INVESTIGATION OF LEACHING PARAMETERS IN THE RECYCLING OF WASTE LI-ION BATTERIES BY HYDROMETALLURGICAL METHOD

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ABSTRACT

INVESTIGATION OF LEACHING PARAMETERS IN THE RECYCLING OF WASTE LI-ION BATTERIES BY HYDROMETALLURGICAL METHOD

With the developing technology, the demand for Li-ion batteries is increasing in many sectors such as automotive, energy and electronic devices. Accordingly, the need for raw materials for Li-ion battery production also arises. With the limited availability of raw materials in this age of consumption, the importance of Li-ion battery recycling is increasing.

In line with this idea, this study focuses on recycling Li-ion batteries by hydrometallurgical method. In the study, the effect of parameters such as the amount of H_2SO_4 and H_2O_2, temperature, presence of H_2O_2 and priority of addition on nickel and cobalt leaching efficiencies in the leaching step, which is one of the hydrometallurgical method stages, was investigated. As a result of the studies, it was observed that nickel and cobalt leaching efficiencies increased with the increase in the amount of H_2SO_4. It was also observed that the leaching efficiencies increased proportionally with the temperature rise. As a result of the sequential studies in which the effect of H_2SO_4 amount and temperature were examined, 94.09% Co and 85.09% Ni leaching efficiencies were obtained.

In the studies, the presence, amount and priority of addition of H_2O_2 in the leaching stage were also among the parameters analysed. It was observed that Nickel and Cobalt yields increased with the presence of H_2O_2. Addition priority of H_2O_2 was also found to be important. When H_2O_2 was added first, H_2O_2 did not affect the leaching efficiency, on the contrary, Nickel and Cobalt leaching efficiencies increased with the addition of H_2SO_4, H_2O_2.

ÖZET

ATIK Li-İYON BATARYALARIN HİDROMETALURJİK YÖNTEMLE GERİ DÖNÜŞÜMÜNDE LİÇ PARAMETRELERİNİN İNCELENMESİ

Gelişen teknoloji ile birlikte otomotiv, enerji ve elektronik aletler gibi bir çok sektörde Li-iyon pillerine talep artmaktadır. Bu doğrultuda, Li-iyon pil yapımı için ham madde ihtiyacı da oluşmaktadır. Tüketim çağındaki bu kısıtlı ham madde mevcudiyetinde de Li-iyon pil geri dönüşümünün önemi artmaktadır.

Bu düşünce doğrultusunda, bu çalışmada Li-iyon pillerinin hidrometalürjik yöntemle geri dönüşümüne odaklanılmıştır. Çalışmada, hidrometalürjik yöntem aşamalarından biri olan liç kademesinde eklenen H_2SO_4 ve H_2O_2 miktarları, sıcaklık, H_2O_2'nin varlığı ve ekleme önceliği gibi parametrelerin Nikel ve Kobalt liç verimlerine etkisi incelenmiştir. Çalışmalar sonucunda, H_2SO_4 miktarının artmasıyla birlikte Nikel ve Kobalt liç verimlerinin arttığı gözlemlenmiştir. Ayrıca, sıcaklık artışıyla da liç verimlerinin orantılı olarak arttığı görülmüştür. H_2SO_4 miktarının ve sıcaklığın etkisinin incelendiği sıralı çalışmalar sonucunda, %94,09 Co, %85,09 Ni liç verimi elde edilmiştir.

Çalışmalarda, liç aşamasında H_2O_2 varlığı, miktarı ve ekleme önceliği de incelenen parametreler arasındadır. H_2O_2 varlığıyla Nikel ve Kobalt veriminin arttığı görülmüştür. H_2O_2'nin ekleme önceliğinin de önemli olduğu görülmüştür. Öncelikle H_2O_2 eklemesi yapıldığında H_2O_2'nin liç verimini etkilemediği, tam tersi H_2SO_4, H_2O_2 eklemesiyle Nikel ve Kobalt liç verimleri artmıştır.

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INTRODUCTION

With the rapidly increasing global energy consumption, reducing the carbon footprint and addressing issues such as climate change has become a priority. To this end, it is necessary to increase renewable energy and nuclear energy to replace fossil fuels. The US Energy Information Administration estimates that renewable energy consumption will be close to the share of liquid fuels in 2050 and will reach approximately 250 quadrillion BTU (Bauer et al. 2022). Though renewable energy sources such as solar and wind energy are environmentally preferable, they are not sustainable due to some disadvantages. One of these disadvantages is the lack of continuous storage. Lithium-ion batteries, which are among the popular electrochemical energy storage devices today, show considerable promise as portable energy that can store energy and have an accessible power supply. Considering the importance of Li-ion batteries in the near future, the Nobel Prize was rewarded in 2019 to John B. Goodenough, Stanley Whittingham and Akira Yoshino, pioneers of Li-ion battery technologies. Li-ion batteries, whose technology is developing today and is expected to move to different dimensions in the near future, have caused a sustainable revolution in human life (Bauer et al. 2022).

Because of the remarkable, major evolution among energy storage devices, the need for efficient rechargeable, lightweight, portable batteries has recently been of great importance. Advances have been made in improving these properties. Many studies and applications in these developments are focussed even on complicated technologies in battery production due to the importance of the issue (Dobó, Dinh, and Kulcsár 2023)

Moreover, due to this global problem, first European countries and then all countries of the world have realized the significant impact of greenhouse gases on climate change. With this realization, they have supported the development of renewable clean energy systems. Developments such as wind, solar and electric vehicles are examples of these. The technological development of Li-ion batteries has been determined by many devices such as smartphones, electric vehicles, tablets, computers, and energy storage systems that have become popular in recent days. In addition, it is of great importance to reduce greenhouse gases increasing with the increasing consumption of fossil fuels. In addition, electric vehicles in the automotive sector will save energy by using clean energy. In battery production; parameters such as battery size, weight, long battery life, safety and low cost have become important for manufacturers (H. J. Kim et al. 2020).

These batteries are composed of 3 to 12 cells and have a voltage of 3-36 V depending on the area of use. One of these areas of use is electric transport systems. It is used even in small transport vehicles such as bicycles and scooters and is becoming increasingly important. In the automotive sector, li-ion batteries are widely used in hybrid vehicles, plug-in hybrid and electric vehicles and their development is still continuing. The use of li-ion batteries in vehicles such as buses and trucks used in the transport sector has become widespread. Countries are emphasising on green energy policy with the increasing consumption of fossil fuels. With this policy, the demand for various storage devices is increasing. As storage equipment, Li-ion batteries offer mini-storage up to 40 MWh in facilities larger than about 2 kWh (Bauer et al. 2022).

In addition, Li-ion batteries are widely used in the automotive and energy sectors and are highly preferred for grid storage systems due to their high energy and power densities. The Li-ion battery market is expected to reach 253 million dollars by 2030 with the production of electric vehicles (Yu et al. 2022).

The operating principle of Li-ion batteries is based on the charge-discharge process like other electrochemical batteries (Wu, n.d.). In terms of content, it generally contains Li, Co, Mn and graphite compound elements (Gaines, Richa, and Spangenberger 2018).

The fundamental principle of operation of a rechargeable Li-ion battery is shown in Figure 1. The electrolyte (lithium salt) that provides ion flow is located between two electrodes. The separator (membrane), which provides insulation of the electric current between the two electrodes, is also included with the electrolyte. During the charging and discharging process of the battery, lithium ions in the electrolyte move between the electrodes and mix with the active material. During battery charging, lithium ions are oxidised and released by separating from the positive electrode (cathode). During oxidation electrons are released and these electrons are captured by the current collector. Lithium salts are also mixed into the active material at the negative electrode. In the discharge of the battery, this flow is reversed. The active materials in the positive electrode (cathode) consist of mixed oxides such as metal oxides. The active material in the negative electrode (anode) is graphite and amorphous carbon compounds. As shown in Figure 1, during the charging of li-ion batteries, lithium ions are transferred from the positive electrode to the negative electrode with the help of electrolyte and membrane. The electrons that provide electricity generation are captured by the copper current collector at the positive electrode and pass to the aluminum side of the current collector at the negative electrode with the help of an external cable. During discharge, this flow is reversed (Bauer et al. 2022).

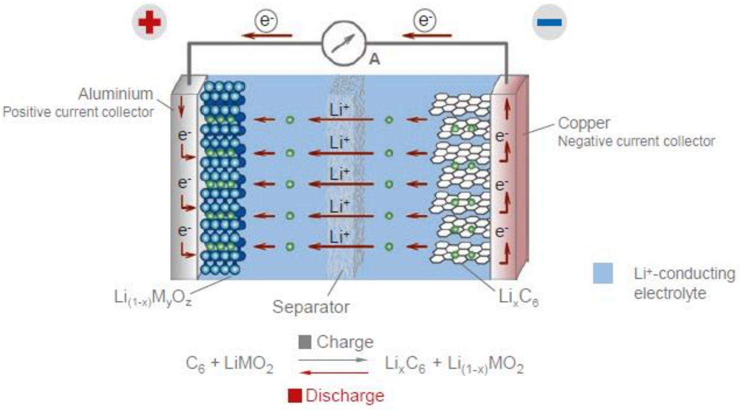


Figure 1. Working Principle of Li-ion batteries (Misenan et al., n.d.).

Li-ion batteries basically consist of five main parts. These are; the shell part that surrounds the battery from the outside; the internal components are the positive electrode (anode), the negative electrode (cathode), the separator that provides insulation and the electrolyte part that provides electron flow (An 2019).

Shell: It is the outer part that ensures the safety of the internal mechanism of the Li-ion battery. It usually consists of stainless steel or concentrated nickel plated steel. This part is recovered by mechanical separation method in recycling (An 2019).

Cathode: It is called the positive electrode in the battery mechanism. It is an active material consisting of mixed oxide. Mostly, this active material is carefully and thinly coated on aluminum foil, which is the current collector. The conductive material polyvinylidene fluoride (PVDF) is used to bind these two components. The active material in the cathode must oxidize the transition metals to achieve charge balance (Brückner, Frank, and Elwert 2020). There are three types of cathode-active materials.

These are

- $LiMO_2$ compounds consisting of Nickel, Cobalt, Manganese, and Aluminium metal (M) components: layered oxides,
- LiM_2O_4 compounds composed of nickel, manganese metal (M) components: spinels,
- $LiMPO_4$ compounds consisting of Iron, Manganese, Cobalt, Nickel metal (M) components: phosphates (Brückner, Frank, and Elwert 2020). With the widespread use of li-ion batteries in different sectors, manufacturers have focused on increasing the high energy density of electrode materials. $LiCoO_2$ type batteries are the first preferred Li-ion batteries due to their high energy density and easier production compared to other batteries. These types of batteries are widely used in mobile devices such as laptops, phones, watches. This type of commercially available li-ion battery consists of approximately 90% $LiCoO_2$, 8% conductive material and 4% PVDF (An 2019).

Recently, NMC (NiCoMn) containing batteries have started to be used with the use of Nickel to increase battery capacity and Manganese to improve battery stability and are still under development. On the other hand, LFP (LiFeP) batteries have attracted the attention of manufacturers with their low cost and safety advantages and have started to be investigated (Brückner, Frank, and Elwert 2020).

Anode: The anode has a similar structure to the cathode in function. It is a structure coated with PVDF and active material as a binder on copper foil, which acts as a current collector. Graphite is generally used as an active material. Pyrolysis carbon, glass carbon, petroleum coke, carbon fiber are other materials used in the anode. Graphite is widely used in today's salable li-ion batteries due to its low cost. However, efforts are also being made to improve the material properties of graphite in order to increase the storage capacity of the batteries currently used (An 2019).

Separator: This part is used to prevent short circuit between the anode and cathode due to electricity. The separation efficiency of the separator directly affects the capacity, safety and number of cycles of the battery. A good separator plays an important role in improving the performance of the battery. In addition, a separator should have a favourable pore structure, good mechanical strength and not overheat. Separators used in li-ion battery systems used in industry are polypropylene, polyethylene containing materials (An 2019).

Electrolyte: an important role in providing the charge transfer between anode and cathode in the battery. It consists of high purity lithium salts and organic solvents. The most widely used lithium salts used for these batteries: Lithium Carbonate, Lithium hexafluorophosphate, Lithium tetrafluoroborate, Highly concentrated $LiN(SO_2CF_3)_2$/dinitrile. The most common organic solvents used in salable batteries are: methyl ethyl carbonate, dimethyl carbonate, propylene carbonate. In addition, the electrolyte used determines the specific capacity, operating temperature and cycle efficiency of the battery (An 2019). In the light of this information, the parts of li-ion batteries are given in Table 1. As can be seen in Table 1, the internal structure of li-ion batteries consists of the 4 parts mentioned above.

Table 1. Characteristic texture of Li-ion batteries (Dobó, Dinh, and Kulcsár 2023).

Cell conponents	Chemical Composition	% wt.	Additional information
External casing	Fe-Ni alloy	20-25	Steel case typical of cylindrical cells
	Al	10	Aluminum case found in prismatic cells
Cathode		25-30	-
Aluminum	Al (Current collector foil)	5-8	-
Binder	Usually PVDF	1-2	Alternatives: PTFE, butadiene-styrene rubber(SBR) or modified cellulose (e.g. CMC)
Metal oxide	Li	1,5-7	LCO gives better performances but is highly expensive. It is replaced by NMC, LMO (where Mn gives structural stability) or C-coated LFP (LiFePO4) that is safer.
	Co LCO ($LiCoO_2$)	5-20	
	Ni LNO (LiNiO2) NCA ($LiNi_{0,8}Co_{0,15}Al_{0,05}O_2$)	5-10	
	Mn LMO ($LiMnO_2$) NMC ($LiNi_xCo_yMn_zO_2$)	5	
Polymeric separator	Microporous PP or PE	4-10	-
Electrolyte		10-15	Ethylene carbonate (EC) is the most used organic solvents, combined with other to lower its high melting T.
Li salts	$LiPF_6$, Li_2CO_3, $LiClO_4$	-	
Organic solvents	DMC-EC, PC-DME	-	
Anode		15-25	-
Copper	Cu (Current collector foil)	8-10	
Binder	Usually PVDF	1-2	Inert, thermo-resistant and current-resistant binder helping the adhesion.
Graphite		15-17	Low stroge capacity of graphite (373 mAh/g)

Li-ion batteries used in industry can have different cell structures: pouch, prismatic, button. A visual of these cell types is given in Figure 2. As can be seen in the figure and as mentioned above, the li-ion anode is generally composed of graphite, which retains lithium in its layers. Graphite is attached to the copper plate with PVDF binder chemical. This similar structure is also present in the cathode. Carbon-containing component and Li transition metal oxides (such as Lithium Cobalt Oxide-$LiCoO_2$, Lithium Iron Phosphate-$LiFePO_4$, Nickel Manganese Cobalt oxide $LiNi_xCo_yMn_zO_2$-NMC) are coated on Aluminium foil with the help of PVDF (Dobó, Dinh, and Kulcsár 2023).

