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Recycling of lithium-ion batteries

The effects of a reducing agent on the efficiency and kinetics of metal leaching

Master's thesis in Materials Chemistry

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Front cover: One dismantled battery cell. The cathode material is scraped off and left visible is the current collector. Also visible in the figure are the separator represented by the thin white plastic sheet and the copper used as current collector on the anode to the left.

Abstract

Lithium-ion batteries are vital in today's society which is becoming more and more dependent on green energy production and energy storage. Rechargeable batteries have different types of cathode materials according to their respective primary application. Lithium is used in all cathode materials and besides lithium the common metals include cobalt, nickel, manganese and aluminum. When the life-cycle for a battery is ending it is recycled and the valuable metals are recovered. The recycling of batteries is a growing industry with different ways to extract valuable metals and other components from spent batteries.

This thesis focuses on the hydrometallurgical waste treatment process which is one of four ways to recycle batteries. The hydrometallurgical waste treatment process consists of different process steps, but this thesis focuses on leaching. Leaching is an important step for effective recovery of metals from consumed lithium-ion batteries. This thesis aims to examine the effect of a reducing agent on the leaching of metals from cathode material. The effect hydrogen peroxide has on the efficiency and kinetics of the leaching process are investigated and compared to leaching with sulfuric acid. Furthermore, the effect of temperature on the leaching kinetics is studied. Seven different cathode materials studied in this thesis: Lithium Cobalt Oxide (LCO), Lithium Nickel Oxide (LNO), Lithium Manganese Oxide (LMO), Mixed Nickel Manganese Cobalt (NMC), NMC 111, NMC 442 and NMC 811.

The study showed encouraging results for most cathode materials. The effect of hydrogen peroxide is increased efficiency of the leaching and faster reactions. LiNiO_2 show decreased leaching efficiency when hydrogen peroxide is used because crystalline Nickel Oxide (NiO) is produced. In the other cathode materials containing nickel the efficiency and leaching rate are improved when hydrogen peroxide is used. The study showed that an increase in temperature increased the leaching efficiency for all cathode material in 2M H_2SO_4 except the leaching of manganese from NMC 442.

Keywords: Reductive leaching, hydrometallurgical recycling, hydrogen peroxide, Li-ion batteries, NMC, cobalt recovery

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Abbreviations

CAGR	Compound Annual Growth Rate
CNT	Carbon Nanotubes
DMAC	N,N-dimethylacetamide
DMF	N,N-methylformamide
DMSO	Dimethylsulfoxide
FCC	Face-Centered Cubic
HOMO	Highest Occupied Molecular Orbital
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
LCO	Lithium Cobalt Oxide
LiB	Lithium ion Battery
Li-ion	Lithium ion Battery
LMO	Lithium Manganese Oxide
LNO	Lithium Nickel Oxide
LUMO	Lowest Unoccupied Molecular Orbital
NCA	Nickel Cobalt Aluminum
NCO	Nickel Cobalt Oxide
NMC	Nickel Manganese Cobalt
NMP	N-methylpyrrolidone
PE	Polyethylene
PEO	Polyethylene Oxide
PP	Polypropene
PVD	Physical Vapor Deposition
PVdF	Polyvinylidene Fluoride
WEEE	Waste Electrical and Electronic Equipment
XRD	X-Ray Diffraction

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1

Introduction

Lithium-ion batteries (Henceforth referred to as LiB) is a common battery type in modern society and the batteries contain valuable metals such as cobalt, nickel, copper, etc. Recently the lithium has also been considered valuable and the recovery of it has been of interest. This chapter gives a background about lithium before the theory of LiBs and the recycling of LiBs are presented. Furthermore, the overall aim and demarcations of the thesis are presented in this chapter.

1.1. Background

A monumental challenge arises for the modern society in the form of a transition from fossil fuels i.e. coal and oil to renewable energies. This shift of energy sources is necessary if sustainability of the earth is to be preserved, mainly because of the emission of carbon dioxide from fossil fuels that drives the global warming. Numerous renewable energy sources have a disadvantage in common, they are unable to store the energy produced until the consumers demand it. Therefore, these technologies need an energy storage ability for example batteries. Batteries are available in many different types and forms, with various technologies. Examples of different batteries are Nickel-Cadmium, Alkaline and LiBs to mention a few.

Lithium is an important component of lithium batteries as the name hints, but the raw material can be used in other applications such as the glass and ceramics industries, polymer production and pharmaceutical production among others [1]. According to a report from 2018 the total production of lithium was estimated to be 43 000 tons and the consumption 41 500 ton during 2017 [2]. The share for each individual market can be seen in Figure 1 along with the mass in metric tons for each sector.

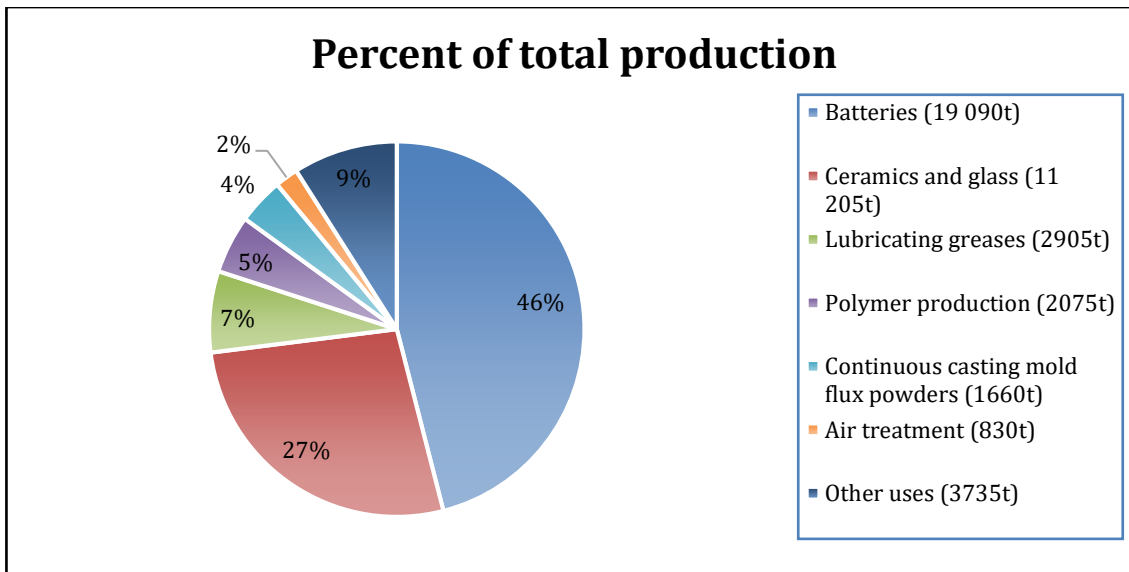


Figure 1: Showing the share of the produced lithium for each market during 2017. Data obtained from [2].

Lithium batteries are batteries that utilizes lithium as an anode in either solid or liquid form [3]. Batteries with metal lithium as anode are referred to as primary lithium batteries [4]. When lithium is used in the form of ions in batteries they are referred to as either rechargeable or secondary lithium batteries (LiBs) [3]. The most commercialized rechargeable battery type in the world applies a cathode made of LiCoO_2 [1, 3, 5, 6, 7].

In principle a lithium-ion battery is made up of the following key components: a cathode, current collector, electrolyte, an anode and a separator [1]. The reports of how much of the total weight each component accounts for in a battery vary between sources. It has been reported that the cathode corresponds to 10-45 weight % (wt%), the anode for 5-30 wt%, the current collector on the anode 2-15 wt%, the current collector on the cathode 2-25 wt%, the electrolyte for 1.2-20 wt% and the separator for 0.5-14 wt% [1] [8] [9] [10] [11] [12] [13]. The battery consists of more components outside the battery cell, e.g. the packaging, battery management system and electrical contacts. The weight percent of each component are influenced by the type of battery and the producer of the battery. Figure 2 shows how a lithium-ion battery is built with its main components.

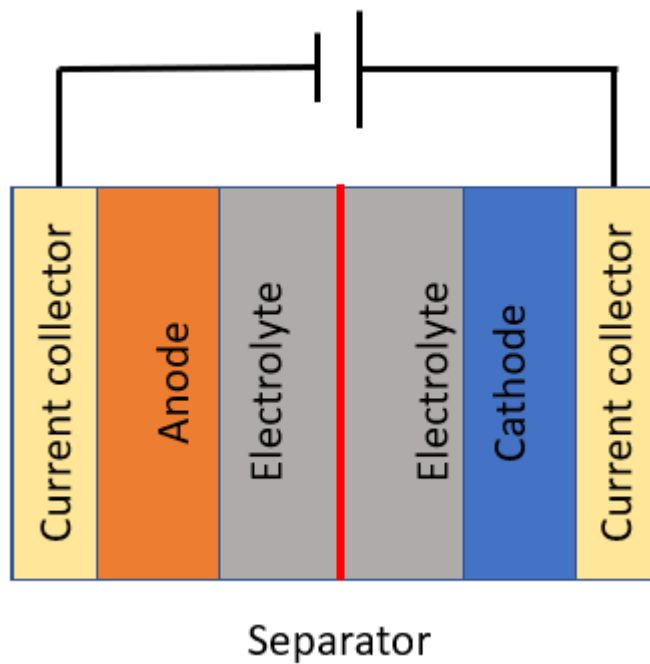


Figure 2: A schematic drawing of a lithium-ion battery with its principal components.

The cathode is the positive electrode receiving electrons from the negative electrode, which is called anode. The electrolyte is a substance, usually a salt, that produces an electrically conducting solution when dissolved in a liquid. The electrolyte is used between the electrodes where ions travel when they are released from an electrode. The separator is applied to keep the anode and cathode apart inside the battery thus preventing a short circuit [1]. A current collector is used on both the anode and cathode to support the electrode material. The components will be more extensively explained in the section 1.2.1.

However, in a rechargeable lithium battery the anode and cathode are not always the same electrode. This is depending on the state of the battery i.e. if it is supplying electrical energy to an application or recharging. This phenomenon is called intercalation, which describes the oxidation/reduction of the electrodes [14]. The term describes a reversible interaction between a material with interstitial sites in its structure and a guest species [15]. In lithium-ion batteries the guest ions are lithium ions that moves back and forth between the anode and cathode through the electrolyte. The material that was used when the breakthrough for intercalation came was titanium sulfide (TiS_2) [3] [5] [14] [16]. The aforementioned compound LiCoO_2 is an intercalator with high capacity and was used in the battery introduced on the market by Sony Corporation in 1991 which has since become the most used rechargeable battery [17].

The production of lithium metal has increased with an average of 5.1% each year under the time span ranging from 1980-2008 [18]. In a report published in 2019 it is estimated that the production of lithium increased by 22% under 2018 compared to the production in 2017 [19]. According to the report the reason for the increase in production is because lithium is used in new batteries.

The increased demand for lithium ion batteries can be seen when looking at Compound Annual Growth Rate (CAGR) for different applications where lithium is used. The CAGR calculations are based on data from the *Mineral Commodity Summaries* published by U.S. Geological Survey every year. Equation *a* was used to calculate the CAGR.

$$CAGR = \left(\frac{\text{Lithium used in process year (n) (tonne)}}{\text{Lithium used in process year (0) (tonne)}} \right)^{\frac{1}{\text{year (n)} - \text{year (0)}}} - 1 \quad (a)$$

The CAGR are based on data from 2012 and 2018 which were published in 2013 and 2019 respectively. The CAGR for different sectors are presented in Table 1. Since the data used for the estimation of the changes in the market for Li has been collected by the same institute the CAGR calculation might not give a true picture of the market but rather an indication how it has changed over time. In Appendix I the data can be reviewed.

*Table 1: The CAGR for categories where lithium is used. Data published in [19] [20] [21]. *Denotes that the first data for the category was published 2013.*

Category	CAGR 2012-2018
Glass and Ceramics	14.35 %
Li-ion batteries	40.16 %
Air treatment	6.86 %
Lithium/Lubricating greases	8.42 %
Polymers	25.84 %
Other uses	-4.11 %
Continuous casting mold flux powders*	6.96 %

The demand for lithium is increasing every year. The recycling of lithium from products are at present less than 1% [1] [22]. Therefore, extensive research is investigating and developing the four methods in which lithium-ion batteries can be recycled. These four methods are pyrometallurgical treatment, mechanical treatment, hydrometallurgical treatment and last a combination of thermal pretreatment and hydrometallurgical treatment [1]. This study will focus on hydrometallurgical treatment of spent Li-ion batteries.

1.2. Theory

Chapter 1.2 presents in-depth information about the components in a Li-ion battery with focus on the cathode active material and the hydrometallurgical waste treatment principle.

1.2.1. Main components in batteries

As presented in section 1.1 the main components of a lithium-ion battery are: Anode, Cathode, Separator, Electrolyte and Current collector. Here every component will be described more extensively with further details about different materials that can be used at each position in the battery and what the research in the respective area are focused.

1.2.1.1. Anode

In the first Li-ion batteries commercialized by Sony, the anode was made of graphite and it remains the most common anode material today [1] [3]. The structure of the anodes in LiBs are based on copper foil covered with graphite. Graphite is used as anode in LiBs because it is a cheap environmentally friendly material [3] [23] with low working potential as well as high specific capacity [23] [24]. Problems with graphite anodes are capacity loss under long-time electrochemical cycles leading to problems using it in electric vehicles and in energy storage

applications [23] [24]. Graphite is a part of the group carbonaceous materials which can have different form and shape. Common types are hard carbon, soft carbon and carbon nanotubes [1] [3]. Another material that has been used as anode in a commercialized battery is a composite consisting of Sn/Co/C [3].

Since the introduction of the graphite/copper structure other materials have been studied as anodes. The list of desired characteristics for new anodes is long and it includes the following characteristics among others [1]:

- The anode should have good reversibility for the lithiation/ delithiation at low electrode potential and a good capacity retention.
- Excellent electronic and ionic conductivity to permit the diffusion of electrons and Li-ions.
- High compatibility with the electrolyte and binder system.
- High energy density

All new anodes are susceptible for the intercalation with lithium ions since this is necessary for the charging/ discharging of the batteries. Anodes are divided into three different groups according to their respective type of intercalation. The three are: Intercalation-, alloy- and conversion type [1]. The first group have the mechanism for intercalation as described in section 1.1. Alloy type of anodes are produced when Li ions electrochemical alloy with an alloy-type material (M) according to reaction (1) [1].



Conversion type of anodes are based on a redox reaction with Li_2O [25]. Both Julien et al. and Swiatowska et al. have reviewed research conducted in this field. They both reviewed articles focusing on applying Silicon (Si), Germanium (Ge) and Tin (Sn) as anodes [1] [3]. The similarity among these metals is their position in the periodic table, they all have the same amount of valence electrons and therefore have good properties to be used as anodes. However, a problem with anodes based on these metals is that the SEI layer undergo big changes in volume during lithiation/delithiation [1] [3].

1.2.1.2. Cathode

The cathode made up of *Lithium Cobalt Oxide* (LCO), $LiCoO_2$, was developed and tested in 1980 [26]. It was the first cathode where the charge-discharge cycle reaches the potential range 3.6-4.2V [3]. As mentioned in section 1.1 LCO is the most used cathode in sold Li-ion batteries. The reason behind the properties of LCO is the thermodynamically stable structure and the strong Co-O bond which reduces the bond distance in the unit cell [3]. This gives the advantages with LCO which is a decent rate capacity and the best energy density of the tested cathodes [1]. The main disadvantages with LCO is the potential to overheat [1] and the loss of oxygen when the battery is running at a different potential range compared to the normal range of 3.6-4.2V [3]. Figure 3 shows the structure of $LiCoO_2$ where the red balls represent oxygen, blue atoms cobalt and purple lithium respectively. Primary applications where LCO is used are in small scale electronics [13].

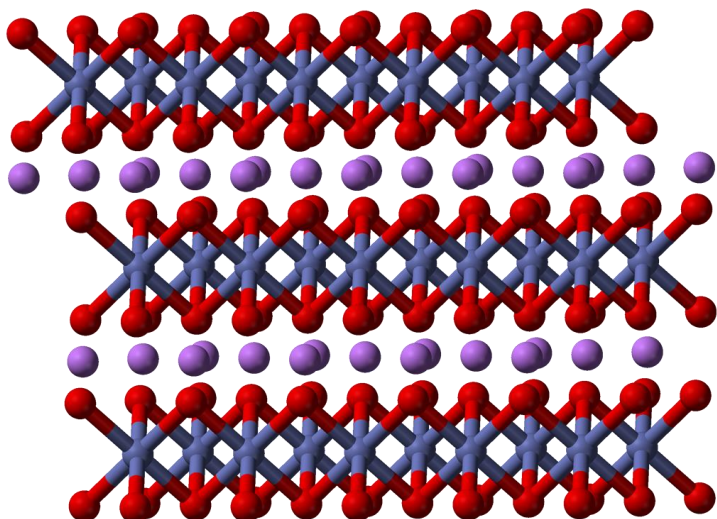


Figure 3: Ball-and-stick model of the structure of LiCoO_2 . Image available under public domain [27].

Lithium Nickel Oxide (LNO), LiNiO_2 , has similar structure as LCO, is made of cheaper metals and develop a high cell potential close to 4V which is the advantage with LNO cathodes [3]. However, the downsides with LNO is bigger than the advantages, therefore there is no commercialization of batteries containing LNO cathodes, but they are used at lab scale. Examples of problems with LNO are that irreversible phase transitions can occur during lithiation-delithiation [28] and that it is difficult to synthesize LiNiO_2 with the nickel ions in the right valence state and crystallized in the right order [1] [29]. The structure of LNO can be displayed with Figure 3 with one difference, the blue balls represent Ni-ions instead of Co-ions.

Nickel Cobalt Oxide (NCO), $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$, is a cathode material that is rich in nickel but with the addition of cobalt ions. They have promising electrochemical properties as a result of the incorporation of cobalt ions into the LNO-structure. NCO becomes stabilized when $y=0.3$ [1] as a result of the strong Co-O bindings that forms a robust structure [3]. The changes in structure compared to LCO and LNO gives NCO a higher electric capacity but slightly lower discharge voltage [3]. A study showed problems with NCO cathodes as they are inclined to lose oxygen on deep lithium extraction in the cobalt-rich phases [30].

Nickel Cobalt Aluminum (NCA), $\text{LiNi}_{1-y-z}\text{Co}_y\text{Al}_z\text{O}_2$, has a similar structure to NCO but with the difference of being doped with aluminum ions. The doping with Al ions improves the electrochemical properties as a result of the contribution from the improved structural stability and thermal stability [3]. Drawbacks with NCA is that there is some problem obtaining homogenous material for the NCA cathodes [31]. NCA cathodes are widely used in batteries produced by SAFT. These batteries are applied in electric vehicles from TESLA [13], the space industry and in the military among other applications [3].

Nickel Manganese Cobalt (NMC), $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ [3] or $\text{Li}(\text{Ni}_{1/2-y}\text{Mn}_{1/2-y}\text{Co}_{2y})\text{O}_2$ [1], is a promising cathode material based on the idea of using different metals to minimize the drawbacks of each component while maximizing the advantage of each metal. The manganese ions help improve the thermal stability as long as they stay in the +4-valence state [3]. The amount of Mn^{4+} ions must equal the amount of Ni^{2+} otherwise the cathode will lose its charge neutrality and the Mn^{4+} ions will change valence state to Mn^{3+} which is more unstable due to high spin configuration of the electrons [1] [3]. The NMC with the composition of

$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ developed by Ohzuku's group [32] are considered the golden standard in NMCs [1]. The benefits are that it shows good stability during lithiation/ delithiation at higher temperatures, low cost and high energy density [3] [33]. The market for NMC cathodes is forecasted to increase along with the increased demand for electric vehicles [33]. In Figure 4 the crystal structure of an NMC cathode is displayed.

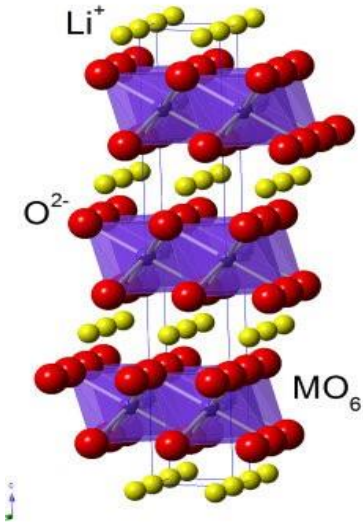


Figure 4: The crystal structure of $\text{LiNi}_y\text{Co}_z\text{Mn}_{1-y-z}\text{O}_2$ cathode. The Ni, Mn and Co atoms are randomly distributed on M sites. Figure available via license CC BY-NC-ND 3.0 [34].

Lithium Manganese Oxide (LMO), $\text{Li}_x\text{Mn}_2\text{O}_4$, is a cathode with a spinel structure [1]. When $x > 1$ the material will be distorted due to Mn^{3+} ions which will change the structure of LMO and change properties of the material [1]. Therefore, it is common to use LMO with the constitution of LiMn_2O_4 . It is a cheap and non-toxic material with a structure that enables intercalation of lithium ions [1]. The advantage with this type of cathode is that it is safe and possess high power density [1]. A disadvantage with LMO is that when it is cycled at high temperatures the particles will start to crack [35]. The number of cracks in the structure correlates with the degradation of the capacity [35]. Under an environment with high temperatures the dissolution of Mn^{2+} ions will also contribute to the capacity degradation escalating the loss of capacity [35]. LMO has been used in electric vehicles but is becoming less common [13]. Figure 5 shows the crystalline structure for LMO and the pathways for lithium diffusion.

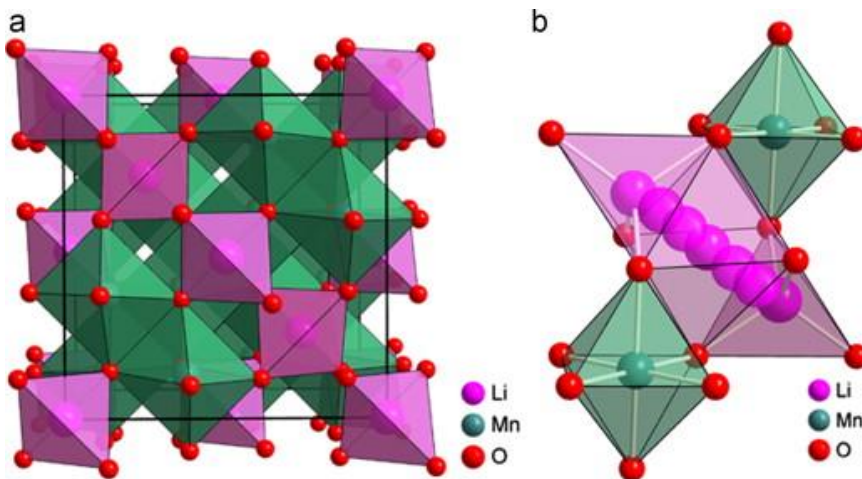


Figure 5: (a) Crystalline structure of spinel LiMn_2O_4 . (b) Its corresponding lithium diffusion pathways. Figure available via licence CC BY-NC-ND 3.0 [36].

1.2.1.3. *Current Collector*

A challenge with LiBs is to increase their power- and energy density to develop them further. To be able to do it the batteries need superior ion and electron kinetics which is something the current collector can improve [37]. The main purpose of current collectors is to collect the current and deliver it i.e. the electrons to the external circuit. Furthermore, it should support the electrode material and display good resistance against corrosion [1] [38]. Corrosion can be avoided by keeping the electrochemical potential of the metal between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO) of the electrolyte [37]. The most used current collectors are electrolytic copper foils on the anode and aluminum foils on the cathode [1] [37] [38]. These materials have excellent current transport properties. A study from 2006 showed that the use of Lithium bis(oxalate)borate (LiBOB) as electrolyte helps the formation of a passive film on the surface of the aluminum used as current collector [39] [40]. This protects the metal from pitting corrosion.

The research is now focused on 3D current collectors and on different techniques to prepare the current collectors to improve their performance. The use of 3D current collectors is increasing due to the ability to develop thinner coating on the electrodes leading to decreased diffusion time through the coating [37]. Different techniques to improve current collectors on the cathode include physical vapor deposition (PVD) of the current collector on the electrode [41] [42], and usage of carbon nanotubes (CNTs) to prepare the current collector [43]. Techniques to improve the current collectors applied on the anode are using copper foams with high porosity [44], and electrodeposition of porous copper plates [45].

1.2.1.4. *Separator*

The separator is placed in a battery to keep the electrodes apart to avoid a short circuit and ensure cell safety. A separator is a porous membrane which is permeable to the flow of ions between the electrodes [46]. There are different types of separators but the most common are made of nonwoven fabrics or microporous polymeric films [1]. Polyolefins, e.g. Polyethylene (PE), Polypropylene (PP) or a trilayer of PP/PE/PP are used in Li-ion batteries with a liquid electrolyte [46]. In Li-ion batteries with gel polymer as electrolyte the separators are usually Polyvinylidene fluoride (PVdF) or a polyolefin coated with a gelling agent [46]. An important aspect with a trilayer of PE/PP/PE is their respective melting temperature. The melting temperature for PE is 130°C and for PP 165°C. Therefore, the PE will start to melt if a runaway reaction occurs and the temperature is increasing in the battery. PE fill the pores while PP still has mechanical strength to avoid a short circuit within the battery [3]. The research in this area is focusing on improving the properties of the existing separators and developing new made of ceramic composite materials [1] [47].

1.2.1.5. *Electrolyte*

An electrolyte usually contains one or more lithium salts and one solvent or a mixture of different solvents [1] [3]. Components that can be included in the electrolyte are ionic liquids, polymers and additives. Ionic liquids can be added to the electrolyte and they show good properties such as large electrochemical window [48] but some ionic liquids have the undesirable property of being highly flammable [3].

Additives are designed and used in batteries to protect the electrode surface and improve the electrolyte. The performance of graphite electrodes can be enhanced by different modifications to the surface. Examples of modifications of the surface is mild oxidation [49], addition of a polymer coating [50] and chemical vapour deposition of a tin-oxide coating [51]. These performance increasing techniques all have in common that they improve the amount of cycles the battery can endure.

Polymer electrolytes uses a polymer instead of a liquid electrolyte between the electrodes [1]. The conductivity of a polymer electrolyte is dependent on the phase of the polymer. The ionic conductivity is superior in liquid (amorphous) phase and the electronic conductivity prefer the crystalline phase of a polymer [52]. Polymers that can be used in Li-ion batteries are polyesters, polyimines and polyethers [1]. The first polymer electrolyte in LiBs was Polyethylene Oxide (PEO) [3] [52] [53]. PEO shows properties that closely resembles water in some aspects [1]. Polymer electrolytes improves safety as they minimize the need for organic solvents in the electrolyte. They are also less prone to changes in volume during the lithiation/delithiation cycle leading to less tension in the battery [1]. Table 2 shows common substances used in the electrolyte solutions in commercialized LiBs.

Table 2: Components used in the electrolyte solution in commercialized batteries [1] [3].

Role	Substance
Solvent	Ethylene carbonate (EC)
Solvent	Propylene carbonate (PC)
Solvent	Dimethyl carbonate (DMC)
Solvent	Diethyl carbonate (DEC)
Salt	LiPF ₆
Salt	LiBF ₄
Salt	LiBOB

1.2.2. Hydrometallurgical recycling of Li-ion batteries

Hydrometallurgical treatment is one of the four aforementioned ways to recycle spent Li-ion batteries. It utilizes leaching, solvent extraction and precipitation to recover metals from used batteries. However, there are some pretreatment steps applied to the batteries before the hydrometallurgical process. These steps along with the schematic process schemes of possible treatments a used battery can undergo is presented in Figure 6. Recycling companies use different process schemes to reach the product, the chart in Figure 6 is just a general flow chart of how batteries can be recycled.

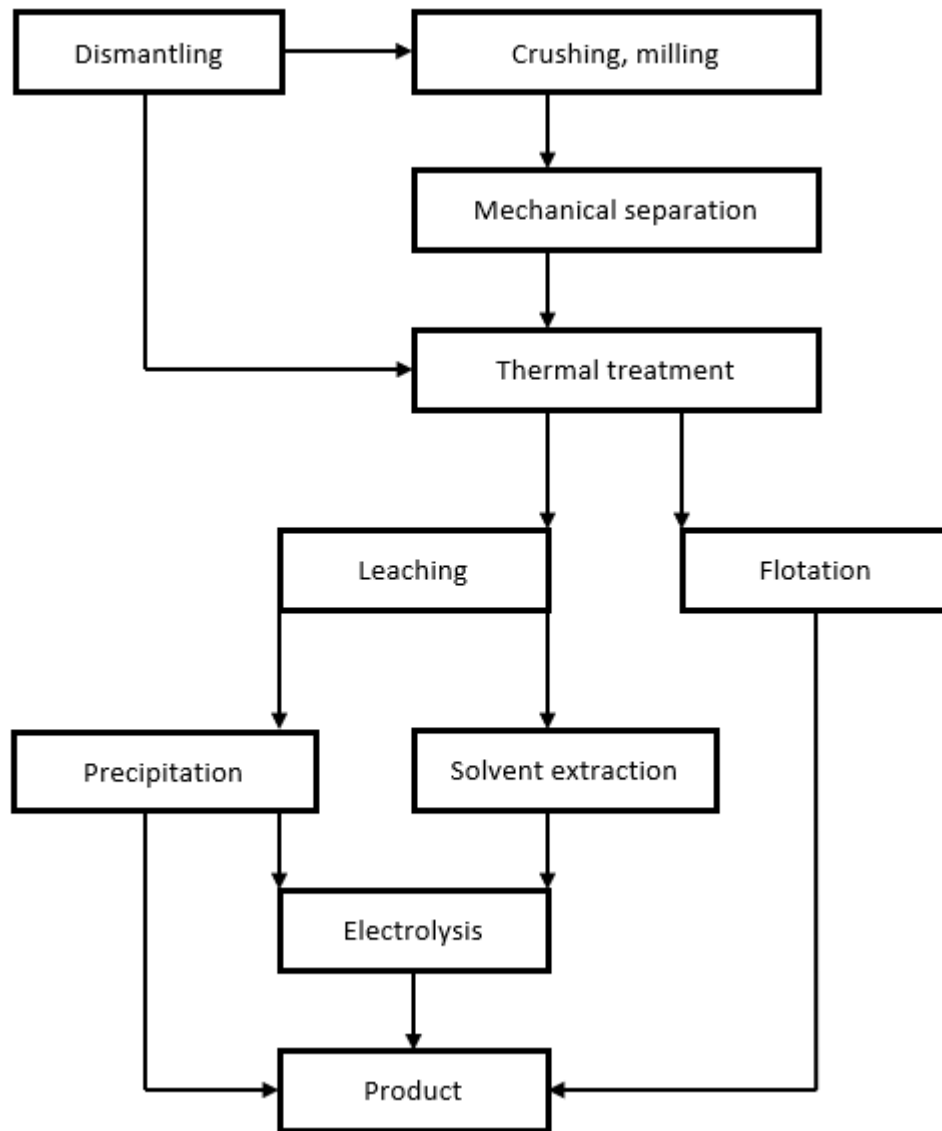


Figure 6: Flow chart for the hydrometallurgical recycling with pretreatment steps [1].

1.2.2.1. Pretreatment steps

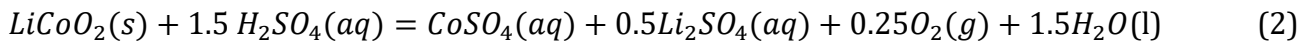
First the batteries are discharged as a precautionary step to avoid short-circuits and self-ignition [1] [54]. The discharge can be done by immersing the battery in a salt solution [55]. Then the batteries are dismantled to separate the active materials of the battery and the peripheral parts like cables and casing which are regarded as the Waste Electrical and Electronic Equipment (WEEE) [56]. The separation of the different components in the battery core is more difficult since they are more closely packed and attached to each other. Research has been conducted on how to separate the current collectors from the black mass by dissolving the organic binder between them. This process can be achieved with the help of organic solvents such as dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMAC), N,N-methylformamide (DMF) and N-methylpyrrolidone (NMP) [1] [54]. The use of an organic solvent has some disadvantages, namely that they are not suitable for scale-up and the electrodes has to be calcinated or pyrolyzed to remove impurities and residues from the organic compounds [54].

The center core of a spent battery goes through a mechanical pretreatment step with the aim of separating the black mass and other materials present in the core. The separation of the

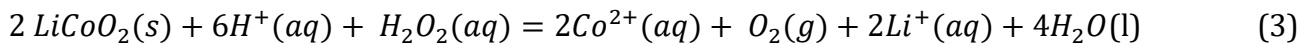
materials can be performed using different processes. Processes used include magnetic separation, crushing, sieving and ultrasound separation [1] [55].

