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Hydrometallurgical Treatment of Spent Lithium-Ion Batteries: A study of optimal conditions for the leaching

Bachelor's thesis in the Chemical Engineering program

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Abstract

The interest of recycling lithium-ion batteries to recover valuable metals has traditionally been focused on economic benefit. Nowadays, the interest has shifted towards a more global perspective on waste disposal because of issues from both environmental impacts and resource supply. The current recycling processes are designed to operate with small lithium-ion batteries from portable electronic devices [1], and do not satisfy the new requirement in environment and recycling efficiency for larger, more advanced lithium-ion batteries from electric vehicles and plug-in hybrid electric vehicles. Therefore, recycling processes must be developed to accommodate an increasing amount of vehicle lithium-ion batteries, that are expected to enter the waste stream in the near future.

Leaching is an essential step for effective recovery of metals from spent lithium-ion batteries during hydrometallurgical treatment. The objective of the present work was to determine the optimal leaching conditions for recovery of metals from spent lithium-ion batteries. The leaching was carried out by using hydrochloric acid. Effects of different concentrations, temperatures, reaction times and solid-to-liquid ratios were examined. With optimal leaching conditions found to be 1 M hydrochloric acid, 60 min leaching time, at 40°C with solid to liquid ratio of 1/20 g/ml.

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1 Introduction

1.1 History

Rechargeable batteries have an essential role in our lives and are related to many daily chores that would be impossible without the ability to recharge. The currently well-known rechargeable batteries are based on the lead acid, nickel-cadmium, nickel-metal-hydride and lithium-ion chemistries [2]. The first commercial rechargeable battery was the lead acid battery invented by the French physicist Gaston Planté in 1860. Lead acid batteries are used in automobiles for starting, lighting and ignition, but also as stationary batteries used for back-up power supply, and traction batteries. Other applications include aircrafts, submarines and hybrid electric vehicles [3]. In comparison, nickel-cadmium (NiCd) batteries were invented by Ernst Waldemar Jungner in 1899, but because of contemporary environmental concerns they only retain their status in aircrafts due to their good safety record. Nickel-metal-hydride batteries eventually replaced the NiCd batteries and are used for medical instruments, hybrid cars and industrial applications [4]. The work on lithium batteries began in 1921 under Gilbert N. Lewis, but the first non-rechargeable lithium battery was not launched commercially until in the early 1970s [5]. The revolution of information technology in the 1980s led to a growing need for rechargeable batteries to be small, lightweight and with greater capacity [6]. Unfortunately, the development failed in the 1980s because of instabilities in the metallic lithium used as anode material, which provides extraordinarily high-energy densities and leads to the growth of lithium dendrites. These then cause a steep drop of cycle life and severe safety issues. The inherent instability of lithium metal caused the research to move to non-metallic solution using lithium ions [7].

1.2 Background and problem

Since Sony launched the first commercial rechargeable lithium-ion battery in 1991 [6], the lithium-ion battery technology has gained on-going attention not only to its material resource [8], but in recent years also to its end-of-life environmental issues [9]. The applications of lithium-ion batteries have been widely integrated in society, and are used for high-tech products such as e-bikes, laptop computers, smartphones, digital cameras, hybrid and electric vehicles, stationary energy storage and electric grid applications etc. [8], [10]–[12]. Lithium-ion batteries have been considered the best technology for sustainable transportation due to their significant potential to lower greenhouse gas (GHG) emissions [1], [2], [12]. The lithium-ion batteries have many advantages over conventional batteries, such as high power and energy density, high potential, long storage life, low self-discharge, no memory effects, wide operating temperature

range [13], all of which makes them an excellent candidate in the growing demand for hybrid electric vehicles and plug-in hybrid electric vehicles [1].

The global sales of electric battery vehicles are predicted to increase from 5 million in 2015 to a projected 100 million in 2045 [14]. Spent batteries are expected to contribute to a huge amount of waste at the end of their life cycle in the near future [9]. The batteries will end up in municipal solid wastes, waste to incineration facilities, and recycling facilities [9]. However, Lithium-ion batteries contain hazardous materials such as toxic and flammable electrolyte [15], which are expected to accumulate at increasing rates in nature due to their increased use. An increase in used lithium-ion batteries without proper handling would mean increased potential harm to the environment, safety and health, due to the ability to spontaneously ignite which depends on the batteries are not completely discharged and are improperly handled, and the potential to release toxic elements during landfill disposal. The main elements leached from Lithium-ion batteries into environment are cobalt, nickel and lithium, if the metals present in a high enough dose will lead to toxic effects for human health [9]. Moreover, raw material mining from nature needs more energy than the energy required by the recycling processes. For instance, the energy consumption and CO₂ emission can be 70% higher if LiCoO₂ is produced from ore extraction, than from recycled material [15]. Furthermore, lithium is available only in specific geographic regions (almost 70% of the global lithium deposits are concentrated in Argentina, Bolivia and Chile) [1], where geopolitical issues and price market fluctuations makes sustainable supply uncertain [16][2]. Additionally, lithium supply may not overcome lithium production due to continuously growing demand for lithium-ion batteries [15].

Beside environmental and geopolitical perspectives, government regulations force a strict policy in battery recycling, due to the growing concern for environmental issues and the unique geopolitical lithium availability, with European governments imposing more strict regulations than other countries. According to the EU Battery directive 2006/66/EC, the recycling rate of spent lithium-ion batteries was obliged to reach at least 50% by weight of lithium batteries and accumulators by 1 January 2014 [1], [15].

From an economic perspective, for a high energy cell (100Ah), the active material presents 72.2% of the cell price (48.8% and 23.4% for cathode and electrolyte, respectively), which contains various metals such as copper, aluminum, magnesium, nickel, cobalt and lithium. Some of these elements have a high economic value and are recycled because of economic interest, such as cobalt, nickel and copper. According to Alexandre Chagnes and Beata Pospiech, in 2013, the recovery of lithium is economically interesting if the production of lithium reaches one million tons for the lithium-ion battery industry for electric vehicles [1], [9], [16]. Generally, spent lithium-ion batteries contain 5-20% cobalt, 5-10% nickel, 5-7%

lithium, 5-10% other metals (copper, aluminum, iron, etc.) 15% organic compounds and 7% plastics [13]. The extraction of 28 tons of spent lithium-ion batteries will yield one ton of lithium, which corresponds to 250 tons of mineral or 750 tons of brine [17]. The average price for cobalt and lithium in December 2017 was \$72 589 and \$22 914 per ton respectively [18]. Furthermore, according to *Zhang al et. 2018*, the number of available end-of-life vehicle batteries ranges from value \$1.38 million to \$6.76 million in 2035.

Based on the above-mentioned point of view, recycling of spent lithium-ion batteries is necessary and potentially profitable. However, recycling of spent lithium-ion batteries is difficult and uncertain. Designing efficient recycling processes is challenging

as the composition of lithium-ion batteries varies in technology and their application as well as manufacturing [19]. Furthermore, recycling of batteries is strongly dependent on the dynamic of economic benefit and demand for resources available [18], the former depending on the metal market price as well as the cathode materials technologies used in lithium-ion batteries [1].

The current recycling processes are designed for small electronics devices, and focus on recycling of valuable metals in cathodes, such as cobalt, nickel and copper [1], [16], while lithium, aluminum and manganese are lost in slag without further processing. Lithium, in the form of lithium carbonate, is an important raw material for the production of lithium-ion batteries. Since lithium carbonate is one product from recycling of the batteries by hydrometallurgical methods, spent lithium-ion batteries constitute an important secondary resource for the lithium-ion batteries industry [20]. Today, only 3% of lithium-ion batteries are recycled and lithium recovery is less than 1% [20], [21]. However, in the long term, recycling processes need to be developed to improve recycling efficiency for the sake of environmental safety and sustainability, as this maximizes efficiency and minimizes costs but also yields high enough quality lithium to meet the large-scale market demand for advanced lithium-ion batteries [1], [16], [22].

The recycling process can be performed either using high temperature or low temperature separation techniques. The two well-known technologies are pyrometallurgy (high temperature) and hydrometallurgy (low temperature). According to Ekberg and Petranikova, a hydrometallurgical process is the better alternative because it is more environmentally friendly, requires less energy and is more efficient. For instance, lithium can be recovered to almost 100% using a hydrometallurgical process, but will be lost completely in a pyrometallurgical process [16]. The spent lithium-ion recycling process is usually operated through three stages: pre-treatment (dismantling, crushing and separation), secondary treatment (thermal treatment) and metal extraction (acid/alkaline leaching, precipitation, solvent extraction and electrowinning) [16], [23]. The pre-treatment is implemented to separate battery components

such as outer cases, shells, and to concentrate the metallic fraction, but also remove some hazardous source. The secondary treatment is to enhance the separation of the black mass from the current collector carries out by dissolving the organic binder. The metal extraction stage is applied hydrometallurgical processes to recover high purity metal and reach high recycling efficiency [23].

In this study, I first introduce the working principle of lithium ion batteries and their components, then conduct a literature review of industry recycling processes. Finally, the results of the leaching experiment (with focusing on metals Co, Mn, Li and Ni) will be presented with the aim of finding the best conditions for a leaching process, which in turn depends on several parameters such as temperature, concentration of acid, time, and solid-liquid rate.

2 Theory

2.1 Principle of lithium-ion batteries

A rechargeable lithium-ion battery is formed from several cells, each made up by four individuals but connected components (cathode, anode, electrolyte and separator). Cathodes and anodes are electrodes, which store electrical energy as chemical energy. The electrolyte constitutes as a conductive medium to assure mobility of the ionic components between the anode and the cathode during the redox reaction process. The separator may be a thin microporous polymer membrane which is placed between the anode and cathode to prevent contact. The membrane permits lithium-ions to pass through the pores and prevents short-circuits between electrodes. The working principle (see Figure. 1) of a lithium-ion rechargeable battery cell is dealing with multiple charging and discharging processes. In case of a charging process occurring, the two electrodes are connected to an external electrical power source and lithium-ions from the cathode migrate via the electrolyte to the anode internally, while the electrons move through an external circuit in the same direction. The discharging process occurs in the opposite direction. Each electrochemical cell acts as an element of the battery and delivers between 3 and 4 V depending on the applied lithium-ion technology. These cells are placed together parallel forming a block, which delivers the same voltage but with a higher capacity. These blocks are ordered in a series, then a functional battery is formed, which delivers a high voltage [24].

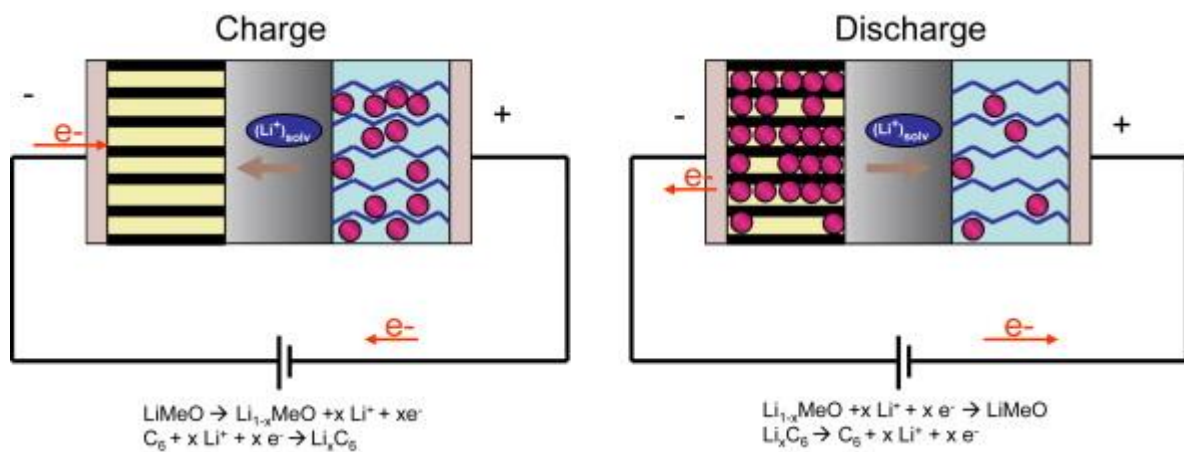


Figure 1. Schematic of the charge- discharge process in a lithium-ion battery [24].