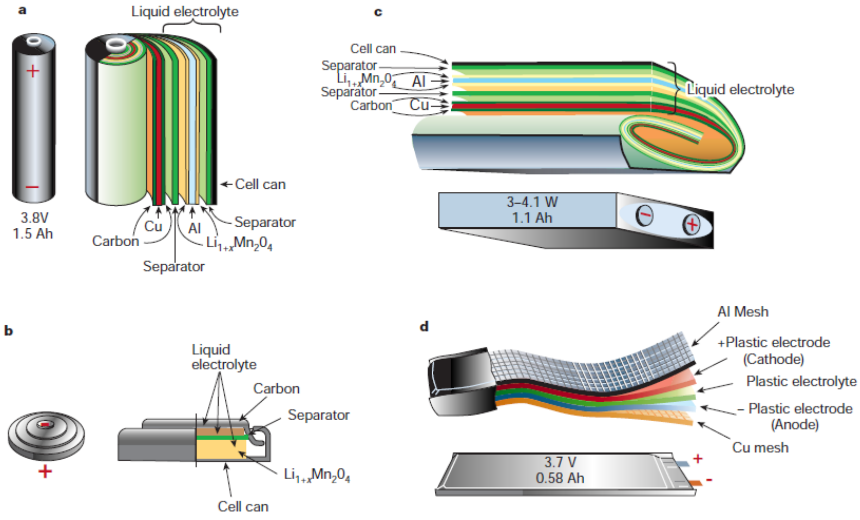
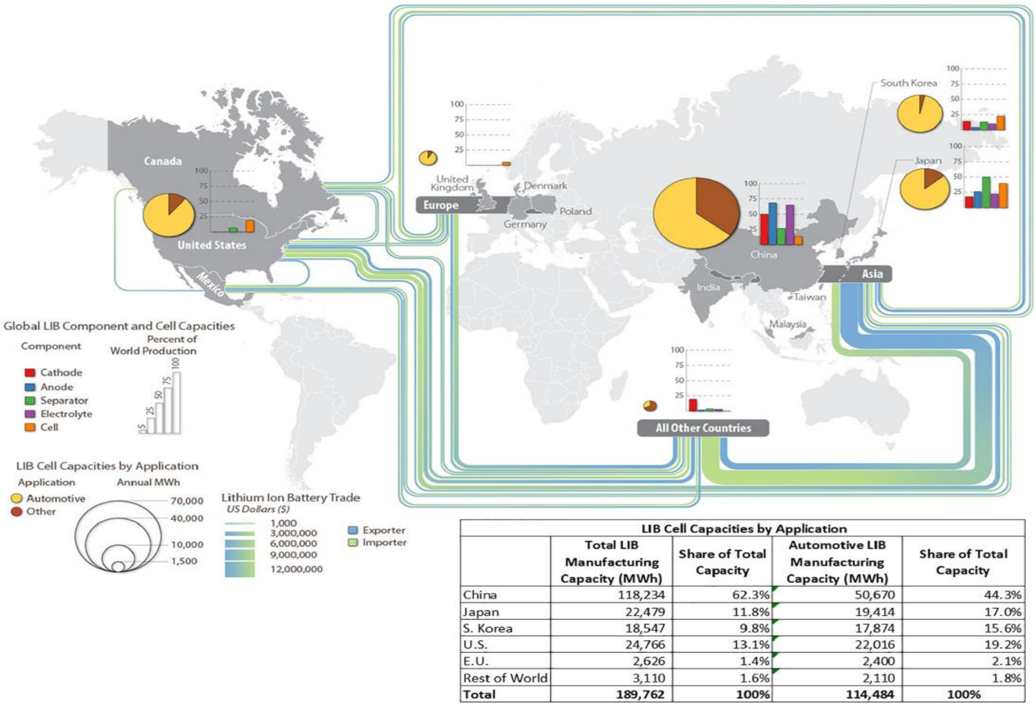


Figure 2. Shape and composition of Li-ion batteries a) Cylindrical, b) coin, c) prismatic, d) thin and flat. (Tarascon and Armand 2001).

Another basic element that diversifies Li-ion batteries is the Li-ion salt used. In fact, this lithium salt has had a direct effect on the naming of the li-ion battery. The lithium-iron phosphate, NMC, the most widely used lithium cobalt oxide, lithium nickel aluminum oxide, which is still under development, and LFP, which is popular after NMC, are mentioned above. Based on Avicenne Energy's 2015 data, NMC batteries account for 29% of the global li-ion market, which is much higher today, lithium cobalt oxide batteries account for 29% and lithium iron phosphate batteries account for 23%. The most widely used battery type in China is lithium iron phosphate batteries. Considering that the Chinese market has an important place in the world, this represents two thirds of the li-ion market (Larouche et al. 2020). In general, the cathode material in li-ion batteries has undergone various changes from the past to the present. For example, Lithium cobalt oxide batteries, one of the first li-ion batteries used, are among the most widely used li-ion batteries due to their stable and balanced discharge capacity, ease of production and cost (Windisch-Kern et al. 2022). However, due to the high cost of lithium and cobalt, it was considered to reduce the amount of cobalt in the li-ion battery. With this idea, a battery type such as NMC has been developed. For example, the NMC battery type is named according to the molar ratios of Nickel, Cobalt and Manganese. Such as NMC622-Ni: Co: Mn;6:2:2 or NMC811- Ni:Co:Mn;8:1:1. Another alternative popular battery type today is LFP batteries. LFP batteries offer high stability and lifetime. They have slightly lower energy density than Nickel Cobalt manganese and Lithium Cobalt oxide batteries. For this reason, they are used in small electronic and household appliances, laptops, scoters and bicycles. In high energy demanding vehicles and energy storage systems, li-ion batteries such as NMC are used. On the other hand, lithium manganese oxide batteries are less costly than other batteries because they do not contain Co. In addition, these batteries have good charging properties and potential. Therefore, they are used in small electrical and electronic devices.

Today, Nickel Cobalt Manganese and Nickel Cobalt Aluminium li-ion batteries are more widely used due to the high capacity and energy density provided by nickel. Vehicle giants such as BMW, Renault, Tesla, Volkswagen, etc. mostly prefer this type of battery (Windisch-Kern et al. 2022).

The countries in the Li-ion battery market and their production capacities are given in Figure 3.



LIB Cell Capacities by Application

	Total LIB Manufacturing Capacity (MWh)	Share of Total Capacity	Automotive LIB Manufacturing Capacity (MWh)	Share of Total Capacity
China	118,234	62.3%	50,670	44.3%
Japan	22,479	11.8%	19,414	17.0%
S. Korea	18,547	9.8%	17,874	15.6%
U.S.	24,766	13.1%	22,016	19.2%
E.U.	2,626	1.4%	2,400	2.1%
Rest of World	3,110	1.6%	2,110	1.8%
Total	**189,762**	**100%**	**114,484**	**100%**

Figure 3. Li-ion battery manufacturing capacities and trading in the World in 2016 (Mayyas, Steward, and Mann 2019).

As shown in Figure 3, Li-ion battery production is higher in China, Japan, the United States and South Korea. Countries in Asia, such as China and South Korea, started to use Li-ion batteries in almost all application areas in 2016 and increased their capacity by 84%. The USA ranks 2nd in the world in li-ion battery production with a production capacity share of 13%. With the recent li-ion battery investments in Tesla and Nevada, it has risen from 4th to 2nd place. Europe, on the other hand, has remained at 2.1% production capacity compared to other producers in the world. In this case, it may allow car manufacturers in Europe to develop a regional supply chain. Vehicle manufacturers using these batteries in Europe have started to market their vehicles worldwide. Li-ion battery production facilities in Europe are planned in countries such as Poland, Germany and Sweden. In fact, there are already companies producing batteries today, such as Northvolt (Mayyas et al., 2019).

Some countries are increasing their Li-ion battery production capacities and are also becoming suppliers. For example, China, South Korea and Japan are in the position of suppliers in the world by producing some li-ion battery parts. These parts are electrolyte, electrode and separator, which are considered as the basic parts of li-ion batteries. In the USA, Tesla and Panasonic companies are developing their supply network. Li-ion battery manufacturers in Asia serve the domestic market and exports (Windisch-Kern et al. 2022). Li-ion batteries have a lifetime of 10 years in large electronic devices and 3 years in small electronic devices. About 85% of Li-ion batteries are used in small devices such as phones and laptops, and about 20% are used in vehicles and energy storage systems. Li-ion batteries that have completed their use contain hazardous substances that may affect human health due to the heavy metals they contain. On the other hand, the amount of precious metals (such as nickel lithium, cobalt, etc.) in li-ion batteries is higher than can be found in a naturally occurring ore. These amounts vary from manufacturer to manufacturer and battery type. However, most batteries contain approximately 8% plastic, 15-20% organic, 6% Nickel, 5% Lithium, 5-20% cobalt. Considering these amounts, environment and living health, recycling of li-ion batteries gains importance. In addition, this issue is even more important in order to use limited raw material resources more sparingly. In addition, it offers a different raw material option by obtaining precious metals such as lithium, nickel, cobalt, manganese at concentrations that cannot be obtained from natural resources (Dobó, Dinh, and Kulcsár 2023).

Waste li-ion battery sources and lifetimes are shown in Figure 4. Li-ion batteries have a shorter lifetime than other battery types. As mentioned above, they have a lifetime of 10 years for large electronic devices and 3 years for small electronic devices. Nickel-cadmium batteries and lead acid batteries have a lifetime of 16-19 years and 6-11 years respectively. In 2012, the amount of waste li-ion batteries was 10700 tonnes and in 2020 this value will reach 250000 tonnes. In 2025, it is thought to be 464000 tonnes. Waste battery collection in Europe, America and Australia is approximately 4% on a per producer basis. The reason why this rate is so low is the lack of awareness of the battery consumers, the lack of collection habits and the resale of used electronics (Kaya 2022).

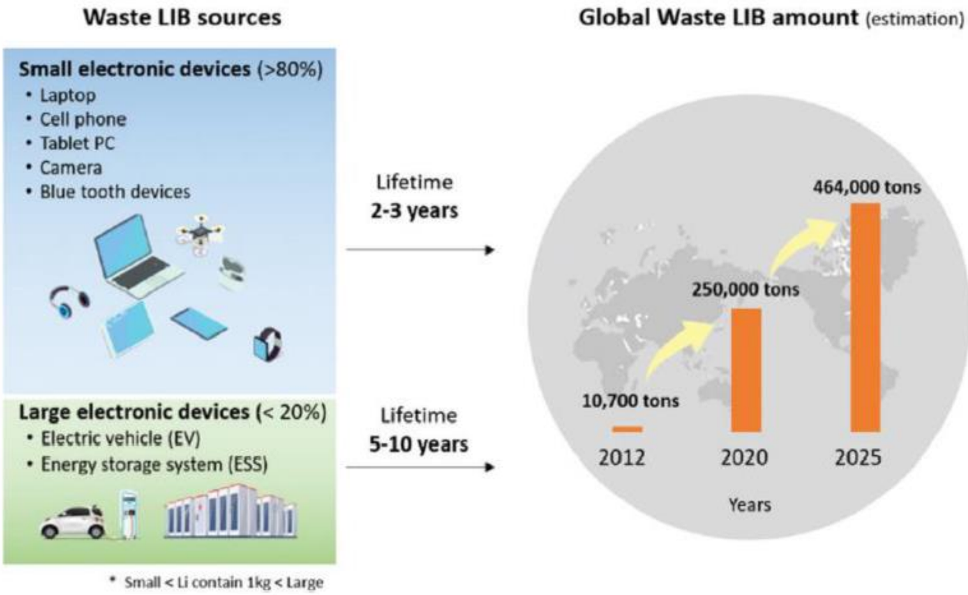


Figure 4. End of life Li-ion battery supply in worldwide (Kaya 2022).

As the use of Li-ion batteries becomes more widespread in electric vehicles and electronics, the demand is expected to increase gradually. Thus, the need for li-ion battery recycling will also increase with the idea of being sustainable. Today, li-ion batteries are considered as hazardous waste. In fact, the export of these wastes is limited according to the Basel Convention due to the risk of fire during storage and transport. For these reasons, collection, landfilling and export of li-ion batteries are not widespread. After use, although the materials in li-ion batteries are waste, they have economic value. In addition, these precious metals have limited resources in the world. Li-ion battery recycling by hydrometallurgical methods can recover the metals in it at an acceptable recycling percentage. In addition, this method also supports the reduction of carbon footprint by minimising greenhouse gas emissions. With the recent increase in the amount of consumption, recycling is no longer optional for countries. Because this situation has become a necessity due to environmental and economic factors (Kaya 2022).

There are three different basic methods for recycling waste or used li-ion batteries. These are; direct, pyrometallurgy and hydrometallurgy. Direct recycling aims to recover the active components or precious metals in li-ion batteries directly by using mechanical methods. Pyrometallurgy is a recycling method that includes the processing of waste li-ion batteries at high temperatures and subsequent separation steps. Hydrometallurgy, on the other hand, includes process steps such as dissolving the valuable components in waste or spent li-ion batteries in aqueous solution, purifying and concentrating the target metal compounds in solution. Hydrometallurgical and pyrometallurgical methods are the most widely used methods in the industry. Although direct recycling methods are not used as a basic process, they can be included in pre-purification processes in pyrometallurgy or hydrometallurgy. In addition, direct recycling methods have been limited to small scale studies (Dobó, Dinh, and Kulcsár 2023). In the light of the above information, the contents of recycling methods are given in Figure 5.

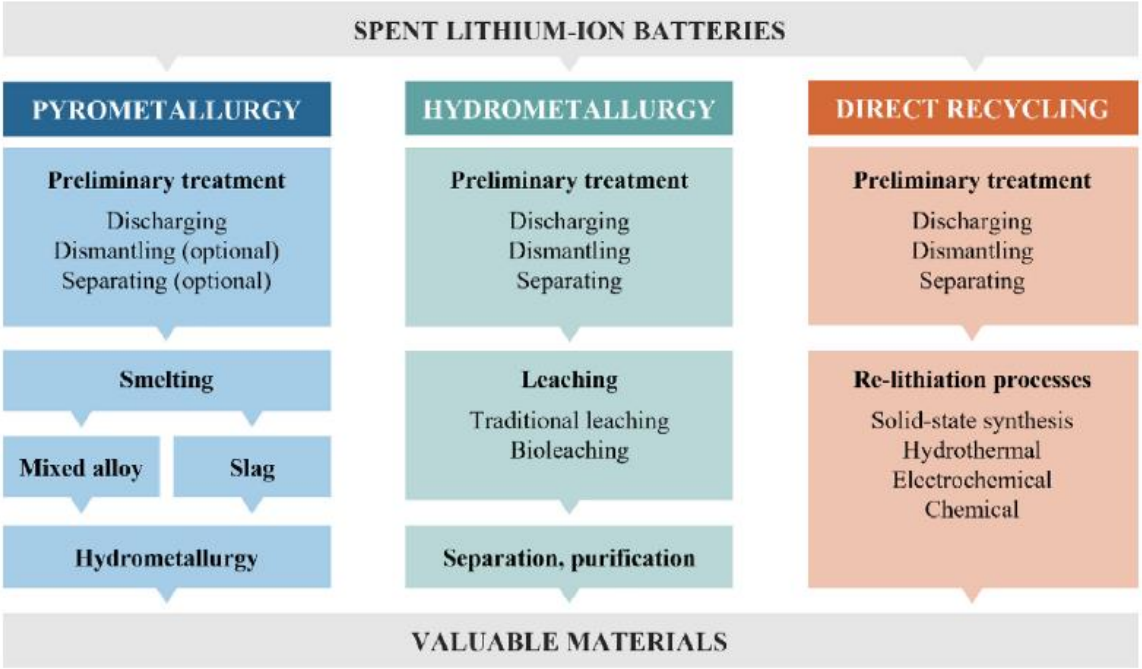
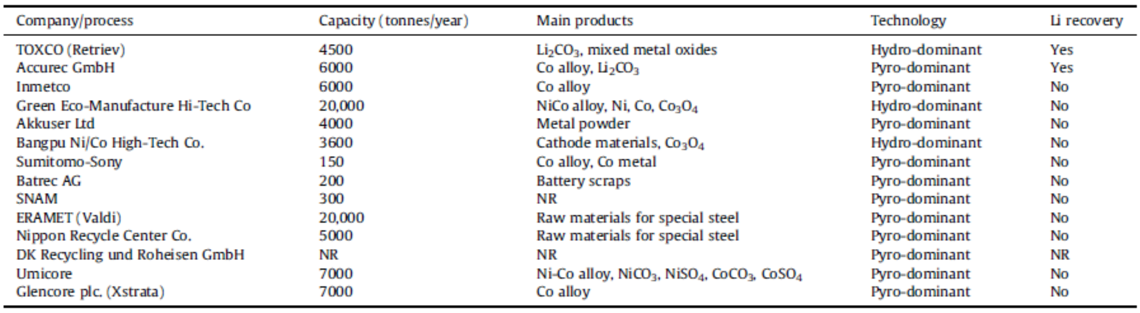


Figure 5. Stage of Li-ion batteries recycling methods in several processes (Dobó, Dinh, and Kulcsár 2023).

