**Aalto University
School of Chemical
Engineering**

Janiika Emmi Katariina Eronen

RECOVERY OF LITHIUM FROM LITHIUM-ION BATTERY WASTE

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Sustainable Metals Processing

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Supervisor   Professor Mari Lundström

Instructors   M.Sc. Antti Porvali
                    M.Sc. Miamari Aaltonen

Author Emmi Eronen	
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Thesis supervisor Professor Mari Lundström	
Thesis advisor(s) / Thesis examiner(s) M.Sc Antti Porvali & M.Sc Miamari Aaltonen	
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Abstract

Recovery of lithium from spent lithium-ion batteries has recently been of interest due to increasing demand of portable electronics, electric vehicles and energy storage systems. Currently few industrial processes recover cobalt, nickel and lithium from battery waste using hydrometallurgical methods. However, future waste batteries will challenge the present processes due to more complex technology and decreasing amount of metals to be recovered.

Leaching of spent Li-ion batteries have been studied using strong mineral acids such as sulfuric, hydrochloric and nitric acid. In comparing experiments hydrochloric acid has performed best. Also, organic acids can be used as leaching reagents. Solvent extraction and ion exchange can be used to selectively concentrate metals containing solution whereas chemical precipitation, electrowinning and/or cementation methods are used for the recovery of metals from spent Li-ion batteries. Impurities are often precipitated from the leach liquor by neutralization with NaOH solution. Cobalt, nickel and lithium can be separated from complex metal containing solution by solvent extraction using different extractants such as Cyanex 272 or P507.

In this work precipitation and solvent extraction were investigated to recover mainly cobalt, nickel and lithium from leach liquor. Temperature (30, 40 and 50 °C) and pH (5.0, 5.5 and 6.0) dependency were studied in the purification step of leach liquor. Iron, aluminum and copper were precipitated together using 2 M sodium hydroxide solution at 50 °C when equilibrium pH was 5. Temperature (30, 40 and 50 °C) and pH dependency were studied in the precipitation of cobalt, manganese and nickel as hydroxides (pH 7.5, 8.0 and 8.5) and carbonates (pH 7.0, 7.5 and 8.0). Cobalt, manganese and nickel were precipitated in one stage using 2 M sodium carbonate solution at 50 °C when equilibrium pH was 8. Lithium was precipitated successfully by adding stoichiometric amount of saturated sodium carbonate solution at 50 °C. Before lithium recovery the liquor was evaporated in order to increase the concentration of lithium. Lithium carbonate recovery efficiency was 59% and calculated estimation of the purity 95%.

Solvent extraction has been studied widely in the separation of cobalt and nickel. In this work, the separation of cobalt and manganese from nickel and lithium was performed with 40% saponified Cyanex 272. Optimal parameters were 2:1 organic-to-aqueous ratio, contact time 15 min, equilibrium pH 5.3 and temperature 30 °C. 98% of cobalt and 99% of manganese were separated from nickel and lithium in one extraction stage. Cobalt and manganese were stripped in single stage with 2 M H_2SO_4 and the efficiencies were 96% and 93%, respectively. Scrubbing before stripping was recommended for future experiments. Conceptual flowchart for the recovery of metals was suggested according to results and literature.

Keywords LIBs, lithium-ion battery, hydrometallurgy, recycling, circular economy, leaching, chemical precipitation, solvent extraction

Tekijä Emmi Eronen	
Työn nimi Litiumin talteenotto litium-ioni akkumurskeesta	
Laitos Kemian tekniikan ja metallurgian laitos	
Professuuri Hydrometallurgia ja Korroosio	**Professuurikoodi** MT-85
Työn valvoja Professori Mari Lundström	
Työn ohjaaja(t)/Työn tarkastaja(t) DI Antti Porvali & DI Miamari Aaltonen	
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Tiivistelmä

Viime aikoina kiinnostus litiumin talteenottoa kohtaan litium-ioni-akkumurskeesta on kasvanut. Syynä kiinnostuksen kasvuun on kannettavan elektroniikan, sähköisten ajoneuvojen ja energian varastointisysteemien kysynnän kasvu. Tällä hetkellä muutama teollisuudessa oleva prosessi ottaa koboltin ja nikkelin lisäksi litiumin talteen akkumurskeesta hydrometallurgisesti. Kuitenkin tulevaisuuden paristot sekä akut tulevat olemaan haaste nykyisille kierrätysprosesseille entistä monimutkaisemman teknologian ja pienenevien metallipitoisuuksien vuoksi.

Akkumurskeen liuotusta on tutkittu käyttäen vahvoja mineraalihappoja kuten rikki-, suola- ja typpihappoa. Vertailevissa tutkimuksissa suolahappo on liuottanut parhaiten eri metalleja. Mineraalihappojen lisäksi liuotusreagensseina on tutkittu orgaanisia happoja. Neste-nesteuuttoa ja ioninvaihtohartseja voidaan käyttää liuoksen selektiivisessä metallin rikastuksessa, kun taas kemiallista saostusta, elektrolyyttistä rikastusta ja/tai sementaatiota käytetään metallin talteen otossa. Yleisesti epäpuhtaudet poistetaan neutralisoinnilla eli lisäämällä natriumhydroksidia liuokseen, jolloin rauta, alumiini ja kupari saostuvat. Koboltti, nikkeli ja litium voidaan erottaa kompleksisesta metalliliuoksesta neste-nesteuutolla käyttäen erilaisia uuttoaineita kuten Cyanex 272:ta tai P507:ää.

Tässä työssä tutkittiin kemiallista saostusta ja neste-nesteuuttoa päämetallien eli koboltin, nikkelin ja litiumin talteen ottamiseksi ja erottamiseksi. Raudan alumiinin ja kuparin saostuksessa tutkittiin lämpötilan (30, 40 ja 50 °C) ja pH:n riippuvuutta (5.0, 5.5 ja 6.0). Rauta, alumiini ja kupari saostettiin yhdessä 50 asteessa lisäämällä 2 M natriumhydroksidia kunnes pH oli 5. Koboltin, mangaanin ja nikkelin saostuksen lämpötila- (30, 40 ja 50 °C) ja pH-riippuvuutta tutkittiin lisäämällä natriumhydroksidi ja -karbonaatti liuoksia. Metallit saostettiin yhdessä 50 °C:ssa lisäämällä 2 M natriumkarbonaattia kunnes tasapaino pH oli 8. Litiumin kristallointi suoritettiin 50 °C:ssa lisäämällä stoikiometrinen määrä kyllästettyä natriumkarbonaatti liuosta. Ennen litiumin talteenottoa litiumin konsentraatiota nostettiin haihduttamalla pohjaliuosta. Litium karbonaatin saanto oli 59 % ja laskettu arvio puhtaudesta oli 95 %.

Neste-nesteuuttoa on tutkittu laajasti koboltin ja nikkelin erotusmenetelmänä. Tässä työssä koboltin ja mangaanin erotus nikkelistä ja litiumista suoritettiin 40 % saippuoidulla Cyanex 272:lla. Optimaaliset parametrit olivat 2:1 orgaaninen-vesiliuos suhde, kontaktiaika 15 min, tasapaino pH 5.3 ja lämpötila 30 °C. 98 % koboltista ja 99 % mangaanista saatiin erotettua nikkelistä ja litiumista yhdellä uuttovaiheella. Yksivaiheisella strippauksella talteen saatiin 96 % koboltista ja 93 % mangaanista. Puhdistusta suositellaan ennen strippausta jatkokokeita varten. Tulosten ja kirjallisuuden perusteella esitettiin vuokaavio metallien talteen ottamiseksi akkumurskeesta.

Avainsanat Litium-ioni-akku, hydrometallurgia, kierrätys, kiertotalous, liuotus, kemiallinen saostus, neste-nesteuutto

Foreword

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Tsirp Tsirp!

Espoo, 16th of May 2017.

Emmi Eronen

Abbreviation List

Lithium-ion battery	LIB
End-of-life	EOL
Polyvinylidene fluoride	PVDF
Lithium cobalt oxide	LCO
Lithium manganese, nickel, cobalt oxide	MNC
Lithium manganese spinel	LMO
Lithium iron phosphate	LFP
Lithium nickel, cobalt, aluminum oxide	NCA
Solid-to-liquid ratio	S:L
Solvent extraction	SX
Equilibrium pH	pH_e
Initial pH	pH_i
Synergistic solvent extraction	SXX
Organic-to-aqueous ratio	O:A
Tributyl phosphate	TBP
X-Ray Diffraction	XRD
Inductively coupled plasma atomic emission spectroscopy	ICP-OES
Atomic absorption spectroscopy	AAS

Contents

1   Introduction

Currently the battery industry is growing rapidly due to increasing demand of battery-operated portable and wearable electronics, electric vehicles (EVs) and energy storage systems (Christmann, et al., 2015). The major growth effect of energy storage systems both for grid and residential systems derive mainly from increasing use of renewable energy sources such as wind and solar power (Thackeray, et al., 2012). Due to growth of battery industry the consumption of lithium-ion batteries (LIBs) increases and recycling of end-of-life (EOL) products becomes essential.

Pyro- and hydrometallurgical techniques have been introduced in the recycling of LIBs. The commonly suggested advantages of hydrometallurgical technique over pyrometallurgical are the scalability of the operation, possibility for the recovery of wider quantity of elements and in specific cases low operating costs, high extraction efficiency and release of lower amount of emissions (Swain, 2017). Hydrometallurgical process has the ability to adapt to varying waste composition and lower input volumes (Ekberg & Petranikova, 2015). In LIB recycling the recovery of lithium by pyrometallurgical approach is currently nonexistent (Christmann, et al., 2015). Hydrometallurgical method for the recovery of lithium has been successful and an industrial process has been developed and implemented in France (Tedjar & Foudraz, 2004).

The purpose of this thesis is the recovery of lithium from LIB commercial scrap material, which has been crushed and leached in hydrochloric acid (HCl). This work focuses on seven different metals with the highest concentrations in leach liquor, which are iron (Fe), aluminum (Al), copper (Cu), manganese (Mn), nickel (Ni), cobalt (Co) and lithium (Li). Methods used in the recovery of these elements in this work are chemical precipitation and solvent extraction (SX). In chemical precipitation parameters such as pH and temperature are investigated using two reagents, sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3). SX for the separation of Co is investigated using partially saponified extractant. The goal of this thesis is to investigate, which metals can be precipitated, and which separated via SX. The optimal conditions for metal recovery using precipitation are presented in this work. The separation of Co is investigated using Na-Cyanex 272 as an extractant. A process flowchart for the recovery of seven investigated metals is suggested according precipitation and SX results. Furthermore, quality of gained products in the precipitation process is presented.

2 Lithium-ion batteries

Lithium is most commonly used in battery as positive electrode material due to its light weight, high energy density, low auto-discharge rate, large temperature range and excellent cycle life. The substantial increase of lithium consumption in battery industry and EOL waste of batteries have raised an interest towards the recovery of lithium from spent LIBs. LIB is often referred to as secondary or rechargeable battery, whereas non-rechargeable lithium battery is referred to as lithium primary battery. The availability of LIBs has decreased the market size of primary lithium batteries. (Christmann, et al., 2015) According to Sociedad Quimica y Minera de Chile (SQM), in 2014 LIBs accounted for 46% of total lithium demand, Figure 1 (SQM, 2014). The reserve of lithium in the world was estimated to be close to 14 000 000 tons. Lithium mine production, excluding U.S. production, in 2015 was estimated to be 32 500 tons worldwide. (USGS, 2016) Automobile companies developing lithium-based batteries for EVs and companies developing energy storage systems are expected to raise the use of lithium compounds significantly (Christmann, et al., 2015).
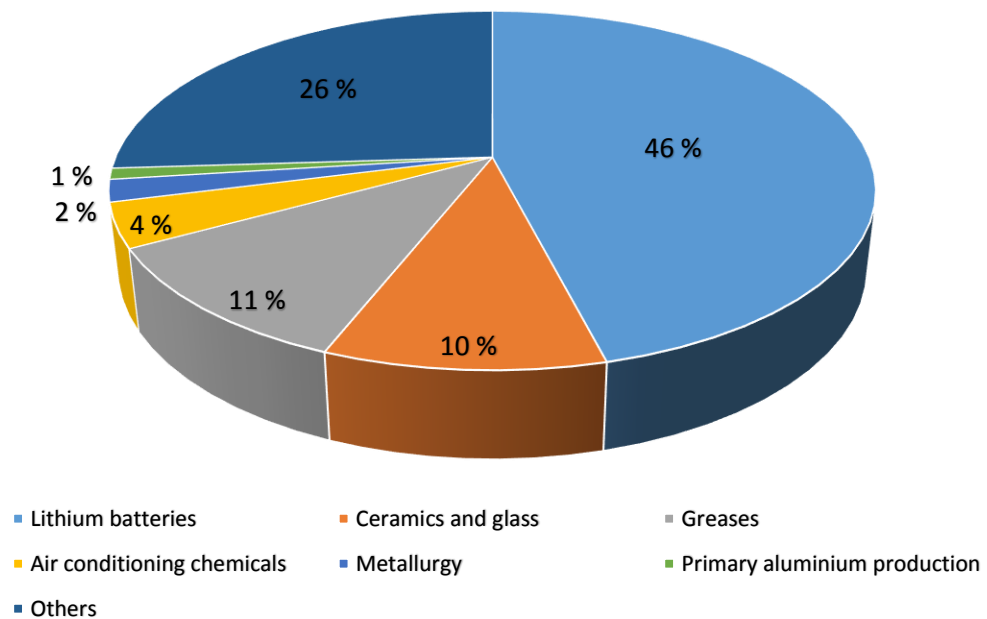
Figure 1. Total demand of lithium in 2014 divided into different categories (SQM, 2014).

2.1 Technology

Battery is a device containing basic electrochemical units, which are referred to as cells providing electrical energy. A battery cell consists of four main components: positive electrode (i.e. cathode when discharged), negative electrode (i.e. anode when discharged), separator and electrolyte (Figure 2). The separator is located between the anode and the cathode preventing physical contact and shortcuts while the electrolyte enables transfer of ions between the electrodes. The electrolyte is generally aqueous solution such as water or other solvent with dissolved salt, acids or alkalis. Occasionally reactions between anode and electrolyte are avoided by applying non-aqueous electrolytes. (Linden & Reddy, 1995)
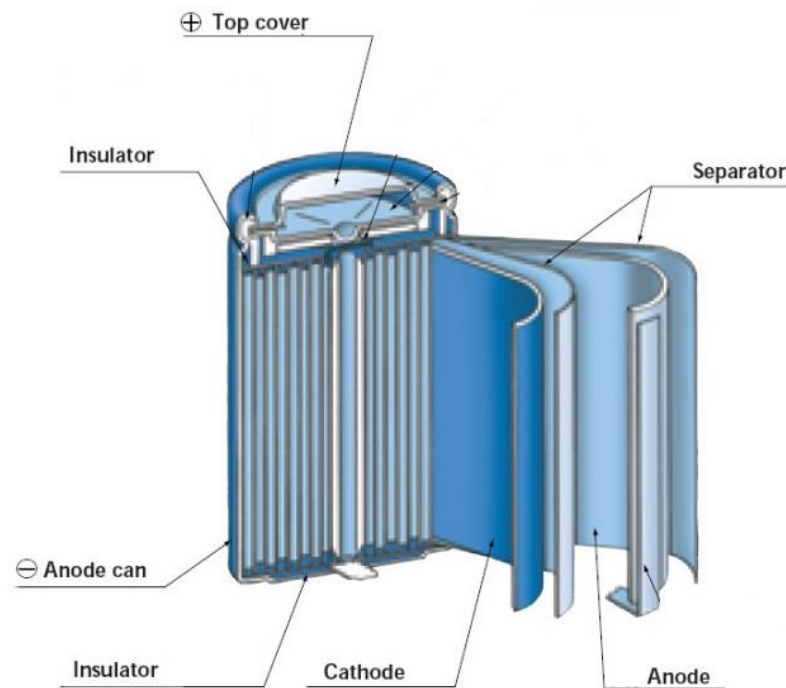
Figure 2. Schematic assembly of cylindrical portable lithium-ion battery (modified from (EPBA, 2007)).

In a cell an electrochemical oxidation-reduction reaction converts the chemical energy of active materials directly into electric energy (Linden & Reddy, 1995). During the electrochemical reaction, the negative electrode or anode is oxidized and positive electrode or cathode is reduced, respectively. Oxidation occurs as electrons are transferred from the electrode to electrolyte and reduction occurs as electrons are transferred from the electrolyte to the electrode. In LIBs, the

cathode transfers lithium-ions to the anode during charging and receives ions during discharging. In the anode, same process occurs vice versa. (Chagnes, 2015a)

2.2 Materials

LIBs are extremely heterogeneous and contain various materials from metals to plastics. The European Portable Battery Association (EPBA) offers product information of different batteries and an indicative material composition for LIBs. According to EPBA (2007) a typical portable LIB contains aluminum foil 15 - 25%, carbon 0.1 - 1%, copper foil 5 - 15%, diethyl carbonate (DEC) 1 - 10%, ethylene carbonate (EC) 1-10%, methyl ethyl carbonate (MEC) 1 - 10%, lithium hexafluorophosphate ($LiPF_6$) 1 - 5%, graphite as powder 10 - 30%, lithium cobalt oxide ($LiCoO_2$ or LCO) 25 - 45%, polyvinylidene fluoride (PVDF) 0.5 - 2%, steel, nickel and polymers in balance (EPBA, 2007). Table 1 presents the metal compositions of LIB powder in different literature sources.

Table 1. Element composition (wt.%) in different types of pretreated spent LIBs.

Reference	LIB type	LIB Fraction (wt.%)							
		Li	Co	Ni	Cu	Al	Mn	Fe	P
Ferreira et al. (2008)	LCO batteries (without steel case)	2.45-8.88	30.8-42.9	0.02	13	6.5-10.0	<0.01	0.03-0.10	-
Chen et al. (2011)	Anode and cathode films of portable LIBs	3.34	26.77	0.34	1.24	5.95	1.1	3.76	-
Huang et al. (2016)	Hybrid cathode powder of $LiFePO_4$ and $LiMn_2O_4$	4.35 ±0.05	17.18 ±0.12	-	-	-	33.45 ±0.15	-	9.36 ±0.07
Takacova et al. (2016)	Portable LIBs (80 wt.% of LIBs and 20 wt.% polymer LIBs)	3.65	22.43	1.54	1.33	0.72	1.49	1.27	-

LIBs contain a thin film of aluminum as a substrate material for cathode and a thin film of copper for anode. Both electrodes are coated with active materials. The active materials in anode are usually Li-based compounds, graphite, carbon or silicon. (Warner, 2015) The cathode is coated with lithium metal oxide material and the most widely used compound in portable LIBs is LCO, which has the highest energy density of all commonly known cathode materials. Currently LCO is the market predominant cathode material. NMC or lithium nickel/manganese/cobalt oxide (Li$(Ni_{0.33} Mn_{0.33} Co_{0.33}) O_2$) is the second most important material used in secondary batteries. Other

well-known options for active materials in cathodes are LMO or lithium manganese spinel ($LiMn_2O_4$) and LFP or lithium iron phosphate ($LiFePO_4$). (Christmann, et al., 2015) In automotive batteries, the cost of raw material is lowered by replacing some or all of Co with Ni, Mn or Al (Gaines, 2014) Therefore, NMC, LMO and LFP are major cathode types for EVs (Lowe, et al., 2010). The anode and the cathode contain adhesives such as PVDF and organic additives holding the structure of electrodes and current collectors intact (Ordoñez, et al., 2016). In addition, the separator located between the anode and cathode is usually polyethylene (PE), polypropylene (PP) or combination of PE and PP (Światowska & Barboux, 2015).

The electrolyte in LIBs is usually a mixture of two or three solvents and a lithium salt. The most used salt is $LiPF_6$. Other common alternative salts include lithium perchlorate, lithium hexafluoroarsenate and lithium tetrafluoroborate. In addition to lithium salts, polymer electrolytes are used as alternative electrolytes. The three types of polymer electrolytes are dry solid polymer electrolytes, polymer gels and composites. The dipolar organic solvents such as ethers, alkyl carbonates, lactones, sulfones and nitriles are compatible with LIBs. (Chagnes, 2015b)

Consequently, majority of LIBs have cathode foil made of aluminum, which has LCO deposited on it as cathode active material. Anode foil is made of copper upon, which graphite is deposited by adhesive. Electrolyte contains $LiPF_6$ in an organic solvent(s). Battery cell is covered and protected by stainless steel casing. Efficient recycling process of LIBs is challenging to achieve due to variety of materials and compositions in the waste stream. Optimizing one recycling process for a stream of specific LIB waste may not be suitable for other type or mixed waste LIBs. (Al-Thyabat, et al., 2013)

2.3 Lithium in present recycling processes

Currently, 3% of LIBs are recycled for the purpose of valuable metal recovery (Swain, 2017). According to International Resource Panels hosted by UNEP, the recycling rate of Li from EOL products is less than 1% (UNEP, 2011). Hydrometallurgical processes have been already developed and implemented to recover Li from Li-based batteries. The improvement of current processes and development of new more efficient processes are a necessity to meet the future recycling targets of EOL products. Additionally, the increasing demand of Li could eventually lead to usage of recycled Li as primary Li reserves become poor. (Christmann, et al., 2015)

2.3.1 Pyrometallurgy

Umicore combines pyro- and hydrometallurgy for the recycling of all types of Li-ion and NiMH batteries. Ultra-High Temperature (UHT) technology operates in over 3000 °C generated by plasma. (Morel, 2010) However, Li present ends up into slag and is not recovered (Umicore, 2017). Today the challenge with pyrometallurgical processes is to make the extraction of Li from slag competitive for the manufacturers of LIBs when compared to primary Li production (Christmann, et al., 2015).