1.2.2.2. *Leaching*

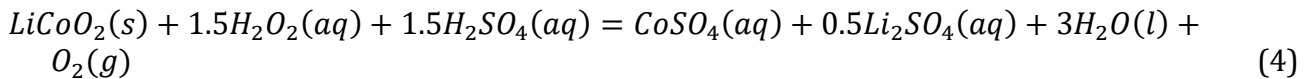
When the black mass with high concentration of the valuable metals is separated from the batteries the hydrometallurgical treatment can be applied. Leaching is the first step in the hydrometallurgical treatment and crucial to achieve high yields of valuable metals. The leaching process is used to convert metals from the cathode into ions in the leaching solution. Different methods can be applied to accomplish the leaching. These methods are Inorganic Acid Leaching, Organic Acid Leaching, Bioleaching, Alkaline Leaching, Intensified Leaching, Selective Leaching and Reductive Leaching [1] [54]. The most common leaching agents in Inorganic Acid Leaching and Reductive Leaching are HNO_3 , H_2SO_4 and HCl [54]. Reaction 2 show the leaching reactions with Sulfuric acid and Hydrochloric acid without any additional leaching media on the most common cathode material LiCoO_2 [1]:



Reductive leaching is done with the addition of a reducing agent in the acid. The reducing agent can be one of hydrogen peroxide, malic acid, ascorbic acid, citric acid, oxalic acid and glucose [57]. The main purpose with the addition of a reductive agent are to change valence state of the metals used in the cathode into a more soluble state and to increase the efficiency of the leaching [1] [54]. Reaction 3 shows a general reaction scheme proposed for the reductive leaching of LiCoO_2 with hydrogen peroxide in the presence of an acid [54]:



Reactions 4 shows the specific leaching reaction for LiCoO_2 in sulfuric acid with hydrogen peroxide as a reductive agent [1].



Presented in Table 3 is a summary of results from earlier studies on leaching with inorganic acids and in some cases addition of H_2O_2 . Table 3 show studies performed on LiCoO_2 and one case where a mixture of cathode material was investigated. However, there is a lack of information on other types of cathode materials in general.

Table 3: Summary of conditions used in studies where leaching with H₂O₂ was performed.

Cathode material	Leaching media	Temperature (°C)/ Time (min)	S/L (g/mL)	Leaching efficiency (%)	Source
LiCoO ₂	2M H ₂ SO ₄ + 5 vol% H ₂ O ₂	75/60	1:100	Li: 99.1; Co: 70.0	[58]
LiCoO ₂	2M H ₂ SO ₄ + 6 vol% H ₂ O ₂	60/60	1:100	Li: 97; Co: 98	[59]
LiCoO ₂	2M H ₂ SO ₄ + 2 vol% H ₂ O ₂	60/120	1:33	Li: 87.5; Co: 96.3	[60]
LiCoO ₂	2M H ₂ SO ₄ + 5 vol% H ₂ O ₂	80/60	1:50	Li: >99; Co: >99	[61]
LiCoO ₂	6 vol% H ₂ SO ₄ + H ₂ O ₂	65/60	1:30	Li: 95; Co: 75	[62]
LiCoO ₂	3M H ₂ SO ₄	70/360	1:5	Li: 98; Co: 98	[63]
LiCoO ₂	3M H ₂ SO ₄ + 1.5M H ₂ O ₂	70/60	N/A	Li: 99; Co: 99.4	[64]
LiCoO ₂	3M H ₂ SO ₄ + H ₂ O ₂	N/A	N/A	Li: 99; Co: 99	[65]
LiCoO ₂	1M HNO ₃ + 1.7 vol% H ₂ O ₂	75/30	1:10	Li: 99; Co: 99	[66]
Mixture	2M H ₂ SO ₄ + 2 vol% H ₂ O ₂	70/300	1:10	Li: 106.7; Co: 96.7; Ni: 97.9	[7]

1.2.2.3. Electrochemical potentials

The leaching yields of metal ions from the spent batteries are controlled by the thermodynamics of the reactions between cathode materials and the reducing agent. The base is the electrochemical potential between the different valence state of the metals and the reducing agent. For low valence ions, e.g. Lithium, an acid is enough to easily leach it but for high valence ions an additional reductive agent is needed to increase the efficiency of the leaching. Equation *b* shows how the electrochemical potential for the cell is calculated and Equation *c* shows how the equilibrium constant is calculated for the system.

$$\Delta E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} \quad (b)$$

$$\log K = \frac{n\Delta E_{cell}^{\circ}}{0.059} \quad (c)$$

Table 4: The half-cell reaction and equilibrium rates for different metals used in the cathode .Table 4 shows the different cathode reactions as well as the cell potential in volt and the equilibrium constant. All cell potentials were calculated using the cell potential for O₂/H₂O₂ as the anode.

Table 4: The half-cell reaction and equilibrium rates for different metals used in the cathode [61].

Half-cell reaction	Potential	Cell potential	K
O ₂ + 2 H ⁺ + 2e ⁻ → H ₂ O ₂	0.699 V		
Ni ⁴⁺ + 2e ⁻ → Ni ²⁺	1.678 V	0.979 V	33
Co ³⁺ + e ⁻ → Co ²⁺	1.83 V	1.131 V	19.2

$\text{Mn}^{4+} + 2\text{e}^- \rightarrow \text{Mn}^{2+}$	1.224 V	0.525 V	17.8
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1.2.2.4. Solvent extraction and precipitation

When the valuable metals are leached, they have to be separated and recovered from the solution. There are different methods that can be used to obtain the separation. Solvent extraction is one way to separate the metals. The method is efficient since the extractants have high selectivity for the different metal ions. Common organic extractants are 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), Bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), hydroxy-oxime derivate (Acorga M5640) and di-(2-ethylhexyl) phosphoric acid (D2EHPA) [1].

The principle is that a substance, usually metal ions, is solved in a system containing two liquid phases, usually one aqueous and one organic phase. The metal ions are extracted from the aqueous phase into the organic phase. This is possible since the solvent in the organic phase is an extracting agent dissolved in a diluent. Different extracting agents uses different ways to extract the desired substance. The extraction can be made through three different mechanisms: Acidic, Basic/ Ion pair and Solvating. Acidic extraction is when the organic acid dissociates and the conjugated base reacts with the cation in the solution, forming a neutral complex. During extraction with Basic/ Ion pair an ion pair is formed between the extractant and the metal complex. The mechanism for solvating is the following: The extraction happens when the extracting agent replaces the water molecule in the inner sphere of the metal atom. Presented in Table 5 are the organic extractants and their respective target metal. [67]

Table 5: The target metal for each extractant [1].

Organic extractant	Target metal for extraction	Mechanism
PC-88A	Co from Ni and Li.	Acidic
Cyanex 272	Co and Ni, possible to extract other metals by changing pH.	Acidic
Acorga M5640	Cu, which is regarded as an impurity.	Acidic
D2EHPA	$\text{Fe}^{3+} < \text{Zn}^{2+} < \text{Cu}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Mn}^{2+} < \text{Mg}^{2+} < \text{Ca}^{2+}$	Acidic

Another method for extraction of metals is precipitation. The principle is that the metal ions forms precipitates with ions present in the solvent. Ions used to make precipitations are OH^- , $\text{C}_2\text{O}_4^{2-}$ or CO_3^{2-} [54] because they form insoluble compounds. If one of these ions are present in the solution it can form a precipitate with the valuable metals. The precipitates are hard to solubilize which enables an easy separation from the leaching solution. Precipitation is mainly used in leaching solutions for formation of precipitates containing Al, Cu and Fe [62]. These metals may hinder the extraction of Co making it necessary to remove them. It is common to combine different methods such as solvent extraction and precipitation to increase the yield and purity of the recovered metals from spent LiBs [54].

Once the metals are recovered, they can be sold on the market or reused in batteries or other applications. Cobalt is the metal with the highest value with an estimated price of 31 \$/kg [68]. A chemical characterization of spent LiBs showed that 1kg battery material consisted of 250g Co, 110g Ni, 31g Li and 120g Cu [69].

1.3. Aim and objective

The aim of this thesis project was to obtain a deeper understanding of how efficient hydrogen peroxide is as a reduction agent in a hydrometallurgical recycling process of LiBs and how it influences the kinetics of the leaching for different cathode materials. Several different parameters namely leaching temperature, leaching time and type of battery were examined. To reach the envisioned aim stated above, the specific objectives of this thesis project have been defined as the following:

- Can hydrogen peroxide improve the efficiency of metal dissolution in leaching?
- For which battery composition does hydrogen peroxide increase the recovery of valuable metals the most?
- At which temperature is the recovery of valuable metals the highest?

1.4. Demarcations

This project only investigates seven different cathode materials. These are pure metals oxides with no or a small amount of impurities. There are a variety of lithium-ion batteries with different structures of cathodes, but this thesis focuses on LiCoO_2 , LiNiO_2 , LiMn_2O_4 , mixed NMC from Volvo batteries, NMC 111, NMC 442 and NMC 811. A fixed ratio between solid phase and liquid phase was used. The solid phase was weighted, and the liquid phase was measured by volume. The ratio was S:L 1:100 to fully investigate the effect of H_2O_2 and to minimize effect of the sampling. Furthermore, the hydrometallurgical process is a complex procedure, but this project focuses on the leaching of the metals which is a separate stage in the hydrometallurgical process. Finally, there is only focus on one reducing agent in this project, hydrogen peroxide.

2

Method

This work was performed on different cathode materials. The hydrogen peroxide used was provided by Nouryon Functional Chemicals AB. This chapter presents the methods used in the experimental work of this thesis. It also describes in detail how the samples were prepared for the different analytical methods used to analyze the samples.

2.1. Materials and reagents

The leaching solutions used in this work consisted of aqua regia (3:1 HCl:HNO₃) for characterization studies and sulfuric acid solutions at a specified concentration for the battery leaching process studies. The cathode materials LiCoO₂, LiNiO₂ and LiMn₂O₄ used in this thesis were pure metal oxides in powder form from Sigma-Aldrich. The mixed NMC was provided by Volvo Car Corporation and the composition was analyzed in a licentiate thesis [68] which presented a composition corresponding to NMC 121 and therefore it will be referred to here as NMC 121. NMC 111 and NMC 811 were provided by Fecupral, spol s r.o. (ltd). H₂O₂ (EKA HP C59) was provided by Nouryon Functional Chemicals AB, the product had a concentration of 59% hydrogen peroxide.

2.2. Procedure in hydrometallurgical experiments

2.2.1. Dismantling

For the battery containing NMC 442 a manual dismantling had to be done to extract the cathode material. First the plastic cover was removed before the batteries were immersed in water and CoSO₄*7H₂O for a few days to totally discharge. Thereafter the batteries were cut open and the anode and cathode were separated. The active cathode material was removed from the Aluminum foil by using a scraper and then collected in a plastic beaker.

2.2.2. Leaching

The leaching solution was prepared with Milli-Q water and sulfuric acid (Sigma-Aldrich 95-97% analytical grade). The hydrometallurgical leaching was carried out in plastic beakers which was placed in a water bath inside a large glass beaker. All experiments were performed in triplicates. The water bath was placed on a combined magnetic stirrer and heater (IKA RCT basic). One magnet was placed inside all plastic beakers before the experiments started. 2M sulfuric acid was added into the plastic beakers before they were placed in the water bath with a closed lid. In the case of reductive leaching the hydrogen peroxide was added into the beaker before the solution was heated. The temperature was held at 25°C, 40°C and 60°C respectively. During leaching the condensed water collected on the lid was returned into the beaker to keep the solid-to-liquid ratio as constant as possible.

After 2 minutes when leaching with H₂O₂ and 5 minutes when leaching with acid samples were taken from the plastic beaker, the stirring was stopped 5 seconds before a syringe was used to take the sample. The sampling continued at 5, 10, 20 and 60 minutes when H₂O₂ was used and at 10, 15, 20, 30, 60, 120 and 180 minutes when only acid was used. A filter was used on the syringe to ensure that only liquid was transferred to a 5 ml tube. 100 µl of the solution was pipetted from the 5 ml tube into a 10 ml ICP vial containing 9.9 ml 0.5M nitric acid (Sigma-Aldrich 70%) creating a dilution factor of 100 while the remaining solution was returned to the plastic beaker to decrease the effect of sampling. For ICP measurements further dilutions were necessary, 1 ml from the diluted sample was transferred into a new 10 ml ICP vial containing 9 ml 0.5M nitric acid diluting the sample to a total factor of 1000. A full list of all experiments is presented in Appendix II.

2.3. Determination of metal concentration in leached samples

An iCAP™ 6000 series Inductively Coupled Plasma – Optical Emission spectrometry (ICP-OES) was used to analyze the metal content in the samples to determine the leaching efficiency. Standard solutions, for a calibration curve, containing 0 ppm, 1 ppm, 5ppm, 10 ppm and 20 ppm were prepared for analyzing the following metals: Co, Ni, Mn and Li. The preparation of a standard solution containing 20 ppm of each metal demanded 1 ml of a solution containing 1000 ppm of one metal. To dilute the standard to 20 ppm 0.5M HNO₃ was used. To obtain lower concentration solutions the 20 ppm solution was diluted. The leaching yield was calculated by using equation (d):

$$\text{Leaching efficiency [\%]} = \left(\frac{\left(\frac{(c \text{ (ppm)})}{1000} \right) * V \text{ (ml)}}{m \text{ (g)}} \right) * 100 \quad (d)$$

V is the total volume of the leaching solution, c is the measured concentration of a certain metal in the solution from the ICP-OES and m is the weight of the metal in the sample. Equation (e) is used to calculate m for each metal:

$$m \text{ [g]} = \left(\frac{M(\text{metal})}{M(\text{cathode})} \right) * m_{\text{cathode}} \quad (e)$$

Where M(metal) are the molar mass for the specific metal and M(cathode) the molar mass for the cathode material.

2.4. X-Ray powder Diffraction

After some leaching experiments powder remained in the solution. The solution was filtrated using a Lafil 400 vacuum filtration system with Whatman Grade GF/B filter paper where the insoluble material was collected. The extraction of the powder from the filter started with an immersion of the filter paper in ethanol in a vial. Following the immersion, the vial was shaken for 10 minutes by an ultrasonic shaker. The precipitated powder was dried at room temperature before X-Ray Diffraction (XRD) analysis. The XRD analysis were carried out using a Bruker D8

Advance X-ray diffractometer. The x-ray wavelength used corresponds to the characteristic Cu K α -radiation of 1.5406Å and a 2 θ range from 10° to 90° was included with a step scan of 0.04°. To avoid a preferential orientation of the crystals the sample was rotated with a speed of 15 rpm during the analysis. The database used to analyze the data was PDF-4+ 2019 from The International Centre for Diffraction Data [71].

2.5. Thermodynamic studies

HSC Chemistry 9 developed by Outotec was used to calculate and plot the thermodynamic data for the different cathode materials [72]. The program was used to plot both Pourbaix diagrams and diagrams for the ΔG -energy of the reactions. The data was used to compare the leaching results with the results from the thermodynamic studies.

3

Results and discussion

The main results from the laboratory work are presented in this chapter. Information about how ICP-OES works are presented in Appendix III. The results from the leaching are arranged according to cathode material.

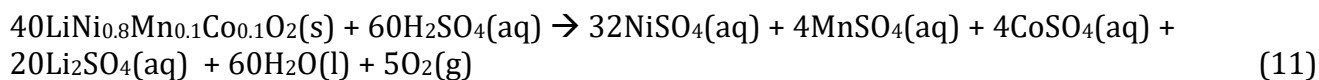
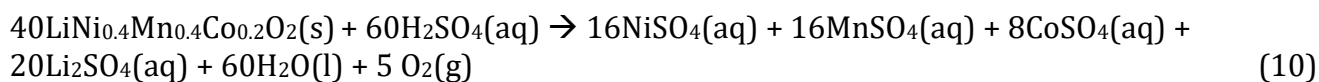
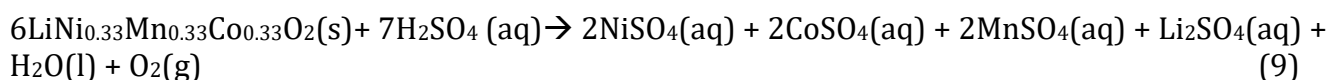
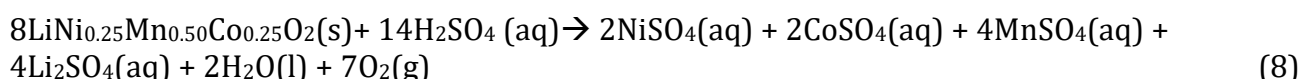
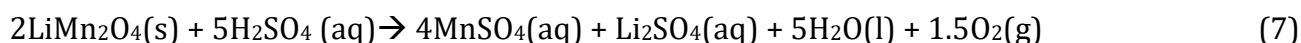
3.1. Thermodynamic studies

In this section the data from HSC Chemistry 9 are presented. First the leaching reactions are presented followed by calculated values for Gibbs free energy and Pourbaix diagrams for the important metals in the cathode materials.

3.1.1. Mechanism of the leaching

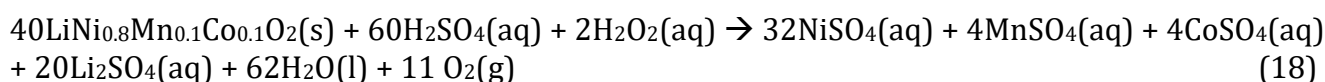
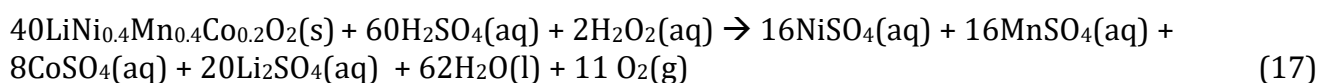
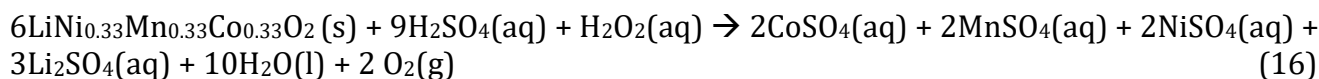
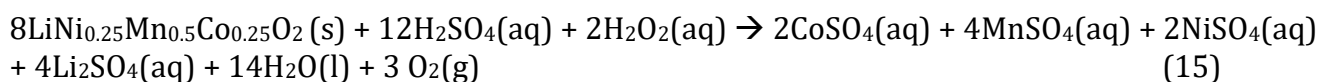
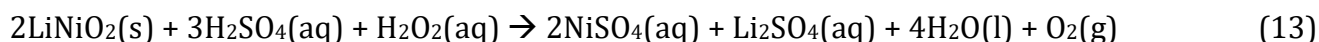
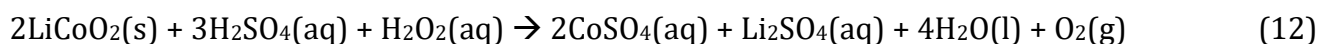
3.1.1.1. *Leaching with 2M H₂SO₄*

Presented in this section are reaction (5)-(11) with the proposed leaching reactions that take place for the different cathode materials when the leaching solution is 2M sulfuric acid. Sulfuric acid reacts with the cathode material to form soluble products of the metal ions. By-products from the reactions are water and oxygen.



3.1.1.2. *Leaching with H₂O₂*

Presented in reaction (12)-(18) are the proposed leaching reactions when hydrogen peroxide is used as a reductive agent in the leaching. An additional factor is that hydrogen peroxide can decompose and form water and oxygen. Sulfuric acids react with the cathode material and hydrogen peroxide is a reductive agent active on the surface of material.



The amount of hydrogen peroxide needed to finish the leaching can be calculated using the ratio between the reagents in each reaction. Table 6 presents how much hydrogen peroxide each reaction need to reach completion calculated based on 0.25g cathode material and 25ml 2M H_2SO_4 . In Appendix IV the data can be reviewed. The volume of hydrogen peroxide in each reaction is very small compared to the total volume of the leaching solution.

Table 6: The calculated volume of hydrogen peroxide necessary to reach a leaching efficiency of 100%.

Cathode	Volume H_2O_2 (ml)
LiCoO₂	0.02969
LiNiO₂	0.02977
LiMn₂O₄	0.02679
NMC 121	0.01516
NMC 111	0.01010
NMC 441	0.003
NMC 811	0.00298

3.1.2. Thermodynamic modeling

A useful way to get insight on how a reaction may occur during the leaching process is by analyzing the thermodynamic equilibrium parameters to investigate if it will happen spontaneously or if it needs a catalyst. In Table 7, Table 8, Table 9 and Table 10 four parameters are presented: the standard Gibbs free energy (ΔG°), the standard enthalpy (ΔH°), the standard entropy (ΔS°) and the rate constant K for leaching with the cathode material. LiCoO_2 and LiMn_2O_4 (estimated) are currently the only cathode materials used in this study available in the database.

The negative values of ΔG° in Table 7 and Table 8 for each reaction indicate that the reactions will proceed naturally in the desired direction to form product. All calculated enthalpies are

negative, therefore the reactions will be exothermic. However, all reactions have negative values for the calculated entropies and will thus move toward a less disordered system.

Table 7: Values of ΔG for chemical reaction of LiCoO_2 in H_2SO_4 at 25-60°C.

Reaction Equation					
$4\text{LiCoO}_2 + 6\text{H}_2\text{SO}_4(\text{l}) = 2\text{Li}_2\text{SO}_4(\text{ia}) + 4\text{CoSO}_4(\text{ia}) + 6\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$					
Reaction Data					
T	ΔH°	ΔS°	ΔG°	K	Log K
°C	kJ	J/K	kJ		
25.000	-920.693	-798.613	-682.586	3.948E+119	119.596
40.000	-934.365	-843.346	-670.272	6.507E+111	111.813
60.000	-953.595	-902.857	-652.808	2.304E+102	102.363

Table 8: Values of ΔG for chemical reaction of LiCoO_2 in H_2SO_4 and hydrogen peroxide at 25-60°C.

Reaction Equation					
$2\text{LiCoO}_2 + 3\text{H}_2\text{SO}_4(\text{l}) + \text{H}_2\text{O}_2(\text{l}) = \text{Li}_2\text{SO}_4(\text{ia}) + 2\text{CoSO}_4(\text{ia}) + 4\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$					
Reaction Data					
T	ΔH°	ΔS°	ΔG°	K	Log K
°C	kJ	J/K	kJ		
25.000	-558.315	-336.403	-458.016	1.775E+080	80.249
40.000	-565.141	-358.736	-452.803	3.433E+075	75.536
60.000	-574.739	-388.440	-445.330	6.750E+069	69.829

From $\Delta G^\circ/T$ diagram in Figure 7, the reaction between LiCoO_2 and sulfuric acid is the preferred reaction, due to that it has the largest negative value on ΔG° .

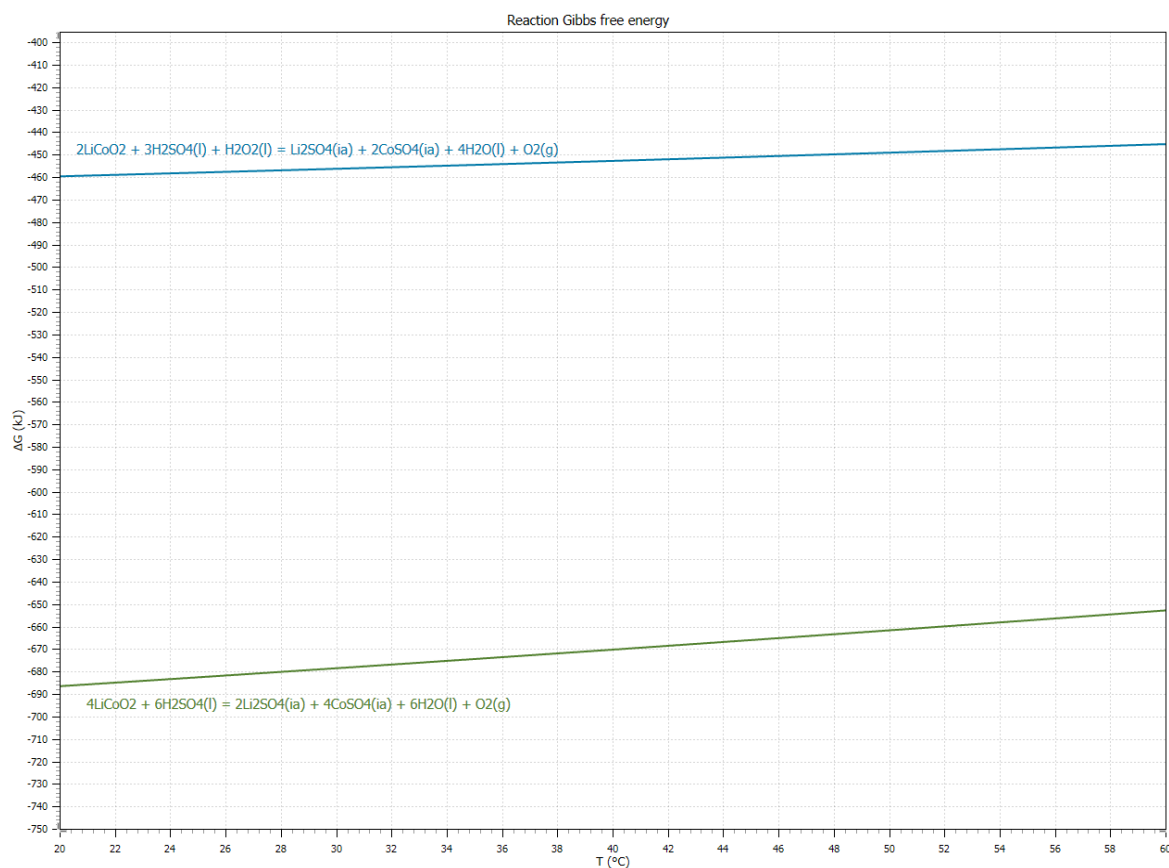
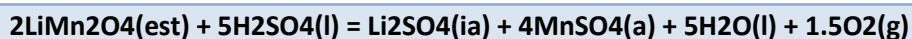


Figure 7: Standard Gibbs free energy changes for the two reactions containing LiCoO_2 .

The ΔG° values in Table 9 and Table 10 are negative for both reactions at the temperatures the leaching is performed at. Therefore, the reactions will happen spontaneously when the cathode is added into the leaching solution. The reactions are exothermic since the ΔH° values are negative. The change in Gibbs free energy due to the reaction in the acid solution containing hydrogen peroxide has significant more negative values than the change in Gibbs free energy due to the reaction without hydrogen peroxide.

Table 9: Values of ΔG for chemical reaction of LiMn_2O_4 in H_2SO_4 at 25-60°C.

Reaction Equation



Reaction Data					
T	ΔH°	ΔS°	ΔG°	K	Log K
°C	kJ	J/K	kJ		
25.000	-497.885	-280.025	-414.396	4.042E+072	72.607
40.000	-508.557	-314.958	-409.928	2.417E+068	68.383
60.000	-521.945	-356.411	-403.206	1.675E+063	63.224

Table 10: Values of ΔG for chemical reaction of LiMn_2O_4 in H_2SO_4 and hydrogen peroxide at 25-60°C.

Reaction Equation



Reaction Data					
T	ΔH°	ΔS°	ΔG°	K	Log K
°C	kJ	J/K	kJ		
25.000	-1983.497	-525.558	-1826.802	1.000E+308	308.000
40.000	-2015.462	-630.192	-1818.118	1.971E+303	303.295
60.000	-2055.540	-754.290	-1804.249	8.171E+282	282.912

Figure 8 shows how ΔG° change over a temperature span from 25°C - 60°C. The reaction with the solution containing hydrogen peroxide is favored as it has the lowest ΔG° value.

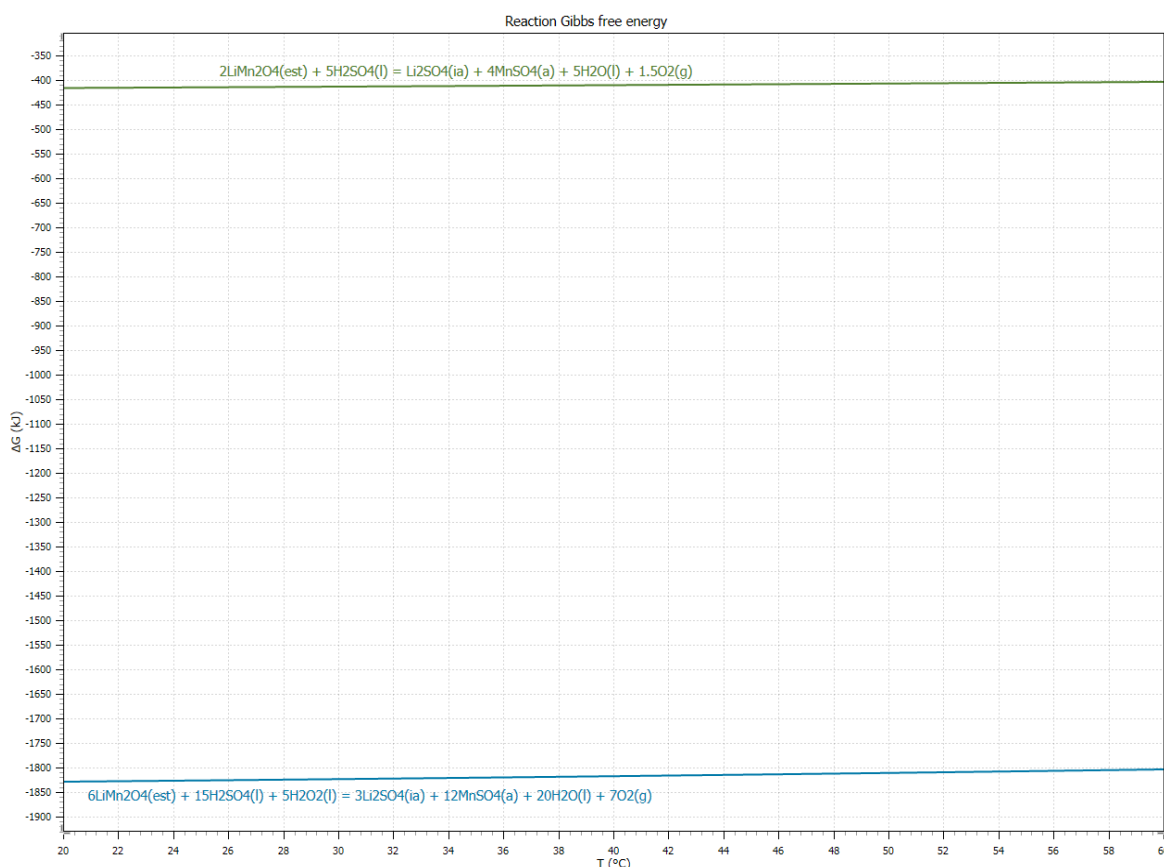


Figure 8: Standard Gibbs free energy changes for the two reactions containing LiMn_2O_4 .

In Figure 9, Figure 10, Figure 11, Figure 12 the speciation of the leached metal ion can be predicted using the Pourbaix diagrams, showing which form of the metal ion will be present at a specific point. The pH in 2M H_2SO_4 is -0.3 and the potential was measured to be 663 mV. When hydrogen peroxide was added the potential dropped to 637 mV. The species of each metal in the leach solutions are Co^{2+} , Mn^{2+} , Li^+ and Ni^{2+} .

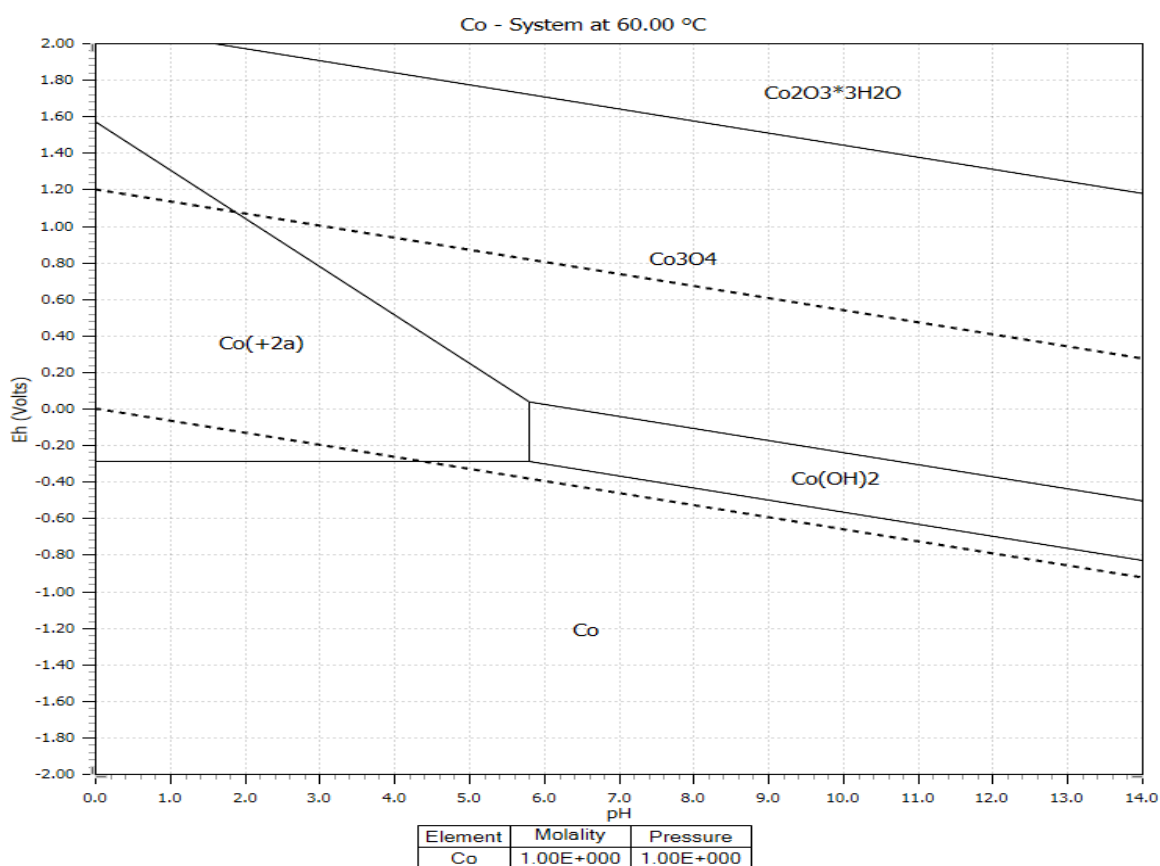


Figure 9: Pourbaix diagram for Cobalt-H₂O system at 60°C.

