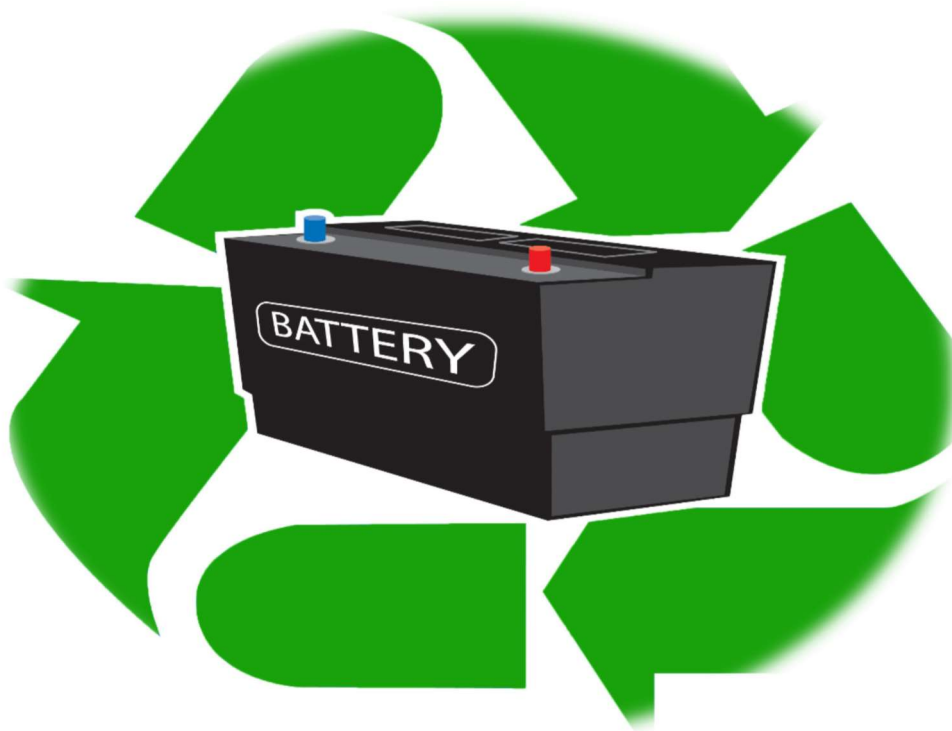




**CHALMERS**  
UNIVERSITY OF TECHNOLOGY

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# Recycling of lithium-ion batteries- Leaching Study



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# Summary

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The project is an evaluation of a recycling process of lithium batteries using a hydrometallurgical treatment method. The focus in this study was to investigate the effect of several parameters on the leaching process. The studied parameters were: acid concentration, temperature and solid to liquid ratio. A kinetic study was performed as well. The work started with theoretical studies to collect information about lithium-ion batteries in general and existing technologies which are used for the recycling. The work continued with experimental studies. The electrodes recovered from the lithium-ion battery were crushed. The black mass was then leached with sulphuric acid. Several parameters such as different temperature, acid concentration, time and solid to liquid ratio were studied.

# Preface

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Lithium-ion batteries are widely used today in many applications. One of the most important challenges caused by the wide usage of lithium-ion batteries is their waste when they are spent. The motivation for the recycling is due to the presence of valuable chemical components such as cobalt, copper, lithium and a mixture of organic electrolyte, as well as the legislative requirements to recycle spent batteries accompanied by a prohibition of their landfilling. Recycling of lithium batteries helps to avoid the environment's pollution and gives some economic benefits.

This project has been performed as thesis work during my study in the Chemical Engineering program at Chalmers University.

First and foremost, I would like to thank all my family members, I have received intensive and unlimited support from them.

Special thanks go to my supervisor, Martina Petranikova and my examiner Britt-Marie Steenari at Chalmers University for their patience, guidance and support during this work. I would also like to thank Gabriele Lombardo for his support and help during this project.

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# 1 Introduction

The world is witnessing tremendous development and increasing growth in the use of lithium-ion batteries. The main disadvantage of increasing the use of these batteries is the volume of the waste after they are spent. Recycling of batteries is appropriate for at least two important reasons [1]:

1. Lithium-ion batteries are potential sources of valuable metals such as lithium, cobalt, nickel, and others. Recovery of these metals provide a good economic benefit.
2. Recovery of metals from secondary sources saves the primary raw materials (ores) and decreases the effect of mining on the environment.

There are various methods and technologies used in this field. In this project, a couple of used technologies will be discussed, but the focus has been to study and analyze leaching as part of the hydrometallurgical treatment. The hydrometallurgical treatment is one of the methods used for recycling of spent lithium-ion batteries.

A spent lithium-ion battery contains several valuable metals like Li, Co, Ni and Mn and others. Recovery of these materials gives big environmental and economic benefits. Recycling is a main topic for the research group Industrial Materials Recycling within Chalmers University of Technology. The group works on a project related to recycling of lithium-ion batteries together with a car manufacturer. The experiments were performed using Chalmers lab facilities. In the leaching process the effects of different parameters: time, temperature, acid concentration and solid to liquid ratio on Li, Co, Mn, Ni, Cu and Al recovery from electrode material, the so called black mass, were studied.

## 1.1 Problem description

In this assignment, we investigated various parameters to determine the effect of studied parameters on the leaching process. The leaching process is the important step of hydrometallurgical treatment and it was studied in this project by applying the following parameters:

- Different temperature 25, 40 and 60 °C
- Leaching time up to 120 minutes.
- Two different concentrations of sulphuric acid, 0.5 respective 1 M.
- Different mass ratios of solid to liquid, 1:50 and 1:20.

In the leaching process the behaviour of Co, Mn, Ni and Li was studied.

## **1.2 Limitations**

There are various options used in implementing of leaching:

1. Based on the leaching media
2. Based on the pressure
3. Based on the performance

Within this project and due to limited time, only a part of case 1 was investigated using a mineral acid (sulfuric acid). To get a more sufficient result, the leaching process can be determined with a wider range of all studied parameters/conditions. However, this was not possible in the limited time of this project.

## 2 General about lithium batteries

### 2.1 The history of lithium batteries

In 1912, Gilbert Newton Lewis, an American physical chemist, started a pioneer work in lithium- metal batteries, but the first primary lithium-metal batteries were available in the 1970s by the Exxon Company [2].

During the 1970s and 1980s, a lot of research was focusing in developing and converting the primary lithium-metal batteries to rechargeable batteries with high power density. In the 1980s, rechargeable lithium-metal batteries were commercialized for the first time but failed due to security risks associated with lithium metal which caused violent reactions to temperature changes during charging [3].

The first rechargeable lithium-metal battery was made of a titanium disulphide cathode and a lithium-aluminium anode [3].

Research continued striving to solve the problem that was associated with using lithium metal. It was found that it was impossible to use that technology in rechargeable batteries and that it was necessary to find a better and safer alternative. After a lot of research in this field the result was to replace lithium metal. Research resulted into the development of Li-ion batteries, in which lithium compounds and salts are used instead of metallic lithium.

Nowadays the most common active material is  $\text{LiCoO}_2$  as the cathode material and carbon as the anode material [3] [4].

The first so called Lithium-ion battery was developed by Asahi Chemicals and was marketed for the first time by Sony Corporation in 1991. The new batteries received immediate a huge success due to their good performance, low weight, high gravity power density 120-150 Wh / kg and high cell voltage (3.6V) [4][5][6].

Today there are several types of lithium-ion batteries available on the market. The difference between all these types is linked to their cathode materials.

