.

When Co and Ni were separated from Li some crud formation was noticed. The crud was most likely caused by the preneutralization of the extractant with quite concentrated NaOH.

The problems might be avoided if the neutralization were to be done with either a more dilute NaOH or with some other chemical. Up to 80 % of Co and Ni were removed from the solution. The efficiency is not enough to create pure Li in the raffinate, and on the other hand the high yield for Co and Ni are needed for improving the economic efficiency of the process. In order to increase the efficiency, more stages at higher pH and increased temperature should be considered. At higher pH, there will most likely be more co-extraction of Li and a scrubbing stage should be again added.

Fluoride in the process seemed to be extracted at the same time as Mn and Al. This was unexpected. The fluoride concentration in the aqueous feed decreased and the fluoride was detected from the organic phase. This proves that fluoride was actually extracted and not removed by some other way. Fluoride was not stripped efficiently with sulfuric acid from the loaded organic. If the fluoride starts to accumulate into the organic phase, there would be even more health and safety risks. Thus, it is suggested that the fluoride be removed in the pretreatment steps before leaching with for example some kind of thermal treatment if possible. This way major health and safety concerns could be avoided.

In conclusion, the suggested flowsheet was proven to be a viable option for recovering valuable metals with high purity from spent LIBs. High extraction efficiencies were achieved for Cu, Fe, Mn and Al. The extraction of Co and Ni still needs some optimizing but the with co-extraction method with Versatic 10 was deemed promising. The removal of fluoride also still needs to be considered and researched in more detail.

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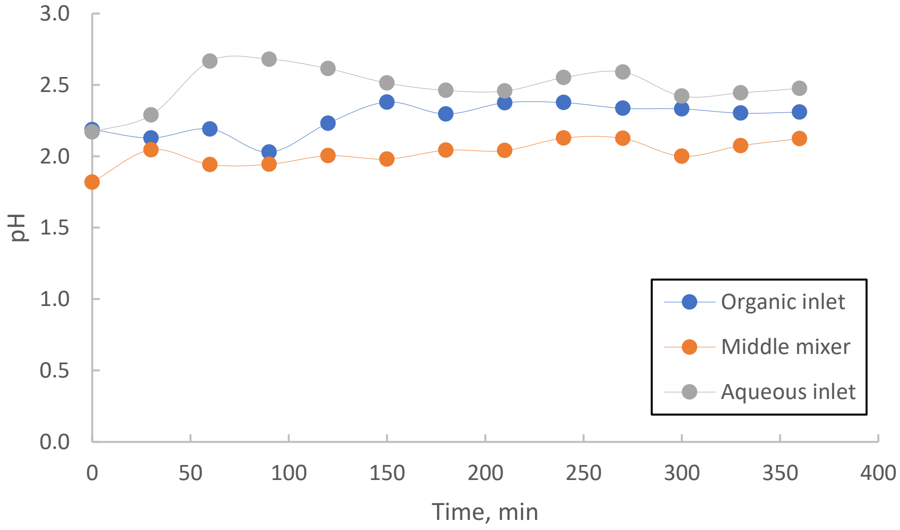
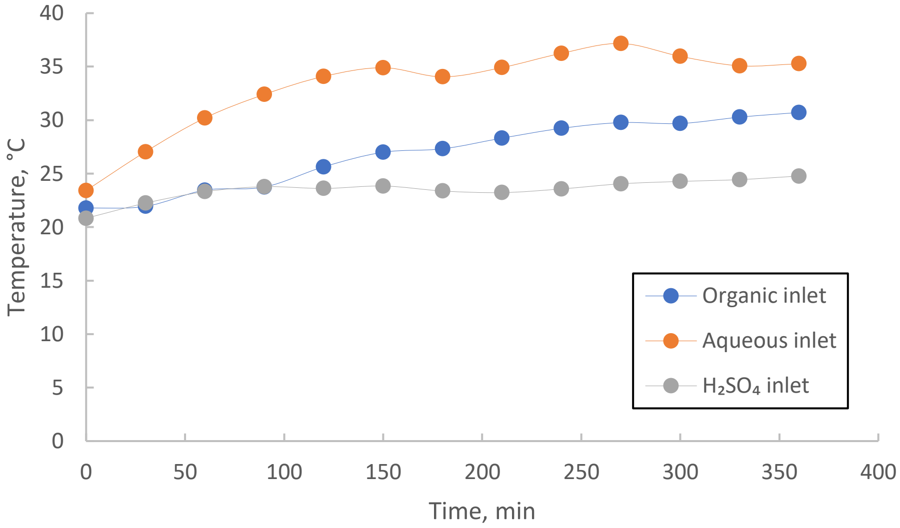
APPENDICES

APPENDIX I	Measured pH values and temperatures during D2EHPA runs.
APPENDIX II	Measured pH values and temperatures during Versatic 10 runs.