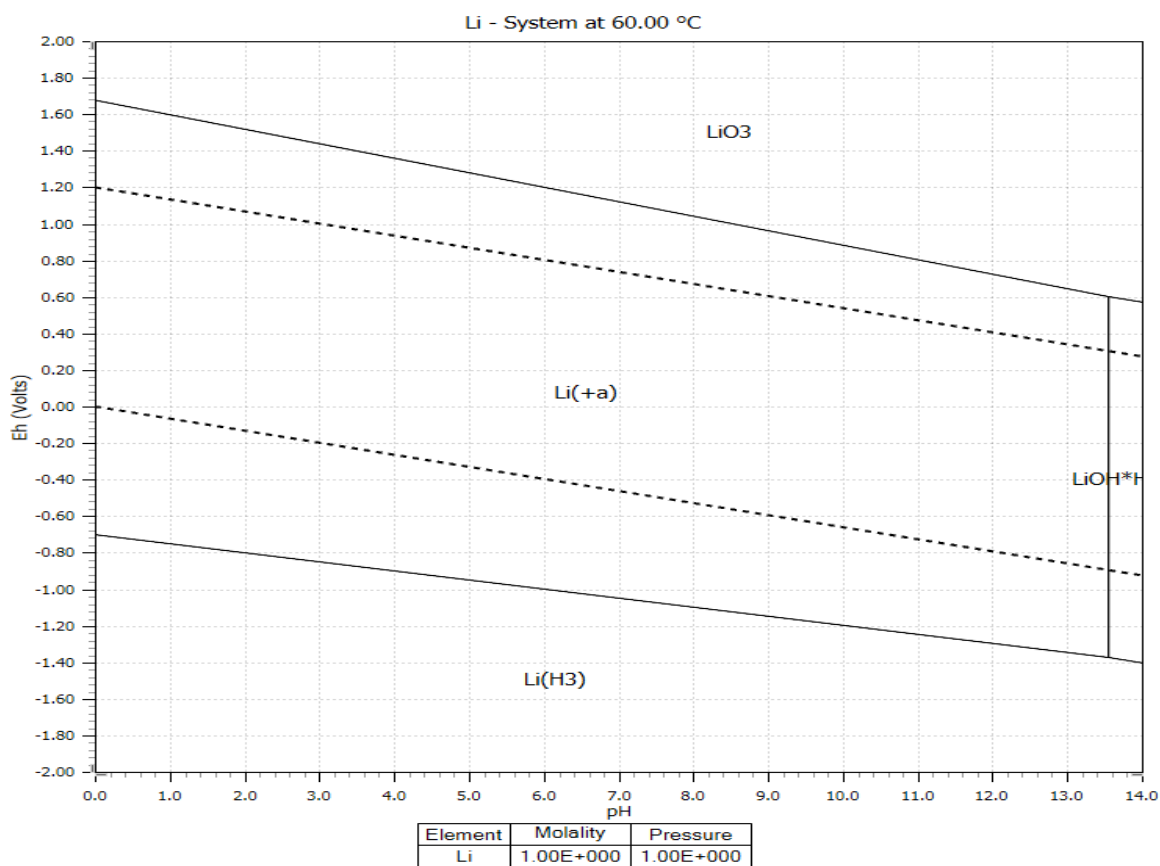


Figure 10: Pourbaix diagram for Lithium-H₂O system at 60°C.

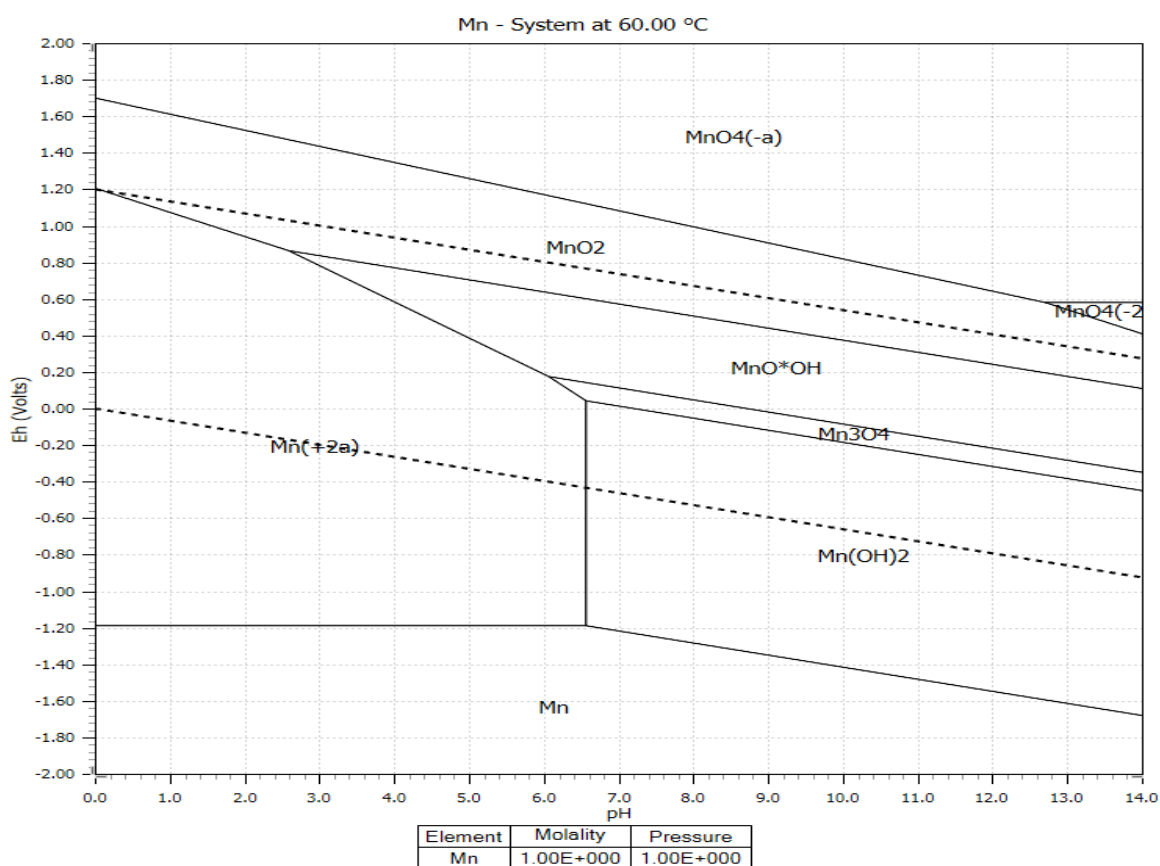


Figure 11: Pourbaix diagram for Manganese-H₂O system at 60°C.

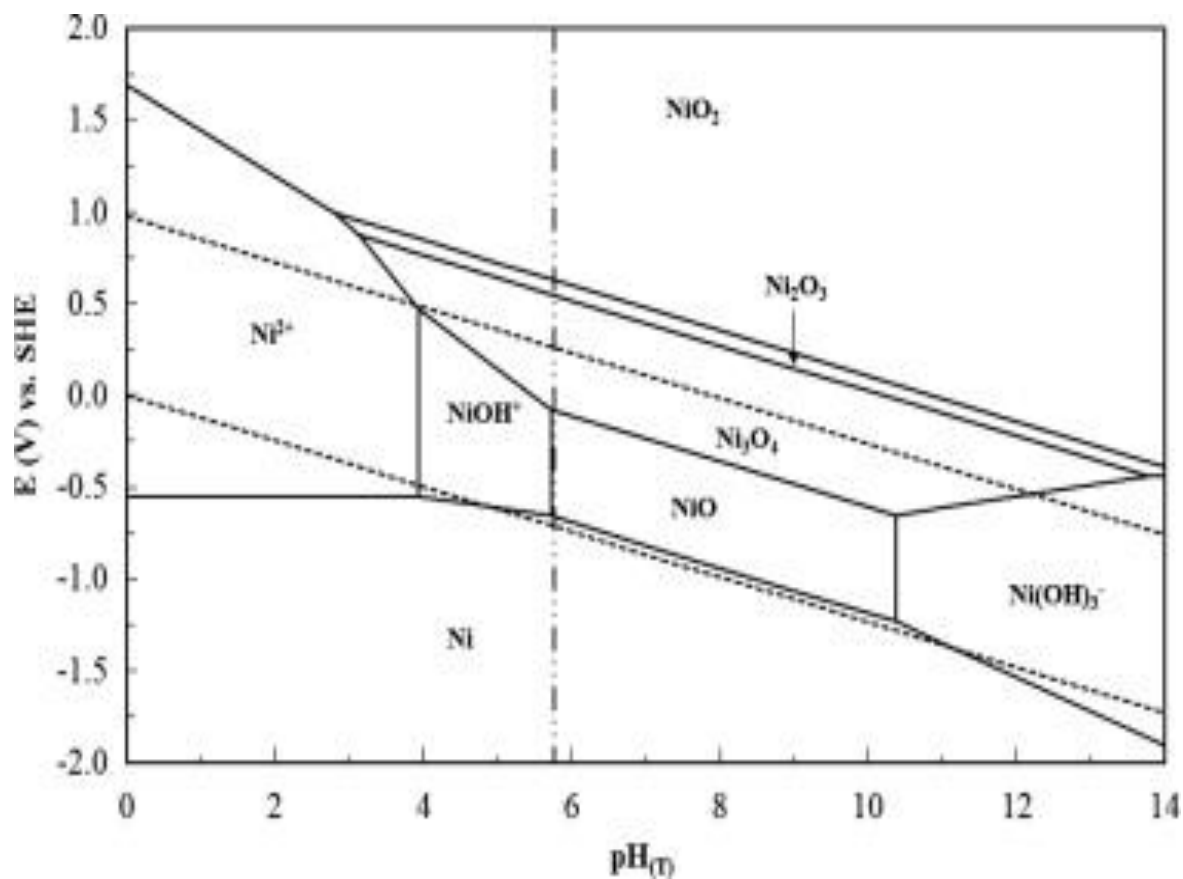


Figure 12: Pourbaix diagram for Nickel-H₂O system at 60°C. [73]

In Figures 9-12 the desired oxidation state of each metal were presented according to pH and potential of the leach solutions. Presented in Table 11 are the oxidation state of each metal in a specific cathode material. These are the oxidation state when the metal oxide powder is introduced in the leach solution.

Table 11: Oxidation state of each metal in different cathode materials.

Cathode	Li	Co	Ni	Mn	O
LiCoO ₂	+1	+3			-2
LiNiO ₂	+1		+3		-2
LiMn ₂ O ₄	+1			+3/+4	-2
LiNi _{1-y-z} Mn _y Co _z O ₂ [74]	+1	+3	+2	+4	-2

3.2. Leaching of LiCoO₂

3.2.1. 2M H₂SO₄ – no addition of H₂O₂

In Figure 13 and Figure 14 the leaching efficiencies measured in percent are presented from 0-180 minutes. All points represent the average from a triplicate of samples with the standard deviation plotted for each point. Figure 13 shows the leaching efficiency for cobalt. Figure 14 presents the leaching efficiency for lithium.

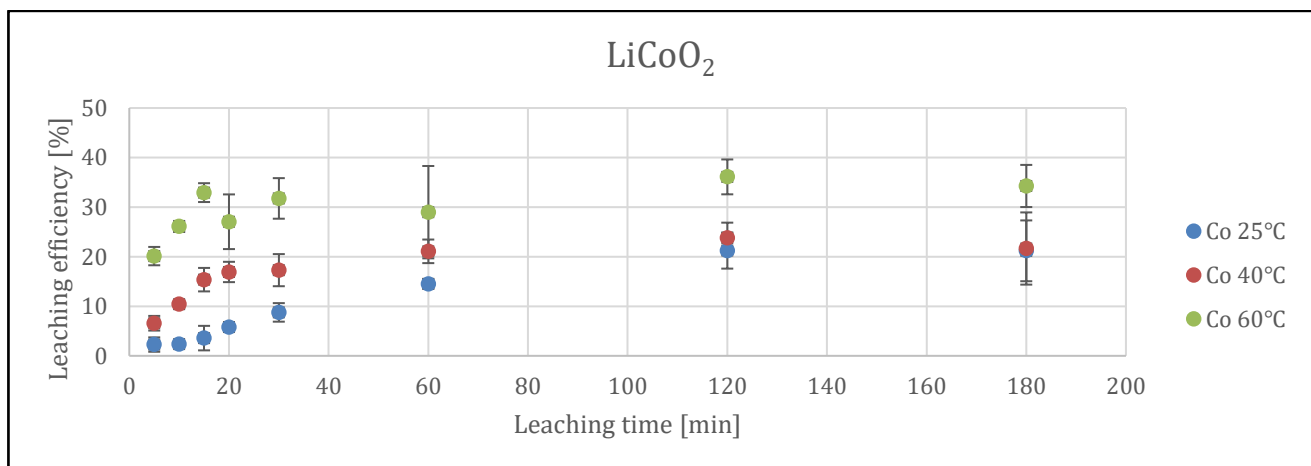


Figure 13: Leaching of LiCoO₂. Kinetic curves of cobalt leaching in percent plotted against time.

The leaching curves presented in Figure 13 show that the maximum leaching yields for all temperatures used are reached at 120 minutes. After 120 minutes the leaching yield was ca 35% at 60°C. The leaching efficiency are visibly highest at 60°C. Generally, the leaching of Co reaches lower values compared to the leaching of Li. The point at 60 minutes for 60°C shows a rather high standard deviation since one of the samples had considerably lower amount of cobalt in the solution due to heterogeneous character of the sample.

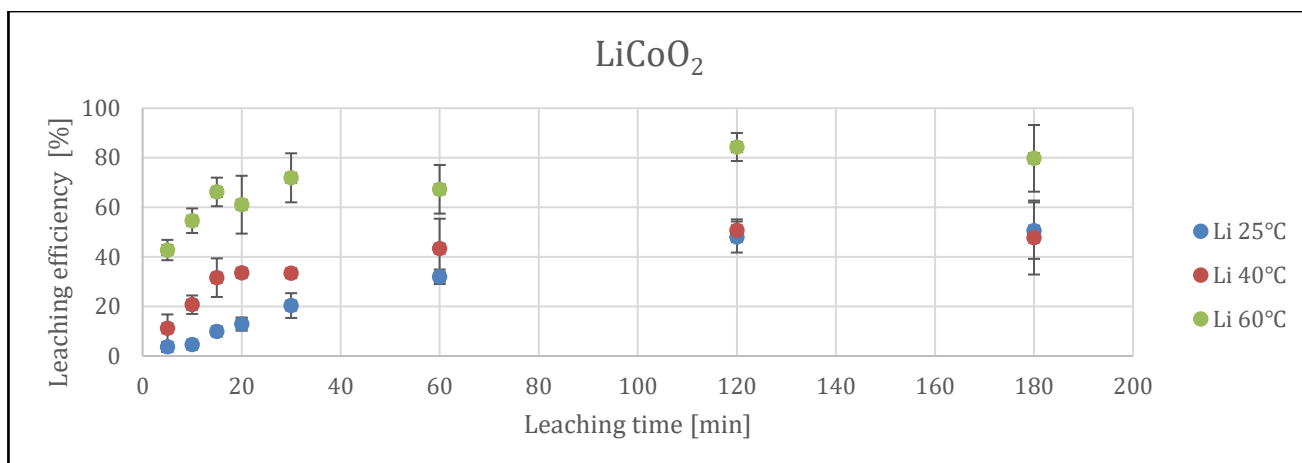


Figure 14: Leaching of LiCoO₂. Kinetic curves of lithium leaching in percent plotted against time.

After 60 minutes the leaching efficiency has reached its maximum value for all three temperatures in Figure 14. A clear increase in leaching efficiency can be seen when the temperature is increased with the highest leaching efficiency at 60 °C.

3.2.2. 2M H₂SO₄ with addition of H₂O₂

Figure 15 A-C and Figure 16 A-C shows the kinetic curves for leaching of cobalt and lithium. Included in each Figure is the corresponding kinetic curve for leaching without a reductive agent for a direct comparison between the leaching efficiencies. As before all the points represent the average from a triplicate of samples and the standard deviation is visible for every point. The leaching with hydrogen peroxide was only done for 60 minutes since the leaching reached 100% in that time span.

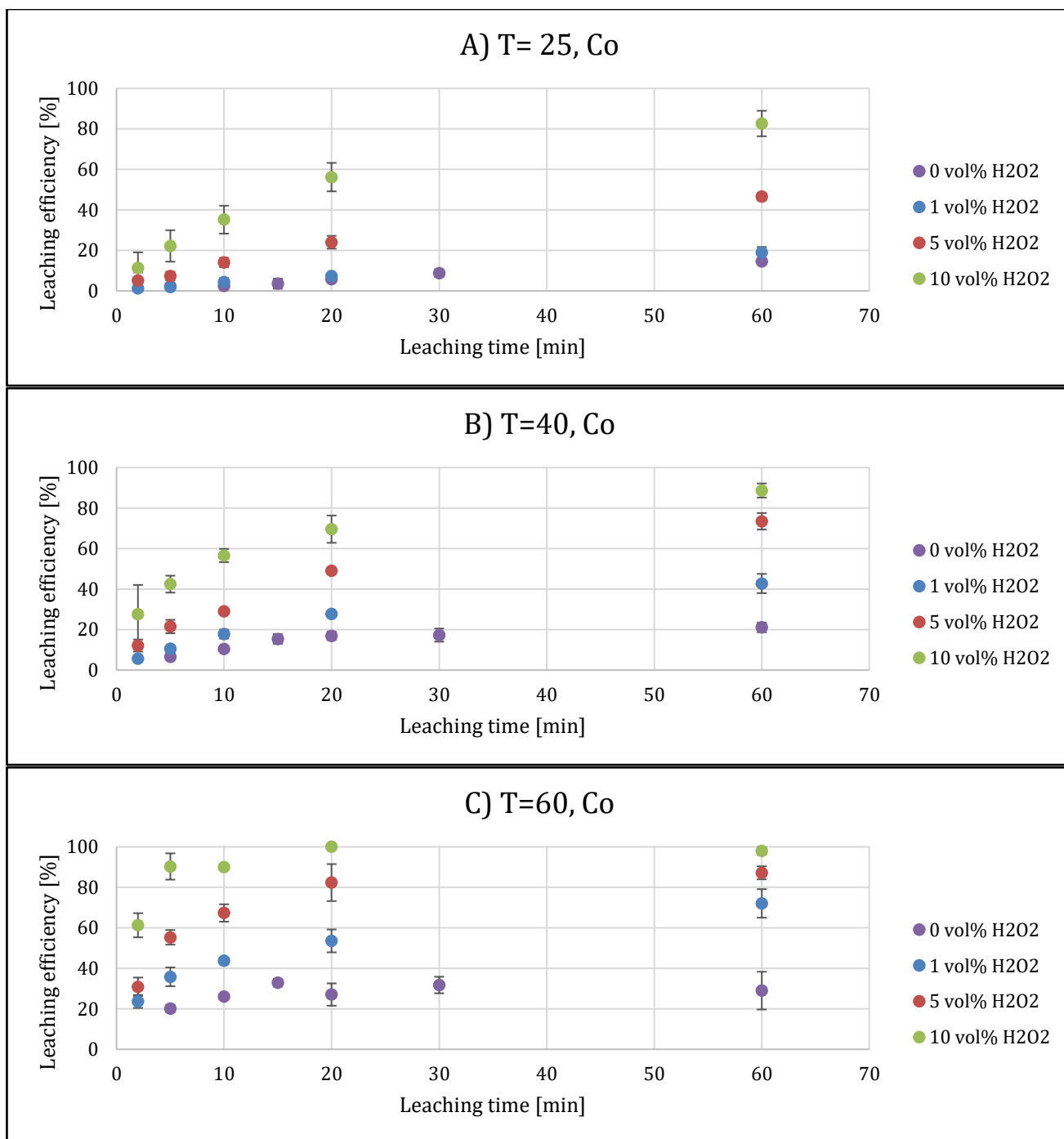


Figure 15: Leaching of LiCoO_2 . Kinetic curves for cobalt leaching at 25°C. B) Kinetic curves for cobalt leaching at 40°C. C) Kinetic curves for cobalt leaching at 60°C.

The effect of hydrogen peroxide is visible in Figure 15 A) as it improves the leaching efficiency compared to leaching without hydrogen peroxide. A clear pattern can be seen, the leaching yield improves as the volume of hydrogen peroxide increases. The kinetic curves for 1 vol% H_2O_2 and leaching with only acid are similar up to 60 minutes where the leaching with H_2O_2 was stopped. In Figure 15 B) the kinetic curves for leaching at 40°C with H_2O_2 shows faster and more efficient leaching compared to leaching with just acid. When the amount of H_2O_2 is increased the leaching efficiency follows the same pattern as leaching in 25°C, 10 vol% displays the highest leaching yield.

Figure 15 C) shows that all cobalt is leached when 10 vol% H_2O_2 is used in the leach solution. As before leaching with hydrogen peroxide shows superior leaching efficiency compared to leaching with just acid.

The addition of hydrogen peroxide has improved the leaching of LiCoO_2 considerably. The kinetic curves for leaching of cobalt all show better efficiency than without a reductive agent. In 60°C all cobalt is leached when 10 vol% hydrogen peroxide is used. In section 3.1.2 the oxidation state of cobalt was determined to be +3 when LiCoO_2 is in powder form. However, the desired oxidation state is the one in Figure 9 which is +2. Hydrogen peroxide has accomplished a reduction in oxidation state from +3 to +2 for cobalt and completed the leaching.

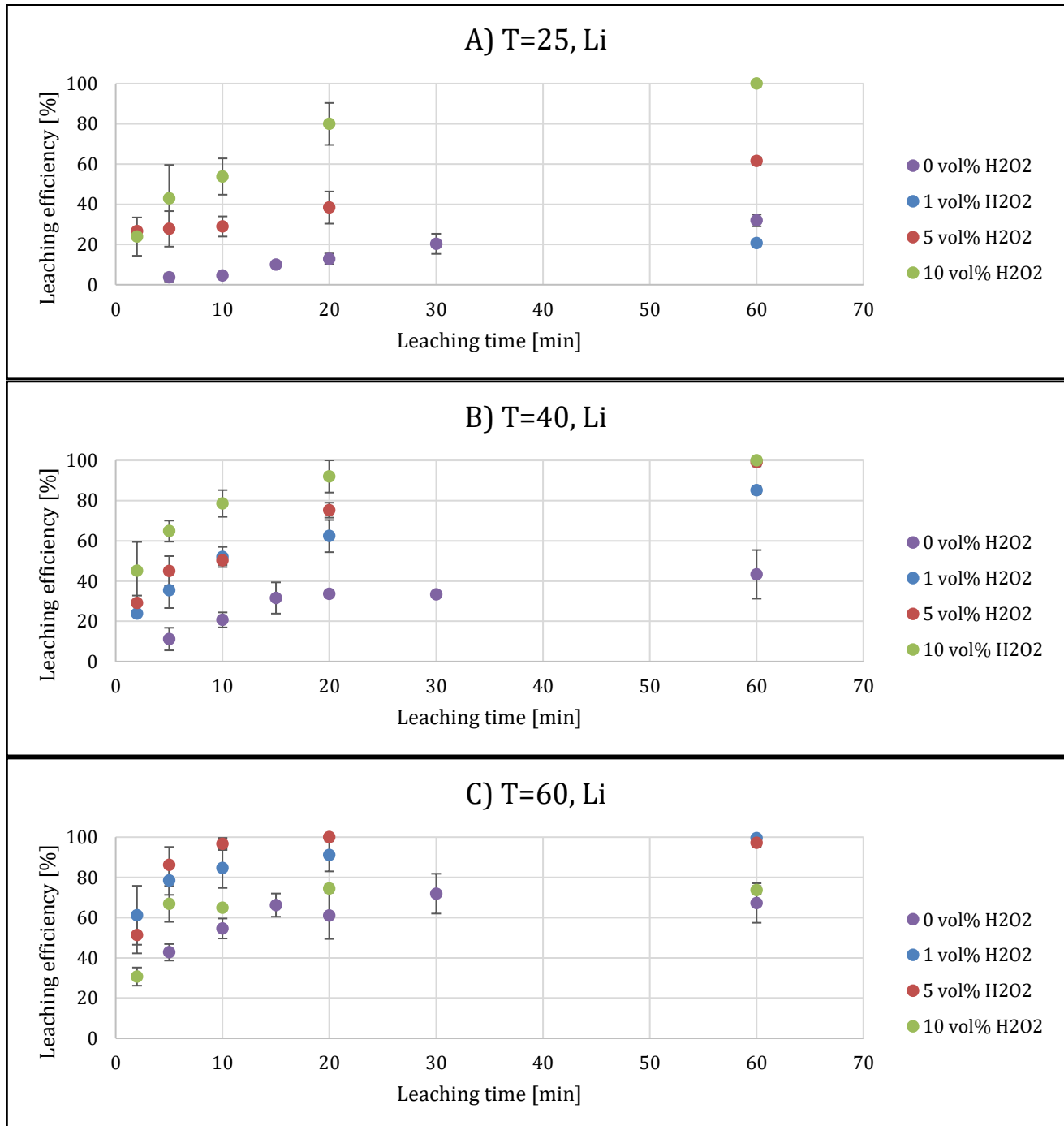


Figure 16: Leaching of LiCoO_2 . A) Kinetic curves for lithium leaching at 25°C . B) Kinetic curves for lithium leaching at 40°C . C) Kinetic curves for lithium leaching at 60°C .

As can be seen in Figure 16 A) the leaching efficiency for lithium reaches 100% within an hour when 10 vol% H₂O₂ is added to the leaching solution. For the sample where 1 vol% H₂O₂ was used the ICP-OES had trouble measuring the lithium content and therefore only one point is available. The single point is showing lower leaching efficiency compared to leaching with only acid in the same time frame.

Figure 16 B) shows that the kinetic curve for all samples containing hydrogen peroxide has increased leaching efficiency compared to leaching without a reductive agent.

The kinetic curves in Figure 16 C) show a decrease in the leaching efficiency for 10 vol% H₂O₂ which display similar efficiency as leaching with no reductive agent. As for leaching with 1- and 5 vol% H₂O₂ they both reach 100% efficiency, with 5 vol% reaching it under 20 minutes.

Visible in Figure 10 is that lithium is monovalent, and it does not change oxidation state during the leaching with hydrogen peroxide. The addition of hydrogen peroxide still increases the leaching efficiency in the investigated temperature range. This is an effect of the increased leaching of cobalt. The structure of the metal oxide powder is changed when the cobalt is leached making liberation of lithium from the structure itself easier.

3.3. Leaching of LiNiO₂

3.3.1. 2M H₂SO₄ – no addition of H₂O₂

In Figure 17 and Figure 18 the leaching efficiency for LiNiO₂ are presented. The points are the average from a triplicate of samples with the respective standard deviation presented at each point. Figure 17 present the leaching efficiency for nickel. Figure 18 displays the leaching efficiency for lithium.

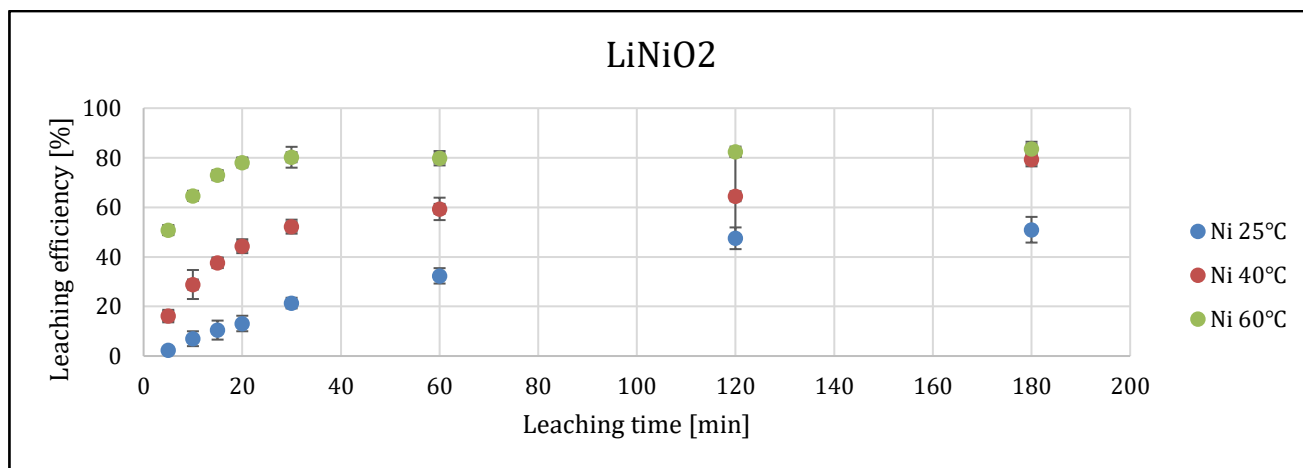


Figure 17: Leaching of LiNiO₂. Kinetic curves of nickel leaching in percent plotted against time.

For nickel the leaching efficiency increases throughout the experiment for 25°C and 40°C. However, the percentage of which the leaching efficiency increases slows down after 60 minutes. The leaching efficiency for 60°C reaches a plateau after 30 minutes with only small improvements to the leaching efficiency from that point.

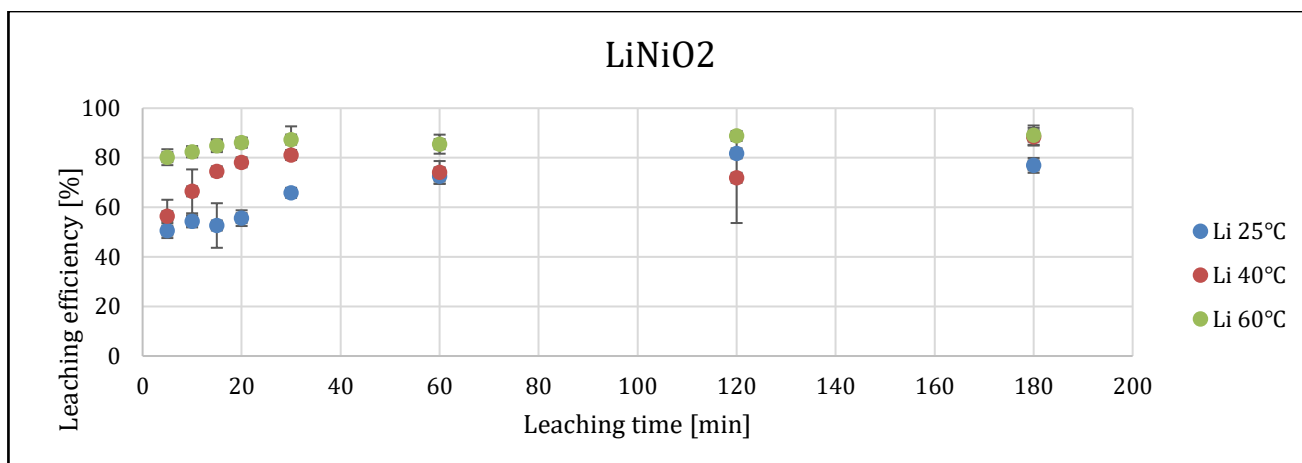


Figure 18: Leaching of LiNiO₂. Kinetic curves of lithium leaching in percent plotted against time.

For the samples in 25°C the leaching efficiency increases during the first 120 minutes before it decreases in the end. The leaching efficiency for 40°C increases under the first 30 minutes and thereafter it does not increase before the last measurement. For 60°C the leaching efficiency is high from the beginning with only an increase under the first 30 minutes before it reaches a plateau.

3.3.2. 2M H₂SO₄ with addition of H₂O₂

Figure 19 A-C and Figure 20 A-C shows the kinetic curves for leaching of nickel and lithium. The leaching with hydrogen peroxide was only done for 60 minutes since equilibrium was achieved at a shorter time compared to leaching with no addition of hydrogen peroxide. Every figure has an additional kinetic curve for 0 vol% H₂O₂ for a direct comparison between leaching with and without H₂O₂.