### 2.2 The difference between lithium metal and lithium-ion batteries

There are two different types of lithium batteries: primary and secondary.

Lithium metal batteries belong to the primary type of batteries (non-rechargeable), where the anode is made of metallic lithium [7]. These batteries have a typical gravimetric density of 250 Wh/kg and are good alternatives for use with digital cameras, medical devices and military purposes.

The lithium-ion battery is a secondary advanced type of lithium batteries. Theses batteries have a typical gravimetric density of 150 Wh/kg.

A lithium-ion battery consists of a positive electrode “cathode” which can be made of different types of material, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and others. The negative electrode “anode” active material is carbon or graphite [8].

The function of lithium metal and lithium-ion batteries is to convert the chemical energy stored in the battery's active materials to electrical energy through an electrochemical reaction. The function differs only during recharging. In the lithium-ion battery, the process proceeds in the opposite direction. That means during recharging of the lithium-ion battery, electrical energy is transformed to chemical energy by a reversible electrochemical reaction [6].

### 2.3 Application areas of lithium-ion batteries

There are different types and shapes of rechargeable batteries. From its first appearance until today, lithium-ion batteries remain leading and dominant in the electronic market. Lithium-ion batteries are widely used in portable products such as mobile phones, cordless phones, MP3 players, GPS receivers, camcorders, vacuum cleaners, laptops, etc. The use of lithium-ion battery is so wide that it exceeds the portable device and it increases significantly over time, see Figure 1 below.

An important application area for these batteries is storage of electrical energy produced from wind mills and solar panels. The electricity generated during the night is stored in batteries to be used in the peaks in electricity demand.

A new and quickly developing area of use of lithium-ion batteries is in electrical vehicles, where the performance and capacity of the batteries are the key factors for designing of these vehicles.

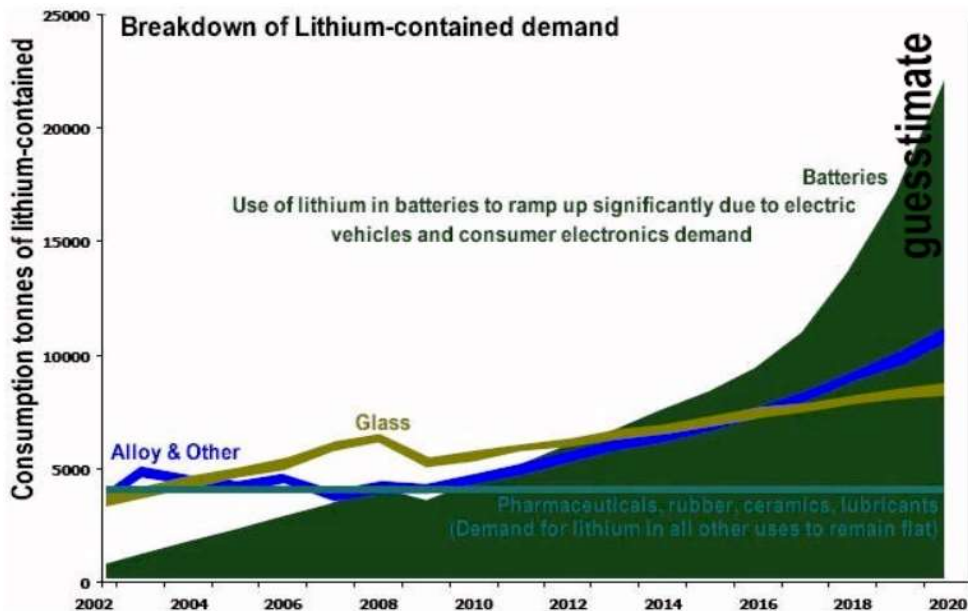


Figure 1: Forecast of lithium-ion batteries demand [8].



## 2.4 Lithium-ion batteries advantages and disadvantages

Advantages [5] [10] [12]

Lithium-ion batteries have a higher volumetric and gravimetric energy storage capacity compared to the other batteries such as nickel cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), and valve-regulated lead acid (VRLA) battery system, see Figure 2 below).

1. Smaller and lighter. The used materials are lighter that gives a better performance.
2. High energy density. Higher energy density leads to a longer operating time.
3. Low self-discharge that leads to longer duration. A special advantage of lithium-ion batteries is their self-discharge that is less than 3% per month.
4. Does not have a memory effect. This means the lithium-ion batteries are not required to be empty before a new charge.

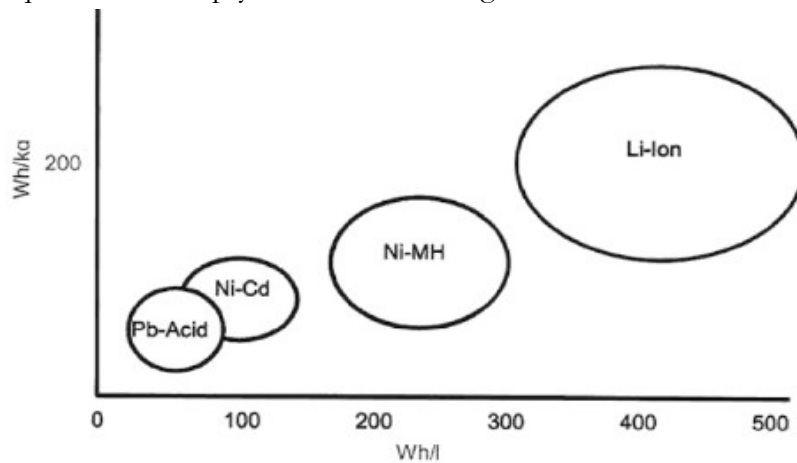


Figure 2: Energy density (Wh / l) and specific energy (Wh / kg) for rechargeable battery systems [5].

Disadvantages [5]

1. Short lifetime of the portable battery, approximately for 3 years (average lifetime for NiMH battery is 5 years).
2. Expensive
3. A special protection circuit is required to avoid overcharging
4. Sensitive to high temperature.

## 2.5 Construction of lithium-ion batteries

A lithium-ion battery contains of electrochemical cells consisting of four parts, namely anode, cathode, electrolyte and separator [6], see figure 3 below.

**Negative electrode** called anode. The anodes that are based on graphite are widely used nowadays due to their long life, availability and relatively low cost [6] [11].

**Positive electrode** called cathode. The cathode active material is a metal oxide that can be made with different chemistries such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMnO}_x$ ... etc. [6] [11].

**Electrolyte** with is the medium where the ions are moving in between the anode and the cathode. The electrolyte contains a lithium salt e.g.  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ , etc. The lithium salt is dissolved in a dipolar aprotic organic solvent such as ethylene carbonate and methyl carbonate [6] [11].

**Separator** which is a porous polymeric membrane. The function of the separator is to allow lithium ions to pass through the pores and prevent short circuit formation between the cathode and the anode [6] [11].

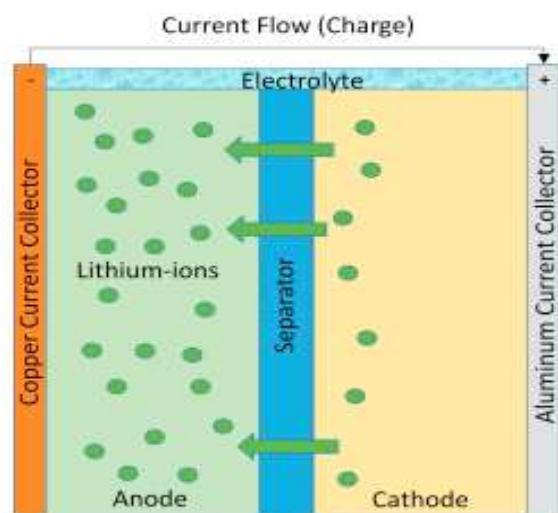


Figure 3: Electrochemical cell components in lithium-ion battery [11].