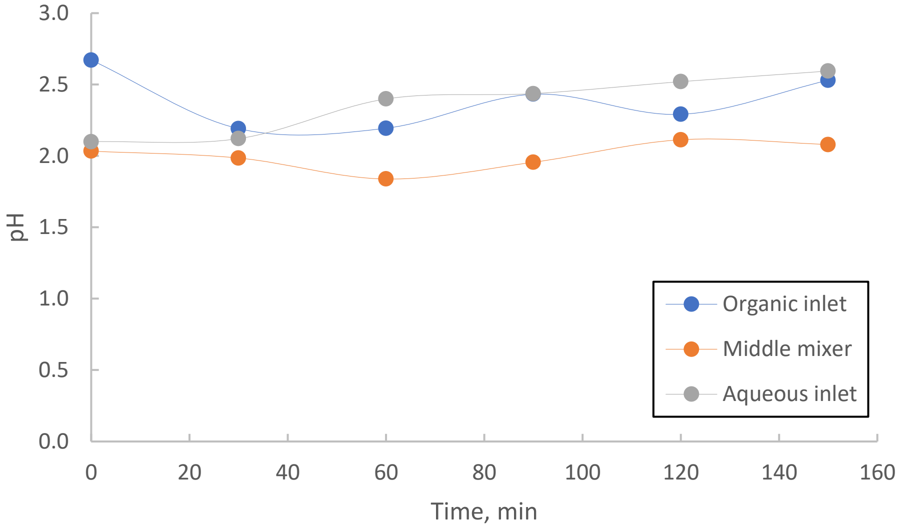
APPENDIX I: Measured pH values and temperatures during D2EHPA runs.

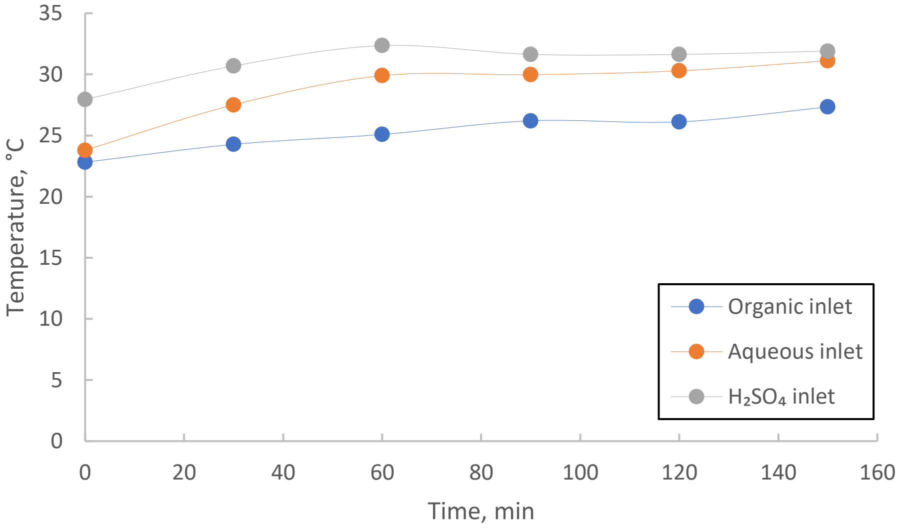
Measured pH values and temperatures during Run #1 with 30 vol-% D2EHPA. There were 3 stages in loading with a phase ratio of 1, a target pH of 2.5, and a residence time of 6 minutes. The shown values are averages of measured values at a certain time.