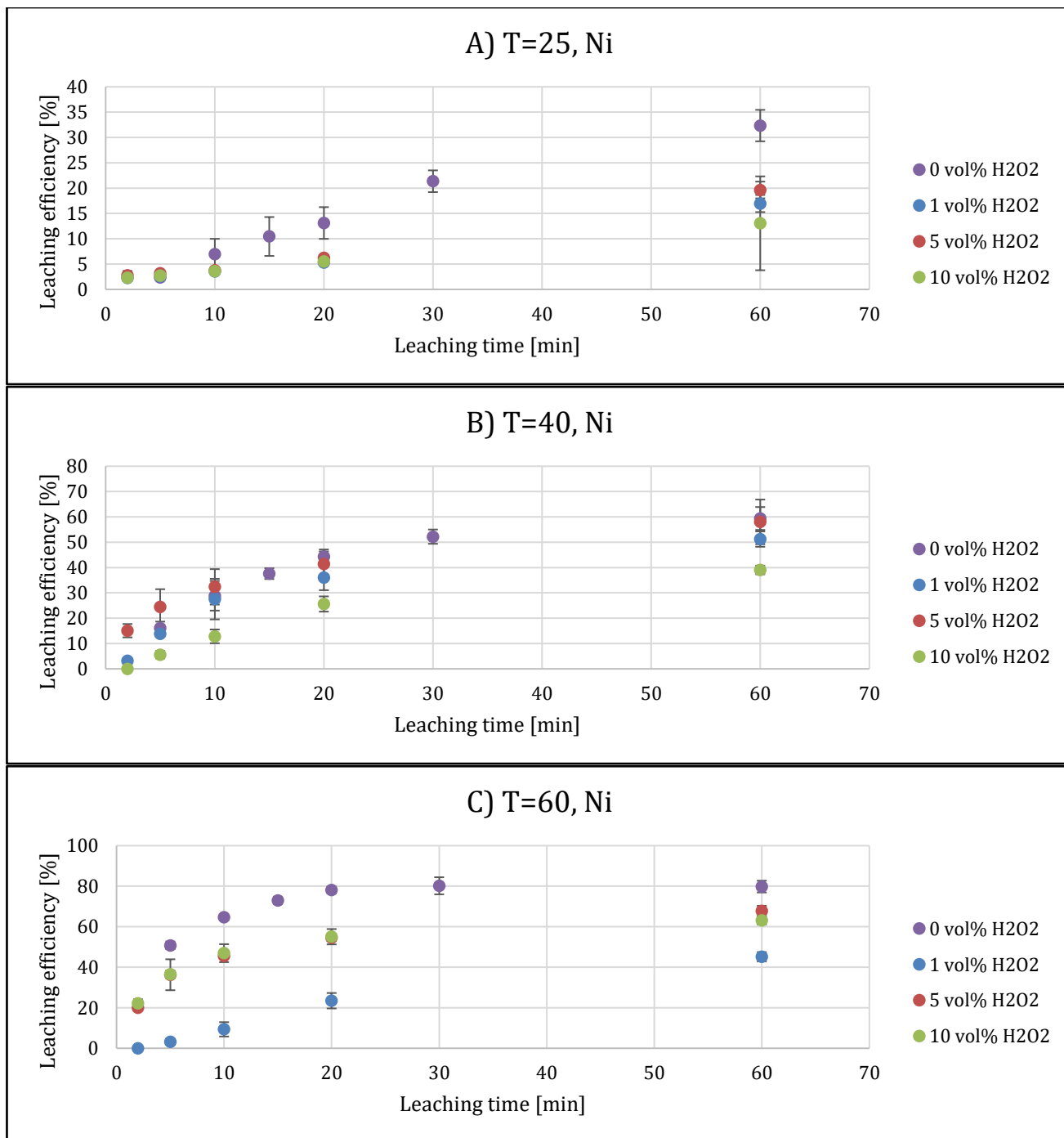


Figure 19: Leaching of LiNiO₂. A) Kinetic curves for nickel leaching at 25°C. B) Kinetic curves for nickel leaching at 40°C. C) Kinetic curves for nickel leaching at 60°C.

For all temperatures leaching with 0 vol% H₂O₂ has the best recovery rate of nickel and best leaching yield of nickel. The kinetic curves in Figure 19 A) shows that in 25°C all samples containing hydrogen peroxide have lower efficiency but only small differences between them before 60 minutes of leaching where they are separated by 6% leaching efficiency. In Figure 19 B) the kinetic curve for 5 vol% H₂O₂ follows the curve for 0 vol% closely while the curve for 1 vol% displays a slightly lower yield and 10 vol% has the lowest effectiveness. When leaching in 60°C the solutions with 5- and 10 vol% hydrogen peroxide has similar kinetic curves until 60 minutes as presented in Figure 19 C). The solution containing 1 vol% H₂O₂ has the lowest leaching efficiency which is significantly lower compared to the other kinetic curves.

The leaching efficiency of nickel is decreased when hydrogen peroxide is used. This is clearly visible at 25°C and 60°C where 0 vol% hydrogen peroxide has significantly better efficiency. At 40°C the solutions with hydrogen peroxide have efficiencies closer to 0 vol% but they do not reach the same yield as leaching without hydrogen peroxide. Sulfuric acid is more efficient changing the oxidation state of nickel from +3 to +2. This is the only cathode material where hydrogen peroxide does not improve the leaching efficiency.

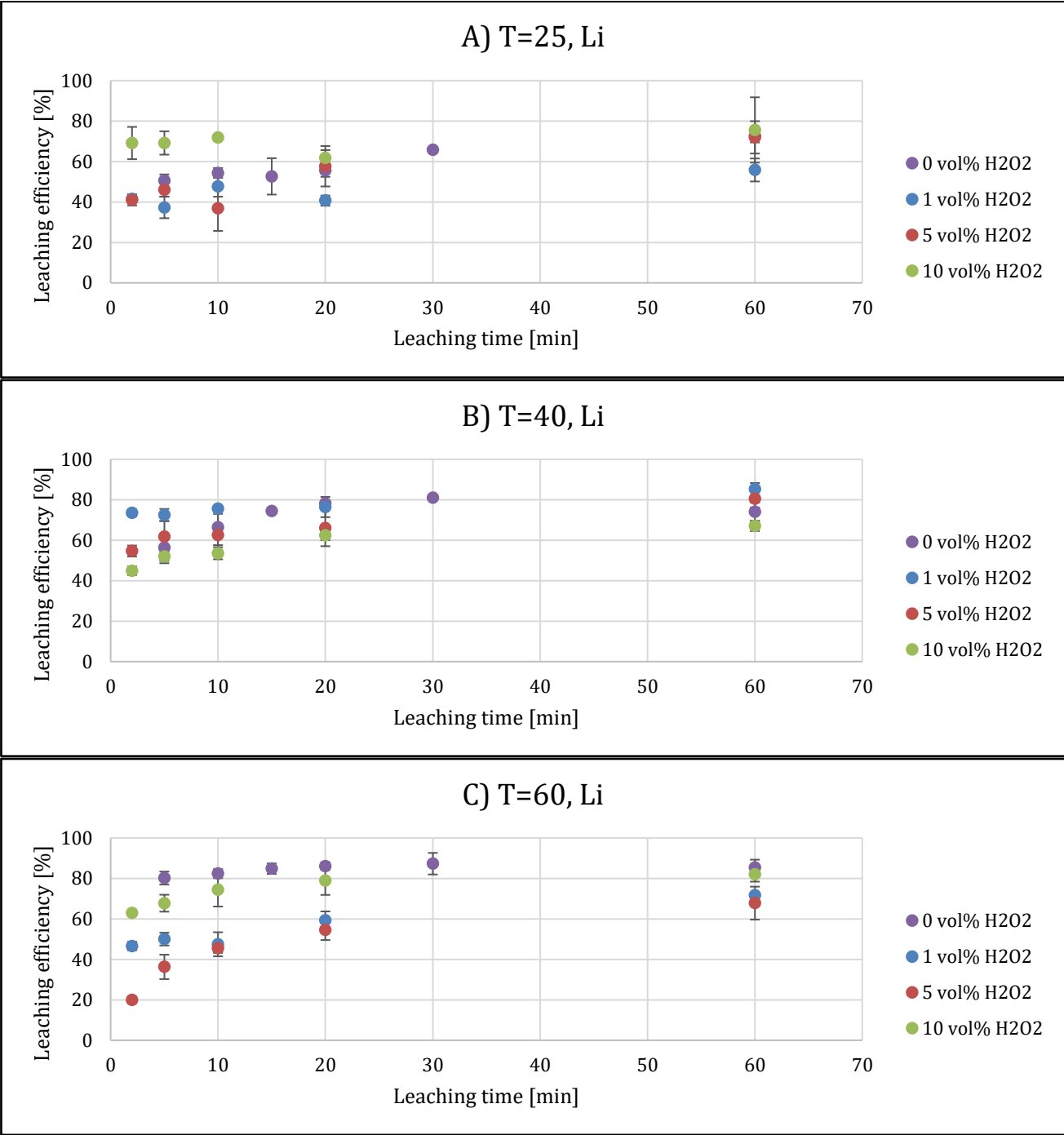


Figure 20: Leaching of LiNiO₂. A) Kinetic curves for lithium leaching at 25°C. B) Kinetic curves for lithium leaching at 40°C. C) Kinetic curves for lithium leaching at 60°C.

Leaching with 1- and 5 vol% hydrogen peroxide in 25°C has lower efficiency compared to leaching with 0% H₂O₂ as can be seen in Figure 20 A). The solution containing 10 vol% H₂O₂

reaches a high leaching efficiency from the beginning but only improves marginally from the 2-minute mark to the 60-minute mark.

Figure 20 B) shows that the solutions with 1- and 5 vol% hydrogen peroxide have a higher leaching yield compared to 10 vol% hydrogen peroxide. The leaching efficiency for 0 vol% H_2O_2 are in the middle of the solutions containing hydrogen peroxide.

Figure 20 C) shows that leaching in 60°C with 0 vol% hydrogen peroxide is the most effective way to form Li_2SO_4 , with a leaching efficiency of 80% after 2 minutes. Of the solutions containing H_2O_2 , the one with 10 vol% displays the best kinetic curve.

The effect of hydrogen peroxide on leaching of lithium from LiNiO_2 is small and shows a minor improvement of efficiency at 25°C and 40°C . The sulfuric acid is more efficient to use if lithium is to be leached from LiNiO_2 at 60°C . For LiNiO_2 the leaching of nickel is not improved by hydrogen peroxide and a consequence leaching of lithium does not improve either.

3.3.3. XRD analysis of solid residue

The addition of hydrogen peroxide had the opposite effect from what was expected so the residue after the leaching was investigated further. The XRD data of the solid residue from the sample leached with 10 vol% H_2O_2 in 60°C is shown in Figure 21. The figure contains multiple peaks but after analyzing with the database PDF-4+ 2019 the peaks were matched to two different compounds, Nickel Oxide and Lithium Nickel Oxide. The respective peaks for these two compounds are shown in Figure 22 and Figure 23.

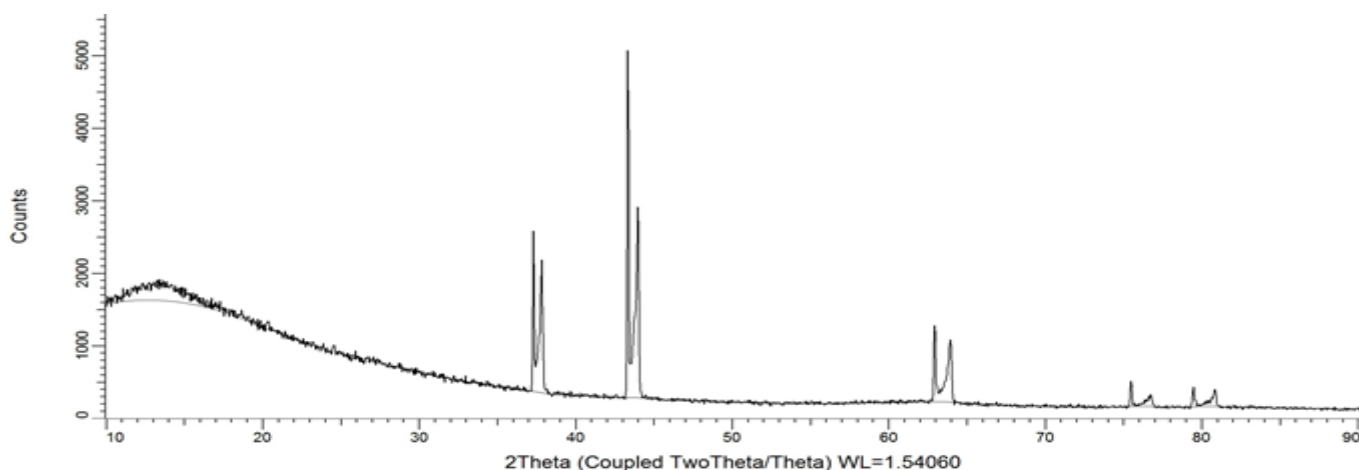


Figure 21: XRD analysis from the remaining powder after leaching of LiNiO_2 .

The red peaks in Figure 22 represent $\text{Li}_{0.55}\text{Ni}_{1.45}\text{O}_2$. The peaks from the analyzed samples fit with $\text{Li}_{0.55}\text{Ni}_{1.45}\text{O}_2$. The crystals have a rock-salt structure with Face-Centered Cubic (FCC) unit cells. The ratio of nickel and lithium is changed compared to the pure cathode material highlighting how extraction of lithium is easier from the material. Since not all cathode material is leached the residue was expected to contain some form of LiNiO_2 .

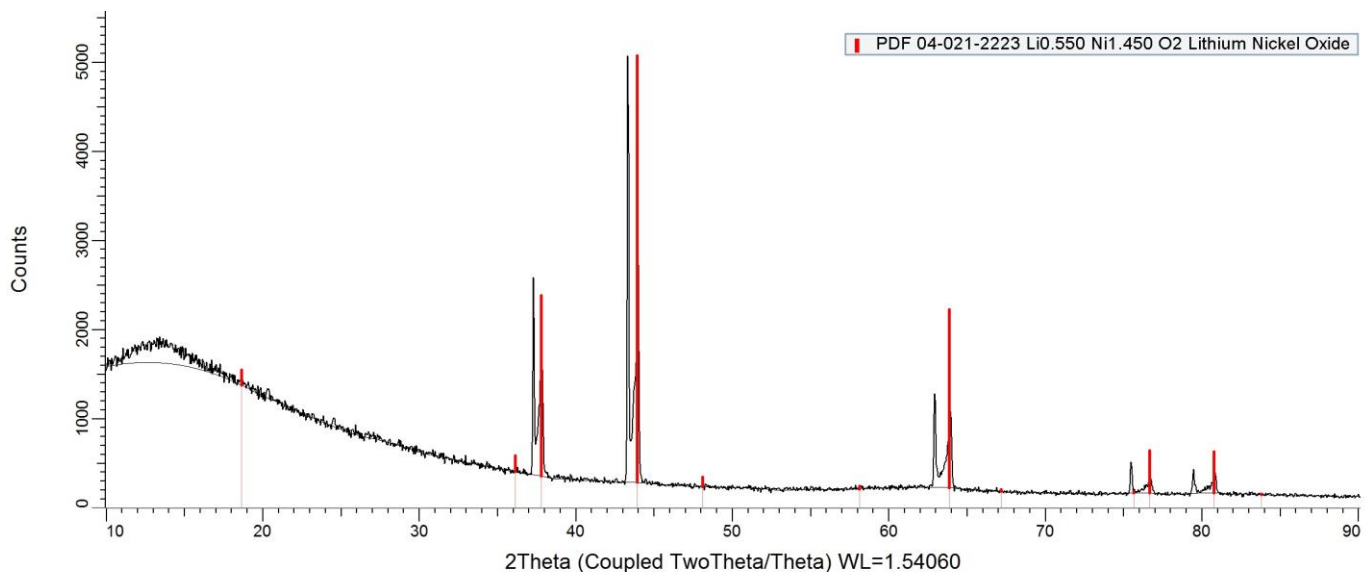
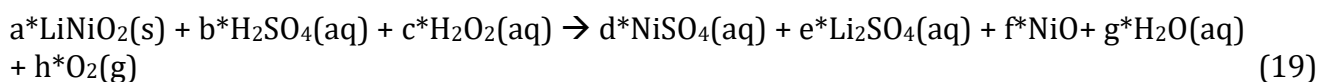


Figure 22: The corresponding peaks for LiNiO₂ marked in the XRD data.

The blue peaks in Figure 23 represent synthetically made NiO. The data from the sample fits well with the peaks for NiO from the PDF-4+ 2019 database. The crystals are organized in an FCC unit cell for nickel oxide. The presence of NiO in the residue was unanticipated but it showed what happened to the nickel ions during leaching with hydrogen peroxide. According to Figure 12 NiO is the favored form of nickel when pH 6-10 and the potential -0.5V-0.0V. The pH is very unlikely to change from pH 0 to pH 6 when the S:L values are small and there is excess amount of acid in the system making a change in potential more likely. One possible explanation is that a protective layer forms around some nickel ions and change the pH for it. Nickel is reduced by hydrogen peroxide, but it does not follow the proposed reaction (13) for the leaching. Therefore, a new reaction has to be suggested for the leaching. Reaction (19) show the new proposed reaction. However, the stoichiometric coefficients are unknown.



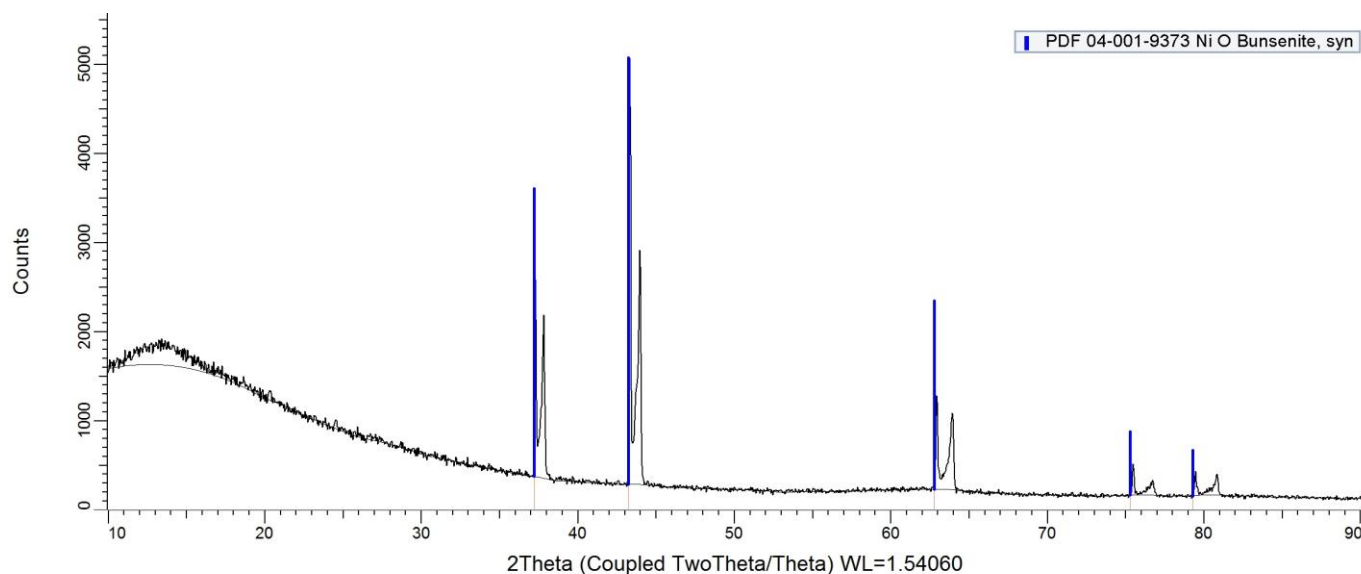


Figure 23: The corresponding peaks for NiO marked in the XRD data.

3.4. Leaching of LiMn_2O_4

3.4.1. 2M H_2SO_4 – no addition of H_2O_2

Figure 24 and Figure 25 shows the kinetic curves for leaching of manganese and lithium. All points represent an average from three samples with the standard deviation visible.

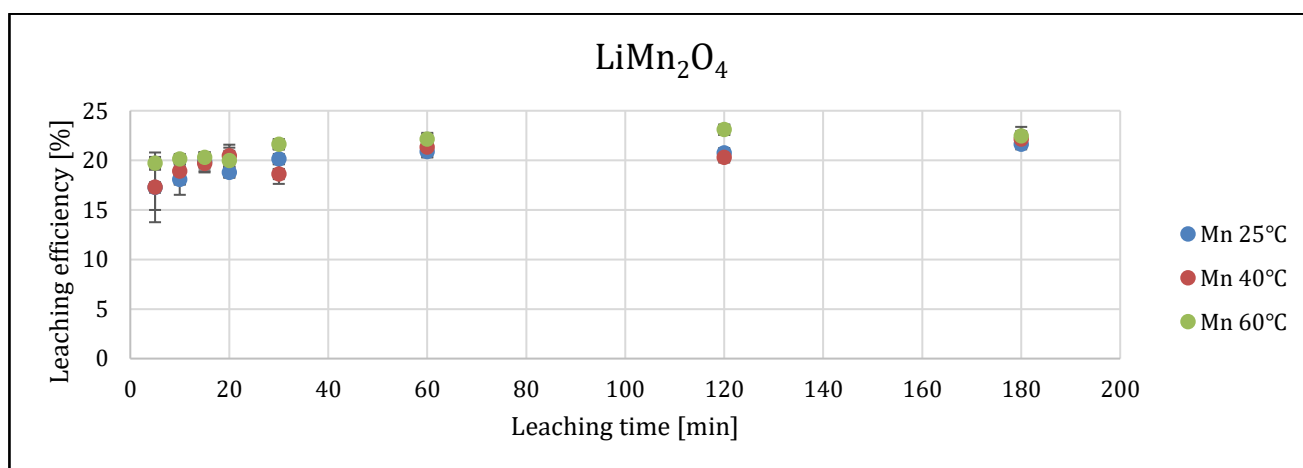


Figure 24: Leaching of LiMn_2O_4 . Kinetic curves of manganese leaching in percent plotted against time.

The leaching efficiency for manganese is almost unaffected by leaching time and an increase in temperature as shown in Figure 24. There are only small differences between the leaching efficiency at 5 minutes and 180 minutes for all temperatures.

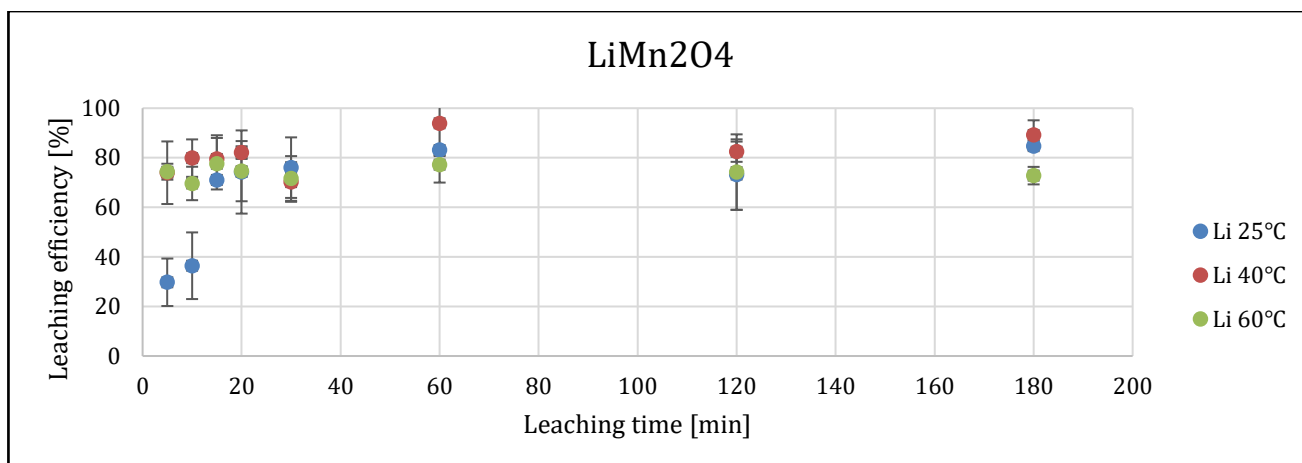


Figure 25: Leaching of LiMn_2O_4 . The kinetic curves of lithium leaching in percent plotted against time.

Figure 25 shows the leaching of lithium from LiMn_2O_4 which reaches its highest efficiency after 15 minutes in both 25°C and 60°C. In 40°C it takes 60 minutes before the peak is reached. There are no significant improvements during the leaching time when leaching in 60°C, for 25°C and 40°C there are improvements during the first 60 minutes of leaching.

3.4.1. 2M H_2SO_4 with addition of H_2O_2

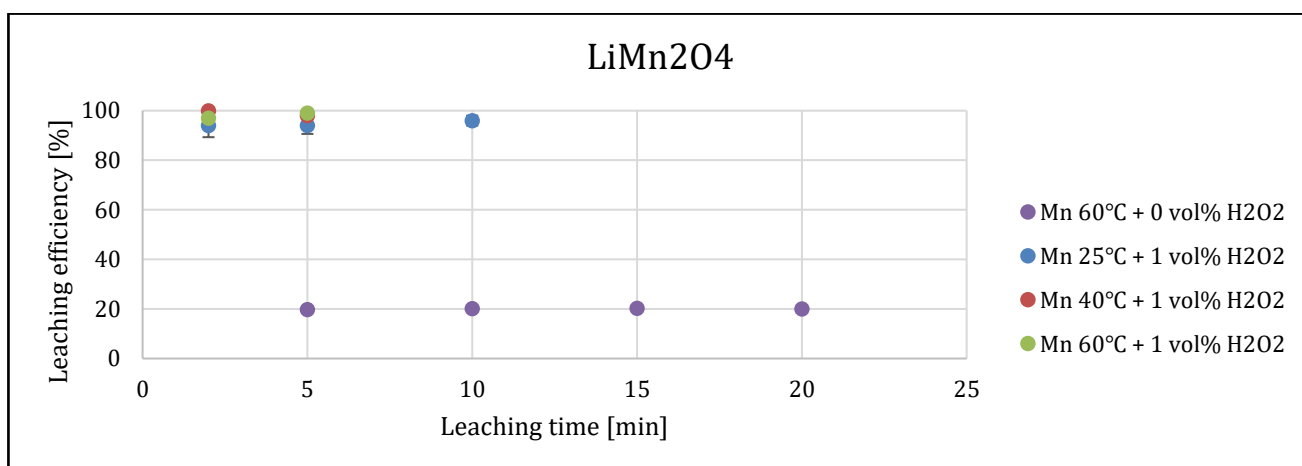


Figure 26 and Figure 27 shows the kinetic curves for leaching of manganese and lithium from LiMn_2O_4 . The leaching with hydrogen peroxide was only done for 10 minutes since equilibrium was achieved at a shorter time compared to leaching with no addition of hydrogen peroxide.

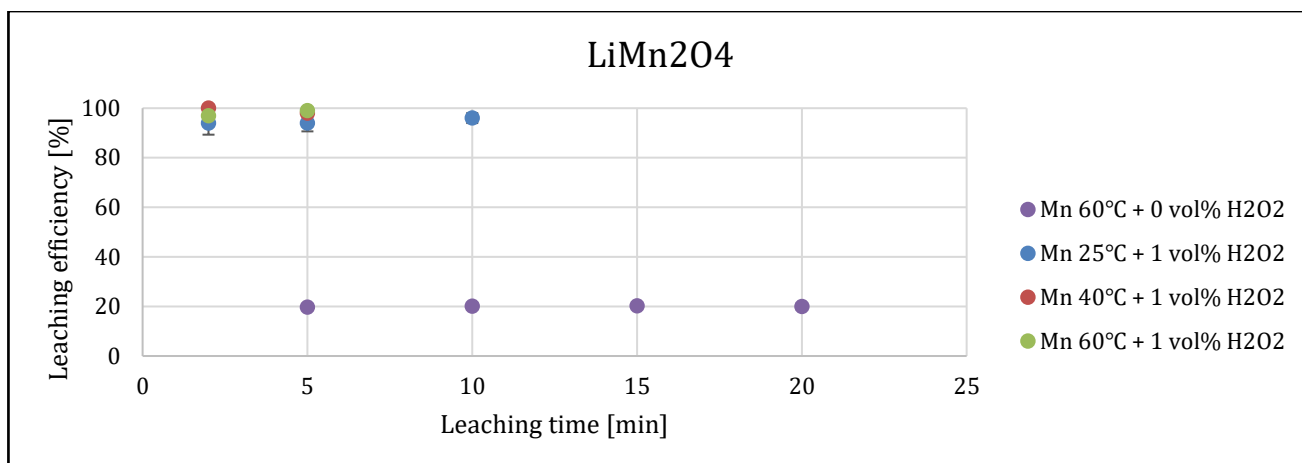


Figure 26: Leaching of LiMn₂O₄. The kinetic curves of manganese leaching in percent plotted against time.

Presented in Figure 26 are the kinetic curves for leaching of manganese with hydrogen peroxide present. The x-axis is substantially shorter than in other graphs as the leaching was complete in less than 10 minutes. With hydrogen peroxide the leaching reaches close to 100% after just 5 minutes compared to 22% without hydrogen peroxide.

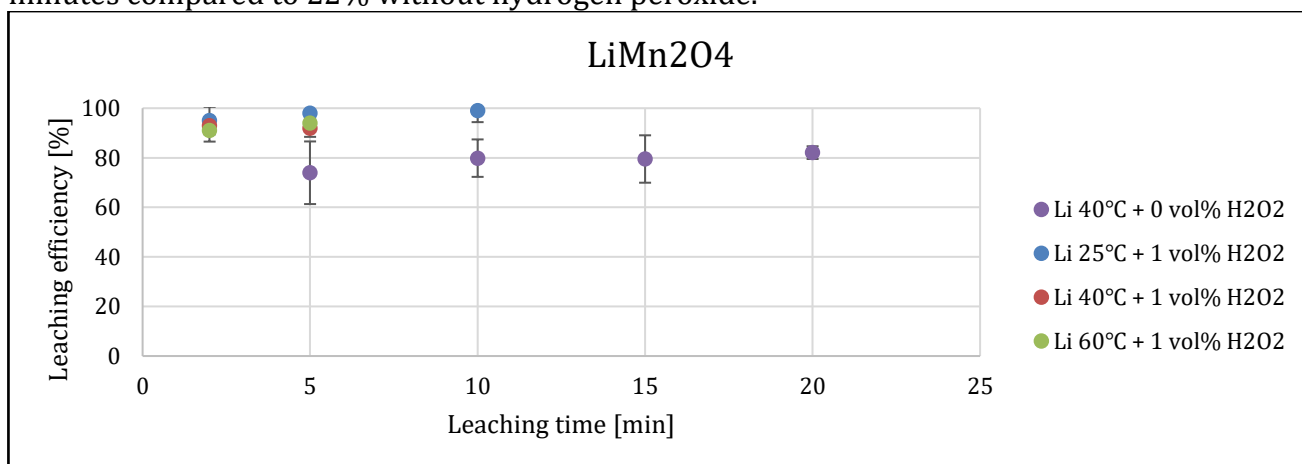


Figure 27: Leaching of LiMn₂O₄. The kinetic curves of lithium leaching in percent plotted against time.

The leaching of lithium is presented in Figure 27. The metal oxide powder was leached within 10 minutes and therefore the x-axis is significantly shorter than for other graphs. In Figure 24 lithium has the highest leaching efficiency at 40°C and for comparison it is included in Figure 27. All samples containing hydrogen peroxide has higher leaching efficiency than the samples with 0 vol% H₂O₂ after 2 minutes.

In section 3.1.2 the Gibbs free energy value was calculated for the leaching reaction of LiMn₂O₄. The large negative value for the reaction with hydrogen peroxide showed that the reaction was spontaneous but not the swiftness of the reaction. After less than 5 minutes the metal oxide powder was totally leached, and result was a transparent solution. The effect of hydrogen peroxide was evident even at low volume and at all temperatures for LiMn₂O₄ for both manganese and lithium.

3.5. Leaching of NMC 121

3.5.1. 2M H₂SO₄ – no addition of H₂O₂

A battery containing NMC 121 was provided by Volvo Car Corporation and had been dismantled and scraped beforehand. However, the particle size was bigger which is a difference compared to many of the fine powders used for leaching of the other cathode materials. The material is also more heterogenous. Presented in Figure 28, Figure 29, Figure 30 and Figure 31 are the leaching result for NMC 121 in sulfuric acid.

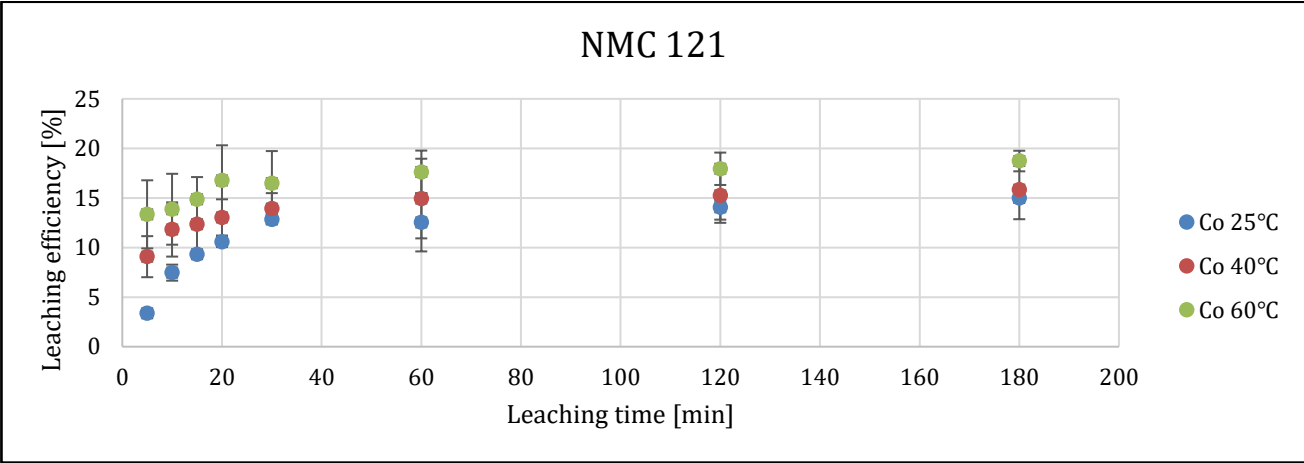


Figure 28: Leaching of NMC 121. The kinetic curves for cobalt plotted against time.