## 2.6 Principles of lithium ion batteries

The function of the battery is realized by transferring lithium ions between cathode and anode. During charging of the lithium-ion battery, the current carried by lithium ions ( $\text{Li}^+$ ) of the positive electrode (cathode) is transferred to the negative electrode (anode). At the discharge, the process goes in the opposite direction i.e. the lithium ions are shifted from negative to positive electrodes [6] [12] see figure 4 in the next page.

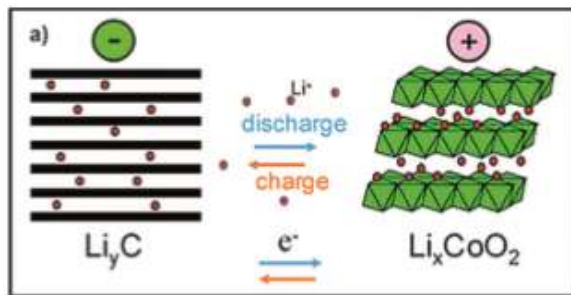


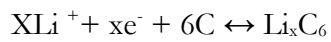
Figure 4: The charge-discharge cycle of rechargeable batteries [12].

The figure 4 explains the charge - and discharge process in lithium-ion battery which have  $\text{LiCoO}_2$  as positive electrodes material and carbon as negative electrodes material. The chemical reaction that happens during the charge and discharge is shown below [13],

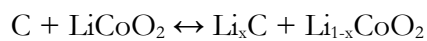
The positive electrode half-reaction (cathode reaction),  $\text{LiCoO}_2$  as an example:



The negative electrode half-reaction is:



Overall cell reaction:



## 3 Recycling of spent lithium-ion batteries

### 3.1 Background

In 2000, the global production of lithium-ion batteries was about 500 million cells. The annual amount of waste from lithium-ion batteries was estimated to around 200 to 500 million tonnes [14]. The waste contains 5–15% wt. Co and 2.7% wt. Li in addition to several different materials, based on the amount of consumption mentioned earlier.

It is worth mentioning that the increase of lithium-ion batteries consumption in the period 2000 to 2010 has become 800% worldwide. USA allotted a total production for lithium-ion batteries amounting to 12.7 billion mobile phones, 94.4 million laptops and 768.9 million digital cameras.

In the year 2020, it is expected that the amount and weight of discarded lithium-ion batteries will exceed 25 billion units and 500 thousand tons. This is due to industry focus and the growing interest of electric cars.

The increase in waste volume of batteries because of increased manufacturing, the use of batteries in addition to environmental awareness, considering the risks that could have an impact on the environment, have led to the development of a program to recycle spent batteries [14].

### 3.2 Why battery recycling is important:

- By a recycling process, several different valuable metals as cobalt, nickel, lithium and others are recycled and give economic benefits [6].
- Recovery of the batteries protect the environment from several risks like pollution [15].

### 3.3 Recycling processes for spent electric vehicle lithium-ion battery

Recycling of lithium-ion batteries is a complex process because of the huge amount of different materials that are used in the production of these types of batteries. In theory, it is possible to almost completely recover a lithium-ion battery, but in practical terms, the separation of materials mixture is complicated.

In 2013, a hydrometallurgical process was developed by Recupyl S.A that is stated to have 90% recovery rate. This method can be used to recycle a spent lithium-ion battery but the multiple steps involved in the process have been an obstacle for the process to be used in the industry sector [16].

Nowadays a pyrometallurgical process is the most used method in the industry for recycling of spent lithium-ion batteries. This process is expensive and requires large

quantities of energy but currently they are more common than the hydrometallurgical process due to existing infrastructure. [6].

### **3.3.1 Pyrometallurgical treatment**

In general, the pyrometallurgical processing is applied to recovery of metals from spent Li-ion batteries at high temperatures (up to 1200°C). Such approach is widely used in the recycling of lithium-ion batteries and it is more common than hydrometallurgical treatment.

The advantages of such approach is that the purity of the final products is relatively high, the performance is relatively simple and in addition to the process and production volumes are also high.

On the other hand pyrometallurgical processes require a large amount of energy and can have a negative impact on the environment. The gas emissions such as CO and volatile organic compound need an additional treatment and there is also generation of CO<sub>2</sub>. Another negative effect is the dust formation due to material handling and transportation. [6] [17]. The main disadvantage of pyrometallurgical treatment is disability to recover several metals such as aluminium, manganese, and especially lithium since they become incorporated in a slag. Pyrometallurgical treatment is applied by Accurec (Germany), Umicore (Belgium), and Xstrata.

### **3.3.2 Hydrometallurgical treatment**

Hydrometallurgical process have been applied in metal recovery from primary raw material and it is also applied for the recovery of valuable metals from the secondary sources. Hydrometallurgical treatment offers several significant advantages for metals recovery. The process does not require much energy (up to 100 °C) and the cost to carry out the process is lower to compare to pyrometallurgical process [6] [21]. In addition to that, the environmental impact is lower as well as gas emissions, dioxin and dust potential.

An important advantage of using such approach is that very high purity of the final products can be achieved. The only obstacle for performing such process in the industry is the complexity [6].

Hydrometallurgical treatment of Li-ion batteries requires the discharging of the batteries, which is then followed by dismantling, mechanical pre-treatment to separate some battery components (covers, foils, etc.) from the metal bearing material (black mass – mixture of active material). After the physical processes, a series of chemical processes based on acidic leaching is carried out for the recovery of the metals from the battery [18], see figure 5 below.

Leaching is the first important step in the chemical process and it is used to recover the solute from a solid by using of appropriate solvents. After the leaching step, different chemical methods such as solvent extraction, precipitation, ion-exchange and electrowinning can be used for separation and recovery of metals with a high purity of the end products [6].

Hydrometallurgical treatment is used by Recuply (France) and Retrie Technologies (Canada) [6].

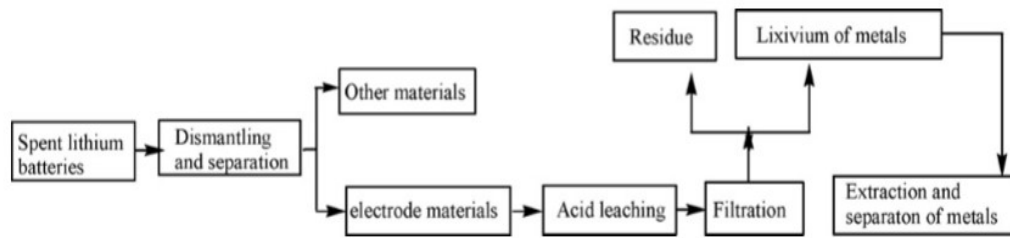


Figure 5: A schedule of all steps for recycling a spent lithium-ion battery [18].

### **Dismantling and physical processes**

The purpose of the physical processes is to separate battery components based on different properties such as density, conductivity, magnetic behaviour, etc. [18]. The process consists of different steps such as discharging and crushing, see the general procedure at figure 6.

