Utilization of Deep Eutectic Solvents (DES) in Recovery of Li-based Black Mass

Master Thesis in Sustainable Energy System

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CHALMERS UNIVERSITY OF TECHNOLOGY
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Cover: Four leaching agents / deep eutectic solvents, DES, after leaching black mass. The leaching conditions 2 h, 90°C and solid to liquid ratio 20 g/l. From left to right OA-ChCl, OA-ChCl + water, OA-TMA and MA-ChCl + water.

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Abstract

This study was conduced with a characterization of 12 combinations of solvents. These solvents consisted of the acids citric acid monohydrate, CA, oxalic acid dihydrate, OA, and malic acid, MA. The acids were mixed with the chloride based salts ammonium chloride, NCl, aluminum chloride hexahydrate, ACH, choline chloride, ChCl, and tetramethylammonium chloride, TMA, in the ratios 1:1, 1:2 and 2:1. The categorizations for the observed solvents, also called Deep eutectic solvents (DES), were pH and optical viscosity.

After determining the characteristics for each solvent, the solvents with the lowest observed viscosity and the lowest pH were used for the leaching of black mass, with the goals of having low water consumption and high leaching yield of Ni, Co and Mn. The lithium based black mass had the cathodic structure NMC 111 or NMC 622. The five solvents used for leaching were OA-ChCl, OA-TMA, OA-ACH, CA-ChCl and MA-ChCl with the following experimental properties: leaching duration of 2h, 90°C, ratio 2:1, solid to liquid ratio, S/L, 20 g/l and the black mass NMC111. Thereafter, a parameter optimization was performed by changing the leaching temperature between 60, 90, 120 and 150°C as well as the ratios between 1:1, 1:2 and 2:1. The other experimental properties were 2h duration, 90°C, S/L 50g/l and the black mass NMC622. Further, a kinetic study was performed where the leaching duration changed between 1/3, 2/3, 1, 2, 4, 6, 18 and 24h, and the best parameters from the parameter optimization were used.

Keywords: pH, optical viscosity, DES, HBA, HBD, LIB and Leaching

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Elin Strömberg, Lillestrøm Norway, 2024-05-20

List of Acronyms

Acronyms in alphabetical order are listed below and these acronyms are used throughout the master thesis:

ACH	Aluminum chloride hexahydrate
CA	Citric Acid monohydrate
ChCl	Choline Chloride
DES	Deep Eutectic Solvents
EV	Electric vertical
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
IPS-OES	Inductively coupled plasma - optical emission spectrometry
LIB	Lithium-ion Battery
MA	Malic acid
NCl	Ammonium chloride
OA	Oxalic acid dihydrate
OES	Optical emission spectrometry
TCA	Tricarboxylic acid
TMA	Tetramethylammonium chloride
XRF	X-ray fluorescence

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1

Introduction

Most of the world, 196 parties, has agreed through the Paris Agreement, to keep the global temperature increase well below 2°C compared to the preindustrial levels [1]. To stay below this agreed limit, a reduction in emitted greenhouse gases must occur [1]. One way to limit greenhouse gases is to transform the transport sector. The European Parliament and Council have mandated that all registered cars and vans must be emission free after 2035. This legislation will make the transport sector in the European Union more sustainable [2].

A category of technology that has low emissions are electrical vehicles (EV), hybrid electric vehicles (HEVs) and plug-in hybrid electrical vehicles (PHEVs) [3]–[5]. These vehicles use lithium-ion batteries (LIBs) instead of combustion engines [5]. LIBs fit in the transportation sector because they have high power density, high efficiency and can operate at wide temperature ranges [5]. Furthermore, it is expected that around the year 2040 more than half of the vehicles fleet will be electrically driven [4].

The global production capacities of LIBs in the beginning of 2019 were 316 GWh, where 73% were produced in China and 12% were produced in the US [4]. In addition it is expected that the global production capacity will increase to 500 GWh by 2025 [6]. The big consumption of LIBs has resulted in the prediction that the demand will exceed the supply after 2023 [4], leading to increased prices of the metals used. To minimize the cost in production, lithium, cobalt and nickel must be recycled from spent LIBs and thereby used as secondary resources [4], [5]. It is also crucial to prevent the metals in spent LIBs metals from contaminating the environment through traditional waste disposal methods such as landfills, incinerations, and stabilizations [7]. These methods may lead to soils and groundwater contamination as well as the release of toxic gases into the atmosphere [7]. Moreover, such traditional methods will waste valuable metals. To address these issues, the US has prohibited landfilling of spent LIBs, treating them as hazardous materials, and the European Union has committed itself to recycling at least 50% of its waste batteries [7]. Therefore, finding sustainable ways to recycle LIBs is imperative, and extensive research has been conducted to develop environmentally friendly leaching solutions for the recycling of metals in the batteries. For example, leaching with organic acid has proven highly efficient in extracting valuable metals from LIBs [7]–[11].

1.1 Motivation

The Institutt for energiteknikk, IFE, has been involved in a project “SUMBAT” which is funded by Norwegian Research Council under the "Grønn Platform" funding program. SUMBAT aims to lay the foundation for a sustainable battery value chain in Norway.

The project endeavors to form a consortium of key stakeholders from both industry and academia, fostering collaboration along the entire battery value chain. In the project, the relevant task has been to seek an innovative recycling processes, characterized by low toxicity, low water consumption and low energy demand. This has led to the research presented in this thesis, which covers one of the methods investigated within the project. The goal is to explore one of the most innovative methods utilized in the recycling of black mass.

1.2 Aim

The aim of this report was to study various organic leaching solutions using a well established method for leaching black mass which is a processed powder of cathodes from used lithium ion batteries [9], [10], [12], [13]. In this study 12 combinations of 3 different organic acids and 4 chloride based salts were being used in the ratios 1:1, 1:2 and 2:1. The acids were citric acid, oxalic acid and malic acid and the chloride based salts were ammonium chloride, NCl, aluminum chloride, ACH, choline chloride, ChCl, and tetramethylammonium chloride, TMA. The overall goal of this thesis was to widen the knowledge of Deep Eutectic solvent, DES, as well as to find good solutions for receiving high yield when leaching the metals Mn, Co, Ni and Li, thereby increasing the efficiency of LIBs recycling and reducing their reliance on hazardous elements. The ultimate objective was to identify a solvent that has low toxicity, low water consumption and low energy requirement for the leaching of the black mass.

1.3 Limitations

The scientific field of leaching LIBs is broad. While some research has been conducted and published, much remains to be explored due to the complexity of the subject: thus, certain limitations had to be established. The first limitation was that only the organic acids, citric acid, oxalic acid and malic acid, would be studied. These acids have been used in previous research, but not with all the chosen chloride based salts. This selection allows the results of this study to be compared with the existing ones without risking an overstudy of the solvents. For the same reason, the report is focused on the four chloride based salts: ammonium chloride, aluminum chloride, choline chloride and tetramethylammonium chloride.

The second limitation was that the study would investigate only the leaching of the metals Mn, Co, Ni and Li from the black mass. These metals are present at relatively high concentrations in the cathode of LIBs but are rare in the earth‘s ore. Apart from these valuable metals, the black mass also contains other materials such as Fe, Cu and Al but these are present in relatively low concentrations. The third limitation was that only the cathode part, and thereby the black mass, of the LIBs was targeted during this study. This targeting of the cathode occurs because the economical feasibility to the recover the valuable metals during recycling of the LIB. The cathodes was processed into a powder, known as black masses, before the analysis. Therefore, this report does not delve into details on how the powders were pre-treated. The final limitation is that only the cathode structure of NMC111 and NMC622 were targeted.

1.4 Issues Specification

The specific issues that is covered in this thesis is:

- What are the melting points of the studied Deep Eutectic Solvents and what are their pHs and are their optical observed viscosity when they reached a liquid state?
- Which combination of DES are the best for extraction of Mn, Co, Ni and Li from black mass?
- At what temperature, and ratio is the highest efficiency for the extraction achieved?
- How does time affect the leaching results?

2

Theory

The purpose of the chapter *2 Theory* is to provide the understanding needed by five different theory sections. The first section is an introduction of the categorization of lithium-ion batteries, LIBs. The second section presents the recycling methods of the LIBs cathode followed by a description of Deep Eutectic Solvent, DES. The last two sections are the descriptions and properties of the chosen acids and chloride based salts.

2.1 Lithium-Ion Batteries

Lithium-ion batteries generate electricity through charge and discharge introduced by the movement of Li-ions which are shown in the global reaction equation 2.1. The reaction occurring at the anode is represented by equation 2.3, [4], where electrodes commonly are made of graphite [14]. The cathodic reaction is represented by equation 2.2 where the cathodic structure is $LiCoO_2$ [4].

$$LiCoO_2 + 6C \leftrightarrow Li(1-x)CoO2 + C_6Li_x \tag{2.1}$$

$$LiCoO_2 \leftrightarrow Li_{(1-x)}CoO_2 + xLi^+ + xe^- \tag{2.2}$$

$$6C + xLi^+ + xe^- \leftrightarrow C_6Li_X \tag{2.3}$$

Commercial used lithium-ion batteries (LIBs) can have different cathodic structures, these structure are divided into five groups based on the composition, $LiCoO_2$ (LCO), $LiNi_xCo_yMn_{1-x-y}O_2$ (NMC) [5], [15], [16], $LiNi_xCo_yAl_{1-x-y}O_2$ (NCA), $LiFePO_4$ (LFP) [5], [14], [16] and $LiMn_2O_4$ (LMO) [5], [16]. The LCO structures of the cathode are the most expensive and are commonly used in electronic devices, however the structures NCM, NCA and LFP are the most common in EVs [5], [14]. The lithium-ion batteries are constructed by the cathode which is 35% of the LIBs and thereby the biggest and most expensive component [4], [7]. Furthermore, the batteries are made of anode, 10%, electrolyte, 9%, separator, 12% and outer shell, 22% [4], [7].

2.2 Current Methods for Cathode Recycling

The composition of the cathode varies depending on the manufacturer [5] but the cathode roughly consists of 5–7 wt% lithium, 5-20 wt% cobalt [5], [17], 5–7 wt% nickel, 15 wt% organics and 7 wt% plastics [5]. The recycling of the cathode is important due to the content of the valuable metals and if the recycling is effective, it is both more economical and environmentally friendly than extracting the metals than from the ore [5]. Furthermore, life expectancy of the LIBs in EV is around 5-10 years [5], [14].

When LIBs becomes unsuitable for EV, the recycling process starts. The recycling can be divided in two different categories, echelon utilization and material extraction. Echelon utilization is when the batteries are reused in an application that fits the reused power to density ratio [5], [14]. When the power to density ratio decreases below 80% of the original value, the echelon utilization process starts due to the battery no longer being suitable for EV. The battery can thereby be used as a component in smart grids and/or energy storage systems until the power density is reduced to 40 % [5].

After the power to density ratio decreases below 40%, [5], the processes of material extraction, element recycling, of the spent LIBs starts. The battery is first fully discharged to be safe for pretreatment. The pretreatment consists of mechanical separation, mechanochemical treatment, dissolution treatment [4] or thermal treatment [5]. After the pretreatment, the next step is metal extraction, which is carried out either by pyrometallurgy or hydrometallurgy processes [4], [5].

Pyrometallurgy processes require high temperatures, and result in high energy consumption. The main goal of pyrometallurgy is that the pretreated LIBs are heated so that the compounds can go through phase transitions [7], [8], [14], [17]. Metals like Ni and Co, [14], can quite easily form stable alloys under the heat treatment at around 1000°C, after which the metal alloys can be extracted as pure metals. However Li will end up in the slag [7], [14]. The metal recovery is poor due to the bad recovery of lithium as well as the extracted metals have low purity [14].

Hydrometallurgy processes use leaching to extract the metals [5], [17]. This procedure has low energy consumption, results in high purity and low recovery costs but it is a complex technique due to many steps in the process [14]. There are a couple of different leaching techniques, alkali leaching, leaches with ammonia-based solvents, bioleaching, which uses biological microorganisms and acid leaching [5], [7]. Acid leaching can be done either with inorganic e.g. hydrochloric acid, HCl, sulphuric acid, H_2SO_4, nitric acid, HNO_3 etc [4]. Or by organic acids e.g. citric acid, formic acid, malic acid, ascorbic acid, oxalic acid or glycine etc [4]. Inorganic acids can generate hazardous gases like Cl_2, SO_3 and NO_x, and it also requires a large amount of water [7]. Organic acids are weaker than the inorganic acids [5], but they are more stable and leave a smaller environmental footprint [18], [19].

2.3 Deep Eutectic solvents, Properties and Types

In hydrometallurgy processes, Deep Eutectic Solvents, DES, can be used since they are more environmentally friendly solvents. DES have low to no toxicity and are cheap and easy to synthesize [6], [18]–[21]. DES are a combination of a hydrogen bond acceptor, HBA, [6], [19], [22] e.g. choline chloride [22] and a hydrogen donor, HBD, [6], [19], [22] e.g. citric acid [22]. Studies have shown that the HBD has strong influences on the pH, and that the HBA has strong effects on the solvent's acidity [19]. The main categorisation property of DES is that the melting point is lower than the melting point of the hydrogen donor and acceptor respectively. [19]. Some combinations of DES can even be in liquid phase below 25°C, for example urea and choline chloride, ratio 2:1, melting point is 12°C

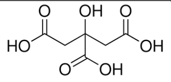
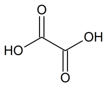
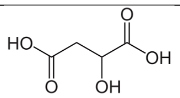
[14].