Figure 28 displays a similar pattern for the different leaching temperatures, their respective kinetic curve increases the most during the first 60 minutes before they reach equilibrium with only small improvements during the last 2 hours. Leaching in 60°C shows the best efficiency, however it is below 20%.

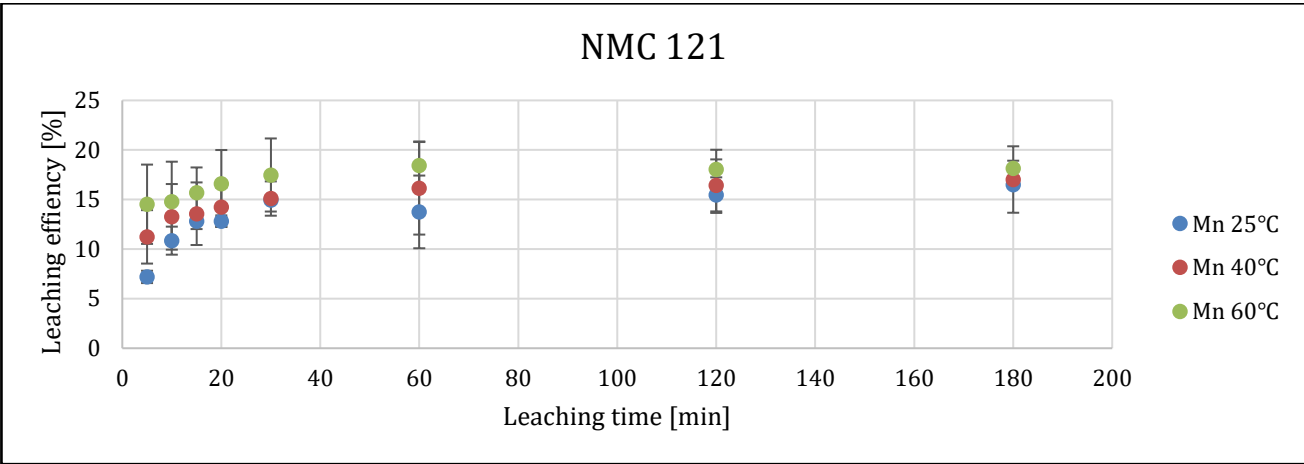


Figure 29: Leaching of NMC 121. The kinetic curves for manganese plotted against time.

Leaching of manganese follows the same pattern as leaching of lithium and cobalt. A leaching temperature of 60°C provides the most efficient leaching as can be seen in Figure 29. The kinetic curves rise the most during the first 60 minutes before it levels out. After 180 minutes all temperatures show similar leaching efficiency albeit with 60°C having slightly higher efficiency than the other temperatures.

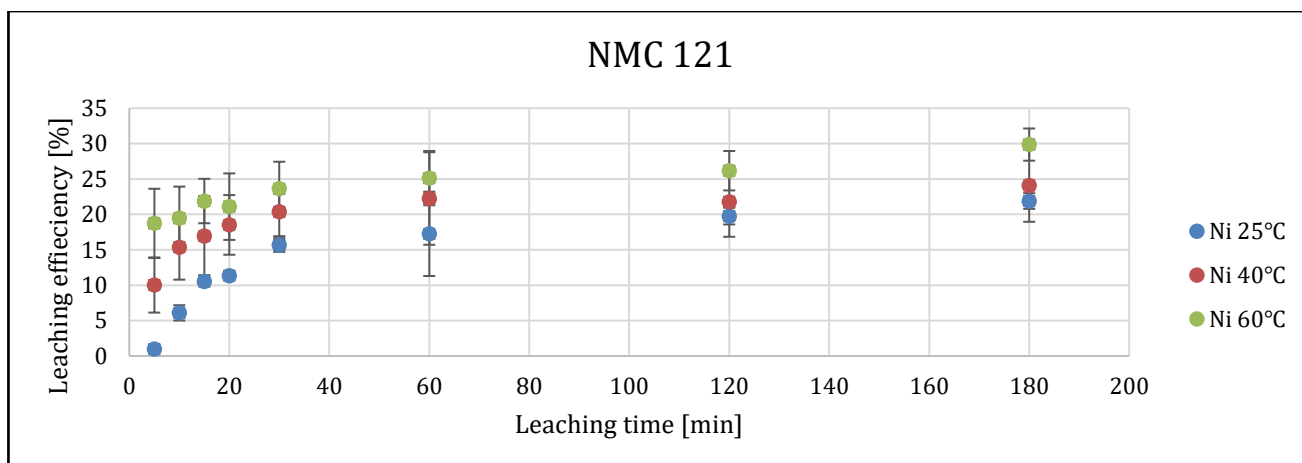


Figure 30: Leaching of NMC 121. The kinetic curves for nickel plotted against time.

In Figure 30 the leaching temperature of 60°C displays the best recovery of nickel from NMC 121. For 25°C the leaching is almost 0% after 5 minutes with a slow start to the leaching, however after 180 minutes it only has 8% lower efficiency than 60°C.

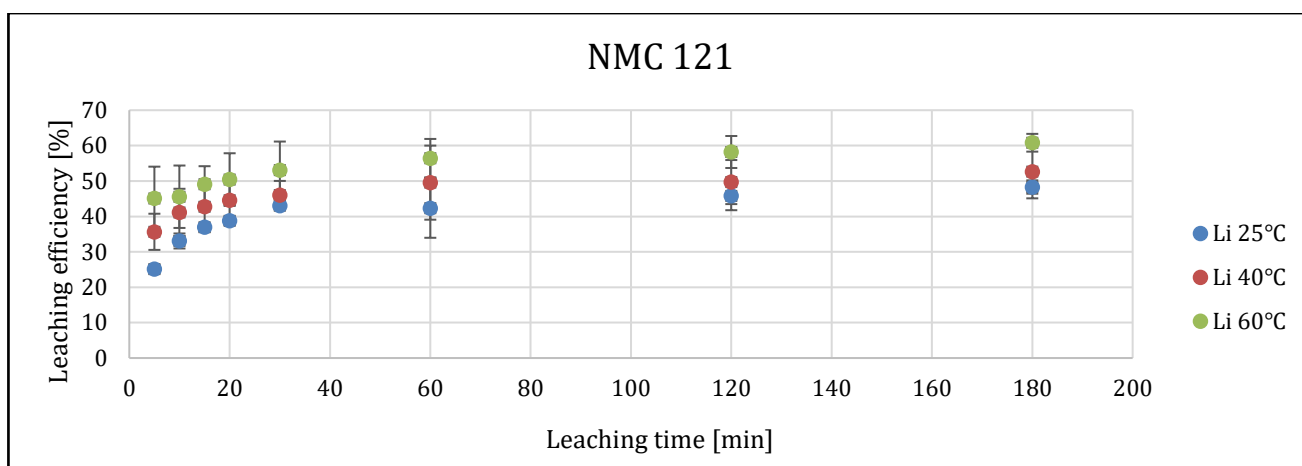


Figure 31: Leaching of NMC 121. The kinetic curves for lithium plotted against time.

During the first 60 minutes of leaching the kinetic curve goes upward before the inclination is leveling out as shown in Figure 31. The leaching temperature of 60°C displays the superior efficiency although it is only somewhat above that for 40°C.

3.5.1. 2M H₂SO₄ with addition of H₂O₂

Figure 32, Figure 33, Figure 34 and Figure 35 shows the kinetic curves for leaching of cobalt, manganese, nickel and lithium. The leaching with hydrogen peroxide was only done for 60 minutes since equilibrium was achieved at a shorter time compared to leaching with no addition of hydrogen peroxide. Included in each Figure is the corresponding kinetic curve for leaching without a reductive agent for a direct comparison between the leaching efficiencies. As mentioned before, all the points represent the average from a triplicate of samples and the standard deviation is visible for every point.

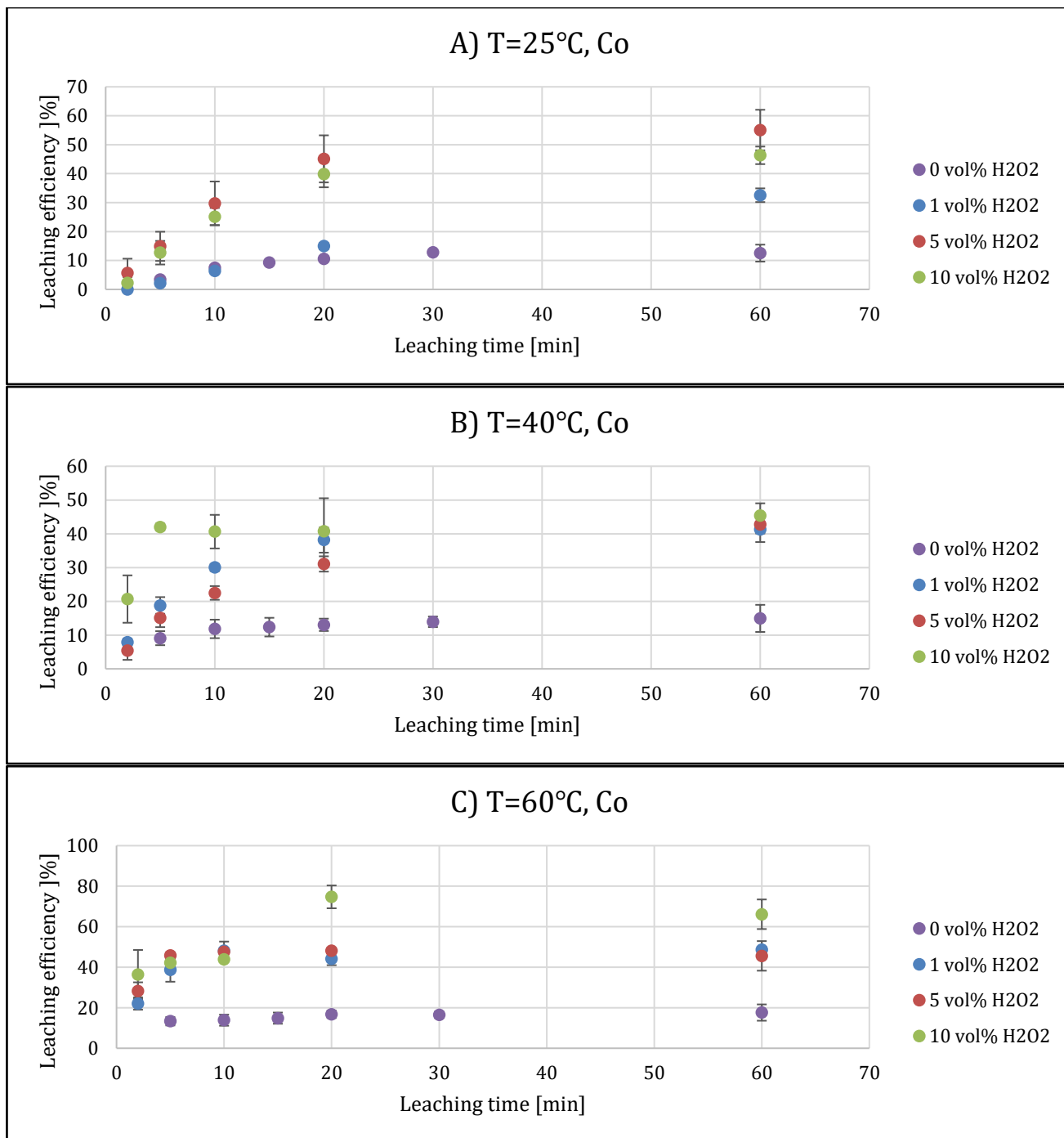


Figure 32: Leaching of NMC 121. Kinetic curves for cobalt leaching A) at 25°C. B) at 40°C. C) at 60°C.

Figure 32 A) present the kinetic curves for leaching in 25°C. Both 5- and 10 vol% hydrogen peroxide have significantly higher efficiency compared to 0- and 1 vol% hydrogen peroxide. In Figure 32 B) the kinetic curves for the solutions containing 1- and 5 vol% hydrogen peroxide follow the same pattern while 10 vol% has better leaching after 5 minutes but after 60 minutes they all show a similar leaching efficiency. The solution without an additional reducing agent provides a lower leaching efficiency. The kinetic curve for 10 vol% hydrogen peroxide shown in Figure 32 C) has the highest leaching efficiency of cobalt from NMC 121 at 60°C. 1- and 5 vol% hydrogen peroxide have a similar pattern and have similar leaching efficiency after 60 minutes. All solutions containing reducing agent demonstrates better kinetic curves than the solution without.

For leaching of cobalt from NMC 121 hydrogen peroxide has a vital role for increasing the leaching efficiency at all temperatures and concentrations. Hydrogen peroxide successfully reduces cobalt from oxidation state +3 to +2 where it can form CoSO_4 .

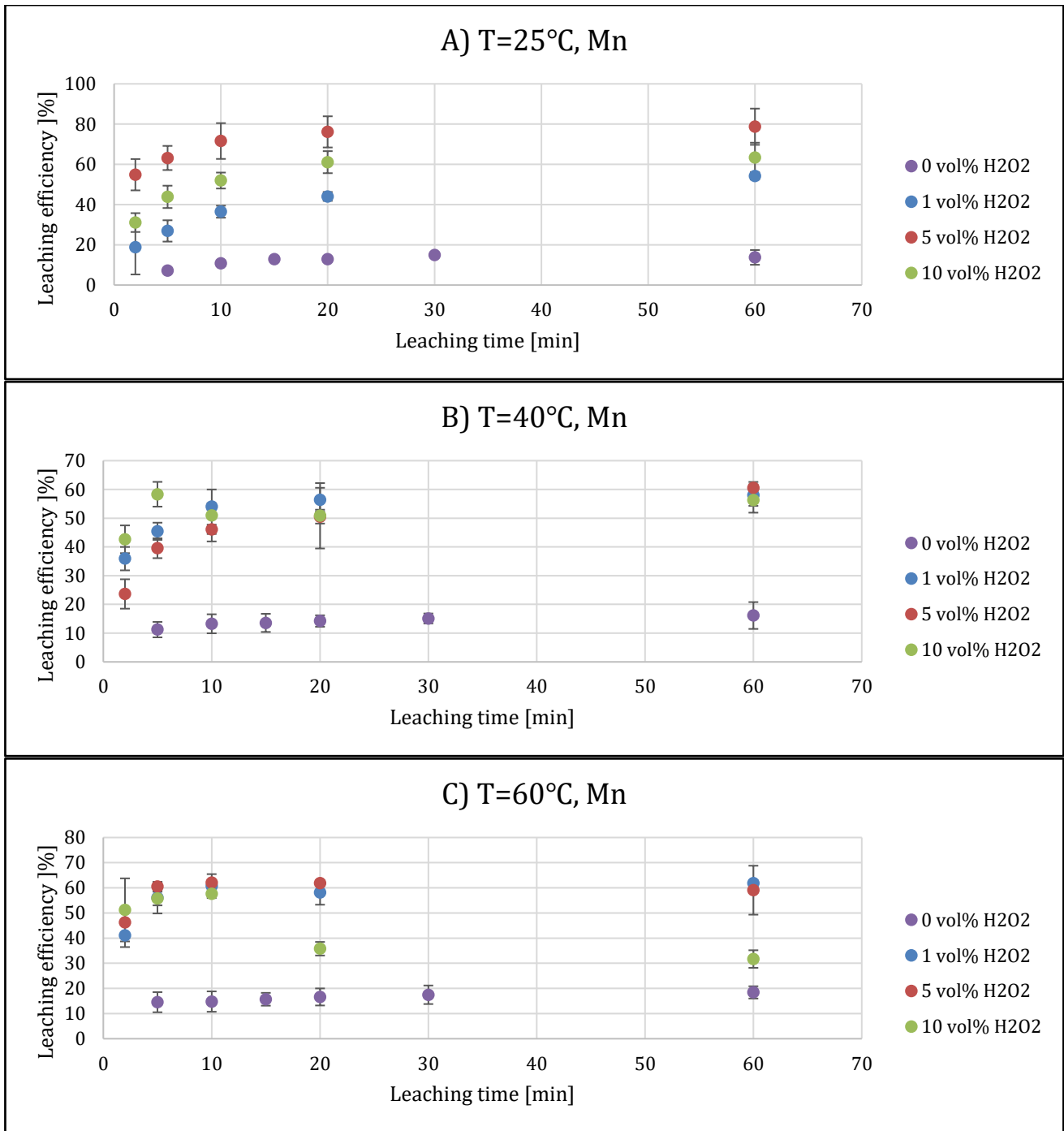


Figure 33: Leaching of NMC 121. Kinetic curves for manganese leaching A) at 25°C. B) at 40°C. C) at 60°C.

Figure 33 A) show a similar pattern for the leaching of manganese. The kinetic curves representing a solution containing hydrogen peroxide with 5 vol% demonstrating the highest leaching efficiency. All solutions with additive have superior efficiency compared to leaching with 0 vol% hydrogen peroxide.

The kinetic curves for solutions with hydrogen peroxide in Figure 33 B) all show better leaching efficiency of manganese than the curve representing 0 vol%. Among the solutions with hydrogen

peroxide they have different values in the beginning of the leaching but after 60 minutes there is only a small difference between them.

In Figure 33 C) an anomaly can be seen for 10 vol% hydrogen peroxide with a significant decrease in efficiency after 20 minutes of leaching which continues to the 60-minute mark. For 1- and 5 vol% the curves have the matching shapes with 1 vol% having a slightly higher leaching efficiency after 60 minutes.

The presence of hydrogen peroxide in the leaching solution aids the leaching of manganese at the temperatures and concentrations investigated for NMC 121. Hydrogen peroxide is able to reduce manganese from +4 to +2 where it is stable and form MnSO_4 . This follows the electrochemical potential for the reaction between hydrogen peroxide and manganese presented in section 1.2.2.3.

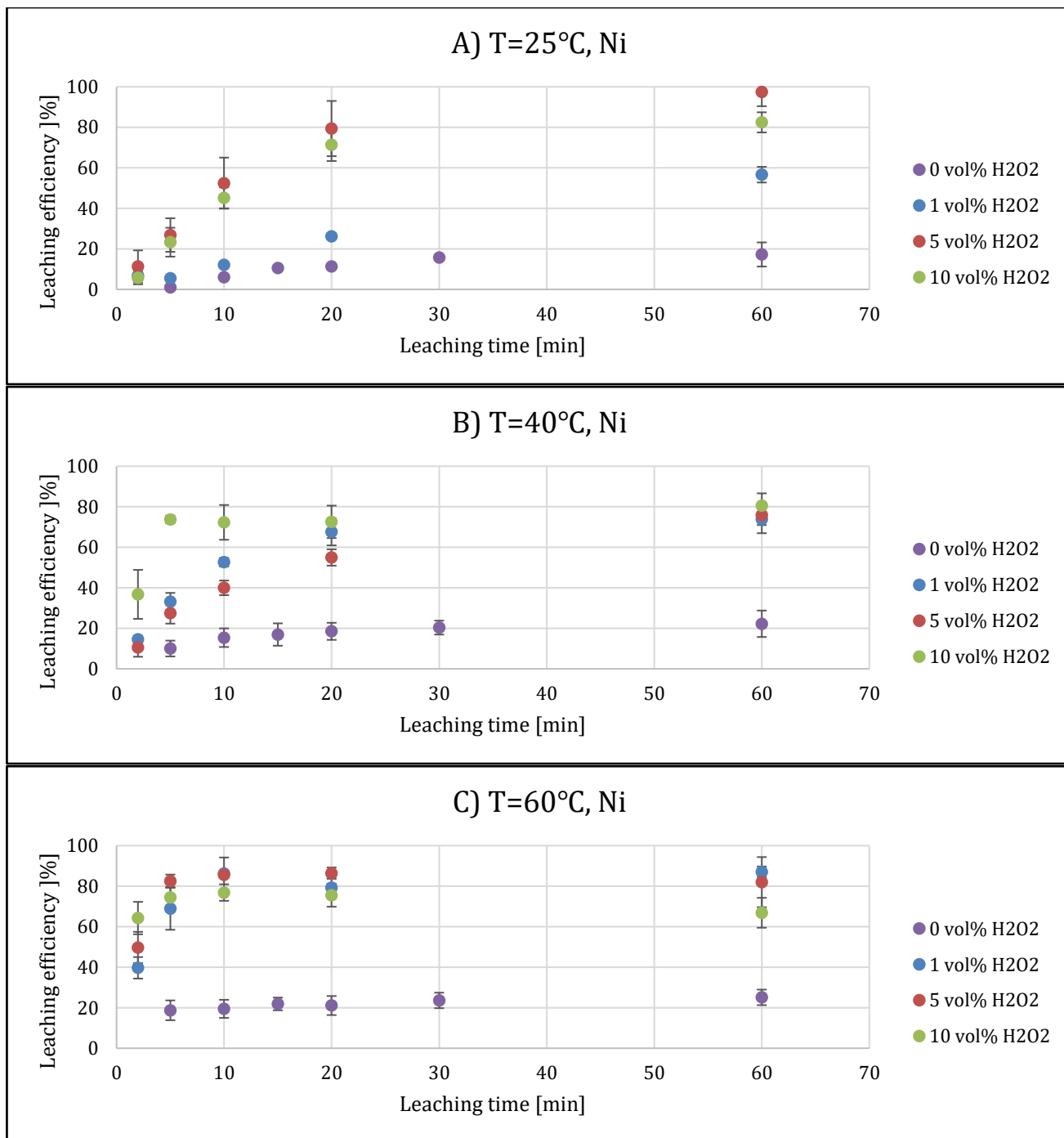


Figure 34: Leaching of NMC 121. Kinetic curves for nickel leaching A) at 25°C. B) at 40°C. C) at 60°C.

Figure 34 A) show how the leaching efficiency for Ni is higher for all solutions with hydrogen peroxide compared to leaching without a reducing agent. The highest leaching efficiency is reached when 5 vol% hydrogen peroxide is used when 97% of the nickel is recovered. In Figure 34 B) the solution containing 10 vol% hydrogen peroxide has the best leaching yield from the beginning but after 60 minutes the 1- and 5 vol% solutions show only a slightly lower leaching efficiency. The kinetic curve for 0 vol% have the lowest leaching efficiency. Figure 34 C) presents how the solution with 1 vol% hydrogen peroxide has the highest leaching efficiency of nickel from NMC 121 in 60°C. The kinetic curve for 10 vol% hydrogen peroxide shows an anomaly when the efficiency decreases after 20 minutes of leaching. All solutions with hydrogen peroxide have significantly higher efficiency compared to the curve for 0 vol% hydrogen peroxide.

The leaching of nickel reaches higher efficiency when hydrogen peroxide is used. The reason for the increase is a consequence from the liberation of other metals from the structure with both cobalt and manganese having increased leaching efficiencies in hydrogen peroxide. When those metals are leached from the structure the acid and hydrogen peroxide can attack nickel ions.

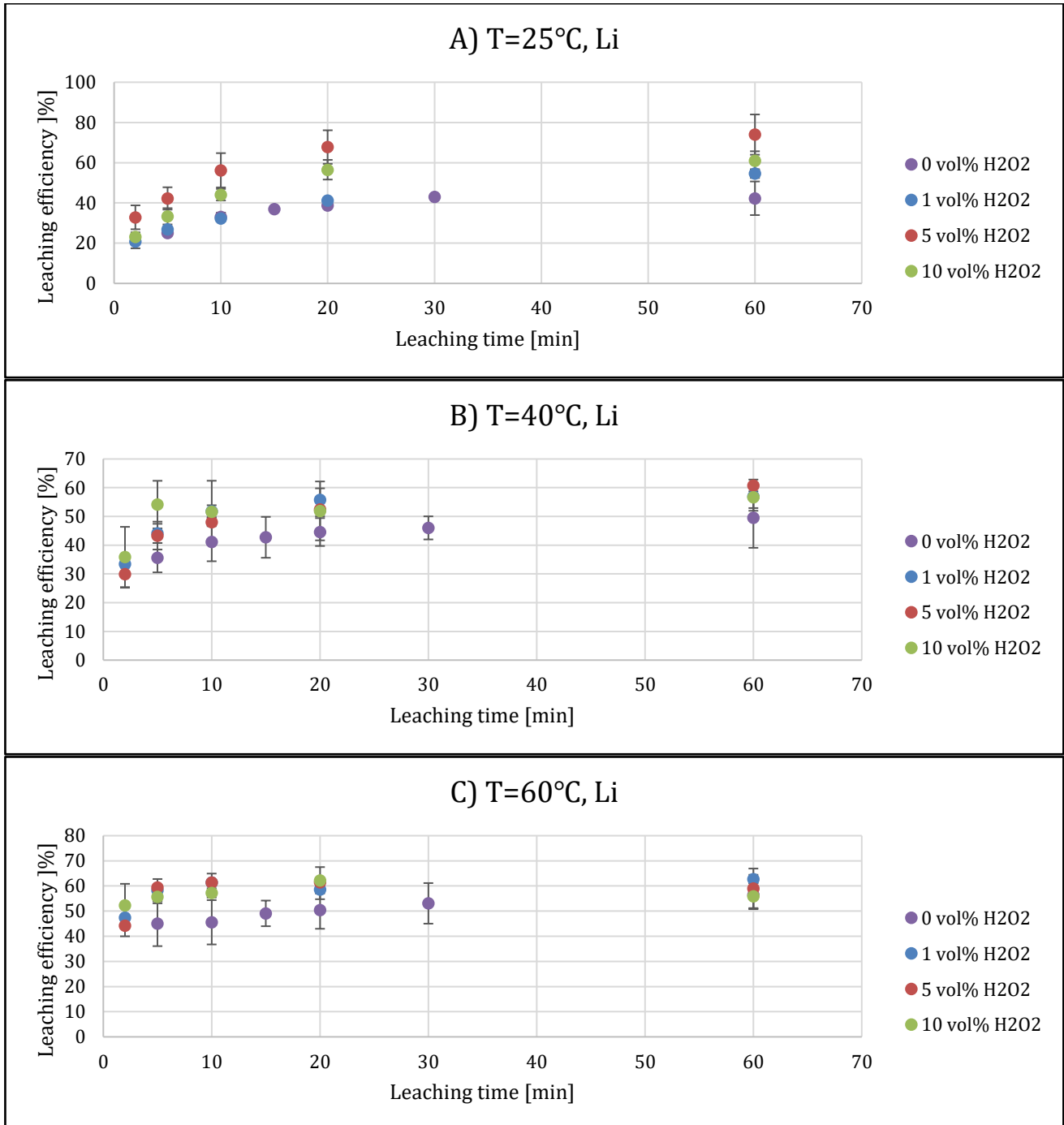


Figure 35: Leaching of NMC 121. Kinetic curves for lithium leaching A) at 25°C. B) at 40°C. C) at 60°C.

The addition of H₂O₂ increases the leaching efficiency in 25°C as presented in Figure 35 A). The kinetic curve with the highest yield is the one for 5 vol% hydrogen peroxide.

Figure 35 B) show the kinetic curves for leaching of lithium in 40°C. All solutions containing hydrogen peroxide have higher leaching efficiency than the one without hydrogen peroxide. 10 vol% has an odd peak after 5 minutes but after that the leaching efficiency decrease before its

highest value is reached after 60 minutes. This can be due to a reaction (15) going backwards since there is a lot of hydrogen peroxide in the solution.

The leaching efficiency in 60°C is presented in Figure 35 C). After 60 minutes of leaching 1 vol% H₂O₂ has the highest leaching efficiency. Both 5 vol% and 10 vol% have the peak after 20 minutes before the efficiency decreases slightly after 60 minutes.

For leaching of lithium, the effect of hydrogen peroxide is most visible at 25°C and 40°C whereas at 60°C the kinetic curve for 0 vol% show equal leaching efficiencies after 60 minutes of leaching. This follows the pattern seen for LiCoO₂ and LiNiO₂.

3.6. Leaching of NMC 111

3.6.1. 2M H₂SO₄ – no addition of H₂O₂

Figure 36, Figure 37, Figure 38 and Figure 39 shows the kinetic curves for leaching of cobalt, manganese, nickel and lithium from NMC 111. As before all the points represent the average from a triplicate of samples and the standard deviation is visible for every point. During analysis of the material it was discovered that the composition of nickel, manganese and cobalt was close to 412 instead of 111.

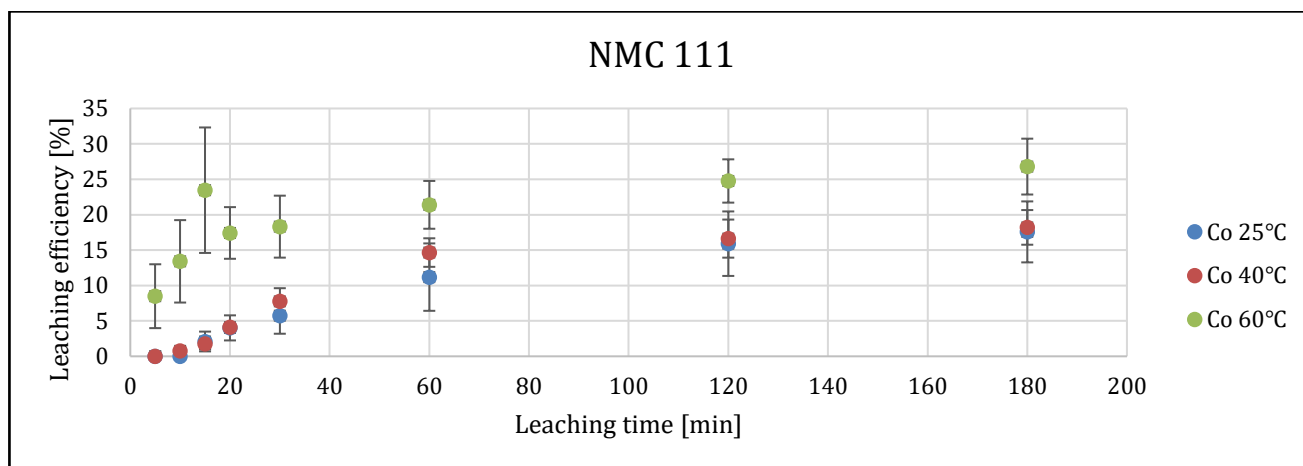


Figure 36: Leaching of NMC 111. The kinetic curves for cobalt plotted against time.

The kinetic curves for 25°C and 40°C again show almost identical leaching performances while 60°C gives a superior leaching efficiency in comparison as shown in Figure 36. All temperatures give a slow leaching with less than 30% of the available cobalt leached after 180 minutes. The points representing leaching in 60°C have noticeably higher standard deviation than the other points during the first 30 minutes of leaching.

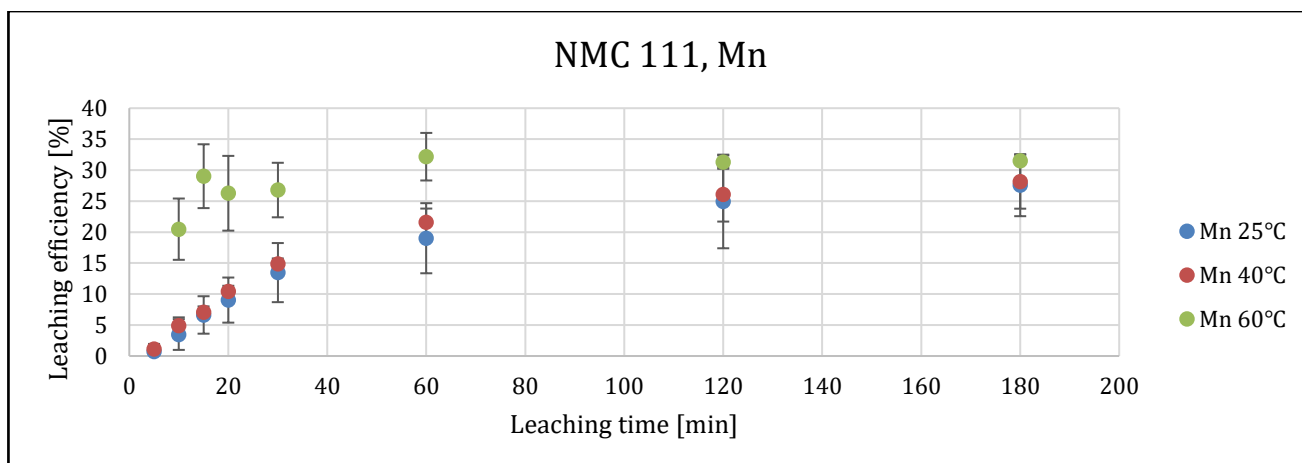


Figure 37: Leaching of NMC 111. The kinetic curves for manganese plotted against time.