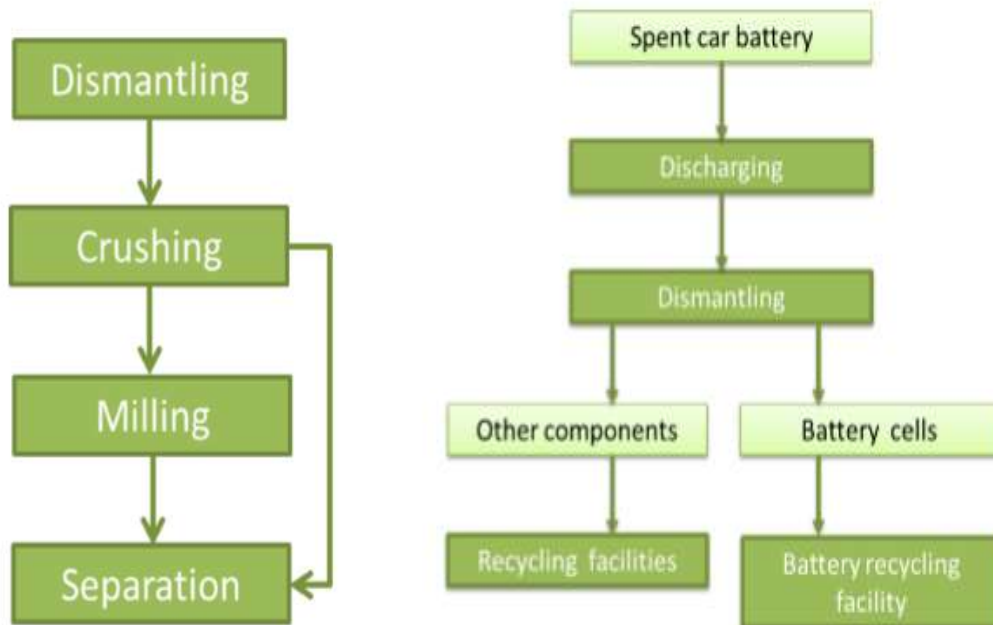


Figure 6: Pre-treatment procedure for a spent portable and car lithium-ion battery [6].

### **Chemical processing**

The chemical processes are carried out first with leaching in acidic media (inorganic and organic acids). After leaching there are different methods that can be used for metal recovery from the leachates. Such methods are: solvent extraction, precipitation, ion-exchange and electrowinning see figure 7 in the next page [6].

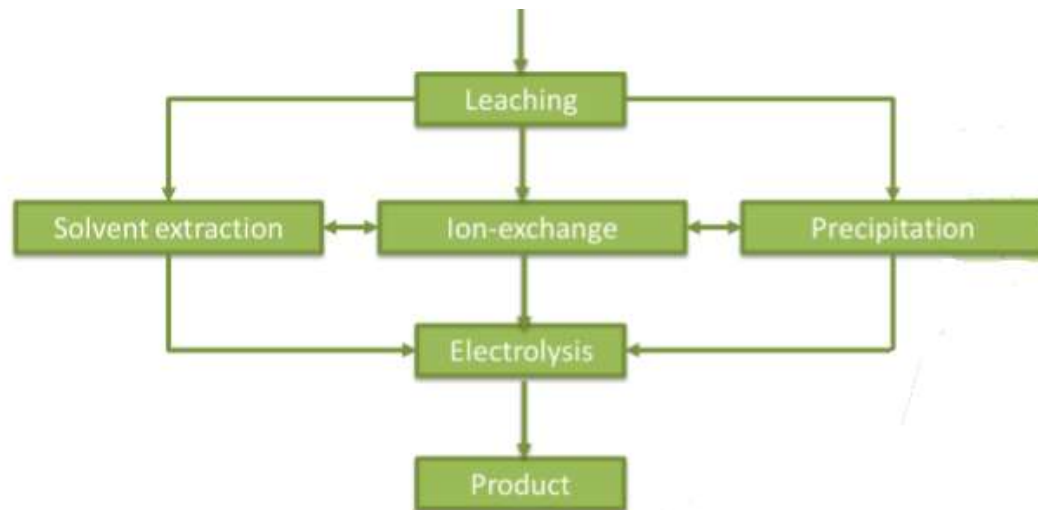


Figure 7: Ordering steps of chemical hydrometallurgical process [6].

## Leaching

Leaching is the first chemical step in recycling of lithium-ion batteries. The process is based on solubilizing all metals. For this purpose, inorganic or organic acids can be applied. Hydrochloric acid (HCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and nitric acid (HNO<sub>3</sub>) are usually used as the leaching medium. There are a lot of parameters such as the concentrations and the type of the leaching media, pH, solid to liquid phase ratio, temperature, etc. that influence the leaching efficiency of the metals. It was found out that using HCl as leaching media gives the highest leaching efficiency due to the ability of chloride ions to destabilize the formation of a surface layer [6]. To increase the leaching efficiencies, reductive agents have been used in several studies.

Reductive agents such as hydrogen peroxide is commonly used in the leaching by HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>. The addition of hydrogen peroxide generates oxygen that promotes cobalt oxide dissolution by reducing Co<sup>3+</sup> to Co<sup>2+</sup>. At the same time the leaching efficiencies of lithium and cobalt can be increased. For example, Zhang et al.<sup>31</sup> reported that 40% of cobalt and 75% of lithium was leached out by HNO<sub>3</sub> without addition of hydrogen peroxide, while the addition of 1.7 vol% H<sub>2</sub>O<sub>2</sub> increased the leaching efficiency to 99% for both metals [6].

Organic acids (citric acid, DL-malic acid) can be used as a leaching agent for the recovery of metals like lithium and cobalt from a spent lithium-ion battery.

For example, Li et al.<sup>10</sup> reported that the use of 1.25 M citric acid and 1 vol% hydrogen peroxide at 90 °C efficiently leached the black mass within 30 min [6].

## Precipitation

Directly after leaching precipitation can be applied to recover/remove some metals from an aqueous solution. The precipitate can be recovered by centrifugation or filtration process. Precipitation by NaOH is usually used to remove impurities such as Cu, Al, and Fe from the leachate before solvent extraction of Co and Ni. Lithium is usually precipitated by using Na<sub>2</sub>CO<sub>3</sub> or CO<sub>2</sub> after cobalt and nickel removal.

For example, the Recupyl process is based on removal of copper contamination by cementation with steel shot, cobalt is recovered by adding sodium hypochlorite

(NaClO) to precipitate  $\text{Co}^{3+}$  hydroxide, which is then separated by filtration. Sodium hydroxide is used to recover aluminium. The lithium in the aqueous solution is precipitated by reducing the pH of the solution to 9 and adding  $\text{CO}_2$  that reacts with lithium ions [6].

### **Solvent extraction**

Solvent extractions is usually used to recover metal ions such as Co, Mn and Ni from spent lithium-ion batteries. Organic extractants such as di-(2-ethylhexyl) phosphoric acid (D2EHPA), bis-(2,4,4-tri-methyl-pentyl) phosphinic acid (Cyanex 272), trioctylamine (TOA), diethylhexyl phosphoric acid (DEHPA) or 2-ethylhexyl phosphonic acid mono-2- ethylhexyl ester (PC-88A) have been used to recover the metal ions from leaching liquors. The main advantage of solvent extraction is the ability to extract a specific metal from a solution i.e. a specific metal such as nickel, cobalt or others can be extract separately from a solution with a high purity [19]. As previously mentioned, Cyanex 272, D2EHPA, and PC-88A are usually used to recover cobalt and separate it from nickel and lithium. The advantage of that extractant is low co-extraction of lithium, which can be recovered with a relatively high purity by precipitation. Electrowinning has been applied to recover nickel [6].



## 4 Method

This chapter of the thesis work presents the procedure and the method that has been used to achieve the goal of this study. It also discusses and describes in details the project plan and how the work is performed step by step.