Tablo 2. Waste Li-ion battery recycling industrial processes (Liu et al. 2019).



Company/process	Capacity (tonnes/year)	Main products	Technology	Li recovery
TOXCO (Retriev)	4500	Li_2CO_3, mixed metal oxides	Hydro-dominant	Yes
Accurec GmbH	6000	Co alloy, Li_2CO_3	Pyro-dominant	Yes
Inmetco	6000	Co alloy	Pyro-dominant	No
Green Eco-Manufacture Hi-Tech Co	20,000	NiCo alloy, Ni, Co, Co_3O_4	Hydro-dominant	No
Akkuser Ltd	4000	Metal powder	Pyro-dominant	No
Bangpu Ni/Co High-Tech Co.	3600	Cathode materials, Co_3O_4	Hydro-dominant	No
Sumitomo-Sony	150	Co alloy, Co metal	Pyro-dominant	No
Batrec AG	200	Battery scraps	Pyro-dominant	No
SNAM	300	NR	Pyro-dominant	No
ERAMET (Valdi)	20,000	Raw materials for special steel	Pyro-dominant	No
Nippon Recycle Center Co.	5000	Raw materials for special steel	Pyro-dominant	No
DK Recycling und Roheisen GmbH	NR	NR	Pyro-dominant	NR
Umicore	7000	Ni-Co alloy, $NiCO_3$, $NiSO_4$, $CoCO_3$, $CoSO_4$	Pyro-dominant	No
Glencore plc. (Xstrata)	7000	Co alloy	Pyro-dominant	No

Table 2 summarizes the current industrial recycling process with emphasis on lithium recycling. Companies in the industry have generally aimed at the recovery of Nickel and Cobalt. The Toxco and Accurec companies also aim to recover Lithium. Umicore carries out li-ion battery recovery using pyrometallurgical methods. Toxco recycles waste li-ion batteries mainly using hydrometallurgical methods. This method involves first immersing the waste li-ion batteries in liquid nitrogen and then removing the batteries into a high pH aqueous solution controlled by lithium hydroxide (Liu et al., 2019).

CHAPTER 2

LITERATURE SURVEY

2.1. Methods of Li-ion Battery Recycle

2.1.1. Direct Recycling

The direct recycling method is a recycling method based on physical separation processes that do not disrupt the battery's morphological and chemical structure. In this method, it starts with crushing, which is called mechanical process. At this stage, materials are separated according to their physical properties such as particle size, magnetisation, shape and density. Direct recycling method steps are used in mechanical processes for pre-concentration in advanced hydrometallurgical methods (Brückner, Frank, and Elwert 2020). Some of these processes are heavy liquid separation and froth flotation. In this method, it is necessary to determine the most effective separation methods suitable for the battery structure (Gaines 2018).

Separation of the active material from aluminum foil or copper by physical methods, removal of PDVF, Li addition to the active material and finally heat treatment can be selected as the most suitable for battery recycling (Larouche et al. 2020; Y. Sun 2023).

Furthermore, in order to separate valuable components, magnetic separation can be used to first separate the components from each other or to reduce the particle size. Then, according to the magnetic properties of the material, separation processes can be carried out using magnetic separation; physical separation and other techniques. Even if these concentrated metal materials obtained are not in the desired battery structure, they can be further purified using metallurgical methods. Compared to other recycling methods, direct recycling method is a more environmentally friendly method. It can also be better in terms of cost with less energy and chemical usage (Y. Sun 2023).

Direct recycling method is based on physical and magnetic separation methods without disturbing the anode and cathode material and particle structure. Foam flotation is one of them. Some battery wastes are industrially available as mixed piles. Anode and cathode can be found together in this pile. For this reason, firstly, separation of anode and cathode from each other should be done in direct recycling. The reason for this is that by separating the cathode active material (CAM) from each other, direct recovery of high purity cathode products will be provided. Direct recycling of NMC from battery types is carried out in the following order: battery disassembly; particle size reduction; screening; separation of battery components such as anode and cathode from each other; $LiCO_3$ is added to the NiCoMn-containing active part obtained from direct recycling. Finally, cathode active material is produced by calcination. In this method, lithium is re-dosed into the battery structure by heat treatment (Kaya 2022).

Farasis Energy has developed a leaching process using alkaline solution to remove copper and aluminum impurities after separating the fragmented cathode from other parts. The solution used in this process consists of (5 M NH_4OH) and 1 M LiOH, which causes complexation with O_2 gas content to favour the oxidation of Al and Cu metals. After 12 hours, these impurity-causing components become completely soluble (Larouche et al. 2020).

Many studies have been conducted using this recycling method. Some of these studies are as follows: Steve and Lauren used a liquid Carbon Dioxide extraction system to first separate the electrolyte portion of waste Li-ion batteries. After separation of the electrolyte, the remaining parts of the battery were passed through a crusher to reduce the particle size. The battery waste parts with reduced particle size were passed through an aqueous washing solution and separated by the effect of the current collector with the effect of the mixer and plastic; copper, aluminum current collectors were separated with the help of filtration. Then, binder is separated with the help of hydrothermal (pressurized aqueous system) accompanied by lithium solution (Lithium Carbonate); graphite part is separated by foam flotation method. Finally, the impurity-removed In another study, all PVDF, Aluminum and most conductive carbon residues were completely eliminated by hydrothermal relithiation and washing methods. Then, in the annealing steps, the characterization of the cathode active part was improved and the trace carbon remaining after hydrothermal treatment was completely removed. As a result of this study, 95-98% capacity retention was achieved in the recycled Li-ion battery with this method. In addition, the battery recovered by this method showed a capacity of 155 mAh/g. The average capacity of the batteries produced in the market is in the range of 154-203 mAh/g (Gupta et al. 2023).

In the work of Steve Sloop and his research group; In waste Li-ion battery recycling, the capacity was first reduced. Then, the discharge process was carried out to start the recycling stages. Then, with the help of flotation method, plastic, aluminum and copper collectors were separated from the waste battery in an alkaline environment. The impure Nickel-rich electrode was hydrothermally treated with Lithium ionic aqueous solution in a pressurized vessel with the addition of oxidizing agents such as O_2 and H_2O_2. The H_2O_2 used during this process formed a coating on the battery surface and the battery capacity was positively improved with additives such as Lithium chlorite. The solid material is then gradually dried and the recycling process is completed. As a result of this study, a maximum capacity of 175 mAh/g is obtained from the recycled battery (Sloop et al. 2018).

In another direct recycle study, firstly discharge process was performed for waste batteries. Then, electrolyte, anode and cathode separation was done by disassembling in an argon-filled glove box. Aluminum was separated from the current collector using deionized water from the degraded cathode. After drying at 50 °C for 2 hours, the cathode material was ground into fine powder. Hydrothermal re-lithiation was performed with the ground battery waste at different temperatures (180, 200, 220 °C) and times (1,2,3 hours). The optimum condition for this stage was determined as 220 °C temperature, 2 hours. 4 M LiOH was used in the lithiation process. Afterwards, sintering (800 C, 4 hours, in air) was performed to remove the deformation in the waste battery after use. After all these processes, a performance test was performed on the recycled battery. The recycled battery was found to have a discharge capacity of 150.7 mAh/g. Also, this battery has a capacity retention of 91.2% (Chan, Malik, and Azimi 2023).

2.1.2. Pyrometallurgical Recycling

Pyrometallurgy is based on the high-temperature recovery of metals and other ingredients in batteries. The battery, including components such as plastics and electrodes, are decomposed in a high-temperature, oxygen-rich furnace at temperatures above 1200C. As a result of this decomposition, metal oxide is obtained. These metal oxides need to undergo many processes before they can be used during li-ion battery production (Kader, Marshall, and Kennedy, n.d.). No pre-treatment is required in the recycling of Li-ion batteries by this method (Kaya 2022).

The pyrometallurgical method starts by volatilising the organic component. The anode and cathode react to solubilise the lithium. During the pyrometallurgical process, precious metals are reduced and alloyed (Y. Sun 2023). To summarise the process steps in the pyrometallurgical method;

Roasting; In an oxidising environment, it removes the unwanted carbon and sulphur from the sulphurous or carbonate structure and converts it into an oxidised structure. In this method, the separation of the components in the cathode by a chemical reaction is carried out by roasting. For example, sulphation roasting is carried out to decompose the Lithium Cobalt Oxide compound, which is a li-ion battery.

Calcination; It is based on the logic of thermal processing of solid materials in the absence of O2 or air or with very low amounts of these sources. This step is a common process step used in the metallurgical processing of the material, which is then reduced to the desired form.

Reduction; Lithium metal oxide batteries are finally left to the end after the metal part is separated during pre-purification processes. It is possible to decompose using high temperature to produce lithium metal oxides. However, during this process, excess energy is used due to the use of high temperature. In addition, it is difficult to separate Li-metal oxides in the subsequent extraction stage. Therefore, the precious metals recycled in this method may remain as alloys.

In this method, the process step to recycle used or defective Li-ion batteries is usually short. In the pyrometallurgical method, there is generally no safety risk due to electrolyte leakage. In addition, the most important disadvantage of pyrometallurgy is that Lithium cannot be recovered by separation. Generally, it is mixed into the slag and is included with worthless metals. Even if lithium is separated from the slag by this method, energy consumption is quite high. In addition, the high temperature causes the formation of gases containing CO_2, CO, SO_2, organic compounds and dust, resulting in emissions from these components. In this case, this method requires a good gas cleaning system. For these reasons, the pyrometallurgical process requires energy due to the high temperature and a large amount of capital due to the presence of a good gas cleaning system (Liu et al. 2019).

Many studies have been carried out using this method. In the study of Chang Di and his research group, firstly, waste Li-ion batteries were discharged for safety reasons during recycling. After this process, they manually separated the anode, cathode and separator. Thermal treatment method was used to separate auxiliary chemicals such as PVDF from the waste battery. Aluminum and copper were separated from the waste by physical separation methods. After this process, they used the Sulphate Roasting technique to make the cathode part, which is called the active part of the battery, soluble in the chemical. Water leaching was used to recover the soluble lithium compound ions from the waste battery. Na_2SO_4 salt added in certain proportions during the roasting process was used. In these studies, it was aimed to find the optimum parameters of the Sulphate Roasting process. The parameters studied are as follows: Na_2SO_4 dosage amount, roasting temperature and duration. At the end of all studies, Lithium recovery process with 85.43% efficiency was realised by roasting the waste Li-ion battery with 100% Na_2SO_4 dosage at 750 °C for 90 minutes (X. Chen et al., n.d.; Fan et al. 2019).

In another study, precious metals in Li-ion batteries were recovered using salt roasting method. In this study, firstly, waste batteries were discharged and made ready for recycling. Then, plastic, anode, cathode and separator parts were separated manually. Leaching was performed using NaOH to separate the aluminum in the cathode. Then, roasting process was carried out by mixing the aluminium-separated cathode in the ball mill at the determined amounts of NH_4Cl. Roasting temperature and roasting time were also among the parameters studied. Another key parameter is the cathode material amount / NH4Cl amount ratio. After the roasting process, Cobalt and Lithium, which passed into the soluble chloride structure, were taken to the liquid phase by water leaching. Then, the recycling of battery chemicals was completed by precipitating Cobalt using oxalic acid and then Lithium using Na_2CO_3. Among the parameters studied, 350 °C roasting temperature; 1/2 cathode material amount / NH_4Cl amount ratio; 20 minutes roasting time due to the decrease in Cobalt yield after 20 minutes; were determined as optimum conditions. At the end of all these studies; Cobalt with 98.5% efficiency and Lithium with 87% efficiency were recovered (Fan et al. 2019).

Li et.al. (2016) carried out Li-ion battery recycling studies using oxygen-free roasting and wet magnetic methods. Cobalt $^{+2}$ ion compounds are more stable than Cobalt $^{+3}$ ion compounds. Based on this information, they started battery recycling with oxygen-free roasting method. By using this roasting method, they increased the precious metal +2 ion valences in the battery to +3. During this process, vacuum was used to provide an oxygen-free environment. In addition, different temperatures between 850-1400 °C were studied for 30 minutes. The optimum temperature determined in this section is 850C. Li_2CO_3, C formations were not observed at temperatures above 1000 °C. After the roasting process, the material is taken to the wet magnetic separation stage. Here, in the roasting stage, Lithium, Cobalt, whose form changes, are separated. Cobalt clings to the magnet thanks to its ferromagnetic properties. Since lithium turned into Li_2CO_3 at the end of the roasting process, it passed into the liquid phase in its aqueous solution with a solid/liquid ratio of 1/200. Meanwhile, carbon settles to the bottom. Wet magnetic separation studies were carried out for 4 hours at 20C solution temperature. At the end of the studies, 95.72% of Cobalt, 91.05% of graphite and 98.93% of Lithium were recovered (Li, Wang, and Xu 2016).

Ren et al. (2016) conducted Li-ion battery recycling studies using the melting method. In this method, they used $FeO-SiO_2-Al_2O_3$ slag system. They mixed the copper slag, battery waste and alumina in certain ratios and aimed to recover them by melting method. They used 4/1-10/1 slag/battery waste mixture ratios. They also were completed the $FeO-SiO_2-Al_2O_3$ slag system with alumina additives between 17-21%. It was seen in these studies that Cu recovery efficiency decreases as the slag amount is more than the optimum condition. At the end of the studies, 4/1 slag/battery waste mixture ratio, 30 minutes at 1450 °C was determined as the optimum condition of the melting process. The recycling efficiencies were obtained under these optimum conditions are 98.33% for Cobalt, 98.39% for Nickel and 93.57% for Copper. Nickel was obtained with this recycling is an alloy metal containing Cobalt and Copper (REN et al. 2017).

2.1.3. Hydrometallurgical Recycling

Hydrometallurgical methods are important for the recycling of manufacturing scrap or spent li-ion batteries. Because, the elemental compounds in the battery content are recycled separately in concentrated form. In addition, this method is widely and frequently used in battery recycling. Recently, even after the above-mentioned methods, more efficient and concentrated recovery of the components is provided by hydrometallurgical methods. Compared to the pyrometallurgical method, the hydrometallurgical method is a more profitable process with low capital cost and gas emission, high recycling efficiency and good metal selectivity. It is also a widely used process in industrial plants (An 2019).

In hydrometallurgical processing, precious metals are dissolved and transferred to liquid utilizing a chemical. Afterward, they are separated from each other by various methods. In the recycling of Li-ion batteries by hydrometallurgical methods, it allows the recovery of target metals such as Ni, Co, Li as well as many metals such as Aluminium and Copper. The known hydrometallurgical method steps are leaching, precipitation and solvent extraction (Y. Sun 2023).