DES are usually compared with ionic liquids where they have some similarities and some differences. For example, both DES and ionic liquid have a high viscosity compared to molecular liquids. The high viscosity for DES depends on the interactions between the molecules such as hydrogen bonds and van der Waals interaction [19]. The high viscosity limits the movement of free molecules in the solvent, which can be a limiting factor in metal extractions as well as during DES recycling. The differences between DES and ionic liquids are that DES do not degrade in water, are biodegradable and have low to no toxicity, [18]–[21]. DES also have negligible vapor pressure [18], [20], are non-flammable and have non explosive properties [19]. DES are thermally and chemically (electrochemically) stable, [18], [19], which is important for their applications in extraction and hydrolysis. DES can also be used as an alternative to conventional organic solvents in fractionation, catalysis, preparation in biofuels and separation of azeotropic mixtures [19]. Other properties of DES are that they have quite high density compared to water and organic solvents, where the densities can range between 1.1-2.4 g/cm^3. It has also been studied that an increased temperature results in lower pH for most of the DES. pH is an important physical property, it impacts the chemical reactions and therefore it plays an important role in catalysis, biochemical reactions and metal leaching applications [19]. Furthermore, DES have been shown to result in high solubility of metal oxides, which has been discussed as a result of the hydrogen bond donor. The HBD can act as an oxygen acceptor and can break up the metal oxide bonds [18], [21]. Further research has determined that DES diluted with water have almost identical properties compared to DES without water. Therefore, in practice, DES are usually diluted with water to affect the hydrogen bonds [19]. Moreover, studies have shown that the DES containing carboxylic groups in HBD and chloride ions in the HBA like choline chloride, improve the oxide dissolution, where the chloride ion together with the carboxylic group result in the possibility of proton exchange [21].

2.4 Organic Acids (HBD)

Acids used in this study are citric acid monohydrate, oxalic acid dihydrate and malic acid. Their chemical formula, structure, melting point and hazards are shown in table 2.1.

Table 2.1: Properties of organic acids

Name	Chemical formula	Structure	Melting point	Hazards
Citric acid monohydrate	$C_6H_8O_7 \cdot H_2O$		135°C [23]	Irritant [23]
Oxalic acid dihydrate	$C_2H_2O_4 \cdot 2H_2O$		101-102°C [24]	Corrosive Irritant Health Hazard [24]
Malic acid	$C_4H_4O_5$		127-132°C [25]	Irritant [25]

Citric acid, 2-hydroxypropane-1,2,3-tricarboxylic acid [23], is mainly produced by microorganisms [26], such as fungi, where different hydrocarbon sources are transformed to citric acid by the tricarboxylic acid cycle, the TCA cycle, through a temperature and air controlled process [7].

Citric acid can be used for many different types of metal leaching. It has been used to extract metals in ore, tailings, slag and waste materials [26]. The metals vanadium, uranium, copper, lithium and cobalt have been leached with the help of citric acid from catalyst, electroplating sludge, ore and LIBs respectively [26]. The reason why citric acid has good leaching properties is because it is a tricarboxylic acid and therefore it can release protons in three stages, at different pH. This leads to good coordination ability and chelating properties with metal ions. Citric acid has further weak reducing properties which contributes to good leaching properties [26]. In table 2.2 the acid reaction together with pK$_a$ values for the acids citric acid, oxalic acid and malic acid are visible [7].

Table 2.2: Organic acid reaction and pK_a [7]

Name	**Reaction**	**pK$_a$**
Citric acid	$H_3C_6H_5O_7 \rightarrow H_2C_6H_5O_7^- + H^+$	2.79
	$H_2C_6H_5O_7 \rightarrow HC_6H_5O_7^{2-} + H^+$	4.30
	$HC_6H_5O_7^{2-} \rightarrow C_6H_5O_7^{3-} + H^+$	5.65
Oxalic acid	$H_2C_2O_4 \rightarrow HC_2O_4^- + H^+$	1.25
	$HC_2O_4^- \rightarrow C_2O_4^{2-} + H^+$	4.19
Malic acid	$H_2C_4H_2O_5 \rightarrow HC_4H_2O_5^- + H^+$	3.40
	$HC_4H_2O_5^- \rightarrow C_4H_2O_5^{2-} + H^+$	5.11

Among the chosen acids, oxalic acid is the strongest [13]. Oxalic acid has the pK$_a$ 1.25 [7] and 4.19 [7], [13], which is visible in table 2.2 together with the acid reaction [7]. Oxalic acid, ethanedioic acid [24], can be produced either biologically and/or commercially, but it is mainly produced by fungi. The biological production of oxalic acid is made by fungal metabolism from glucose, and oxalic acid produced commercially uses oxaloacetate hydrolysis for production [7].

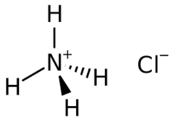
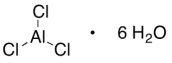
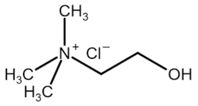
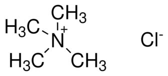
Oxalic acid is a good leaching and chloride based salt and it can leach metals by forming metal oxalate complexes. These complexes are formed due to the fact that oxalic acid is a strong chelating agent. The acid dissolves the metal oxides into the solution after which ion oxalate reacts to form metal oxalate complexes [13]. When lithium is present, simple complexes will form, but for metals like copper, cobalt, manganese and nickel the oxalate complexes will be both simple and complex. Metals in simple oxalates have low solubility and precipitate easily in leaching processes [13].

Malic acid, 2-Hydroxybutanedioic acid [25], has two isomers, L and D [7], [27]. L isomers are formed by biological activites, fungi. Malic acid is also present in animals and vegetables but is mostly found in fruits such as apples [7]. The biological production of malic acid's L isomer comes from the TCA cycle where enzymes convert oxaloacetate into malic acid [27]. In commercial production, both the L and D isomer can be synthesized by hydration in high temperature and pressure of either malic or fumaric acid [7]. Malic acid has two carboxylic groups and the acid reactions along with its pK$_a$ is visible in table 2.2 [7]. Moreover, malic acid can be used when leaching metals in lithium ion batteries by forming complexes. Lastly, malic acid is biodegradable under both anaerobic and aerobic conditions [7].

2.5 Chloride Based Salts (HBA)

The chloride based salts, hydrogen boner acceptor, used in this study are ammonium chloride, aluminum chloride hexahydrate, choline chloride and tetramethylammonium chloride. Their properties such as chemical formula, structure, melting point and hazards can be found in Table 2.3.

Table 2.3: Properties of chloride based salts

Name	Formula	Structure	Melting point	Hazards
Ammonium chloride	$NH_4{}^+Cl^-$		350°C [28]	-Irritant [28]
Aluminum chloride hexahydrate	$ALCl_3 \cdot 6H_2O$		100°C [29]	-Corrosive -Irritant [30]
Choline chloride	$C_5H_{14}NO^+Cl^-$		305°C [31]	-Irritant [31]
Tetramethylammonium chloride	$C_4H_{12}N^+Cl^-$		420°C [32]	-Acute toxic -Irritant -Health hazard -Environmental hazard [32]

Ammonium chloride is highly soluble in water [28], [33]. Ammonium chloride, which is an inorganic compound, [28] which can be utilised for example as a nitrogen source for fertilizers [28], [33], pickling agent for the metals tin and zinc[28], and as a component in pharmaceutical industries [28], [34]. The production of ammonium chloride can either occur by synthetic processes where ammonia reacts with hydrochloric acid, HCl, or destructive distillation of coal with HCl [28], or as a byproduct to the Solvay process which is the production of sodium carbonate [28].

Aluminum chloride reacts strongly in the presence of bases or water, is nonflammable and is associated with a strong smell [35]. Furthermore, the area of use for aluminum chloride is usually for the production of aluminum metal or to create acids in chemical industries [35]. Lastly, aluminum chloride is used as antiperspirants in deodorants[30], [35], disinfectants and wood preservatives [30].

Choline chloride is an organic quaternary ammonium salt, [36]–[38], which is a weak acid [37] and well soluble in both water and ethanol [31]. The uses of choline chloride are many, e.g. as food additives for poulets [36]–[38] or as a flavoring agent. Research has also found that choline chloride can help patients with long term total parenteral nutrition, TPN, by increasing the amount of choline in their bodies. [31]. The production of choline chloride can occur either by chemical synthesis or biotechnological processes with microorganisms [38]. In the chemical processes are, trimethylamine, hydrogen chloride and ethylene oxide reacting to create the desired product of choline chloride [31], [38].

Tetramethylammonium chloride is soluble in water and alcohol [32], [39], [40] but insoluble in ethers [32]. Tetramethylammonium chlorides can act as a clay stabilization for the extraction of oil and natural gas by hydraulic fracturing, cracking rocks underground, [32], [41], as a catalyst [32], [40], inhibitor or as a chemical intermediate [32]. Further uses are as a component in materials like polymers and electronic devices that are sensitive to humidity, where tetramethylammonium chloride is good at absorbing moistuer [40].

2.6 Previous Studies of DES in Metal Recovery

Previous research has had many different goals. Some research has focused on characterization of DES properties while others have focused on receiving high leaching yields of metal extraction from LIBs.

For example, a study done by Skulcova A. et al. *“The pH Behavior of Seventeen Deep Eutectic Solvents”*, [19], tested 17 different combinations of aqueous DES to explore the pH dependency on temperature in the range of 25-60°C [19]. The solvents were studied in different ratios which were diluted to 0.5mol/l of, among others, citric acid-choline chloride, oxalic acid-choline chloride, malic acid-choline chloride and ethylene glycol-choline chloride. The study found that OA-ChCl in ratio 1:1 had the highest dependency on temperature for the pH and the combination that showed the least dependency on temperature was citric acid-choline chloride in the ratio of 2:1 [19].

Another study made by Shafie M H et al. *“Synthesis of citric acid monohydrate-choline chloride based deep eutectic solvents (DES) and characterization of their physicochemical properties”* [42], studied the characterisation of citric acid-choline chloride properties where density, viscosity and surface tension were examined at different temperatures. The DES ratios investigated were 1:3, 1:2, 1:1, 2:1 and 3:1. The results were; a higher ratio of citric acid resulted in higher a density, viscosity and surface tension and a higher ratio of choline chloride increased the melting point of the DES [42].

The leaching properties of different DES have been studied as well. The research paper by Nayaka G. P. et al. *“Use of mild organic acid reagents to recover the Co and Li from spent Li-ion batteries”* [9] focused on Li and Co recovery from black mass. The paper presented a method where 100 mM iminodiacetic acid or malic acid was mixed with 20 mM ascorbic acid and diluted with distilled water. The black mass used was $LiCO_2$, the amount used was 0.2 g for 100 ml leaching solution, with the leaching time 2h and at temperature of 80°C. The study resulted in the leaching yields being >99% for Li and >91% for Co for the chosen DES [9].

Lastly, a study done by Ebrahimi E. et al. *"Solvometallurgical recycling of spent $LiNi_xCo_yMn_ZO_2$ (NCM) cathode material using ternary choline chloride-ethylene glycol-p-toluenesulfonic* *acid deep eutectic solvent"* [43], studied the leaching yield of Li, Mn, Co and Ni from black mass derived from $LiNi_xCo_yMn_zO_2$ based black mass. The study used different DES solutions consisting of choline chloride mixed with oxalic acid, acetic acid, DL-lactic acid or p-toluenesulfonic acid with ethylene glycol. The leaching conditions were 27-100°C, 0-72 h and S/L ratio of 10-50g/l. These leaching conditions were used to study the different leaching yields of Li, Ni, Co and Mn. The study concluded that leaching yields for all metals studied are higher for low S/L ratio, high temperature and long duration [43].

2.6.1 Gaps in Current Research

Described in the previous, section *2.6 Previous studies of DES in metal recovery*, have different research focused on both characterization of properties or/and leaching performance for different types of DES. In the four examples presented above, choline chloride is a chemical used predominantly with various HBDs e.g. citric acid, malic acid and oxalic acid [19], [42], [43]. However, other studies have also focused on choline chloride as HBA with different HBD. A review done by Fan Y et al. titled *Development and challenges of deep eutectic solvents for cathode recycling of end-of-life lithium-ion batteries* [44], presents leaching efficiencies for Li and Co but also for Ni and Mn, where most of the DES consists of HBA-ChCl. The review concluded that further research is needed and proposed some further studies. One of the proposed study areas was viscosity observation, due to its critical role during filtration and leaching efficiency. Another proposal was the observation of extensive sets of temperatures, ratio and time along with varying HBA-HBD and other external additives that can lead to promising leching yields for LIBs [44].

2.7 Analysis Methods

The methods for the analyses for this thesis are XRF and ICP OES. These analysis methods are used for the filtrate recovered after the leaching. The methods are explained in the following subsections.

2.7.1 XRF

XRF, X-ray fluorescence, is an analytical method which uses fluorescence to determine the element composition of a sample in a non destructive way with minimal damage to the sample [45], [46]. XRF analyses are beneficial for elements with an atomic number greater than 9 [46]. XRF analyses are suitable for both solid and liquid samples [45]. The analysis occurs by dislodging an electron in the inner orbitals of the atom, either the K or the L orbital. The dislodging happens because the sample is irradiated with high energy X-ray radiation [45]. To stabilize the now unstable atom, an electrode from a higher energy orbital replaces the dislodged electron in the lower energy orbit [45]. This replacement from a higher to a lower energy state releases fluorescent X-ray, photons, which are specific to each atom. The energy emitted is tracked and forms the basis of the XRF analysis [45]. Thereby, XRF is an excellent analysis method for both qualitative and quantitative elemental composition analyses [45], [46].

Since XRF emits radiation during use, therefore the sample should not be handheld nor should the XRF be pointed towards a body part [45]. Lastly, to minimize the exposure of radiation, it is important to think about time, distance and shielding [45].