2.2 Lithium-ion battery components

2.2.1 The cathode

The cathode is made of a mixture of the active material and pasted onto both sides of aluminium foil. Typically active materials containing 80-85% metal oxide powder, 10% polyvinylidene fluoride (PVDF) binder, and 5% acetylene black. [1], [9].

The most used materials for cathode are intercalation materials. Such compounds have crystal structures to allow the lithium-ions to diffuse freely (Figure 2). The three most common ones are layered rock salt structure (two dimensional, i.e. LiMO_2 , $M = \text{Co, Ni, Mn}$), spinel structure (three dimensional, i.e. LiMn_2O_4), and olivine structure (one dimensional, i.e. LiFePO_4) [25], [26].

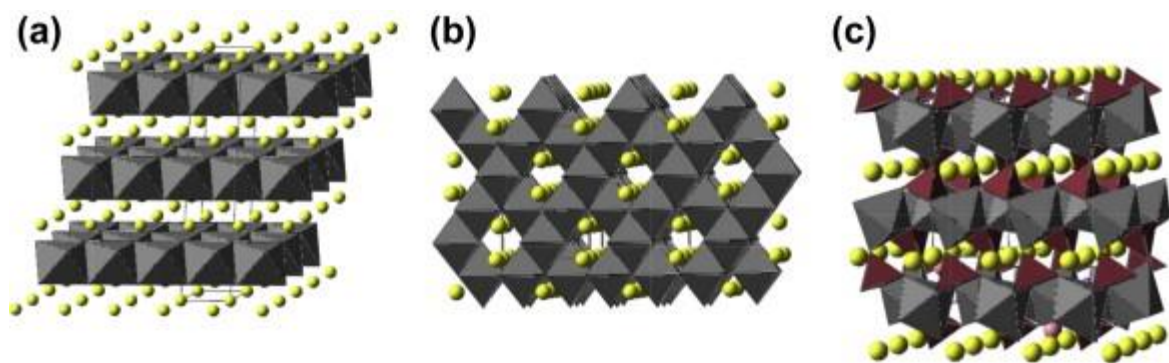


Figure 2. Common structures used in lithium intercalation batteries: a) layered LiMnO_2 , b) spinel structure LiMn_2O_4 , c) olivine structure LiFePO_4 [26].

2.2.2 The anode

The anode consists of a copper foil coated with a paste made of active materials, mainly containing 90% graphite, 4-5% acetylene black and 6-7% organic binder [1], [27]. More than 98 % of commercial negative electrode materials used in Lithium-ion battery system are carbonaceous materials and lithium titanium oxide ($\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LTO}$) [26]. Potential future materials include silicon and/or tin, as they are among the most important in a number of elements known to alloy with lithium. Since a substantial volume expansion occur during charging/discharging processes and leading to high compression and tensile stress within lithium alloy anodes, by shifting the material into Nano-size would solve this problem. Those materials are characterized by better kinetics, higher reversibility of charge/discharge process, and increased life cycle [8].

2.2.3 The electrolyte

The selection of electrolyte materials is important for the performance of lithium-ion batteries, and must be chosen with care to withstand the redox environment at both positive and negative

electrodes. It must also perform stably in a wide voltage range without decomposition or degradation (up to 4.5 V for LIB). The electrolyte should provide high ion mobility and be inert without reactions with battery materials in the involved temperature ranges [8]. There are three main types of electrolytes that are currently used, or under research, in lithium-ion batteries: liquid, solid, and polymer electrolytes [28].

In commercial lithium-ion batteries, the common liquid electrolyte is a mixture of lithium salts and organic solvent, also referred to as the organic liquid electrolyte (Liquid electrolytes). The most important considerations for liquid electrolytes are safety, long-term stability and reaction rate [28].

2.2.4 The separator

The separator may be a thin micro-porous polymer membrane, which is placed between the anode and cathode to prevent contact. The membrane permits lithium-ions to pass through the pores and prevents short-circuits between electrodes. The separators are formed by a multilayer structure of polyethylene and polypropylene [8], [26].

The chemical reaction principle in lithium-ion battery is simple, but the development of electrode materials and improved performances battery systems suitable for the high energy/power requirements in electric vehicles remains a challenge in both cost, energy density, power density, cycle life and safety [12], [26]. Although a lithium-ion battery cell consists of relatively simple components, each cell contains of many different materials. A lithium-ion pack can have 100 or more individual cells (e.g. a Tesla electric vehicle has ~5000 cells per pack), the large number of cells with different materials makes the recycling complicated [22].

3 Lithium-ion battery recycling processes

Recycling processes of spent lithium-ion batteries can be divided into hydrometallurgical treatment and pyrometallurgical treatment, but also include combinations of pyro- and hydrometallurgical treatment that involves pre-treatment steps like thermal or mechanical processing [16], [21]. The high-temperature pyrometallurgical treatment focuses on the formation of metal alloys containing cobalt, nickel, copper and iron, while lithium, aluminium and manganese remain in the slag and can be used for construction materials [16], [20], [22]. To recover lithium, further processing is needed. The pyrometallurgical treatment has disadvantages such as high energy demand and high cost for treatment of waste gases before they enter the environment [9]. Nevertheless, this process cannot recover lithium per se, and the economic profitability is strongly co-dependent on the price of cobalt. Thus, pyrometallurgical processes might not be profitable for recycling of automotive lithium-ion batteries in the future since cobalt is most likely to be replaced by cheaper and more easily obtainable materials like manganese [29].

Hydrometallurgical treatment uses chemical leaching to facilitate material recovery in low temperature [2], and is more environment-friendly due to its low operating temperature, while also enabling high purity yield with high lithium extraction efficiency. Therefore, current efforts have been to promote the development of hydrometallurgical technologies for spent lithium-ion batteries. According to Ekberg and Petranikova 2015, basically, two approaches are implemented to investigate the possibilities of spent lithium-ion batteries recycling, hydrometallurgical treatment and combination of thermal pre-treatment and hydrometallurgical treatment. Both alternatives usually include three stages: mechanical pre-treatment, leaching, and metal-extraction. Thermal pre-treatment is another process included in combined treatment [16], [23].

The purpose of the pre-treatment stage is to remove hazardous components, reduce the volume of waste and concentrate the active materials, which improves recovery rates of target metals and decrease the energy consumption in further pyrometallurgical or hydrometallurgical processes [11]. Separation occurs according to their physical properties like density, shape, conductivity, magnetic properties, etc. [16], [29], [30].

Generally, the recycling of spent lithium-ion batteries from electric vehicles begin with discharging to prevent short-circuiting and self-ignition. One discharging method that is frequently used is to immerse the spent lithium-ion batteries in a salt solution [13], [16], [23].

The second process step is manual dismantling, in order to separate particular cells from the battery cell. Afterwards, battery cell size reduction is achieved by mechanical multistage pre-treatment procedures, such as crushing, sieving, and separation of magnetic materials. The magnetic particles like steel casings [16].

It is difficult to separate active material from aluminium foil because of the strong adhesive force of PVDF binder [13], and PVDF has to be removed due to the fact that it causes complications during the leaching at solid-liquid separation stage. The complications are caused by organic compounds causing a lower lithium extraction due to lithium adsorption. Many methods have been evaluated in order to find an effective way to separate PVDF, including dissolution of the PVDF with an organic solvent, alkaline leaching and thermal treatment. During alkaline leaching, the current collectors such as aluminium foil are dissolved, leaving the active materials and PVDF undissolved [2]. The next stage would thus involve separating the dissolved current collector from the active materials using NaOH solution. Among the organic solvents N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC), N-methylpyrrolidone (NMP) and dimethylsulfoxide (DMSO), NMP has shown to be the most effective one for PVDF, but is impractical for industrial commercial use due to the high cost [16], [30]. The purpose of thermal treatment is to remove organic compounds and graphite and can be processed in incineration or pyrolysis [16]. Controlling incineration temperature and atmosphere is important. At a temperature above 350°C the PVDF decomposes, and beyond 600°C other components like acetylene black, conductive carbon decompose [13]. Thermal treatment has the advantages of including simple and convenient operations. However, the method requires high energy consumption and has a negative air pollution effect causing high CO₂ emissions and hydrogen fluoride (HF) [11], [13], [30]. A more comprehensive review on separation processes is available in the literature [2], [11], [13], [16], [30].

Hydrometallurgical processes include leaching, solvent extraction, chemical precipitation, ion exchange and electrowinning [16]. Among these processes, leaching plays a crucial role in the recycling processes. Leaching is a solid-liquid extraction process where the solid material (black mass from a spent car used in this experiment) is separated from a mixture by dissolving the material in a leaching agent (HCl was used in this experiment) under certain conditions [31]. The leaching agent can be either inorganic acids such as H₂SO₄, HCl and HNO₃, or organic acids such as citric acid, DL-malic acid and Oxalic acid. Leaching efficiency can be increased by adding a reducing agents such as H₂O₂, glucose and NaHSO₃, which reduces the oxidation number of metal ions by donating electrons to them (e.g. Co³⁺, Mn⁴⁺ to Co²⁺, Mn²⁺) [32].

4 Industrial recycling processes

4.1 The Akkuser process

Akkuser is a company running a recycling plant located in Nivala, Finland, which was opened in May 2006. Since the beginning of their operation they recycle all the portable batteries collected in Finland, but also the waste batteries from Sweden, Denmark, Germany, Austria and Poland. Batteries are manually sorted, based on their chemical content, mainly into four battery types, namely, high-grade cobalt lithium-ion batteries, low-grade cobalt lithium-ion batteries, alkaline batteries and Ni-Mh batteries. Akkuser developed a recycling method called Dry-Technology for Ni-Mh, lithium-ion and Li-polymer batteries, and batteries used in mobile phones. It is a mechanical separation process that operates with a two-phase crushing process followed by magnetic and mechanical separation processes. The process does not use water, chemicals or heating, and is therefore zero-emission. Worthy of notice is that Dry-Technology method does not require any pre-processing steps for discharging lithium-ion batteries. The products of metal contents obtained from the process is sold as raw material to metal producers [16], [33].

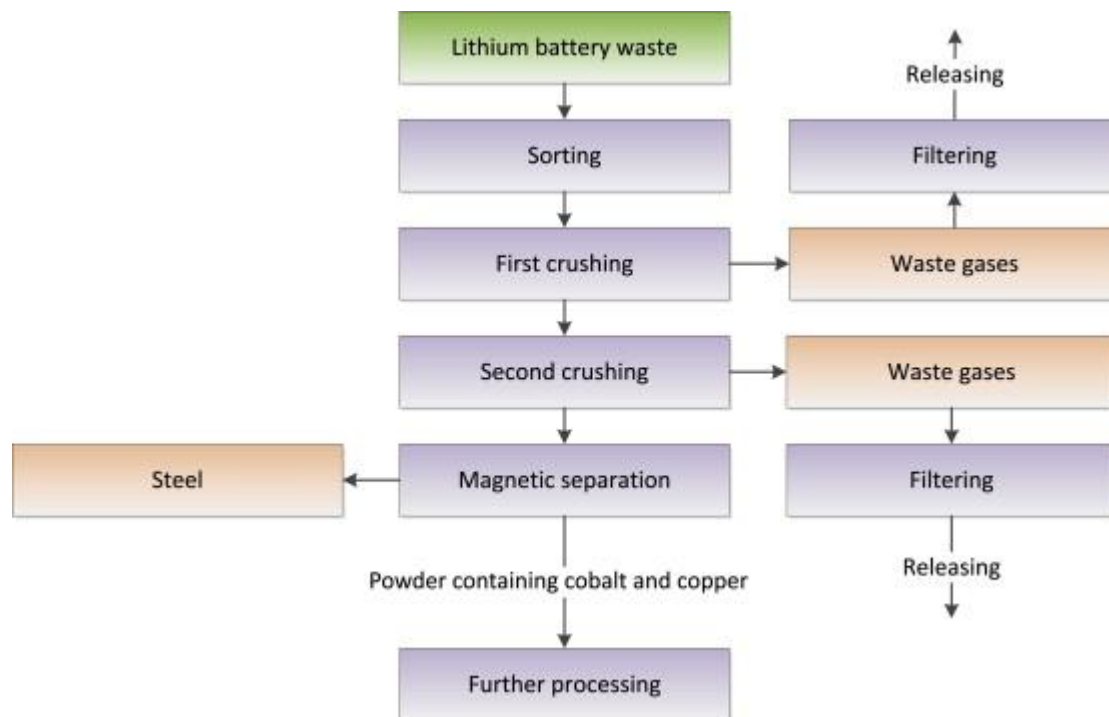


Figure 3. Flow chart for the Akkuser recycling process [15].