With hydrometallurgical processes, it is possible to separately extract the precious metals in li-ion batteries with high purity and efficiency. Battery metals such as Mn, Co, Li, Ni, etc. can be recovered separately and these metals can be converted into cathode active materials (CAM) or cathodic materials that can be used in other battery types. The hydrometallurgical method usually consists of two stages. In the first stage, solid li-ion battery wastes are leached and the precious metals are transferred to the liquid phase. This liquid obtained is called leach filtrate or leachate. In addition, the chemicals used in the leaching stage are alkaline or acidic solutions. Inorganic or organic acids can be used at this stage. In the second stage, the precious metals in the leach filtrate are recovered by separating them with different neutralization methods. These neutralization methods are mainly precipitation and solvent extraction methods, ion exchange and electrolysis methods are also used (Dobó, Dinh, and Kulcsár 2023).

Leaching of Li-ion batteries is the process of dissolving the target metals and other components in the battery with the use of chemicals. This stage is an important and critical stage not only in hydrometallurgy but also in all metallurgical methods (Liu et al. 2019). The reason is; it is seen as a pre-treatment before the subsequent purification and separation processes. Thus, the leaching efficiency also affects the final total recycling efficiency of the metal (An 2019). The leaching process aims to separate the target precious metals and ensure that they are in different forms.

The leaching stage mainly consists of 5 steps:

(1) In the first step, the leaching solubilising agent, such as acid, diffuses in solution to the liquid interface.

(2) Then, the diffused leaching solubilising agent starts to interact with the active components in the waste li-ion battery and diffusion takes place.

(3) Leaching reactions take place on the active substance (such as metal) particles and proceed along the interface.

(4) The dissolved metal ions are separated from the solid.

(5) The dissolved metal ions are dispersed at the solution interface to form ionic elemental compounds (Y. Wang et al. 2020).

In the leaching stage, mainly inorganic and alkaline solutions, but also organic acids are used as solvents (Liu et al. 2019). Figure 6 shows the organic and inorganic acids used as solubilising agents in the leaching stage (Duan et al. 2021). In leaching, inorganic acid is widely used in industry and studies (Dobó, Dinh, and Kulcsár 2023). Moreover, inorganic acid used in the leaching stage provides high efficiency for the recycling of li-ion batteries. Commonly used inorganic acids are hydrochloric acid (HCl), sulphuric acid (H_2SO_4), nitric acid (HNO_3) and phosphoric acid (H_3PO_4). During the leaching process, especially for lithium NiMnCo and lithium iron phosphate batteries, extra reagent or oxidant addition may be required. This helps to reduce metals such as manganese, cobalt and iron during leaching and these chemicals are also referred to as reducing agents. The most commonly used leaching agent is Hydrogen Peroxide (H_2O_2) (Y. Wang et al. 2020).

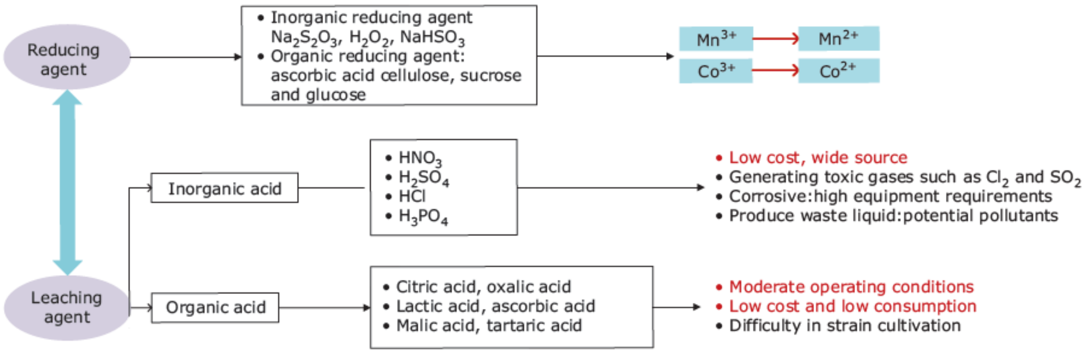


Figure 6. Methods for separating precious metals from CAM (cathode active material) in LİBs (Li-ion battery) waste (Duan et al. 2021).

Leaching temperature and acid concentration are important for leaching efficiency. In order to have high leaching efficiency and separation effect, temperature and acid concentrations should be carefully optimised (An 2019).

Lee et al. (2002) carried out nitric acid leaching studies to recover valuable element compounds such as lithium and cobalt in $LiCoO_2$ containing battery waste. They used Hydrogen Peroxide (H_2O_2) as a reducing agent in the leaching study. They carried out optimisation studies by working at different HNO_3 concentration (0,1-1M), leaching temperatures (25-75 °C), H_2O_2 dosage (0-3,25% vol.) and S/L (solid/liquid ratio) values. Leaching efficiency, It increased in direct proportion with the increase in temperature and HNO_3 amounts. It was observed to decrease with the increase of S/L ratio. In the leaching study using 1 M HNO_3 without H_2O_2 addition, 40% Co, 75% leaching efficiency was obtained. Leaching yields increased with the addition of H_2O_2. The optimum determined leaching conditions are as follows: 1 M HNO_3, 75 °C leaching temperature, 10 g/L (S/L ratio), 1.7% vol. H_2O_2 addition and 30 minutes leaching time. In the leaching study carried out under optimum leaching conditions, dissolution efficiencies above 90% were obtained for Cobalt and Lithium (Lee & Rhee, 2003).

In another study, a leaching study was carried out using hydrochloric acid. In this study, they aimed to recover valuable battery components such as Nickel, Cobalt, Manganese and Lithium in mixed battery wastes of $LiCoO_2$, $LiMnO_4$ and $LiNiCoMnO_2$ types. They studied parameters such as acid concentration, leaching temperature and time, solid/liquid ratio (S/L). Wang et al. observed that the leaching efficiency of all elemental compounds increased with increasing acid concentration and temperature. They also observed that the efficiencies stabilised after a certain acid concentration (4 M HCl) and time (1 hour). When the values above 0.02 S/L ratio were increased, it was observed that the leaching efficiencies decreased. At the end of the studies; 4 M HCl, 80 °C leaching temperature, 0.02 S/L ratio and 1 hour leaching time were determined as optimum conditions. Nickel, Cobalt, Manganese and Lithium leaching efficiencies obtained in the leaching study carried out under these conditions are as it is respectively as follows: %99,8, %99,5, %99,8, %99,9 (R. C. Wang, Lin, and Wu 2009).

Pinna et.al. conducted studies on the recovery of Lithium and Cobalt elemental compounds in $LiCoO_2$-containing used battery waste. Phosphoric acid (H_3PO_4) was used in leaching studies, different from HCl and H_2SO_4. The effects of different H_3PO_4 concentrations, H_2O_2 dosage amounts, temperature values on leaching efficiency were investigated. It was observed that Cobalt and Lithium leaching yields increased with increasing temperature. The same situation was observed for the course of H_3PO_4 concentration. An exponential increase in leaching yields up to 75°C and a small increase in leaching yield between 75-90°C were observed. In the leaching study carried out without the addition of H_2O_2, 28% Co leaching yield was observed, while this value increased to 90% when 2% vol H_2O_2 was added under the same leaching conditions. The optimum leaching conditions determined were; 2% vol. H_2O_2 dosage, H_3PO_4, 2% vol. concentration, 75°C leaching temperature. Leaching efficiencies under these conditions were found to be around 95% (Pinna et al. 2017).

As in the studies mentioned above, different acid types are used in the leaching stage of Li-ion battery recycling. However, due to the high cost of organic and some inorganic acids, the use of sulphuric acid is more common in the sector. For this reason, there are many academic studies examining the use of sulfuric acid in the leaching stage of Li-ion batteries.

Meshram et al. (2015) conducted a leaching study using sulphuric acid during the recovery of valuable element compounds such as 10% Nickel, 35% Cobalt, 11% Manganese and 6.5% Lithium in Li-ion battery (Li-NiCoMn battery). As examined in previous studies, they were examined the effects of parameters such as temperature, H_2SO_4 concentration, leaching pulp density (5-100 g/L) on leaching efficiency. It was observed that the leaching efficiency increased as the H_2SO_4 concentration increased at 0.5-3 M. However, the increase in leaching efficiency up to 1 M H_2SO_4 concentration is exponential. The leaching yield increase between 1-3 M H_2SO_4 concentrations was observed to be very small. Therefore, 1 M H_2SO_4 concentration was determined as the optimum value. It was stated that when a certain leaching pulp density was exceeded, leaching yields started to decrease. It was also observed that the leaching efficiencies increased as the temperatures increased from low to high temperatures. At the end of the studies, 1 M H_2SO_4 concentration, 95 °C leaching temperature, 50 g/L leaching pulp density parameters were determined as optimum conditions. Leaching yields of 93.4% for Li, 66.2% for Co, 96.3% for Ni and 50.2% for Mn were obtained (Meshram, Pandey, and Mankhand 2015).

In another study, sulfuric acid and sulfuric acid co-reducing agent H_2O_2 were used. LiNiMnCo battery waste containing 19% Ni, 20% Co, 7% Li, 19% Mn was used in the study. In this study, in order to observe the effect of H_2O_2 on leaching yields, firstly Sattar et al. carried out a leaching study using only H_2SO_4 without adding H_2O_2. As a result, the leaching yields of Nickel and Lithium were above 92%, while the leaching yield of Cobalt remained at 45%. Even with the addition of 0.5 vol. % H_2O_2, the Cobalt yield increased to 85%. H_2SO_4 concentration was studied at values between 0.5-3 M. Leaching yields increased with increasing H_2SO_4 concentration. Although an increase was observed up to 1.5 M H_2SO_4 concentration for manganese, the leaching efficiency stabilised after 1.5 M H_2SO_4 concentration. In the study carried out under leaching conditions determined without reducing agent (3 M H_2SO_4 concentration, 90°C, 3 h), 68% Co, 92% Ni and Li leaching yields were obtained (Sattar et al. 2019; Zhu et al. 2012).

On the other hand, Zhu et.al. carried out leaching studies using sulfuric acid to recover lithium and cobalt from $LiCoO_2$-containing Li-ion battery waste. They used H_2O_2 as reducing agent to improve Co yield. They investigated the effect of parameters such as H_2SO_4 concentration, temperature and amount of H_2O_2 addition on the recovery efficiency. It was observed that the leaching efficiency increased with increasing temperature. An excessive increase in the reaction temperature did not significantly increase the Li and Co leaching yields. A significant increase in leaching efficiency was observed up to 2 M H_2SO_4 concentration, which was determined as the optimum condition. It was observed that the amount of H_2O_2 addition more than 2% vol. addition did not have a significant effect on the leaching yield. More than 2 M H_2SO_4 concentration did not show a significant increase in leaching efficiencies. 2 M H_2SO_4, 2% vol. H_2O_2 reducing agent, 60°C and 2 h leaching conditions, 94.7% Co and 71% Li dissolution yields were obtained (Zhu et al. 2012).

Kim et.al. conducted a leaching study using H_2SO_4 acid in the recovery of spent waste Li-ion batteries. Unlike the other mentioned wastes, this battery waste contains 2.7% aluminum. In order to eliminate this impurity, firstly 65 mesh size sieving was performed. With this sieving, approximately 95% of Aluminium was eliminated. The remaining 2.7% aluminum was removed by leaching using Sodium Hydroxide. In this way, the impurity was removed and the concentrated Nickel, Cobalt were enriched. In order to recover the Nickel, Cobalt and Lithium in this part, leaching was carried out with the help of H_2SO_4. In the leaching study, the leaching efficiency increased with increasing temperature. However, the leaching efficiency stabilised at temperatures above 60°C. Also, the leaching yields increased with increasing H_2SO_4 concentration. However, after a certain H_2SO_4 concentration (2 M H_2SO_4), the leaching efficiency stabilised. H_2O_2 was used as a reducing agent in the leaching studies. The effect of different amounts of H_2O_2 dosage on the leaching yield was observed. Leaching yields increased with increasing H_2O_2 amount up to 5% vol% H_2O_2 addition. It was observed that H_2O_2 additions more than 5% vol% did not affect the leaching yield. At the end of the leaching studies, approximately 98% dissolution efficiency was obtained (S. Kim et al. 2014).

Nayl et.al. carried out leaching studies using H_2SO_4 acid to recover valuable elemental compounds such as Ni, Co, Li in spent Li-ion batteries. Before this leaching study, Al impurity was removed to concentrate the Ni, Co, Li containing solid. The 0.46%

aluminum in the battery was eliminated with 97% efficiency by NH_4OH leaching. Then, H_2SO_4 leaching studies were carried out to recover the remaining Ni, Co and Li in the battery waste solid. Different leaching parameters were tested in the studies. As in previous studies, it was observed that the leaching efficiencies increased when the H_2SO_4 concentration was increased. After a certain concentration (2 M H_2SO_4), the leaching yields stabilised without increasing. In addition, H_2O_2 was used as reducing agent in the leaching studies. Without the presence of H_2O_2, Co and Ni leaching yields were 42.7% and 82.2%, respectively. With the use of 4 vol% H_2O_2, these yields were 99.6% and 99.4% for Co and Nickel, respectively. However, the leaching yields stabilised after 70°C (Nayl et al. 2017).

Another recycling study was carried out by Swain et.al. A leaching study was carried out using H_2SO_4 acid to leach valuable element compounds such as Co and Li in the $LiCoO_2$ spent battery. Leaching parameters such as H_2SO_4 concentration, H_2O_2 addition amount and temperature were investigated. The leaching yields showed an increase up to 75°C and a slight increase was observed after 75°C. With the increase in H_2SO_4 concentration, an increase in leaching yields was observed in direct proportion, but the Co dissolution yield increased by 1% at concentrations higher than 2M H_2SO_4 concentration. While 34% Co leaching efficiency was obtained in the leaching study carried out without H_2O_2, this efficiency increased to 99% with the addition of 25% vol H_2O_2 (Swain et al. 2007).

Nan et.al. aimed to recover valuable element compounds such as Ni and Co from a mixed nickel-metal hydride (NiMH) and $LiCoO_2$ battery sample. For this purpose, they carried out a leaching study using H_2SO_4 acid and H_2O_2 reducing agent. In the presence of 3 M H_2SO_4, 3 wt% H_2O_2 at 70°C, 90% Nickel and Cobalt leaching efficiency was obtained within 5 hours. The leaching efficiency increased to 99% in more than 5 hours (Nan et al. 2006).

In another study, a Li-ion battery containing 26% Co and 0.34% Ni was recycled. In this study, the focus was primarily on the recovery of Cobalt. Studies were carried out at different H_2SO_4 concentrations and H_2O_2 addition amounts. The leaching temperature was 85°C in all studies. In the studies, the H_2SO_4 concentration was increased from 0.5 M to 4M. Cobalt leaching efficiencies at these concentrations were 20% and 92%, respectively. According to these results, the leaching efficiencies increased with increasing H_2SO_4 concentration. In H_2SO_4 leaching without H_2O_2 reducing agent, Cobalt dissolution efficiency is 50%. With the addition of 10% vol H_2O_2, this yield increased to 91% (L. Chen et al. 2011).

Sun et.al. conducted recycling studies with CoO and LiCoO-containing Li-ion battery wastes. In this study, the focus was on the recovery of Lithium and Cobalt from the waste battery mixture. With this in mind, various experiments were carried out at 0.5-4 M H_2SO_4 concentration ranges, 50-90 °C temperatures and 0-20% vol H_2O_2 addition conditions. It was observed that Co and Li leaching yields increased with increasing H_2SO_4 concentration. At 2 M H_2SO_4 concentration, Co dissolution efficiency was approximately 99%, while at values above this concentration, the leaching efficiency remained constant at 99%. In addition, the leaching yields for Cobalt and Lithium also increased with temperature. However, no significant increase in leaching yields was observed at temperatures above 80 °C. Co dissolution efficiency was found to be 76% without the addition of H_2O_2 reducing agent. With the addition of 5% vol H_2O_2, Co dissolution efficiency reached 99% (L. Sun and Qiu 2011).