Figure 37 show the leaching of manganese from NMC 111. Leaching in 60°C give an initial higher efficiency compared to 25°C and 40°C but after 3 hours the difference is 4%. Manganese leaching is barely affected by an increase on temperature from 25°C to 40°C.

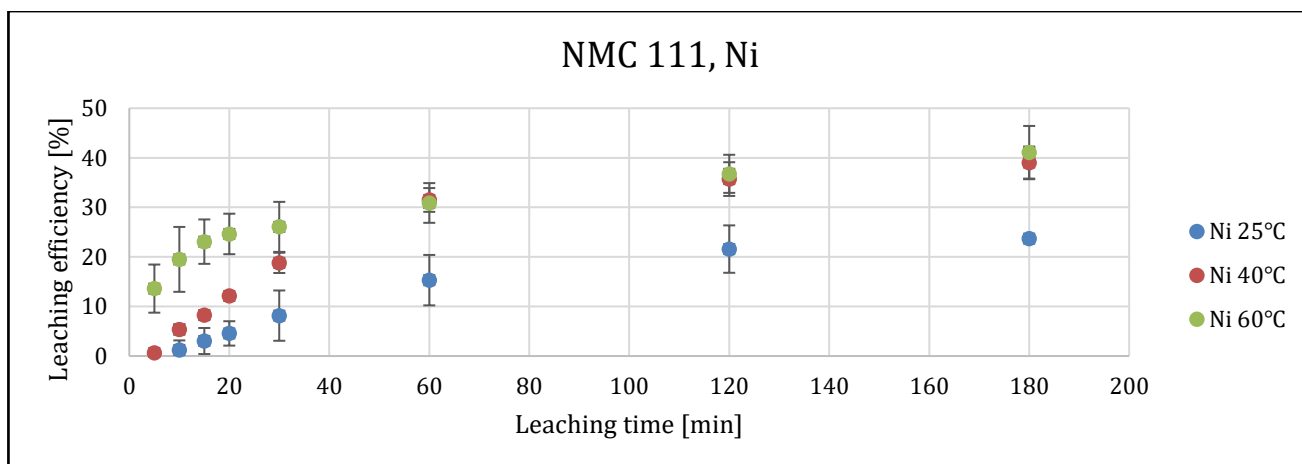


Figure 38: Leaching of NMC 111. The kinetic curves for nickel plotted against time.

For nickel the initial efficiency of the leaching at 60°C is significantly higher than at 40°C but after 60 minutes they both show approximately the same recovery as presented in Figure 38. The temperature of 25°C gives the lowest yield of nickel throughout this experiment.

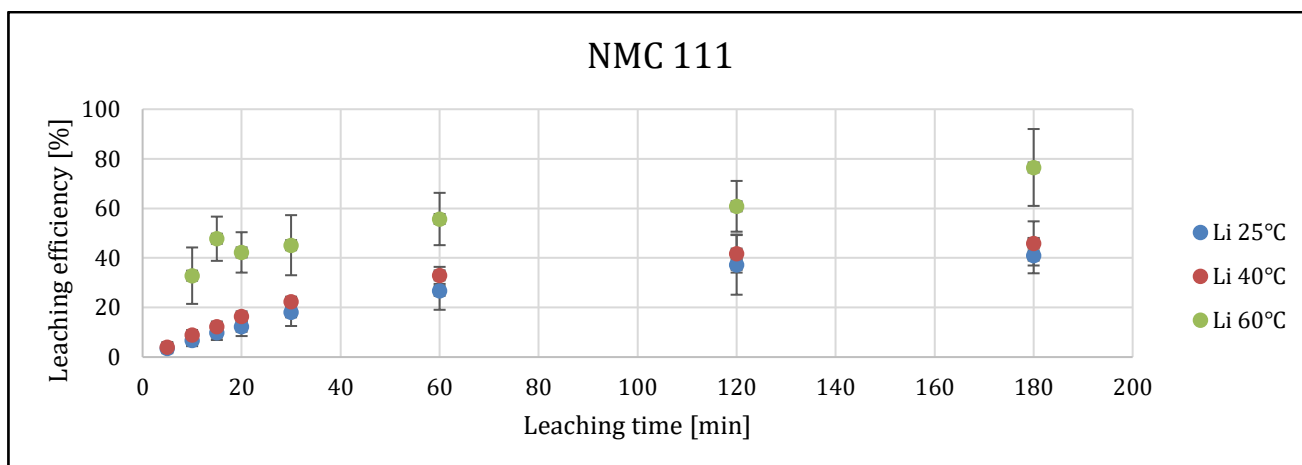


Figure 39: Leaching of NMC 111. The kinetic curves for lithium plotted against time.

In Figure 39 the kinetic curves for lithium at 25°C and 40°C are parallel with 40°C having slightly better leaching efficiency. The kinetic curve for 60°C has no point at 5 minutes because it had unreliable data from the measurement. The leaching of lithium from NMC 111 show good efficiency in sulfuric acid.

3.6.1. 2M H₂SO₄ with addition of H₂O₂

Figure 40, Figure 41, Figure 42 and Figure 43 show the kinetic curves for leaching of cobalt, manganese, nickel and lithium. The leaching of NMC 111 using hydrogen peroxide was only done for 60 minutes as the leaching is completed in a shorter time compared to leaching with no addition of hydrogen peroxide. Included in each figure is the corresponding kinetic curve for leaching without a reductive agent for a direct comparison between the leaching efficiencies. As before all the points represent the average from a triplicate of samples and the standard deviation is visible for every point.

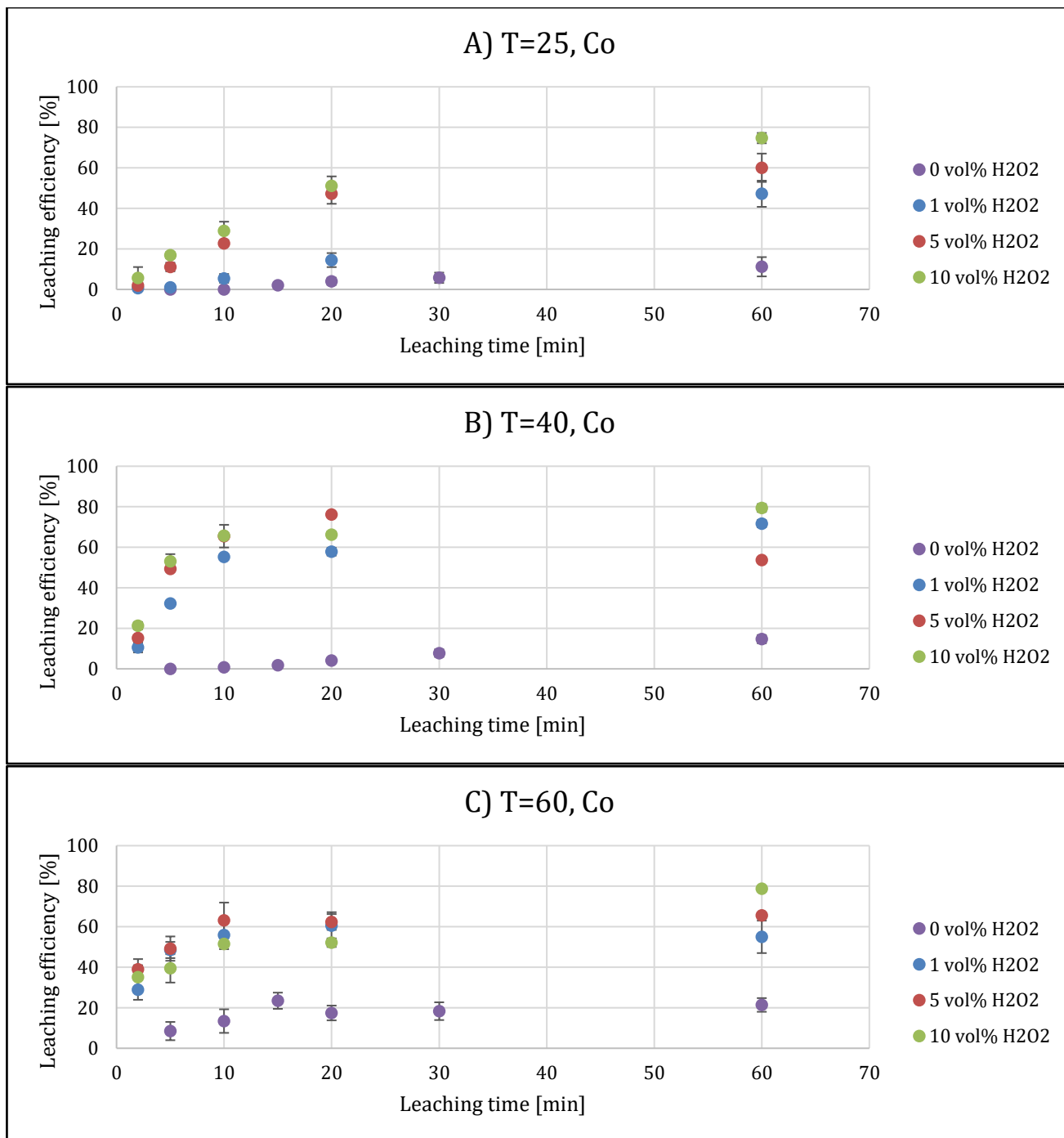


Figure 40: Leaching of NMC 111. Kinetic curves for cobalt leaching A) at 25°C. B) at 40°C. C) at 60°C.

In Figure 40 A) the results from leaching NMC 111 with hydrogen peroxide in 25°C are presented. The kinetic curve for 1 vol% H₂O₂ shows a slow leaching in the beginning before the yield increases between 20 and 60 minutes. The curves representing 5 vol% and 10 vol% H₂O₂ are parallel during the first 20 minutes but 5 vol% drops off in the end.

The kinetic curves for leaching in 40°C are presented in Figure 40 B). All curves representing leaching with hydrogen peroxide have similar pattern from 0 to 20 minutes. The leaching using 5 vol% hydrogen peroxide shows a decrease of leaching efficiency at 60 minutes, but this point can be seen as an anomaly.

All kinetic curves in Figure 40 C) show similar shape with a fast increase of efficiency in the first 10 minutes of leaching. After 60 minutes of leaching 10 vol% hydrogen peroxide shows the highest leaching efficiency of 79% cobalt.

Leaching of cobalt from NMC 111 is improved by the hydrogen peroxide and hydrogen peroxide has a vital role for increasing the leaching efficiency at all temperatures and concentrations. Hydrogen peroxide successfully reduces cobalt from oxidation state +3 to +2 where it can form CoSO_4 . The low pH and positive potential of the solution helped to keep cobalt in oxidation state +2 as could be seen in Figure 9.

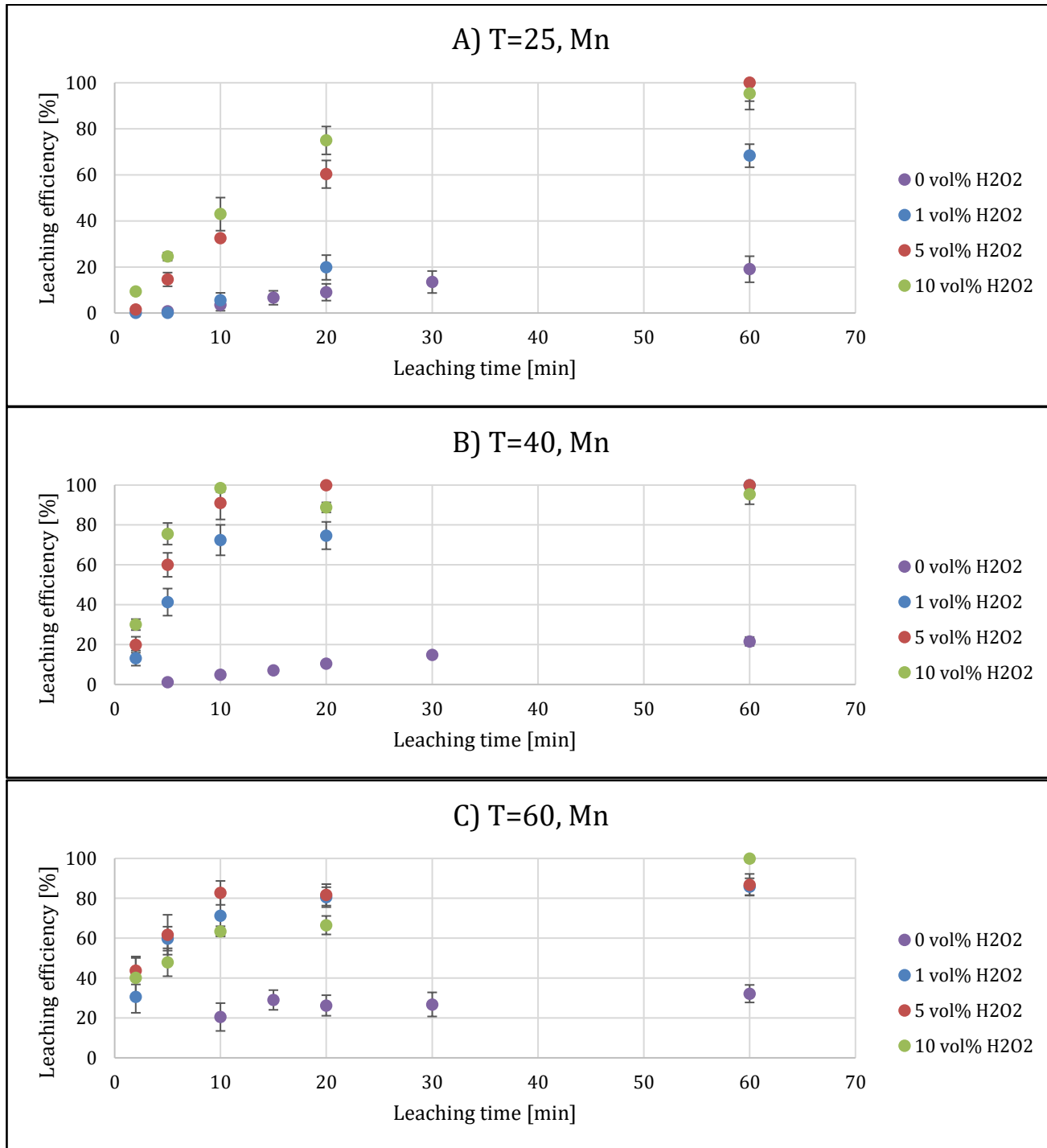


Figure 41: Leaching of NMC 111. Kinetic curves for manganese leaching A) at 25°C. B) at 40°C. C) at 60°C.

In Figure 41 A) the results from leaching of Mn in 25°C are presented. The kinetic curve for 1 vol% H_2O_2 show slow leaching in the beginning before the yield increases between 20 and 60

minutes. The curves representing 5 vol% and 10 vol% H_2O_2 are parallel during the first 20 minutes but 10 vol% drops off in the end.

The kinetic curves for leaching in 40°C are presented in Figure 41 B). After 10 minutes of leaching 10 vol% H_2O_2 reaches complete leaching of manganese while it takes 20 minutes for the 5 vol% solution to reach the same efficiency. Even the 1 vol% solution leached all the manganese from NMC 111.

The kinetic curves in Figure 41 C) representing leaching with hydrogen peroxide have similar shapes with a fast increase of efficiency in the first 10 minutes of leaching. After 60 minutes of leaching 10 vol% hydrogen peroxide shows the highest leaching efficiency.

The presence of hydrogen peroxide in the leaching solution supports the leaching of manganese at the temperatures and concentrations investigated for NMC 111. Hydrogen peroxide is able to reduce manganese from +4 to +2 where it is stable and form MnSO_4 . The oxidation state is as expected from Figure 11 with the leaching solution having low pH and a potential of approximately 0.6V.

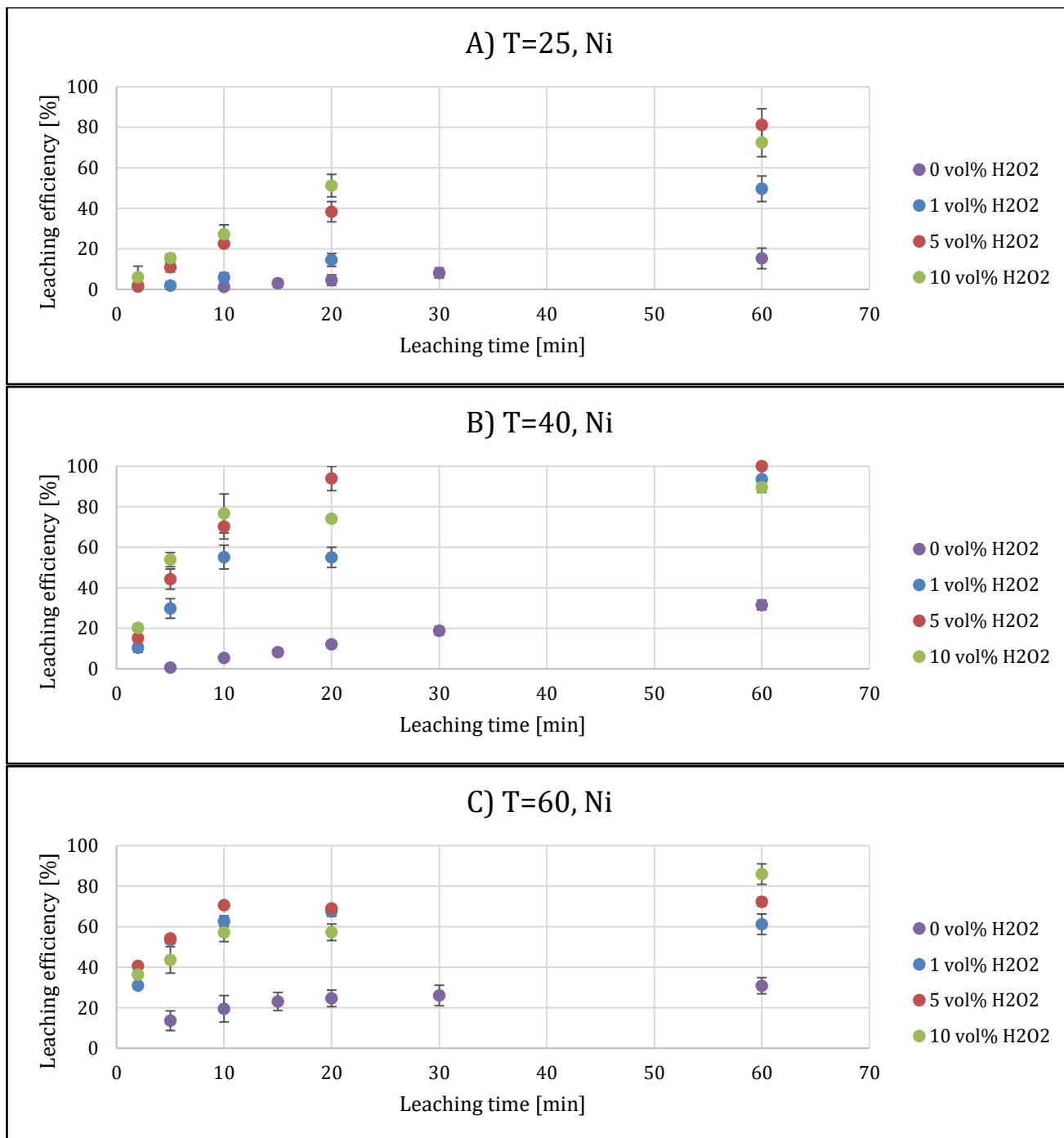


Figure 42: Leaching of NMC 111. Kinetic curves for nickel leaching A) at 25°C. B) at 40°C. C) at 60°C.

Figure 42 A) presents the kinetic curves for Ni leaching in 25°C. The kinetic curve for 1 vol% H₂O₂ has low leaching efficiency in the beginning before the yield increases between 20 and 60 minutes. The curves representing 5 vol% and 10 vol% H₂O₂ follows each other closely during the first 20 minutes but 10 vol% drops off slightly in the end.

Presented in Figure 42 B) are the kinetic curves for leaching in 40°C. 10 vol% hydrogen peroxide expresses good leaching efficiency in the beginning before the leaching yield decreases and after 60 minutes it has lower leaching efficiency than 1 vol%- and 5 vol% hydrogen peroxide.

In Figure 42 C) the kinetic curves representing leaching with hydrogen peroxide at the highest temperature used have similar shapes with a fast increase of efficiency in the first 10 minutes of leaching. After 60 minutes the 10 vol% solution has the highest leaching efficiency followed by 5 vol% and 1 vol%.

The leaching efficiency of nickel is increased when hydrogen peroxide is used. The liberation of other metals from the structure, with both cobalt and manganese having increased leaching efficiencies when leaching with hydrogen peroxide, is the reason nickel leaching reach higher efficiency. The difference in potential between nickel and hydrogen peroxide highlighted in section 1.2.2.3 is another factor driving the reaction towards more NiSO_4 .

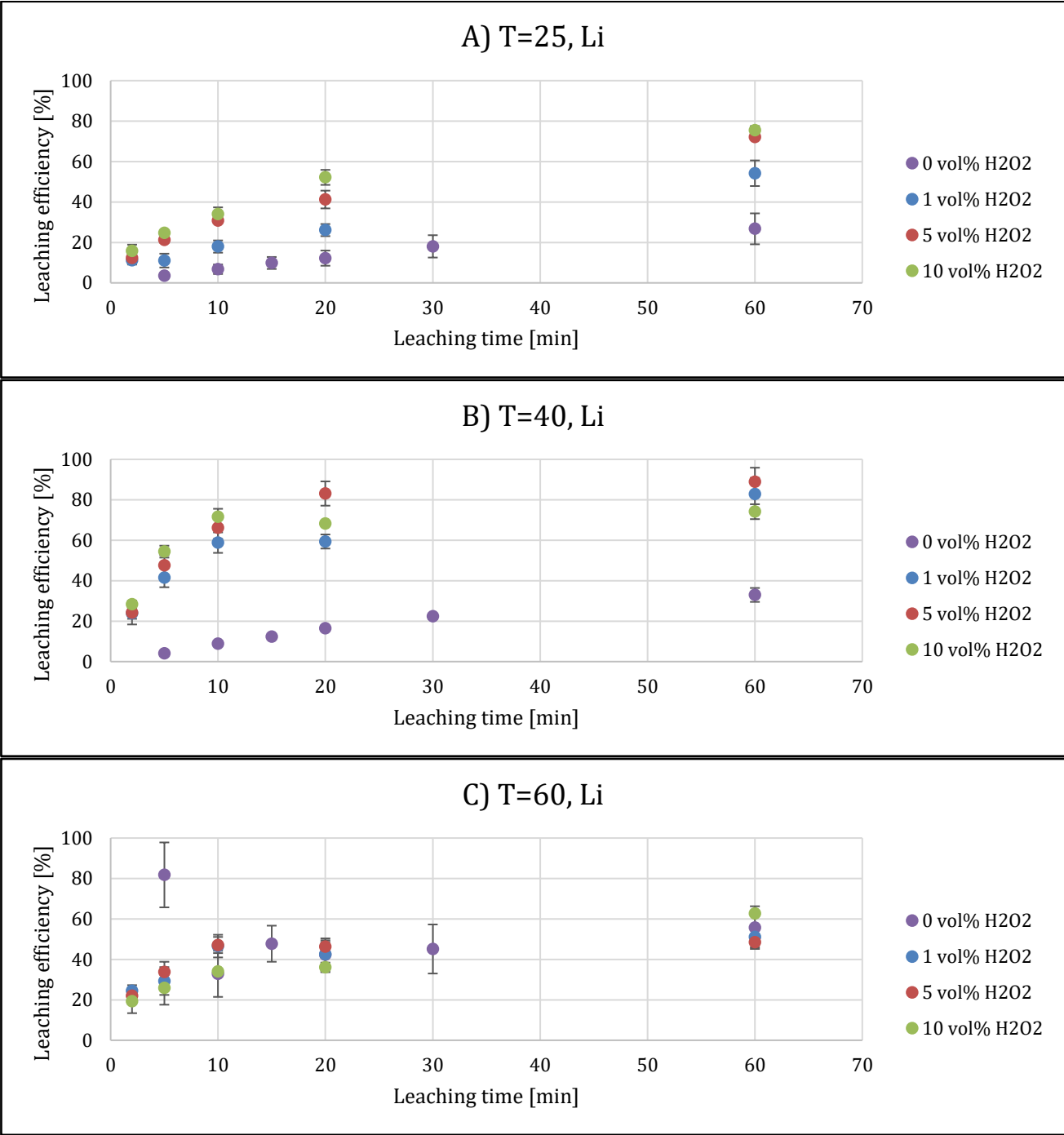


Figure 43: Leaching of NMC 111. Kinetic curves for lithium leaching A) at 25°C. B) at 40°C. C) at 60°C.

The addition of H_2O_2 increases the leaching efficiency at 25°C as presented in Figure 43 A). The kinetic curve with the highest leaching yield is the one for 10 vol% hydrogen peroxide.

Figure 43 B) show the kinetic curves for leaching of lithium at 40°C. The kinetic curves for the leaching with hydrogen peroxide have a fast increase of efficiency during the first 10 minutes. After 60 minutes 5 vol% has the highest leaching efficiency.

The leaching efficiency at 60°C are presented in Figure 43 C). After 60 minutes of leaching the solution with 0 vol% hydrogen peroxide have similar leaching efficiency of lithium as the solutions containing hydrogen peroxide.

For leaching of lithium, the effect of hydrogen peroxide is most visible at 25°C and 40°C whereas at 60°C the kinetic curve for 0 vol% show equal leaching efficiencies after 60 minutes of leaching. This follows the pattern seen for LiCoO₂, LiNiO₂ and NMC 121.

3.7. Leaching of NMC 442

3.7.1. Leaching with H₂SO₄ – no addition of H₂O₂

The kinetic curves for leaching of cobalt, manganese, nickel and lithium from NMC 442 are displayed in Figure 44, Figure 45, Figure 46 and Figure 47. As before all points represent the average from a triplicate of samples and the standard deviation is visible in every point.

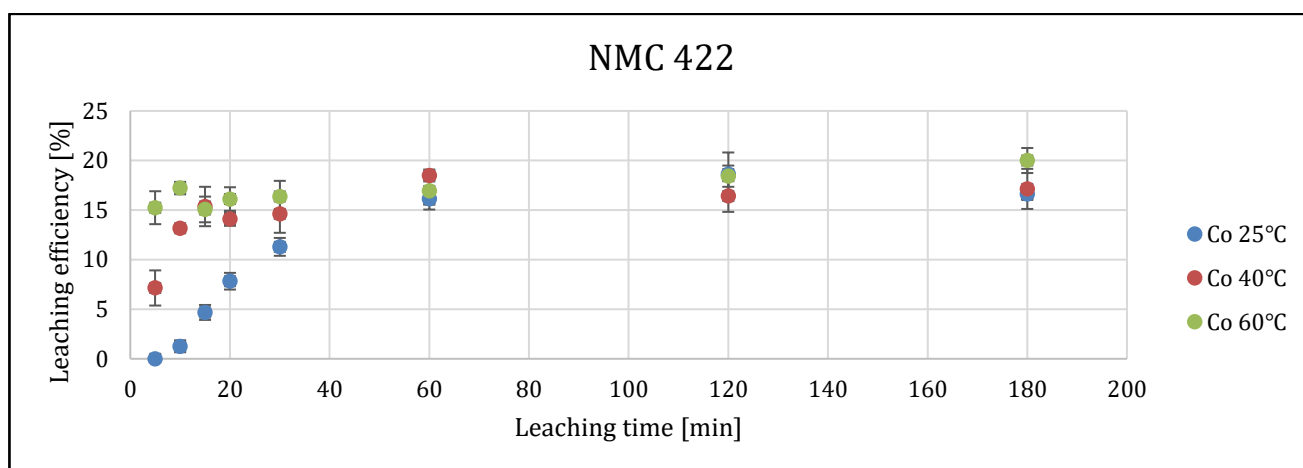


Figure 44: Leaching of NMC 442. The kinetic curves for cobalt plotted against time.

Figure 44 shows the kinetic curves for cobalt leaching from NMC 442. In 25°C the kinetic curve has a steep increase in leaching efficiency during the experiment while 60°C only have a slight increase throughout the experiment after a rapid initial leaching. The curve for 40°C start with a leaching efficiency between those for the experiments at 25°C and 60°C but after 15 minutes of leaching it has reached the same efficiency as 60°C.

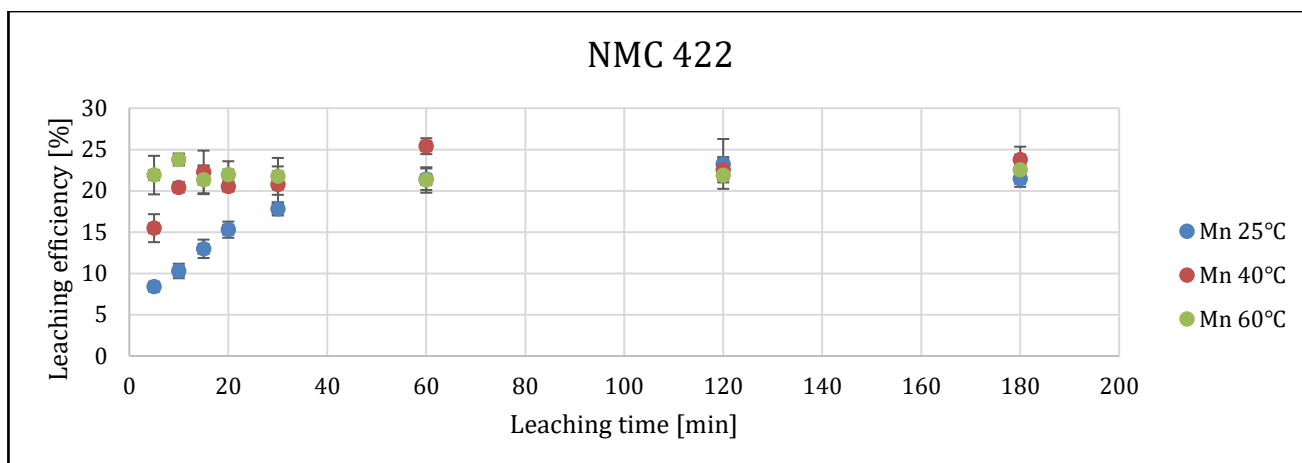


Figure 45: Leaching of NMC 442. The kinetic curves for manganese plotted against time.

The kinetic curves for manganese are shown in Figure 45. The same pattern as in Figure 44 can be seen, the kinetic curve for 25°C start at a low efficiency but after 60 minutes of leaching it has similar efficiency as 40°C and 60°C. 60°C show only a small increase in efficiency during the experiment.

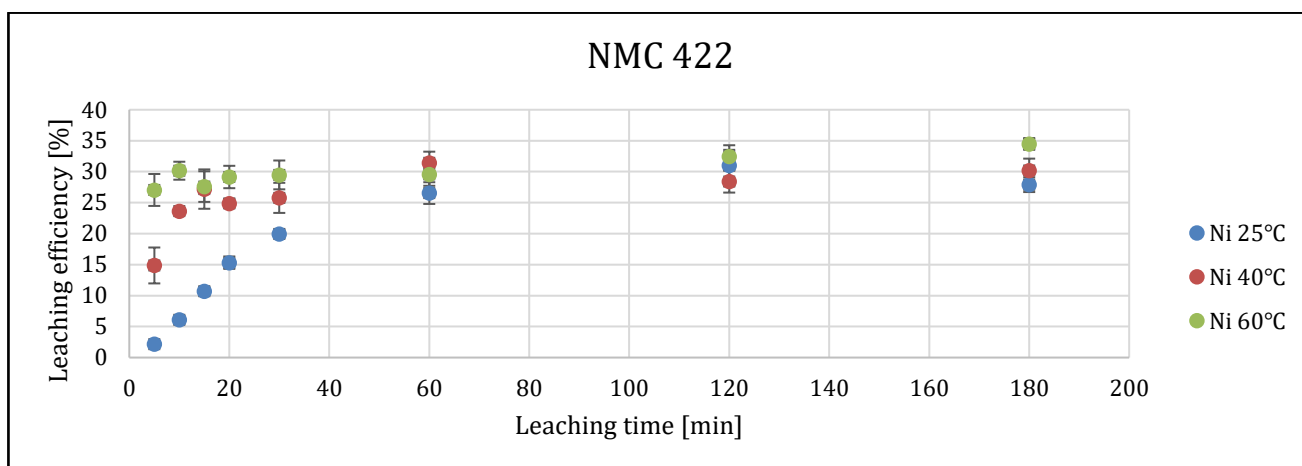


Figure 46: Leaching of NMC 442. The kinetic curves for nickel plotted against time.

The kinetic curves for leaching of nickel are presented in Figure 46. The kinetic curve for 60°C start at the highest efficiency and ends with the highest efficiency as well but after 180 minutes all temperatures are separated by 8%. The kinetic curve for 25°C have very low efficiency after 5 minutes but show a steady increase during the experiment until 120 minutes.