In UHT process the pyrometallurgical phase contains three fractions: an alloy, a slag and gas emissions. Metal alloy contains the valuable metals (Co, Ni, Cu and Fe) from battery waste after smelting. Evidently, some metals end up in slag fraction (Al, Li, Mn and Rare Earth Elements (REE)). The potential for lithium recovery from the slag has been acknowledged. The recovery process has not yet been implemented due to economical challenges. Extraction process of REE has been recently implemented in France. Currently, the rest of the slag is used in the construction industry. The recovered valuable metals such as Co and Ni are further refined in a subsequent hydrometallurgical process and converted into active cathode materials for the production of new LIBs. (UNEP, 2013) It needs to be noted that currently the Li in the produced active cathode materials in the Umicore process originates from chemical addition i.e. primary raw materials and not from the LIB waste.

2.3.2 Hydrometallurgy

Currently, three companies are exploiting hydrometallurgical processes in metals recovery from spent LIBs in industrial scale. It should be noted that solely LMO and LFP cathode materials are currently unattractive to recyclers as cathodes contain no valuable metal (Co and Ni) (Christmann,

et al., 2015). In Table 2, the companies, locations, scrap material, process steps and recovered compounds or metals are shortly presented.

Table 2. Hydrometallurgical recycling processes for LIBs in industry (Tedjar & Foudraz, 2004; Saloojee & Lloyd, 2015; JX Nippon Mining & Metals Corporation, 2009; Acker, 2016)

Company	Location	Recycled material	Hydrometallurgical process steps	Recovery
Recupyl	France	All LIBs	Leaching, cementation and precipitation	Li_3PO_4 or Li_2CO_3 and Co_2O_3 or Co
JX Nippon Mining	Japan	All lithium batteries	Leaching, filtration, SX and lithium crystallization	Li_2CO_3, $NiCO_3$, Co and Mn
Retriev Technologies	USA	All lithium batteries	Separation, filtration and recovery	Cobalt cake, Li brine

According to Recupyl's patent (no. FR 2 868 603), a commercial process has been developed for the recovery of metals from Li-based battery waste. In mechanical separation process step Fe, Cu and plastics are separated from the finer scrap material. The fine material is leached. Mixed oxides, added Li and carbon are separated from soluble Li. Soluble Li is precipitated as lithium phosphate (Li_3PO_4). Another leaching step is needed for the mixed oxides and added Li. After leaching a purification process removes copper and other impurities via cementation and precipitation. The Co from solution containing Co and Li salts is precipitated as Co_2O_3 or recovered by electrolysis where Co is recovered as bimetallic alloy. After Co removal the Li in raffinate can be precipitated as Li_3PO_4 or lithium carbonate (Li_2CO_3). (Tedjar & Foudraz, 2004)

JX Nippon Mining & Metals Corporation carried out a commercial feasibility trial process for the extraction of metals from recycled cathode materials. First the scrap was leached and filtered. Solvent extraction was performed to selectively separate Mn, Co and Ni from the leach liquor. The separated metals were refined. Final products of Co and Mn were recovered using electrowinning. The separated Ni was recovered as nickel carbonate ($NiCO_3$). After the separation of Co, Mn and Ni, the leach liquor contained mainly Li. Lithium was recovered as Li_2CO_3. (JX Nippon Mining & Metals Corporation, 2009)

Retriev Technologies (formerly Toxco Inc.) has a three-step process in use for recycling of spent LIBs. The steps include battery separation, product treatment and slurry filtration. The metals are

separated using hydrometallurgy, yet recovered using pyrometallurgy. Cobalt cake is recovered from spent LIBs using hydrometallurgical approach. (Acker, 2016) Li is recovered as Li brine, which is used in primary lithium production (Ekberg & Petranikova, 2015).

Currently the capacities of hydrometallurgical processes for spent LIBs are minor compared to pyrometallurgical processes where the initial input value is often thousands of tonnes per year. Umicore's UHT process treats 7 000 tonnes of battery waste per year. The amount equals to approximately 250 million mobile phone batteries. (Vliegen, 2010) The capacity in Recupyl's hydrometallurgical battery recycling plant is 110 tonnes of batteries per year (Goonan, 2012). Umicore's process capacity is over 60 times larger than Recupyl's. In a lab scale process model, presented in literature, the amount of processed powder varied from 100 to 250 tonnes per year (Granata, et al., 2012). The lab scale input amount measures up to current commercial process capacity. The recovered products (Li, Co, Mn and Ni) could potentially be used as raw material in the manufacture of new batteries. If the quality of recovered products is not satisfactory enough the products must find alternative market. (Gaines, 2014)

2.4   Future

Multiple factors influence the future availability of Li such as pure product and compound prices, possible new reserves, development in lithium recycling, changes in the geography of lithium industry, possible substitutions for LIBs, progress in battery design and progress in recycling of EOL products. It has been estimated that the demand and supply balance should not be a concern before years 2025-2030. (Christmann, et al., 2015)

The valuable metal content in future batteries is expected to decrease as new more complex future generation LIBs are developed. It needs to be realized that there is a possibility that currently available recycling processes might not be adaptable for future generation LIBs. Compared to the current state, the composition and properties of metals will greatly vary in the future. The development of nanotechnologies in battery design will much likely enhance the performance while using less raw materials. (Lorente, et al., 2016)

Additionally, EVs and energy storage systems are being introduced in large scale and developed at the moment therefore they will not become EOL products in the near future. Even though there might not be demand for lithium recycling in the next 10 years or more the preparations and development of efficient valuable metal recycling should be high priority at the moment. (Gaines, 2014)

3 Pre-treatment and leaching of LIBs

The cathode, anode and separator are laminated to enable electrical contact in the cell. Joining the units through lamination makes batteries extremely compact devices. The pre-treatment processes of LIB waste allow for effective recovery of metals. Common pretreatment of spent LIBs is mechanical separation. However, the disadvantage in mechanical separation of metals is that some components are not fully separated due to complicated structure. (Ordoñez, et al., 2016) Discharging is important step in the dismantling process of spent LIBs due to high reactivity of lithium in air or moisture (Swain, 2017). Different methods have been proposed in literature to dismantle the batteries safely. For instance, Wang et al. (2012) suggested the use of dilute sodium chloride (NaCl) to remove the excess charge. Castillo et al. (2002) proposed refrigeration of spent LIBs with liquid nitrogen. In industrial scale, Retriev Technologies have implemented low temperature recycling plant due to high reactivity of lithium (Swain, 2017). However, not all recycling plants use discharging procedure (Ekberg & Petranikova, 2015). If crushing is executed without discharging the equipment must be protected for possible explosions, which might occur during crushing.

PVDF and carbon cause problems in the recovery processes due to their insignificant solubility to solvents. It is preferred that PVDF and carbon are removed from the LIB waste before the recovery stages. Thermal processing has been used to remove the insoluble organic additives and adhesives, although the products of combustion from incineration were not environmentally friendly. (Ordoñez, et al., 2016) Additionally, Shin et al. (2005) reported that the incineration of $LiCoO_2$ reduced the leaching efficiencies of lithium and cobalt due to the molten aluminum mixed with $LiCoO_2$. Hence incineration should not be performed prior leaching. Incinerated active material was leached in sulfuric acid (H_2SO_4) with addition of hydrogen peroxide (H_2O_2). (Shin, et al., 2005) Alternatively, PVDF and carbon may be removed by filtration after the leaching process. Ordoñez et al. (2016) reviewed that PVDF is often removed by dissolution processes. PVDF dissolves in organic reactants such as dimethyl sulfoxide (DMSO) at 60 °C. (Ordoñez, et al., 2016)

According to literature, ionic liquids (IL) have been used to recover copper foils and glass fibers from waste printed circuit boards (Zhu, et al., 2012). The interest in IL derives from the fact that it is relatively green and safe solvent. Zheng & Li (2014) studied heated ionic liquid for the separation of Al and cathode materials from spent LIBs. Optimal process parameters were 180 °C heating temperature, 300 rpm agitation, and 25 min retention time, peel-off rate of cathode materials from Al foil could reach 99%. (Zeng & Li, 2014)

Majority of Co and Li comes from $LiCoO_2$ active material. A common dismantling procedure on laboratory scale involves separation of cathodes and anodes to recover higher purity products (Tunsu & Retegan, 2016). This trend can be seen in literature where the leached raw material often includes only the cathodes of spent LIBs (Zhang, et al., 1998; Shin, et al., 2005; Dorella & Mansur, 2007; Ferreira et al., 2008; Li et al., 2013; Takacova et al., 2016). After the separation of anodes and cathodes the leaching step is facilitated by increasing the surface area of the raw material. Crushing and grinding processes are used to enhance the leaching of metals. (Shin, et al., 2005; Ma et al., 2013; Ordoñez, et al., 2016; Takacova et al., 2016) The smaller the particle size, the easier the dissolution and the greater the leaching efficiency (Shin, et al., 2005). Generally, pre-treatment process includes discharging, manual dismantling, separation of anodes and cathodes, calcination and grinding or crushing (Li et al., 2013; Chen, et al., 2015). It should be noted that the anodes and cathodes are not always separated before crushing of LIBs. Occasionally, the crushing is performed to the whole spent battery without pre-treatment.

In majority of the investigations LIB waste has been leached using strong mineral acids. The three most used acids include H_2SO_4, HCl and nitric acid (HNO_3). In recent studies by Takacova et al. (2016) and Joulié, et al. (2014) the leaching efficiencies of these three acids were compared. Takacova et al. (2016) compared HCl and H_2SO_4 media in the leaching of Li and Co. Joulié et al. (2014) compared HCl to H_2SO_4 and HNO_3 media in the leaching of Li, Ni, Co and Al. In addition, Zhang et al. (1998) compared H_2SO_4, hydroxylamine hydrochloride ($HONH_2 \cdot HCl$) and HCl media in the leaching of Co and Li. All experiments showed results in the favour of HCl medium in terms of Co and Li leaching efficiency and chemical price. Nevertheless, H_2SO_4 is the most commonly applied medium in base metal hydrometallurgy and has been the most investigated medium for recovering Co, Li and other metals from spent LIBs. Convincing leaching results were obtained with H_2SO_4 at the presence of H_2O_2, which acted as a reducing agent. (Dorella & Mansur, 2007; Ferreira, et al., 2009; Kang et al., 2009; Wang, et al., 2012; Chen, et al., 2015; Yang et al.,2015)

Alternatively, strong mineral acids may be substituted with organic acids as leaching solutions. Organic acids such as citric, malic and aspartic acids were studied by Li et al. (2013) and Ma et al. (2013). The experiments with organic acids were limited to the leaching of Co and Li only. It was observed that citric acid performs well at the presence of H_2O_2 (Li, et al., 2013).

Leaching efficiency in a chosen medium is optimized through various parameters. In most studies the effect of temperature, solid-to-liquid ratio (S:L), concentrations of solutions and reaction time were investigated. (Zhang., 1998; Dorella & Mansur, 2007; Ferreira, et al., 2009; Kang et al.,

2009; Wang et al., 2012; Joulié et al., 2014; Chen et al., 2015; Yang et al., 2015; Takacova et al., 2016)

3.1 Strong mineral acids

As mentioned previously in Chapter 3, H_2SO_4 is the most used leaching medium for the LIB waste material. However, some comparative studies of different leaching media have showed results in favor of HCl. Therefore, the leaching of LIBs with H_2SO_4 and HCl are presented in this work as suitable strong mineral leaching reagents. Other possible reagents such as HNO_3 are excluded from this work.

3.1.1 Hydrochloric acid

In the literature, two different leaching reactions for $LiCoO_2$ in HCl solution were proposed. Ekberg & Petranikova (2016) present the reaction for $LiCoO_2$ leaching in HCl as given in Eq. 1.

$$2LiCoO_2 + 6HCl \rightarrow 2CoCl_2 + 2LiCl + 3H_2O + 0.5O_2 \tag{1}$$
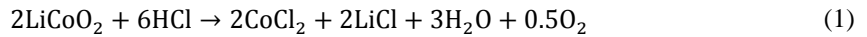
Alternative reaction has been proposed by Takacova et al. (2016). Reaction is given in Eq. 2.

$$2LiCoO_2 + 8HCl \rightarrow 2CoCl_2 + 2LiCl + 4H_2O + Cl_2 \tag{2}$$
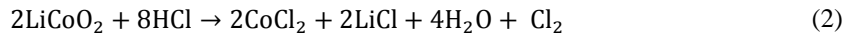
Additionally, Takacova et al. (2016) proposed multiple possible reactions for Co and Li in HCl solution. The reactions are shown in Eq. 3-7. The possible reactions are based on thermodynamic calculations. (Takacova, et al., 2016) It is possible that Eq. 6 was included as carbonate-based electrolytes may react with the meta-stable cathode materials creating Li_2CO_3 impurities. Additionally, in recent studies the Li_2CO_3 has been considered as a protective layer for cathodes in LIBs. (Bi, et al., 2016)

$$Li_2O + 2HCl \rightarrow 2LiCl + H_2O \tag{3}$$

$$CoO + 2HCl \rightarrow CoCl_2 + H_2O \tag{4}$$

$$Co_2O_3 + 6HCl \rightarrow 2CoCl_2 + 3H_2O + Cl_2 \tag{5}$$

$$Li_2CO_3 + 2HCl \rightarrow 2LiCl + H_2O + CO_2 \tag{6}$$

$$Co_3O_4 + 8HCl \rightarrow 3CoCl_2 + 4H_2O + Cl_2 \tag{7}$$
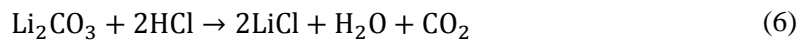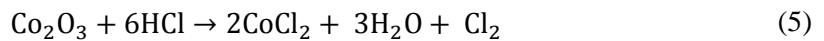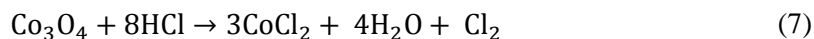
Joulié et al. (2014) compared three different leaching mediums for Li, Ni, Co, Al oxide (NCA) powder; H_2SO_4, HCl and HNO_3. First the effect of acid type, concentration, reaction time and temperature were studied to determine the most efficient conditions for the leaching of Li, Ni, Co and Al. In order to compare the different acid media, the material was leached for 18h in 2 M acid concentration at 25 °C. Under these conditions the leaching efficiency of Li, Ni, Co and Al was 70 - 80% with HCl. Efficiency with H_2SO_4 and HNO_3 acids was 80% for Li and approximately 40% for other metals. The results of acid comparison clearly indicated that HCl was the most efficient medium in the leaching of studied metals. In HCl solution the leaching conditions were optimized by investigating different parameters. Four acid concentrations 1, 2, 3 and 4 M were studied. The leaching time in the experiments was either 3 h or 18 h and temperatures were 25 °C or 90 °C. S:L ratio was fixed at 5% (w/v). At room temperature, only 80% of the metals were leached in 18 h experiment with 4 M HCl concentration and 70% with 2 M HCl concentration. As temperature was increased to 90 °C and HCl concentration fixed at 2 M, the leaching efficiency of all metals increased over 80%. It was concluded that leaching yields increased with the increasing temperature to a certain extent. The optimized parameters were adjusted to 4 M HCl concentration, 90 °C, 18 h and 5% (w/v) S:L ratio. The complete leaching efficiency (100%) was achieved under these conditions for Li, Ni, Co and Al. (Joulié, et al., 2014)

Zhang et al. (1998) studied H_2SO_4, $HONH_2 \cdot HCl$ and HCl in the leaching of Co and Li. The most suitable medium was HCl due to its lower cost and better accessibility. However, high efficiencies were achieved with $HONH_2 \cdot HCl$ as well. Leaching efficiencies were studied by adjusting different parameters such as solution concentration, temperature, leaching time and S:L ratio. The highest yields were achieved with 4 M HCl solution at 80 °C. S:L ratio was optimized to 1:100 and the leaching time to 1 h. The pH of the liquor was approximately 0.6. Under these conditions over 99% of Co and Li were leached from raw material. The results indicated that the increase in temperature and reaction time enhanced the leaching of all the metals in HCl solution. The S:L ratio had no obvious effect on yields. (Zhang, et al., 1998) However, it is notable that the optimized S:L ratio of 1:100 was very low. It would be a challenge to create a feasible industrial process with such a low S:L ratio.

Castillo et al. (2002) noted that after two hours of leaching 80% of Li was dissolved at low concentrations (0.1 M) of HCl. During the first hour 25% Mn was co-leached. It was

acknowledged that, in order to prevent Mn dissolution, the concentration of HCl should be decreased resulting in the decrease of reaction rates. (Castillo, et al., 2002)

Takacova et al. (2016) optimized the leaching conditions of Li and Co after comparing HCl and H_2SO_4 leaching media. Optimized conditions were 2 M HCl, temperature 60 - 80 °C, leaching time 90 min, S:L ratio 1:50 and agitation 300 rpm. Under these conditions almost 100% of Co and Li were leached from raw material. Complete leaching of Li was achieved with both media; 2 M of HCl and 2 M of H_2SO_4 at 60 - 80 °C. The leaching efficiency of Co was 50 - 60% with H_2SO_4 and almost 100% at 80 °C with HCl. However, Li leaching was more efficient with H_2SO_4 acid at low concentrations (0.1-0.5 M) than with HCl under the same concentrations (20 °C). (Takacova, et al., 2016)

3.1.2   Sulfuric acid

In multiple studies H_2SO_4 was shown to dissolve Co from raw materials at high efficiency, especially at the presence of H_2O_2 (Dorella & Mansur, 2007; Ferreira et al., 2008; Kang et al., 2009; Wang, et al., 2012; Chen, et al., 2015; Yang et al.,2015)

The addition of H_2O_2 in to H_2SO_4 solution is enhancing the leaching process of metals from spent LIBs. The reducing agent in the solution improves the efficiency of metal recovery due to reduction of Co ions. Hydrogen peroxide converts Co^{3+} to Co^{2+} with evolved oxygen (Shin, et al., 2005; Ferreira et al., 2008). The added percentages of H_2O_2 varies from 1-1 vol.% (Ferreira et al., 2008; Chen, et al., 2015).

Chen et al. (2011) studied the leaching of Co, Li, Al, Cu, Fe, Mn and Ni in H_2SO_4 solution. First, the raw material was leached with NaOH in order to selectively dissolve Al^{3+}. At optimal conditions 99.9% of Al was leached. The reaction time was 4h and temperature 25 °C. NaOH addition was 5 wt% and S:L ratio 1:10. After the removal of Al, the remaining metals were leached with H_2SO_4. The optimal leaching conditions were 4 M of H_2SO_4 and 10 vol.% of H_2O_2. S:L ratio was 1:10 and temperature 85 °C. Leaching efficiency for Co was 95% and for Li 96%. In the S:L ratio study, the leaching efficiencies decreased when ratio was above 1:10 while decreasing the S:L ratio had only a minor effect on yields. (Chen, et al., 2011)

Shin et al. (2005) used H_2SO_4 and H_2O_2 to leach Li and Co from battery waste. The 2 M concentration of H_2SO_4 with the addition of H_2O_2 (15 vol.%) led to leaching efficiency of 100% within 10 min of leaching time. Temperature was 75 °C, agitation 300 rpm and S:L ratio 50:1. Small concentrations of Cu and Al were dissolved into the liquor, 0.46 g/l and 0.79 g/l

respectively. It was noted that acid is not able to dissolve PVDF and hence the binder remains in the cake. Additionally, carbon was not soluble and floated on top of the liquor. The electrolyte ($LiPF_6$) degrades into lithium fluoride and phosphor pentafluoride during crushing. The organic solvents such as propylene carbonate (PC) and DEC were evaporated. Such process was suggested as a commercial scale plant. (Shin, et al., 2005)

3.2 Organic acids

Citric acid ($C_6H_8O_7$), malic acid ($C_4H_6O_5$) and aspartic acid ($C_4H_7NO_4$) has been investigated as leaching solutions (Li et al., 2013; Ma et al., 2013). Additionally, oxalic acid ($C_2H_2O_4$) has been used as leaching solution of spent LIBs (Ekberg & Petranikova, 2015).

Ma et al. (2013) studied the leaching of cobalt-bearing waste with $C_6H_8O_7$ system. Leaching efficiency for Co was over 99%, yet efficiency of Fe, Mn and Cu were relatively low compared to leaching in H_2SO_4 solution medium. (Li et al., 2013). Li et al. (2013) compared the leaching efficiencies of three different organic acids. $C_6H_8O_7$, $C_4H_6O_5$ and $C_4H_7NO_4$ were used as leaching media with the presence of H_2O_2. Recovery of Co and Li was optimized by varying the concentrations of solutions, the S:L ratio, the temperature and reaction time. Results showed that nearly 100% of Li and 90% of Co were recovered from the raw material when leaching with $C_6H_8O_7$ or $C_4H_6O_5$. $C_4H_7NO_4$ was significantly less effective due to its weak acidity and lower solubility in water. For $C_6H_8O_7$ and $C_4H_6O_5$, the recovery yields were high when S:L was 20 g/l and temperature 90 °C. The presence of H_2O_2 enhanced the recovery as shown in multiple investigations. (Li, et al., 2013)

4 Recovery methods

Complex systems often require a combination of precipitation and SX to recover various metals selectively from LIB leaching liquors (Zhang, et al., 1998; Chen, et al., 2015; Dorella & Mansur, 2007; Ma, et al., 2013; Nguyen, et al., 2015). The general approach is to remove impurities by chemical precipitation prior SX in order to obtain pure products in SX step. In order to recover compounds after SX from aqueous solutions, the precipitation or reduction by e.g. electrowinning is used again. Zhang, et al. (1998) used SX directly for metal separation from LIB leaching solution without purifying the solution via precipitation first.