4.2 The Umicore process

Umicore is a recycling company located in Belgium. With a plant capacity of 7000 t/year, they are a leading supplier of key materials for rechargeable batteries used in portable electronics, hybrid and electrical vehicles. Umicore offers very pure battery grade cobalt oxide as precursor for lithium cobalt oxide for portable devices. Further, offers very pure battery grade cobalt and nickel sulphate for production of nickel cobalt aluminum oxides (NCA), and nickel manganese cobalt oxides (NMC), for automotive field. By the combination of a unique Ultra High Temperature (UHT) pyro-metallurgical treatment and state-of-the-art hydro-metallurgical process, Umicore enables recycling of all kinds and all sizes of lithium-ion and NIMH batteries. The UHT-process provides two end products, namely a metal alloy containing cobalt, nickel and copper, and a slag containing aluminum, manganese and lithium, which can be used in construction industry or further processed for metal recovery. The UHT process is different from other pyrometallurgical processes because of the ability to reach a higher metal recovery efficiency than existing pyrometallurgical processes, and the fact that spent lithium-ion batteries do not require any potentially hazardous pre-treatments. Furthermore, electrolytes, plastics and metals can be used as an energy source, which reduces energy consumption and CO₂ emission; by using a gas cleaning system, all organic compound decompositions are detected and kept near zero emission waste [2], [34].

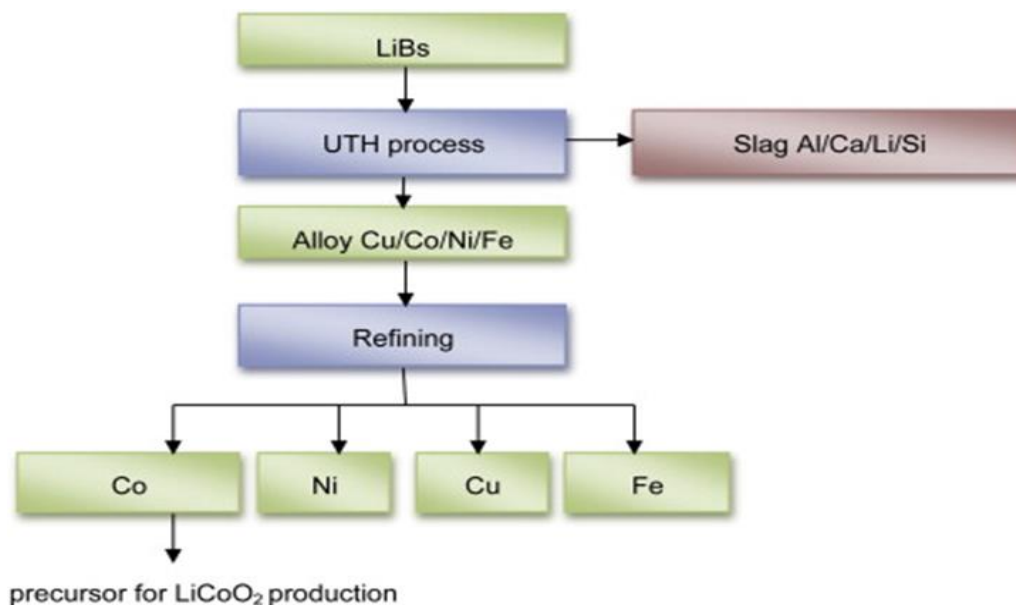


Figure 4. Flow chart for the Umicore Process [16].

4.3 The Accurec process

The Accurec plant is located in Germany [16], and hosts a recycling capacity for spent lithium-ion batteries equaling 2000 annual metric tons. The process involves mechanical pre-treatment, where lithium-ion batteries are classified, sorted, dismantled and subsequently pyrolysis treated to dispose of organic component. Afterwards, batteries are deactivated, makes them safe for further processing. The deactivated cells are mechanically crushed and then forwarded to sieving, followed by magnetic as well as air mediated separation, where concentrates of copper, aluminum and steel are retrieved [35]. The remaining electrode materials are then heat treated under vacuum and condensed to obtain metallic Co-Mn alloy and lithium containing slag [2], [16], [35].

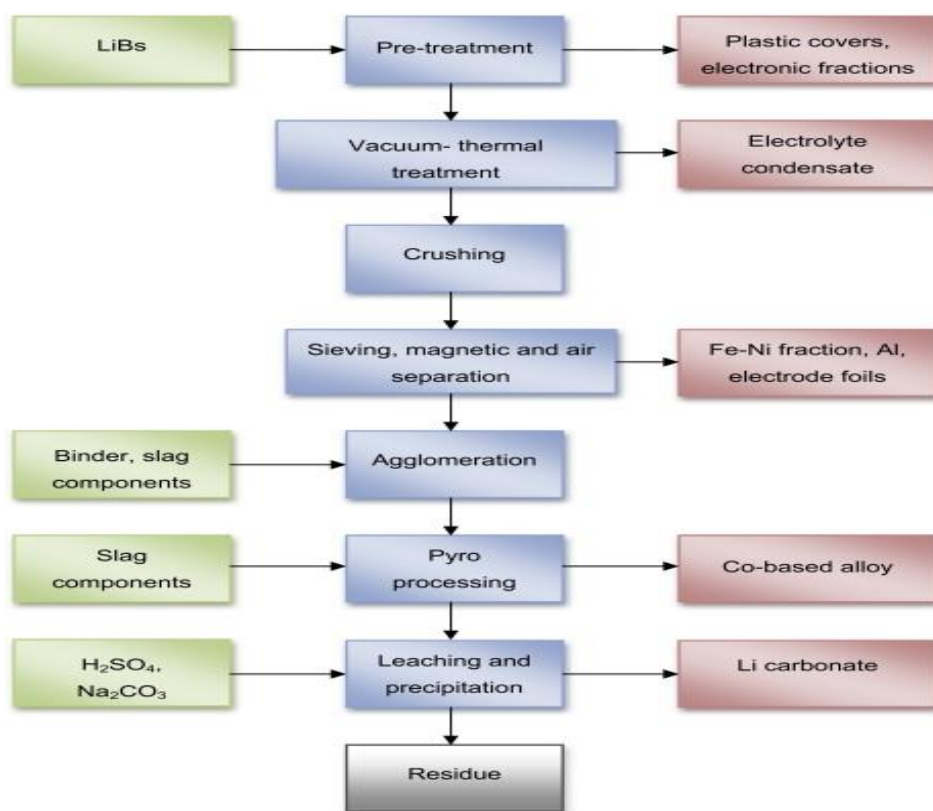


Figure 5 Flow Sheet of Accurec recycling process [16].

4.4 The Retrieval process

The Retrieval process has been commercially applied in Canada since 1993 [16], and primarily recycles lithium metal primary and lithium-ion secondary batteries [20]. Battery packs from hybrid and electric vehicle are first manually dismantled, then fed by conveyor together with other electronic batteries to an automated crusher, which operates using liquid nitrogen to prevent fugitive emissions and to reduce the reactivity. This step produces three types of materials: plastic components are obtained after the initial crushing stage; solid meal is obtained

by separation on a shaker table and is sold to other metallurgical plants for further recovery processing; the product of metal-enriched liquid is solidified using filtering technology with final products forming a cobalt filter cake and a lithium rich filtrate, which is then sent off-site for further metal purification [16], [20], [35], [36].

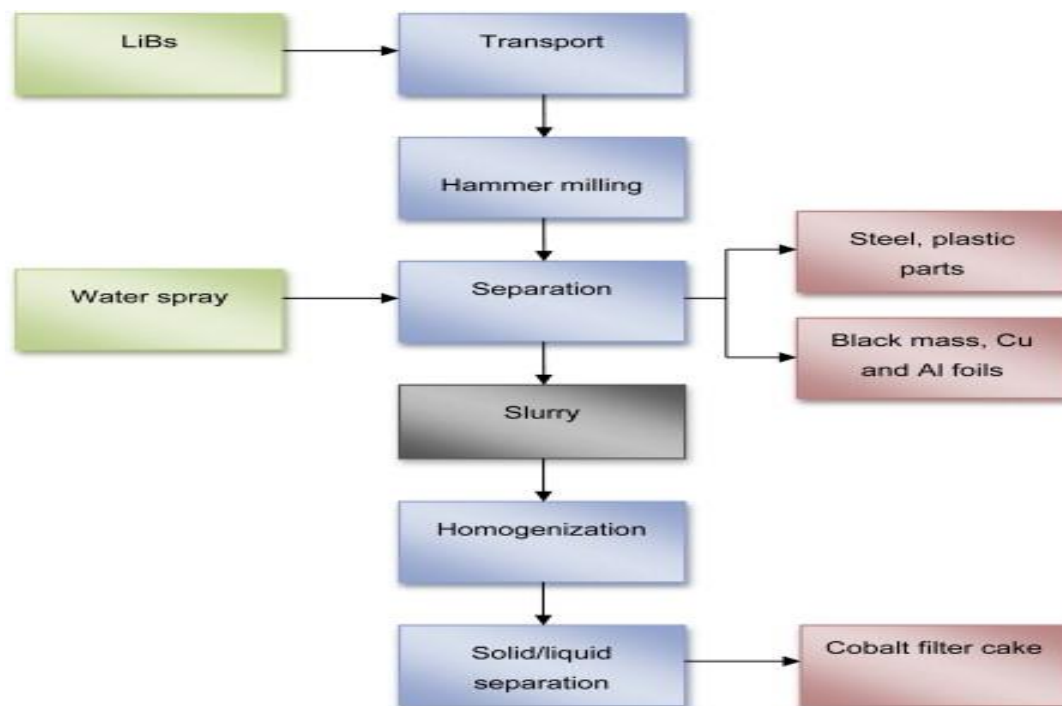


Figure 6 Flow chart for the Retrieve process [16].

4.5 The Recupyl process

Recupyl is an international company that focuses on in hybrid and electric vehicle battery recycling, and has operations in France, Poland and Singapore. The Recupyl process is, also known as the VALIBT process for recycling lithium-ion batteries. The process starts with mechanical treatment, which is operated under an inert environment in a confined chamber, effectively eliminating the reactivity of lithium. The products after mechanical treatment are paper, plastic, steel, copper and black mass. The fine black mass is leached with water. Lithium is precipitated as Li_2CO_3 by using the CO_2 from the mechanical treatment. The suspension of metal oxides is dissolved in sulfuric acid, copper impurities are cemented out with steel shots. Iron is obtained from the solution by precipitating with increasing the pH value from less than 3 to 3.85 by addition of soda. The NaClO is used to oxidize the purified solution to precipitate Co^{3+} hydroxide. Another way to separate cobalt can be carried out by electrolysis. Finally, the lithium that is left in the solution is precipitated with CO_2 gas [16].