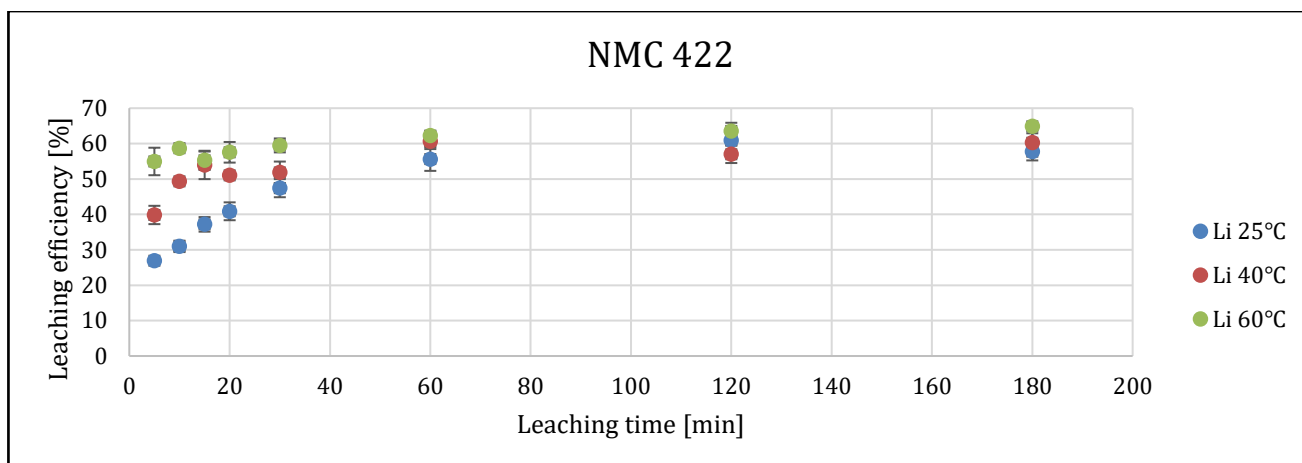


Figure 47: Leaching of NMC 442. The kinetic curves for lithium plotted against time.

Figure 47 present the kinetic curves for leaching of lithium. The kinetic curve for 25°C start with the lowest efficiency but after 120 minutes it has reached 60% efficiency. The kinetic curve for 60°C starts with the highest leaching efficiency but show only small increase in leaching during the experiment.

3.7.2. Leaching with H_2SO_4 with addition of H_2O_2

Figure 48 A-C, Figure 49 A-C, Figure 50 A-C and Figure 51 A-C shows the kinetic curves for leaching of cobalt, manganese, nickel and lithium. Every Figure has the corresponding kinetic curve for leaching without a reductive agent for a direct comparison between the leaching efficiencies. The points represent the average from a triplicate of samples and the standard deviation is plotted for every point.

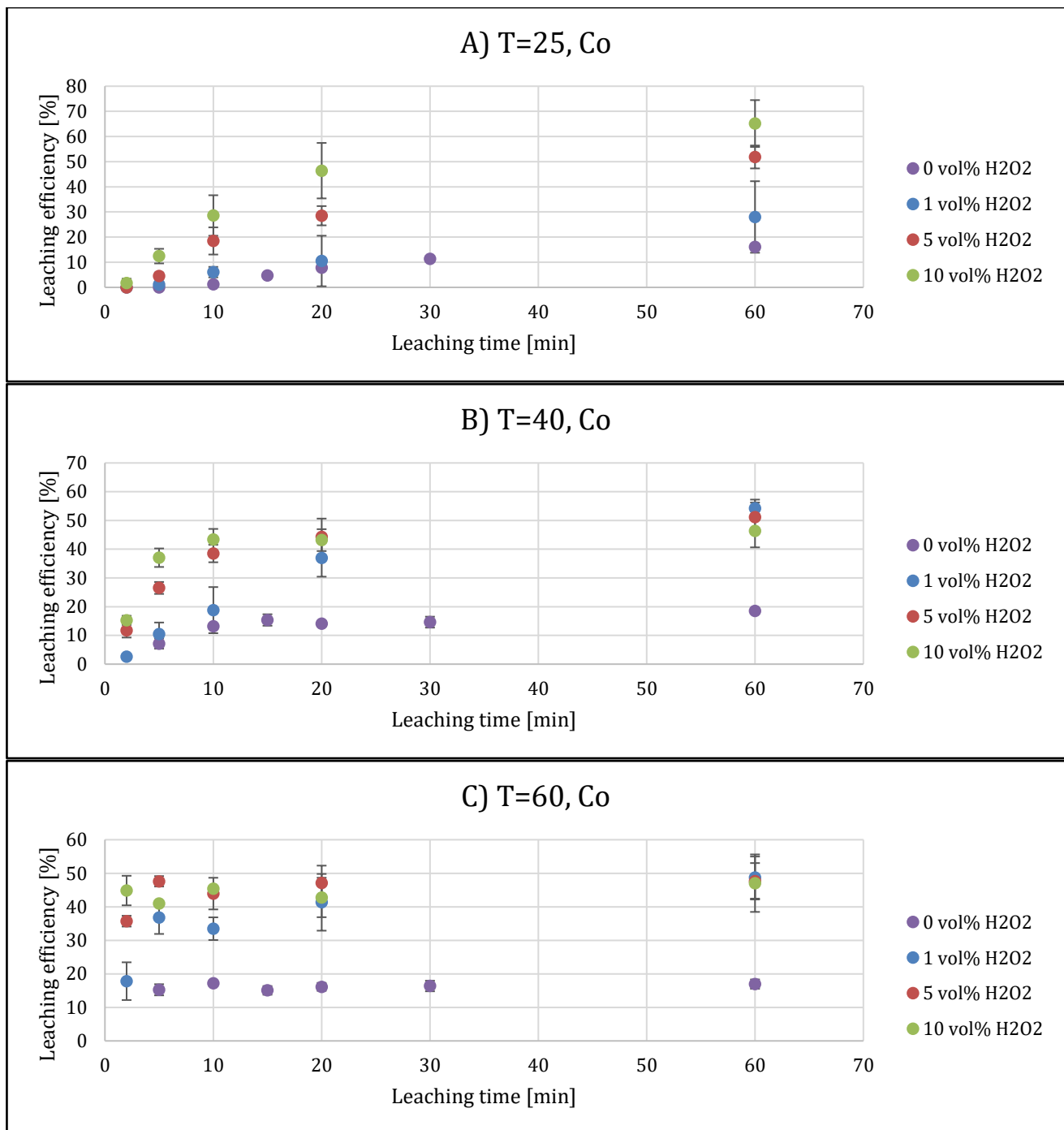


Figure 48: Leaching of NMC 442. Kinetic curves for cobalt leaching A) at 25°C. B) at 40°C. C) at 60°C.

Visible in Figure 48 A) is that increasing the amount of hydrogen peroxide gives an increased leaching efficiency. 10 vol% H₂O₂ has the highest leaching efficiency followed by 5 vol% H₂O₂, 1 vol% H₂O₂ and 0 vol% H₂O₂.

In Figure 48 B) it is harder to find a pattern for the kinetic curves other than that the efficiency increases during the experiment, in the beginning 5 vol% H₂O₂ and 10 vol% H₂O₂ follow each other before 1 vol% H₂O₂ ends with the highest efficiency. All samples with hydrogen peroxide have better leaching efficiency than without H₂O₂.

Figure 48 C) show only a small increase in leaching efficiency for 5 vol% H₂O₂ and 10 vol% H₂O₂ whereas 1 vol% H₂O₂ start with a low efficiency and ends with an efficiency similar to 5 vol% H₂O₂ and 10 vol% H₂O₂.

Hydrogen peroxide has increased the leaching of cobalt from NMC 442. It manages to improve the recovery of cobalt at all temperatures and concentrations of hydrogen peroxide compared to leaching without it. The increase in leaching show H_2O_2 reduces cobalt from oxidation state +3 to +2 where it forms CoSO_4 .

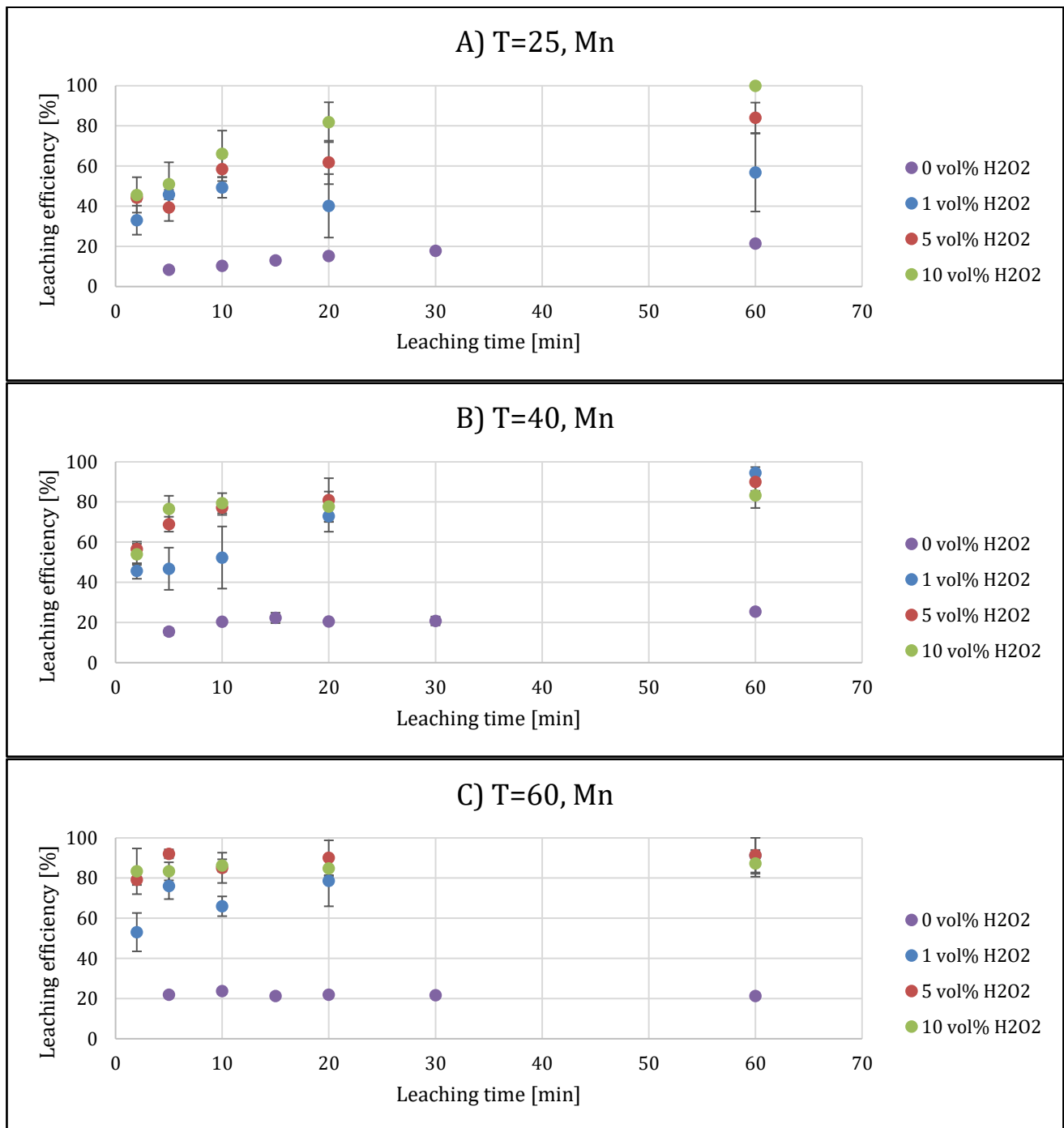


Figure 49: Leaching of NMC 442. Kinetic curves for manganese leaching A) at 25°C. B) at 40°C. C) at 60°C.

In Figure 49 A) the kinetic curves are easily separated with 10 vol% H_2O_2 showing the highest values and the other follow in descending order according to the volume of hydrogen peroxide in the sample. In 10 vol% H_2O_2 all manganese is leached. The curve for 1 vol% H_2O_2 show a slight decrease in efficiency at 20 minutes before it increases in the end.

The kinetic curves for 40°C are displayed in Figure 49 B). Throughout the experiment 5 vol% and 10 vol% H₂O₂ show similar efficiency while 1 vol% H₂O₂ start at a much lower efficiency but after the experiment is finished it has the highest leaching efficiency.

Figure 49 C) present the kinetic curves for leaching at 60°C, the curves representing 5 vol% and 10 vol% H₂O₂ have very high leaching efficiencies from the start and only show minor improvements when the time increase. 1 vol% H₂O₂ start with a slightly lower value but after 60 minutes it reaches similar efficiency as 5 vol% and 10 vol% H₂O₂.

The addition of hydrogen peroxide to the solution has increased the leaching of manganese from NMC 442. The effect can be seen at all tested temperatures and concentrations of hydrogen peroxide. Almost all of the manganese is leached from powder form to the aqueous form MnSO₄, showing the change of oxidation state manganese goes through. As presented in Table 11 manganese starts in oxidation state +4 but in MnSO₄ it has oxidation state +2.

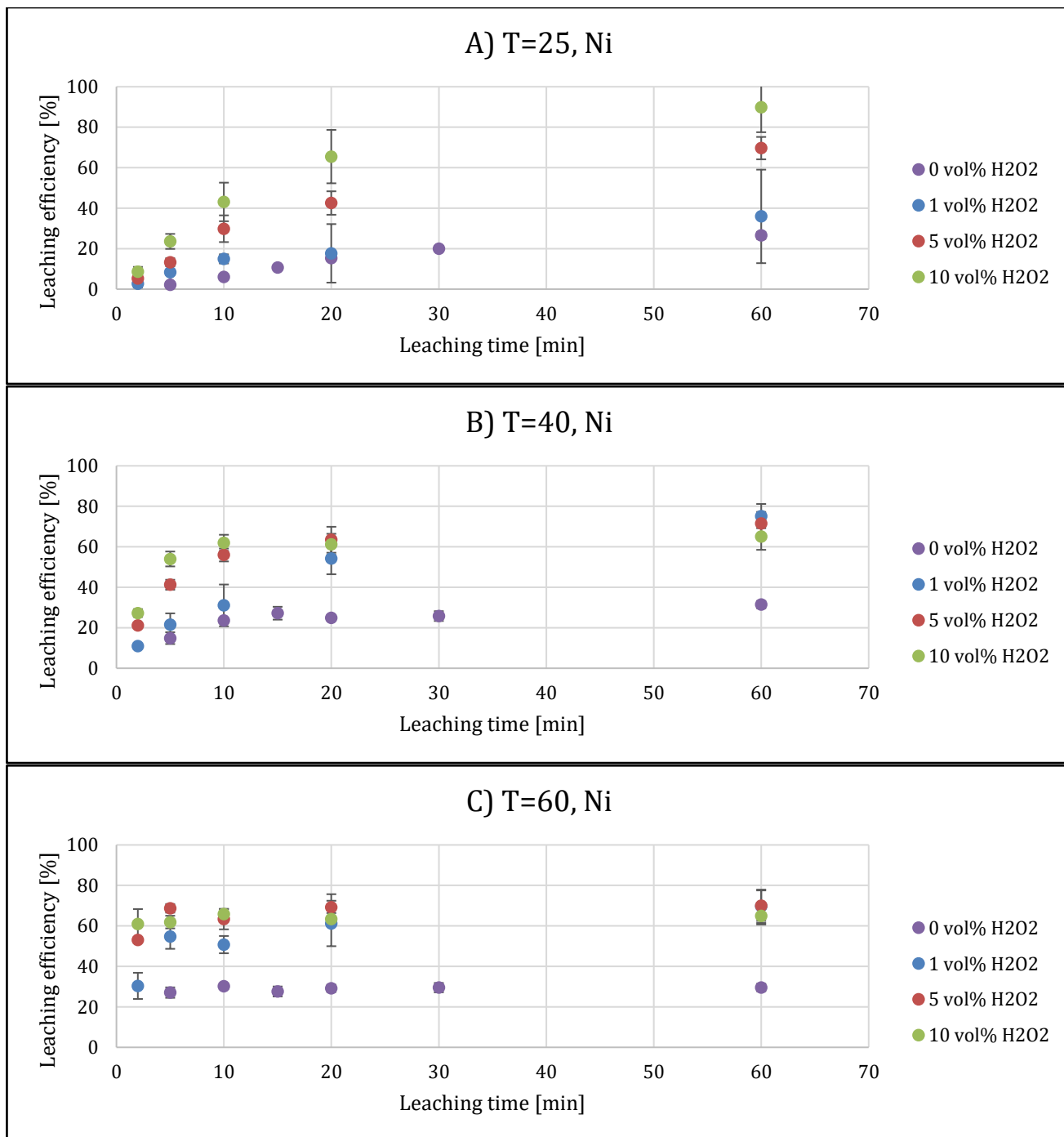


Figure 50: Leaching of NMC 442. Kinetic curves for nickel leaching A) at 25°C. B) at 40°C. C) at 60°C.

Figure 50 A) show the influence of increasing volume of hydrogen peroxide for leaching at 25°C. 10 vol% H₂O₂ have the highest leaching efficiency followed by 5 vol% H₂O₂, 1 vol% H₂O₂ and 0 vol% H₂O₂.

The leaching curves presented in Figure 50 B) represent the experiments at 40°C. 5 vol% H₂O₂ and 10 vol% H₂O₂ show similar leaching efficiency throughout the experiment. 1 vol% H₂O₂ start at a lower efficiency but after 60 minutes it ends with the highest efficiency.

In Figure 50 C) the kinetic curves for 5 vol% H₂O₂ and 10 vol% H₂O₂ both show a high leaching after 2 minutes, but the efficiency does not improve significantly during the experiment. 1 vol% H₂O₂ start with a low value but after 60 minutes it has reached an efficiency similar to 5 vol% and 10 vol% H₂O₂.

Hydrogen peroxide increases the leaching efficiency for nickel from NMC 442. Nickel is already in oxidation state +2 as presented in Table 11 so a reduction in oxidation state is not necessary. However, the increased leaching of cobalt and manganese helps nickel to be more easily leached from the structure of the cathode material.

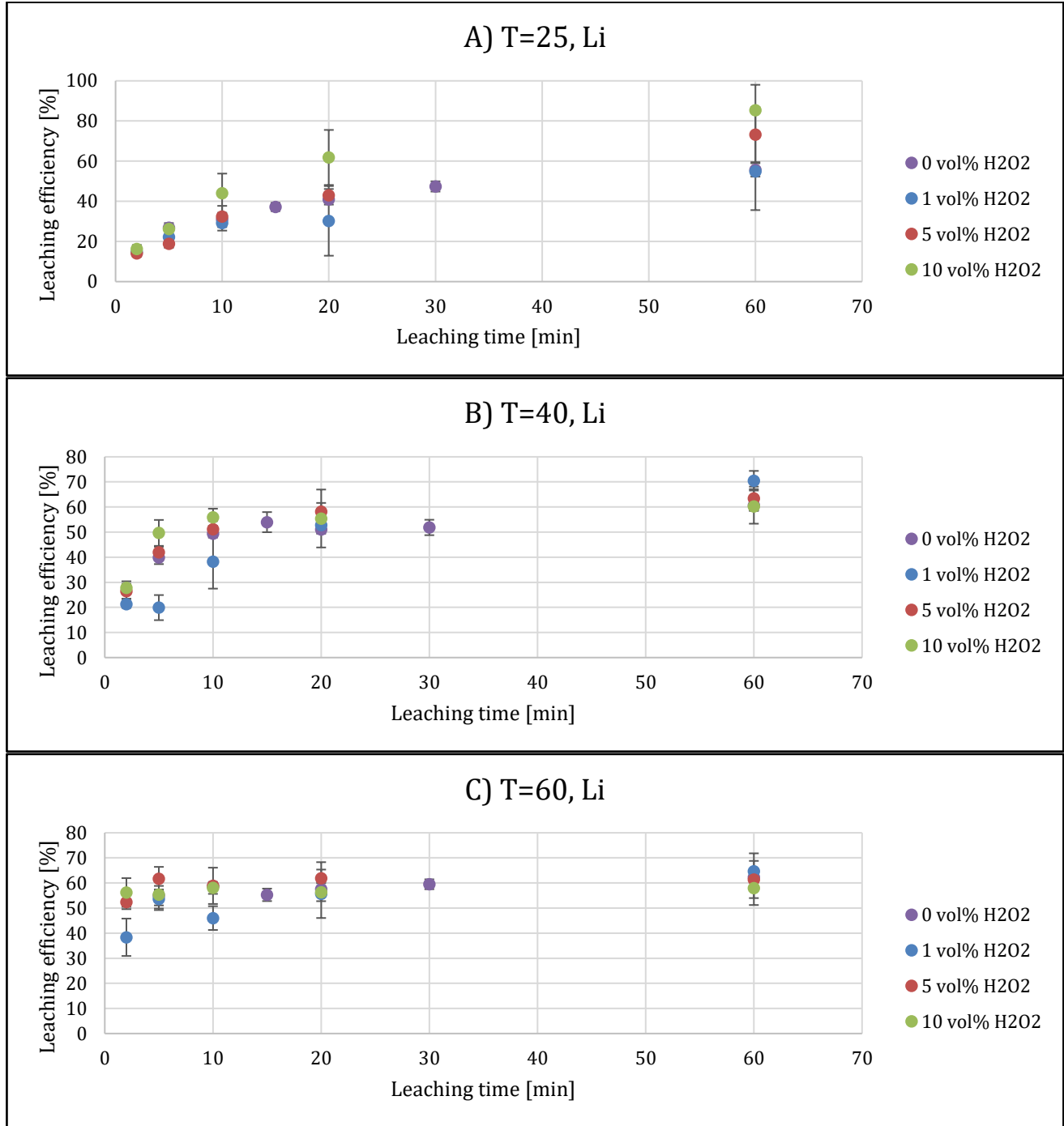


Figure 51: Leaching of NMC 442. Kinetic curves for lithium leaching A) at 25°C. B) at 40°C. C) at 60°C.

In Figure 51 A) the kinetic curves of H₂O₂ show a low leaching efficiency from the start before steady improvements during the experiment. Highest efficiency is reached with 10 vol% H₂O₂ while 0 vol% and 1 vol% H₂O₂ has the same recovery rate after 60 minutes. The kinetic curves in Figure 51 B) show a different pattern. 1 vol% H₂O₂ has decreased efficiency after 5 minutes but when the experiment is finished it has the highest efficiency. The kinetic curve for 0 vol% H₂O₂ follow the curves for 5 vol% and 10 vol% H₂O₂.

Figure 51 C) show that during the experiment neither 0 vol%, 5 vol% nor 10 vol% H₂O₂ show a significant increase in leaching efficiency. However, 1 vol% H₂O₂ has the lowest value after 2 minutes but during the experiment it increases and after 60 minutes it has reached a leaching efficiency of 64%.

The effect hydrogen peroxide has on the leaching is most noticeable at 25°C. For the leaching at 60°C the kinetic curve for 0 vol% H₂O₂ showed a leaching efficiency similar to samples containing hydrogen peroxide. This can be seen for other cathode materials as well.

3.8. Leaching of NMC 811

3.8.1. Leaching with H₂SO₄ – no addition of H₂O₂

Presented in Figure 52, Figure 53 and Figure 54 are the kinetic curves for leaching of cobalt, nickel and lithium from NMC 811. For this cathode material there was a problem with the measurement of manganese in the ICP-OES as it did not detect any leached manganese when 2M sulfuric acid was used. All experiments were done in triplicates to and the points represent an average from those experiments with standard deviation plotted.

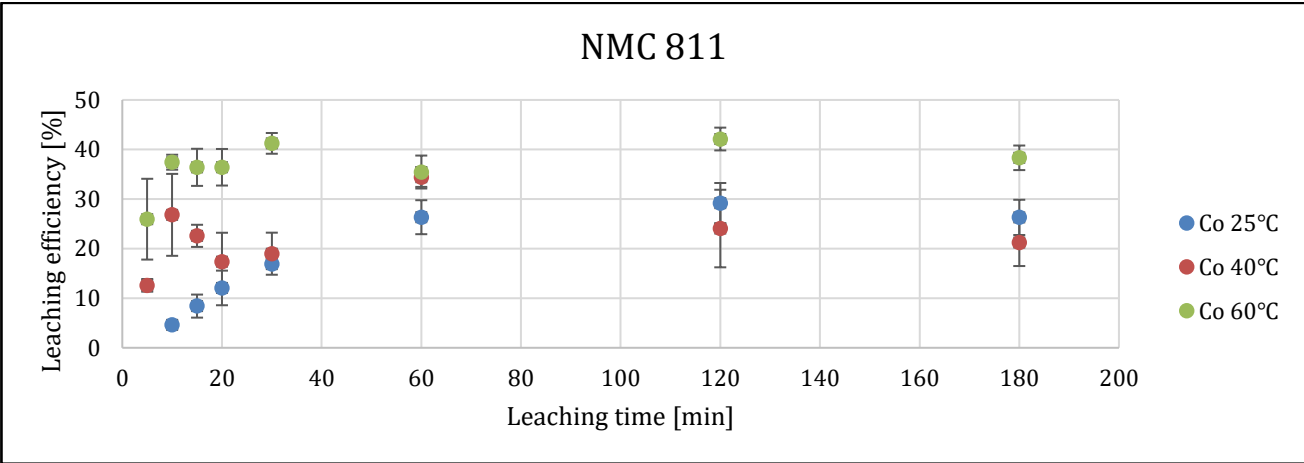


Figure 52: Leaching of NMC 811. The kinetic curves for cobalt plotted against time.

In Figure 52 the kinetic curves for cobalt are presented. 60°C has the highest leaching efficiency when the leaching is finished. The curve representing 25°C has its peak after 120 minutes before a small decrease at the 180-minute mark. For 40°C the curve shows no clear pattern, first having a small peak after 10 minutes and then another after 60 minutes before the efficiency decrease. The reason for this may be problems occurring when diluting the samples.

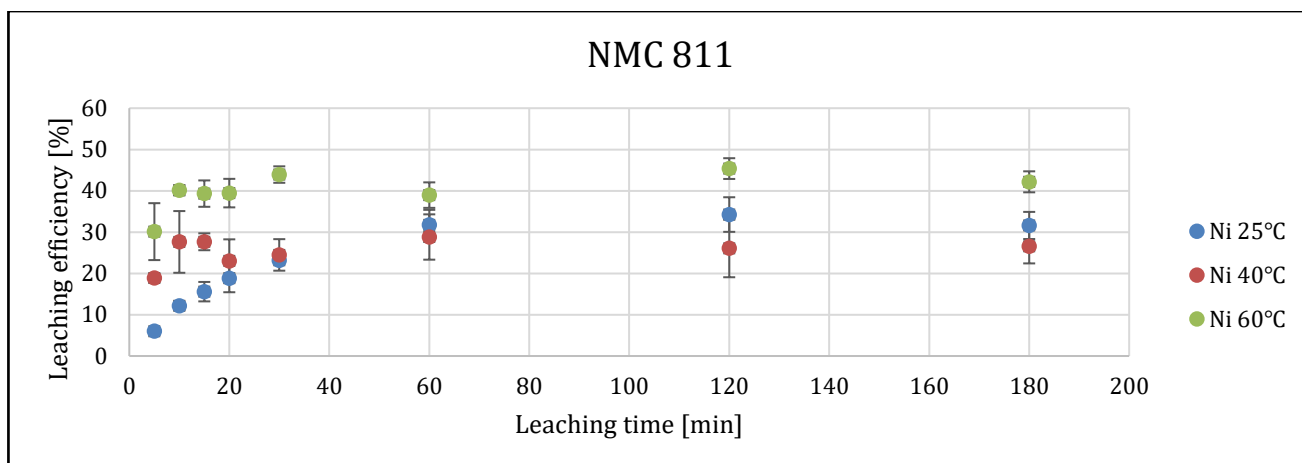


Figure 53: Leaching of NMC 811. The kinetic curves for nickel plotted against time.

Figure 53 shows the kinetic curves for leaching of nickel from NMC 811. The curve representing 25°C show an improving efficiency during the first 120 minutes of leaching whereas the curves for 40°C and 60°C both have only small increases in leaching efficiency during the experiment. After 180 minutes the best leaching efficiency is reached at 60°C.

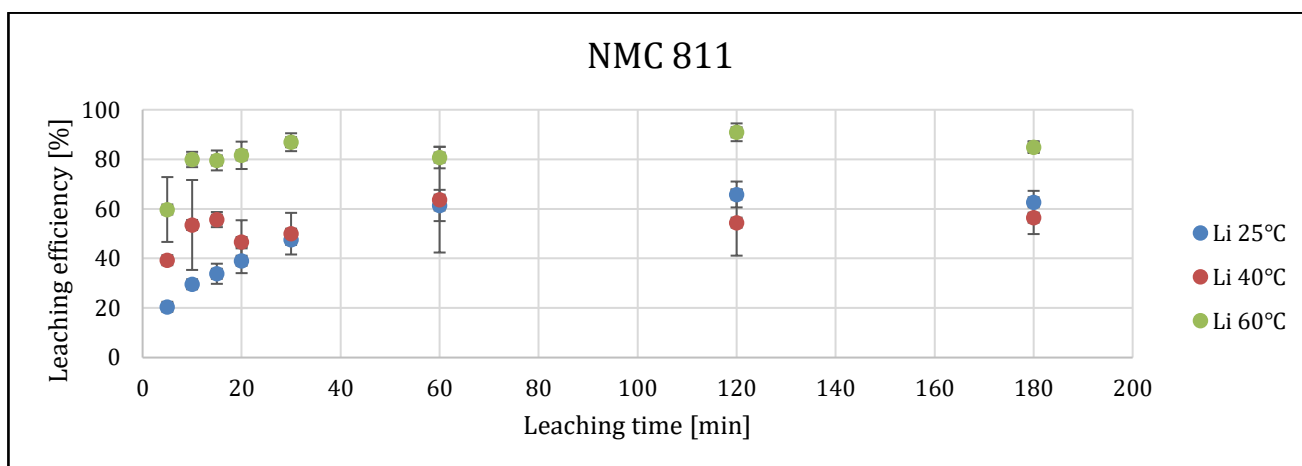


Figure 54: Leaching of NMC 811. The kinetic curves for lithium plotted against time.

The kinetic curves for leaching of lithium from NMC 811 are presented in Figure 54. The highest leaching efficiency is reached at 60°C with over 90% after 120 minutes. The kinetic curve for 40°C reach its peak at 60 minutes before a slightly lower efficiency is measured afterwards. For 25°C the leaching efficiency is low in the beginning before reaching an efficiency of 60% in the end.

3.8.2. Leaching with H_2SO_4 with addition of H_2O_2

In this section the results from leaching NMC 811 with hydrogen peroxide is presented. Figure 55, Figure 56, Figure 57 and Figure 58 display the leaching of cobalt, manganese, nickel and lithium. All points represent the average of a triplicate with the standard deviation plotted.

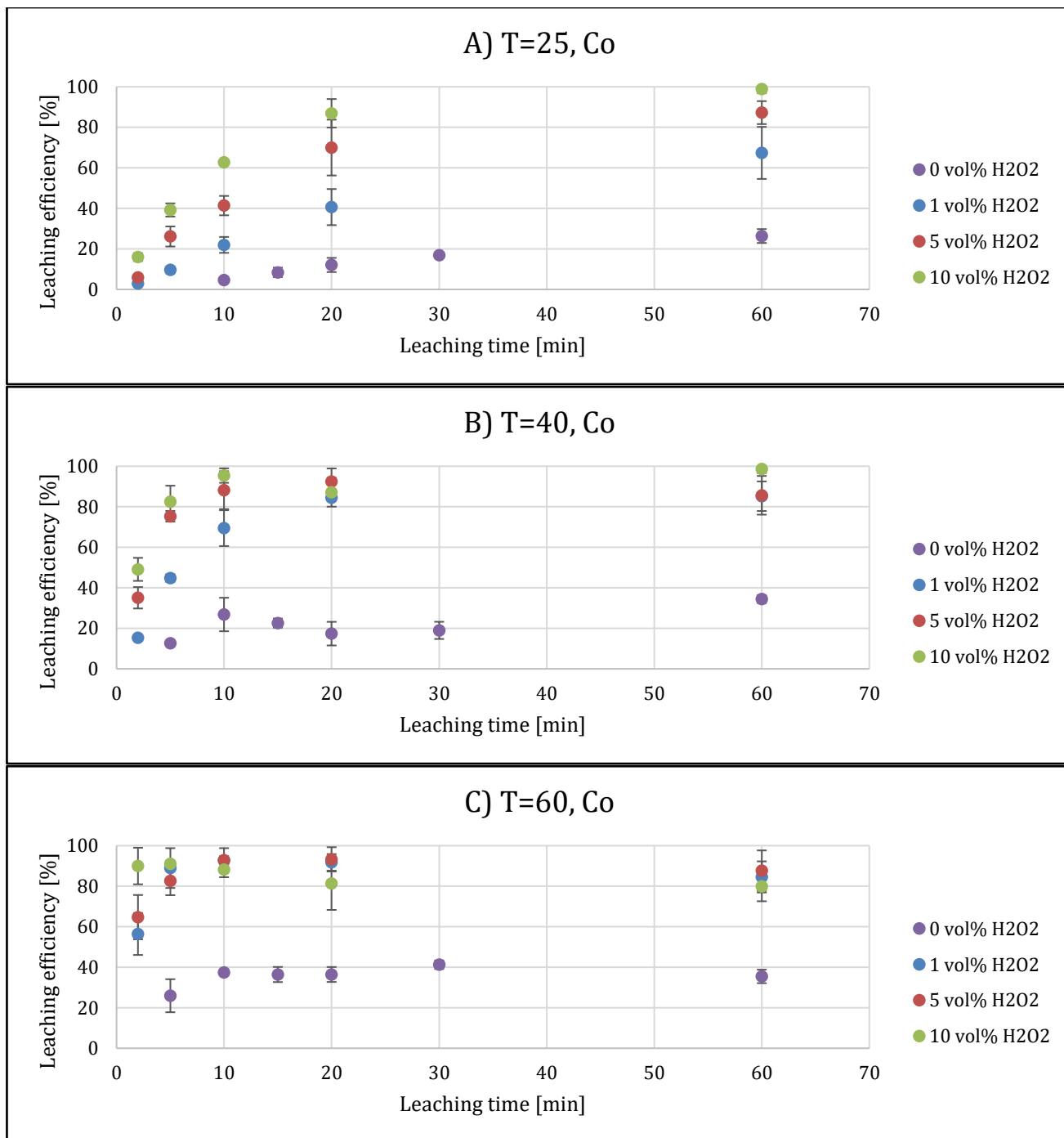


Figure 55: Leaching of NMC 811. Kinetic curves for cobalt leaching A) at 25°C. B) at 40°C. C) at 60°C.