Joulié et al. (2014) recovered metals solely through precipitation from product liquid solution (PLS). When compared to SX, it was concluded that precipitation is easier to implement as an industrial scale process. Although, efficient separation of metals is challenging. Chen et al. (2015) acknowledged that if the optimal equilibrium pH (pH_e) increases gradually after each extraction or precipitation step there is no need for back and forth adjustments of pH values. Therefore, the amounts of reagents used during the process of precipitation or extraction decrease. (Chen, et al., 2015) On the contrary to precipitation, Pranolo et al. (2010) used solely synergistic solvent extraction (SSX) in a very complex system for the recovery Fe, Cu, Al, Co, Ni and Li. However, it should be noted that most of the studies are conducted in laboratory scale and not intended for design of industrial scale plant. The studies do not generally take into account the chemical prices, mass balance and product quality thus a direct indication of the feasibility of leaching, precipitation or SX processes for metal production from LIBs is not attained.

Table 3 summarizes the sample types, leaching steps and recovery steps of different laboratory scale investigations. The sample type, leaching of the raw material and recovery stages are presented with main conditions and parameters.

Table 3. Summary of leaching parameters and recovery methods used in laboratory scale investigations for LIB leaching.

| Reference | Sample type | | | | | | Recovery step | | |
	Raw material	Treatment	Solutions	T (°C)	S:L ratio (g/ml)	Results	Methods	Reagents	Results
Zhang et al. (1998)	Mainly LiCoO$_2$	Anode and cathode separation	HCl, NH$_2$OH·HCl, H$_2$SO$_3$	80	1:100	Co (< 90%) and Li (< 90%) with 4 M HCl and 2 M NH$_2$OH·HCl. H$_2$SO$_3$ resulted in low yields.	Precipitation + SX	D2EHPA, PC-88A, Na$_2$CO$_3$	PC-88A more selective over Co. Co (< 99.9%) and Li (12.6%) with 0.9 M PC-88A. Li (< 80%) precipitated with Na$_2$CO$_3$.
Chen et al. (2015)	Mixed cathode material	Discharging, dismantling, calcination, grinding	H$_2$SO$_4$ + H$_2$O$_2$	80	1:20	Ni^{2+} (4.29 g/l), Co^{2+} (7.18 g/l), Mn^{2+} (5.68 g/l), Li$^+$ (1.49 g/l), Cu^{2+} (1.78 g/l) and Fe^{3+} (1.96 g/l) leached. No yields presented.	Precipitation + SX	NaOH, KMnO$_4$, Na$_3$PO$_4$ and Mextral®5640H, Mextral®272P	Cu (≈ 100%) and Co (97.8%) extracted with Mextral. Fe (100%), Mn (99.2%), Ni (99.1%) and Li (95.8 %) precipitated.
Pospiech (2016)	Synthetic leach liquor	-	-	-	-	Synthetic aqueous phase contained ([Co^{2+}] = 0.01 M, [Li$^+$] = 0.01 M)	Synergistic SX	Cyanex272 and TBP	Selectivity of Co over Li is significantly greater when Cyanex 272 is used together with TBP in the extraction system.
Pranolo et al. (2010)	Synthetic leach liquor	-	-	-	-	Synthetic aqueous phase contained Ni^{2+} (0.15 g/l), Co^{2+} (16.9 g/l), Li$^+$ (3.8 g/l), Cu^{2+} (0.4 g/l) Al^{3+} (0.7 g/l) and Fe^{3+} (0.6 g/l).	SX + Ion-exchange resin	Ionquest 801, Acorga M5640, Cyanex272	Complete (100%) extraction of Cu, Al and Fe with Ionquest 801 and Acorga M5640. Extraction of Co (>90%) with Cyanex272. Li and Ni separated with Dowex M4195.
Joulié et al. (2014)	NCA material	-	HCl	90	5% (w/v)	100% Li, Ni, Co and Al leached by 4 M HCl.	Precipitation	NaOH, NaClO	Recovered Co (100%) and Ni (99.99%) completely. Lithium could be recovered as carbonate or phosphate salt.
Ma et al. (2013)	Cobalt-bearing waste	Crushing, grounding and sieving	H$_2$SO$_4$ + H$_2$O$_2$, C$_6$H$_8$O$_7$ + H$_2$O$_2$	85	1:20	Co (<99 %) separately leached with 2.5 M H$_2$SO$_4$ and 2.5 M C$_6$H$_8$O$_7$ (+ 10 vol.% of H$_2$O$_2$) Leaching efficiency of other metals with C$_6$H$_8$O$_7$ was low.	Precipitation + SX	D2EHPA	Over 93% of Fe, Mn and Cu extracted wtih D2EHPA from H$_2$SO$_2$ (co-extraction of Co 35%). C$_6$H$_8$O$_7$ system suitable for SX. Although, recovery yields low.

Figure 3 and Figure 4 present suggested conceptual flow charts for the recovery of metals. In Figure 3, the recovery of eight elements are shown using cementation and chemical precipitation methods. Different variations of chemicals are suggested in each process step in order to recover metals. (Wang, et al., 2011) In Figure 4, a flow chart is presented for the recovery of six metals, leached in H_2SO_4, by using SX and ion-exchange resin (Pranolo, et al., 2010).
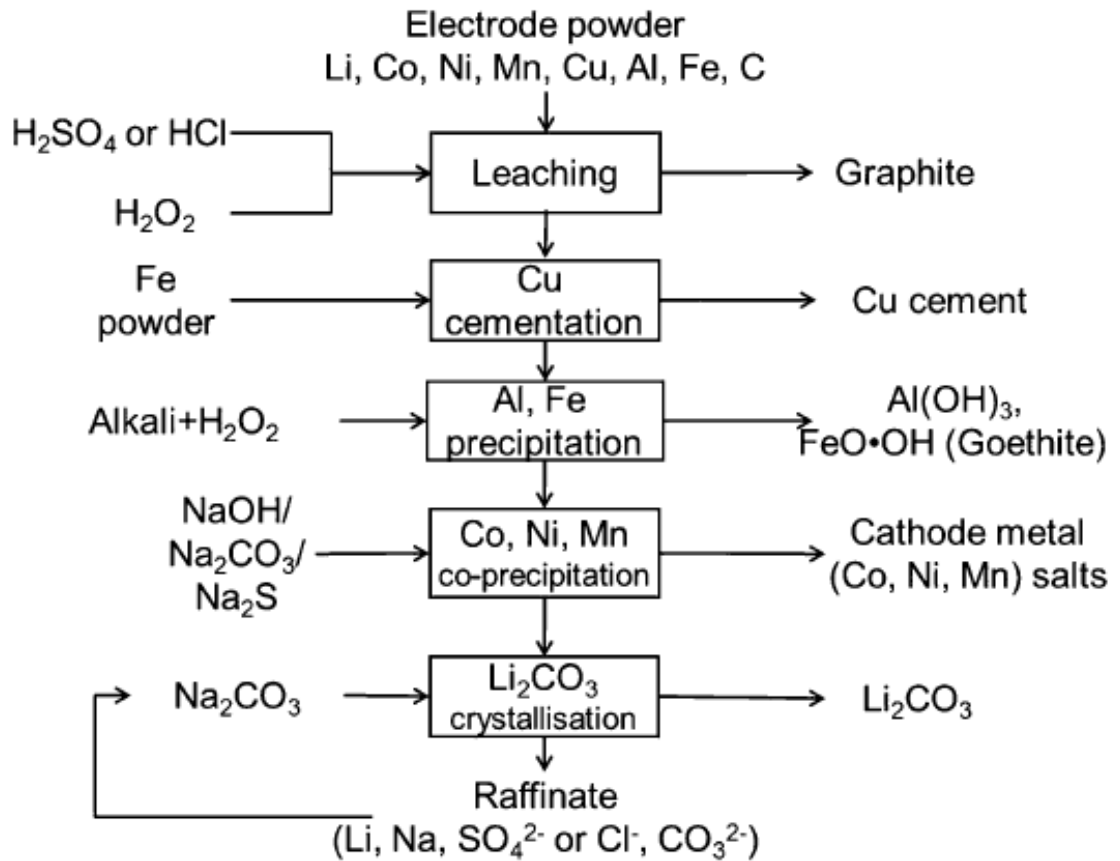
Figure 3. Potential flowchart for the recovery of Cu, Al, Fe, Co, Ni, Mn and Li from LIB scrap powder (Wang, et al., 2011).
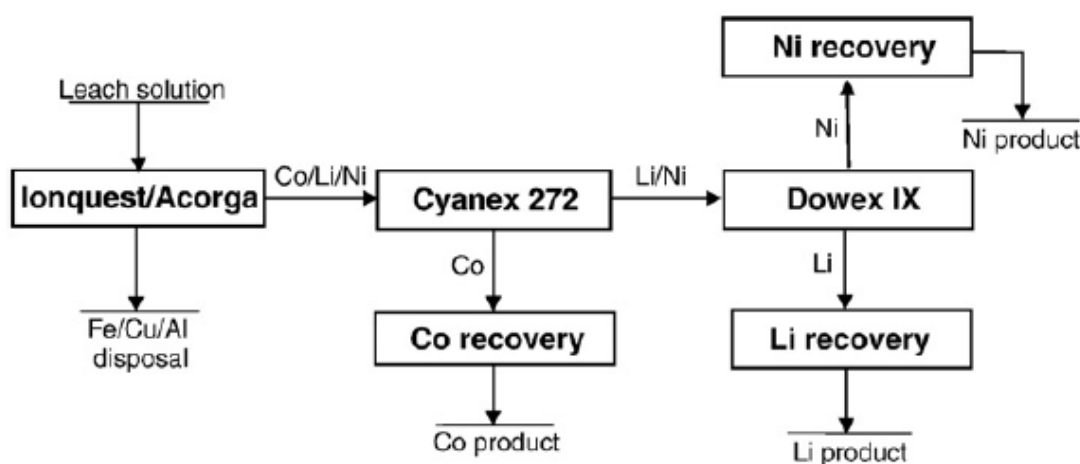
Figure 4. Suggested flow chart for the recovery of Fe, Al, Cu, Co, Ni and Li in H_2SO_4 via SX and ion exchange resin (Pranolo, et al., 2010).

4.1 Chemical precipitation

NaOH is the most common precipitation reagent used and conventionally also known as "neutralization agent". (Ekberg & Petranikova, 2015) Precipitation is mainly used to remove and recover impurity metals such as Al, Fe, and Cu from acidic leach liquor of spent LIBs. Additionally, several experiments have shown that Co, Li, Mn and Ni can be precipitated selectively from the leach liquor using different reagents (Joulié, et al., 2014; Chen, et al., 2015; Wang, et al., 2016). It should be noted that even if SX was used for the separation of metals, the recovery of metals is commonly performed via chemical precipitation.

Joulié et al. (2014) separated Li, Ni and Co by chemical precipitation method (Sections 4.1.3 and 4.1.4). Al remained as an impurity in recovered Co and Ni compounds. The main challenge in chemical precipitation was to efficiently separate elements, which have similar solubility in chloride medium. However, it was noted that selective precipitation of similar metals was achievable by pH variations and/or the presence of reactive compounds. After each precipitation step the compounds were recovered from solutions by filtration. (Joulié, et al., 2014)

4.1.1 Impurity removal

In general, the precipitation of impurities (Fe, Al and Cu) in acidic media has been achieved by adding NaOH at pH values lower than 6 (Figure 5). Alternatively, all the impurity metals can be removed successfully as carbonate compounds (Figure 6). In carbonate precipitation sodium carbonate (Na_2CO_3) was used as a reagent. It was acknowledged that precipitation performance

is highly dependent on the pH value of the solution. Impurities were efficiently removed in specific pH values without major co-precipitation of valuable metals. However, if impurity removal was performed at higher pH values, loss of valuable metals was inevitable. In NaOH precipitation experiment the decrease in Li concentration was noted to be caused by absorption of Li and not precipitation of lithium hydroxide (LiOH). (Wang & Friedrich, 2015)
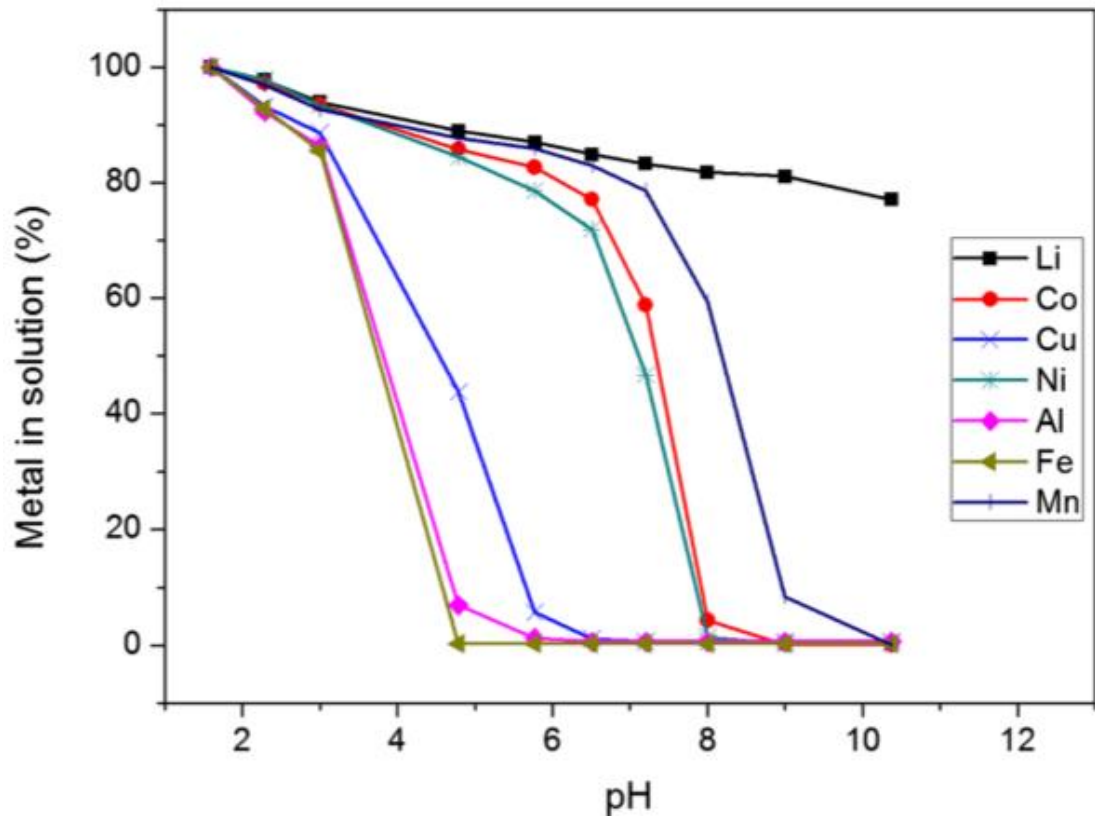
Figure 5. The precipitation of metal ions from H_2SO_4 leach liquor using NaOH (200 g/l) at 40 °C temperature (Wang & Friedrich, 2015).
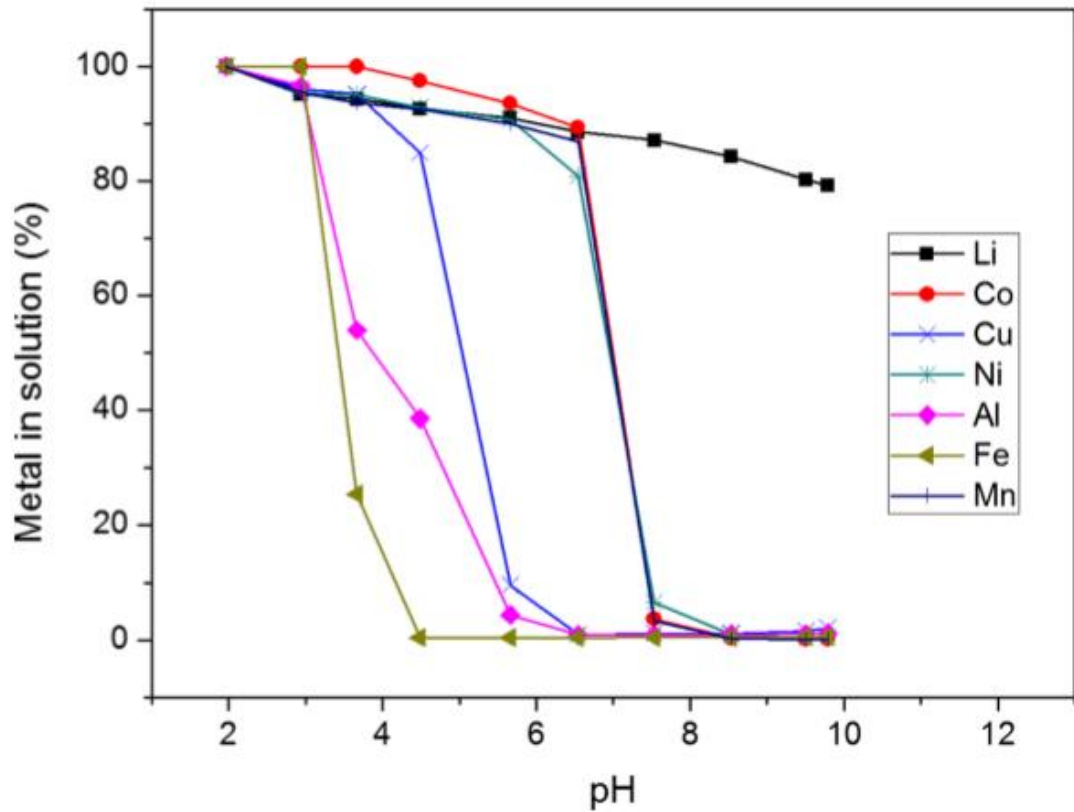
Figure 6. The precipitation of metal ions from H_2SO_4 leach liquor using Na_2CO_3 (200 g/l) at 40 °C temperature (Wang & Friedrich, 2015).

Fe removal is common challenge in hydrometallurgy. Generally, ferric ions (Fe^{3+}) are removed first from the leach liquor by addition of NaOH until pH is approximately 3.0 (Chen, et al., 2015). Ferrous ions (Fe^{2+}) precipitate when pH is over 8.5 (Figure 7). At low pH values the ferrous ions are poorly soluble. (Noubactep, 2013) Huang et al. (2016) used a novel method to remove ferric ions by flotation from leach liquor of hybrid cathodes. Ferric was recovered from HCl solution as ferric chloride ($FeCl_3$). (Huang, et al., 2016) Additionally, SX has been used to remove Fe ions (Section 4.2.3).
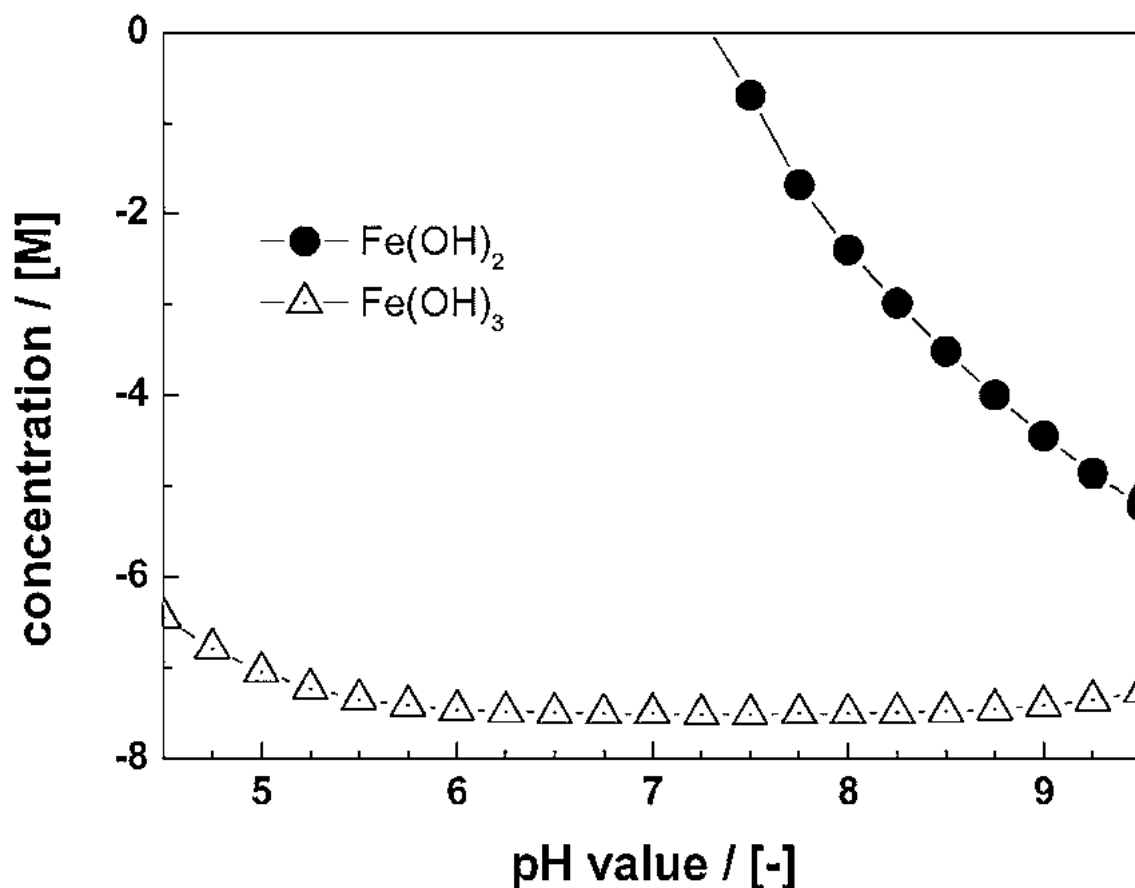
Figure 7. Solubility and pH dependency of iron hydroxides between pH 4.5 and 9.5 (Noubactep, 2013).