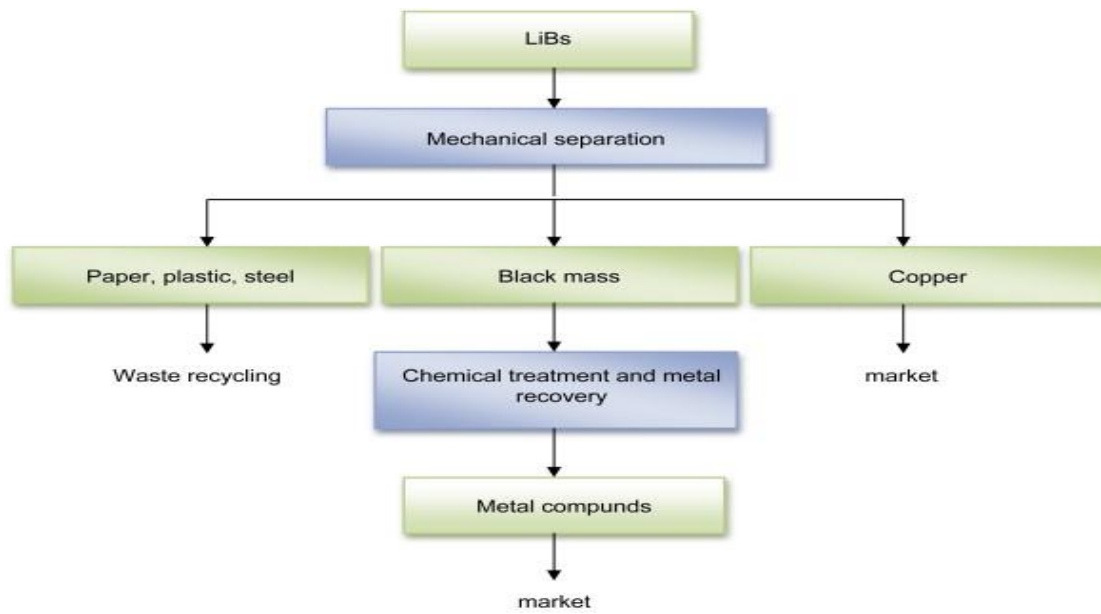


Figure 7 Flow chart for the Recupyl process [16].

5 Experimental

5.1 Materials and agents

The black mass used in this study was recovered from lithium-ion battery cells of a used car. After dismantling, cathode and anode were ground with an IKA M20 universal mill crusher for five minutes. The leaching agent was hydrochloric acid 37%, (Sigma Aldrich). Nitric acid 65% (Sigma Aldrich) was used for the dilution of the samples to measure the concentration of metal. Hydrochloric and nitric acids were dilute using Milli-Q water to the desired concentrations (see Table 1 in section 5.2) for the experiments.



Figure 8. The battery powder used in experiment.

5.2 Determination of metal content in black mass

To characterize the original metal content, 0.2 g of black mass was dissolved with 50 ml aqua regia solution and then diluted 1000 times with nitric acid. Prior to the measurement, the Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP-OES, ICAP 6500, Thermo Fischer) was calibrated using four standard solutions for target metals (0ppm, 5ppm, 10ppm, 20ppm). The standard solution was obtained by adding 1 ml of Al, Ni, Mn, Co, Cu and Li (1000ppm metal solution) to 44 ml 0.5 M HNO_3 solution (total 50, 20 ppm), which was then sequentially diluted with 0.5 M of HNO_3 to make the remaining three target solutions. A reference (0ppm) was obtained by using a pure sample with only 0.5 M HNO_3 .

5.3 The leaching process

Black mass samples were added to the leaching agent in a plastic beaker. The solutions were continuously stirred with electromagnet at 550 rpm with cover, and at temperature 25°C, 40°C and 60°C. For temperature 40°C and 60°C, plastic beakers were placed into a water bath over an electric heater with a thermometer to control the reaction temperature. The leaching agent concentrations were 0.5 and 1 M. The following constant leaching conditions were used: S:L = 1:50; 1:20 g/mL, the leaching time of 120 min. Liquid samples were taken out at the fixed reaction times 5, 15, 30, 60 and 120 min from each experiment to monitor the leaching process.

Triplicates were made for each experiment and total 360 samples were obtained. Procedure: 0.3 ml of liquid samples were taken and filtered. 0.1 ml were taken from the filtered liquid and diluted with 9.9 ml 0.5 M HNO₃ (diluted 100 times, 60 samples). 1 ml of solution is taken and diluted with 9 ml 0.5 M HNO₃ (diluted 1000 times, 60 samples). After 120 min, the leach solution and insoluble residues were immediately separated by vacuum filtration using a Lafil 400 vacuum filtration system with Whatman Grade GF/B filter paper (12.5 Cm size) was used in this study. The liquid samples were analysed by using ICP-OES to determine the metal concentration of the Co, Mn, Li and Ni, and to identify the optimal conditions for leaching. The solid residues from filtration were left to dry and then they were weighed. The leaching recovery rate was calculated according to the following formula:

$$\text{LEACHING EFFICIENCY} = [(C(M) * V * X) / m(M)] * 100\%$$

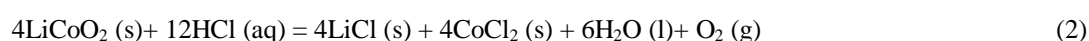
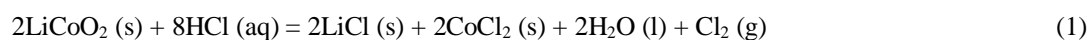
Where C is the concentration of metal M (M=Co, Mn, Li, Ni) in the liquid samples, V (L) is the volume of the leaching agent, m (M, g) is the mass of metal M in the black mass.

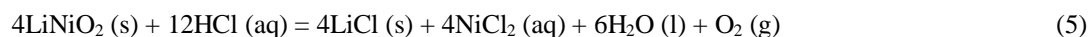
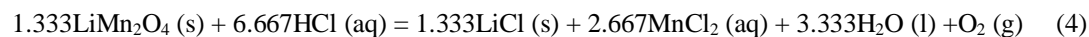
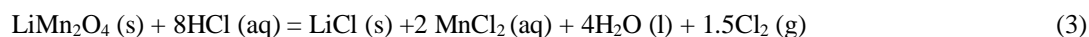
Tabell 1. Parameters for the leaching processes.

| Concentrations [mole] | Temperature [°C] | Leaching times and sampling [min] | Solid to liquid ratio [g/ml] |
|--------------------------|------------------|--------------------------------------|---------------------------------|
| 0.5 | 25, 40, 60 | 5, 15, 30, 60,120 | 1:50 |
| 1 | 25, 40, 60 | 5, 15, 30, 60,120 | 1:50 |
| 0.5 | 25, 40, 60 | 5, 15, 30, 60,120 | 1:20 |
| 1 | 25, 40, 60 | 5, 15, 30, 60,120 | 1:20 |

5.4 Thermodynamic studies

In order to predict the feasibility and spontaneity of reactions during the leaching process, a thermodynamic equilibrium calculation is necessary, which depends on thermodynamic parameters: Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS). The thermodynamic parameters were calculated by using the software HSC Chemistry 9. The mechanism of reactions between black mass and hydrochloric acid solution that might occur are:





From $\Delta G^0/T$ diagram in Figure 9, it can be determined the reaction (2) is preferable, due having the most negative change in $\Delta G^0/T$.

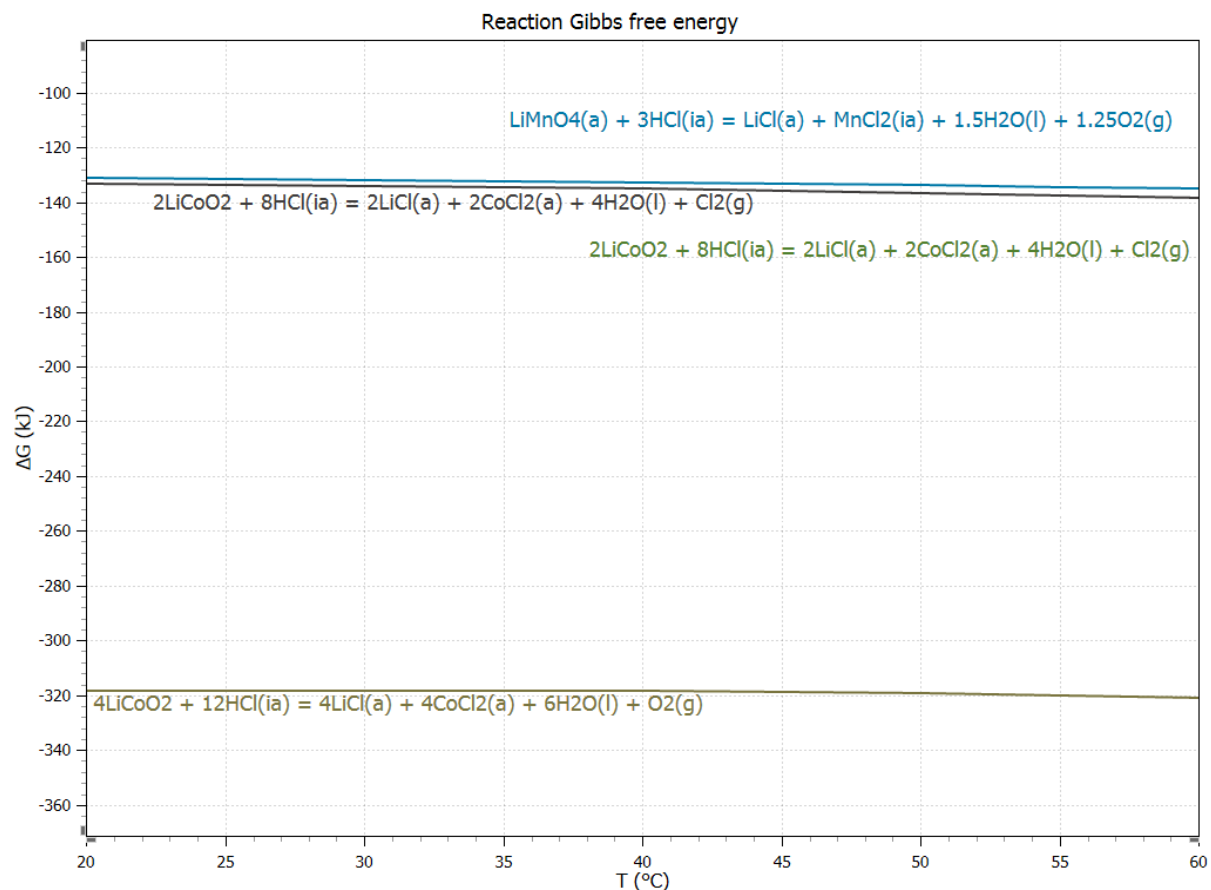


Figure 9. Standard Gibbs free energy changes of the possible reactions as a function of temperature in range 20°C - 60°C. a = solid, ia = aqueous, l = liquid, g = gas.

The negative values of ΔG^0 (Tables 2-5) for each reaction, indicate that the processes will proceed spontaneously in the forward direction to form more products. The calculated enthalpy has negative values in Tables 2, 3 and 5, which means that the reactions occurring during the recovery of different elements are exothermic. In Table 4 however, the positive enthalpy value identifies the reaction as endothermic.