### 4.1 Method chosen

The main method used to perform this work is dividing the project into several sub-tasks to facilitate the work, see figure 8 below. Each sub-task has been solved independently either by searching for previous studies in the field or by discussing the problems with the project supervisor. At the end, all the project parts were conducted together.

The following figure presents the structure of this work and the main sub-task in chapters of the report.

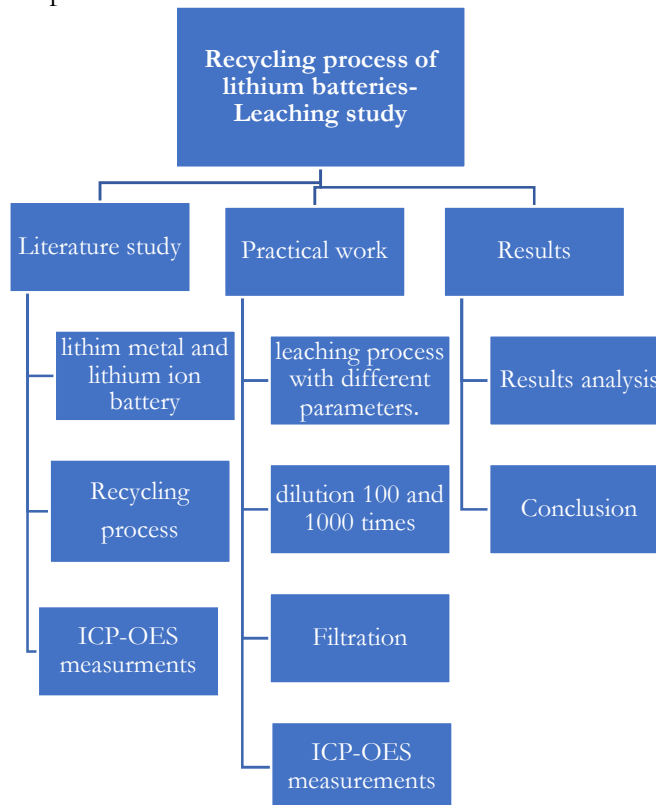


Figure 8: The structure of this thesis with main sub-task.

## 5 Practical Work

The purpose of the practical work was to study the leaching process and investigate different parameters to find good conditions for leaching.

### 5.1 Materials and Equipment

Two sheets of cathode and anode that were previously discharged and disassembled from a spent car lithium-ion battery were obtained as sample materials for the work, see figure 9 below. An IKA M20 universal mill was used to grind cathode and anodes sheets. A timer was used to measure the leaching during different times. 0.5 and 1 M sulfuric acid was prepared and used to dissolve the sample from battery. A heating plate with temperature control was used for heating up the prepared leaching solution. 0.5M nitric acid was used to prepare samples for measurements. ICP-OES machine was used to measure the concentrations of the metals in the solutions.



Figure 9: Sheets of cathode and anode from spent car lithium-ion battery. The battery is cut into small pieces and mixed to powder.

#### 5.1.1 ICP-OES instruments

ICP-OES (inductively coupled plasma-optical emission spectrometry) is a technique used to determine the concentrations of elements in aqueous solutions. This is done using a plasma and a spectrometer. The technology has become available since 1974 and is used mostly in research and analysis [21].



Figure 10: ICP-OES machine.

## 5.2 Leaching Method

Sulfuric acid with two different concentrations were prepared. 50 mL of sulfuric acid was added to a plastic jar. 1g of powder that contains cathode and anode materials was added into sulfuric acid at  $t=0\text{min}$ . The solution in the plastic jar was heated to  $25^\circ\text{C}$  and the timer was started immediately. A magnet was used constantly for stirring of the solution during the heating process.

To investigate the time effect on the process, a sample of the solution was taken at time intervals of 5, 15, 30, 60 and 120 minutes. A syringe with an attached filter was used to take a volume of 0.1 mL from the solution at the time intervals mentioned above.

The experiment was repeated but with other parameters, see Tabell 1 below. The prepared samples of all experiments were collected in different test tube rack, diluted 100x and 1000x and was then used in the measurements.

Concentration	Temperature ( $^\circ\text{C}$ )	Leaching time and sampling (min)	Solid to liquid ratio (g: mL)
0.5M	25,40,60	5,15,30,60,120	1:50 and 1:20
1M	25,40,60	5,15,30,60,120	1:50 and 1:20

Table 1: Parameters applied on leaching process during the experiments.

### **5.3 Preparing of standards solution**

For measurements of leaching results, four standard solution with concentration of 0ppm, 20ppm, 15ppm and 5ppm were prepared from certified 1000 ppm solutions of the following metals Li, Mn, Co, Ni, Al and Cu. The standard solutions are necessary and are used as reference.

The first standard solution with a concentration of 20 ppm was prepared by adding 1ml of each metal's solution Li, Mn, Co, Ni, Al and Cu in a test tube and then dilute to 44 ml using 0.5 M HNO<sub>3</sub>.

The solution with a concentration of 10ppm was prepared by transferring 25ml of the first standard solution to a new test tube and then dilute to 50ml with 0.5 M HNO<sub>3</sub>.

For the third standard solution with 5ppm, 20 ml of the standard solution with concentration of 10ppm was transferred to empty test tube and diluted to 40 ml using 0.5 M HNO<sub>3</sub>. The last standard solution with 0ppm was prepared by adding only 50ml 0.5 M HNO<sub>3</sub>.

#### **5.3.1 Samples dissolved for analysis**

To know the metals contents in the solid samples, 0.2g of powder was dissolved in 50 ml of aqua regia and then diluted 1000 times with nitric acid. The solutions were used to measure metal concentrations by Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP-OES).

#### **5.3.2 Preparing of the samples for measurements**

Using a pipette, the samples from all experiments (paragraph 5.2) were prepared for ICD-OES measurements by diluting all of them first to 100x and then to 1000x using different volumes of nitric acid (0.5 M HNO<sub>3</sub>).

#### **5.3.3 ICP-OES measurements**

For ICP-OES measurements, the samples that were diluted 100 times or 1000 times was available to use. The standard solution and the samples from the experiments had been inserted together in the ICP-OES machine. The machine measured each sample and respective standard solution separately and documented the measurement result on the PC that is connected to the machine.

The PC was prepared with information about the already known concentrations of the standard solutions and the numbering of each samples. As mentioned before, the ICP-OES machine can measure the concentration of several metals in a solution. We had from the beginning to select which metals we want to measure from the periodic table on the PC.

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Ppm is the concentrations unit of standard solution and equals the unit of mg/l.

## 6 Results and discussion

From ICP-OES measurements, the concentrations of all metals in the leaching solution had been documented and then analysed for calculation of the leaching efficiency. The analysis was done for the samples that was diluted 100x and 1000x but the focus in the results will be on the samples that been diluted 100x because these have higher concentrations of the metals.

The results present the leaching of lithium, nickel, cobalt and magnesium, but the focus was mostly on the lithium and nickel. These metals were selected because they showed highest concentration in samples from the measurements.

### 6.1.1 Results of the samples dissolved for analysis

Metals contents in the samples that were measured by ICD-OES in paragraph 5.3.1 have been calculated using formula 1, see Appendix A. The percentage of each metals presented in the Table 2 below.

Metal	Average percentage in sample (wt %)
Li	3.05
Ni	8.27
Co	5.01
Mn	13.7
Cu	13.5
Al	10.0

Table 2: Weight percentage of all metals content in the sample.