In oxalic acid Fe^{3+} can be removed with Fe-powder as poorly soluble ferric or ferrous oxalate. Effects of molar ratio (Fe/Fe^{3+}), ultrasound time, rection time and reaction temperature were investigated. The iron removal efficiency was 96.25% with optimal parameters (Molar ratio = 5, ultrasound power = 150 W, ultrasound time = 10 min, T = 50 °C, stirring speed = 300 rpm, reaction time 1 h). (Liu, et al., 2017)

Li et al. (2013) precipitated Fe^{3+}, Al^{2+} and Cu^{2+} from HCl leach liquor by addition of NaOH. The results indicated that the loss of Co and removal of impurities increase with increasing pH. At pH 5.5 the impurities were precipitated as hydroxides with the efficiency of 90 - 100%. The loss of Co was only 5%. It was acknowledged that the pH should be controlled in the range of 4.5-6.0. In pH over 6 the loss of Co reached significant levels and in pH under 4.5 the removal of impurities was not efficient enough. (Li, et al., 2013)

Chen et al. (2015) studied the recovery of iron from 2 M of H_2SO_4 solution containing 2 vol.% of H_2O_2. The pH_e value was adjusted by adding of 1 M NaOH dropwise. Under optimized conditions

nearly 100% of ferric ions were precipitated. The complete recovery was achieved at pH 3.0, temperature 60 °C, reaction time 1h and agitation of 300 rpm. It was noted that co-precipitation of other metals was unusual under pH 3.0. The precipitation of iron hydroxide ($Fe(OH)_3$) was presented in Eq 8. (Chen, et al., 2015)

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \tag{8}$$

Chen et al. (2011) precipitated Cu from acidic solution (H_2SO_4 with addition of H_2O_2) as $Cu(OH)_2$ by addition of NaOH until pH reached 5.5. $Cu(OH)_2$ reaction is given in Eq. 9. (Chen, et al., 2011).

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \tag{9}$$

From Figure 8 the soluble metal concentration and pH dependency of $Cu(OH)_2$ can be seen.
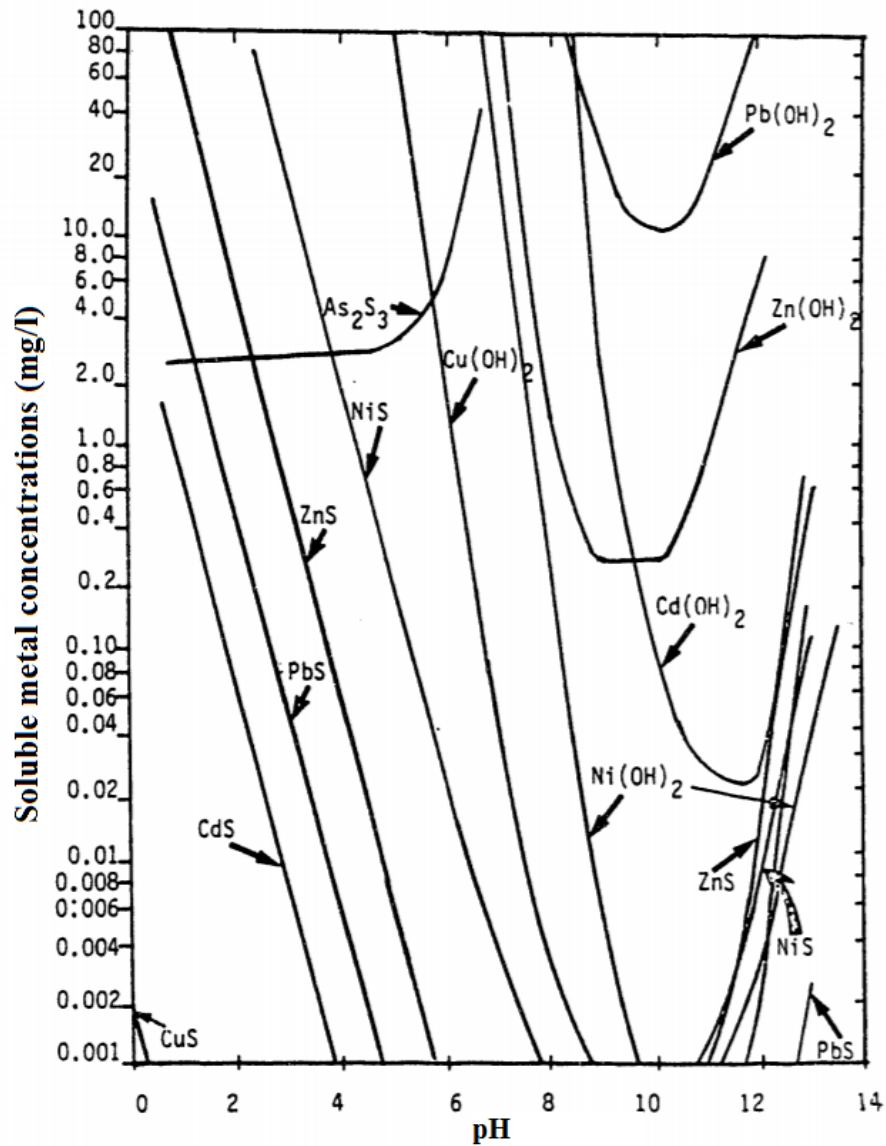
Figure 8. Solubility of metal hydroxides and sulfides as a function of pH (Peters & Shem, 1993)

Kang et al. (2010) precipitated Cu from acidic (H_2SO_4 with addition of H_2O_2) solution before the precipitation of Co. Cu^{2+} ions were possible to precipitate as sulfides due to low solubility of copper sulfide (CuS) in acidic solution (Figure 8). With addition of sodium sulfide (Na_2S), 99.9% Cu was precipitated from the leachate. During the precipitation of Cu 11% of Al was co-precipitated. The precipitation of Cu^{2+} ions is presented in Eq. 11. (Kang, et al., 2010)

$$Cu^{2+} + H_2S \rightarrow CuS + 2H^+ \tag{10}$$

However, it should be noted that in HCl solution where substantial amount of chloride ions was present Cu precipitated as atacamite or paratacamite ($Cu_2(OH)_3Cl$) (Sharkey & Lewin, 1971). Additionally, Cu can be removed by cementation (Section 4.4)

Wang & Friedrich (2015) precipitated Al as aluminum hydroxide ($Al(OH)_3$) as given in Eq. 11. The precipitation of Al was completed approximately at pH 6 (Figure 5). (Wang & Friedrich, 2015)

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \tag{11}$$

4.1.2 Manganese

Manganese has been precipitated as oxides, dioxides, sulfides, hydroxides and carbonates (Wang & Friedrich, 2015; Chen et al, 2015; Castillo et al., 2007). Manganese hydroxide ($Mn(OH)_2$) precipitation by pH adjustment is shown in Figure 5. Manganese carbonate ($MnCO_3$) solubility and pH dependency is shown in Figure 6.

Huang et al. (2016) precipitated Mn as manganese oxides (MnO_2/Mn_2O_3) in HCl solution. Mn was precipitated by saturated solution of potassium permanganate ($[KMnO_4] = 0.35$ M). Above pH 2 the efficiency decreases probably due to incomplete oxidation. The co-precipitation of Li was less than 5%. The reactions between Mn^{2+} and $KMnO_4$ are given in Eq. 12 and 13. (Huang, et al., 2016)

$$2KMnO_4 + 3Mn^{2+} + H_2O \rightarrow 5MnO_2 + 2K^+ + 4H^+ \tag{12}$$

$$KMnO_4 + 4Mn^{2+} + 10H_2O \rightarrow 5MnO(OH) + K^+ + 15H^+ \tag{13}$$
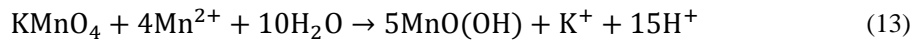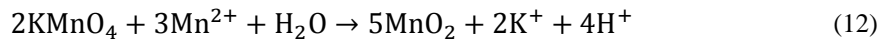
Chen et al. (2015) precipitated Mn^{2+} (5.68 g/l) from a leachate (H_2SO_4 with added H_2O_2) by drop-wise addition of 0.5 M $KMnO_4$ solution. Before the precipitation of Mn, the Fe ions were precipitated using 1 M NaOH solution and Cu was extracted using Mextral®5640H extractant. To optimize the precipitation, the effects of pH and molar ratio of Mn^{2+} and $KMnO_4$ were studied. The reaction time (1 h), temperature (25 °C) and agitation (300 rpm) were constants. The precipitation efficiency of Mn was 99.2% when equilibrium pH equals 2.0 and molar ratio of ratio of Mn^{2+} and $KMnO_4$ was 2.0. (Chen, et al., 2015)

Castillo et al. (2002) precipitated Mn from acidic solution (HNO$_3$) as Mn(OH)$_3$. Solution pH was raised to 5.2 to precipitate the impurities of Ni and Fe. NaOH was added until pH reached 10.0 to precipitate Mn as hydroxides. (Castillo, et al., 2002)

4.1.3 Cobalt

Cobalt has been precipitated as cobalt hydroxide (Co(OH)$_2$), cobalt oxide (Co$_2$O$_3$) and cobalt oxalate (CoC$_2$O$_4$) in acidic media. The pH dependency of Co hydroxide and carbonate precipitation is shown in Figure 5 and Figure 6, respectively. Wang & Friedrich (2015) investigated the precipitation of Co as hydroxide, carbonate and sulfide compound together with Mn and Ni.

Joulié et al. (2014) studied the precipitation of Co in HCl solution. Precipitation of Co^{2+} as hydroxide in the presence of Ni^{2+} was relatively difficult due to very similar pKs values. The pKs value for Co(OH)$_2$ is 14.2 and for nickel hydroxide (Ni(OH)$_2$) is 14.7. The selective precipitation was performed when Co^{2+} was oxidized to Co^{3+}. Co$_2$O$_3$ has lower solubility in acidic media (pKs = 40.5) and can be precipitated without the co-precipitation of Ni compounds. In acidic medium the Co^{2+} requires an oxidant in order to transfer to Co^{3+} hence sodium hypochlorite (NaClO) was added. Selective precipitation of Co(OH)$_2$ was affected by pH, and stoichiometric ratio of NaClO and Co. Co was precipitated at pH 3.0. Above pH 3.0 the Ni(OH)$_2$ was co-precipitated. Co$_2$O$_3$ contained Ni as impurity. The precipitation efficiency of Co was 99.99% with over 90% purity. The precipitation of Co^{3+} ions is given in Eq. 15. (Joulié, et al., 2014)

$$2Co^{2+} + ClO^- + 2H_3O^+ \rightarrow 2CO^{3+} + Cl^- + 3H_2O$$
$$2Co^{3+} + 6HO^- \rightarrow Co_2O_3, 3H_2O \tag{14}$$
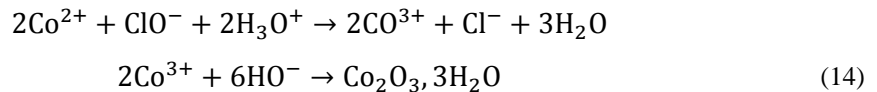
For Co recovery ammonium oxalate ((NH$_4$)$_2$C$_2$O$_4$) or sodium oxalate (Na$_2$C$_2$O$_4$) are commonly used reagents in precipitation. Kang et al. (2010) precipitated Co as CoC$_2$O$_4$ from H$_2$SO$_4$ solution with addition of H$_2$O$_2$. CoC$_2$O$_4$ has a low solubility in acids and is precipitated when the molar ratio of oxalic acid (H$_2$C$_2$O$_4$) to Co^{2+} was 3:1 in the solution. The precipitation of Co ions is given in Eq. 16. (Kang, et al., 2010)

$$Co^{2+} + H_2C_2O_4 \rightarrow CoC_2O_4 + 2H^+ \tag{15}$$

4.1.4 Nickel

Ni can be recovered from acidic solution as hydroxide, sulfide or carbonate compound (Wang & Friedrich, 2015; Chen, et al., 2015; Joulié, et al., 2014). The pH dependency of Ni hydroxide and carbonate precipitation is shown in Figure 5 and Figure 6, respectively.

Joulié et al. (2014) reported that the selective precipitation of Ni^{2+} in acidic media (HCl) was possible. Challenge was the simultaneous precipitation of Ni^{2+} and Co^{2+}. The solubility of Co was changed by oxidizing the Co^{2+} to Co^{3+}. $Ni(OH)_2$ was completely (100%) precipitated above pH 11. $Ni(OH)_2$ contained Co and Al as impurities. The purity of the recovered Ni was over 90%. (Joulié, et al., 2014)

Chen et al. (2015) precipitated Ni from leachate (H_2SO_4 with added H_2O_2) by treating the solution sequentially with NaOH. Original leachate contained $[Ni^{2+}]$ = 4.29 g/L. The purity of Ni compound recovered was 99.13%. Ni was recovered as $Ni(OH)_2$. The precipitation of Ni ions is given in Eq. 17. (Chen, et al., 2015)

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2 \qquad (16)$$

4.1.5 Lithium

Generally, Li is crystallized by saturated Na_2CO_3 or carbon dioxide (CO_2) after all other metals have been separated from the leach liquor by SX and/or chemical precipitation (Ekberg & Petranikova, 2015). Zhang et al. (1998) and Nguyen et al. (2015) studied that Li can be recovered as Li_2CO_3 using saturated Na_2CO_3 from chloride or sulfate solutions in temperature near 100 ℃. Wang et al. (2011) acknowledge that the solubility of Li_2CO_3 in 20 °C is 13.3 g/l and in 100 °C 7.2 g/l. The efficient recovery of Li_2CO_3 was possible when solution was first concentrated and when the recovery was carried out at near 100 °C. (Wang, et al., 2011) Additionally, Li can be precipitated as Li_3PO_4 using trisodium phosphate (Na_3PO_4) as precipitator (Chen et al., 2015). It should be noted in the recovery of Li that the battery grade Li_2CO_3 purity should be 99.5% or higher (Tran & Luong, 2016).

Zhang et al. (1998) recovered Li from aqueous phase after the extraction of Co from HCl leachate. Aqueous phase was treated with Na_2CO_3 reagent to precipitate Li as carbonate. Since solubility of Li_2CO_3 is inversely proportional to temperature, the temperature was adjusted to 100 °C. The recovery efficiency of lithium was 80% with 0.07% co-precipitation of Co. (Zhang, et al., 1998)

Zhao et al. (2011) separated Co and Mn from Li in one SX stage in H_2SO_4 (addition of H_2O_2) leach liquor. Co and Mn were extracted from Li with Cyanex 272 and PC-88A at pH_e 5.2-5.3. After the extraction of Co and Mn nearly all the Li remained in the aqueous phase. Li was recovered as Li_2CO_3. (Zhao, et al., 2011)

Chen et al. (2015) precipitated Fe from the leaching liquor (H_2SO_4 + H_2O_2) using NaOH as reagent. Cu^{2+} ions were extracted using Mextral®5640H and recovered as pure Cu product. Mn was precipitated using $KMnO_4$. Ni loaded Mextral®272P was used as extractant to separate Co^{2+} ions from Ni and Li. Co was recovered as pure Co product. At this stage, the aqueous phase contained only Li and Ni. Remaining metal ions were recovered as Li_3PO_4 and $Ni(OH)_2$, respectively. (Chen, et al., 2011)

Meshram et al. (2015) recovered Li as Li_2CO_3 after the recovery of Co, Mn and Ni. Before the precipitation of Li the filtrate was 50% concentrated due to low concentration of Li after the removal of Co, Mn and Ni. Excess of Na_2CO_3 solution was added until pH reached 14, solution was filtered and Li_2CO_3 was recovered. Washing of the precipitate was performed using hot water to avoid major dissolution of Li_2CO_3. The precipitation of Li is presented in Eq. 24. (Meshram, et al., 2015)

$$2Li + Na_2CO_3 \rightarrow Li_2CO_3 + 2Na^+ \qquad (17)$$
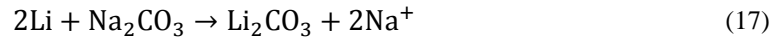
Huang et al. (2016) precipitated Li as Li_3PO_4 from HCl solutions. Saturated Na_3PO_4 was used as reagent. Precipitation efficiency increased with increasing addition of Na_3PO_4. Recovery efficiency of 93.68% was achieved with 0.2 M addition of Na_3PO_4 while pH was adjusted to 7.0. Precipitation with Na_2CO_3 was also investigated in HCl medium. The efficiency was approximately 85% due to higher solubility of Na_2CO_3. The reaction is presented in Eq. 16. (Huang, et al., 2016)

$$3Li^+ + PO_4^{3-} \rightarrow Li_3PO_4 \qquad (18)$$

Higuchi et al (2016) investigated selective recovery of Li from different cathode materials. To recover Li from leach liquor powder of Na_2CO_3 was used as reagent. The mixture was shaken for 15 h at 50 °C. Lithium was recovered from Co-type cathode material as Li_2CO_3 with purity of 100%. Lixiviation was used to improve the purity of precipitate. Recovery efficiency after crystallization was 85.3% and total recovery 65.7% due to lixiviation. It was acknowledged that 99.5% purity is the objective in recovery of Li. Purification by lixiviation is used in commercial production of Li_2CO_3. (Higuchi, et al., 2016)

Zhu et al. (2012) investigated the recovery of Co and Li from spent LIBs by chemical precipitation. The scrap material was leached in H_2SO_4 solution with addition of H_2O_2. Lithium was crystallized using saturated Na_2CO_3 solution. Molar ratio of Na_2CO_3 to Li ions was 1.1:1.0. Excess addition of Na_2CO_3 showed no obvious increase in Li recovery. (Zhu, et al., 2012)

4.2   Solvent extraction

In order to recycle metals from LIB waste efficiently, unit processes with high selectivity towards different metals are necessary. Chen et al. (2015) noted that using precipitation as a method to recover metals may be ineffective due to the complicated aqueous systems involved. The complex systems often contain metals with similar properties such as solubility, which hinders the recovery efficiency (Joulié, et al., 2014). There is a wide variety of SX extractants available, which can provide high selectivity for the removal of specific metal(s) into organic phase even for complex metal solutions. After extraction of metal into the organic phase, effective stripping back to the aqueous solution is required in order to make SX process feasible.