Li-ion batteries are used in many sectors such as automotive, energy recovery and storage, electronic devices. With this wide range of applications, the demand for Li-ion batteries is also increasing. As a result of this situation, the need for raw materials for Li-ion batteries arises. It is possible that the current raw material opportunities will be limited in a short time. With these considerations, the recycling of Li-ion batteries, which are used in every field, gains importance. With this motivation, studies on the recovery of Li-ion batteries have been carried out.

In this studies, leaching, one of the first chemical steps of Li-ion battery recovery, was carried out. In this leaching study, the effects of leaching parameters such as H_2SO_4 concentration, temperature and H_2O_2 addition amounts on nickel and cobalt leaching yields were investigated as mentioned in the above studies. Meta Nikel Kobalt Madencilik A.Ş., a subsidiary of Zorlu Holding, produces an intermediate product called MHP (Mixed Hydroxide Precipitation), which is used as raw material in various sectors such as batteries and defence industry. MHP is a solid containing Nickel and Cobalt Hydroxides. It is thought that the Nickel and Cobalt recovered in this study will contribute to the product in the plant as well as being used as raw material in battery production. Based on this idea, Nickel and Cobalt recovery has been focused on in leaching studies.

CHAPTER 3

METHODS AND MATERIALS

3.1. Materials

Nickel and Cobalt recovery studies were carried out in the black mass waste battery samples of Li-ion batteries whose content is given in Table 3. In the studies, leaching studies were carried out as one of the first chemical stages of hydrometallurgical method. In leaching studies; parameters such as temperature, H_2SO_4 concentration, H_2O_2 dosage amount and effect were analysed. The amount of H_2SO_4 was determined by stoichiometric calculations and the effects of 50% less than the theoretical required amount of H_2SO_4, 50% less than the theoretical required amount of H_2SO_4, 50% more than the theoretical required amount of H_2SO_4 on leaching yields were examined. In addition, the effect of 60, 80, 100°C temperatures on the leaching yields together with the H_2SO_4 amounts were also analysed. In addition, the effect of H_2O_2 presence and addition order on the leaching efficiency were also investigated. The theoretical required amount of H_2O_2 and H_2SO_4, determined by stoichiometric calculations, was added in various black mass/H_2O_2 by mass (BM/H_2O_2), black mass/H_2SO_4 (BM/H_2SO_4) by mass ratios (theoretical H_2SO_4 and H_2O_2; BM/H_2SO_4; BM/H_2SO_4). The BM/H_2SO_4 and BM/H_2O_2 ratios studied were 0.75 and 1.

Tablo 3. Chemical content of Black Mass utilized for leaching.

Element	Ni	Co	Al	Cu	Mn	Li
mg/L	147110	74923	53002	51442	62758	30537
wt. %	14,71	7,49	5,30	5,14	6,28	3,05

The black mass sample, the content of which is given in Table 3, contains valuable elemental compounds in the anode and cathode parts of Li-ion batteries.

Information about the chemicals used in the leaching studies such as sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) is given in Table 4.

Tablo 4. Properties of Chemicals used for leaching.

Chemicals	Formula	Moleculer Weight (g/mol)	Purity (%)	Brand Name
Sulfuric acid	H_2SO_4	98,08	98-99	Hicri Ercili
Hydrogen Peroxide	H_2O_2	34,01	30	Ataman Chemicals

3.2. Methods

In this study, leaching studies, one of the first chemical steps of hydrometallurgical recycling methods, were carried out. The process steps related to the study are described in the following sub-headings.

3.2.1. Required H_2SO_4 and H_2O_2 Addition Calculation

The amounts of sulphuric acid and hydrogen peroxide required for the black mass (Li-ion battery waste sample) were determined by stoichiometric calculations. The following reaction equations were utilised during stoichiometric calculations.

Sulfuric acid leaching studies reaction equations without hydrogen peroxide:

Main reactions:

$4LiNiO_{2(s)} + 6H_2SO_{4(aq)} \rightarrow 4NiSO_{4(aq)} + 2\ Li_2SO_{4(aq)} + 6H_2O_{(g)} + O_{2(g)}$ (Equation 1)

$4LiCoO_{2(s)} + 6H_2SO_{4(aq)} \rightarrow 4CoSO_{4(aq)} + 2\ Li_2SO_{4(aq)} + 6H_2O_{(g)} + O_{2(g)}$ (Equation 2)

Side Reaction:

$2\ Al_{(s)} + 3\ H_2SO_{4(aq)} \rightarrow Al_2(SO_4)_{3(aq)} + 3\ H_{2(g)}$ (Equation 3)

$Cu_{(s)} + 2\ H_2SO_{4(aq)} \rightarrow CuSO_{4(aq)} + H_{2(g)}$ (Equation 4)

$2\ Fe_{(s)} + 3\ H_2SO_{4(aq)} \rightarrow Fe_2(SO_4)_{3(aq)} + 3\ H_{2(g)}$ (Equation 5)

$4LiMnO_{2(s)} + 6H_2SO_{4(aq)} \rightarrow 4MnSO_{4(aq)} + 2\ Li_2SO_{4(aq)} + 6H_2O_{(g)} + O_{2(g)}$ (Equation 6)

Sulfuric acid leaching studies reaction equations with using hydrogen peroxide:

Main reactions:

$2LiNiO_{2(s)} + 3H_2SO_{4(aq)} + H_2O_{2(aq)} \rightarrow 2NiSO_{4(aq)} + Li_2SO_{4(aq)} + 4H_2O_{(g)} + O_{2(g)}$ (Equation 7)

$2LiCoO_{2(s)} + 3H_2SO_{4(aq)} + H_2O_{2(aq)} \rightarrow 2CoSO_{4(aq)} + Li_2SO_{4(aq)} + 4H_2O_{(g)} + O_{2(g)}$ (Equation 8)

Side Reaction:

$2\ Al_{(s)} + 3\ H_2SO_{4(aq)} + H_2O_{2(aq)} \rightarrow Al_2(SO_4)_{3(aq)} + 6H_2O_{(g)}$ (Equation 9)

$Cu_{(s)} + H_2SO_{4(aq)} + H_2O_{2(aq)} \rightarrow CuSO_{4(aq)} + 2H_2O_{(g)}$ (Equation 10)

$2\ Fe_{(s)} + 3\ H_2SO_{4(aq)} + 3H_2O_{2(aq)} \rightarrow Fe_2(SO_4)_{3(aq)} + 6H_2O_{(g)}$ (Equation 11)

$2LiMnO_{2(s)} + 3H_2SO_{4(aq)} + H_2O_{2(aq)} \rightarrow 2MnSO_{4(aq)} + Li_2SO_{4(aq)} + 4H_2O_{(g)} + O_{2(g)}$ (Equation 12)

3.2.2. Experimental Presedure

The experimental flow of the leaching studies is described below:

- The determined amount (20 g) of black mass sample of waste Li-ion batteries was taken into a 500 ml beaker.
- Water was added so that the pulp density was 2/37 g/ml (5% solid/liquid ratio) with the presence of acid.
- The black mass water mixture was stirred with magnetic stirrer for homogeneous distribution.

- Then the calculated amount of acid was added to the mixed black mass water mixture.
- The mixture in the beaker was heated to reach the target temperature.
- After reaching the target temperature, the leaching process was continued for the determined time.
- After the leaching process was finished, solid and liquid were separated. Then the weight and volume measurements of the leaching filtrate were taken.
- The leached solid (black mass) was washed with approximately 450 ml of distilled water. Then the solid-liquid was separated and the weight and volume of the wash filtrate were measured.
- The washed leached solid was dried in an oven at 105°C and the dried solid was weighed.
- The efficiency was calculated with the use of the weighed leaching filtrate, washing filtrate and dry leached solid.

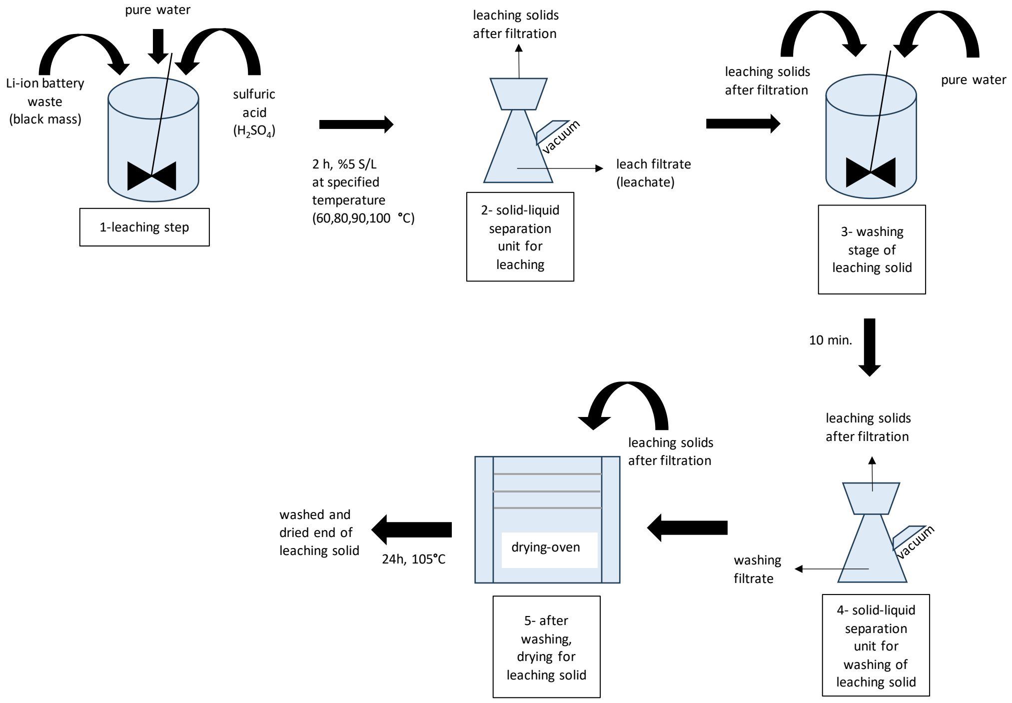


Figure 7. Flow of experiments.

Leaching, filtration and post-drying solid stages in the experimental flow, which are also shown schematically above, are given in Figure 8. Figure 8 a) shows the experimental setup after the addition of pure water and acid to provide 5% S/L ratio of li-ion battery waste. Figure 8 b) is the filtration set up to separate the valuable element compounds which are transferred to the liquid after the leaching stage from the waste solid. Figure 8 c) is the post-washing filtration setup to remove the remaining leaching leachate on the waste solid after filtration. Figure 8 d) shows the dried solid after solid washing.

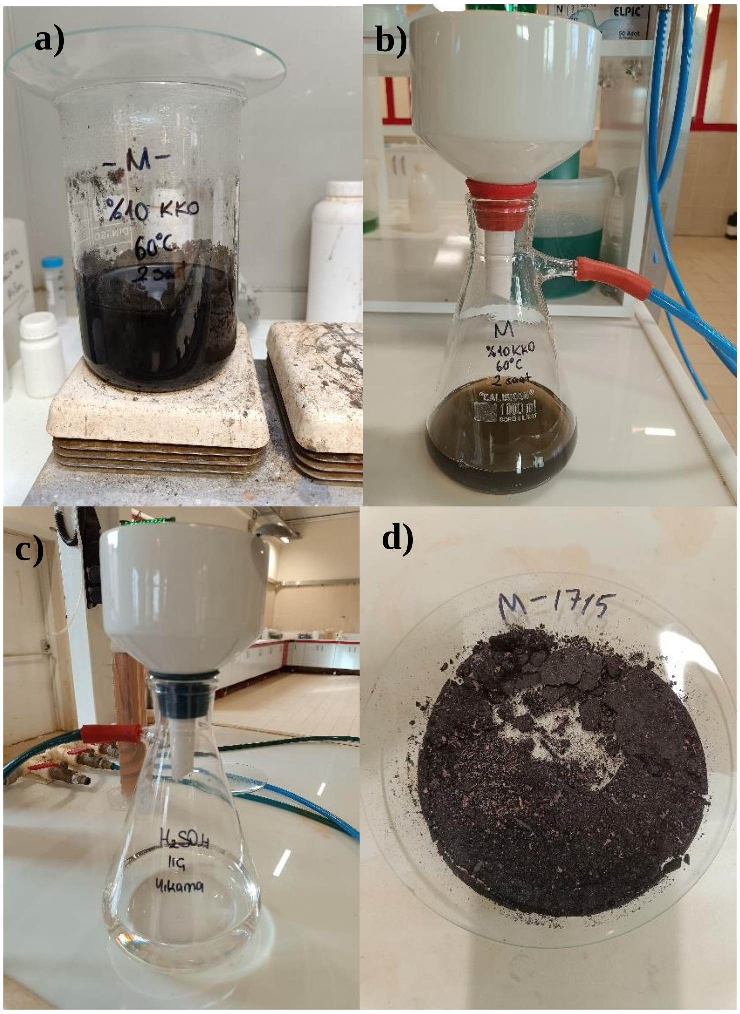


Figure 8. Experimental stages.

3.2.3. Leaching Efficiency Calculation

The leaching efficiency calculation is based on the solid by mass amounts of the initial Li-ion battery waste sample (black mass) and the residual solid after leaching (leached black mass). The leaching efficiency based on the initial Li-ion waste battery sample by mass and the residual leached solid by mass was calculated using the following Equation 13.

$$\text{leaching efficiency} = \frac{output}{input} \times 100 \qquad \text{(Equation 13)}$$

output: amount of leached Li-ion battery waste sample by mass
input: amount of initial Li-ion battery waste sample by mass

3.2.4. Analysis of Sample

In the studies, leaching experiments were carried out for the recovery of valuable element compounds such as Nickel and Cobalt in the waste Li-ion battery sample. In the leaching studies, ICP-OES equipment Agilent 5900 was used to determine the elemental contents of the initial Li-ion waste battery sample, leaching filtrate and residual battery after leaching.

CHAPTER 4

RESULT AND DISCUSSION

4.1. Effect of H_2SO_4 Amount

In the leaching studies, the effect of H_2SO_4 amount on nickel and cobalt leaching efficiency was investigated. In the studies, the theoretical required amount of H_2SO_4, 50% less than the theoretical required amount of H_2SO_4 and 50% more than the theoretical required amount of H_2SO_4 were calculated by using equation 1, 2, 3, 4, 5, 6. In addition, 20 g of Li-ion waste battery sample (black mass) was used in all leaching studies. In addition, acid amounts were calculated considering this 20 g black mass solid. As a result of this calculation, the theoretical required amount of H_2SO_4 is 22,13 g 50% less than the theoretical required amount of H_2SO_4 was calculated as 11,06 g and 50% more than the theoretical required amount of H_2SO_4 was calculated as 33,19 g. These amounts were taken as variable parameters and solid/liquid ratio (S/L), time and temperature values were fixed. All studies were carried out at 2/37 (5%) S/L for 2 hours. The effect of these H_2SO_4 amounts on the leaching efficiency at 3 different temperatures such as 60, 80, 100°C was analysed. At 60°C, parameters such as S/L ratio, temperature and time were fixed and the above given H_2SO_4 amounts were considered as variable parameters. These experiments were also carried out at 80 and 100°C temperatures. The leaching efficiencies of Nickel and Cobalt were analysed individually. The highest 94,09% leaching efficiency of cobalt was obtained in the study using 50% more H_2SO_4 than the theoretical required amount at 100°C. As the amount of acid was increased to 50% less than 50% more than the theoretical required amount, the leaching efficiency of Cobalt increased from 54,82% to 94,09%. Nickel efficiency in the same studies increased from 32.58% to 85.09%, the highest Ni efficiency value obtained. This shows that the amount of H_2SO_4 is an important parameter in leaching. The mass balances of the above mentioned studies are given in Appendix A.