Table 2. Values of ΔG^0 for chemical reaction of LiCoO_2 in HCl at 298-333 k.

| Reaction Equation | | | | | |
|---|------------------|-------------------|------------------|------------|--------|
| $2\text{LiCoO}_2 + 8\text{HCl(ia)} = 2\text{LiCl(a)} + 2\text{CoCl}_2\text{(a)} + 4\text{H}_2\text{O(l)} + \text{Cl}_2\text{(g)}$ | | | | | |
| Reaction Data | | | | | |
| T °C | ΔH kJ | ΔS J/K | ΔG kJ | K | Log K |
| 25,000 | -115,372 | 61,476 | -133,701 | 2,666E+023 | 23,426 |
| 40,000 | -96,660 | 122,705 | -135,085 | 3,424E+022 | 22,535 |
| 60,000 | -70,934 | 202,322 | -138,338 | 4,919E+021 | 21,692 |

Table 3. Values of ΔG^0 for chemical reaction of LiCoO_2 in HCl at 298-333 k.

| Reaction Equation | | | | | |
|---|------------------|-------------------|------------------|------------|--------|
| $4\text{LiCoO}_2 + 12\text{HCl(ia)} = 4\text{LiCl(a)} + 4\text{CoCl}_2\text{(a)} + 6\text{H}_2\text{O(l)} + \text{O}_2\text{(g)}$ | | | | | |
| Reaction Data | | | | | |
| T °C | ΔH kJ | ΔS J/K | ΔG kJ | K | Log K |
| 25,000 | -327,855 | -31,854 | -318,358 | 6,021E+055 | 55,780 |
| 40,000 | -299,945 | 59,472 | -318,568 | 1,390E+053 | 53,143 |
| 60,000 | -261,707 | 177,817 | -320,946 | 2,116E+050 | 50,325 |

Table 4. values of ΔG^0 for chemical reaction of LiMn_2O_4 in HCl at 298-333 k.

| Reaction Equation | | | | | |
|--|------------------|-------------------|------------------|------------|-------|
| $\text{LiMn}_2\text{O}_4\text{(Est)} + 8\text{HCl(ia)} = \text{LiCl(a)} + 2\text{MnCl}_2\text{(ia)} + 4\text{H}_2\text{O(l)} + 1,5\text{Cl}_2\text{(g)}$ | | | | | |
| Reaction Data | | | | | |
| T °C | ΔH kJ | ΔS J/K | ΔG kJ | K | Log K |
| 25,000 | 37,868 | 153,226 | -7,816 | 2,341E+001 | 1,369 |
| 40,000 | 49,619 | 191,675 | -10,404 | 5,439E+001 | 1,736 |
| 60,000 | 65,746 | 241,586 | -14,739 | 2,047E+002 | 2,311 |

Table 5 the value of ΔG^0 for chemical reaction of LiMn_2O_4 in HCl at 298-333 K.

| Reaction Equation | | | | | |
|---|------------------|-------------------|------------------|------------|--------|
| $,333\text{LiMn}_2\text{O}_4\text{(Est)} + 6,667\text{HCl(ia)} = 1,333\text{LiCl(a)} + 2,667\text{MnCl}_2\text{(ia)} + 3,333\text{H}_2\text{O(l)} + \text{O}_2\text{(g)}$ | | | | | |
| Reaction Data | | | | | |
| T °C | ΔH kJ | ΔS J/K | ΔG kJ | K | Log K |
| 25,000 | -46,971 | 49,495 | -61,728 | 6,538E+010 | 10,815 |
| 40,000 | -40,819 | 69,626 | -62,623 | 2,796E+010 | 10,447 |
| 60,000 | -32,530 | 95,284 | -64,274 | 1,198E+010 | 10,078 |

The particular species of the metal ions can be predicted using E-pH diagrams, showing that the elements are present in ionic form of Co^{2+} and Mn^{2+} until pH 5.8 and pH 6.5, respectively, in hydrochloric acid, while lithium is in the ionic form of Li^+ until pH 13.6.

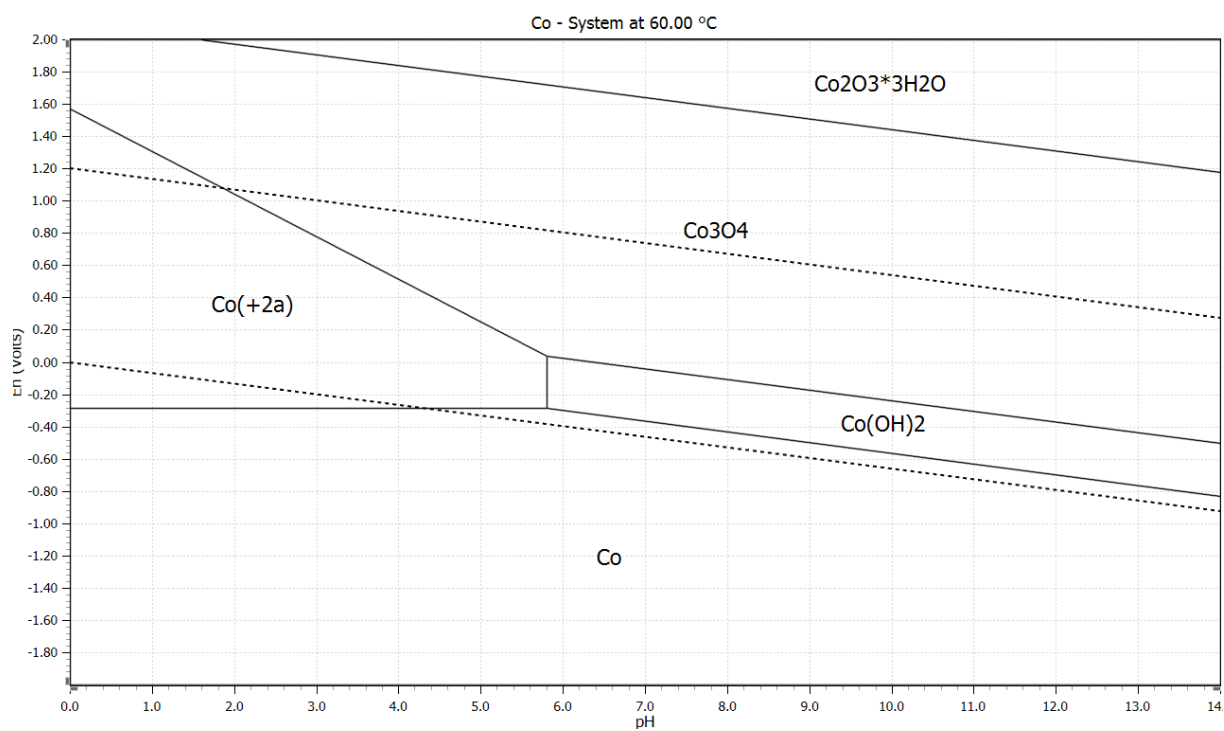


Figure 10. E-pH diagram for Co-H₂O at 60°C.

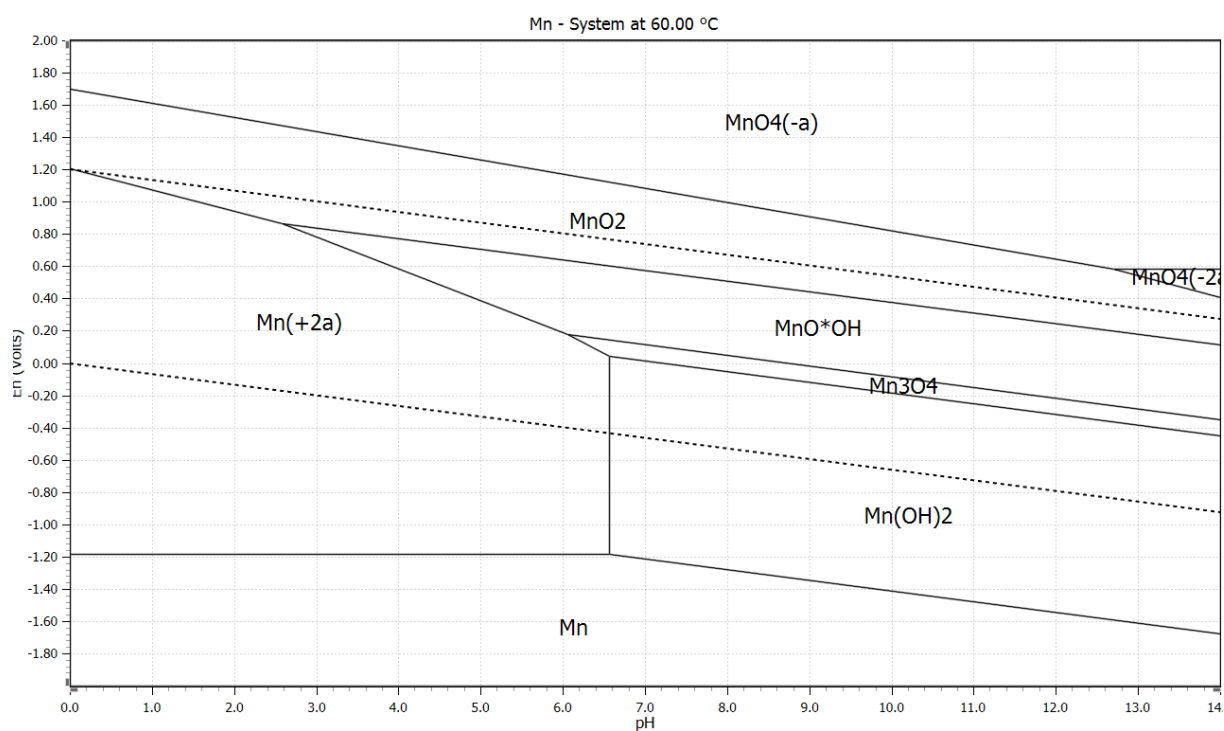


Figure 11. E-pH diagram for Mn-H₂O system at 60°C.

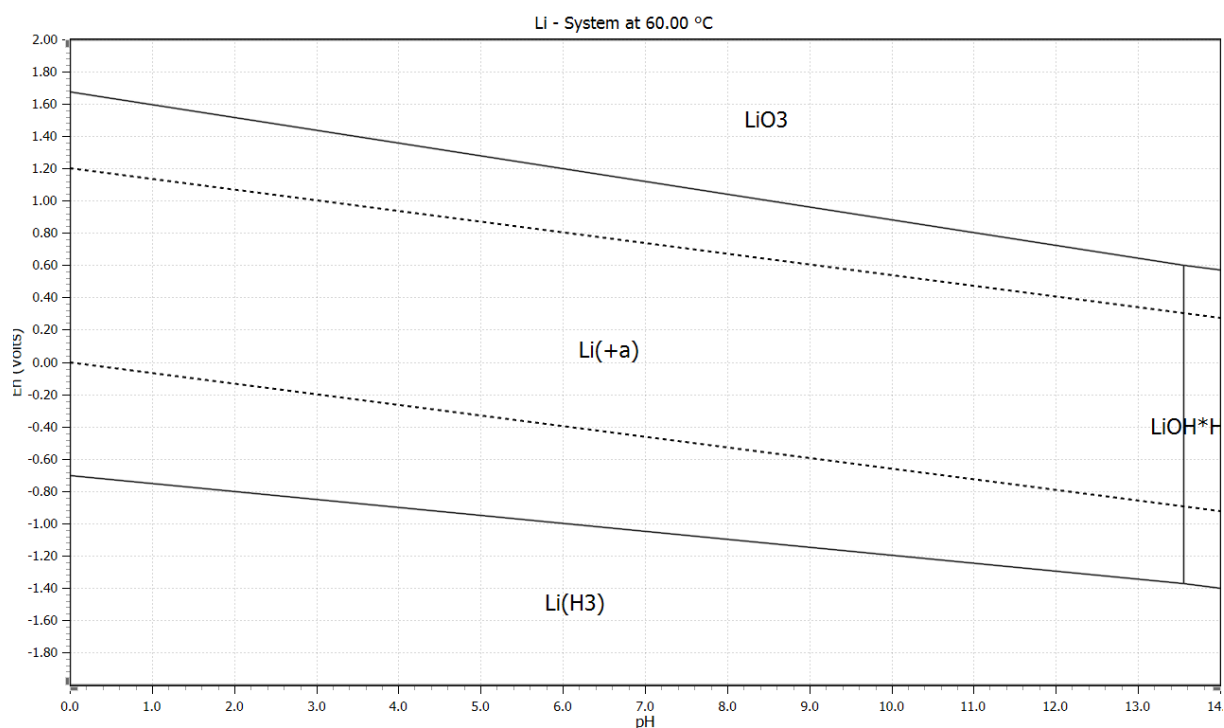


Figure 12. E-pH diagram for Li-H₂O system at 60°C.