SX or also known as liquid-liquid extraction is a common process able to selectively produce high purity raffinates. SX is executed using two media immiscible to each other, the aqueous and the organic phase. The aqueous phase contains the dissolved metal ions or metal ion complexes. The organic phase contains the extractant, which is able bind the metal ions. (Free, 2013) A diluent is often needed for the organic phase due to viscosity of extractant (Chagnes, 2015a). The basic steps of SX, extraction, scrubbing and stripping, are demonstrated in Figure 9. To extract the metal, the organic phase is loaded. The organic and the aqueous phases are mixed intimately to selectively extract the metal ions from the aqueous phase into the organic phase. When the desired metal ions are attained in the organic phase, the two media can be separated again by settling. The loaded organic phase is scrubbed to remove impurities and stripped into a concentrated aqueous solution. Stripping is often performed at near zero pH allowing the equilibrium to shift and metal ion to dissociate from extractants. (Free, 2013)
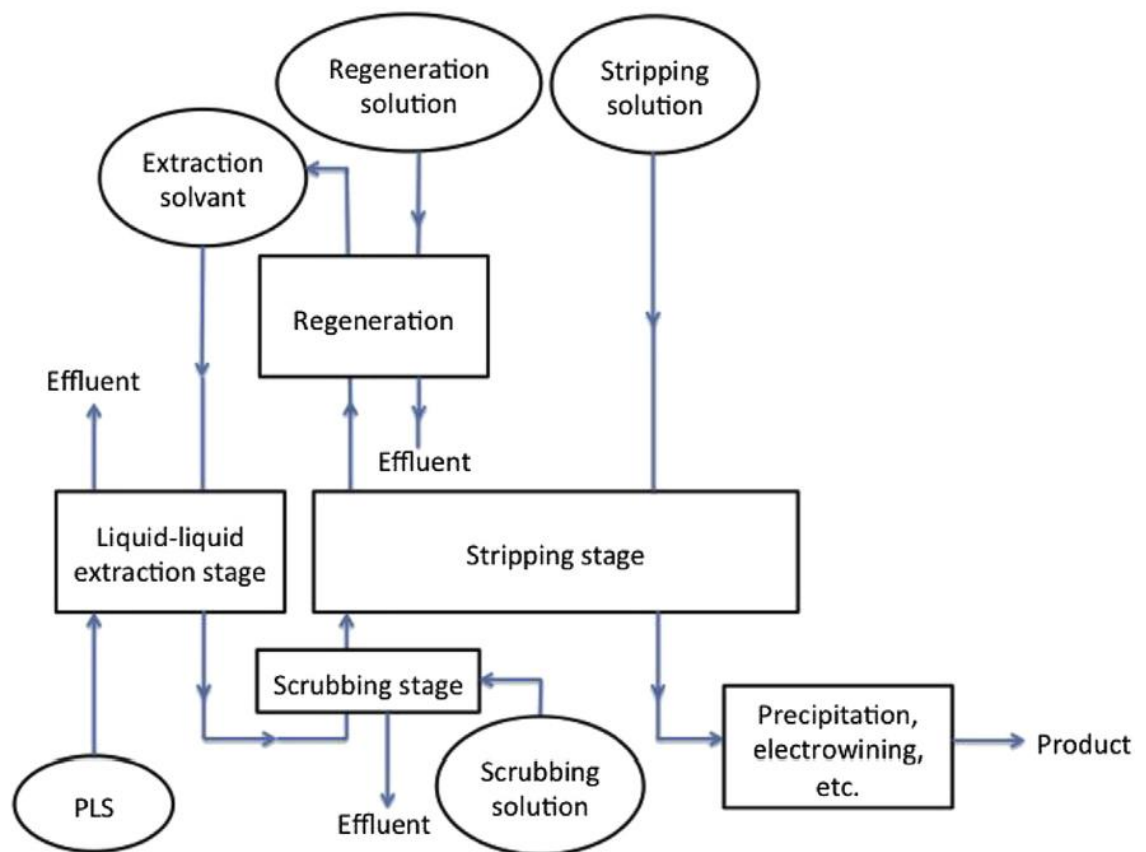
Figure 9. Conventional flowchart of SX with different stages. Pregnant leach solution (PLS) is the solution produced after leaching. (Chagnes, 2015a)

The interactions of ions in aqueous and organic medium have thermodynamic equilibrium constraints. These constraints determine the maximum extraction. Successful extraction is achieved when the pH favors only the desired metal. In addition, the concentrations and organic-to-aqueous (O:A) ratio matter. The McCabe-Thiele diagrams are used to determine graphically the theoretical number of equilibrium stages for extraction or stripping. The diagrams can be created based on the constraints of thermodynamic equilibrium, constraints of flows and concentrations. (Free, 2013)

SX processes are either performed to synthetic solutions or actual leach liquors obtained from spent LIB waste as seen in Table 3. Pranolo et al. (2010) studied mixed extractant system using synthetic liquor. More often real leaching liquor is used to investigate the actual conditions of real LIB waste stream. (Zhang, et al., 1998; Chen, et al., 2011) The trend in the recovering of metals has mainly been the separation of Co and Li. However, recent studies have focused on other metals such as Fe, Al, Cu, Ni and Mn as well (Pranolo, et al., 2010).

4.2.1 Extractants

Ion-exchange, solvation and coordination extractants are the three main extractant types used in SX (Free, 2013). Phosphoric acids are widely used in literature for the extraction of metals from LIB waste. Several organic extractants such as di-(2-ethylhexyl)phosphoric acid (D2EHPA), 2-ethylhexylphosphoric acid mono-2-ethylhexyl ester (PC-88A, Ionquest 801 or P507), di-2,4,4-trimethylpentyl-phosphinic acid (Cyanex 272), Acorga M5640, Mextral®5640H and Mextral®272P have presented promising results in separation of metals from spent LIBs (Zhang, et al., 1998; Dorella & Mansur., 2007; Chen, et al., 2015; Pranolo, et al., 2010). Usually before the solvent extraction of Co, Ni and Li, the impurities such as Cu, Al and Fe have been removed from the leach liquor using precipitation. However, SX may also be used for the removal of impurities. Some studies show that mixed extractant systems exhibit increased selectivity and enhance the synergistic effects when compared to single extractant systems (Zhao, et al., 2011; Pranolo, et al., 2010). Saponification or neutralization of acidic extractants has been performed in order to improve the selectivity (Swain, et al., 2006). Chen et al. (2011) used P507 as extractant, which was saponified by NaOH solution. Saponification is discussed in more detail in Section 4.2.2.

D2EHPA and PC-88A were studied by Zhang et al. (1998) in the extraction of Co from Li. The results showed that extraction of Co over Li was greater with PC-88A than when compared to D2EHPA. Chen et al. (2015) extracted Co from Li using Ni loaded Mextral®272P as an extractant. Mextral®5640H was used to selectively extract Cu. Pranolo et al. (2010) proposed a mixed solvent extractant system to recover metals from leach liquor of spent LIBs. The system included multiple SX stages for the recovery of all studied metals (Co, Li, Fe, Ni, Al and Cu). In the first SX stage all Fe, Al and Cu was extracted using Ionquest 801 as extractant and Acorga M5640 as synergist. It was suggested yet not investigated that the co-extraction of Co, Ni and Li could be scrubbed. After the first SX stage the raffinate contained only Li, Co and Ni. In the second SX stage, Co was completely separated from Li and Ni using Cyanex 272. Co was recovered as pure Co product. It was suggested that an ion-exchange resin (Dowex M4195) could be used for the separation of Ni and Li. (Pranolo, et al., 2010)

Acidic extractant operates by cation exchange of hydrogen ions. A general reaction of extraction for any acidic extractant e.g. Cyanex 272 is given in Eq. 19 (Ekberg & Petranikova, 2015).

$$Me_{aq}^{n+} + n\overline{HL} \leftrightarrow \overline{ML_n} + nH_{aq}^{+} \tag{19}$$
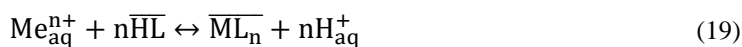
where "Me" is metal ion and "HL" denotes acidic extractant molecule.

4.2.2 Saponification of extractant

Cyanex 272 is widely used cation exchanger for the recovery of Co from complex metal ion systems. It performs especially well in the extraction of Co from Ni, which is difficult to do efficiently. Cyanex 272 exists as a dimer, whereas the sodium salt of Cyanex 272 (Na-Cyanex 272) is in a form of a monomer (Swain, et al., 2006). Saponification of acidic extractants such as Cyanex 272 is advantageous, since the saponification increases the pH of the organic phase thus pH_e of the system is increased resulting in more efficient and selective recovery of metal ions. Additionally, saponification minimizes co-extraction of impurities. In HCl leach liquor the saponification of Cyanex 272 is preferred as saponification improves the recovery rates of Co and Mn. The saponification rate (SR) or neutralization degree of the solvent should preferably vary from 30 to 50%. (Shin, et al., 2012) Converting more than 50% of acidic solvent into a salt often requires a phase modifier to prevent third phase formation (Cytec Industries Inc., 2008).

The recovery of metal ions using Cyanex 272 is dependent on pH_e value measured from the aqueous phase after extraction. The pH dependency can be seen in Figure 10. The separation of Co and Mn together from other metals could be achieved using Na-Cyanex 272 in HCl or H_2SO_4 leach liquor (Figure 11). The co-extraction of lithium should remain low (<10%), yet the co-extraction of Ni might increase to 20% as shown in Figure 11. Li starts to extract after pH 7 thus the separation of metals from Li with Cyanex 272 is relatively easy. The order of metal extraction in sulfuric solutions using Cyanex 272 was $Mn^{2+} = Co^{2+} > Ni^{2+} > Li^+$ (Mansur, 2011).
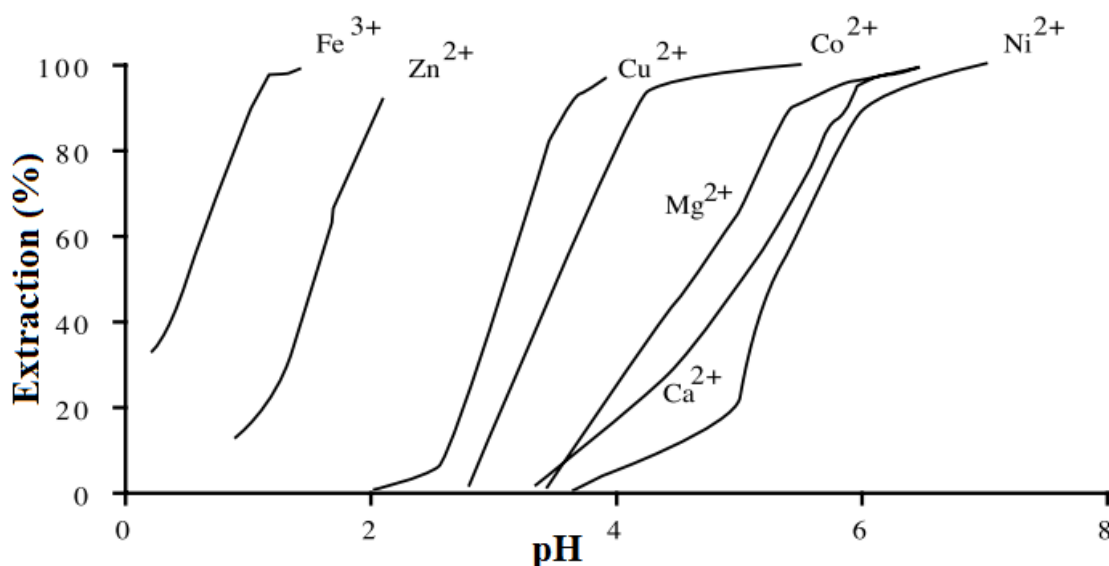
Figure 10. Equilibrium pH dependency in the extraction (%) of metals from chloride solutions using Cyanex 272 (Cytec Industries Inc., 2008).
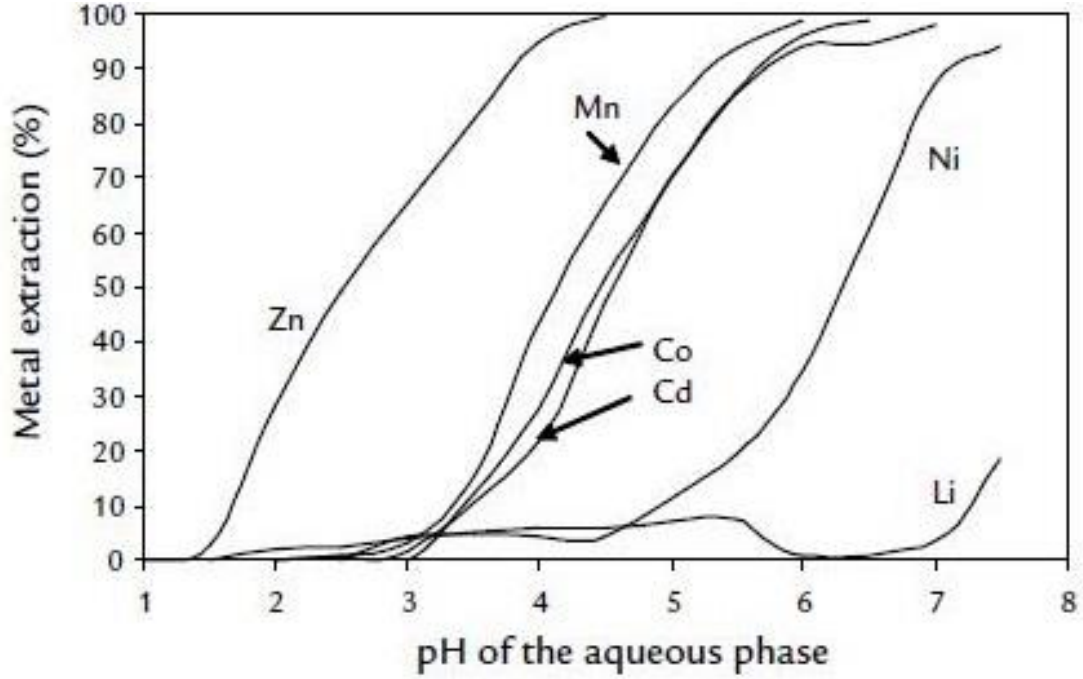
Figure 11. Equilibrium pH dependency in the extraction (%) of metals from sulfuric solutions using Cyanex 272 (Mansur, 2011)

The saponification reaction is given in Eq. 20 (Ekberg & Petranikova, 2015).

$$Na_{aq}^+ + \frac{1}{2}(HA)_{2org} = NaA_{org} + H_{aq}^+ \tag{20}$$
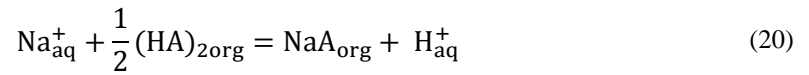
where "HA" denotes the extractant, "org" denotes organic phase and "aq" denotes aqueous phase.

The extraction reaction including saponified extractant is given in Eq. 21.

$$Me_{aq}^{n+} + xA_{org}^- + \frac{y}{2}(HA)_{2org} = Me(A)_{n.}(x+y-n)(HA)_{org} + (n-x)H_{aq}^+ \tag{21}$$
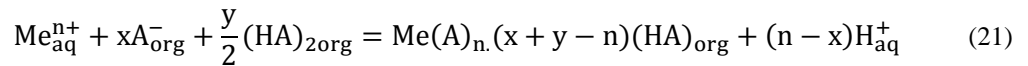
Furthermore, it should be noted that the organic phase can be regenerated by washing with distilled water. Painuly (2015) studied the use of regenerated Cyanex 272 and results showed no significant change in extractability for up to 10 cycles. Regeneration was carried out by washing the organic phase twice with water. (Painuly, 2015)

4.2.3 Separation of impurities

Impurities are mainly precipitated from leach liquors. The presence of impurity ions in leach liquor hinders the separation of valuable metals. SX of Fe, Cu and Al was studied by Pranolo et al. (2010). Of all impurities, Cu is most commonly separated via SX.

Pranolo et al. (2010) studied unconventional recovery method of impurity metals (Fe, Al and Cu). Mixed solvent extractant system was used for a synthetic aqueous feed solution containing $[Co^{2+}]$ = 16.9 g/l, $[Li^+]$ = 3.8 g/l, $[Fe^{3+}]$ = 0.6 g/l, $[Ni^{2+}]$ = 0.15 g/l, $[Al^{3+}]$ = 0.7 g/l and $[Cu^{2+}]$ = 0.4 g/l. The organic solution contained 7% Ionquest 801 and 2% Acorga M5640. Shellsol D70 was used as a diluent. According to McCabe-Thiele diagrams three theoretical stages are needed for the extraction of Fe, Al and Cu when O:A is 1:2 and pH 4.0. The metal extraction order was following: $Fe^{3+} > Cu^{2+} > Al > Co$, Ni, Li. Ionquest 801 alone would have led to high co-extraction of Co while Cu was completely extracted. Using the mixed extractant system the complete separation of Fe^{3+}, Cu and Al from Co, Ni and Li was achieved at pH 4.0-4.5. (Pranolo, et al., 2010)

Table 4 shows that the extraction of metals decreases with the increase in O:A ratios due to limited capacity of the organic phase. Fe has the strongest affinity to the organic phase as the separation factor increases along with increasing O:A. The separation factors of Al and Cu over Co improve with increasing O:A as well, yet only up to O:A 2:1. Factors decrease at O:A 1:5. The decrease can be explained by crowding effect of Fe^{3+} as organic capacity was reduced. Kinetics study determine that the extraction of Fe^{3+}, Al and Cu from Co, Ni and Li was most suitable at 40 °C instead of room temperature due to increase in Al extraction. (Pranolo, et al., 2010)

Table 4. Metal separation factors over Co at pH 4.0 (Pranolo, et al., 2010)

Element	O:A ratio	Concentration (mg/l)		Extraction (%)	Sep. factor (M/Co) ($\times 10^4$)
		Aqueous	Organic		
Fe	2:1	0	336	>99.9	1.9
	1:1	0	680	>99.9	11.1
	1:2	2	1343	99.7	58.4
	1:5	5	3280	99.3	134
Al	2:1	0	344	>99.9	1.9
	1:1	1	680	>99.8	2.2
	1:2	31	1341	95.5	3.6

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	1:5	414	1397	42.0	0.7
Cu	2:1	3	238	99.4	0.1
	1:1	3	419	99.2	0.4
	1:2	50	734	88.0	1.2
	1:5	282	870	38.2	0.6
Co	2:1	13,362	1183	15.1	-
	1:1	15,781	483	3.0	-
	1:2	16,236	19	0.06	-
	1:5	16,450	8	0.01	-

Chen et al. (2015) selectively separated and extracted Cu using Mextral®5640H as extractant diluted in kerosene. Prior to extraction Fe ions were precipitated from the leachate (2 M of H_2SO_4 and 2 vol.% of H_2O_2) by NaOH solution. Optimal conditions for extracting Cu were following: reaction time 300 s, concentration of Mextral®5640H was 10 vol.%, the O:A was 1:2, pH was 1.94 and temperature was a constant 25 °C. If pH was increased over 2.0 the other metals would start to co-extract. Under these conditions nearly 100% of Cu can be extracted while the co-extraction of other metals remain insignificant. (Chen, et al., 2015)

4.2.4 Separation of Co via SX

Separation of Co has been studied widely due to its high value compared to other metals in leaching liquors. In general, Co is separated from raffinate containing Co, Ni and Li when other metals have been removed from the leach liquor. For the separation of Co from other metals organophosphorous acids have been studied with successful results.

Pranolo et al. (2010) recovered Co from feed solution containing $[Co^{2+}] = 16.9$ g/l, $[Li^+] = 3.8$ g/l and $[Ni^{2+}] = 0.15$ g/l using Cyanex 272. The organic solution in the experiment contained 15% (v/v) Cyanex 272 in Shellsol D70. The separation of Co from Ni and Li was achieved at pH 5.5-6.0. (Pranolo, et al., 2010)

Chen et al. (2015) extracted Co from Li with counter-current extraction using Ni loaded Mextral®272P as an extractant. Prior to Co extraction, Fe ions were precipitated, Cu was extracted and Mn precipitated. The remaining solution contained only Li, Co and Ni. Concentration of Co^{2+} was 7.18 g/l in the leachate at the start of the experiment. Conclusion was that separation of Co, Ni and Li benefited from higher pH_e values. Optimal conditions for the extraction were 20 vol.% of Mextral®272P, O:A 1:1, reaction time of 300 s, pH_e of 4.5 and

temperature of 25 °C. The extraction efficiency of Co was 97.8% with co-extraction of 0.72% Ni and 0.78% Li. The loaded organic was treated with 5 g/l Na_2CO_3 and 0.1 M H_2SO_4 solutions to scrub Li^+ and strip Co^{2+}. Results for the recovery of the Co and Li were approximately 99% and 100%, respectively. In addition, the Co extraction isotherm was studied. McCabe-Thiele diagram revealed that three counter-current extraction stages were needed to extract 99% of Co. Leachate contained 3.63 g/l Co^{2+} and O:A was 1:2. Table 5 shows the separation of Co over Ni in different pH_e values. The greater the separation factor between different metals, the more efficient was the separation. Separation factors were studied in a solution containing 15 vol.% of Mextral®272P in kerosene. Agitation was 300 s and O:A was 1:1 at 25 °C. (Chen, et al., 2015)

Table 5. Separation factors of Co over Ni at different pH_e values (Chen, et al., 2015)

Factors	Equilibrium pH				
	2.51	3.48	4.50	5.47	5.99
D_{Co}	0.64	6.41	21.73	54.56	54.57
D_{Ni}	0.0005	0.0068	0.016	0.23	0.96
$\beta_{Co/Ni}$	1273	942.27	1357.95	237.20	56.84

Chen et al. (2011) dissolved the battery waste with H_2SO_4 and H_2O_2. Co was separated from Li and Ni using SX method. The experiment was executed mixing the aqueous and organic media in 125 ml separatory funnel. The initial pH was adjusted before equilibration and mixing was performed by shaking the system manually for 10 min. Fe, Mn and Cu were precipitated from the leach liquor in advance. The extractant P507 was saponified before extraction. Saponification rate of over 25 wt% in P507 caused viscosity problems, hence 25 wt% was chosen as saponification rate. The pH_e 3.5 was chosen as optimal value since co-extraction of Li and Ni was only 8%. Co was stripped from the organic medium while Li and Ni remained in aqueous medium. After stripping Co was recovered as CoC_2O_4 by adding excess of $(NH_4)_2C_2O_4$ until pH was 1.5. The Co recovery efficiency was 99%. It was acknowledged that the increase in O:A ratio increased the extraction of Co, yet the co-extraction of Li and Ni increased simultaneously. (Chen, et al., 2011)

4.2.5 Separation of Co via SSX

Separation of Co and Li was studied using SSX with a mixture of Cyanex 272 and tributyl phosphate (TBP) in kerosene. Instead of using single extractant, a mixture of extractants is used to improve synergistic effects, recovery efficiencies and metal selectivity. The SSX was performed on synthetic leach liquor. In Figure 12 the SSX effect can be seen compared to single

extractant SX. The graph shows that the mixture of extractants increased the extraction efficiency of Co^{2+}. Co-extraction of Li^+ remained low. At pH 5.3 nearly 90% of Co^{2+} was extracted with 10% co-extraction of Li^+. (Pospiech, 2015)
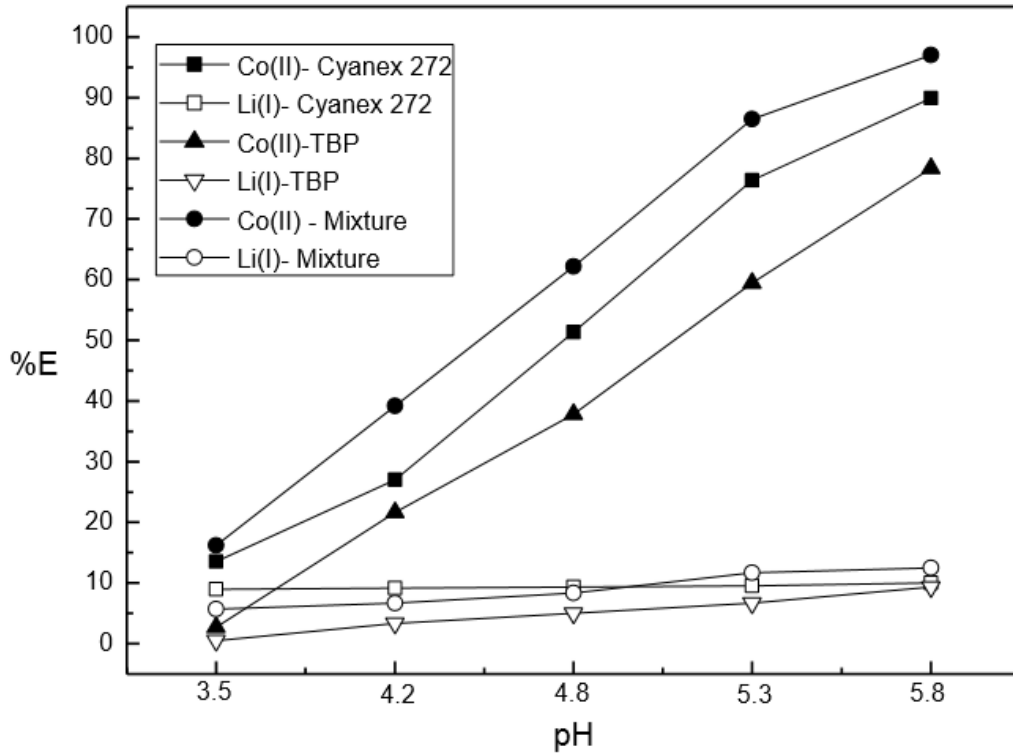
Figure 12. Extraction (%) of Co and Li using single extractant (Cyanex 272 / TBP) or mixture of extractants investigated in different pH values. Aqueous phase contained Co^{2+} and Li^+ 1:1. (Pospiech, 2015)

Pospiech (2015) concluded that the mixture of TBP and Cyanex 272 had synergistic effect on Co. TBP has been used previously as extractant and phase modifier. It was acknowledged that TBP and other solvating agents also extract Co^{2+} from chloride solutions. The reaction is given in Eq. 24. (Pospiech, 2015)

$$Co_{aq}^{2+} + 2Cl_{aq}^- + 2S_{org} \rightarrow (CoCl_2 \cdot 2S)_{org} \tag{22}$$
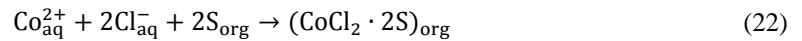
where S is TBP.