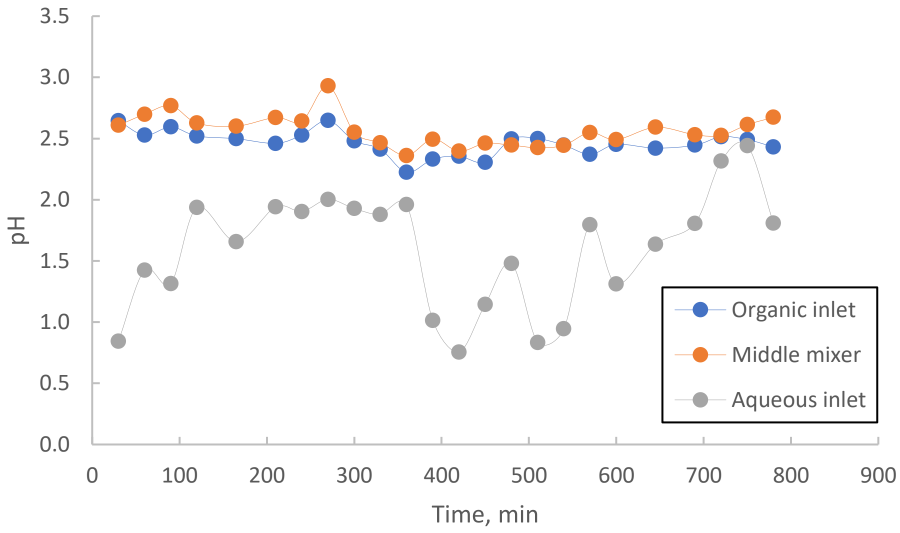


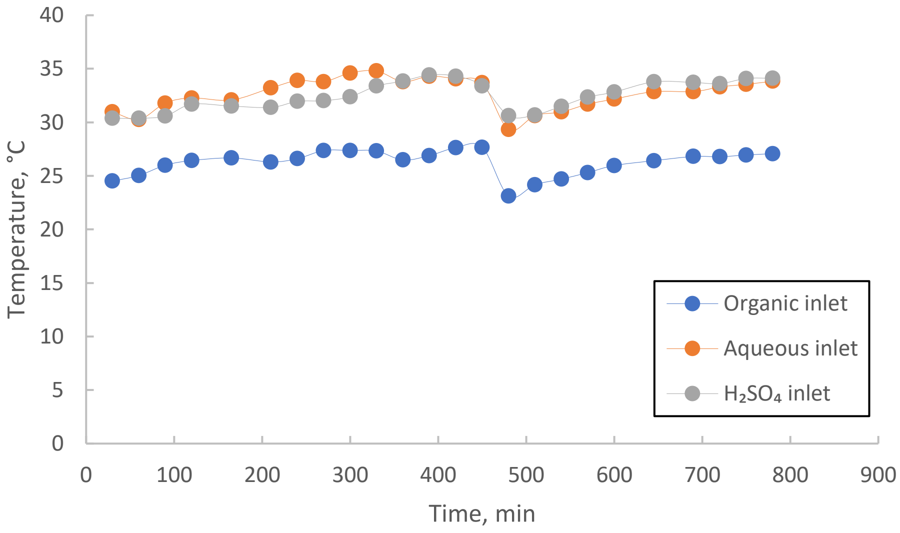
Measured pH values and temperatures during Run #2 with 30 vol-% D2EHPA. There were 3 stages in loading with phase ratio of 1.5, a target pH of 2.5, and a residence time of 6 minutes. The shown values are averages of measured values at a certain time.