2.7.2 ICP OES

Inductively coupled plasma - optical emission spectrometry, ICP-OES, is an analytical method for determining elemental composition. ICP-OES can analyze powders, solids, liquids and suspensions, but the samples need to be dissolved or digested before the analysis [47]. The method uses a plasma of argon gas and an optical emission spectrometer [47], [48]. The sample is pumped through a nebulizer, into a spray chamber, then into the argon plasma and is analyzed by the spectrometer. The plasma has a high temperature, around 6000-7000K but can reach up to 10 000K [48]. This high temperature atomizes and ionizes the sample, where the electrons absorbs the emitted energy from the plasma and thereby moves to a higher energy orbit. When the electrons later return to the stable orbit, light / photons, is emitted due to the difference in energy between the orbits. The emitted light wavelength and intensity are measured by the optical emission spectrometer, OES,creating a spectrum unique to each element [47], [48]. ISP-OES is beneficial for quantitative chemical analysis and a wide range of elements can be measured at the same time. Limitations include the requirement for samples to be fully dissolved or digested, and the possibility of spectral overlap among specific elements [47].

3

Methods

This thesis is based on experiments where DES are investigated in various ways to find the properties for the highest leaching efficiency of the black mass and thereby ensuring the recycling of the metals Ni, Mn and Co from the LIBs. In section *3.1 Materials*, the materials needed for the experiments are presented, thereafter the methodology continues with an explanation of the different experiments, which is divided into five distinct steps. The first step is to investigate the DES properties pH and viscosity, section *3.2 Viscosity and pH*, whilst the second step is choosing the most promising ones, section *3.3 Selecting Solvents* and the third step of the experiments is the leaching, section *3.4 Leaching*. Steps four and five involve an optimization of the parameters and a kinetic study. These last steps are described in *3.5 Parameter Optimization and Kinetic Study*.

3.1 Materials

The materials needed for the experiments are an oil bath, a magnetic stirrer, a heater, a 250 ml round flask with three necks, two 150 ml e-flasks, one condenser, two thermometers, one pH indicator, pH paper, a 250 ml Büchner flask, a 17g 4 g Büchner glass filter from JENAER GLAS SCHOTTu.GEN MAINZ, a 17g 3 g Büchner glass filter from JENAER GLAS SCHOTTu.GEN MAINZ, a handheld XRF model NITON XL5 Plus, acids, chloride based salts and black masses provided by Hydrovolt, Norway in the composition NMC 111 and NMC 622. The setup was designed so that the magnetic stirrer and heater were combined. The heater regulated the temperature in the oil bath with the help of a thermometer which was attached to the heater. The pH indicator, sensION TM + PH31, from HACH, had the operating range of 0°C to 80°C and pH rangeed between 0 and 14. The calibration of the pH indicator was conducted in 5 day intervals. pH paper from VWR BDH chemicals was used in the scale 1-11 with the interval 1.

The chemicals with the respective CAS-No and manufacturer were citric acid monohydrate for decalcifying, CAS-No 5949-29-1 from VWR BDH chemicals, oxalic acid dihydrate Suprapur® CAS-No 6153-56-6 from Supelco®, malic acid TECHNICAL, CAS-No 6915-15-7 (617-48-1) from VWR BDH chemicals, ammonium chloride for analysis, CAS-No 12125-02-9, from Supelco®, aluminum chloride hexahydrate, Reagent Grade, CAS-No 7784-13-6, Alfa Aesar, choline chloride high purity, CAS-No 67-48-1 from VWR BDH chemicals and tetramethylammonium chloride for synthesis, CAS-No 75-57-0 from Sigma-Aldrich.

Two types of black mass, both received from Hydrovolt, a Norwegian EV battery recycling company, were studied. The black masses were named "NMC111" and "NMC622" where the numbers refer to the stoichiometric ratio between Ni, Mn and Co. The black masses elemental composition analysis were conducted by NTNU and are presented in table 3.1.

Table 3.1: Black mass elemental composition in wt.%

	Al	**Co**	**Cu**	**Fe**	**Mn**	**Ni**	**Li**
NMC 111	0.035	10.67	3.79	0.55	8.12	10.93	3.44
NMC622	1.86	5.21	3.19	0.02	4.97	16.41	2.87

3.2 Viscosity and pH

The 12 solvents, also referred to as solutions and DES, were the combinations of the HBD, citric acid (CA), oxalic acid (OA) and malic acid (MA) with the HBA, ammonium chloride (NCl), aluminum chloride (ACH), choline chloride (ChCl) and tetramethylammonium chloride (TMA). These solvents were prepared in the ratios 1:1, 1:2 and 2:1 for the study of viscosity in the temperature interval 25-100°C and the observation of the pH in the temperature interval 25-85°C if the solvents were in liquid state within the given range. Viscosity and pH were observed for every 5°C increase in temperature. Figure 3.1 visualizes a simplified picture of the laboratory setup. There, a round flask with three necks was used. In the two outer necks a pH indicator and a temperature indicator were attached and in the middle neck a condenser was placed to reduce the evaporation. The round flask was positioned in a heated oil bath and the solvents were stirred with a magnetic stirrer at 300 rpm.

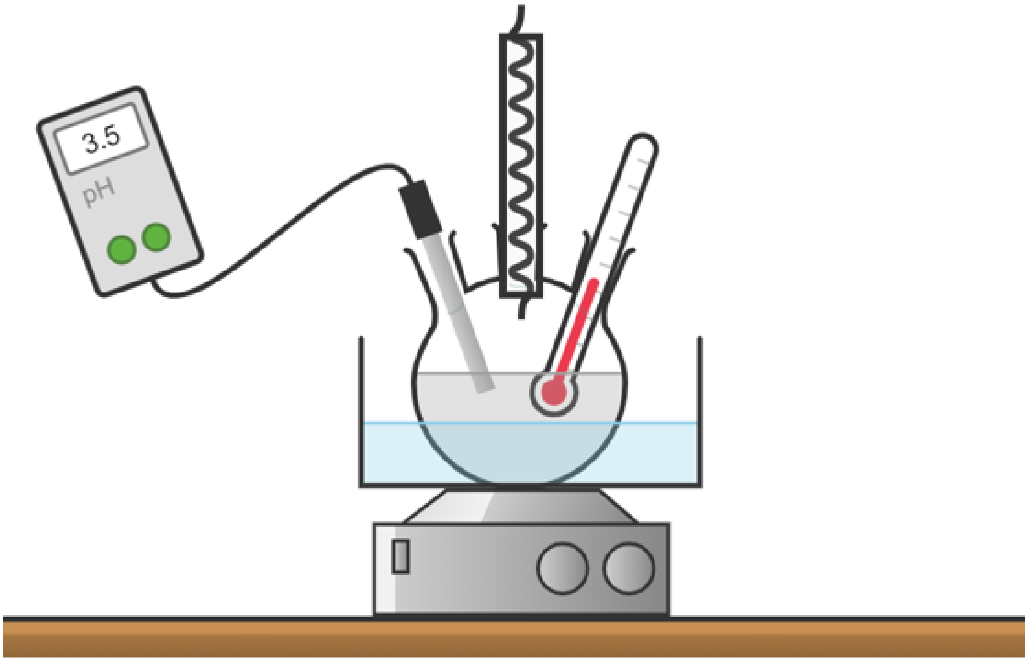


Figure 3.1: *A simplified picture of the laboratory set up. The round flask had. from left to right a pH probe, a condenser and a thermometer attached to the three necks. The round flask was immersed in a heated oil bath with an attached magnetic stirrer*

3.3 Selecting solvents

In the second step, the selection of five solvents was based on the result of *3.2 Viscosity and pH*. These five solvents demonstrated the most promising properties based on low viscosity and low pH at low temperatures.

3.4 Leaching

The third step involved the five selected solvents from 3.3. The leaching was conducted in the same setup as described in figure 3.1 except for the pH indicator being removed. The leaching was carried out by first preparing the 5 different solvents by steering the solvents in an e-flask at 300 rpm and at 90°C for a minimum time of 30 minutes. Thereafter 50 ml of the solvent was transferred to the round flask, mentioned above figure 3.1, together with black mass for the solid to liquid ratio, S/L ratio, 20 g/l. The leaching temperature was 90°C and the duration was 2 h. After the leaching, the samples were filtered with a 17g 4g filter and analyzed with XRF to determine the elemental composition. The leaching efficiencies for the metals Ni, Mn, Co, Al, Fe and Cu, denoted as η, were calculated in $\%$. This calculation was performed by dividing the mass of the leached sample in grams, $m_{leached}$, with the total mass of black mass in grams used for leaching, $m_{blackmass}$, these masses, $m_{leached}$ and $m_{blackmass}$ was multiply with the weight present, wt_i, of the diffrent metals thereafter, the expression is multiplied with 100, equation 3.1.

$$\eta = \frac{m_{leached} \cdot wt_i}{m_{blackmasswt \cdot wt_i}} \cdot 100(\%) \tag{3.1}$$

3.5 Parameter Optimization and Kinetic Study

The best leaching agents were used in the fourth and fifth step. The selection was based on the highest efficiency of the metals Ni, Mn and Co and desired properties like viscosity. Step four was parameter optimization of the best leaching agent and step five was a kinetic study. In both these last steps the solid to liquid ratio S/L was changed to 50 g/L and the stirring occurred at 300 rpm. The change in the S/L ratio was made to create a more filter cake, which would be denser and therefore easier to analyze with the XRF. The parameter optimization purpose was to investigate how the leaching would react depending on different temperatures; 60, 90, 120 and 150°C, and different ratios; 1:1, 1:2 and 2:1. The best parameters were then used for the kinetic study, where the duration was changed between 1, 2, 4, 6, 18 and 24h.

4

Results of Characteristic

The results are divided into two sections: *4.1 Viscosity* and *4.2 pH*. For simplicity, section *4.1 Viscosity* is divided into three subsections based on the three different acids.

4.1 Viscosity

The first part of the study was carried out as described in section *3.2 Preparation of Solvents, Viscosity and pH*. The acids citric acid, CA, oxalic acid, OA and malic acid, MA, were mixed with the chloride based salts ammonium chloride, NCl, aluminum chloride, ACH, choline chloride, ChCl and tetramethylammonium chloride, TMA, where the phases and viscosities were tracked at different temperatures. The transformation from solid to liquid usually happened in the sequence: solid, attached, melt and liquid phase during mixing. During the attached phase, the solvent was adhered to the round flasks / e-flasks and the magnetic stirrer was not able to stir properly. After the attached phase came the melting phase/process. The definition of the melting processes was when the solvents became glossy and/or transparent and the mixture became very viscose, with the magnetic stirrer was not rotating fully. The liquid phase occurred when the mixture appeared and behaved like a liquid. When the liquid phase was achieved, the solvents were further heated to determine the viscosity change, where the overall trend with increasing temperature was that the viscosity decreased with increased temperature.

The tables in the following subsections are the phases of the solvent tracked by color. Yellow represents solid phases, green attached phases, pink melt phases and blue liquid phases. Additionally, the tables also define viscosities observed optically after the liquid states were achieved. The scale had the interval 1-4 where 1 was the viscosity of a liquid honey or more viscose, 2 represented a viscosity like syrup, 3 was like oil and 4 had a viscosity like water. The distinction between oil and water was determined by whether the solution swirled around inside the round flask when rotating, if not, the viscosity was marked as oil.

4.1.1 Citric Acid and HBA

Table 4.1 presents the solvents containing citric acid combined with various HBAs that were heated up within the temperature interval of 25-100°C. For CA-NCl and CA-ACH in ratios 1:1 and 1:2 the solvents remained in solid state throughout the given temperature range. For CA-NCl and CA-ACH in ratio 2:1, a phase change from solid occurred, for NCl an attached phase was reached whilst the melt phase was reached for ACH at 100°C. Table 4.1 continues to describe the combinations of CA-ChCl and TMA in the ratios

1:1, 1:2 and 2:1 which all transformed into liquid state in the interval 25-100°C. The lowest melting point for the solvents was achieved by the presence of choline chloride. In general, the viscosity was lower for the solvents containing ChCl than for TMA. The lowest viscosity was observed for citric acid and choline chloride, ratio 2:1, followed by choline chloride 1:1 and tetramethylammonium chloride 2:1.

Table 4.1: Solvents of citric acid-HBA, phases and viscosity

		Temperatures in Celsius															
Solvents	ratios	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
CA-NCl	1:1	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	-
	1:2	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	-
	2:1	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩
CA-ACH	1:1	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	-
	1:2	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	-
	2:1	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟥
CA-ChCl	1:1	🟩	🟩	🟩	🟦	🟦 -	🟦 1	🟦 2/3	🟦 2/3	🟦 2/3	🟦 2/3	🟦 2/3	🟦 3	🟦 3	🟦 3	🟦 3	🟦 3
	1:2	🟩	🟩	🟩	🟥	🟥	🟥	🟦	🟦 1	🟦 2	🟦 2	🟦 2	🟦 2	🟦 2	🟦 2	🟦 2	🟦 2/3
	2:1	🟨	🟩	🟩	🟩	🟥	🟦	🟦 1	🟦 -	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4
CA-TMA	1:1	🟨	🟩	🟩	🟥	🟥	🟥	🟥	🟥	🟦	🟦 2	🟦 2	🟦 2	🟦 2	🟦 2	🟦 2	🟦 2/3
	1:2	🟨	🟨	🟩	🟩	🟩	🟥	🟥	🟥	🟥	🟦	🟦 1	🟦 1	🟦 1	🟦 1	🟦 1/2	🟦 2/3
	2:1	🟨	🟨	🟩	🟥	🟥	🟥	🟥	🟥	🟦	🟦 1	🟦 2	🟦 2	🟦 3	🟦 3	🟦 3	🟦 4

Colors represent different phases, yellow= solid, green= attached, pink= melting, blue= liquid. Viscosity scale 1-4 where 1 has high viscosity (honey or thicker) and 4 has low viscosity (like water).

It is further important to understand in what range the solvents can operate and how other properties affect the solvents after they have been taken away from the oil bath.