For SSX of Co the Eq 25 is given by Pospiech (2015).

$$Co_{aq}^{2+} + HA_{org} + S_{org} + Cl^- \rightarrow CoAClS_{org} + H_{aq}^+ \tag{23}$$

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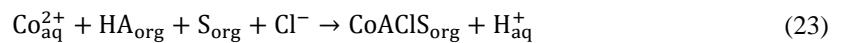
Zhang et al. (1998) were first to introduce the separation and recovery of metal values from spent LIBs. Solvent extraction method was used to separate Co from Li in the HCl solution. Experiment was carried out in 50 ml centrifuge tube or 500 ml separatory funnel at 25 °C. Equilibrium was attained after 30 minutes. The liquor contained 17.25 g/l of Co and 1.73 g/l of Li with the addition of 0.29 M D2EHPA and 0.3 M PC-88A in kerosene. Results showed that complete extraction of Co occurred when pH was higher than 6.5 and under pH 5.5 no extraction of lithium was observed. Above pH 5.5 Li began to co-extract. Experiments showed that the extraction of Co over Li was greater with PC-88A compared to D2EHPA (Table 6). (Zhang, et al., 1998)

Table 6. Separation factors of Co over Li with D2EHPA and PC-88A as extractants. Different values of O:A, pH_e and concentrations are present. (Zhang, et al., 1998)

Extractant	O:A	Equilibrium pH	Separation factor ($\beta_{Co/Li}$)
0.29 M D2EHPA	2.2:1	6.71	7.1×10^2
0.29 M D2EHPA	2.2:1	7.17	6.5×10^2
0.3 M PC-88A	2.5:1	7.03	8.8×10^4
0.3 M PC-88A	2:1	7.05	1.3×10^5

Feed solution: [Co] = 17.25, [Li] = 1.73 (g/l); pH = 0.6

Additionally, SSX and separation of valuable metals was investigated using Cyanex 272 and PC-88A. Extraction was performed using a mechanical shaker to mix the aqueous and organic phases (O:A was 1:1). The leaching medium was H_2SO_4 with addition of H_2O_2. The combination of Cyanex 272 and PC-88A was used to separate Co, Mn and Li from cathodic material of spent LIBs. The liquor medium in the experiment was H_2SO_4. The selectivity of Co^{2+} from Mn^{2+} was studied as co-extraction of Li was insignificant under experimented conditions. Extraction mechanism, pH isotherms, separation and stripping were studied with mixed and single extractant system. The order of extraction was reported to be Mn > Co >> Li, regardless of whether mixed or single extractant system was used. EDTA was used to improve selectivity between Co and Mn. It was concluded that Co and Mn can be separated using the mixed extractant system with equimolar of EDTA. The concentration of extractant mix was 0.5 M and the pH was 5.0. The separation factors of Co^{2+} and Mn^{2+} were investigated using Cyanex 272 (HA) or PC-88A (HL) alone, the mixture of Cyanex272 and PC-88A (HL + HA) and with the addition of EDTA. In Table 7 the calculated distribution ratios (D) and separation factor (SF) are presented. (Zhao, et al., 2011)

Table 7. Distribution factors and separation factor for Mn^{2+} and Co^{2+} in different SX systems from sulfate solutions (Zhao, et al., 2011).

Factors	Value					
	HL	HA	HL + HA	HL-EDTA	HA-EDTA	HL-HA-EDTA
D(Mn)	11.68	2.75	40.1	18.35	3.45	39.2
D(Co)	2.34	0.84	7.58	0.064	0.059	0.055
SF	4.99	3.27	5.29	286.7	58.47	712.7

The synergistic reaction is given in Eq. 26 (Zhao, et al., 2011).

$$2H_2A_{2(o)} + Me_{aq}^{2+} + 1.5H_2L_{2(o)} \rightarrow MeH_3A_2L_3 + 2H_{(a)}^+ \tag{24}$$
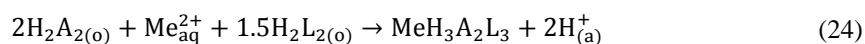
where "H_2L_2" denotes the extractant with synergistic effect.

4.2.6 Separation of Ni via SX

Nguyen et al. (2015) separated Ni and Li successfully from H$_2$SO$_4$ leach liquor using PC-88A as an extractant. Over 99.6% of Ni was extracted in two counter-current stages when O:A ratio was 1:1 and pH adjusted to 6.5. The purity of the recovered Ni was 99.9%. Li was scrubbed from loaded organic with dilute Na$_2$CO$_3$ solution. The McCabe-Thiele diagram showed that two scrubbing stages were required in order to achieve scrubbing efficiency of 99.6%. Li was recovered as Li$_2$CO$_3$ using saturated Na$_2$CO$_3$ solution. Temperature during Li precipitation was 100 °C. Figure 13 demonstrates the separation and recovery of Ni and Li from leach liquor. It can be acknowledged that multiple stages of extraction, scrubbing and stripping is necessary to attain good recovery and high purity compounds. (Nguyen, et al., 2015)
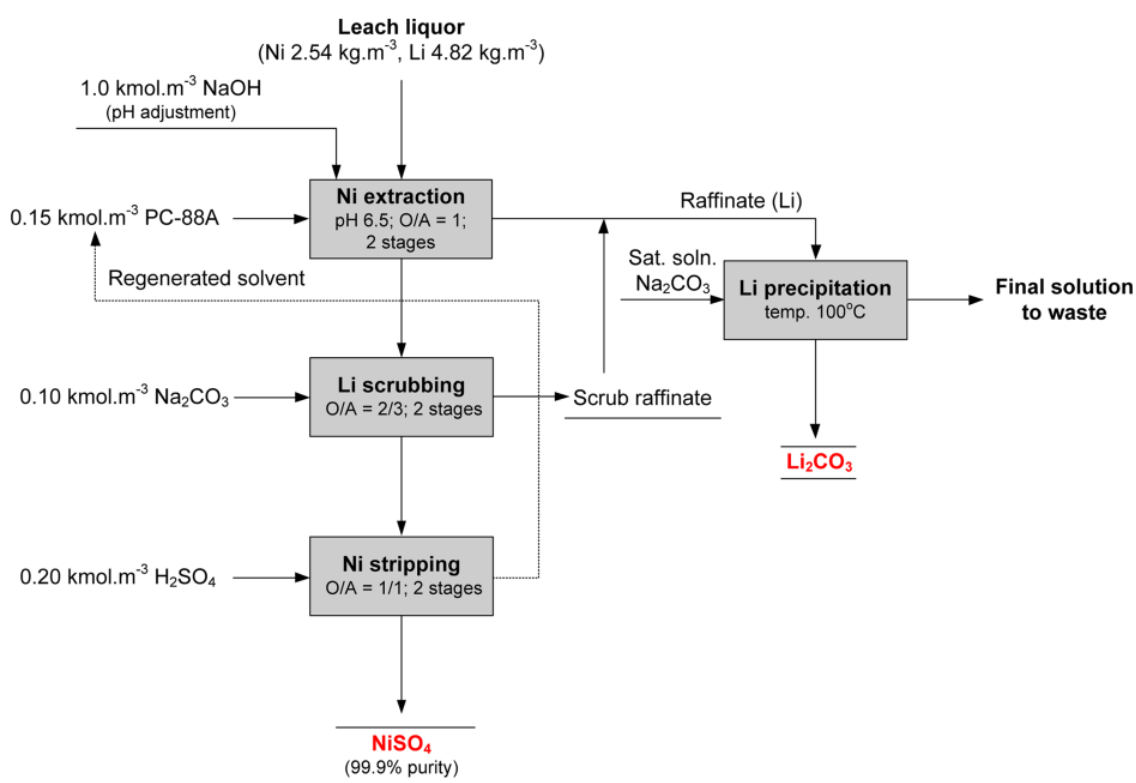
Figure 13. Recovery of Ni and Li from H₂SO₄ leach liquor of the cathodes of spent LIBs (Nguyen, et al., 2015).

4.2.7   Stripping

After specific metal(s) is extracted via SX to the organic phase stripping is needed to remove the ions from organic medium. Stripping is known as "backextraction". Addition of acid to the system releases the metal ions from the extractant and enables the recovery of the metal ion(s). (Chagnes, 2015a) As mentioned in Section 4.2 scrubbing can be performed prior to stripping. In SX system scrubbing is needed especially if co-extraction has been high and separation of metals has decreased. In addition to extraction, McCabe-Thiele diagrams are suitable for scrubbing and stripping studies as well. (Nguyen, et al., 2015)

Factors affecting scrubbing are scrub solution concentrations, temperature and number of scrubbing stages. Nguyen et al. (2015) investigated the scrubbing of lithium with Na_2CO_3 solution. It was noted that external pH control was not needed in the scrubbing. Lithium was scrubbed to obtain high purity nickel. Phase disengagement and precipitation of Ni at high pH values (pH <8.7) caused challenges during scrubbing thus scrubbing should be performed at lower pH values. Optimal concentration of Na_2CO_3 solution was 0.10 kmol/m³. In general, high organic-to-scrub solution ratio is beneficial in scrubbing. However, optimal organic-to-scrub solution ratio

in the scrubbing of Li was 2:3 with two counter-current stages. Scrub raffinate could be reused for example in lithium recovery step. (Nguyen, et al., 2015)

Pranolo et al. (2010) studied the stripping kinetics and concluded that stripping of Al and Cu was fast using 80 g/l H_2SO_4. The stripping of Fe required higher acid concentration of 200 g/l of H_2SO_4. Based on McCabe-Thiele diagrams two stages of stripping was needed to recover Al, Cu and Fe. (Pranolo, et al., 2010)

Zhao, et al. (2011) achieved the complete stripping of Co and Mn in a single stage. Li remained in the aqueous phase since the conditions were not optimized for extraction of Li. The stripping was successful when concentrations of HCl and H_2SO_4 were more than 0.04 M and 0.01 M, respectively. Stripping efficiency of H_2SO_4 was stronger than HCl in mixed Cyanex 272 and PC-88A system. Co and Mn were stripped as Co^{2+} and Mn^{2+}. (Zhao, et al., 2011) Nguyen et al. (2015) stripped Ni from loaded organic with 0.2 kmol/m^3 H_2SO_4. Stripping efficiency was 99.9% with two stage counter-current process (O:A = 1:1).

Chen et al. (2011) recovered Co as CoC_2O_4 using $(NH_4)_2C_2O_4$ after solvent extraction. The strip solution was neutralized (pH = 0.8) with concetrated NaOH. Ammoniun oxalate was added until pH reached 1.5 and Co was recovered. Molar ratio of Co^{2+} and ammoniun oxalate affected the stripping. Under the optimum ratio (1.15:1.0) 99% of Co was precipitated. (Chen, et al., 2011)

4.3   Ion-exchange resins

The ion-exchange resins perform similarly to SX. However, in ion-exchange the organic compound is in a stationary medium such as resin beads. Porous polymeric beads enable the loading of dissolved metal ions. Loaded beads are then stripped of the organic compound. Ion-exchange beads include amines, carboxylates, phosphonates and sulfonates. (Free, 2013)

Sorption or desorption can be used for lithium recovery from leachates during hydrometallurgical processes. Sorption of commercial ion exchange resins were studied with synthetic leachate containing solely lithium compounds. Amberlite IR 120 exchange resin (sodium and hydrogen) was tested in the recovery of LiCl, Li_2CO_3 and Li_2SO_4 from aqueous solutions. Amberlite IR 120 is a strong acidic cation exchange resin based on styrene divinylbenzene copolymer spheres functionalized with sulfonic acid. Operation range of resin is pH 0-14 and exchange capacity 1.8 eq/l. The sorption of Amberlite H (hydrogen) and Amberlite Na (sodium) were tested with different lithium salts. Sorption yields of Amberlite Na were similar (approximately 20%) with varying pH values and different lithium salts. Sorption yields of Amberlite H were clearly higher

for Li_2CO_3 and Li_2SO_4 (over 25%). The sorption experiments were carried out for 24 hours. Solution contained 0.2 M lithium. (Lemaire, et al., 2014)

Pranolo et al. (2010) extracted Fe, Al and Cu from Co, Li and Ni using SX with different extractants (Section 4.2.3). Subsequently Co was separated from Li and Ni using Cyanex 272. It was suggested that Li and Ni could be recovered as pure products from raffinate by ion-exchange resin (Dowex M4195). However, the separation was not investigated. (Pranolo, et al., 2010)

4.4 Cementation

Cementation is used to recover dissolved metals from aqueous medium and is based on the differences in the electrode potentials of the metals. In cementation, the dissolved more noble metal is reduced back to its metallic state. Simultaneously the less noble metal dissolves donating the electron for metal ion precipitation. (Free, 2013) Different process parameters have effects on cementation efficiency such as initial concentration, agitation, time, temperature and pH (Nazim, et al., 2012).

Nazim et al. (2012) investigated the effect of Cu concentration, temperature and pH in Cu cementation. The optimum conditions were determined by optimization toolbox of MATLAB 7.0 software. In theoretical calculations and in experimental tests initial copper concentration was 2248 ppm, temperature 54 °C and pH 3.46. Theoretical and experimental recoveries were 90.88% and 89.42%, respectively. (Nazim, et al., 2012)

Cu^{2+} cementation reaction using Fe powder is presented in Eq. 27 (Nazim, et al., 2012).

$$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu \qquad (25)$$

Wang & Friedrich (2015) removed Cu^{2+} from leach liquor by adding Fe powder with particle size of "200 Mesh". The solution was heated and stirred (150 rpm). It was acknowledged that the reaction of Cu cementation was mostly controlled by boundary layer diffusion. Considering the dissolution of Fe powder in high temperatures optimal temperature for the Cu cementation was 60 °C. (Wang & Friedrich, 2015)

5   Experimental methods and materials

The aim of the experimental part is to build up a process flowsheet for the recovery of Li, Co and Ni from LIB waste. The experimental methods used are precipitation and SX. The precipitation of different metals in HCl leach liquor was studied using two different reagents, NaOH and Na_2CO_3. Additionally, solvent extraction was investigated as a method to separate Co, Mn, Ni and Li from each other.

5.1   Raw material

Different leaching solutions and leaching conditions were studied earlier in METYK project (Aaltonen, 2017). The leachate raw material was provided by METYK project in order to enable the research described in this work. The process development described in this work was performed for CloseLoop project. High extraction of Li and Co was achieved with HCl, H_2SO_4 and HNO_3 reagents. The leaching of the LIB waste was carried out with 4 M HCl according to the conclusive results.

Commercially crushed and sieved battery waste was obtained for this research. Prior to leaching, XRD analysis was performed to powder material. Figure 14 presents reference XRD analysis obtained from literature. In the scrap material from literature, anode and cathode materials were separated from Cu and Al before grinding, screening and XRD analysis. Figure 15 presents XRD analysis of the scrap material used in this work. The intensity (counts per second) is significantly higher in analysis obtained from literature than in analysis of scrap material used in this work. This could be explained by the relatively small diameter of sample used in the analysis. Additionally, the batteries in reference XRD analysis (Figure 14) were dismantled manually (Chen, et al., 2011) and the obtained powder probably has higher purity compared to powder used in this work. Higher purity of the material could explain the higher intensity. From the Figure 14 and Figure 15, it can be concluded that the position, shape and ratio of spikes match. The powder material is mainly $LiCoO_2$ and graphite. The material probably contains other active materials as well, which the XRD analysis was not able to differentiate from the background or analyzed peaks.
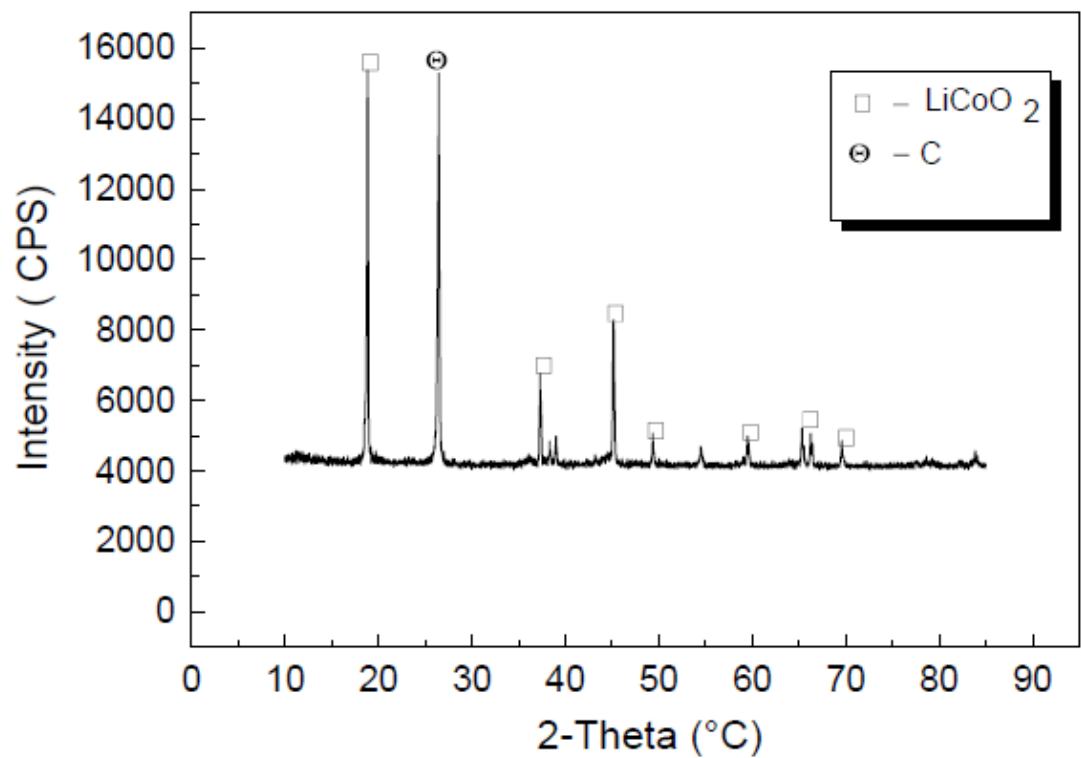
Figure 14. XRD analysis of powder scrap material of spent LIBs (modified from (Chen, et al., 2011)).
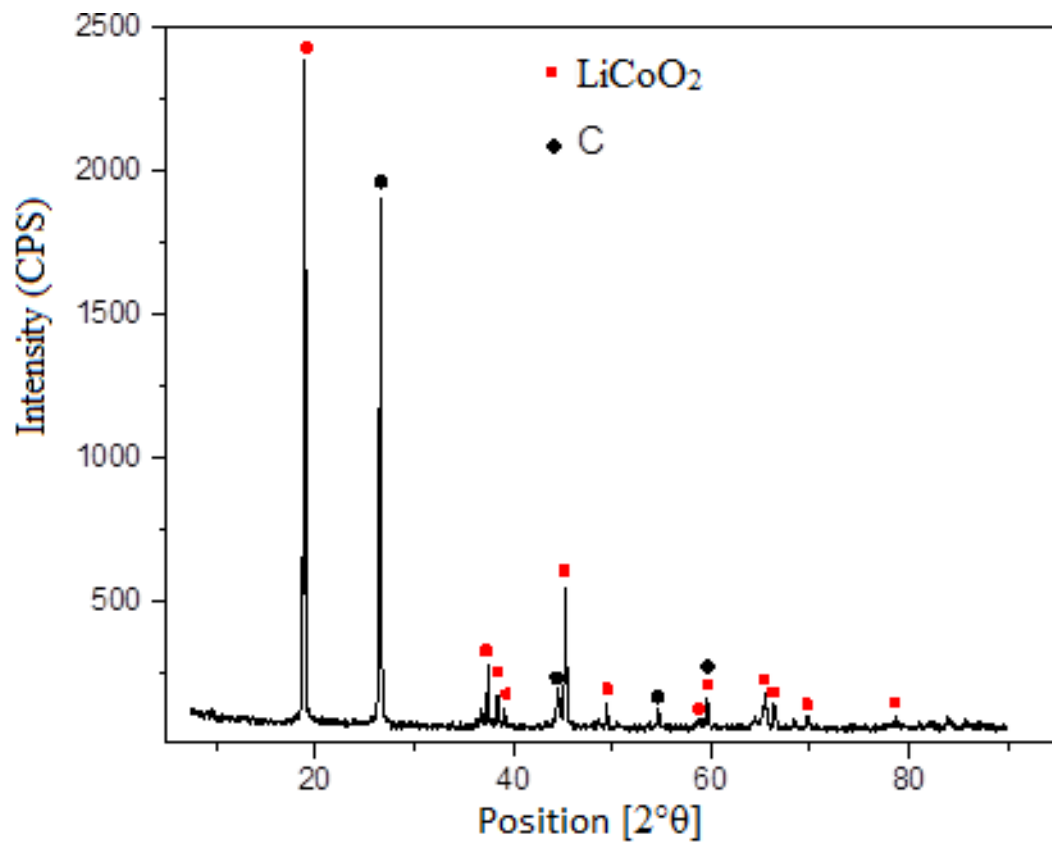
Figure 15. XRD analysis of powder scrap material of spent LIBs.