In Figure 55 A) the kinetic curves are ordered according to increasing amount of hydrogen peroxide. The lowest leaching efficiency is reached with 0 vol% while the highest is reached with 10 vol% where all cobalt is leached. All curves start at a low value and increases during the leaching time.

Visible in Figure 55 B) is that 10 vol% H₂O₂ has the highest leaching efficiency at 40°C. The curves representing leaching with H₂O₂ all show a significant increase during the first 10 minutes of the leaching. 1 vol% H₂O₂ and 5 vol% H₂O₂ have the same leaching efficiency after 60 minutes.

The kinetic curves presented in Figure 55 C) all reach their respective maximum value before 60 minutes. 5 vol% H₂O₂ has the highest leaching efficiency of 93% after 10 minutes before it

decreases slightly. The kinetic curve for 10 vol% H₂O₂ show no increase in efficiency during the experiment but rather a small decrease from the 5-minute mark.

It is clear the addition of hydrogen peroxide to the leaching solution improves the leaching efficiency of cobalt from NMC 811. Once cobalt is released from the structure of the cathode material it is reduced and form CoSO₄(aq).

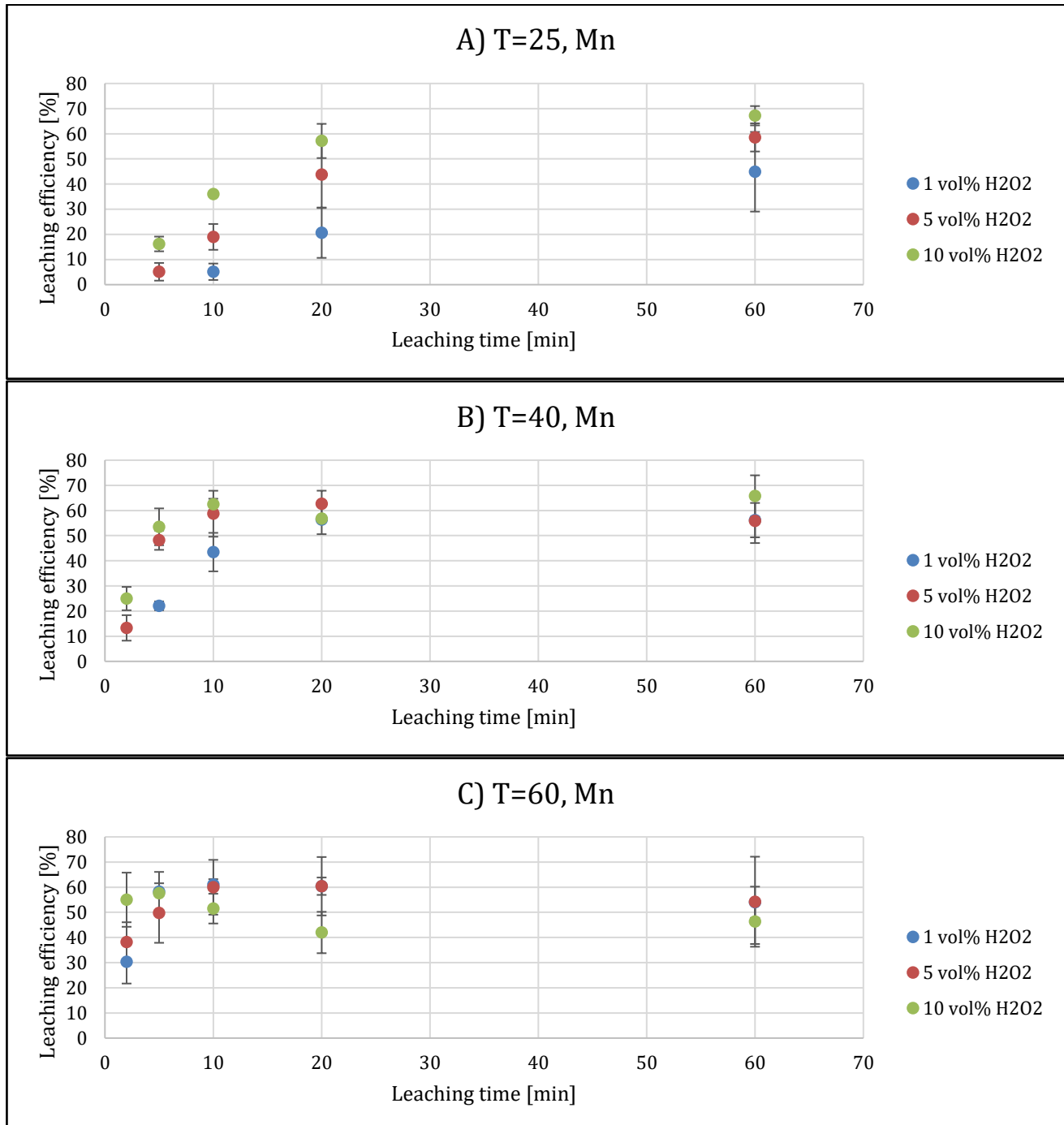


Figure 56: Leaching of NMC 811. Kinetic curves for manganese leaching A) at 25°C. B) at 40°C. C) at 60°C.

The kinetic curves in Figure 56 A) have parallel shapes with 10 vol% H₂O₂ displaying the highest leaching efficiency. All curves start with a low leaching efficiency and show an increase in efficiency throughout the leaching time.

In Figure 56 B) the kinetic curves for 5 vol% H_2O_2 and 10 vol% H_2O_2 have similar shape with 10 vol% having the highest leaching efficiency after 60 minutes. 1 vol% H_2O_2 is missing a value at 2 minutes and has a low efficiency after 5 minutes but after 60 minutes it has comparable leaching efficiencies to 5 vol% H_2O_2 .

Figure 56 C) show how all the kinetic curves reaches maximum leaching efficiency before 60 minutes. The kinetic curve for 10 vol% H_2O_2 show an upward trend between 2 and 5 minutes but then it displays a downward trend. 1 vol% H_2O_2 and 5 vol% H_2O_2 show similar efficiencies after 60 minutes.

During leaching with only acid no leached manganese could be detected by the ICP-OES and therefore no comparison can be done. This however shows the importance of adding hydrogen peroxide to the leaching solution to enable extraction and recovery of manganese from NMC 811. The manganese extracted from the structure was reduced and formed $\text{MnSO}_4(\text{aq})$ according to reaction (18).

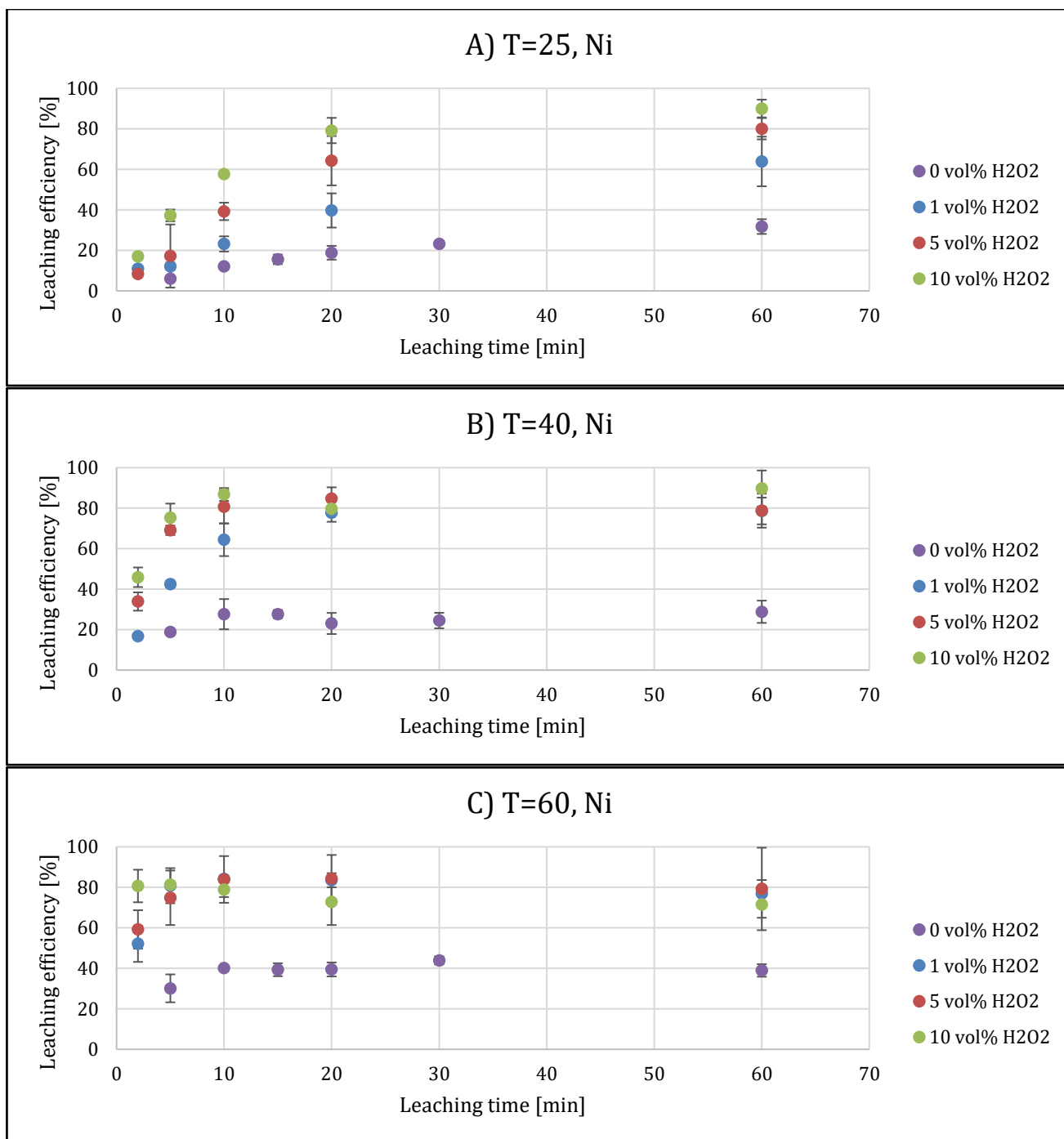


Figure 57: Leaching of NMC 811. Kinetic curves for nickel leaching A) at 25°C. B) at 40°C. C) at 60°C.

Figure 57 A) shows how the leaching efficiency increases as more hydrogen peroxide is added to the solution. 10 vol% H₂O₂ has the highest leaching efficiency with 90%. All solutions containing H₂O₂ display higher efficiency compared to leaching without any addition of a reducing agent. In Figure 57 B) the kinetic curves for 5 vol% H₂O₂ and 10 vol% H₂O₂ are parallel during the first 10 minutes of leaching but in the end 10 vol% H₂O₂ reaches the highest efficiency. 1 vol% H₂O₂ start with a low value but ends with a leaching efficiency of 79%. Presented in Figure 57 C) are the kinetic curves for leaching of nickel from NMC 811 at 60°C. As can be seen the leaching efficiency for 10 vol% H₂O₂ show no increase since the maximum leaching yield was reached during the first minutes of leaching, whereas both 1 vol% H₂O₂ and 5 vol% H₂O₂ have improved efficiencies as the leaching time increase.

In NMC 811 there is a majority of nickel ions in the cathode structure making it necessary to reach high leaching efficiencies of nickel. As nickel is leached from the structure it makes the other metal ions more easily available for the acid and hydrogen peroxide to reduce. The nickel ions form $\text{NiSO}_4(\text{aq})$ during leaching as presented in reaction (18).

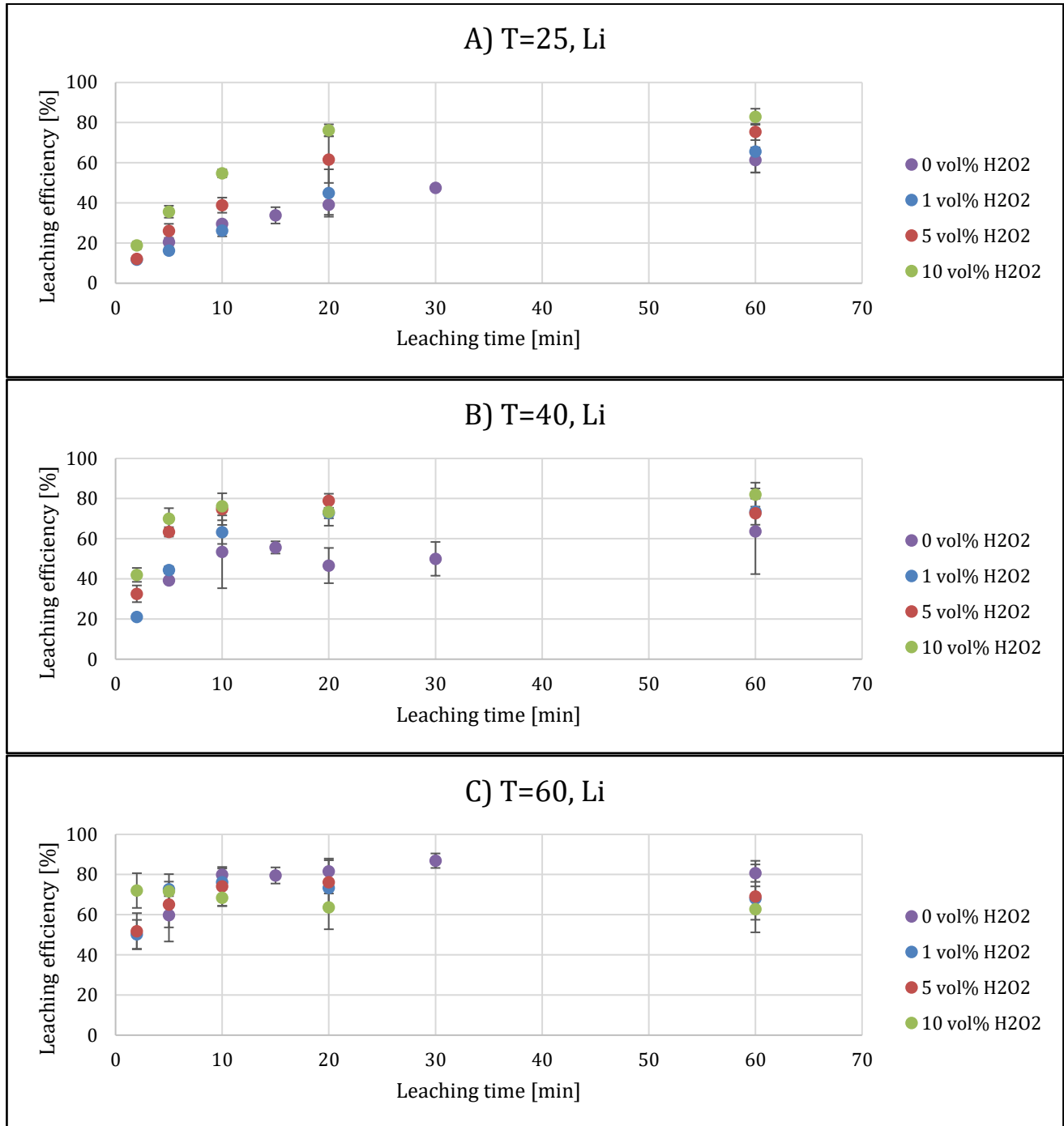


Figure 58: Leaching of NMC 811. Kinetic curves for lithium leaching A) at 25°C. B) at 40°C. C) at 60°C.

In Figure 58 A) 10 vol% H_2O_2 has the highest leaching efficiency followed by 5 vol% H_2O_2 , 1 vol% H_2O_2 and 0 vol% H_2O_2 . The kinetic curves all have similar patterns during the experiment. Figure 58 B) presents kinetic curves for leaching in 40°C where 10 vol% H_2O_2 reaches the highest leaching efficiency. 1 vol% H_2O_2 and 5 vol% H_2O_2 have comparable leaching values after 60 minutes while 0 vol% H_2O_2 has the lowest efficiency.

The kinetic curve for 10 vol% H_2O_2 in Figure 58 C) shows no improvement as the leaching time increases. After 60 minutes of leaching 0 vol% H_2O_2 gives its highest leaching efficiency of 80%. 1 vol% H_2O_2 and 5 vol% H_2O_2 both reach their respective maximum before the 60 minute-mark.

The effect of hydrogen peroxide on the leaching of lithium is visible at 25°C and 40°C where the recovery of lithium is increased. For 60°C leaching without any addition of hydrogen peroxide displays the highest leaching efficiency. This follows the pattern seen for other cathode materials.

4

Conclusion

The effect of hydrogen peroxide could be observed in the results from the leaching experiments. For the investigated cathode materials, it improved the efficiency and leaching rate for all but one material. Hydrogen peroxide is a known reducing agent and as the theory and previous studies predicted the addition of it increased the leaching.

All cathode materials except LiNiO_2 had an increase in leaching of the valuable metals. Three cathode materials were totally leached into the solution when hydrogen peroxide was used: LiCoO_2 , LiMn_2O_4 and NMC 811. The cathode material with the biggest increase in both efficiency and rate due to hydrogen peroxide was LiMn_2O_4 . When the leaching conditions were set at 25°C with 1 vol% H_2O_2 the highest leaching yield was reached in less than 5 minutes. When the leaching conditions were set at 60°C with 10 vol% H_2O_2 a leaching yield of 100% was reached for LiCoO_2 .

During the leaching the temperature and leaching efficiency are connected, when the temperature is increased the leaching efficiency improves. The results from leaching with 2M H_2SO_4 in 60°C showed the highest leaching efficiency for all tested cathode materials with one exception, manganese from NMC 442.

For cathode materials with high concentration of cobalt the leaching yield was high when 60°C and 10 vol% H_2O_2 was used in the leaching solution. The reason for this is the strong nature of the Co-O bond in the cathode materials making it necessary to leach at a high temperature. The metal with the highest value is cobalt, making it the targeted metal in the leaching process. The conclusion for leaching of manganese is that highest yields of it are obtained at 25°C but at different concentrations of H_2O_2 depending on the cathode material. The change of oxidation state for manganese is the reason the leaching efficiency increases when H_2O_2 is added to the leaching solution.

For nickel the maximum yield is often reached at 25°C but with different concentrations of H_2O_2 . The difference in electrochemical potential between nickel and hydrogen peroxide is the reason the leaching yields increase when H_2O_2 is used in the leaching.

The leaching yield of lithium with H_2O_2 increased at 25°C and 40°C but at 60°C leaching without H_2O_2 often showed higher yield. Since lithium is monovalent it was more easily leached by sulfuric acid and at higher temperature H_2O_2 had no effect on the leaching of lithium.

The results from this thesis can be adopted in the growing LiBs industry and for recycling of different types of cathode materials with the use of hydrogen peroxide. Hydrogen peroxide has been a versatile reducing agent that can be applied on different types of cathode materials and improve the leaching efficiency. The recycling process is practical and possesses a high recovery rate of valuable metals making it commercially viable. One way to evaluate the hydrometallurgical treatment with reductive leaching using hydrogen peroxide is to do a life

cycle assessment of the process. That would give an indication of the impact the treatment has on the environment and could be used to compare the treatment to other recycling processes.

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A.

Appendix I

1. Data for CAGR calculations

Data is taken from Mineral Commodity Summaries published each year by United States Geological Survey [19] [20] [21].

Category	Percent of total production 2012	Use of Li in 2012 (tonne)	Percent of total production 2018	Use of Li 2018 (tonne)	Years	CAGR
Batteries	22	6204	56	47040	6	0.40163
Ceramics and glass	30	8640	23	19320	6	0.14353
Lubricating greases	11	3102	6	5040	6	0.08426
Air treatment	4	1128	2	1680	6	0.06864
Polymers	3	846	4	3360	6	0.25843
Other uses	23	6486	6	5040	6	-0.04117
Continuous casting mold flux powders*	6	1800	3	2520	5	0.06961

B.

Appendix II

1. Leaching experiments

Cathode material	Acid	Temperature	Stirrer speed	Time at which samples were taken [min]	Reductive agent
LiCoO ₂	2M H ₂ SO ₄	25°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
LiCoO ₂	2M H ₂ SO ₄	40°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
LiCoO ₂	2M H ₂ SO ₄	60°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
LiNiO ₂	2M H ₂ SO ₄	25°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
LiNiO ₂	2M H ₂ SO ₄	40°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
LiNiO ₂	2M H ₂ SO ₄	60°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
LiMn ₂ O ₄	2M H ₂ SO ₄	25°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
LiMn ₂ O ₄	2M H ₂ SO ₄	40°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
LiMn ₂ O ₄	2M H ₂ SO ₄	60°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
NMC 121	2M H ₂ SO ₄	25°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
NMC 121	2M H ₂ SO ₄	40°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
NMC 121	2M H ₂ SO ₄	60°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
LiCoO ₂	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
LiCoO ₂	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
LiCoO ₂	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
LiCoO ₂	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
LiCoO ₂	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
LiCoO ₂	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
LiCoO ₂	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂

LiCoO₂	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
LiCoO₂	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
LiNiO₂	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
LiNiO₂	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
LiNiO₂	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
LiNiO₂	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
LiNiO₂	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
LiNiO₂	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
LiNiO₂	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
LiNiO₂	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
LiNiO₂	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
LiMn₂O₄	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
LiMn₂O₄	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
LiMn₂O₄	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 121	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 121	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 121	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 121	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 121	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 121	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 121	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 121	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 121	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 111	2M H ₂ SO ₄	20°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
NMC 111	2M	40°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	

	H ₂ SO ₄				
NMC 111	2M H ₂ SO ₄	60°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
NMC 111	2M H ₂ SO ₄	20°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 111	2M H ₂ SO ₄	20°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 111	2M H ₂ SO ₄	20°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 111	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 111	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 111	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 111	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 111	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 111	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 442	2M H ₂ SO ₄	25°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
NMC 442	2M H ₂ SO ₄	40°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
NMC 442	2M H ₂ SO ₄	60°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
NMC 442	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 442	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 442	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 442	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 442	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 442	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 442	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 442	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 442	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 811	2M H ₂ SO ₄	25°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
NMC 811	2M H ₂ SO ₄	40°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	

NMC 811	2M H ₂ SO ₄	60°C	300 rpm	5, 10, 15, 20, 30, 60, 120, 180	
NMC 811	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 811	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 811	2M H ₂ SO ₄	25°C	300 rpm	2, 5, 10, 20, 60	1 vol% H ₂ O ₂
NMC 811	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 811	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 811	2M H ₂ SO ₄	40°C	300 rpm	2, 5, 10, 20, 60	5 vol% H ₂ O ₂
NMC 811	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 811	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂
NMC 811	2M H ₂ SO ₄	60°C	300 rpm	2, 5, 10, 20, 60	10 vol% H ₂ O ₂

C.

Appendix III

1. Inductively Coupled Plasma – Optical Emission Spectrometry

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is a technique that is used to analyze samples containing aqueous and organic liquids and solids to determine the concentration of the elements present in the sample. The sample are exposed to high temperatures in ICP-OES which causes dissociation into atoms and collisional excitation to take place. When the atoms are in their excited state they decay back to the lower states through either thermal or emission energy transitions. The intensity of the light emitted is measured in ICP-OES to help determine the concentration of a specific element in the sample. [75]

Liquid from the vials in the sample racks is transferred to the nebulizer by an autosampler coupled with a pump. In the nebulizer the liquid is transformed into an aerosol by using high-speed gas to break up the liquid. The aerosol is lead to the torch before it is injected into the argon plasma where the temperature is 6000-7000K [75] [76]. The aerosol is vaporized, atomized, desolvated and excited/ionized by the plasma.

The torch consists of different concentric tubes made of quartz in which the argon gas and the aerosol are flowing through before merging in the flame. The aerosol is transported in the center of the torch with the argon gas flowing on the outside of the inner tube. In the tube furthest away from the center, gas flows to keep the walls on the tubes cool. The top of the torch is surrounded by a copper coil coupled with a radio frequency (RF) generator. The alternating current of the RF generator creates an oscillation inside the coil. A consequence from this is an electric field and an alternative magnetic field that accelerate electrons into a circular trajectory. When a spark is applied to the top of the torch some electrons are stripped from the argon gas. These electrons are accelerated by the magnetic field before they collide with other argon atoms, breaking down the gas into the plasma containing argon ions, argon atoms and electrons. This mixture is known as inductively coupled plasma discharge. The discharge is kept inside the torch as a result of the RF energy. When the sample are injected in the torch it punches a hole through the discharge [75]. Figure 59 shows the schematic flow in the torch of ICP-OES.

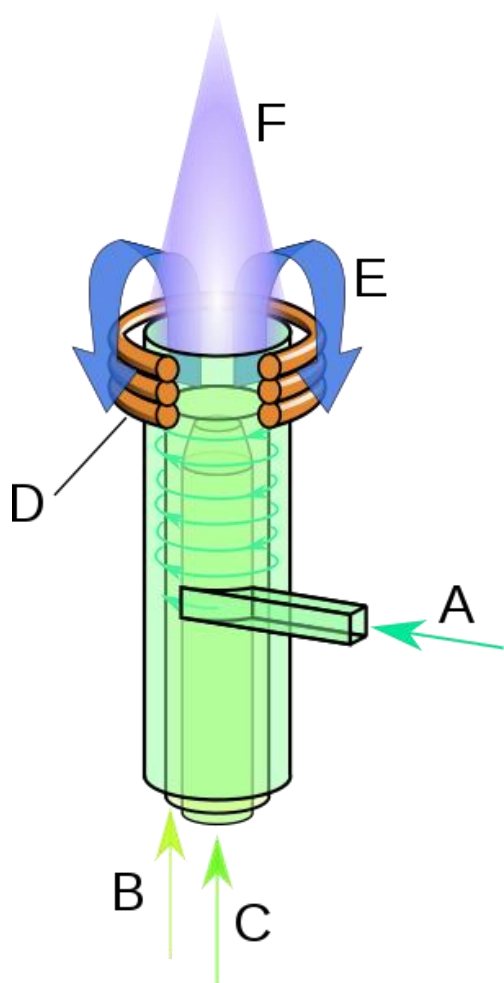


Figure 59: The construction of Inductively Coupled Plasma torch. A: outer gas flow in the quartz tube. B: discharge gas flow. C: flow of carrier gas with sample. D: induction coil which forms the strong magnetic field inside the torch. E: force vectors of the magnetic field. F: the plasma torch (the discharge). Image available under CC-BY-4.0 [77].

When the aerosol has passed through the discharge it is in an excited state as a result of the energy transition. The excited ions and electrons will emit light when they return to their ground state. The emitted light is polychromatic since there are different elements emitting light at different wavelengths. To analyze the light either a polychromator or a monochromator can be used. A polychromator can be used to analyze multiple wavelengths at once while a monochromator is used to measure one wavelength at a time. When the light has passed through the monochromator/polychromator it is detected by a photosensitive detector. [75]

Quantitative information from ICP-OES is received using plots with emission intensity plotted against concentration. These plots called calibration curves are prepared with known amounts of the metals searched for in the samples. With the calibration curve and the measured intensity of an element the concentration of the element in the sample can be calculated. [75]

The advantages with Optical Emission Spectroscopy are the high matrix tolerance, wide linear dynamic range, high speed of analysis and the possibility to excite several different elements at once [75] [78]. Disadvantages are that when several elements are excited simultaneously the emission wavelengths increase in number which can cause interferences between the emission lines [75].

D.

Appendix IV

1. Calculations of amount H_2O_2 needed for leaching of LiCoO_2

	2LiCoO_2	$+ 3\text{H}_2\text{SO}_4$	$+ \text{H}_2\text{O}_2$	$\rightarrow$	2CoSO_4	$+ \text{Li}_2\text{SO}_4$	$+ 4\text{H}_2\text{O}$	$+ \text{O}_2$
M (g/mol)	97.87	98.1	34.0147					
m (g)	0.25	4.905	0.04343					
n (mol)	0.002554	0.05	0.001277					
c (mol/dm ³)		2						
V (ml)		25	0.02969					
ρ (g/ml)			1.463					

2. Calculations of amount H_2O_2 needed for leaching of LiNiO_2

	2LiNiO_2	$+ 3\text{H}_2\text{SO}_4$	$+ \text{H}_2\text{O}_2$	$\rightarrow$	2NiSO_4	$+ \text{Li}_2\text{SO}_4$	$+ 4\text{H}_2\text{O}$	$+ \text{O}_2$
M (g/mol)	97.631	98.1	34.0147					
m (g)	0.25	4.905	0.04355					
n (mol)	0.002561	0.05	0.00128					
c (mol/dm ³)		2						
V (ml)		25	0.02977					
ρ (g/ml)			1.463					

3. Calculations of amount H_2O_2 needed for leaching of LiMn_2O_4

	$6\text{LiMn}_2\text{O}_4$	$+ 15\text{H}_2\text{SO}_4$	$+ 5\text{H}_2\text{O}_2$	$\rightarrow$	12MnSO_4	$+ 3\text{Li}_2\text{SO}_4$	$+ 20\text{H}_2\text{O}$	$+ 7\text{O}_2$
M (g/mol)	180.812	98.1	34.0147					
m (g)	0.25	4.905	0.03919					
n (mol)	0.00138	0.05	0.001152					
c (mol/dm ³)		2						
V (ml)		25	0.02679					
ρ (g/ml)			1.463					

4. Calculations of amount H_2O_2 needed for leaching of NMC 121

	$8\text{LiNi}_{0.25}\text{Mn}_{0.5}\text{Co}_{0.25}\text{O}_2$	$+ 12\text{H}_2\text{SO}_4$	$+ 2\text{H}_2\text{O}_2$	$\rightarrow$	4MnSO_4	$+ 2\text{NiSO}_4$	$+ 2\text{CoSO}_4$	$+ 4\text{Li}_2\text{SO}_4$	$+ 14\text{H}_2\text{O}$	$+ 3\text{O}_2$
M (g/mol)	95.8166	98.1	34.0147							
m (g)	0.25	4.905	0.0222							
n (mol)	0.002609	0.05	0.000652							
c (mol/dm ³)		2								
V (ml)		25	0.01516							
ρ (g/ml)			1.463							

5. Calculations of amount H₂O₂ needed for leaching of NMC 111

	6LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂	+9H ₂ SO ₄	+H ₂ O ₂	→	2MnSO ₄	+2NiSO ₄	+2CoSO ₄	+3Li ₂ SO ₄	+10H ₂ O	+2O ₂
M (g/mol)	95.8872	98.1	34.0147							
m (g)	0.25	4.905	0.01480							
n (mol)	0.002607	0.05	0.000434							
c		2								
(mol/dm ³)										
V (ml)		25	0.01010							
ρ (g/ml)			1.463							

6. Calculations of amount H₂O₂ needed for leaching of NMC 442

	40LiNi _{0.4} Mn _{0.4} Co _{0.2} O ₂	+60H ₂ SO ₄	+ 2H ₂ O ₂	→	16MnSO ₄	+16NiSO ₄	+8CoSO ₄	+20 Li ₂ SO ₄	+62H ₂ O	+11 O ₂
M (g/mol)	96.1802	98.1	34.0147							
m (g)	0.25	4.905	0.00442							
n (mol)	0.002599	0.05	0.000129							
c (mol/dm ³)		2								
V (ml)		25	0.0030							
ρ (g/ml)			1.463							

7. Calculations of amount H₂O₂ needed for leaching of NMC 811

	40LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂	+60H ₂ SO ₄	+2 H ₂ O ₂	→	4 MnSO ₄	+32 NiSO ₄	+4CoSO ₄	+20 Li ₂ SO ₄	+62H ₂ O	+11 O ₂
M (g/mol)	97.2828	98.1	34.0147							
m (g)	0.25	4.905	0.00437							
n (mol)	0.002569	0.05	0.000128							
c (mol/dm ³)		2								
V (ml)		25	0.002987							
ρ (g/ml)			1.463							