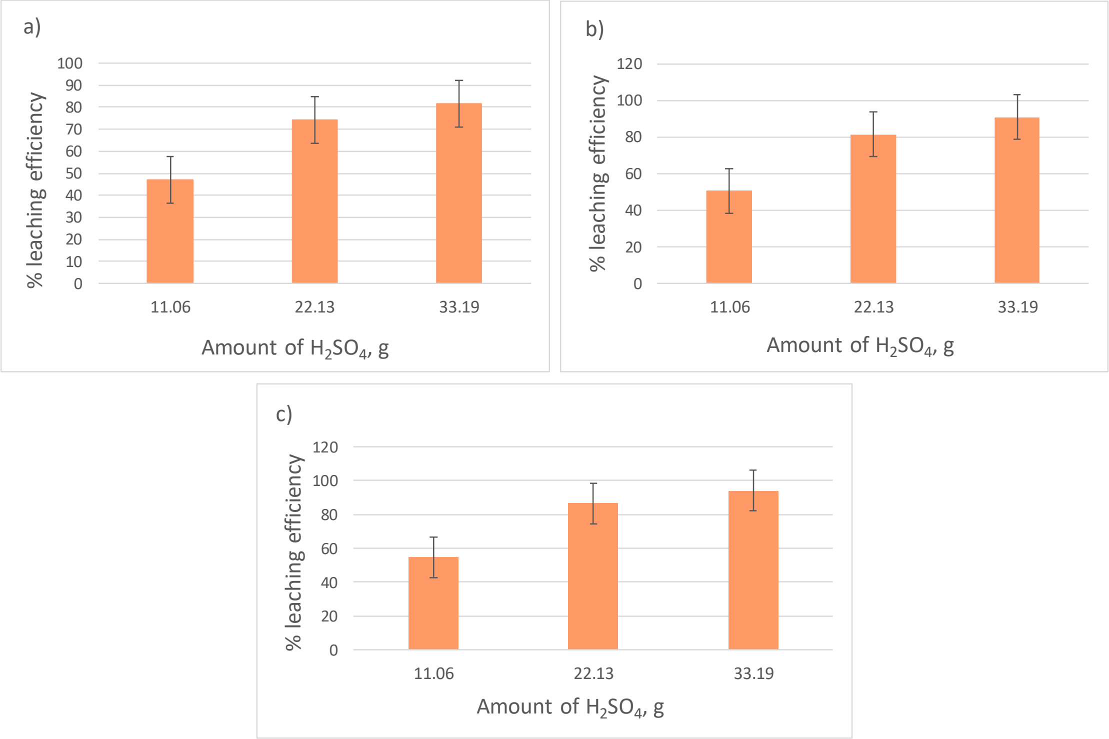


Figure 9. Effect of H_2SO_4 amount on leaching efficiency of Cobalt, leaching conditions: S:/L ratio, 2/37 (%5); time, 2h; temperature, a) 60ºC b) 80ºC c)100ºC.

Figure a)60 ºC; b)80 ºC; c)100 ºC shows the effect of different H_2SO_4 addition amounts on Nickel and Cobalt efficiencies at the indicated temperatures. It was observed that Cobalt efficiency increased with increasing H_2SO_4 addition amount at Figure a)60 ºC. The increase in Cobalt efficiency with increasing amount of H_2SO_4 was also observed in Cobalt efficiencies at 80 and 100 ºC. This is explained by the increase in the amount of dissolved solids with the increasing amount of acid, which increases the Cobalt leaching efficiency.

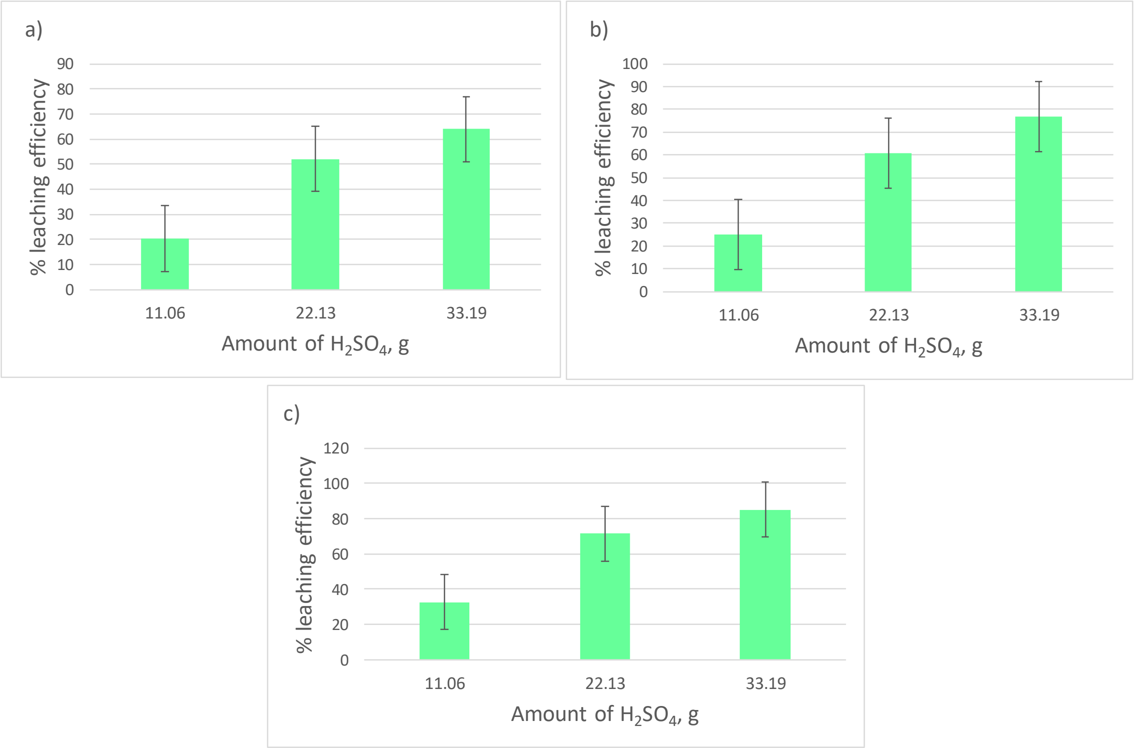


Figure 10. Effect of H_2SO_4 amount on leaching efficiency of Nickel, leaching conditions: S:/L ratio, 2/37 (%5); time, 2h; temperature, a)60°C b)80°C c)100°C.

As observed for cobalt leaching efficiencies, Figure 10 a) shows that nickel leaching efficiency increases with increasing acid content at 60 °C. The same situation was also observed for the leaching studies carried out at 80 °C and 100 °C. This situation observed in Figure 9 and Figure 10 is explained by the fact that with increasing acid content, the solid content of the dissolved and leached black mass (Li-ion waste battery sample) increases and indirectly the leaching efficiency also increases. As in the studies of Meshram et.al. and Sattar et.al., as the amount of H_2SO_4 used in the leaching process increases, the efficiency increases in direct proportion (Sattar et al., 2019, Meshram et al., 2015).

4.2. Effect of Leaching Temperature

In these studies where the effect of temperature was investigated, S/L ratio (5%), time (2h) and 3 different acid amounts were fixed. In these conditions where acid amounts were fixed separately, 3 different temperatures were determined as variable parameters. These temperatures were 60, 80 and 100ºC. The effects of these temperatures on nickel and cobalt leaching efficiency were examined. The results of the studies are given in Figure 11.

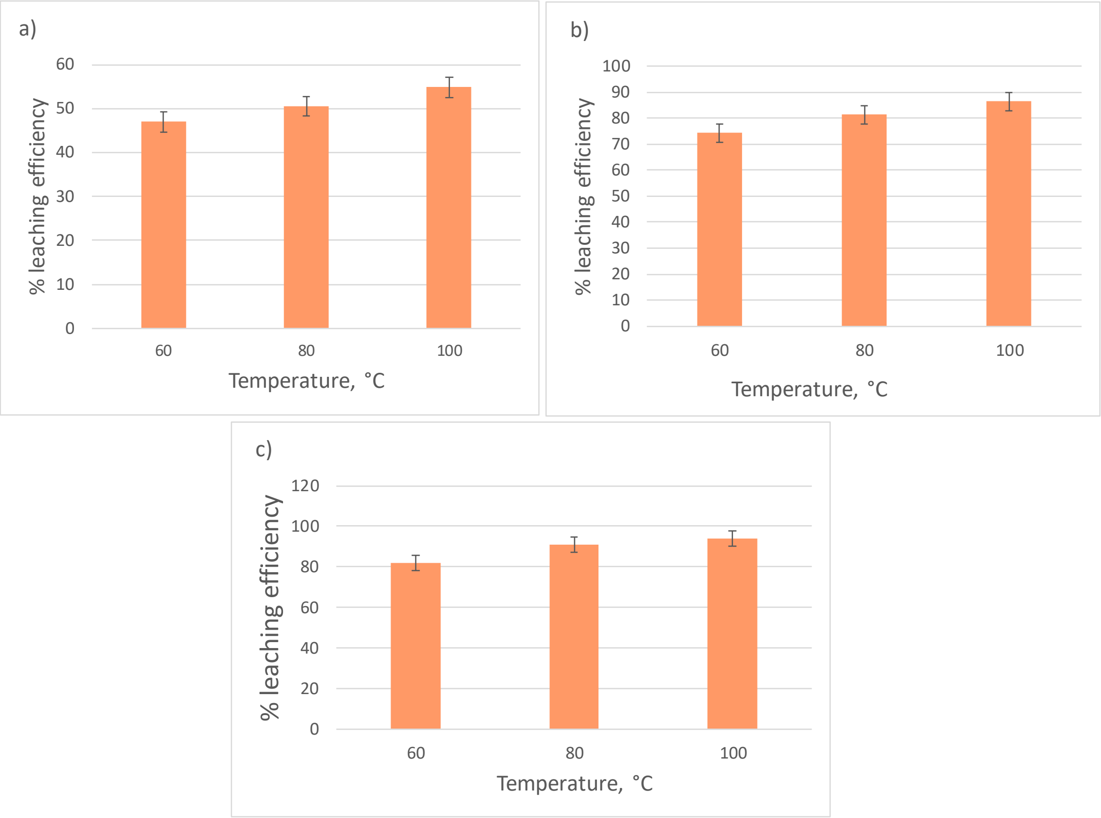


Figure 11. Effect of temperature amount on leaching efficiency of Cobalt, leaching conditions: S:/L ratio, 2/37 (%5); time, 2h; temperatures 60; 80; 100ºC, Amount of H_2SO_4 a) 11,06 g b) 22,13 g c) 33,19 g.

In Figure 11, Cobalt efficiency change at different temperatures at the same acid concentration and experimental conditions is analysed. In Figure 11 a), Cobalt efficiencies at different temperatures such as 60; 80; 100 ºC with the addition of 11,06 g H_2SO_4 acid are analysed. This situation was also examined separately at 22.13 g and 33.19 g H_2SO_4 addition amounts. At the same acid concentration and experimental conditions, it was observed that the cobalt efficiency increased with increasing temperatures.

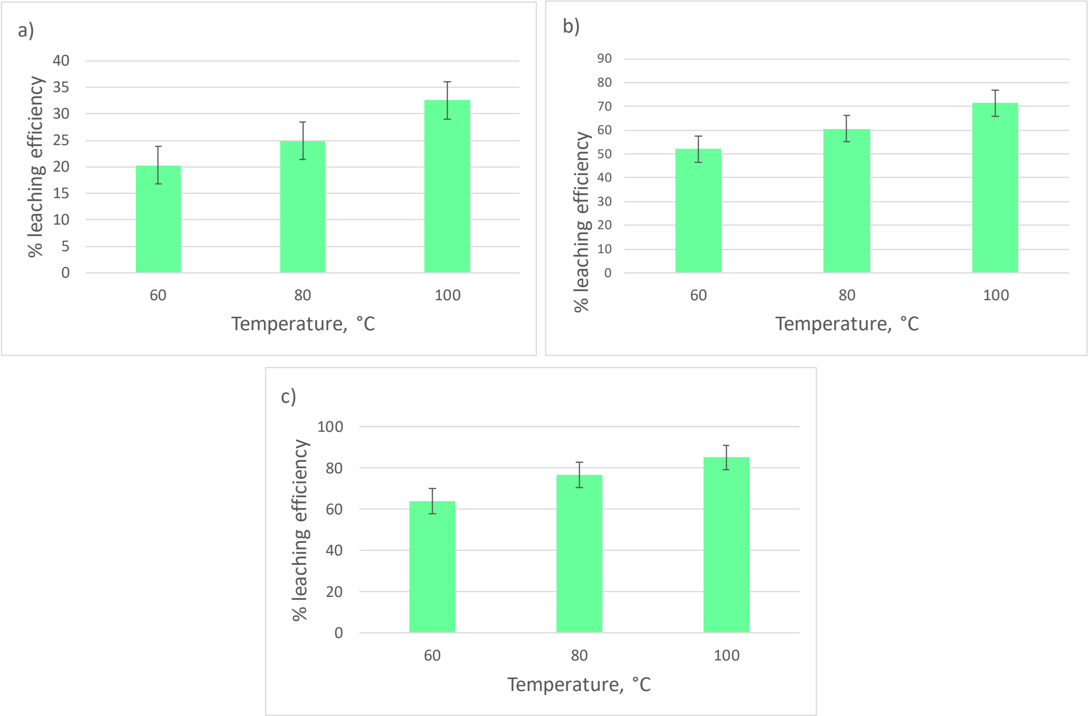


Figure 12. Effect of temperature amount on leaching efficiency of Nickel, leaching conditions: S:/L ratio, 2/37 (%5); time, 2h; temperature, 60; 80; 100ºC, Amount of H_2SO_4 a) 11,06 g b)22,13 g c) 33,19 g.

Figure 12 shows the Nickel efficiency change at different temperatures at the same acid concentration and experimental conditions. For example; in Figure 12 b), the effect of different temperature changes at 60, 80 and 100 ºC on Nickel leaching efficiency with the addition of 22.13 g H_2SO_4 was analyzed. Here, as seen in Figure 11, it was observed that Nickel leaching efficiency increased with increasing temperature.

In the studies, 10-15% increase in Cobalt leaching efficiency was observed with increasing temperature at fixed S/L ratio, time and acid amounts. For example, the cobalt efficiency was 74.36% at 60ºC and 86.43% at 100ºC (experimental parameters: 22.13 g H_2SO_4, 2h, 5% S/L). As seen in Figure 12 The efficiency of Nickel under the same conditions was 52.16% at 60ºC and 71.41% at 100 ºC. As seen in Lee et.al and Meshram et.al studies, it is seen that the Cobalt and Nickel leaching efficiencies increase with increasing temperature. This means that the dissolution efficiency of H_2SO_4 increases with increasing temperature. Therefore the amount of H_2SO_4 reacting with black mass increases (Swain et al., 2007,L. Chen et al., 2011).