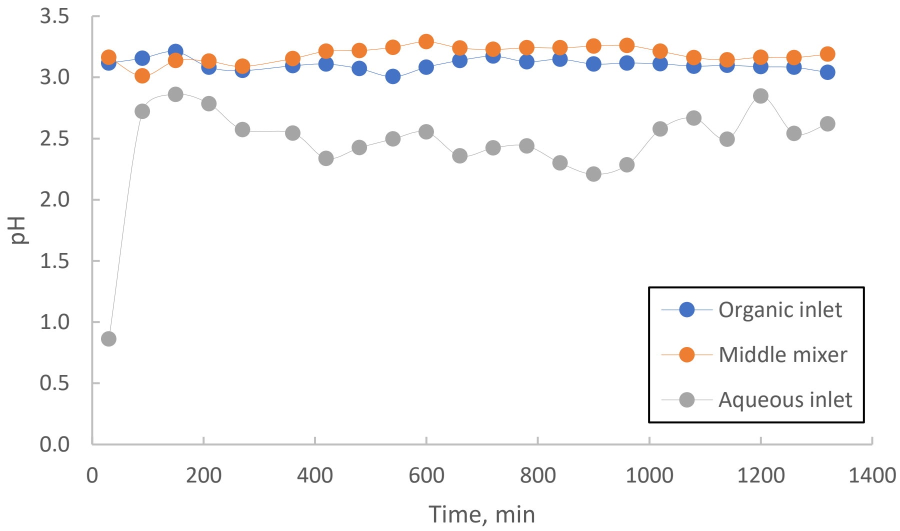


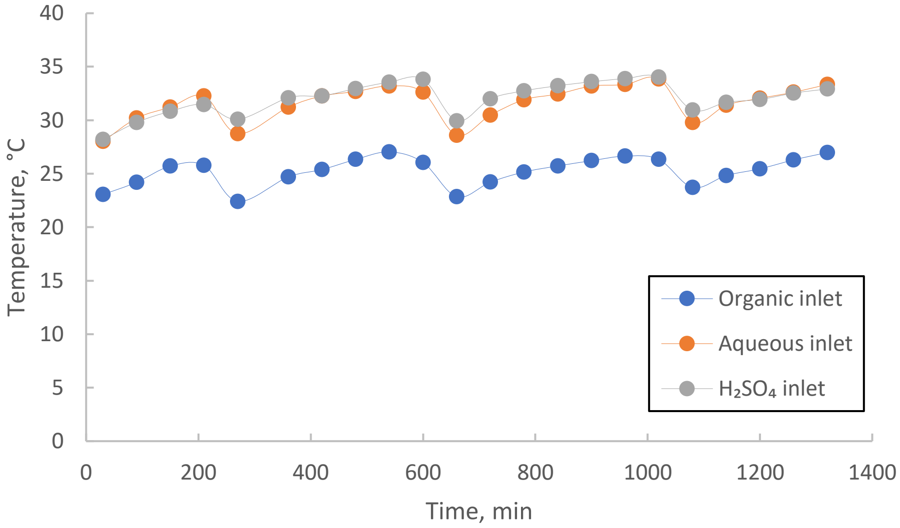
Measured pH values and temperatures during Run #3 with 30 vol-% D2EHPA. There were 5 stages in loading with phase ratio of 1.5, a target pH of 2.5, and a residence time of 6 minutes. The shown values are averages of measured values at a certain time.





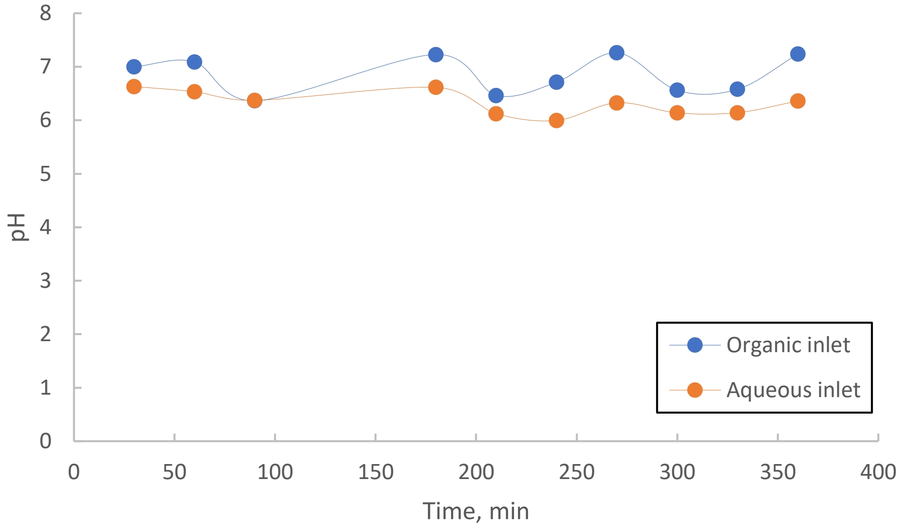
Measured pH values and temperatures during Run #4 with 30 vol-% D2EHPA. There were 5 stages in loading with phase ratio of 1.5, a target pH of 3, and a residence time of 6 minutes. The shown values are averages of measured values at a certain time.