## 6.2 Leaching results

Based on the results from ICP-OES measurements, the leaching efficiency for all metals in the leaching solutions was calculated by using formula 2, see Appendix A. The best conditions of leaching were identified by studying the results from measurement at pre-defined parameters, i.e. temperature, concentration, time and solid to liquid ratio.

### 6.2.1 The effect of time

The leaching process was studied during two hours to investigate which time gives the highest efficiency. The graphs below show the time interval on the x axis and the calculated leaching efficiency of the metals on the y axis. The focus in this part was on lithium, nickel, cobalt and magnesium leached with concentration of 0.5M. Graphs 11, 12 and 13 show that the leaching efficiency increases over time. The best efficiency was obtained at 120 minutes.

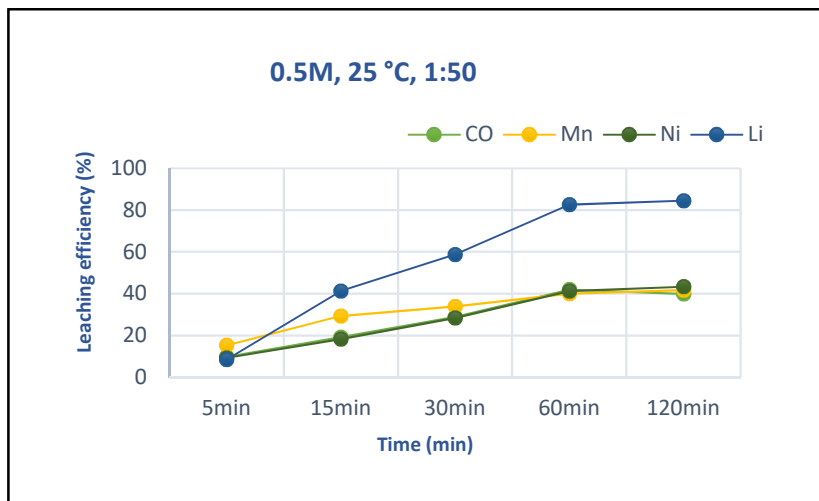


Figure 11: Time influence on leaching at 25°C.

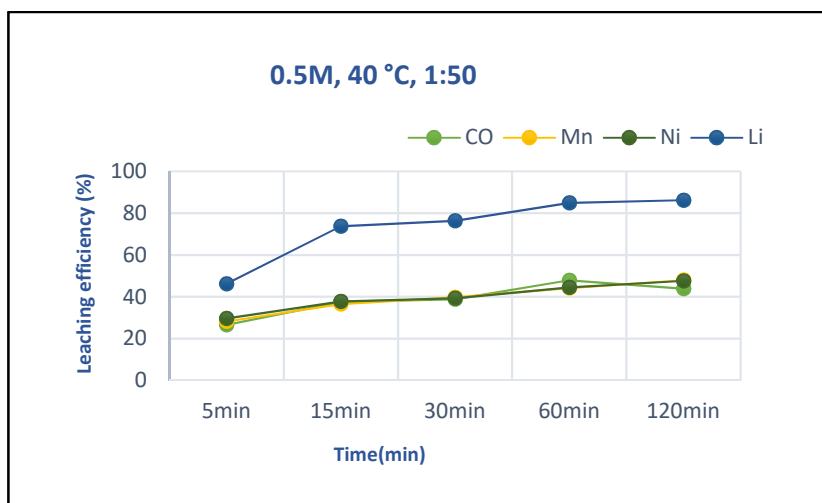


Figure 12: Time influence on leaching at 40°C.

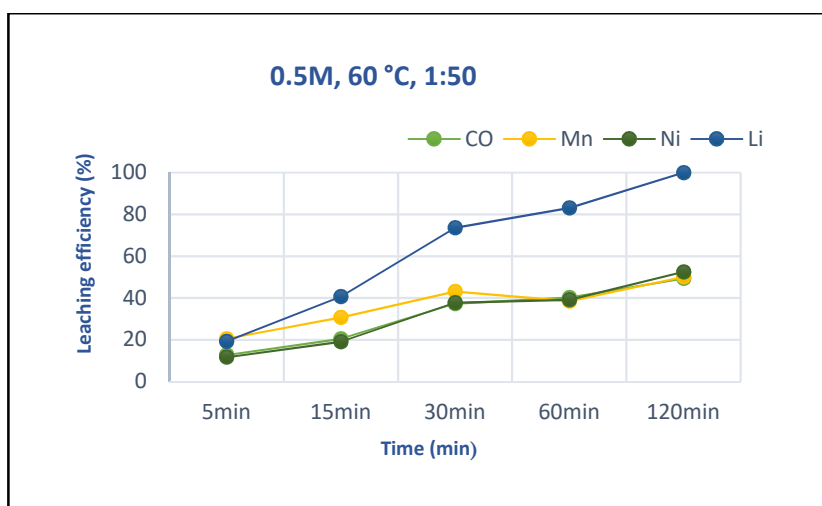


Figure 13: Time influence on leaching at 60°C.

### 6.2.2 The effect of acid concentration

In the graphs below the impact of acid concentration for leaching is shown. Two different acid concentrations had been used, 0.5 M respective 1 M, at different temperatures. It had been decided to study the concentration impact at time 120 minutes, because that gave the highest efficiency in all measurements.

Graph 14 shows no significant impact of acid concentrations at 25°C on the efficiency.

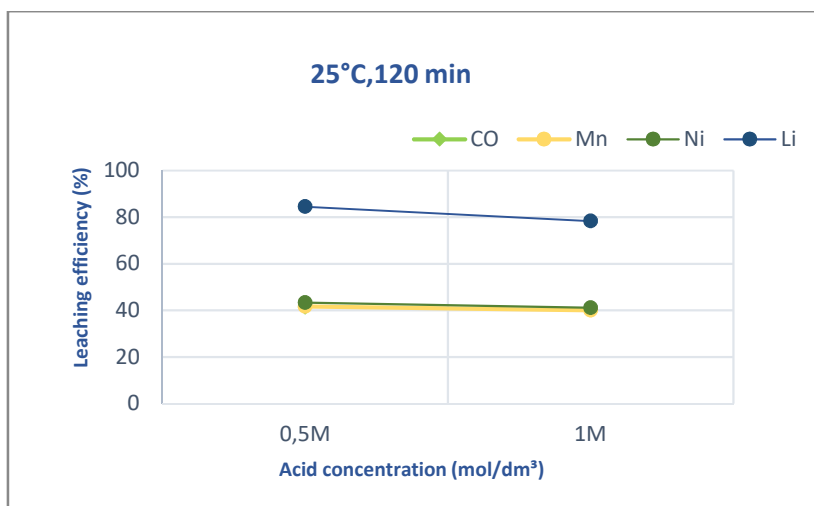


Figure 14: The influence of acid concentration on the leaching efficiency at 25°C and 120 min.

By increasing the temperature to 40 °C, respective 60 °C, a better efficiency on all metals except Lithium could be observed at acid concentration 1 M, see graphs 15 and 16 below.