The combination of CA-NCl in the ratio 2:1, reached a liquid state at 120°C. The solvent was then transferred to a storage container and crystallized very fast. For CA-NCl in ratios 1:1 and 1:2 a heated water bath was used instead of a heated oil bath, and melting point could not be noted for these ratios. The same water bath was used for ACH in the ratios 1:1 and 1:2. The oil bath was thereafter used for CA-ACH 2:1, and the solution reached a liquid state at 115°C. If the heating continued, rapid gas development occurred when the temperature increased above 125°C. Moreover, the melting process to create the DES solvent CA-ChCl for the ratios 1:1 and 1:2 was considered to be exothermic as the temperature of the solvent exceeded the temperature in the oil bath, this is further explained in *B Laboratory Notes for Citric Acid and Choline Chloride*. After heating CA-ChCl, ratios 1:1, 1:2 and 2:1 were easily transferred to the storage containers whilst the ratio 2:1 crystallized over the course of some days and ratio 1:1 and 1:2 stayed in liquid state for longer. Lastly, when CA-TMA were mixed, all ratios contained some undissolved TMA after the solvent turned into liquid. In addition, when the solvents were removed from the oil bath, all ratios crystallized fast and the ratios 1:1 and 2:1 were very sticky.

4.1.2 Oxalic Acid and HBA

Table 4.2 describes the states of the solvents containing oxalic acid and HBA when the solvents were heated up in the temperature interval 25-100°C in the ratios 1:1, 1:2 and 2:1. Almost all the solvents reached a liquid state, except for OA-ACH in the ratios 1:1

and 1:2, but these solvents started to melt within the given temperature range. Furthermore, the solvents containing NCl melted at higher temperatures compared to those with ChCl and TMA. For example, the ratio 1:1 turned to liquid state at 90°C, the ratio 1:2 at 100°C and 2:1 at 95°C, table 4.2.

All DES containing OA-ChCl became liquid at room temperature, 25°C, a trend not observed with CA-ChCl, as noted in table 4.1. In addition, all the solvents had low viscosity throughout the temperature interval. These same trends can be seen for OA-TMA, table 4.2, in which the mixtures have become liquid at lower temperatures and had lower viscosity than those containing CA-ChCl, table 4.1.

Table 4.2: Solvents of oxalic acid-HBA, phases and viscosity

		Temperatures in Celsius															
Solvents	ratios	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
OA-NCl	1:1	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟥	🟦	🟦 2	🟦 1*
	1:2	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟦 3
	2:1	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟦	🟦 2
OA-ACH	1:1	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟥	🟥
	1:2	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟥	🟥
	2:1	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟦	🟦 3	🟦 4	🟦 4	🟦 4
OA-ChCl	1:1	🟦	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4
	1:2	🟦	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4
	2:1	🟦	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4
OA-TMA	1:1	🟨	🟩	🟩	🟦	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4
	1:2	🟨	🟨	🟨	🟨	🟩	🟦	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4
	2:1	🟨	🟨	🟩	🟥	🟦	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4

*Colors represent different phases, yellow= solid, green= attached, pink= melting, blue= liquid. Viscosity scale 1-4 where 1 has high viscosity (honey or thicker) and 4 has low viscosity (like water), * dried*

The DES containing ammonium chloride proved to be quite difficult to transfer to the storage containers. For the 1:1 ratio, almost all the liquid had evaporated, leaving a very sticky residue. For the ratios 1:2 and 2:1, the solvents crystallized quickly and therefore had to be scraped out from the round flask. The solvents containing aluminum chloride in the ratios 1:1 and 1:2 needed also to be scraped out for transfer to the storage containers. However, for the ratio 2:1 it was possible to pour the solvent to the storage container, but it crystallized after some minutes. All solvents containing OA-ChCl and OA-TMA in all ratios were easily transferred to storage containers. For the solvents containing ChCl in the ratios 1:1 and 1:2, the mixtures were still liquid after one day. All the solvents containing TMA crystallized over time.

4.1.3 Malic Acid and HBA

Table 4.3 describes the physical observations of the solvents containing malic acid and the HBAs, heated within the temperature range of 25-100°C. Differences and similarities between table 4.3 and tables 4.1 and 4.2 are evident. DES containing malic acid and ammonium chloride or aluminum chloride remain solid throughout the entire temperature range for the ratios 1:1 and 1:2, similar to the DES containing CA, but differing from those containing OA. Furthermore, malic acid containing DES in the ratio 2:1 for both ammonium chloride and aluminum chloride remained solid throughout the entire interval, as noted in table 4.3, in contrast to tables 4.1 and 4.2. Additionally, all the ratios and combinations involving choline chloride and tetramethylammonium chloride transitioned to a liquid state at roughly the same temperature as the DES containing CA and they also had similar viscosities. Table 4.3 shows that the lowest viscosity was reached for choline chloride across all ratios.

Table 4.3: Solvents of malic acid-HBA, phases and viscosity

		Temperatures in Celsius															
Solvents	ratios	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
MA-NCl	1:1	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
	1:2	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
	2:1	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
MA-ACH	1:1	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
	1:2	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
	2:1	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
MA-ChCl	1:1	🟩	🟥	🟥	🟦	🟦 1	🟦 2	🟦 2/3	🟦 3	🟦 3	🟦 3	🟦 3/4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4
	1:2	🟩	🟥	🟥	🟦	🟦 1/2	🟦 1/2	🟦 3	🟦 3	🟦 3/4	🟦 3/4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4	🟦 4
	2:1	🟩	🟥	🟥	🟥	🟦	🟦 2	🟦 2	🟦 2/3	🟦 3	🟦 3	🟦 3	🟦 3/4	🟦 4	🟦 4	🟦 4	🟦 4
MA-TMA	1:1	🟨	🟨	🟨	🟩	🟩	🟩	🟥	🟥	🟦	🟦 1	🟦 2	🟦 2	🟦 3	🟦 3	🟦 3	🟦 3
	1:2	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟥	🟥	🟦	🟦 1	🟦 2	🟦 2	🟦 2	🟦 2	🟦 2
	2:1	🟨	🟨	🟨	🟨	🟨	🟩	🟩	🟥	🟦	🟦 1	🟦 2	🟦 2	🟦 3	🟦 3	🟦 3/4	🟦 4

Colors represent different phases, yellow= solid, green= attached, pink= melting, blue= liquid. Viscosity scale 1-4 where 1 has high viscosity (honey or thicker) and 4 has low viscosity (like water).

As previously described for the other acids, notations of the properties are needed. Starting with the solution containing MA and NCl, the liquid state was reached at a higher temperature than the observed interval. For the ratio 1:1, the liquid state was reached at 120°C for ratio 1:2 and 2:1 at 125°C. Moreover, MA and NCl based mixtures in all ratios crystallized fast when being removed from the oil bath. The DES containing MA and ACH were also in a liquid state above the interval studied in table 4.3. The solutions were all liquid in a temperature above 140°C whilst the mixture with ratio 1:2 was liquid already at 135°C. Gas development occurred when the temperature rose above 140°C for all ratios. The solutions containing either choline chloride or tetramethylammonium chloride were all easy to transfer to a storage container when removed from the oil bath. Choline chloride based solvents remained in liquid phase for at least a day after the experiments were performed. Further, the solution of MA-TMA were all sticky and lastly, ratio 1:2 crystallized fast when it was removed from the oil bath.

4.2 pH

In the experiments, the pH could be measured if liquid phases were obtained in the temperature range of 25-85°C. These measured pH levels were noted and are expressed in more detail in section *A PH*. The results are also presented in the form of two figures: one for CA solvents, figure 4.1, and one for MA solvents, 4.2, both these figures show a change in the pH values for the mixtures. The pH values observed for OA mixtures had the same pH and no graph was needed. It is important to note that for the pH measurements for CA-TMA and for all solutions containing OA and MA, measurements were conducted with pH paper due to limitations in the pH probe, this is further explained in *A pH*.

Figure 4.1 shows the measured pH values for all solutions containing CA that reached a liquid state under 85°C. The overall trend was that the pH value decreased with increasing temperatures, which was valid for all solutions except CA-TMA in which the pH level increased with increasing temperature. This increase could be an error within the measurement with the pH probe. The results in figure 4.1 are further explained in *A.1 Citric acid together with HBA*.

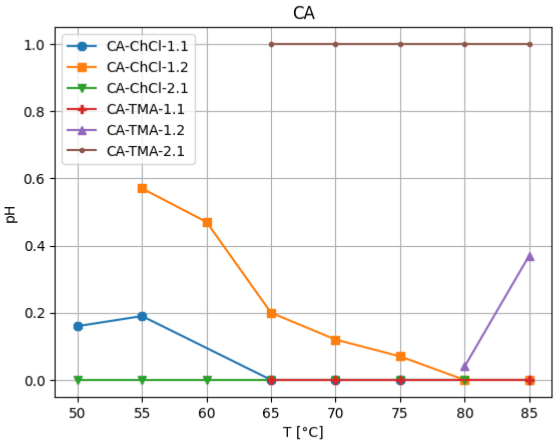


Figure 4.1: *pHs dependency of temperature where the blue line is CA-ChCl in ratio 1:1, orange CA-ChCl ratio 1:2, green CA-ChCl ratio 2:1, red CA-TMA ratio 1:1, purple CA-TMA ratio 1:2 and brown CA-TMA in ratio 2:1.*

Figure 4.2 shows the pH dependency of temperature for the solution containing MA together with HBA, where the maximum pH values are 2. Furthermore, figure 4.2 shows that the pH decreased with increasing temperature where the lowest traceable pH was 1 due to the pH probe limitation. The results in figure 4.2 can be further investigated in *A.3 Malic acid together with HBA*.

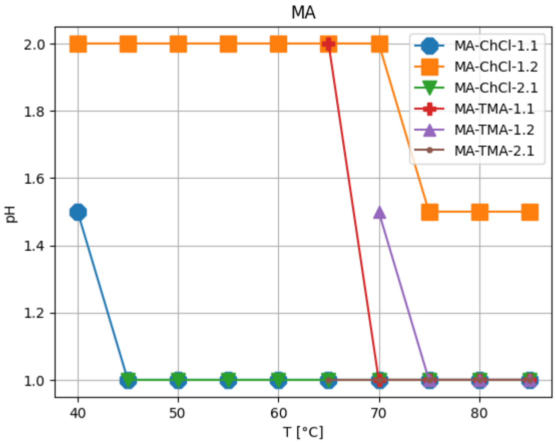


Figure 4.2: *pHs dependency of temperature where the blue line is MA-ChCl in ratio 1:1, orange MA-ChCl ratio 1:2, green MA-ChCl ratio 2:1, red MA-TMA ratio 1:1, purple MA-TMA ratio 1:2 and brown MA-TMA ratio 2:1.*

All the mixtures containing OA had the same pH values and therefore a graph was not needed for these measurements. In appendix A.2 the pH values can be seen in detail. However, to summarize the mixtures OA-ChCl all ratios, OA-TMA all ratios and OA-ACH in ratio 2:1, all had the observed pH at 1.

5

Results of Leaching and XRF

As described in the method section, the leaching experiments were designed as three parts. The initial leaching with five different leaching solutions is presented in section *5.1 Selection*, parameter optimization is presented in section *5.4 Parameter optimization* and a kinetic study is discussed in section *5.5 Kinetic study*. Between each section, a selection is made regarding which DES/leaching agents that were to advance to the next step. This selection is based on the highest leaching efficiency, η, for Ni, Mn and Co. However, the conditions of the solvents are also taken into consideration.

5.1 Selection

From the results given in previous sections, *4.1 Viscosity* and *4.2 pH*, OA-ChCl, OA-TMA, OA-ACH, CA-CHCl and MA-ChCl with the ratio 2:1 are the most promising DES. These solvents and ratios were selected because they can be compared, they have low viscosity values, low pH and are relatively easy to handle when heated. Therefore, these solvents are used for the first leaching experiment, investigating which of these solvents has the highest leaching efficiency for the metals Ni, Mn and Co.

Table 5.1 describes the leaching efficiency for the solvents OA-ChCl, OA-TMA, OA-ACH, CA-CHCl and MA-ChCl within the experimental setup of a duration of 2 h, at 90°C and 20 g/l of black mass. The table shows that the best leaching agent is OA-ACH where the leaching efficiency for Ni is 90%, Mn 94% and Co 81 %. The second best leaching agents is CA-ChCl where the leaching efficiency is 66% for Ni, 73% for Mn and 66 % for Co. The leaching agents that had the lowest leaching efficiency for Ni were OA-ChCl and OA-TMA where it was 0%, MA-ChCl had the lowest efficiency for Mn, 51%, and OA-TMA had the lowest efficiency for Co, 42%.

Table 5.1: Leaching efficiency in percentages (20 g/l)

	OA-ChCl	OA-TMA	OA-ACH	CA-ChCl	MA-ChCl
Al [%]	26	1700	39 000	0	0
Co [%]	49	42	81	66	44
Cu [%]	81	104	112	51	49
Fe [%]	0	0	0	0	0
Mn [%]	57	54	94	73	51
Ni [%]	0	0	90	66	44

Black mass leaching with solid to liquid ratio 20 g/l, duration 2 h and 90°C

5.2 Discussion of Selection for Parameter Optimization

Results from *5.1 Selection* showed that the OA-ACH mixture had the highest yield for the leaching for the targeted metals. However, it is not possible to optimize the relevant parameters for this solvent, due to the operational challenges of OA-ACH such as ratio and temperature. The ratios 1:1 and 1:2 do not melt at 90°C, table 4.2. The OA-ACH mixture could not be tested for the designed parameter optimization experiments as the mixture in ratio 2:1 was liquid only above 90°C. One of the goals of this task, which is the baseline of this thesis, was to find a leaching agent that can operate at low temperature with high yield, requires low water consumption and has low toxicity. Furthermore, tests at higher temperatures would not work for OA-ACH due to the fact that when the temperature reaches around 120°C, the solvent will start to boil. Most likely, this happens due to the decomposition of ACH, and crystallization/solid formation occurs. Therefore, CA-ChCl, was chosen for the parameter optimization study and then also for the kinetic study.