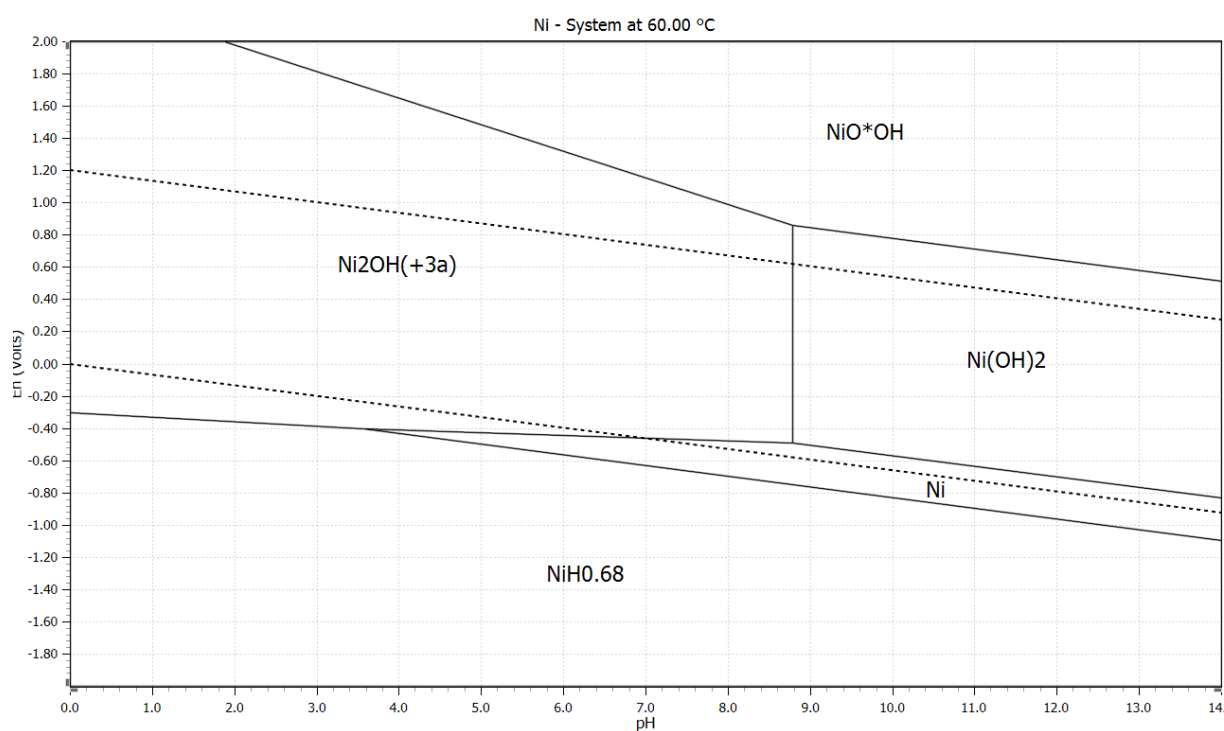


Figure 13. E-pH diagram for Ni-H₂O system at 60°C.

6 Results and discussion

6.1 Materials composition

The metal contents in black mass in the present work were dissolved using aqua regia and solution was analysed using ICP-OES technique. Experiments were done in triplicates. The results and standard deviations are shown in Table 6. According to these results, Mn is the main element in the black mass, followed by Ni, Co and Li.

Table 1. Chemical composition of the spent lithium-ion batteries.

| Metal | Metal content in the battery powder [%] |
|-------|---|
| Co | 5.0 ± 0.3 |
| Mn | 13.7 ± 0.8 |
| Li | 3.0 ± 0.1 |
| Ni | 8.3 ± 0.5 |

6.1.1 Effect of temperature on the HCl leaching process

The effect of temperature during leaching condition with parameters 0.5 M and 1 M HCl at S/L ratio 1/50 and time 60 min is shown in Figure 14. The leaching efficiencies were significantly affected when the temperature increased from 25°C to 40°C and 60°C for 0.5 M HCl. The effect of temperature applied could be supported by thermodynamic calculations of standard free Gibbs energy changes and the results given in Tables 2–5, where the values of each metal ion is more negative with increased temperature. From the plot it can be seen that the leaching efficiencies increased most in the beginning, a later increasing more slowly until their maximum was reached. From 41%, 64%, 79% and 39% at 25°C for Co, Mn, Li and Ni increasing to 100% respectively at 60°C.

The leaching efficiencies were positively affected by increasing the acid concentration from 0.5 M to 1 M. As the E-pH diagrams show (Figures 10–13), the metals of Co, Mn, Li and Ni can be dissolved when present in an acidic region. However, the efficiencies were not correlated to temperature. The efficiency for Co was around 93% at 25 °C, slowly increasing to 100% at 60°C. The leaching efficiency of Mn reached its maximum of 100% at 40°C, then decreased slightly to 96% at 60°C. Nickel leaching efficiency increased significantly from 73% at 25°C, to 90% at 40°C, with no further increase in efficiency towards 60°C.

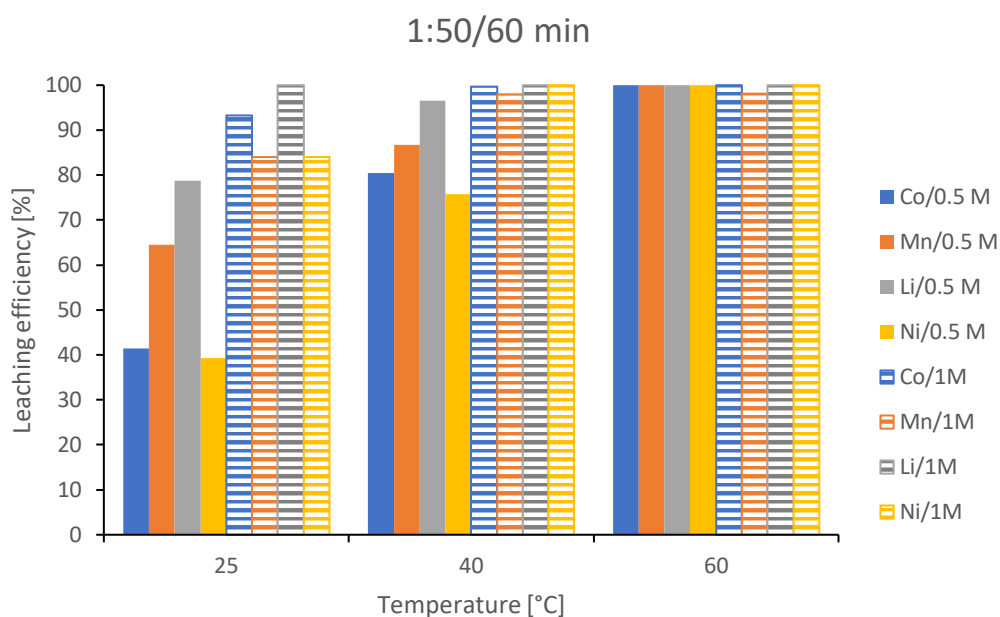


Figure 14. Effect of temperature on the leaching efficiency of Co, Mn, Li and Ni (s/l: 1/50 g/mL, 0.5 and 1 M HCl, leaching time 60) at 25°C, 40°C and 60°C.

The leaching efficiency under leaching conditions 0.5 and 1 M HCl, S/L ratio 1/20 at 60 min are shown in Figure 15, with the best result at 60 °C for both concentrations of HCl. It shows that in the lower concentration 0.5 M HCl, the leaching efficiency for Co, Mn, Li and Ni, did not increase significantly from 25°C (28%, 38%, 51% and 26%), to 40°C (32%, 37%, 57% and 29%). However, it can be seen in the plot that the leaching efficiencies increased when the temperature increased to 60°C, with leaching efficiencies reaching 56%, 57%, 82% and 53% respectively. In the case of the higher concentration 1 M HCl, the leaching efficiency was already high from 25°C (79%, 91%, 96% and 82%) increase to 40°C (92%, 100%, 100% and 97%) and reached 100% at 60°C.

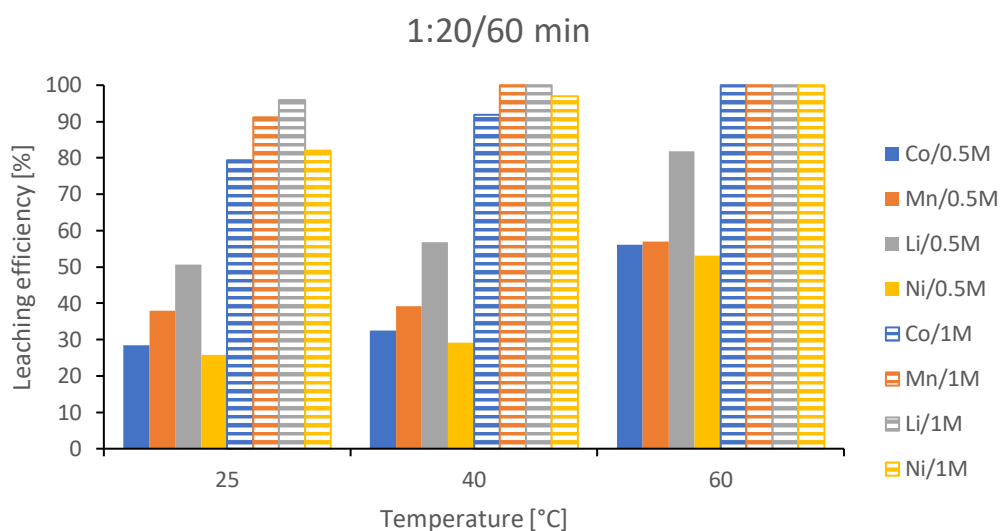


Figure 15. Effect of temperature on the leaching efficiency of Co, Mn, Li and Ni (s/l: 1/20 g/mL, 0.5 and 1 M HCl, leaching time 60) at 25°C, 40°C and 60°C.

However, the plots (Figs. 14 and 15) show that, when the concentration of HCl is low, the efficiencies are more affected by temperature in condition S/L ratio 1/50 than in 1/20. In addition to that, the efficiencies were not much different from each other when it came to concentration of 1 M HCl. And from these plots, it can be seen that the main factor affecting leaching efficiency is the acid concentration. Since most of the target metals were achieved 100% leaching efficiencies at 40°C, it was chosen to be the optimal leaching temperature.

6.1.2 Effect of HCl concentration

The effects of HCl concentrations on the leaching process of studied elements can be seen in Figs. 16-21. The effect of acid concentrations was studied by using 0.5 M and 1 M of HCl with varied temperatures at 25°C, 40°C and 60°C, S/L ratio of 1/50 and 1/20, and time intervals of 5, 15, 30, 60 and 120 min. The kinetic curves of Co, Mn, Li and Ni show that the optimal concentration for leaching was 1 M HCl in this study.

As seen in Fig. 16, the kinetic curve of leaching efficiencies for Co and Ni were increased quite similar. In the first 30 min increased rapidly in both concentrations, there after the one with higher concentration increased rapidly while the lower one. At the point of 60 min, the leaching efficiencies for Co, Mn, Li and Ni increased from 41%, 64%, 88%, and 39% to 93%, 84%, 100% and 84% respectively. At this point, the leaching efficiencies still increased significantly. with the exception of Li with 1 M HCl, At 30 min leaching time Li reached leaching efficiency 97%.

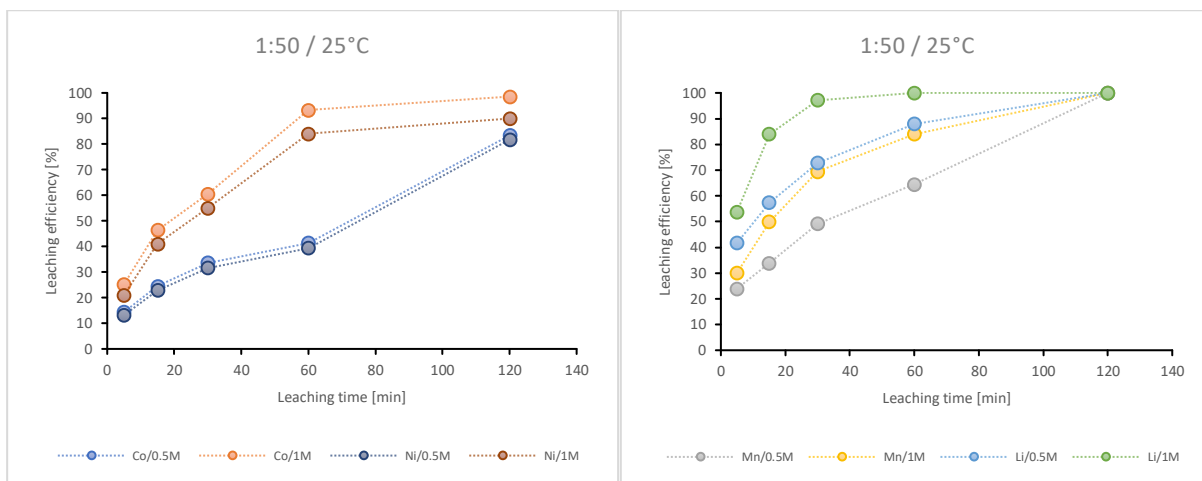


Figure 16. Effects of HCl concentration on the leaching efficiency of Co, Mn, Li and Ni (leaching parameters: s/l: 1/50 g/mL, temperature at 25°C).