4.3. Effect of H_2O_2 Presence

The mentioned leaching studies as above were carried out without Hydrogen Peroxide (H_2O_2). In light of the research articles and studies, leaching studies were carried out with H_2O_2 added in various amounts to observe the effect of the presence of H_2O_2 on Nickel and Cobalt leaching efficiency. To observe this effect, firstly, the theoretical amounts of H_2SO_4 and H_2O_2 required by stoichiometry were calculated using equations 7,8,9,10,11,12. The theoretical required amounts of H_2SO_4 and H_2O_2 are 16.74 g and 18.75 g, respectively. In addition, the leaching study was also carried out using the theoretical required amount of H_2SO_4 (22.13 g H_2SO_4) without H_2O_2 addition for the same experimental conditions. Leaching studies were also carried out with acid and H_2O_2 additions at different mass black mass/ H_2SO_4 (BM/ H_2SO_4) and mass black mass/ H_2O_2 ratios. These BM/ H_2SO_4 and BM/ H_2O_2 ratios have the same value and are as follows: 0.75 and 1. The amounts of H2SO4 and H_2O_2 with BM/ H_2SO_4 ratio of 0.75 are 26.65 and 26.53 for 20 g black mass, respectively. The amounts of H_2SO_4 and H_2O_2 with BM/ H_2SO_4 ratio of 1 are 21.04 and 20.41 for 20 g black mass, respectively. In addition, the effect of different addition sequences of H_2SO_4 and H_2O_2 on the leaching efficiency was also investigated. In these studies, water was added to the black mass (Li-ion waste battery sample) sample to achieve a 5% S/L ratio. Then, H_2O_2 was added first and then H_2SO_4 was added. The same study was also tested in the reverse order of addition. Fixed experimental conditions were 5% S/L ratio, 2 hours of leaching time at 90ºC.

Table 5. Efficiency summary table of leaching studies in the presence of H_2O_2.

<table>
<tr><th>Amount of H_2SO_4</th><th>Amount of H_2O_2</th><th>Co % efficiency</th><th>Ni % efficiency</th><th>Information of Experiment</th></tr>
<tr><td>22.13 g</td><td>-</td><td>81.72</td><td>66.26</td><td rowspan="4">In the leaching study, firstly H_2SO_4 acid was added and then H_2O_2 was added.</td></tr>
<tr><td>16.74</td><td>18.75</td><td>89.08</td><td>76.24</td></tr>
<tr><td colspan="2">$BM/H_2SO_4=BM/H_2O_2=0.75$</td><td>97.42</td><td>92.87</td></tr>
<tr><td colspan="2">$BM/H_2SO_4=BM/H_2O_2=1$</td><td>94.95</td><td>86.04</td></tr>
<tr><td colspan="2">$BM/H_2SO_4=BM/H_2O_2=1$</td><td>84.77</td><td>69.33</td><td rowspan="3">In the leaching study, firstly H_2O_2 was added and then H_2SO_4 acid was added.</td></tr>
<tr><td colspan="2">$BM/H_2SO_4=BM/H_2O_2=0.75$</td><td>84.67</td><td>67.87</td></tr>
<tr><td>16.74</td><td>18.75</td><td>73.46</td><td>49.90</td></tr>
</table>

other experimental conditions: %5 S/L ratio, 2 h, 90°C

A summary table of Nickel and Cobalt leaching efficiencies of the experiments carried out to observe the effect of H_2O_2 used in leaching studies is given in Table 5. As indicated in Table 5, the Nickel and Cobalt efficiencies obtained by adding the theoretical amount of H_2SO_4 without H_2O_2 are 66.26% and 81.72%, respectively (experimental conditions in this study were 90 °C, 5% S/L ratio and 2 hours leaching time). Cobalt efficiency increased to 89.08% and Nickel efficiency increased to 76.24% with the addition of the theoretically required amount of H_2SO_4 and H_2O_2. These efficiencies increased with increasing the addition amounts of H_2SO_4 and H_2O_2. Nickel efficiency increased to 86.04% and Cobalt efficiency increased to 94.95% with the increase of 21.04 g H_2SO_4, 20.41 g H_2O_2 addition amount ($BM/ H_2SO_4=BM/ H_2O_2=1$). With the addition of 26.65 g H_2SO_4 and 26.53 g H_2O_2 ($BM/ H_2SO_4=BM/ H_2O_2=0.75$), Nickel and Cobalt efficiencies increased to 92.87% and 97.42%, respectively. This H_2O_2 effect was also clearly observed in the studies of Zhu et.al, Naly et.al., Swain et.al., Sun et.al. In their studies, it was observed that the leaching efficiencies increased by about 20-25% (Zhu et al. 2012) (Nayl et al. 2017) (Swain et al. 2007) (Nan et al. 2006) (L. Sun and Qiu 2011). The increase in efficiency with the addition of H_2O_2 was explained by the fact that it assists and supports H_2SO_4 in the reduction of Co^{+3} ions to Co^{+2} to form the $CoSO_4$ compound (Sattar et al. 2019).

Another investigated issue was the order or priority of the addition of H_2SO_4 and H_2O_2 in the leaching stage. As seen in Table 5, when the theoretically required amount of H_2O_2 is added first and then the theoretically required H_2SO_4 is added, Nickel and Cobalt leaching efficiencies were obtained 49.90% and 73.46%, respectively. When this addition order was reversed (first H_2SO_4, then H_2O_2 addition), Nickel and Cobalt efficiencies were 76.24% and 89.08%, respectively, as given above. Thus, the importance of the priority of adding H_2SO_4 and H_2O_2 in the leaching stage was observed. This is explained by the amphoteric property of H_2O_2 which has both reducing and oxidising properties in reactions. This causes it to show amphoteric reactivity (Sankaralingam et al. 2018). At the beginning of the leaching study, the pH value of the black mass sample mixed with pure water was in the range of 5-6. When H_2O_2 is added to this mixture firstly, the added H_2O_2 does not show acidic properties since it is amphoteric. This does not affect the dissolution efficiency of black mass. However, when H_2SO_4 acid is first added to the black mass-pure water mixture, the pH decreases to approximately 1-2 depending on the amount of H_2SO_4. Then, when H_2O_2 was added, since the mixture was acidic, H_2O_2 also showed acidic properties and supported and assisted H_2SO_4 (Sankaralingam et al. 2018).

CHAPTER 5

CONCLUSION

This study investigated the effect of leaching parameters on nickel and cobalt leaching efficiency in hydrometallurgical recycling of Li-ion battery wastes. H_2SO_4 addition amount, temperature, H_2O_2 presence, addition amount, H_2SO_4 and H_2O_2 addition priority are among the leaching parameters were investigated.

The leaching studies observed that nickel and cobalt leaching efficiencies increased with increasing the amount of H_2SO_4. When the theoretical amount of H_2SO_4 added was increased by 50%, Nickel efficiency increased by 15% from 71.41% to 86.09% under the same experimental conditions except for the amount of H_2SO_4. Cobalt efficiency was increased by about 8% from 86.43% to 94.09% under the same operating conditions. Nickel and Cobalt leaching efficiencies were also increased with increasing temperature in the conducted leaching studies at equal H_2SO_4 amounts. In the studies where 50% more acid was added than the theoretically required amount of H_2SO_4, the leaching efficiency of Nickel at 60°C was 64.02%, while this efficiency increased to 85.09% at 100°C. Under the same leaching conditions, the efficiency of Cobalt increased from 81.8% to 94.09%. Considering these results, it is seen that the amount of acid used in leaching studies and leaching temperature are important parameters for Nickel and Cobalt leaching efficiency.

Another parameter analyzed was the presence and additional amount of H_2O_2 during leaching. Without the addition of H_2O_2, 66.26% Ni and 81.71% Co leaching efficiencies were obtained with the theoretical required amount of H_2SO_4 addition. To see the effect of H_2SO_4, leaching study was carried out under the same experimental conditions with the theoretical required amount of H_2SO_4 and H_2O_2 additions and 76.24% Ni, 89.08% Co leaching efficiency was obtained. In this case, it is seen that the use of H_2O_2 reducing agent has a positive effect on leaching efficiency. It was also observed that there was an increase of approximately 10-15% in nickel and cobalt leaching efficiency with increasing the amount of H_2O_2 compared to the theoretical amount of H_2O_2 addition. It was observed that the addition amounts of H_2SO_4 and H_2O_2 are important in leaching studies, as well as the priority of the addition of H_2SO_4, H_2O_2. At the beginning of the leaching study, when the theoretically required amount of H_2O_2 was first added to the black mass-pure water mixture and then the theoretically required amount of H_2SO_4 was added, Nickel and Cobalt leaching efficiencies were 49.90% and 73.46%, respectively. Under the same experimental conditions, at the same amount of H_2SO_4 and H_2O_2, with the opposite addition priority, these efficiencies were 76.24% for Nickel and 89.08% for Cobalt. During this addition, due to the amphoteric structure of H_2O_2, nickel and cobalt efficiencies were increased by approximately 15-20%.

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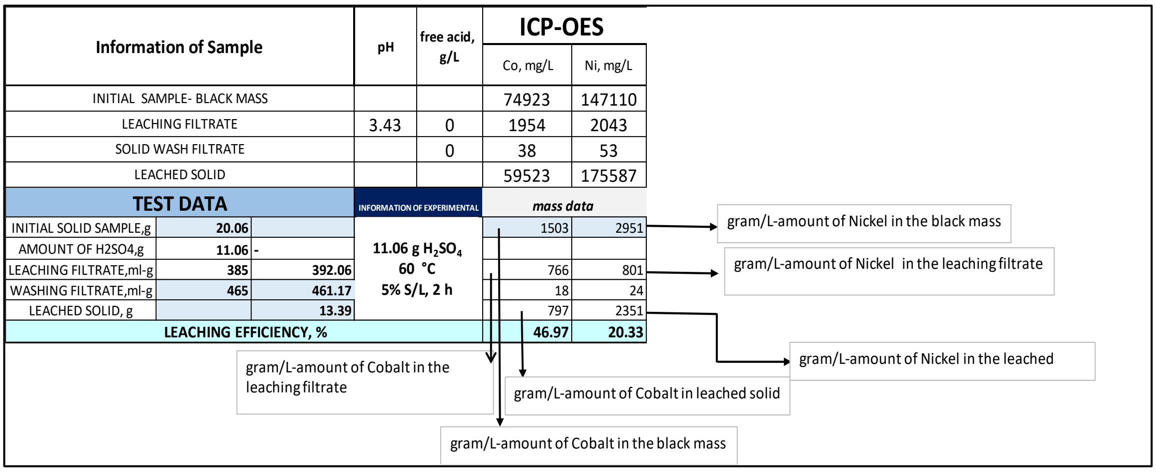
APPENDIX A

MASS BALANCE OF EXPERIMENTS

Table A.1. Mass balance of leaching for experiment 1 (operating condition; %5 S/L; 60°C; 2h; 11,06 g H_2SO_4).



Information of Sample	pH	free acid, g/L	ICP-OES Co, mg/L	ICP-OES Ni, mg/L
INITIAL SAMPLE- BLACK MASS			74923	147110
LEACHING FILTRATE	3.43	0	1954	2043
SOLID WASH FILTRATE		0	38	53
LEACHED SOLID			59523	175587

TEST DATA			INFORMATION OF EXPERIMENTAL	mass data	
INITIAL SOLID SAMPLE,g	20.06		11.06 g H_2SO_4 60 °C 5% S/L, 2 h	1503	2951
AMOUNT OF H2SO4,g	11.06	-			
LEACHING FILTRATE,ml-g	385	392.06		766	801
WASHING FILTRATE,ml-g	465	461.17		18	24
LEACHED SOLID, g		13.39		797	2351
LEACHING EFFICIENCY, %				46.97	20.33

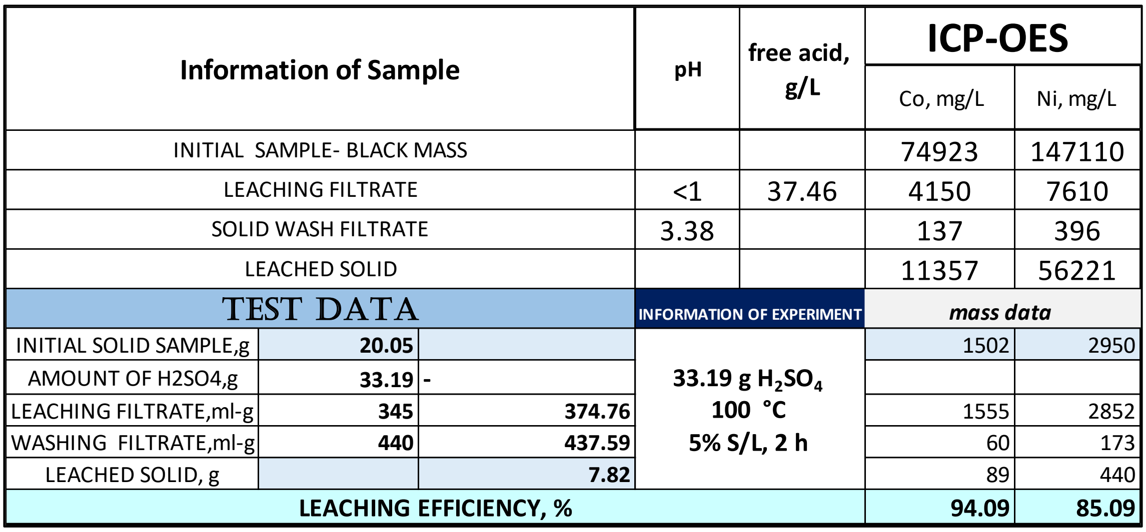
Table A.2. Mass balance of leaching for experiment 2 (operating condition; %5 S/L; 60°C; 2h; 33,19 g H_2SO_4).

Information of Sample			**pH**	**free acid, g/L**	**ICP-OES**	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			<1	43.1	3572	5358
SOLID WASH FILTRATE				0	210	524
LEACHED SOLID					28620	111080
TEST DATA			**INFORMATION OF EXPERIMENTAL**		***mass data***	
INITIAL SOLID SAMPLE,g	**20.04**		**33.19 g H_2SO_4** **60 °C** **5% S/L, 2 h**		1501	2948
AMOUNT OF H2SO4,g	**33.19**					
LEACHING FILTRATE,ml-g	**325**	**354.14**			1265	1898
WASHING FILTRATE,ml-g	**415**	**414.31**			87	217
LEACHED SOLID, g		**9.55**			273	1061
LEACHING EFFICIENCY, %					**81.80**	**64.02**

Table A.3. Mass balance of leaching for experiment 3 (operating condition; %5 S/L; 80°C; 2h; 11,06 g H_2SO_4).