5.3 Challenges and Proposed Mitigation Actions

The biggest challenge during the leaching was the filtration of the solvents; OA-ChCl, OA-TMA, OA-ACH, CA-ChCl and MA-ChCl. The problem was that some of the solvents were too viscose or hardened during the filtration and therefore they could not be filtered through the filter glass. The solvents that could go through the filter glass easily were OA-ChCl and OA-TMA, and the rest, OA-ACH, CA-ChCl and MA-CHCl needed additional effort for the filtration. The different techniques were tested to facilitate the filtration such as addition of distilled water during filtration, addition of distilled water during leaching and heating the setup during filtration in the same time as the filter glass properties changed.

The first proposed solution was to add distilled water during the filtration. This worked to filter the solvents but a significant amount of water was needed, e.g. for CA-ChCl, 55ml distilled water was needed for 50 ml solvent. The second method was to add distilled water before the leaching process started, the amount of water added was 10vol% of the total volume. However, additional water for filtration was also needed and the total amount of water added was 18ml for 45 ml of solvent.

The third method was to heat up the setup with a heating gun, which did not give efficient results. The heating reduced the viscosity of the solvent mixtures, but it did not help enough to enable the smooth filtration, therefore dilution was needed. However, less distilled water was needed for the filtration when the setup was heated and the leaching agent diluted. 11ml of distilled water was used compared to the former amount of 18 ml and 55ml. Another reason this modification may have led to low water consumption was the switch from 17g 4g glass filter to a 17g 3g glass filter. The chosen combination was the setup with a heating gun and dilution because it required the least amount of water. This setup was used for the rest of the experiments, parameter optimization and kinetic study.

Table 5.2 presents the leaching efficiencies for the three proposed actions, adding distilled water during filtration, adding distilled water during leaching and heating the setup. Table 5.2 shows the amount of water needed as well as the leaching yield of CA-ChCl at 90°C, 2 h and 50 g/l of NMC 111 black mass.

In table 5.2 it is seen that the leaching efficiencies for ´filtration + dilution´ and ´heating + dilution´ have similar leaching yields for all the metals, Al, Co, Cu, Fe, Mn and Ni. This shows that the heating of the setup does not change the leaching yields achieved. However, the sample using ´10vol% + dilution´ had for all metals a higher leaching yield. This shows that when water was added before the leaching the leaching yield would increase. However, one of the objectives of this study was to find a leaching mixture that required low water consumption, therefore the experiments were continued with the procedure where heating and dilution were combined because that resulted in the lowest water consumption.

Table 5.2: Filtration option tested for CA-ChCl

	Filtration	filtration + dilution	10vol%	10vol% + dilution	heating + dilution
Al [%]	-	0	-	0	0
Co [%]	-	36	-	79	38
Cu [%]	-	31	-	72	52
Fe [%]	-	0	-	166	106
Mn [%]	-	35	-	68	33
Ni [%]	-	37	-	80	39
water added	0ml	55ml	0ml	18ml	11ml

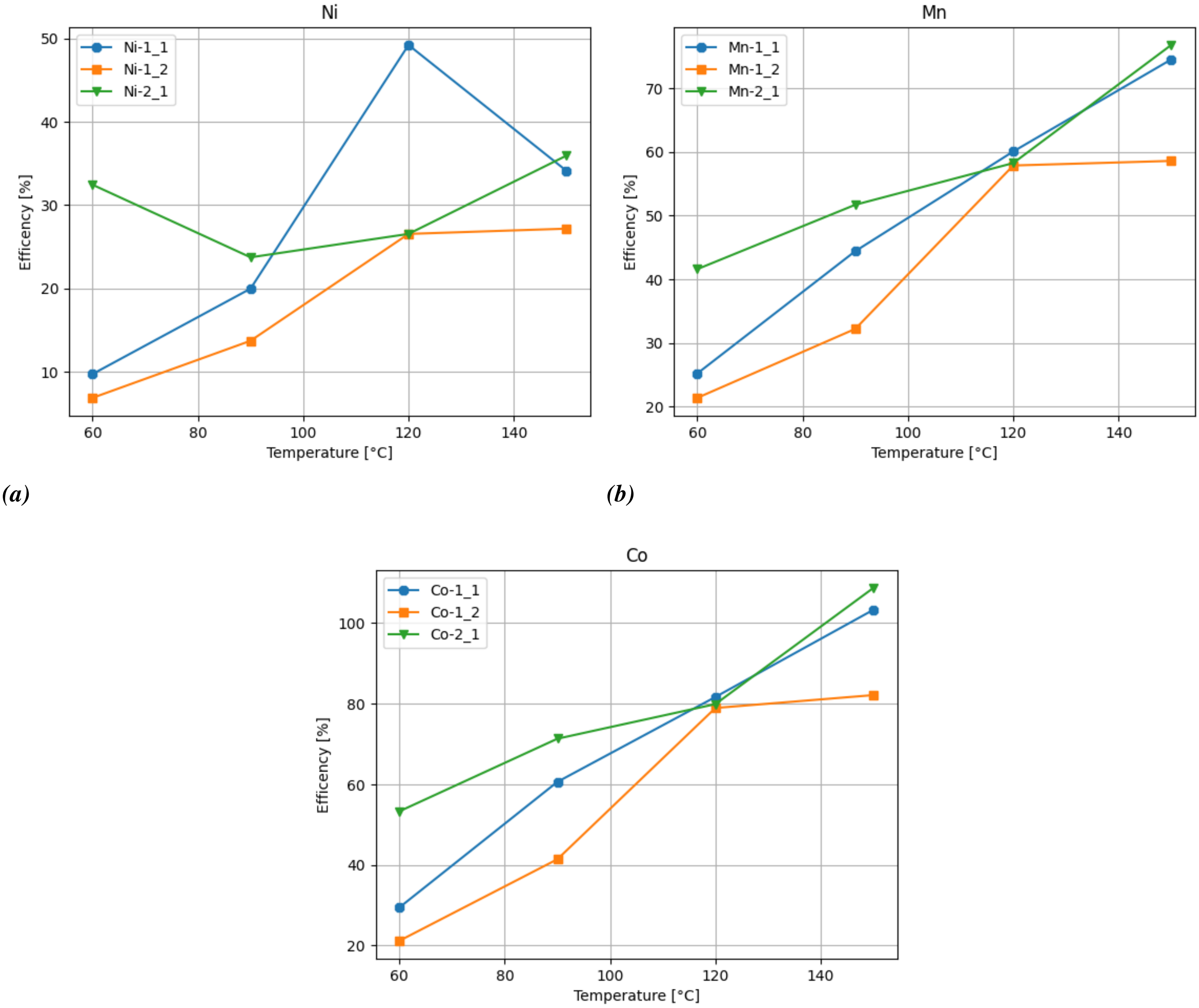
- no filtration

5.4 Parameter Optimization

Figure 5.1 represents the leaching efficiency for the metals Ni, Mn and Co in different settings. The temperature was varied between 60°C and 150°C with a 30°C interval. The ratios were also changed between 1:1, 1:2 and 2:1. Leaching efficiency can be seen in the data set for the figures in appendix *C Parameter Optimization Table* where the leaching efficiency of the other main metals, Al, Cu and Fe, are described.

One of the trends in figure 5.1 is that with increasing temperature the leaching efficiency is increasing. This is true for all the graphs except the graphs for Ni in the ratio 1:1 and 2:1, figure 5.1a. The graph for the ratio 1:1 increases to a leaching yield of 60% when the temperature was increased to 120°C, but then the leaching yield decreased to 34% at a temperature of 150°C. For the ratio 2:1 the leaching efficiency was roughly 32% at 60°C and it decreased to roughly 24% at 90°C. For the rest of the graphs leaching yield is increasing with increasing temperature. Another trend for figure 5.1 is that the ratio 2:1 has the highest leaching efficiency for almost all temperatures except for 120°C where the ratio 1:1 had the highest leaching efficiency for all the metals Ni, Mn and Co. Furthermore, it is worth noting that the leaching efficiency of 1:2 seems to have reached a plateau at 120°C but because of the increase of leaching efficiency between 120°C and 150°C, this is not that significant.
Important notes, in figure 5.1c there is a leaching yield for the ratios 1:1 and 2:1 above 100% which is not possible. This shows that a possible error occurs when analyzing the

sample with XRF which is further discussed in section *8.1 Sources of Errors*. The second note, in figure 5.1a, is that the leaching yield of Ni is very high for the solvent in ratio 1:1 at the temperature 120°C, which will not be considered as the best result, even if the highest leaching yield of Ni is achieved, because of the decrease of efficiency when the temperature increases to 150°C.



(a)

(b)

(c)

Figure 5.1: *Leaching efficiency dependencies of temperature and ratio, duration 2h and S/L 50g/l of Hydro black mass. Figure (a) leaching efficiency of Ni, figure (b) Mn and figure (c) Co*

5.5 Kinetic Study

The kinetic study was conducted with the method presented in *3.5 Parameter Optimization and Kinetic Study*. This study was conducted to understand how the duration affects the leaching yields and is described in figure 5.2. The kinetic trend can be observed by the data points. The red dots represent the data of Ni, while blue represents Mn and green represents Co in terms of leaching efficiency. The overall trend for each targeted metal was that the leaching yield increases overtime, figure 5.2. The figure also shows that the leaching efficiency of Ni and Co follow each other where the leaching efficiency for Co was only some percentages lower than the one for Ni. The leaching efficiency for Mn is roughly, and for the most times, 8% units lower that of the others.

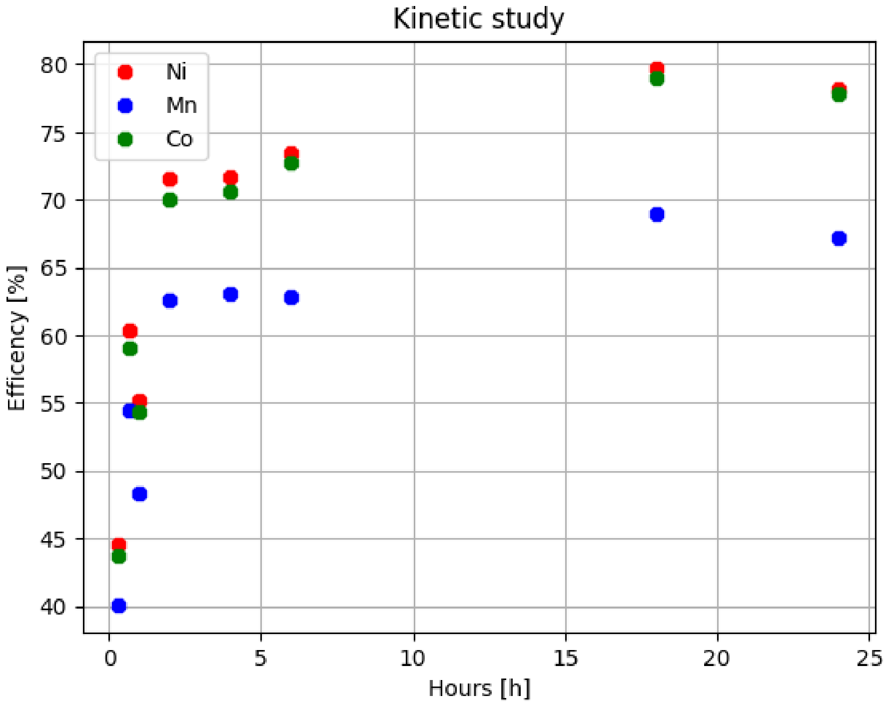


Figure 5.2: *Kinetic study for CA-ChCl 2:1. Data from the metals Ni, Mn and Co are the red, blue and green dots respectively. Leaching parameters 150°C and 50g/l of NMC622*

6

ICP-OES results

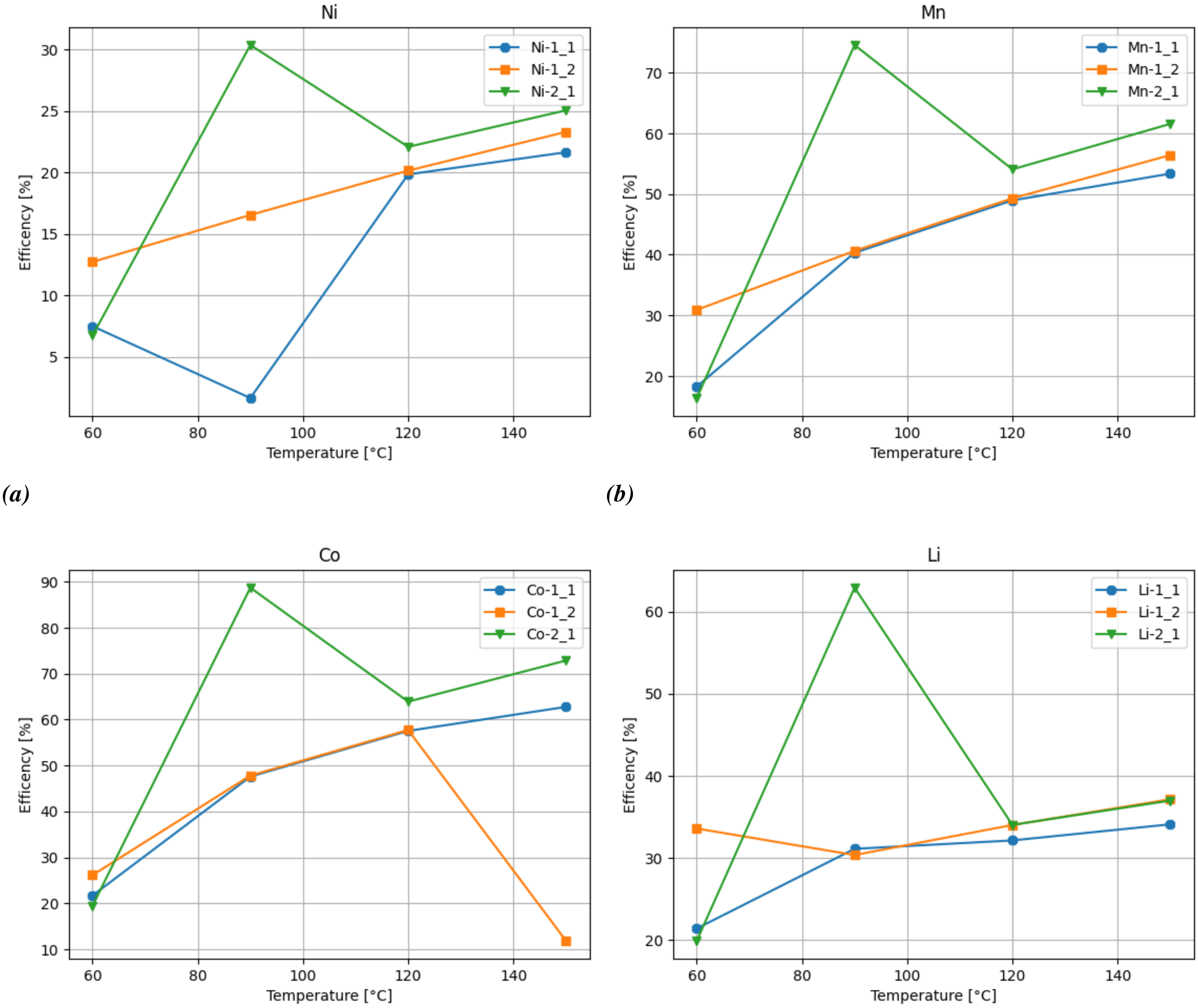
In the two following section, *6.1 Parameter Optimization* and *6.2 Kinetic Study*, the samples CA-ChCl in ratio 1:1, 1:2 and 2:1, are re-analyzed with ICP-OES. This re-analyse were conducted to understand how the leaching yield of Li is affected with ranging ratios, temperature and time. Further, the re-analyzes were also conducted to compare the results between XRF and ICP-OES. The results of the XRF are the foundation of the report, but the ICP-OES results will be used to validate the XRF results when it comes to the parameter optimization and kinetic study.