In this work, the powder scrap material and Li_2CO_3 precipitate were analyzed using X-ray diffraction (XRD). XRD analysis is used for identification of crystal structures and atomic spacing. X-rays are directed toward the sample and diffracted X-rays are detected, processed and counted. XRD can identify unknown minerals by comparing the detection data with standard reference file of inorganic compounds. Homogeneous and single phase powder material is best for XRD analysis. (Dutrow & Clark, 2016)

PANanalytical X'PERT powder X-ray Analysis (NL) was used for the scrap material analysis in this work. The data obtained from XRD was analyzed by PANanalytical HighScore Plus software. In XRD analysis Cu k-α was used as radiation source. The scan area was 10 - 90 [$2°\theta$] and rate 5.3 [$2°\theta$]/per min. Acceleration voltage and current were 45 kV and 40 mA, respectively. The background was determined using a default polynomial function and peaks were fitted using default profile fit function.

The raw material used in the experiments of this work was the PLS1 obtained from leaching of spent LIBs. The leaching was performed at Laboratory of Hydrometallurgy and Corrosion in Department of Chemical and Metallurgical Engineering at Aalto University. The experiments were carried out as part of research project by Alexander Chernyaev. The PLS used in this work was a combination of several PLSs originating from 4 M HCl leaching of LIBs conducted at four different temperatures (50, 60, 70 and 80 °C) with SD% of 5, 7.5 and 10 g/l, where SD denotes solids density. Leaching time was 3 h. (Aaltonen, 2017)

In this work, the solution samples and precipitates were analyzed by Milomatic Oy. Precipitates were total leached with aqua regia and metals were analyzed from solution. Metals except Al were analyzed with atomic absorption spectroscopy (AAS). The brand and model of AAS instrument was Varian AA240. Al was analyzed with inductively coupled plasma atomic emission spectroscopy (ICP-OES). The brand and model of ICP-OES instrument was Perkin Elmer 7100 DV. In extensive analyses (25 metals) alkali metals were analyzed with ICP-OES and other metal with AAS.

Concentrations of all analyzed metals from PLS1 are presented in Table 8. In this work, the investigated metals were limited to metals with highest concentrations in the leach liquor (Al, Fe, Cu, Mn, Ni, Co and Li). The influence of minor metal concentrations was not investigated.

Table 8. Analyzed metal concentrations in the leach liquor before metal recovery. The metals in focus are bolded.

Metal	Concentration (mg/l)
Al	**1510**
As	< 2
B	< 2
Ba	28.3
Ca	39.3
Cd	< 0.5
Co	**16817**
Cr	< 2
Cu	**2145**
Fe	**741**
K	21.6
Li	**2548**
Mg	40.0
Mn	**2146.5**
Mo	< 2
Na	24.8
Ni	**1996**
P	< 2
Pb	12.6
S	51.2
Sb	< 2
Se	10
Sn	86
Ti	17.0
V	< 2

5.2 Experimental setup

The experiments for this work were performed at Laboratory of Hydrometallurgy and Corrosion in Department of Chemical and Metallurgical Engineering in School of Chemical Technology at

Aalto University. The PLS used as the initial liquid raw material for all experiment was the LIB scrap powder leached in HCl introduced in Table 8.

5.2.1 Setup in precipitation experiments

In all the precipitation experiments Titronic 500 titrator, VWR hotplate 7x7 CER HOT/STIR and three different pH meters were used. Titronic 500 is a manual titrator manufactured by Lab Synergy. VWR hotplate/stirring was used to adjust and maintain the temperature and apply the magnetic stirring during experiments. Hanna edge multiparameter pH meter - HI2020 was used for measuring pH in acidic solutions. Additionally, Mettler Toledo SevenEasy pH meter was used in the acidic solution experiments and slightly alkali solutions. VWR Phenomenal pH meter was used for pH measurements in alkali solutions. Before each experiment, the pH meters were tested with buffer solutions and calibrated if needed.

Solution samples were retrieved using an automated Labsystems 4500 finnpipette. Solution sample preparations included either one or two filtration stages. For 15 ml volume sample two stages of filtration was necessary and for 10 ml sample only syringe filtration was needed. First filtration stage was vacuum filtration and it was carried out using a Büchner funnel and a Büchner flask. The filter media used was Whatman Grade 42 filter paper, which has a pore size of 4.2 µm. Whatmann Grade 42 was ashless (<0.01) paper. After vacuum filtration, the samples were filtered through syringe filter with particle retention of 1.2 µm. In the purification step the syringe filter unit used was Whatman FP 30/1.2 CA. Later in the precipitation experiments Whatman FP 30/0.45 CA-S unit was used to ensure the validity of analyses through better solution preparation. Solution samples from carbonate precipitation experiments were prepared for analyses by adding 0.3 ml of HNO_3. The addition of HNO_3 kept metals soluble during the analyses.

The precipitates were recovered after each experiment by vacuum filtration and washed with distilled water (25 °C) to remove any residues. In Li_2CO_3 recovery the cake was washed with 60 °C distilled water to avoid the dissolution of precipitate during washing. The precipitates were dried in oven with the filter paper at approximately 110 °C until completely dry. The drying time varied from 1.5 to 2 h depending on the height and the moisture content of the cake. The precipitates obtained from the precipitation process experiments were exceptionally dried at 60 °C. The weighing accuracy of precipitates was two decimals (0.01 g).

The experiments were not conducted in a closed system thus the evaporation was considered in the calculations and results. Evaporation was acknowledged at elevated temperatures (40 and 50°C). The evaporation was taken into account roughly by heating distilled water to target

temperatures and measuring the volume difference after 1 h retention time. Evaporated volumes during experiments were approximated. Possible reactions with air were not investigated in this work.

5.2.2   Setup in SX experiments

SX experiments were carried out in 200 ml separatory funnels (Figure 16). The denser layer in Figure 16 was aqueous and top layer organic phase. The separation of Mn and Co from Ni and Li was investigated using partially saponified Cyanex 272 (Na-Cyanex 272). All the experiments were conducted to purified solution (Section 5.4.1).
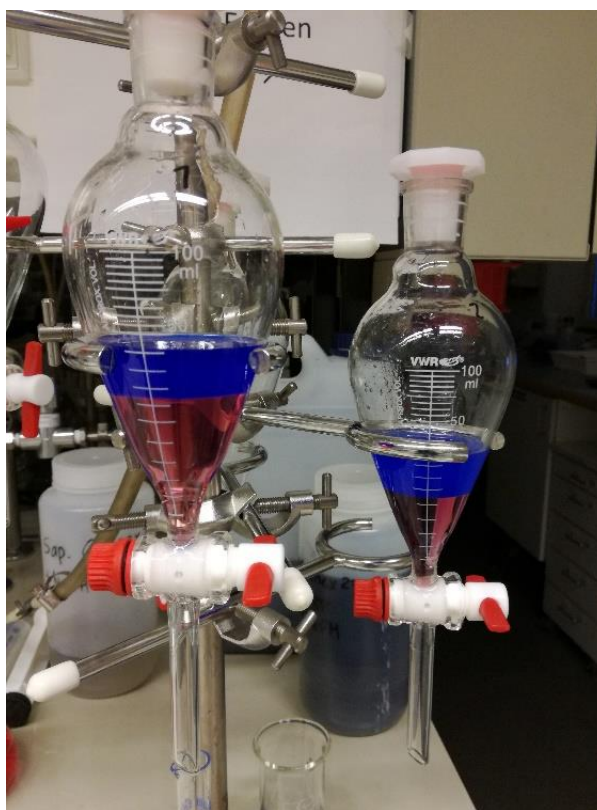
Figure 16. SX experiments were carried out in separatory funnels. Picture has been taken prior to extraction. Funnel on the left has O:A of 1:1 and funnel on the right has O:A of 2:1. Organic phase was the blue solution on top and aqueous phase was below.

The extraction and stripping processes were implemented in Stuart SBS40 shaking water bath. The temperature in the bath during extraction was constant 30 °C. The agitation in the shaking water bath was adjusted to maximum level (400 rpm) in each experiment. In all experiments the contact time during extraction and stripping was constant 15 min.

After extraction, the organic and aqueous phase were separated in separatory funnels. The equilibrium pH (pH_e) of aqueous phase was measured with Mettler Toledo Seven Easy pH meter. Experiments were carried out in duplicate.

5.3 Chemicals

All the chemicals used in precipitation and SX experiments are listed in Table 9 with name, chemical formula, manufacturer and purity.

Table 9. List of chemicals used in experiments with name, chemical formula, manufacturer and purity.

Name	Chemical formula	Manufacturer	Purity (%)
Sodium hydroxide	NaOH	Caelo	97
Sodium carbonate (anhydrous)	Na_2CO_3	Fluka	$\geq$99.5
Sulfuric acid	H_2SO_4	Sigma-Aldrich	95
Nitric Acid	HNO_3	Sigma-Aldrich	65
Kerosene	C12-15H26-32	Aldrich	>95
Tributyl phosphate (TBP)	$(CH_3(CH_2)_3O)_3PO$	Sigma-Aldrich	$\geq$99.0
Cyanex 272	$C_{16}H_{34}PO_2H$	Cytec Industries Incorporated	85

5.4 Precipitation method

PLS1 volume in the beginning of precipitation experiments was constant 100 ml. Solution was poured in a 500 ml beaker and placed on a heating plate. In all experiments the stirring was adjusted to 300 rpm. The solution was heated up to the target temperature (30, 40 or 50 °C) prior to the titration. During titration, the solution temperature was kept constant.

After obtaining the optimal precipitation temperatures, pH values and reagents from all tests the precipitation process was completed from start to finish. First impurities (Fe, Al and Cu) were removed using 2 M NaOH, which resulted in PLS2. Mn, Co and Ni were precipitated as carbonates using 2 M Na_2CO_3, which resulted in PLS3. Finally, Li was recovered as Li_2CO_3 by adding saturated Na_2CO_3. Three obtained precipitates and two solution samples were analyzed.

5.4.1 Precipitation of impurities

First the precipitation of Al, Fe and Cu was studied at three temperatures (30, 40 and 50 °C) and three pH values (5.0, 5.5 and 6.0). PLS1 volume of 100 ml was heated to specific temperature. Temperature was kept stable during the whole experiment. 2 M NaOH was added until pH reached 5.0. In these experiments, initial pH value (pH_i) represents the pH value adjusted before retention time. The pH_i value was set in such a way that the equilibrium pH value will stabilize near target pH value. The pH_e value was attained after the pH_i was set and all the ongoing reactions had stabilized. It was assumed that retention time of 30 min between pH_i and pH_e was enough to attain equilibrium during the experiments. Additionally, the change in pH values were monitored during 30 min to ensure that shifting remains relatively slow or stops completely. After purification step the PLS2 solution volume was measured to be approximately 189-200 ml.

Solution samples of 15 ml in volume were retrieved after each predetermined pH level. The samples were vacuum and syringe filtered (Section 5.2.1). Even though mainly Al, Fe and Cu were removed from the leach liquor, it was preferred that all the investigated metals (Li, Co, Cu, Mn, Ni, Al and Fe) were analyzed from the samples to study the co-precipitation.

5.4.2 Hydroxide precipitation

After the purification step where majority of Al, Fe and Cu were removed, the precipitation of still soluble metals was investigated by adding 2 M NaOH to PLS2. The continued precipitation was investigated at three temperatures (30, 40 and 50 °C) and in three pH values (7.5, 8.0 and 8.5). Original solution in these experiments was the tail liquor from the purification step. Temperature and agitation were constant during the experiments. It was assumed that 30 min retention time ensured the transition from pH_i to pH_e. Solution samples of 15 ml were retrieved after each target pH level. The samples were vacuum and syringe filtered (Section 5.2.1).

5.4.3 Carbonate precipitation

After the purification step where majority of Al, Fe and Cu were removed, the precipitation of remaining soluble metals was investigated by adding 2 M Na_2CO_3 to PLS2. The continued precipitation was investigated at three temperatures (30, 40 and 50 °C) and in three pH values (7.0, 7.5 and 8.0). Original solution in these experiments was the tail liquor from the purification step. Temperature and agitation were constant during the experiments. It was assumed that 30 min retention time ensured the transition from pH_i to pH_e. Solution samples of 15 ml were retrieved after each target pH level. The samples were vacuum and syringe filtered (Section 5.2.1).

5.4.4 Recovery of Li₂CO₃

After precipitation of Fe, Al, Cu, Mn, Ni and Co, Li was recovered from the filtrate by adding stoichiometric amount of saturated Na_2CO_3 solution. The analysis showed that the filtrate contained 1.2 g/l of Li. Li fraction was 99.1% of all analyzed metals.

Recovery was carried out at 50 °C. Solubility of Li_2CO_3 is presented in Table 10. Taking into account, the solubility of Li_2CO_3, concentrating the filtrate was necessary to recover at least some of the Li. First 300 ml filtrate was concentrated to 100 ml at approximately 70 °C. It was calculated that the concentration of Li increased to 3.1 g/l and after adding stoichiometric amount of saturated Na_2CO_3 the concentration of Li_2CO_3 could reach a value of 16.6 g/l as M(Li) is 6.94 g/mol and M(Li_2CO_3) is 73.89 g/mol. Li concentration of 3.1 g/l was decided to be enough to recover at least 0.66 g Li_2CO_3. To be exact the calculated amount of possible Li_2CO_3 precipitate was 0.58 g according to solubility data in Table 10. See Appendix E: Table E1 for detailed calculations.

Table 10. Solubility of Li₂CO₃ in water at different temperatures (National Center for Biotechnology Information , 2017).

Solubility of Li₂CO₃ in water					
Temperature (°C)	20	40	60	80	100
Solubility (g/100ml)	1.31	1.16	1.00	0.84	0.71

5.5 SX method

For solvent extraction experiments diluent, phase modifier and different extractants are needed. According to literature kerosene has been used as diluent (Section 4.2). TBP has been used as phase modifier and Cyanex 272 as an extractant in the recovery of Co (Section 4.2.5). Saponification of extractant such as Cyanex 272 has been beneficial due to increasing metal extraction (Section 4.2.2).

5.5.1 Diluent

Diluents are used in SX systems mainly due to viscosity of extractants (Chagnes, 2015a). Sulfonated kerosene was used as diluent in all SX experiments. In previous research, sulfonation of kerosene has been beneficial in the recovery of uranium and decreased the co-extraction of impurities (Silem & Boualia, 1990).

Sulfonated kerosene was prepared by mixing concentrated sulfuric acid and kerosene at liquid to liquid ratio of 1:1 (v/v) for 1 h in 500 ml separatory funnel. After separation of the two immiscible phases the process was repeated. Finally, the separated kerosene was washed with distilled water at 1:1 ratio (v/v) approximately 10 min. The pH of the kerosene was measured to ensure efficient washing. In all SX experiments the organic phase consisted 70 vol.% of sulfonated kerosene.

5.5.2 Phase modifier

TBP is used as a phase modifier in the SX system. Phase modifier prevents the formation of a third phase in the extraction system. Additionally, TBP might have a synergistic effect on the SX system as described in Section 4.2.4. In SX experiments the organic phase consisted 10 vol.% of TBP. It should be noted that alkaline hydrolysis of TBP occurs in the contact of TBP and NaOH. The hydrolysis reaction should be avoided when preparing the organic phase.

It is recommended that the saponification process is performed prior to the preparation of whole organic phase if the organic phase consists of Na-Cyanex 272 and TBP. Adding the NaOH to mixture including TBP will lead to alkaline hydrolysis reaction and unwanted formation of sodium salt. The reaction was avoided by adding the TBP after the saponification of extractant was completed. According to literature, alkaline hydrolysis of TBP leads to formation of sodium dibutylphosphate (NaDBP) and butanol. Three layers can be observed in the mixture of NaOH and TBP. Top layer consists of diluent, middle layer mainly product of hydrolysis and bottom layer unreacted NaOH along with hydrolysis products. (Srinivas, et al., 1994)

5.5.3 Extractant

In Section 4.2.2 the importance of pH_e in SX system was described. Having partially saponified acidic extractant facilitate the extraction of different metals in different pH_e values. The SX experiments with purified solution were conducted using partially saponified Cyanex 272. The stock solution of Cyanex 272 was provided by Cytec Industries Incorporated. In this work solvent was not purified.

The Na-Cyanex 272 was prepared mixing 10 ml (20 vol.%) of Cyanex 272 with 35 ml of sulfonated kerosene. Stoichiometric amount of NaOH was added to the mixture to attain 40% saponification of the extractant. Saponification ratio can be calculated using Eq. 20 where one H^+-ion is replaced with Na^+-ion. Molecular weight of Cyanex 272 is 290 g/mol and density 0.92 g/cm^3 (Cytec Industries Inc., 2008; Biswas & Singha, 2007). The calculations resulted in 14.4 ml addition of 3 wt.% of NaOH to achieve the 40% saponification. The mixture was shaken for 1h

and aqueous and organic phases were separated. TBP (V = 5 ml) was added to the organic phase after the separation. In reality the saponification ratio is less than in theory, because not all H^+-ions react with Na^+-ions.

Stripping of the extractant was performed similarly in each experiment. After extraction, the organic and aqueous phases were separated and the organic phase was mixed with stripping reagent. The first strip was performed using 2 M H_2SO_4 and if necessary a second strip using 10% NaOH. The strip solution to organic phase ratio was constant 1:1 during SX experiments.

6 Results

6.1 Hydroxide precipitation of Fe, Al and Cu

The purification of the leach liquor was achieved using precipitation method to remove impurities. 2 M NaOH was used as reagent to adjust the pH and to precipitate impurities as hydroxides. The assumed reaction for impurity ions (Al, Fe and Cu) are given in Eq. 26 - 28. However, Cu could precipitate as atacamite as mentioned in Section 4.1.1.

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \qquad (26)$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \qquad (27)$$

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \qquad (28)$$

The unfavorable co-precipitation reactions are given in Eq. 29-31.