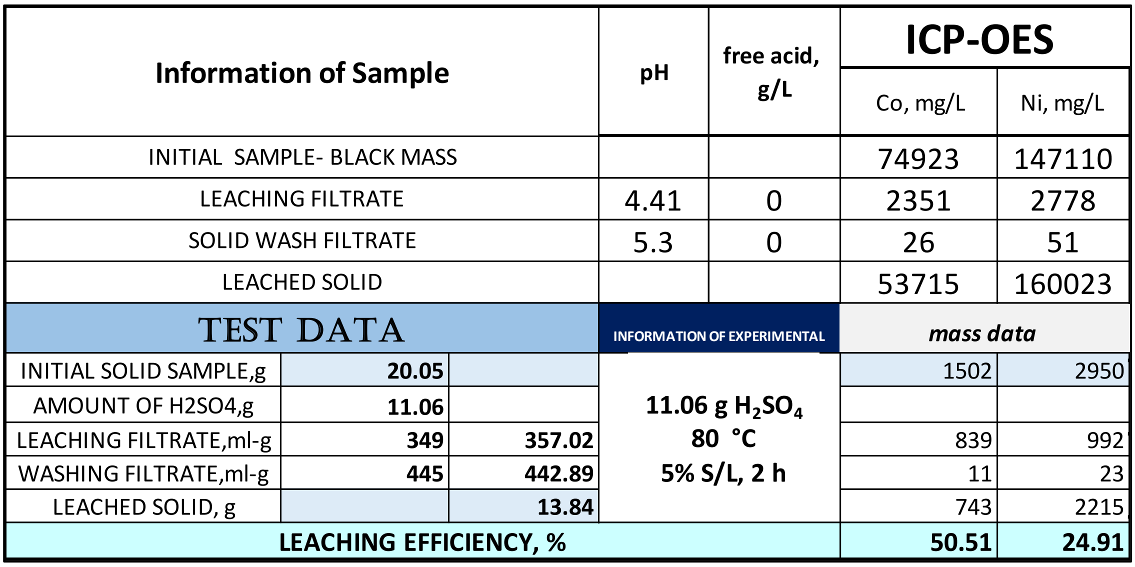
Information of Sample			**pH**	**free acid, g/L**	**ICP-OES**	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			3.16	0.08	1976	2190
SOLID WASH FILTRATE			5.17	0	20	44
LEACHED SOLID					49405	144757
TEST DATA			**INFORMATION OF EXPERIMENTAL**		***mass data***	
INITIAL SOLID SAMPLE,g	**20.04**		**11.06 g H_2SO_4** **100 °C** **5% S/L, 2 h**		1501	2948
AMOUNT OF H2SO4,g	**11.06**					
LEACHING FILTRATE,ml-g	**365**	**371.42**			734	813
WASHING FILTRATE,ml-g	**470**	**468.49**			9	21
LEACHED SOLID, g		**13.73**			678	1988
LEACHING EFFICIENCY, %					**54.82**	**32.58**

Table A.4. Mass balance of leaching for experiment 4 (operating condition; %5 S/L; 80°C; 2h; 33,19 g H_2SO_4).



Information of Sample			pH	free acid, g/L	ICP-OES	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			<1	37.46	4150	7610
SOLID WASH FILTRATE			3.38		137	396
LEACHED SOLID					11357	56221
TEST DATA			INFORMATION OF EXPERIMENT		*mass data*	
INITIAL SOLID SAMPLE,g	**20.05**		**33.19 g H_2SO_4** **100 °C** **5% S/L, 2 h**		1502	2950
AMOUNT OF H2SO4,g	**33.19**	-				
LEACHING FILTRATE,ml-g	**345**	**374.76**			1555	2852
WASHING FILTRATE,ml-g	**440**	**437.59**			60	173
LEACHED SOLID, g		**7.82**			89	440
LEACHING EFFICIENCY, %					**94.09**	**85.09**

Table A.5. Mass balance of leaching for experiment 4 (operating condition; %5 S/L; 80°C; 2h; 11.06 g H_2SO_4).



Information of Sample			pH	free acid, g/L	ICP-OES	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			4.41	0	2351	2778
SOLID WASH FILTRATE			5.3	0	26	51
LEACHED SOLID					53715	160023
TEST DATA			INFORMATION OF EXPERIMENTAL		*mass data*	
INITIAL SOLID SAMPLE,g	**20.05**		**11.06 g H_2SO_4** **80 °C** **5% S/L, 2 h**		1502	2950
AMOUNT OF H2SO4,g	**11.06**					
LEACHING FILTRATE,ml-g	**349**	**357.02**			839	992
WASHING FILTRATE,ml-g	**445**	**442.89**			11	23
LEACHED SOLID, g		**13.84**			743	2215
LEACHING EFFICIENCY, %					**50.51**	**24.91**

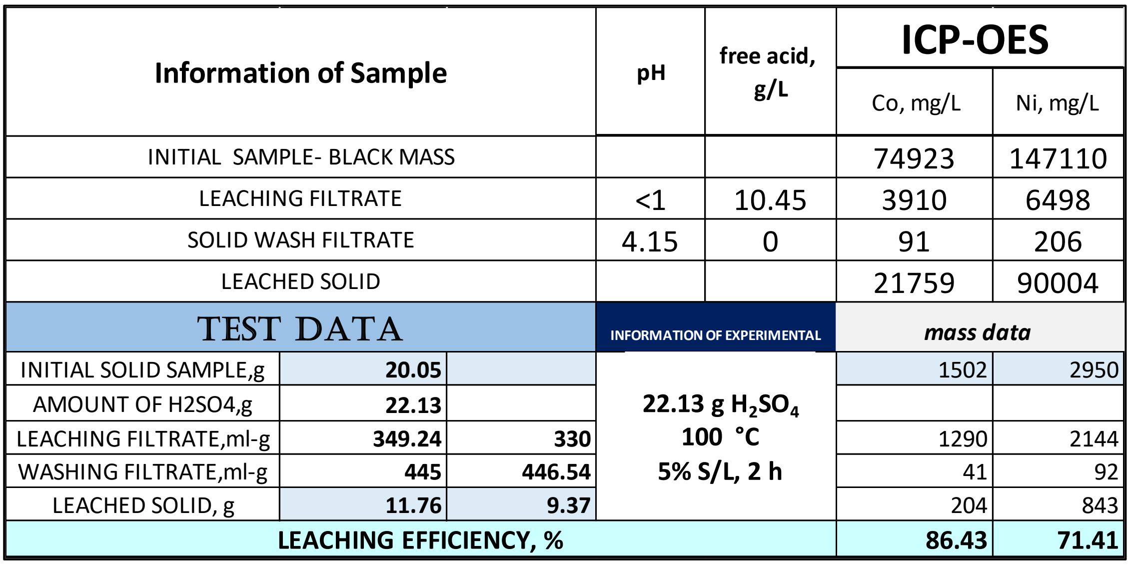
Table A.6. Mass balance of leaching for experiment 6 (operating condition; %5 S/L; 80°C; 2h; 33,19 g H_2SO_4).

Information of Sample			**pH**	**free acid, g/L**	**ICP-OES**	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			<1	42.6	4273	7388
SOLID WASH FILTRATE			3.97		133	392
LEACHED SOLID					16402	81499
TEST DATA			INFORMATION OF EXPERIMENTAL		***mass data***	
INITIAL SOLID SAMPLE,g	**20.06**		**33.19 g H_2SO_4** **80 °C** **5% S/L, 2 h**		1503	2951
AMOUNT OF H2SO4,g	**33.19**					
LEACHING FILTRATE,ml-g	**325**	**353.6**			1511	2612
WASHING FILTRATE,ml-g	**432**	**431.2**			58	169
LEACHED SOLID, g		**8.4**			138	685
LEACHING EFFICIENCY, %					**90.83**	**76.80**

Table A.7. Mass balance of leaching for experiment 7 (operating condition; %5 S/L; 60°C; 2h; 22,13 g H_2SO_4).

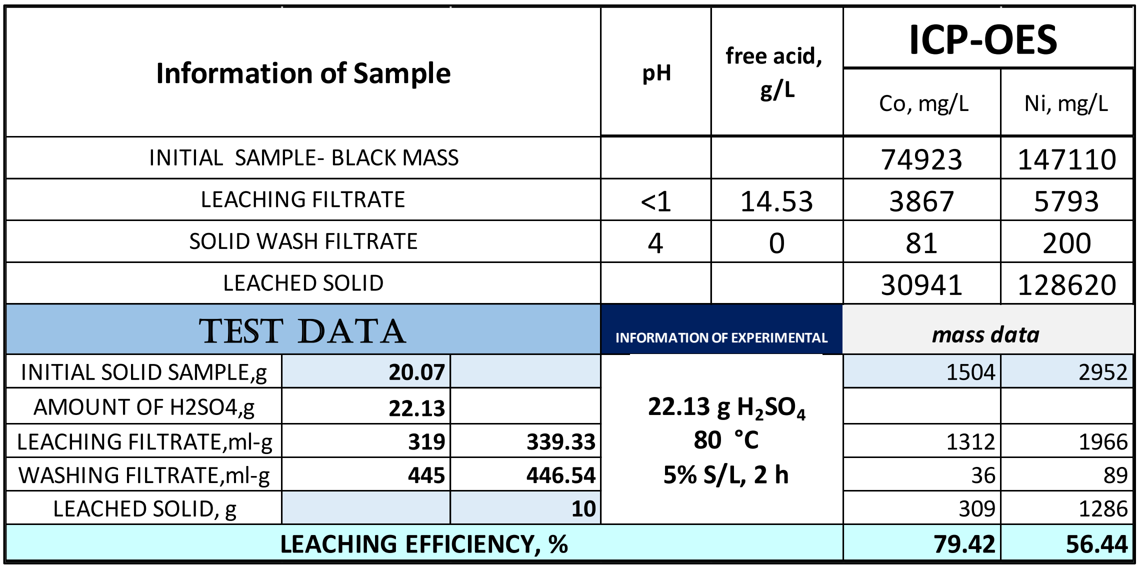
Information of Sample			**pH**	**free acid, g/L**	**ICP-OES**	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			<1	16.65	3529	4807
SOLID WASH FILTRATE					133	392
LEACHED SOLID					49125	179970
TEST DATA			INFORMATION OF EXPERIMENTAL		***mass data***	
INITIAL SOLID SAMPLE,g	**20.05**		**22.13 g H_2SO_4** **60 °C** **5% S/L, 2 h**		1502	2950
AMOUNT OF H2SO4,g	**22.13**					
LEACHING FILTRATE,ml-g	**335**	**355.32**			1254	1708
WASHING FILTRATE,ml-g	**437**	**435.9**			58	171
LEACHED SOLID, g		**7.84**			385	1411
LEACHING EFFICIENCY, %					**74.36**	**52.16**

Table A.8. Mass balance of leaching for experiment 8 (operating condition; %5 S/L; 100°C; 2h; 22,13 g H_2SO_4).



Information of Sample			**pH**	**free acid, g/L**	**ICP-OES**	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			<1	10.45	3910	6498
SOLID WASH FILTRATE			4.15	0	91	206
LEACHED SOLID					21759	90004
TEST DATA			INFORMATION OF EXPERIMENTAL		***mass data***	
INITIAL SOLID SAMPLE,g	**20.05**		**22.13 g H_2SO_4** **100 °C** **5% S/L, 2 h**		1502	2950
AMOUNT OF H2SO4,g	**22.13**					
LEACHING FILTRATE,ml-g	**349.24**	**330**			1290	2144
WASHING FILTRATE,ml-g	**445**	**446.54**			41	92
LEACHED SOLID, g	**11.76**	**9.37**			204	843
LEACHING EFFICIENCY, %					**86.43**	**71.41**

Table A.9. Mass balance of leaching for experiment 9 (operating condition; %5 S/L; 80°C; 2h; 22,13 g H_2SO_4).



Information of Sample			**pH**	**free acid, g/L**	**ICP-OES**	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			<1	14.53	3867	5793
SOLID WASH FILTRATE			4	0	81	200
LEACHED SOLID					30941	128620
TEST DATA			INFORMATION OF EXPERIMENTAL		***mass data***	
INITIAL SOLID SAMPLE,g	**20.07**		**22.13 g H_2SO_4** **80 °C** **5% S/L, 2 h**		1504	2952
AMOUNT OF H2SO4,g	**22.13**					
LEACHING FILTRATE,ml-g	**319**	**339.33**			1312	1966
WASHING FILTRATE,ml-g	**445**	**446.54**			36	89
LEACHED SOLID, g		**10**			309	1286
LEACHING EFFICIENCY, %					**79.42**	**56.44**

Table A.10. Mass balance of leaching for experiment 10 (operating condition; %5 S/L; 80°C; 2h; 22,13 g H_2SO_4).

Information of Sample			pH	free acid, g/L	ICP-OES	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			<1	12.98	3977	6369
SOLID WASH FILTRATE			3.91	0	100	233
LEACHED SOLID					27007	110349
TEST DATA			**INFORMATION OF EXPERIMENTAL**		***mass data***	
INITIAL SOLID SAMPLE,g	**20.06**		**22.13 g H_2SO_4** **80 °C** **5% S/L, 2 h**		1503	2951
AMOUNT OF H2SO4,g	**22.13**					
LEACHING FILTRATE,ml-g	**320**	**344.61**			1370	2195
WASHING FILTRATE,ml-g	**445**	**442.02**			44	103
LEACHED SOLID, g		**9.68**			261	1068
LEACHING EFFICIENCY, %					**82.61**	**63.80**

Table A.11. Mass balance of leaching for experiment 11 (operating condition; %5 S/L; 80°C; 2h; 22,13 g H_2SO_4).

Information of Sample			pH	free acid, g/L	ICP-OES	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			<1	11.75	3934	6375
SOLID WASH FILTRATE			4.83		103	231
LEACHED SOLID					25723	105307
TEST DATA			**INFORMATION OF EXPERIMENTAL**		***mass data***	
INITIAL SOLID SAMPLE,g	**20.07**		**22.13 g H_2SO_4** **80 °C** **5% S/L, 2 h**		1504	2952
AMOUNT OF H2SO4,g	**22.13**					
LEACHING FILTRATE,ml-g	**325**	**348.55**			1371	2222
WASHING FILTRATE,ml-g	**475**	**470.07**			48	109
LEACHED SOLID, g		**9.76**			251	1028
LEACHING EFFICIENCY, %					**83.30**	**65.19**

Table A.12. Mass balance of leaching for experiment 12 (operating condition; %5 S/L; 80°C; 2h; 22,13 g H_2SO_4).

Information of Sample			**pH**	**free acid, g/L**	**ICP-OES**	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			<1	13.87	3840	5879
SOLID WASH FILTRATE			3.62		87	190
LEACHED SOLID					30302	133750
TEST DATA			**INFORMATION OF EXPERIMENTAL**		***mass data***	
INITIAL SOLID SAMPLE,g	**20.05**		**22.13 g H_2SO_4** **80 °C** **5% S/L, 2 h**		1502	2950
AMOUNT OF H2SO4,g	**22.13**					
LEACHING FILTRATE,ml-g	**320**	**344.41**			1323	2025
WASHING FILTRATE,ml-g	**450**	**444.12**			39	85
LEACHED SOLID, g		**10.02**			304	1340
LEACHING EFFICIENCY, %					**79.79**	**54.56**

Table A.13. Mass balance of leaching for experiment 13 (operating condition; %5 S/L; 80°C; 2h; 22,13 g H_2SO_4).

Information of Sample			**pH**	**free acid, g/L**	**ICP-OES**	
					Co, mg/L	Ni, mg/L
INITIAL SAMPLE- BLACK MASS					74923	147110
LEACHING FILTRATE			<1	11.1	3781	6092
SOLID WASH FILTRATE			4.03		81	173
LEACHED SOLID					28423	113027
TEST DATA			**INFORMATION OF EXPERIMENTAL**		***mass data***	
INITIAL SOLID SAMPLE,g	**20.05**		**22.13 g H_2SO_4** **80 °C** **5% S/L, 2 h**		1502	2950
AMOUNT OF H2SO4,g	**22.13**					
LEACHING FILTRATE,ml-g	**342**	**363.45**			1374	2214
WASHING FILTRATE,ml-g	**467**	**465.3**			38	80
LEACHED SOLID, g		**9.6**			273	1085
LEACHING EFFICIENCY, %					**81.84**	**63.21**

The leaching efficiency of Nickel and Cobalt in the table is calculated based on the initial gram-mass of black and gram-mass of leached solid. The gram-Nickel and gram-Cobalt passing from solid to liquid at the end of leaching can be seen from the value in the explanation section of gram-nickel in the leaching filtrate and gram-cobalt in the leaching filtrate, respectively.