6.1 Parameter Optimization

In Figure 6.1, the re-analyzed results from the ICP-OES is shown. The figure 6.1 is divided into 4 sub figures 6.1a, 6.1b, 6.1c and 6.1d which present the leaching yields of the metals Ni, Mn, Co and Li respectively. In all these sub figures, figures 6.1a, 6.1b, 6.1c and 6.1d, it can be seen that the leaching yield of CA-ChCl in ratio 2:1 had the highest leaching yield for almost the whole temperature interval. With the exception at 60°C where the highest leaching yield is obtained for the ratio 1:1 for all the observed metals.

In the sub figures of figure6.1 a spike in the leaching efficiencies can be seen at 90°C for the ratio 2:1. This spike has the highest leaching efficiency for the respective metals in the targeted interval, for Ni the leaching efficiency was roughly 30%, Mn 75%, Co 88% and for Li roughly 63%. Thereafter, at the temperature 120°C, the leaching efficiency decreased to 22% for Ni, 54% for Mn, 63% for Co and 34% for Li. Therefore, it is uncertain if the best leaching efficiency is obtained at this temperature. The second highest leaching efficiency was received by CA-ChCl in ratio 2:1 at a temperature of 150°C which is the same parameter that the *5.4 Parameter Optimization* resulted in.

The differences between the parameter optimization obtained with XRF and ICP-OES are that in figure 5.1 the leaching efficiency was received by the ratios 1:2 reaching a plateau at 120°C which can not be seen in figure 6.1 and that in figure 5.1 the data points more in sequence with each other compared with the data in figure 6.1. However, the leaching yields were in roughly the same percentages for each of the metals Ni,Co and Mn. More detailed data for figure 6.1 can be seen in *C*.



(a) ***(b)*** ***(c)*** ***(d)***

Figure 6.1: *Leaching efficiency dependencies of temperature and ratio, duration 2h, S/L 50g/l of Hydro black mass and analysed with ICP-OES. Figure (a) leaching efficiency of Ni, figure (b) Mn, figure (c) Co and figure (d) Li*

6.2 Kinetic Study

The kinetic study with the data from the ICP-OES was the sample re-analyze from the procedure presented in *3.5 Parameter Optimization and Kinetic Study*. This re-analyze was conducted to understand how the duration affects the leaching yields as well as to see if the results from the XRF and ICP-OES differed from each other. The data from the ICP-OES kinetic study is presented in figure 6.2. The kinetic trend can be observed by the data points. The red dots represent the data of Ni, while blue represents Mn and green represents Co in terms of leaching efficiency. The overall trend for each targeted metal was that the leaching yield increased overtime, figure 6.2. The figure also shows that the leaching yields of the metals Ni, Co, MN and Li followed each other over time.

This is different from figure 5.2 where the leaching efficiency of Mn always was some percentages lower than for Ni and Mn. Another difference between the two figures is that the leaching yield in figure 5.2 ranges between 40 and 80%, compared with the leaching yield received in figure 6.2 where the leaching yield ranges between 32.5 to 52.5% for all metals.

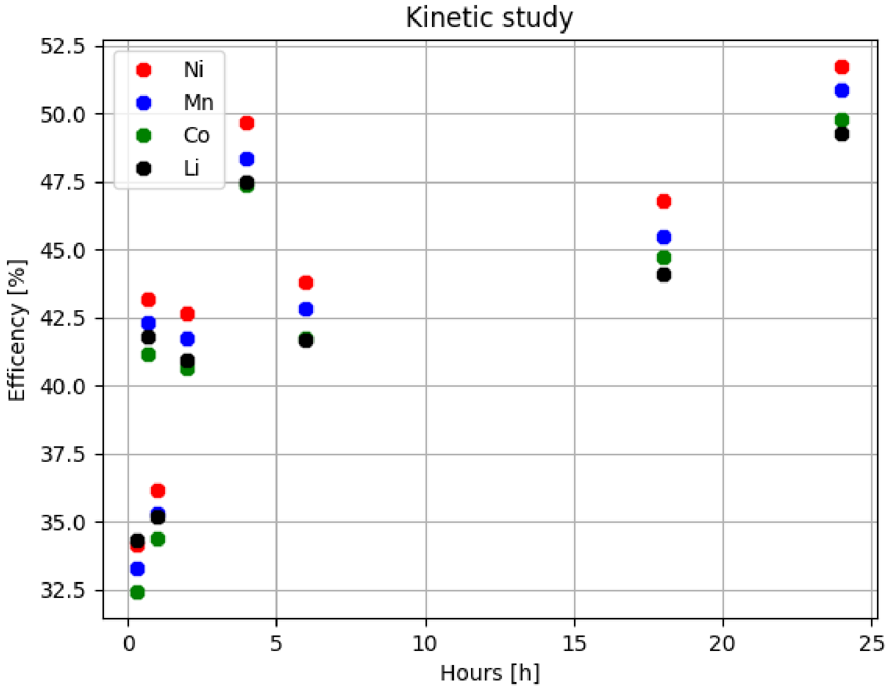


Figure 6.2: *Kinetic study for CA-ChCl 2:1. Data from the metals Ni, Mn, Co and Li are the red, blue, green and black dots respectively. Leaching parameters 150°C, 50g/l of NMC622 and analyzed with ICP-OES.*

7

Conclusion

To conclude, this thesis started with investigating the melting points, viscosities and pH levels of the solvents containing either CA, OA or MA together with the chloride salts NCl, ACH, ChCl and TMA in the ratios 1:1, 1:2 and 2:1. For these solvents, the melting points, viscosities and pH levels varied significantly. Generally, the melting points were high for solvents containing NCl and ACH for all ratios compared to those containing ChCl and TMA, which had lower melting points for all ratios. The solvents containing NCl were mostly in a solid state for the entire temperature interval, 25- 100°C. However, the solvents OA-NCl in all ratios, became liquid around 90-100°C. The solvents containing ACH were mostly solid when the temperature increased to 100°C. Yet, the combination of OA-ACH in ratio 2:1 had a melting point observed at 80°C. The melting points of ChCl were generally lower than the TMA's for the respective acid. For CA-ChCl in ratio 1:1, 1:2 and 2:1 the melting point was around 40-55°C compared to 65-70°C, all ratios. For OA-ChCl, the melting points was 25°C for all ratios compared to the melting points for OA-TMA, which was around 40-50°C. Lastly, the melting points for MA-ChCl was around 40-45°C compared with 65-70°C for MA-TMA.

When considering the optical viscosity, the trend is that increasing temperature decreased the viscosity of the solvents. For the acid CA, the optical viscosity varied from thick like honey and lean as water (1-4). For the solvents containing OA were the viscosity in general leaner, the majority of the observed optical viscosities had a value of 4 which was a viscosity like water. Lastly, for the solvents containing MA, the optical viscosity varied like for CA. The pH levels were low for all DES with the maximum value of pH 2 and the lowest, <0. The pH was generally lower for CA and OA than for MA containing solvents.

From these observed properties five promising solvents were selected OA-ChCl, OA-TMA, OA-ACH, CA-ChCl and MA-ChCl all in the ratio 2:1 for the initial leaching tests. Of these, OA-ACH had the highest leaching efficiencies of Ni, Mn and Co with 80% 94% and 81% respectively in the initial leaching tests. The second best mixture was CA-ChCl with the leaching yields of Ni 66%, Mn 73% and Co 66%. Although OA-ACH had the highest leaching yields, CA-ChCl was used for parameter optimization and kinetic study as several limitations were observed in the OA-ACH system. From the parameter optimization studies, it was found that the optimal ratio of CA-ChCl was 2:1 and the optimal temperature was 150°C. Lastly, during the kinetic study it was observed that CA-ChCl reaches high leaching yield at 2h and thereafter, time is not as important due to the curve of time versus leaching efficiency flattening for all the important metals, Ni, Mn, Co and Li.

8

Discussion

The goal of this study was to find a leaching agent that had low environmental impact like low toxicity, enabling low water consumption and low energy demand. Therefore, DES was considered as an innovative and promising leaching agent group.

Previous research on black mass leaching with DES has often involved using water to dilute the DES. This thesis has demonstrated that adding water before the leaching process increases the leaching yields for Ni, Mn and Co from approximately 37%, 35% and 36% to 80%, 66% and 79% respectively, with the experimental parameters over 2h, 90°C, NMC 111, S/L ratio: 50g/l and using the solvent CA-ChCl in ratio 2:1. However, one of the goals was to minimize water consumption, and therefore the DES was not diluted before the leaching. This resulted in lower efficiencies, and the water saved was 7 ml. Our world faces a shortage of clean water, which is why ensuring access to clean water for all is one of the 17 goals of the UN for a sustainable future. Although this thesis shows that water is necessary for effective filtration, even when the setup is heated, water savings compared to the other methods used in this thesis was still achieved. If the process is scaled up, the minimal amount of water will be used as well. Saving clean water is vital for sustainable development, as all sorts of processes require clean water, which must be shared among them and other applications.

Furthermore, DES are less toxic than other leaching agents, for example, the hazards associated with CA and ChCl are only irritants. These hazards are mild compared to those of other chemicals. However, they create a solvent with a very low pH which can be harmful if not handled properly. In addition, the black mass contains metals which can lead to health issues with prolonged exposure. Thereby, DES toxicity is not major compared to other agents.

DES, which are combinations of a HBD and a HBA, are characterized by the lower melting points compared to those of each HBA and HBD respectively. Therefore, creating DES requires less energy than liquifying individual HBA and HBD components because the melting points are lower. This thesis has shown that the melting point for CA-ChCl, in all ratios, are around 40-55°C compared with the melting point of CA which is 135°C and the melting point of ChCl is 305°C. A similar trend was observed for OA-ChCl, where the melting points in all ratios were 25°C instead of OA‘s melting point of around 101°C. Thus,the creation of DES significantly reduces the melting point. This reduction leads to lower energy consumption than if the components were used alone. Additionally, DES, as a part of a hydrometallurgy process, also results in lower energy consumption compared with pyrometallurgy processes which require high temperatures, around 1000°C.

Hydrometallurgy processes generally have lower energy consumption, but the processes are complex. This thesis has focused solely on the leaching of the black masses. However, recovery ways such as precipitation of the components is equally important and are discussed in section *8.2 Future Research.*

In conclusion, this thesis has demonstrated that to meet the criteria of low energy consumption, low toxicity and low water consumption while achieving high leaching efficiency,CA-ChCl emerges as a promising solvent.

8.1 Sources of Errors

The method used is well tested and employed in previous research. Despite this, errors may have occurred in obtaining the results. The main potential error could have arisen during physical observation of viscosities. The experiments were conducted over a lengthy period, both within each separate experiment and across the span from the first to the last experiment. This may have led to an unintentional and unconscious change in the reference standards for viscosity over time. To mitigate this risk, physical observation measurement was used for clarification of the viscosities. For the viscosity measurements labeled 1, 2, 3 and 4, the stability of the liquid was a critical factor. When a spoon was dragged across the liquid and the liquid‘s trace remained visible for a few seconds, the viscosity was classified as either 1 or 2, depending on the duration it stayed in place. If not, the viscosity was classified as either 3 or 4. The distinction between 3 and 4 depended on whether the solvent could swirl around in the flask; if it could, the viscosity was noted as 4, and if it could not, it was noted as 3. However, these measurements only provided an indication of how viscous the liquids were. A more rigorous analysis would yield greater accuracy.

Another source of error was the reheating of the leaching agent and the black mass. When the DES and black mass were mixed, the DES was removed from the oil bath for volume measurement and then returned to the oil bath with the black mass. This process resulted in the leaching agent, DES and black mass, cooling down and then needing to be reheated until it reached the target temperature. The duration of this reheating could vary, depending on the temperature in the oil bath, which changed during the parameter study. It was estimated that there was a maximum time difference of 10 minutes from when the DES was removed from the oil bath until DES and black mass were reheated to the target temperature. This time difference may have affected the result, as the leaching timer was set when the mixture had reached the desired leaching temperature. However, this error is assumed to be minor when the duration increases above 1 h.