As observed in Fig. 17, the efficiencies of 0.5 M HCl increased rapidly in the first 60 min, thereafter increasing more slowly. From the plots of 1 M HCl, it can be seen that the efficiencies increased sharply between 15-30 min, thereafter slowed down until 60 min with exception of Li, after which the efficiencies remained constant (Li after 30 min). The efficiencies at the point of leaching time 60 min increased from 81%, 87% and 76% to 100%, for CO and Ni, and Mn 98%, while Li increased from 93% to 100% at 30 min.

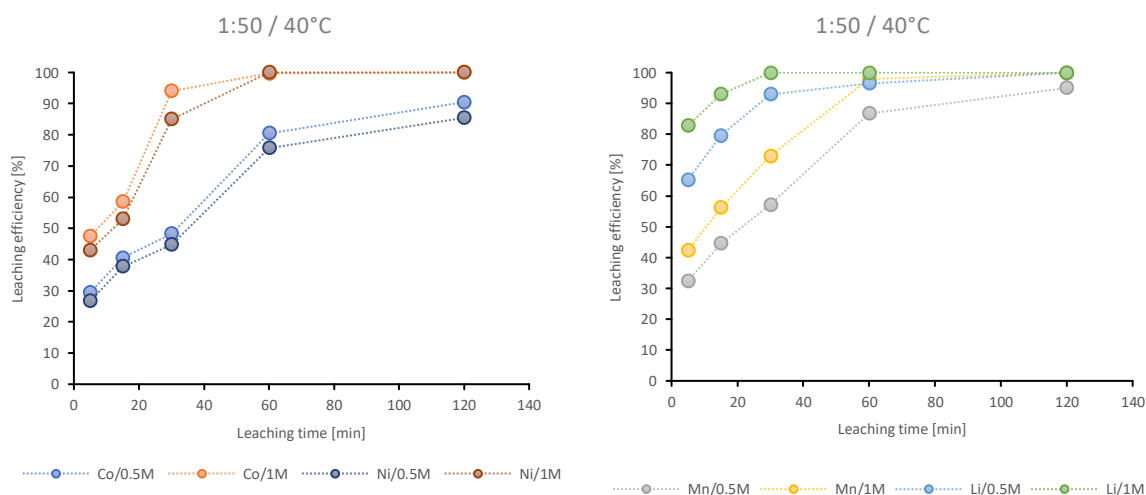


Figure 17. Effects of HCl concentration on the leaching efficiency of Co, Mn Li and Ni (leaching parameters: s/l: 1/50 g/ml, temperature at 40°C).

Compared to Fig. 17, the results shown in Fig. 18 show corresponding efficiency at 60°C. As visible, Li is leached relatively fast, up to 94% in the first 5 min, reaching 100 % at a leaching time 15 min. Overall, it can be seen that the leaching efficiencies of both concentrations increased fast within the first 30 min, then slowed down and remained constant after 60 min.

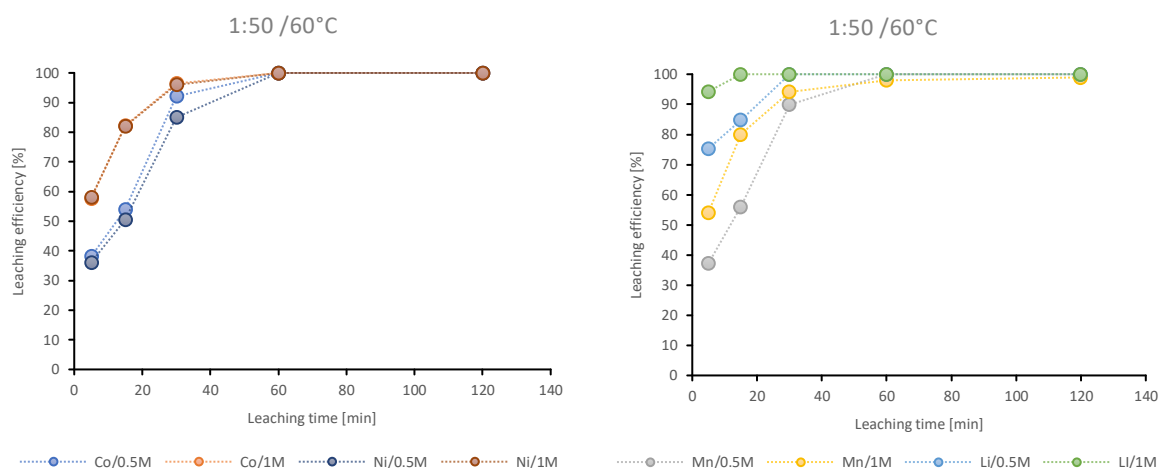


Figure 18. Effects of HCl concentration on the leaching efficiency of Co, Mn, Li and Ni (leaching parameters: s/l: 1/50 g/mL, temperature at 60°C).

As seen in Figs. 19 and 20, the kinetic curves increased in a similar fashion despite different temperatures (25°C and 40°C). The leaching process with 0.5 M HCl for Co, Mn, Li and Ni was fast within 5–30 min, then slowing down and remaining almost constant until 120 min. At 1 M HCl, the leaching process for all the elements was rapid during the first 60 min, with subsequent slowed downs towards 120 min.

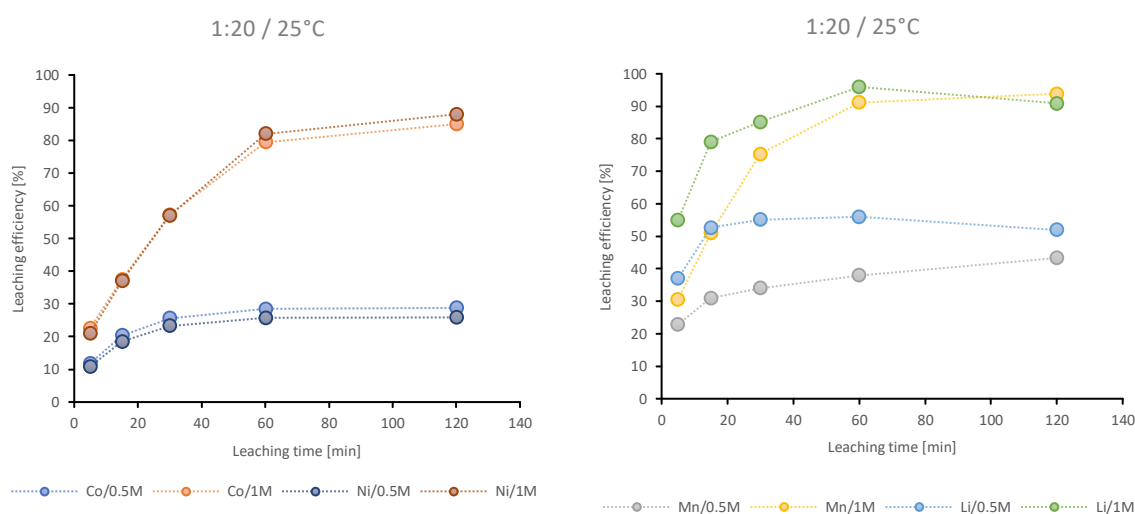


Figure 19. Effects of HCl concentration on the leaching efficiency of Co, Mn, Li and Ni (leaching parameters: s/l: 1/20 g/mL, temperature at 25°C).

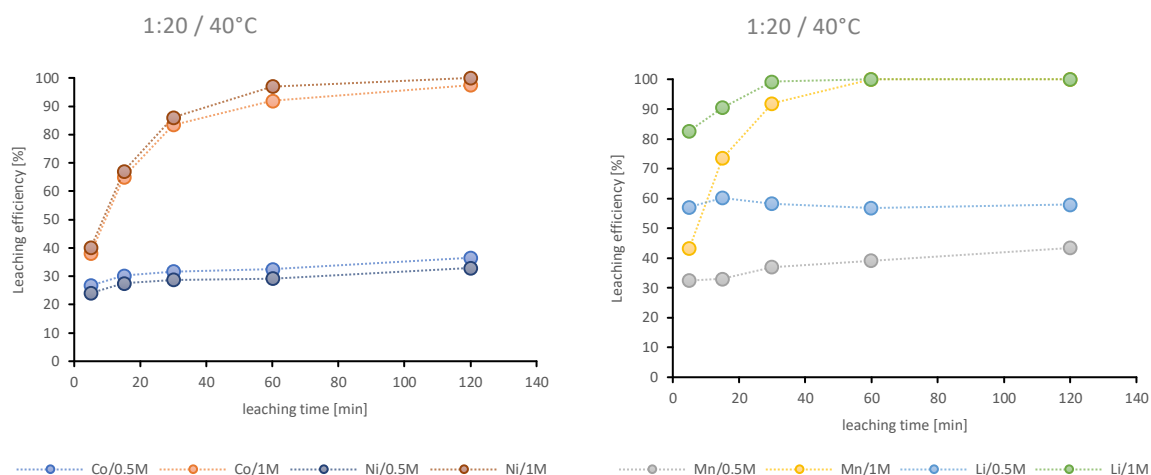


Figure 20. Effects of HCl concentration on the leaching efficiency of Co, Mn, Li and Ni (leaching parameters: s/l: 1/20 g/mL, temperature at 40°C).

Figure 21 presents the results at 60°C. As seen in the plot for Li at 0.5 M HCl, it decreased slightly in the first 15 min, thereafter increasing slowly. The fluorine ions in the leachate may be the explanation, it could create LiF and then re-dissolve. The leaching efficiencies of Co, Mn, Li and Ni at 15 min leaching time increased from 40%, 42%, 76% and 39%, to 92%, 96%, 100% and 96% respectively, when the acid concentration was increased from 0.5 M to 1 M. this indicates that the concentration of acid strongly affect leaching efficiency, with the optimal concentration of HCl in this leaching experiment determined to be 1 M HCL.

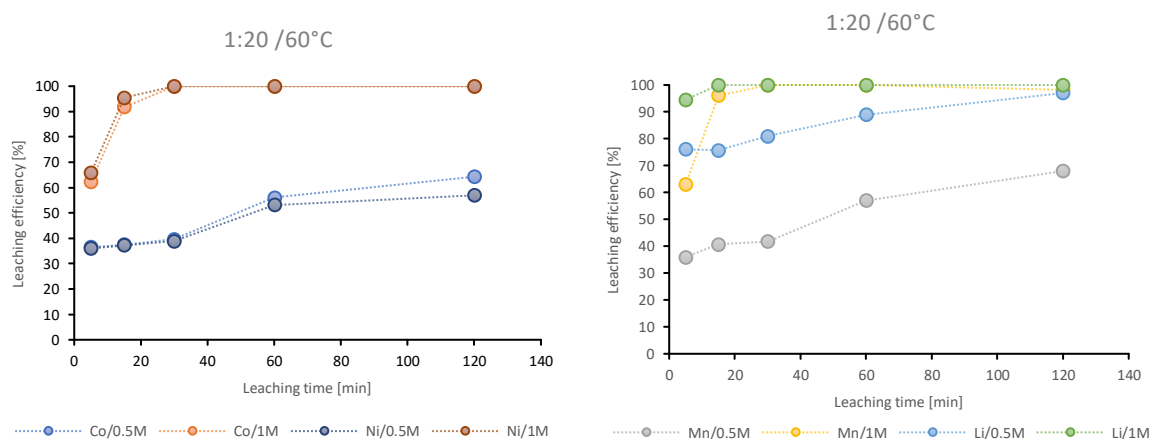


Figure 21. Effects of HCl concentration on the leaching efficiency of Co, Mn, Li and Ni (leaching parameters: s/l: 1/20 g/mL, temperature at 60°C).