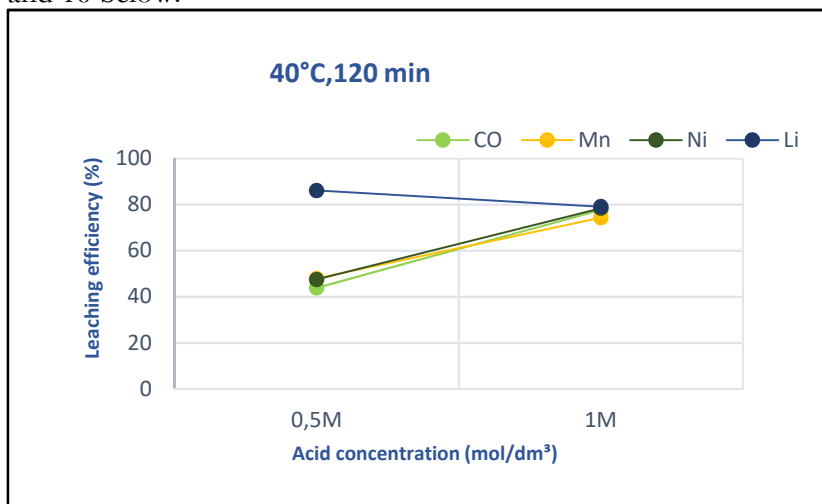


Figure 15: The influence of acid concentration on the leaching efficiency at 40°C and 120 min.



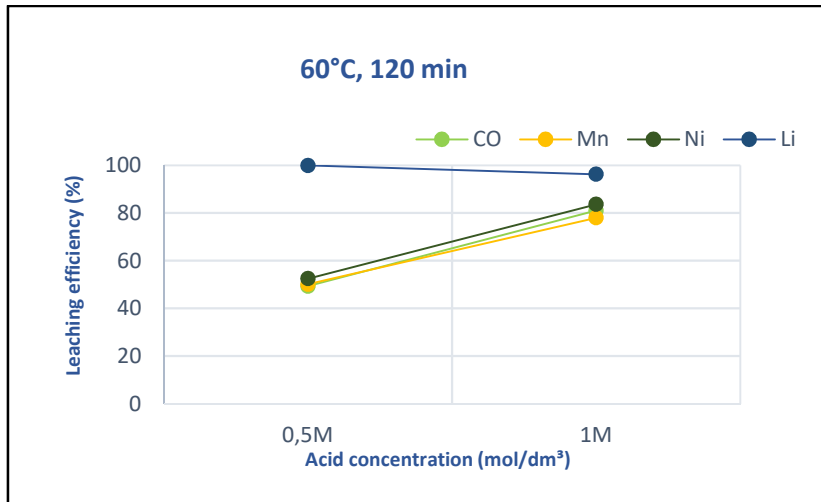


Figure16: The influence of acid concentration on the leaching efficiency at 60 °C, 120 min.

### 6.2.3 The effect of temperature

The leaching efficiency had also been studied with focus on temperature.

The results show a significant impact on leaching at three different temperatures 25 °C, 40 °C and 60 °C, see the graphs 17 and 18 below. As it is presented below the best result was obtained at 60 °C.

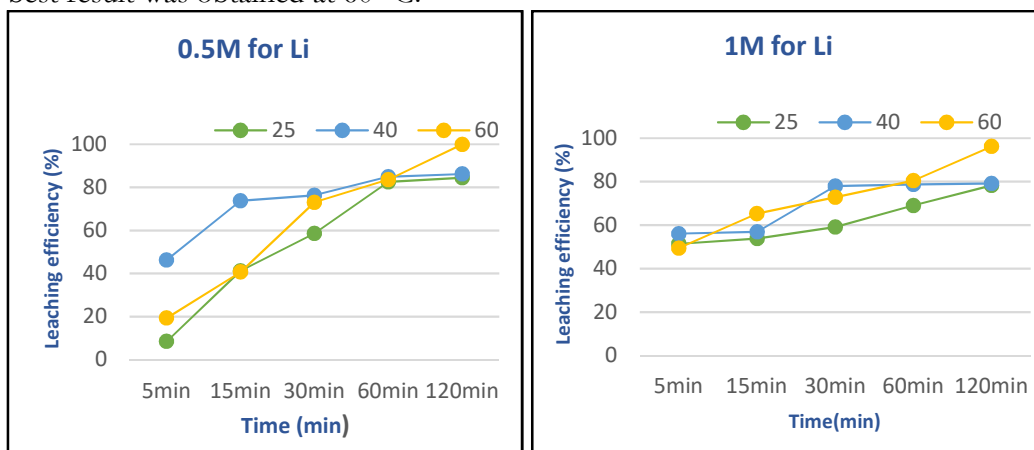


Figure 17: Leaching efficiency of lithium at different temperatures with 0.5 M and 1M sulphuric acid.

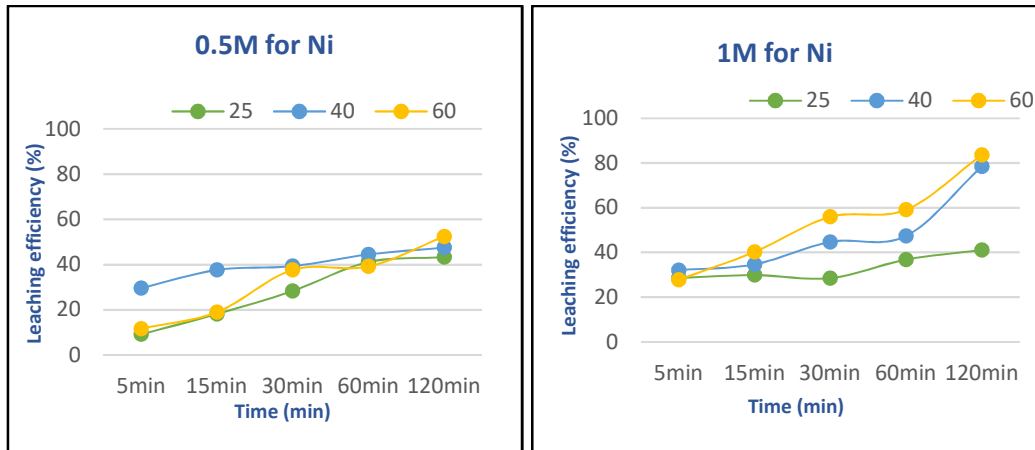


Figure 18: Leaching efficiency of nickel for different temperatures with 0,5 and 1M sulphuric acid

#### 6.2.4 The effect of solid to liquid ratio

To study the effect of the ratio between solid and liquid on the leaching efficiency, two different ratios were investigated; 1:20 respective 1:50. From graphs 19, 20 and 21 below it can be seen that the efficiency was lower when 1:20 was used than with 1:50. One reason to that the ratio of 1:50 gave a higher efficiency can be a higher effect of acid, i.e. the release of metal ions is caused by reaction with  $H^+$ -ions. To avoid this situation higher concentration 2-3M of the acid can be used with the ratio of 1:20.

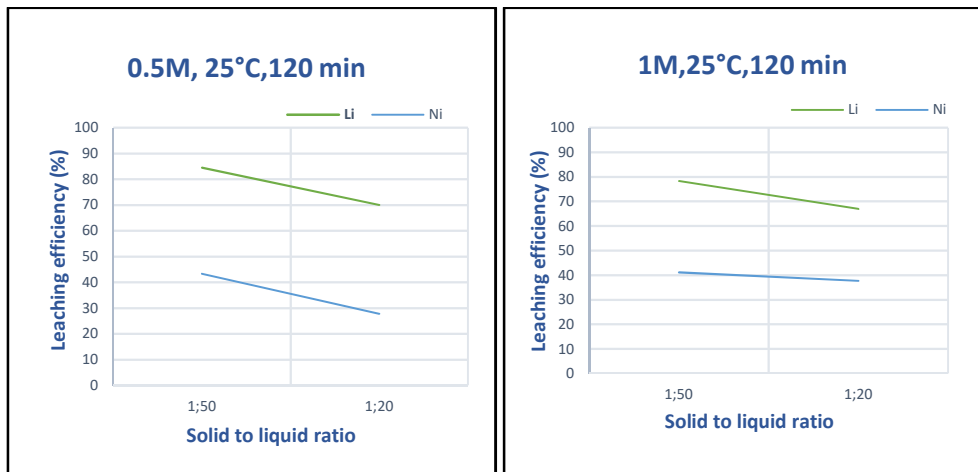


Figure 19: Behaviour of solid to liquid ratio at 25 °C, 0.5 M and 1M.