A third source of error may have been the measurement of volume and weight of all the solvents. Due to the high viscosity of the solvents, the majority was hard to pour out from the measurement equipment and different containers. Therefore, it is not certain that exactly 50ml solvent was used in each experiment and that the final obtained volume/weight of the filtrate was complete. The weight of the retrieved filtrate matters because it was used to calculate the leaching efficiencies. A higher weight of the filtrate results in a higher leaching yield.

Lastly, during the XRF analysis, the black mass which was used as the reference, was analyzed in solid state, but the samples with the leaching agents were in liquid state. This means that when the leaching yield is calculated is the calculation based on a comparison for a solid and a liquid state, this may affect the results. For future studies it would be beneficial to digest the black mass so the XRF could compare samples in the same state. This is also the reasoning why the samples in the parameter optimization and kinetic study were analysed with both XRF and ICP-OES.

8.2 Future Research

Research on using DES for the recycling of LIBs is relatively new, and much remains unknown. This thesis has explored the properties and leaching capabilities of various solvents containing CA, OA and MA in combination with NCl, ACH, ChCl and TMA. This work aimed to continue mapping which solvents could be effective for LIB recycling and other types of metal extractions. However, further research is needed regarding both the property classification and the leaching process. This thesis focused on optically observed viscosities and the pH levels. These properties were observed with some limitation of the analytical equipment, thus, only pH paper and optical observations were used. Further research should focus on a more exact determination of the pH and viscosity for the solvents CA, OA and MA along with the chloride based salts NCl, ACH, ChCl and TMA.

One of the findings from this thesis is that different solvents leach the metals in varying ratios. For example, OA-ChCl and OA-TMA show a lower potential to recover Ni compared with OA-ACH and CA-ChCl. Furthermore, the recovery of Mn for CA-ChCl is 10 percentage units lower than that for Ni and Co for CA-ChCl in ratio 2:1 and 150°C. Thus, it is crucial to further research the mapping of solvents‘ abilities to leach different types of metals. Even if a solvent exhibits poor leaching yields as a leaching agent for LIBs recycling, it may hopefully still be useful for other metal extraction applications.

Finally, further research should also focus on the precipitation of metals after they have been leached from the black mass (or other sources). These precipitation studies could be of two main types: one for selective precipitation for each metal, where the metals can be reused and precipitated in high yields as pure metal salts. The second approach is to precipitate some chosen metals together. For example, in the closed loop recycling of LIB it is not necessary to precipitate all metals individually since they will be mixed again during the production of new cathodes. Therefore, if the cathode structure may be NMC in 1:1:1 or 6:2:2 ratio, it would be feasible to co-precipitate Ni, Mn and Co, which also applies to other cathode structures.

Bibliography

[1] United Nation Climate change, *The Paris Agreement*, Jan. 2024. [Online]. Available: `https://unfccc.int/process-and-meetings/the-paris-agreemen`.

[2] McPHIE Tim and CRESPO PARRONDO Ana, *Zero emission vehicles: first 'Fit for 55' deal will end the sale of new CO2 emitting cars in Europe by 2035*, Oct. 2022. [Online]. Available: `https://ec.europa.eu/commission/presscorner/detail/en/ip_22_6462`.

[3] L. Li, L. Zhai, X. Zhang, *et al.*, "Recovery of valuable metals from spent lithium-ion batteries by ultrasonic-assisted leaching process," *Journal of Power Sources*, vol. 262, pp. 380–385, Sep. 2014, ISSN: 03787753. DOI: `10.1016/j.jpowsour.2014.04.013`.

[4] A. Mohanty, S. Sahu, L. B. Sukla, and N. Devi, "Application of various processes to recycle lithium-ion batteries (LIBs): A brief review," in *Materials Today: Proceedings*, vol. 47, Elsevier Ltd, 2021, pp. 1203–1212. DOI: `10.1016/j.matpr.2021.03.645`.

[5] Q. Wei, Y. Wu, S. Li, R. Chen, J. Ding, and C. Zhang, *Spent lithium ion battery (LIB) recycle from electric vehicles: A mini-review*, Mar. 2023. DOI: `10.1016/j.scitotenv.2022.161380`.

[6] R. Morina, D. Callegari, D. Merli, G. Alberti, P. Mustarelli, and E. Quartarone, "Cathode Active Material Recycling from Spent Lithium Batteries: A Green (Circular) Approach Based on Deep Eutectic Solvents," *ChemSusChem*, vol. 15, no. 2, Jan. 2022, ISSN: 1864564X. DOI: `10.1002/cssc.202102080`.

[7] R. Golmohammadzadeh, F. Faraji, and F. Rashchi, *Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents: A review*, Sep. 2018. DOI: `10.1016/j.resconrec.2018.04.024`.

[8] G. P. Nayaka, J. Manjanna, K. V. Pai, R. Vadavi, S. J. Keny, and V. S. Tripathi, "Recovery of valuable metal ions from the spent lithium-ion battery using aqueous mixture of mild organic acids as alternative to mineral acids," *Hydrometallurgy*, vol. 151, pp. 73–77, 2015, ISSN: 0304386X. DOI: `10.1016/j.hydromet.2014.11.006`.

[9] G. P. Nayaka, K. V. Pai, J. Manjanna, and S. J. Keny, "Use of mild organic acid reagents to recover the Co and Li from spent Li-ion batteries," *Waste Management*, vol. 51, pp. 234–238, May 2016, ISSN: 18792456. DOI: `10.1016/j.wasman.2015.12.008`.

[10] L. Sun and K. Qiu, "Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries," *Waste Management*, vol. 32,

no. 8, pp. 1575–1582, Aug. 2012, ISSN: 0956053X. DOI: `10.1016/j.wasman.2012.03.027`.

[11] X. Chen, C. Guo, H. Ma, *et al.*, “Organic reductants based leaching: A sustainable process for the recovery of valuable metals from spent lithium ion batteries,” *Waste Management*, vol. 75, pp. 459–468, May 2018, ISSN: 18792456. DOI: `10.1016/j.wasman.2018.01.021`.

[12] L. Li, J. Ge, F. Wu, R. Chen, S. Chen, and B. Wu, “Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant,” *Journal of Hazardous Materials*, vol. 176, no. 1-3, pp. 288–293, Apr. 2010, ISSN: 03043894. DOI: `10.1016/j.jhazmat.2009.11.026`.

[13] L. M. Rouquette, M. Petranikova, and N. Vieceli, “Complete and selective recovery of lithium from EV lithium-ion batteries: Modeling and optimization using oxalic acid as a leaching agent,” *Separation and Purification Technology*, vol. 320, Sep. 2023, ISSN: 18733794. DOI: `10.1016/j.seppur.2023.124143`.

[14] A. Zhu, X. Bian, W. Han, *et al.*, “The application of deep eutectic solvents in lithium-ion battery recycling: A comprehensive review,” *Resources, Conservation and Recycling*, vol. 188, Jan. 2023, ISSN: 18790658. DOI: `10.1016/j.resconrec.2022.106690`.

[15] S. Liu, L. Xiong, and C. He, “Long cycle life lithium ion battery with lithium nickel cobalt manganese oxide (NCM) cathode,” *Journal of Power Sources*, vol. 261, pp. 285–291, Sep. 2014, ISSN: 03787753. DOI: `10.1016/j.jpowsour.2014.03.083`.

[16] K. P. Chandra and P. R. Budarapu, “Design and analysis of Lithium-ion pouch cell with LMO-NMC blended cathode using coupled thermo-electro-chemical model,” *Journal of Energy Storage*, vol. 78, Feb. 2024, ISSN: 2352152X. DOI: `10.1016/j.est.2023.109958`.

[17] P. Meshram, B. D. Pandey, and T. R. Mankhand, “Recovery of valuable metals from cathodic active material of spent lithium ion batteries: Leaching and kinetic aspects,” *Waste Management*, vol. 45, pp. 306–313, Feb. 2015, ISSN: 18792456. DOI: `10.1016/j.wasman.2015.05.027`.

[18] T. Li, Y. Xiong, X. Yan, *et al.*, “Closed-loop cobalt recycling from spent lithium-ion batteries based on a deep eutectic solvent (DES) with easy solvent recovery,” *Journal of Energy Chemistry*, vol. 72, pp. 532–538, Sep. 2022, ISSN: 20954956. DOI: `10.1016/j.jechem.2022.05.008`.

[19] A. Skulcova, A. Russ, M. Jablonsky, and J. Sima, “PEER REVIEWED BRIEF COMMUNICATION The pH Behavior of Seventeen Deep Eutectic Solvents,” Tech. Rep.

[20] B. Behnajady, J. Y. Seyf, S. Karimi, M. Moradi, and M. Sohrabi, “Molecular dynamic (MD) simulation and density function theory (DFT) calculation relevant to green leaching of metals from spent lithium-ion battery cathode materials using glucose-based deep eutectic solvent (DES),” *Hydrometallurgy*, vol. 223, Jan. 2024, ISSN: 0304386X. DOI: `10.1016/j.hydromet.2023.106223`.

[21] Y. Luo, Y. Deng, H. Shi, H. Yang, C. Yin, and L. Ou, “Green and efficient recycling method for spent Ni–Co–Mn lithium batteries utilizing multifunctional deep eutectic solvents,” *Journal of Environmental Management*, vol. 351, Feb. 2024, ISSN: 10958630. DOI: `10.1016/j.jenvman.2023.119814`.

[22] T. Zhang, J. Dao, J. Wang, *et al.*, "Efficient leaching of valuable metals from NCM cathode materials by green deep eutectic solvent," *Journal of Cleaner Production*, vol. 438, p. 140 636, Jan. 2024, ISSN: 09596526. DOI: `10.1016/j.jclepro.2024.140636`. [Online]. Available: `https://linkinghub.elsevier.com/retrieve/pii/S0959652624000830`.

[23] National Library of Medicine, *Citric Acid Monohydrate*, Feb. 2024. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/22230#section=WIPO-PATENTSCOPE`.

[24] National Library of Medicine, *Oxalic Acid dihydrate*, Feb. 2024. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/61373`.

[25] National Library of Medicine, *Malic Acid*, Feb. 2024. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/525`.

[26] M. Zhao, Z. Teng, X. Ma, *et al.*, "Insight into leaching rare earth from ion-adsorption type rare earth ores with citric acid: Performance, kinetic analysis and differentiation leaching," *Journal of Rare Earths*, Feb. 2024, ISSN: 10020721. DOI: `10.1016/j.jre.2024.02.005`. [Online]. Available: `https://linkinghub.elsevier.com/retrieve/pii/S1002072124000401`.

[27] B. Xu, W. Zhang, E. Zhao, *et al.*, "Unveiling malic acid biorefinery: Comprehensive insights into feedstocks, microbial strains, and metabolic pathways," *Bioresource Technology*, p. 130 265, Feb. 2023, ISSN: 09608524. DOI: `10.1016/j.biortech.2023.130265`.

[28] National Library of Medicine, *Ammonium Chloride*, Feb. 2024. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/25517`.

[29] Reagents, *Aluminum Chloride Hexahydrate Reagent*, 2020. [Online]. Available: `https://www.reagents.com/2324461/Product/Aluminum-Chloride-Hexahydrate`.

[30] National Library of Medicine, *Aluminum chloride hexahydrate*, Feb. 2024. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/24564`.

[31] National Library of Medicine, *Choline Chloride*, Feb. 2024. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/6209`.

[32] National Library of Medicine, *Tetramethylammonium chloride*, Feb. 2024. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/6379`.

[33] CAMEO Chemicals, *Ammonium chloride*. [Online]. Available: `https://cameochemicals.noaa.gov/chemical/2422`.

[34] Drugbank Online, *Ammonium chloride*, Sep. 2010. [Online]. Available: `https://go.drugbank.com/drugs/DB06767`.

[35] Procurement Resource Insights That Matter! *Aluminium Chloride Production Cost Reports*. [Online]. Available: `https://www.procurementresource.com/production-cost-report-store/aluminium-chloride`.

[36] BC Sciences, *Choline Chloride*. [Online]. Available: `https://www.bocsci.com/product/choline-chloride-cas-67-48-1-300159.html?utm_term=choline%20chloride&utm_campaign=Inhibitor&utm_source=adwords&utm_medium=ppc&hsa_acc=8252592073&hsa_cam=238212739&hsa_grp=156784714223&hsa_ad=693564486709&`

hsa_src=g&hsa_tgt=kwd-303353430609&hsa_kw=choline%20chloride&hsa_mt=p&hsa_net=adwords&hsa_ver=3&gad_source=1&gclid=CjwKCAjw5v2wBhBrEiwAXDDoJVU47jZJ3nWvEgbCBmR0jUVqFxgh pzMQRB1sXNAIEhw_xoCdtUQAvD_BwE.

[37] MP, *Choline Chloride*. [Online]. Available: https://www.mpbio.com/eu/choline-chloride.

[38] PANGOO, *Choline Chloride Manufacturing Process: An In-Depth Exploration for Livestock Health*, Apr. 2023. [Online]. Available: https://www.pangoo.biz/choline-chloride-manufacturing-process-an-in-depth-exploration-for-livestock-health/.

[39] B.C sciences, *Tetramethylammonium chloride*. [Online]. Available: https://www.bocsci.com/product/tetramethylammonium-chloride-cas-75-57-0-76532.html?utm_term=tetramethylammonium%20chloride&utm_campaign=ADCs&utm_source=adwords&utm_medium=ppc&hsa_acc=8252592073&hsa_cam=334395379&hsa_grp=34206925570&hsa_ad=188596527571&hsa_src=g&hsa_tgt=kwd-317545859996&hsa_kw=tetramethylammonium%20chloride&hsa_mt=b&hsa_net=adwords&hsa_ver=3&gad_source=1&gclid=CjwKCAjw5v2wBhBrEiwAXDDoJWfyj3ppOCXxqRAh8nJQDMGgAlOy7BD7fIz3YYuDcK BwE.