6.1.3 Effect of time on leaching

The graphs from Figs. 16-21, present the leaching efficiency as a function of time. It can be observed that the leaching efficiencies of Co, Mn, Li and Ni being significantly influenced by the leaching time. As seen in Fig. 18, the leaching efficiencies of Co, Mn, Li and Ni increased rapidly in the first 30 min, followed by a slower increase after this point and remaining constant

after 60 min at both concentrations, indicating that the maximum leaching efficiency has been reached. Therefore, the optimal time for leaching is determined to be 60 min.

6.1.4 Effect of solid to liquid ratio

The influence of S/L ratio on the leaching of studied elements was investigated under the following conditions: HCl concentrations with 0.5 M and 1 M, S/L ratio of 1/50 and 1/20, temperature in range 25, 40 and 60°C and a leaching time of 120 min.

The results shown in the Figure 22 indicate the efficiency at different S/L with the leachate 0.5 M HCl. As can be seen, the leaching efficiencies increased to almost double when S/L ratio 1/20 was changed to 1/50 at 25°C and 40°C, and the efficiencies reached 100% of S/L ratio 1/50 at 60°C. These results indicate that the leaching efficiencies were strongly correlated to the on solid-liquid ratio. The effect can be explained by the solid-liquid ratio of 1/50 has more acid available for reactions than 1/20, which results in higher leaching efficiency. The metal mass rate of black material that has been transferred from the solid particles to liquid during this 120 min leaching time is presented in Table 7.

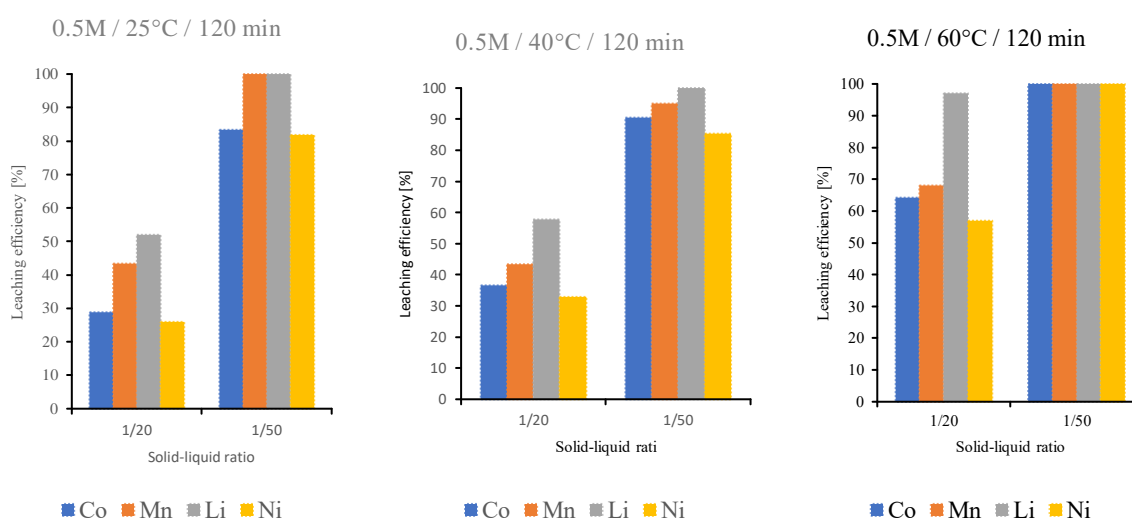


Figure 22. Effects of S/L on the leaching efficiency at 25, 40 and 60°C, 0.5 M HCl, at leaching time 120 min.

Table 2. Metal mass transfer from black material to the liquid after 120 min leaching time with 0.5 M HCl at 25°C, 40°C and 60°C with s/l ratio: 1/20 and 1/50 g/ml.

| | 0.5 M / 25°C | | | | 0.5 M / 40°C | | | | 0.5 M / 60°C | | | |
|------|--------------|------|------|------|--------------|------|------|------|--------------|------|------|------|
| | Co | Mn | Li | Ni | Co | Mn | Li | Ni | Co | Mn | Li | Ni |
| 1/20 | 0.77 | 3.17 | 0.77 | 1.14 | 0.97 | 3.17 | 0.94 | 1.45 | 1.71 | 5.00 | 1.41 | 2.50 |
| 1/50 | 0.86 | 2.89 | 0.64 | 1.39 | 0.93 | 2.67 | 0.63 | 1.45 | 1.12 | 3.09 | 0.71 | 1.73 |

The results of experiments using 1 M HCl are presented in Fig. 23, where it can be seen that the leaching efficiency was already very high at S/L ratio 1/20 at 25°C. When the S/L ratio was decreased to 1/50, the leaching efficiencies increased to 100% for Mn and Li, 99% and 90 % for Co and Ni. At 40°C, the leaching efficiencies already reached 97% for Co, 100% for Mn, Li and Ni of S/L ratio 1/20. When the S/L ratio was decreased to 1/50, Co achieved 100% while Mn, Li and Ni remained the same. Moreover, it can be observed that when the temperature was 60°C, leaching efficiencies for Co and Ni were the same 100% when S/L ratio 1/20 decreased to 1/50, while Mn and Ni increased from 98%, 97% to 99% and 100%, respectively. The results indicate that the leaching efficiencies were not significantly dependent on S/L ratio, but was more dependent on the acid concentration. However, the optimal S/L ratio for leaching was determined to be 1/20. Identification of the optimal leaching conditions may not always take the highest leaching efficiencies into count. An economically effective method is preferred in the industrial process. Calculations of the leaching process cost have identified the primary cost being leaching agents and energy consumption. The mass rate of metal that has been dissolved into the liquid after 120 min leaching is presented in Table 8.

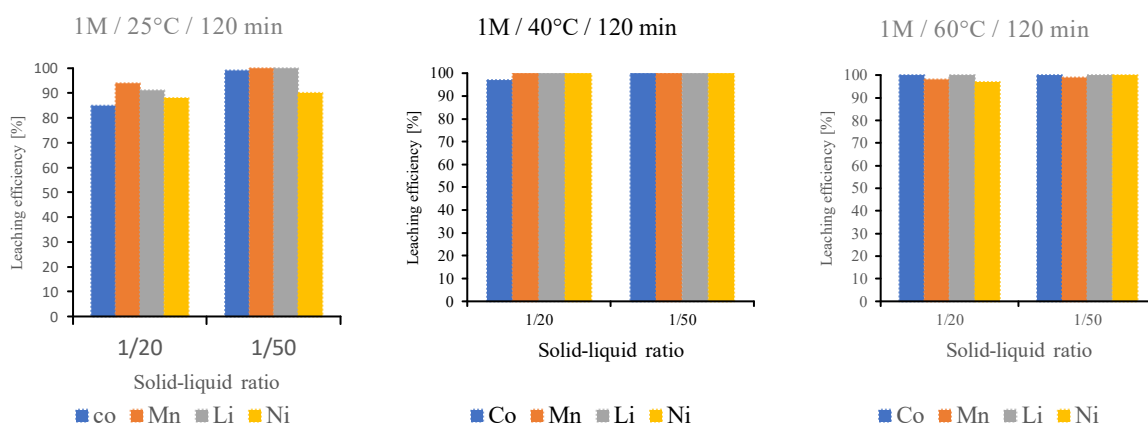


Figure 23. Effects of S/L on the leaching efficiency at 25, 40 and 60°C, 1 M HCl, at leaching time 120 min.

Table 3. Metal mass transfer from black material to the liquid after 120 min leaching time with 1 M HCl at 25°C, 40°C and 60°C with s/l ratio: 1/20 and 1/50 g/ml.

g/L

| 1 M/ 25°C | | | | | 1 M/ 40°C | | | | | 1 M/ 60°C | | | |
|-----------|------|------|------|------|-----------|------|------|------|------|-----------|------|------|------|
| | Co | Mn | Li | Ni | Co | Mn | Li | Ni | | Co | Mn | Li | Ni |
| 1/20 | 2.52 | 7.35 | 1.48 | 3.92 | 2.87 | 8.13 | 1.62 | 4.46 | 1/20 | 3.04 | 8.31 | 1.75 | 4.72 |
| 1/50 | 0.94 | 2.89 | 0.66 | 1.40 | 1.04 | 2.95 | 0.71 | 1.56 | 1/50 | 1.07 | 2.77 | 0.71 | 1.60 |

7 Conclusions

The aim of this study was to investigate the optimal leaching conditions for recovery of Co, Mn, Li and Ni from spent lithium-ion batteries by using a hydrometallurgical treatment. Parameters such as temperature, concentration of hydrochloric acid, leaching time and solid-liquid ratio were implemented as variables when studying the influence on the leaching process. By analyzing of ICP-OES, leaching efficiencies could be calculated and the optimal leaching conditions could be indicated.

From this study, it was indicated that the temperature had a noticeable effect on the leaching process at an S/L ratio of 1/50, with no noticeable effect when using 1 M hydrochloric acid compared to 0.5 M. However, from the examined temperatures of 25°C, 40°C and 60°C, leaching at 40°C seemed to be an optimal temperature of those tested for, from an energy consumption perspective due to the leaching efficiencies not being much different from the one at 60°C. It was also indicated that the concentration of hydrochloric acid had a strong effect on the leaching process, and 1M of HCl seemed preferable over a concentration of 0.5M. It was observed that at a leaching time of 60 min that almost all the metals reached their maximum efficiency, with some exception case of Mn and Ni in leaching with 1 m HCl. The optimal time for leaching was indicated to be 60 min (120 min maximum experiment time). It was further indicated that the leaching efficiencies increased with decreasing solid-liquid ratio when 0.5M of HCl was used, but it was not affected at a concentration of 1M HCl. The optimal solid-liquid ratio for leaching was indicated to be 1/20. Altogether, the most effective leaching conditions under the presented circumstances were indicated in this study to be 1 M hydrochloric acid, 60 min leaching time, at 40°C with solid-liquid ratio of 1/20 g/ml.

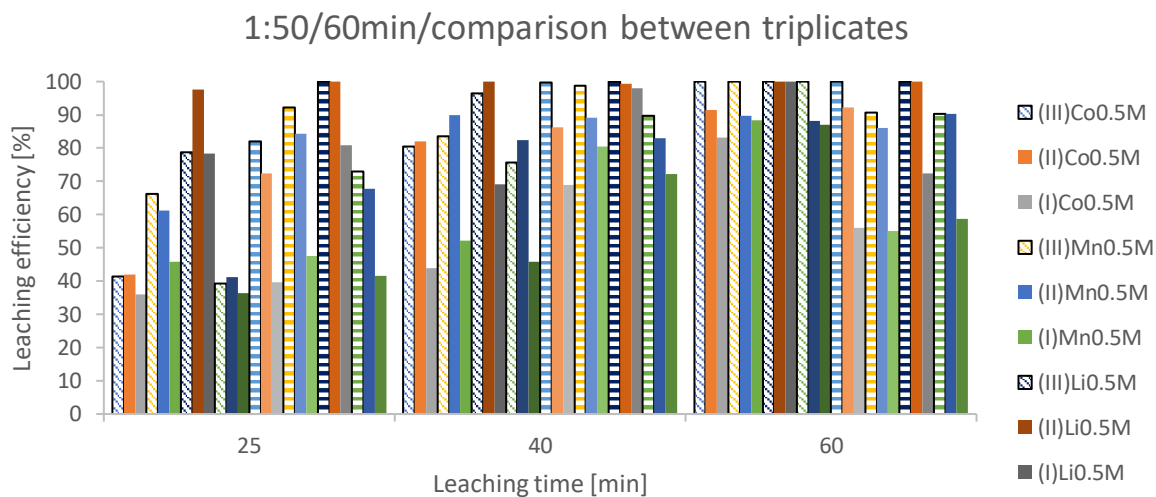
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9 Appendix

Effect of temperature on the leaching efficiency of Co, Mn, Li and Ni (s/l: 1/50 g/mL, 0.5 and 1 M HCl, leaching time 60) at 25°C, 40°C and 60°C.



Effect of temperature on the leaching efficiency of Co, Mn, Li and Ni (s/l: 1/20 g/mL, 0.5 and 1 M HCl, leaching time 60) at 25°C, 40°C and 60°C.