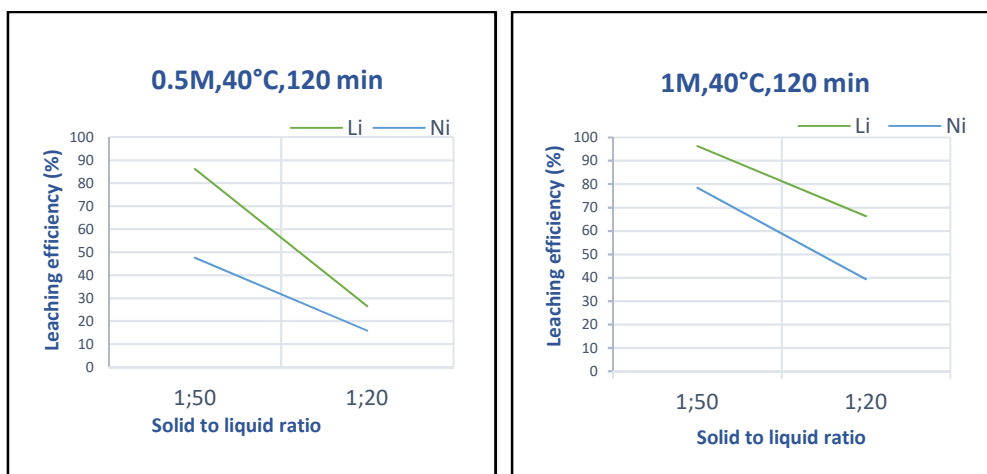


Figure 20: Behaviour of solid to liquid ratio at 40 °C, 0.5 M and 1M.

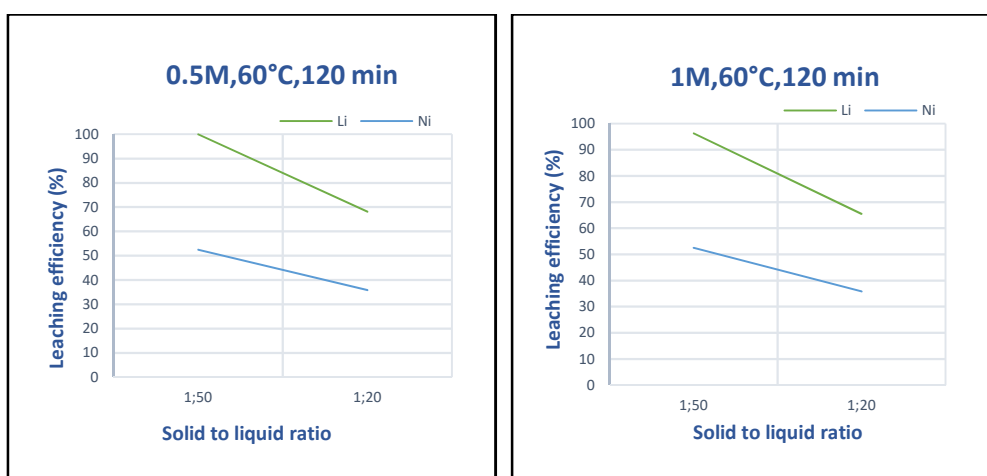


Figure 21: Behaviour of solid to liquid ratio at 60 °C, 0.5 M and 1M.

## 7 Conclusion

The purpose of this project was to study the leaching process in a hydrometallurgical treatment of electrode material from spent lithium ion batteries by using sulfuric acid and investigate the impact of different factors/parameters to decide the optimal conditions of leaching.

More than 50 sample solutions from a spent lithium battery were prepared and used in ICP-OES measurements. From these measurements, the amounts of all metals (Ni, Co, Mn and Li) that dissolved in the leaching solution were determined. The leaching efficiency of the samples was calculated and analysed to decide the optimal parameters for leaching.

By studying the time effect, it had been observed that the leaching efficiency increases over time. The best result was obtained at 120 min. It had been noted that the time effect on lithium is higher compared to for other metals in the studied materials. The optimal temperature for leaching had been observed to be 60 °C for all metals. The efficiency had been significantly improved from 25 °C to 60 °C. However, the concentration of sulfuric acid 1M gave an increased leaching efficiency of the studied metals compared to 0.5M. No significant impact had been observed on lithium. A higher effect was achieved on nickel, cobalt and manganese.

For the ratio of solid to liquid, the highest efficiency had been noted at ratio 1:50.

To summarize up the result of this study, the optimal conditions that result in highest efficiency of the leaching process for all studied metals are 120 min, 60 °C, sulfuric acid concentration 1M and solid to liquid ratio 1:50.

It was noticeable from results, that the leaching efficiency of metals except lithium was not 100%. The metals have not the same leachability. The leachability of lithium is faster than the other metals due to that the efficiency of it reached to 100%. The other metals need more time and temperature to dissolve in sulfuric acid and to leach 100%.

By adding a catalyst to the leaching solution, the kinetic can be improved and the process becomes faster. By this method, the other present metals (nickel, cobalt and manganese) can be leached more efficiently.

It could be worth to mention that the leaching process in a hydrometallurgical treatment is quite complex and requires time, but on the other side very high leaching efficiency can be achieved.

In the industrial environment, there may be other parameters preferred than the optimal ones due to the cost factor, even if these parameters had a lower efficiency. The optimization of the leaching process to recover all the metals from the spent lithium-ion batteries with a high efficiency requires higher acid concentration 2-3M, higher temperature and longer time at lower solid to liquid ratio.

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## 9 Appendix A

### Calculation

#### Formula 1 – Percentage in sample

The percentage of metals in the dissolved sample were calculated by the following formula.

The percentage of metals in the original sample = ((value from ICP-OES measurement\*5000)/ (weight before measurements \*10000000)) \*100

The result for each metal from ICP-OES measurement in g/l multiplied with dilution factor 5000 and divided by the weight before analysis in µg.

The values from ICP-OES and the percentage of metals in the original sample was introduced in Tabell 3 and used then to calculate leaching efficiently for all of metals see Tabell 3.

	g/L
	ICP-OES results
Co	0,2300
Cu	0,6200
Mn	0,6300
Li	0,1400
Al	0,4600
Ni	0,3800
	metal content [%]
sample weight [g]	0,2297
Co	5,0065
Cu	13,4959
Mn	13,7135
Li	3,0475
Al	10,0131
Ni	8,2717

Tabell 3: Results from ICP-OES measurements and calculated metal content.

#### Formula 2 – Leaching efficiency

Leaching efficiency of all metals was calculated by two steps:

1. Step1. The values of metals in the original =the percentage of metals in the original sample/100) \*weight of powder.

See Tabell 3. For percentage of metals in the original sample and Tabell 4 to know the weight.

2. Leaching efficiently= (((The results from ICP-OES /1000) \*volume)/ the values of metals in the original) \*100

For example, the volume of 1:50 ration between solid and liquid presented in Tabell 4. below. The values of metals in the original sample was calculated in step 1.

weight g	volumle m
1,003	50
1,003	49,8
1,003	49,6
1,003	49,4
1,003	49,2

Tabell 4: Weight of powder and the volume of acid for leaching process.