[40] SACHEM, *Unlock the potential of tetramethylammonium chloride (TMACL)*. [Online]. Available: https://www.sacheminc.com/chemicals-by-category/tetramethylammonium-chloride-tmacl/.

[41] United States Patent, *Aften et al. 54 CLAY STABILIZING METHOD FOR OIL*. [Online]. Available: https://patents.google.com/patent/US5099923A/en.

[42] M. H. Shafie, R. Yusof, and C. Y. Gan, "Synthesis of citric acid monohydrate-choline chloride based deep eutectic solvents (DES) and characterization of their physicochemical properties," *Journal of Molecular Liquids*, vol. 288, Aug. 2019, ISSN: 01677322. DOI: 10.1016/j.molliq.2019.111081.

[43] E. Ebrahimi, M. Kordloo, G. Khodadadmahmoudi, A. Rezaei, M. Ganjali, and G. Azimi, "Solvometallurgical recycling of spent LiNixCoyMnzO2 (NCM) cathode material using ternary choline chloride-ethylene glycol-p-toluenesulfonic acid deep eutectic solvent," *Hydrometallurgy*, vol. 222, Oct. 2023, ISSN: 0304386X. DOI: 10.1016/j.hydromet.2023.106184.

[44] Y. Fan, Y. Kong, P. Jiang, *et al.*, "Development and challenges of deep eutectic solvents for cathode recycling of end-of-life lithium-ion batteries," *Chemical Engineering Journal*, vol. 463, May 2023, ISSN: 13858947. DOI: 10.1016/j.cej.2023.142278.

[45] Thermo Fisher Scientific, *What is XRF (X-ray Fluorescence) and How Does it Work?* Jan. 2020. [Online]. Available: https://www.thermofisher.com/blog/ask-a-scientist/what-is-xrf-x-ray-fluorescence-and-how-does-it-work/.

[46] Norges geologiske undersøkelse, "Kvalitetssikring Hovedelementer (isoformert/smeltet prøve)," Tech. Rep., 2005. [Online]. Available: https://www.ngu.no/filearchive/97/NGU_LAB_XRF_anal.pdf.

[47] Eurofins, *Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)*. [Online]. Available: `https://www.eag.com/techniques/spectroscopy/inductively-coupled-plasma-icp-oes/`.

[48] S. Krosse and P. van der Ven, *ICP-OES*. [Online]. Available: `https://www.ru.nl/science/gi/facilities-activities/elemental-analysis/icp-oes/`.

A

pH

The tables in the following subsections are the measured pH of the solvents containing the acids, citric acid, CA, oxalic acid, OA, and malic acid, MA, together with the chloride based salts, ammonium chloride, NCl, aluminum chloride, ACH, choline chloride, ChCl, and tetramethylammonium chloride, TMA. The tables only present the solvents that reached a liquid phase in the range of 25-85°C. The pH was first measured with a pH probe for the solvents containing CA, but the pH probe had limitations and broke after a few uses. The limitations were that the pH probe could not operate in highly viscose solutions, at temperatures higher than 80°C and with pH below 0. Therefore, the pH probe was used for some CA solvents only, and because of the extreme conditions generated by DES, the pH probe was switched to pH paper for all other solvents containing oxalic acid and malic acid.

A.1 Citric Acid Together with HBA

Table A.1 shows that the pHs were low for all the solvents and that the overall trend was that the pH decreased with increasing temperature. Due to the limitations of the pH probe, the pH is represented by <0 if the pHs are below zero. For CA-TMA in the ratio 2:1, the pH paper was used instead of the pH probe. The asterisk, *, identifies these values which can not be directly compared with the other values due to the limitations of the pH paper.

Table A.1: pH of citric acid-HBAs

		Temperatures in Celsius												
Solvents	ratios	25	30	35	40	45	50	55	60	65	70	75	80	85
CA-ChCl	1:1						0.16	0.19	-	<0	<0	<0	-	
	1:2							0.57	0.47	0.20	0.12	0.07	<0	
	2:1						<0	<0	<0	<0	<0	<0	<0	
CA-TMA	1:1									<0	<0	<0	-	
	1:2												0.04	
	2:1									1*	1*	1*	1*	1*

- no data collected
** pH paper was used.*

Table A.1 shows that the maximum pH is observed as pH 1 for all the represented solvents, but the real value might be lower due to the limitations of the pH paper. It can also be seen that if the pH was above 0, the pH decreased when increasing the temperature, as shown for ChCl ratio 1:1 and 1:2.

A.2 Oxalic Acid Together with HBA

The following solutions with oxalic acid had too low pH for the pH probe, therefore, pH paper was used instead. However, these measurements were not as precise as the results for the pH observed for citric acid solvents, due to the range of the pH paper being 1-11. Hence, if the pH was above 1 with a low viscosity and low temperature, the probe would initially be used but due to the results indicated from the pH paper, table A.2, the pHs were too low for the pH probe.

Table A.2: pH of oxalic acid-HBAs

		Temperatures in Celsius												
Solvents	ratios	25	30	35	40	45	50	55	60	65	70	75	80	85
OA-ACH	1:1													
	1:2													
	2:1												<0	<0
OA-ChCl	1:1	1	1	1	1	1	1	1	1	1	1	1	1	1
	1:2	1	1	1	1	1	1	1	1	1	1	1	1	1
	2:1	1	1	1	1	1	1	1	1	1	1	1	1	1
OA-TMA	1:1				1	1	1	1	1	1	1	1	1	1
	1:2					1	1	1	1	1	1	1	1	1
	2:1				1	1	1	1	1	1	1	1	1	1

The values of OA-ACH were measured with pH paper with the lowest value 0.5. All the other values are from pH paper with the lowest value 1.

All combinations of oxalic acid and HDAs had very low pH. For choline choline, all ratios had at least a pH of 1 throughout the entire interval as noted in table A.2. The pHs were also consistently at 1 for the mixtures with tetramethylammonium chloride when the solvents were in a liquid state. Table A.2 indicates that the lowest pH was received by OA-ACH where the pH was <0. This pH measurement was recorded with the pH probe and can not be directly compared with the other values due to the change of measurement method.

A.3 Malic Acid Together with HBA

The solvents consisting of malic acid mixed with the HBAs, choline chloride and tetramethylammonium chloride either had too high viscosity or too low pH for the use of the pH probe and therefore pH paper was used. The lowest detectable pH with pH paper was 1.

Table A.3: pH of malic acid-HBAs

		Temperatures in Celsius												
Solvents	ratios	25	30	35	40	45	50	55	60	65	70	75	80	85
MA-ChCl	1:1				2→1	1	1	1	1	1	1	1	1	1
	1:2				2	2	2	2	2	2	2	2→1	2→1	2→1
	2:1					1	1	1	1	1	1	1	1	1
MA-TMA	1:1									2	1	1	1	1
	1:2										2 → 1	1	1	1
	2:1									1	1	1	1	1

The arrow, → symbolizes the pH being between the value to the right and the value to the left.

For MA-ChCl and MA-TMA in the ratios 1:1 and 1:2, the pH decreases with increasing temperature, table A.3. In addition, for the ratio 2:1 for MA-ChCl and MA-TMA, the observed pH starts already at the lowest detectable value. Furthermore, table A.3 indicates that the highest pH is 2 which was observed for MA-ChCl in the ratio 1:2 until 75°C where it decreased to a pH between 2 and 1, resulting in the mixture having the highest pH of all solvents in table A.3. MA-ChCl in ratio 1:2 also has the highet pH for all mixtures containing CA and OA, tables A.1 and A.2.

B

Laboratory Notes for Citric Acid and Choline Chloride

The following tables, B.1 and B.2, are the laboratory notes from the different experiments conducted by method *3.2 Preparation of solvents, viscosity and pH* . The tables note the temperatures in the oil, T_{oil}, and in the DES solution, T_{DES}. There are also notes about the pH and some minor comments about the phases. Table B.1 presents CA-ChCl in ratio 1:1 and table B.2 for ratio 1:2.

For table B.1, representing CA-ChCl ratio 1:1, it can easily be observed that T_{DES} was higher than T_{oil} in many cases. This trend can be seen in almost the whole temperature interval traced from the T_{oil} temperature 40°C to the T_{oil} of 90°C. The difference in temperature between T_{DES} and T_{oil} was observed at its highest peak with a temperature difference of 8.3°C. Furthermore, the table shows that the pH ranged from pH 0.81 to -1.11. This is further covered in the result section *4.2 PH* and in the appendix section *A PH* and its subsections.

Table B.1: Laboratory notes for CA-ChCl in the ratio 1:1

T_{oil}	T_{DES}	pH	comment
40	43.5	-	
44.0	49.0	-	
50.1	56.9	0.81	
55.0	54.0	-	
55.0	53.8	0.16	
58.0	55.5	0.19	
64.0	64.5	-0.51	
65.6	69.4	-0.81	
69.3	74.1	-1.11	
80.2	85.6	-1.0	
80.2	88.5	-1.11	
80.2	86.5	-1.11 and -0.96	
90.1	92.5	-	
95.5	95.0	-	

Laboratory notes of CA-ChCl in the ratio 1:2 are presented in table B.2. The table shows that the temperatures in the DES, T_{DES}, were higher than the temperature in the surrounding oil, T_{oil}, for many occasions. This is true for almost the whole temperature interval, from the T_oil of 40°C to roughly a T_{oil} of 85.2°C. Furthermore, it can be seen that the pH varied from 0.57 to -0.09. This is further presented in the result section *4.2 pH* and explained in more detail in the appendix section *A PH* and its following subsections. The last column in table B.2 shows some comments about the phases.

Table B.2: Laboratory notes for CA-ChCl in the ratio 1:2

T_{oil}	T_{DES}	pH	comment
27	24.4	-	s
28	25.4	-	start to attach
31.0	28.6	-	−‖−
33.0	30.2	-	−‖−
35.1	33.5	-	−‖−
38.0	38.8	-	melting, mag stop
40.0	40.2	-	melting
43.2	44.2	-	−‖−
44.3	44.8	-	−‖−
45.0	45.6	-	−‖−
46.0	47.4	-	−‖−
46.1	47.9	-	melting 50%
48.2	49.2	-	
49.4	50.0	-	
51.0	53.3	-	
51.0	54.5	-	
51.0	54.1	-	
51.0	53.9	-	l
51.0	53.4	0.48	lumpy l
51.0	52.1	-	
56.1	55.7	0.57	
61.8	60.3	0.47	good l
66.2	66.0	0.20	
68.0	68.0	0.31	
70.0	70.7	0.12	
68.0	74.3	0.07	
80.4	81.2	-0.09	
85.2	85.2	-	
92.0	90.2	-	

C

Parameter Optimization Table

Table C.1 presents the leaching efficiency in percent for CA-ChCl. The leaching efficiency is described for the metals Al, Co, Cu, Fe, Mn and Ni when the leaching temperature changed between 60, 90, 120 and 150°C and the ratios varied between 1:1, 1:2 and 2:1 Furthermore, the S/L ratio was chosen to be 50 g/l for all experiments.

The best leaching efficiency of Ni, Mn and Co was reached for CA-ChCl ratio 2:1 at a temperature of 150°C, which is also shown in figure 5.1. Moreover, table C.1 shows that the leaching efficiency of Fe was above 100 % for almost all tested scenarios. This is not possible and thereby a sign of an analytical error. The table further shows that the efficiency of Al was 0% for all except for CA-ChCl in 90°C and ratio 1:2, where it was 2%. The leaching efficiency of Cu varied between 46 and 60%. Lastly, the leaching efficiencies for Ni, Mn and Co can be seen in figure 5.1.

Table C.1: Leaching efficiency in percentages (50 g/l)

	60°C			90°C			120°C			150°C		
	1:1	1:2	2:1	1:1	1:2	2:1	1:1	1:2	2:1	1:1	1:2	2:1
Al [%]	0	0	0	0	2	0	0	0	0	0	0	0
Co [%]	29	21	53	61	41	71	82	79	80	104	82	109
Cu [%]	43	36	40	60	43	48	48	36	47	50	40	46
Fe [%]	-	-	-	-	-	-	-	-	-	-	-	-
Mn [%]	25	21	42	44	32	52	60	58	58	74	59	77
Ni [%]	10	7	32	20	14	24	50	27	27	34	27	36

Black mass leaching with solid to liquid ratio 50 g/l, 2 h leaching time with varying temperatures between 60-150°C. (- values above 110%)

Table C.2 presents the re-analysed leaching efficiency in percent for CA-ChCl. The leaching efficiency is described for the metals Al, Co, Cu, Fe, Mn and Ni when the leaching temperature changed between 60, 90, 120 and 150°C and the ratios varied between 1:1, 1:2 and 2:1 Furthermore, the S/L ratio was chosen to be 50 g/l for all experiments.

The trend of leaching efficiency for Ni, Mn, Co and Li was that the leaching yield increased with increasing temperature, which is shown in figure 6.1. Moreover, table C.2 shows the leaching efficiency of the metals Al, Cu and Fe as well as the leaching yields of Ni, Mn Co and Li in more detail.

Table C.2: Leaching efficiency in percentages (50 g/l)

	60°C			90°C			120°C			150°C		
	1:1	1:2	2:1	1:1	1:2	2:1	1:1	1:2	2:1	1:1	1:2	2:1
Al [%]	1	9	1	1	3	4	3	5	2	4	4	5
Co [%]	22	36	19	48	48	89	57	58	64	62	12	73
Cu [%]	33	29	34	50	35	94	38	40	32	32	33	37
Fe [%]	-	-	-	-	-	-	-	-	-	-	-	-
Mn [%]	18	30	16	40	41	74	48	49	54	53	56	62
Ni [%]	7	12	6	2	17	30	20	20	22	21	23	35
Li [%]	21	33	19	31	30	63	32	34	34	34	37	37

Black mass leaching with solid to liquid ratio 50 g/l, 2 h leaching time with varying temperatures between 60-150°C. (-not recovered values)

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