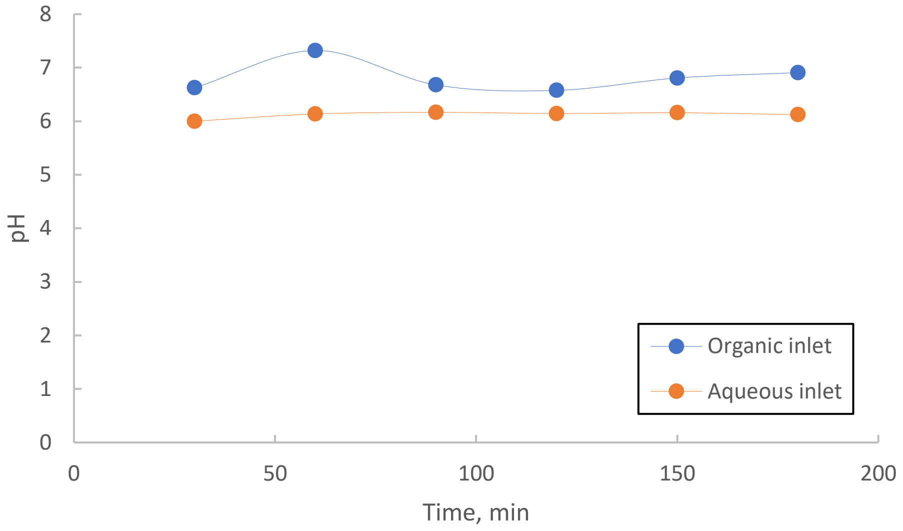


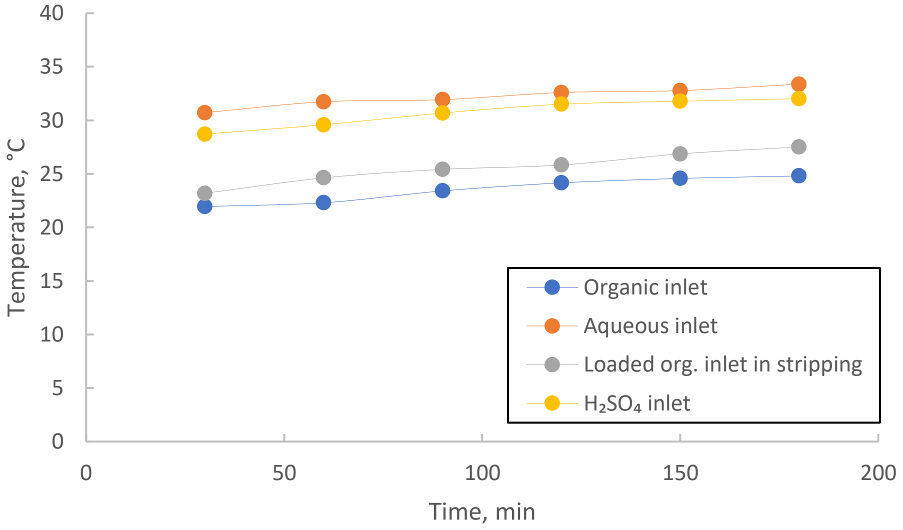
APPENDIX II: Measured pH values and temperatures during Versatic 10 runs.

Measured pH values Run #1 with 40 vol-% Versatic 10. There were 2 stages in loading with phase ratio of 1.5, a target pH of 6.5, and a residence time of 6 minutes. The temperature during Run #1 was room temperature. The shown values are averages of measured values at a certain time.



Measured pH values and temperatures during Run #2 with 40 vol-% Versatic 10. There were 2 stages in loading with phase ratio of 2, a target pH of 6.5, and a residence time of 6 minutes. The shown values are averages of measured values at a certain time.





Measured pH values and temperatures during Run #3 with 40 vol-% Versatic 10. There were 2 stages in loading with phase ratio of 2.5, a target pH of 6.5, and a residence time of 6 minutes. The shown values are averages of measured values at a certain time.