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2 \qquad (29)$$

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2 \qquad (30)$$

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2 \qquad (31)$$

In Figure 17, Figure 18 and Figure 19 the selectivity of Fe, Al and Cu over Li, Co, Mn and Ni differs as pH and temperature varies. According to the results, it was concluded that Fe exists in the form of Fe^{3+} in the leach liquor since all the figures show similar (100%) precipitation efficiency for Fe at studied pH range. The precipitation of Fe^{2+} and Fe^{3+} are explained in Section 4.1.1. At 40 and 50 °C when pH is 5.5 - 6.0 the precipitation of Fe, Al and Cu was in the range of 80 - 100%. At lower temperature (30 °C) the precipitation of impurities was incomplete in lower pH values. The precipitation efficiency of Al and Cu near pH 5 increase from 60% to 80% when temperature increases from 30 to 50 °C. Higher pH values were clearly disadvantageous for Li, Co and Ni as precipitation increases gradually. Precipitation of Mn was insignificant at all temperatures and pH values. Additionally, it seems that small percentages of Li were precipitated as well. Most likely, the absorption of Li causes the apparent decrease seen in graphs (Section 4.1.1).
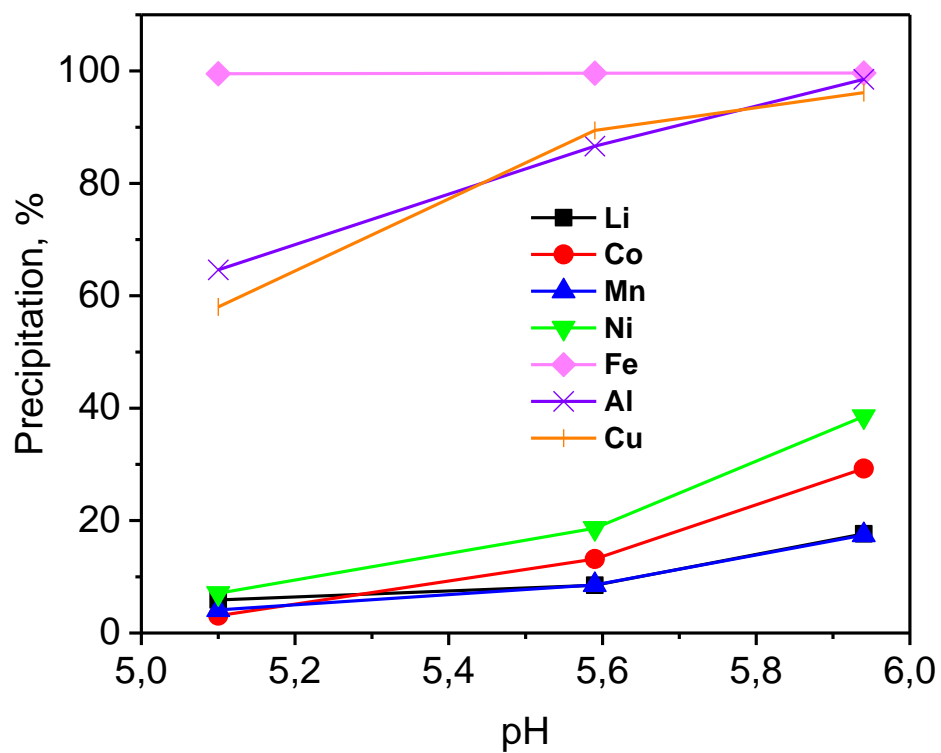
Figure 17. Purification efficiency (%) using 2 M NaOH to precipitate impurities. Temperature was 30 °C and agitation 300 rpm (Samples A3X2, A3Y2 and A3Z2, see Appendix A: Table A4).
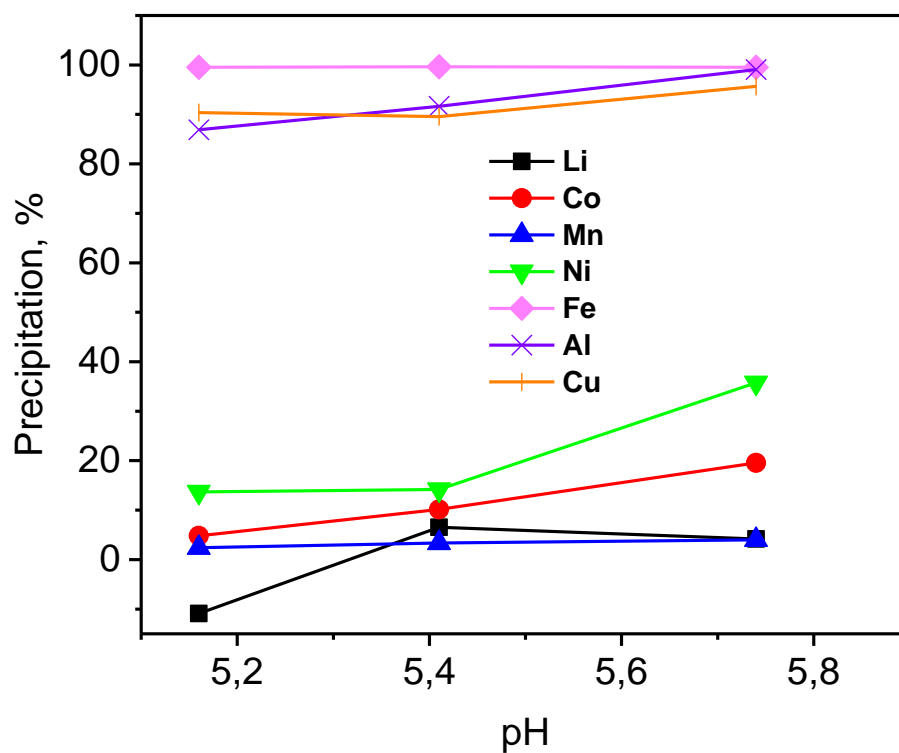
Figure 18. Purification efficiency (%) using 2 M NaOH to precipitate impurities. Temperature was 40 °C and agitation 300 rpm (Sample A4X2, A4Y1 and A4Z1, see Appendix A: Table A4).
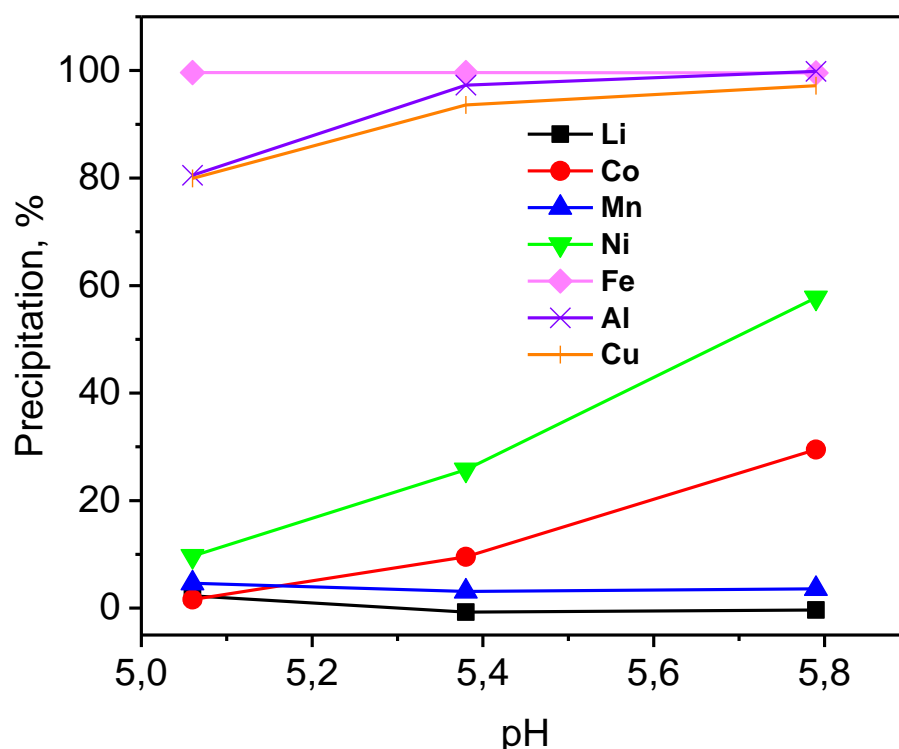
Figure 19. Purification efficiency (%) using 2 M NaOH to precipitate impurities. Temperature was 50 °C and agitation 300 rpm (Sample A5X1, A5Y1 and A5Z1, see Appendix A: Table A4).

In optimal conditions the precipitation of Fe, Al and Cu was high and the co-precipitation of Li, Co, Mn and Ni as low as possible. At 30 °C and near pH 5 the co-precipitation was insignificant. At 40 and 50 °C the co-precipitation was lowest near pH 5, however not as low as in Figure 17. In all purification experiments the impurity removal becomes more efficient as pH increases. However, co-precipitation increases simultaneously. Choosing the optimal conditions for impurity removal is thus a choice between loss of valuable metals and more purified solution (Table 12).

Table 11 summarizes the pH values measured in the purification experiments at different temperatures (30, 40 and 50 °C). The pH_i values were set as close to the target value as possible before the retention time. The pH change between pH_i and pH_e seemed to be coincidental and influenced by parameters. The pH values increase or decrease during the 30 min retention time. In repetitive experiments the fluctuation between pH_e values were minor.

Table 11. Summary of pH values during precipitation in the purification experiments (see Appendix A: Table A2).

Temperature (°C)	Target pH	pH_i	Assumed pH_e	pH difference

30	5.0	5.00	5.10	0.1
	5.5	5.56	5.59	0.09
	6.0	6.00	5.94	-0.06
40	5.0	5.18	5.16	0.16
	5.5	5.49	5.41	-0.09
	6.0	5.99	5.74	-0.26
50	5.0	5.00	5.06	0.06
	5.5	5.51	5.38	-0.12
	6.0	6.01	5.79	-0.21

The decrease and increase in pH values during the results from ongoing reactions. As NaOH reacts with HCl neutralization occurs and pH increases. It can be concluded that at the beginning of NaOH addition the target pH values are more easily exceeded. At higher pH values and higher temperatures the pH_e values were repeatedly lower than target value. The reactions are not occurring instantly, yet after the 30 min retention time the pH change was nonexistent or at least very slow.

Optimal conditions for purification were $T = 50\,°C$ and *target pH* = 5. Table 12 shows the average metal concentrations in PLS2. See Appendix B Table B1 for detailed metal concentrations in samples.

Table 12. Average metal concentrations in PLS2 after purification with 2 M NaOH at 50 °C when equilibrium pH was near 5 (specific PLS2 concentrations in each experiment are presented in Appendix B, Table B1).

Metal concentration (mg/l)	**Li**	**Co**	**Ni**	**Mn**	**Cu**	**Al**	**Fe**
	1209	6986	842	964	111	111.5	1.2

Precipitate obtained from the purification step was analyzed. In Table 13 the obtained hydroxide precipitate (m = 2.53 g) was analyzed and the metal content is presented as ppm (mg/g).

Table 13. Analyses of the precipitate (m = 2.53 g) obtained from the purification step.

ppm (mg/g)	**Li**	**Co**	**Ni**	**Mn**	**Cu**	**Al**	**Fe**
	3.7	99.7	20.8	6.7	73.6	56.5	22.0

In purity calculations, it was assumed that all the metals form assumed compounds and the all of the detected metal amount participates in the formation of the compound. In hydroxide

precipitation Fe, Al and Cu form hydroxide compounds as presented in Eq. 26-28. The purity of the precipitate was calculated to be 32% (see Appendix E: Tables E2-E4). Low purity (32%) was mainly due to co-precipitation of Co even though the co-precipitation percentage during experiment was low. However, the fraction of Co in the raw material (Table 8) was very high compared to other metals (60 wt.%). In Figure 20 is the obtained Fe, Al, Cu -precipitate from optimal purification step.

Figure 20. Obtained Fe, Al, Cu -precipitate from the optimal purification step.

6.2   Hydroxide precipitation of Co, Ni and Mn

Precipitation of metal hydroxides was carried out after the purification step using PLS2 (Appendix B, Table B1). Precipitation of Li, Co, Mn, Ni and Cu were investigated. In the purification step majority of Al, Fe and Cu were removed with minor co-precipitation of Li, Co, Mn and Ni. The assumed reactions are presented in Section 5.4.1.

Continued precipitation of hydroxides was performed after impurity removal. In Table 12 the average metal concentrations after impurity removal are presented. In the Figure 21, Figure 22 and Figure 23 the precipitation percentages of Li, Co, Mn, Ni and left over Cu are presented when 2 M NaOH was added to the solution. The temperature in experiments was adjusted to 30, 40 and 50 °C, respectively. Agitation was constant 300 rpm. At 30 °C efficient precipitation of Co and Ni was successful pH ≥8. At lower pH values the recovery of Co was low (50%). At 40 °C Mn

and Li could be separated from Co and Ni in neutral pH values. However, 20% of Mn was co-precipitated with Co and Ni. Separation of Mn and Li from Co and Ni was concluded to be insufficient. Subsequently Mn and Li separation could be achievable via chemical precipitation or SX. High efficiency of valuable metals was in all temperatures. Li absorption was noticed in purification and in continued precipitation of hydroxides as well. Efficient separation of Mn, Co and Ni from Li was not successful with hydroxide precipitation at studied pH values. All impurities and valuable metals should be efficiently recovered from liquor before crystallization in order to recover as pure Li product as possible.
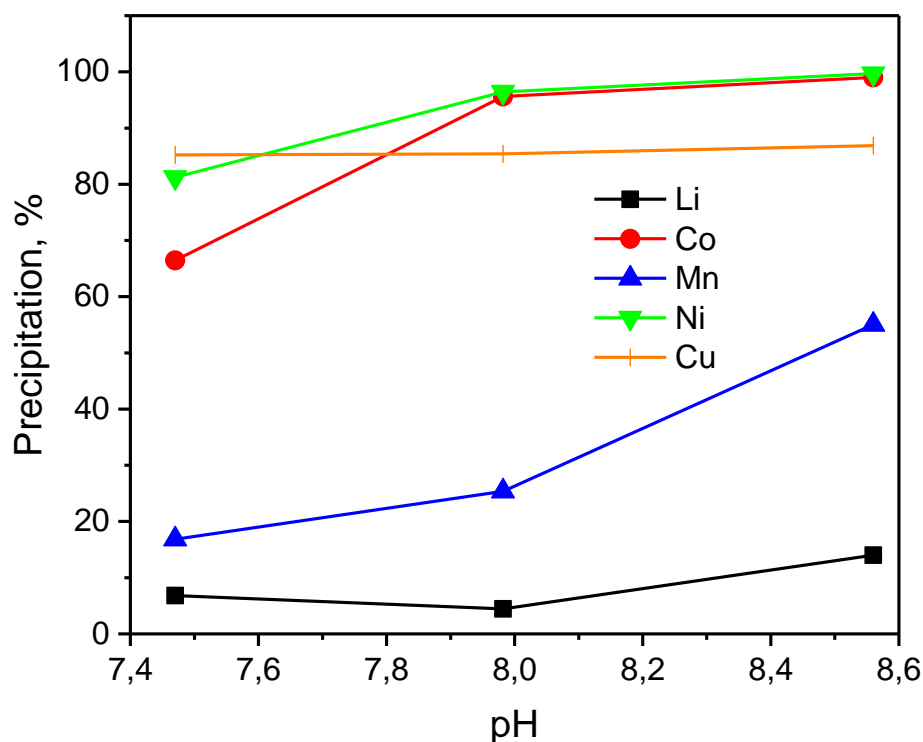
Figure 21. Precipitation after purification step. Reagent used was 2 M NaOH. Temperature 30 °C and agitation 300 rpm (Sample B3X2, B3Y3 and B3Z3, see Appendix C: Table C4).
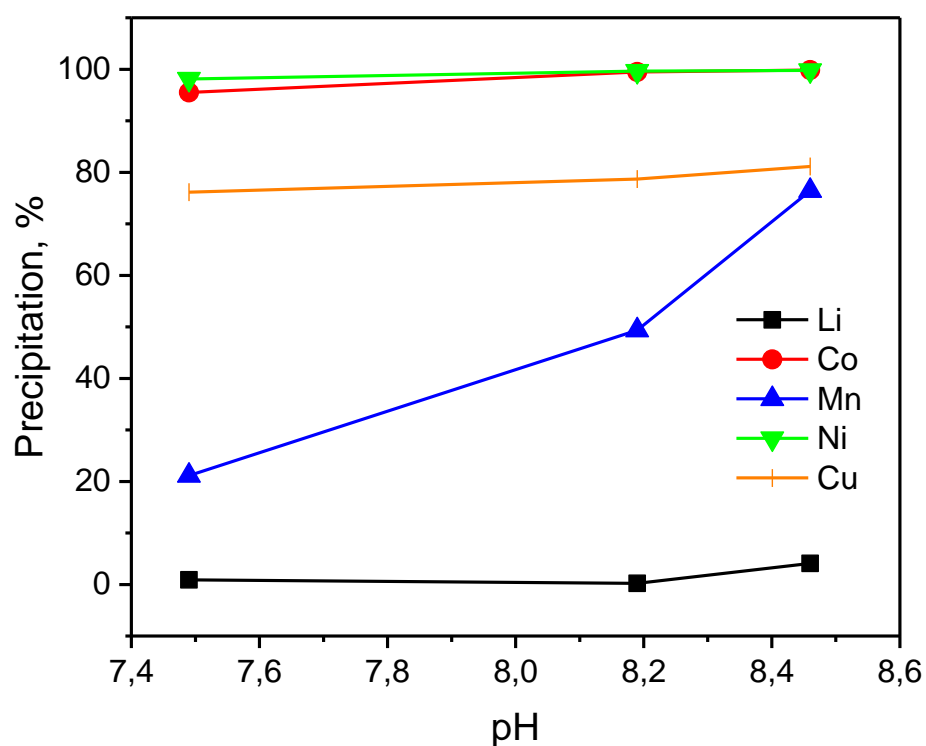
Figure 22. Precipitation after purification step. Reagent used was 2 M NaOH. Temperature 40 °C and agitation 300 rpm (Sample B4X2, B4Y2 and B4Z2, see Appendix C: Table C4).
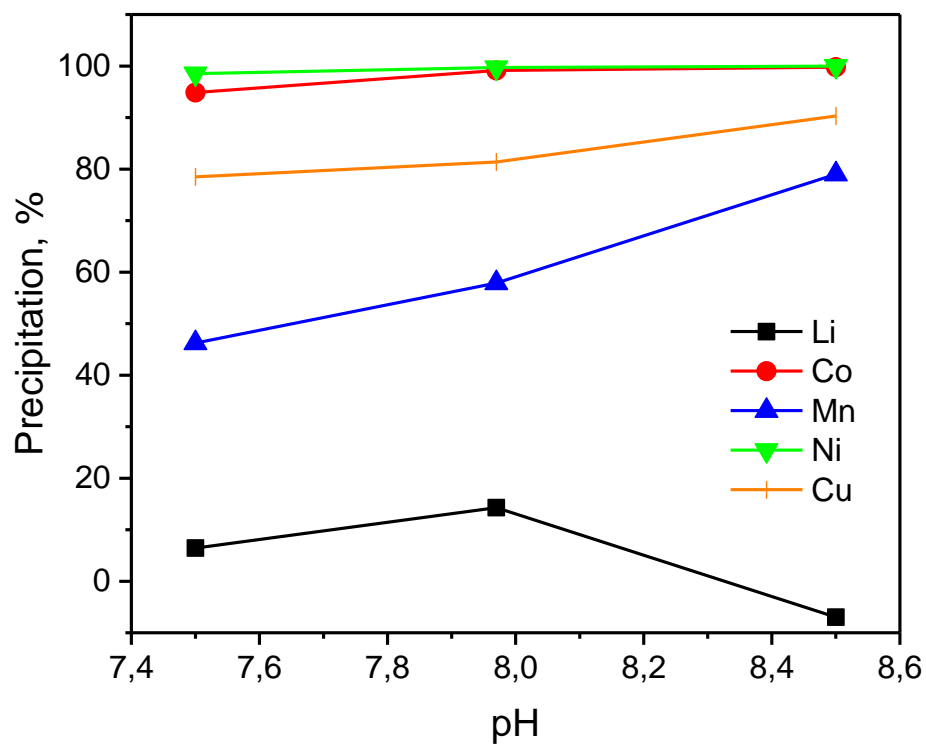
Figure 23. Precipitation after purification step. Reagent used was 2 M NaOH. Temperature 50 °C and agitation 300 rpm (Sample B5X1, B5Y1 and B5Z1, see Appendix C: Table C4).

Separation of metals was discovered to be difficult using 2 M NaOH in studied pH range and temperatures. For Co, Ni and Mn separation from Li was most efficient at 50 °C when pH was adjusted near 8.5. Precipitation efficiency of Mn was 79% in optimal conditions and it was concluded that higher efficiency was needed. Mn and Li separation from Co, Ni and Cu was most successful at 30 °C when pH was near 7.5. Nevertheless, Mn co-precipitation was relatively high, 17%.

The pH values during hydroxide precipitation experiment were investigated (see Table 14). Precise adjustment of the pH values proved to be more difficult than expected. In repetitive experiments the fluctuation between pH_e values were minor. The pH_e was constantly lower compared to target pH value except at 50 °C when target pH was 8.5.

Table 14. Summary of pH values during hydroxide precipitation experiments (see Appendix C: Table C2).

Temperature (°C)	Target pH	pH_i	Assumed pH_e	pH difference
30	7.5	7.5	7.47	-0.03
	8.0	8.01	7.98	-0.03
	8.5	8.66	8.56	-0.01
40	7.5	7.51	7.49	-0.02
	8.0	8.20	8.19	-0.01
	8.5	8.57	8.46	-0.11
50	7.5	7.53	7.50	-0.03
	8.0	8.06	7.97	-0.09
	8.5	8.49	8.5	0.01

Metal concentrations after optimizing the continued NaOH precipitation of PLS are presented in Table 15. Optimal conditions were 50 °C temperature and equilibrium pH of 8.5.

Table 15. Metal concentrations after continued optimal 2 M NaOH precipitation at 50 °C when pH was adjusted to 8.5.

Metal concentration (mg/l)	Li	Co	Ni	Mn	Cu	Al
	1017	722	31.7	568	22.7	<2

6.3 Carbonate precipitation of Co, Ni and Mn

After impurity removal, the PLS2 (Appendix B, Table B1) was used as initial solution in the carbonate precipitation experiments. In Table 12 the average metal concentrations are shown after impurity removal. The results from carbonate precipitation experiments are shown in Figure 24, Figure 25 and Figure 26 with varying temperature 30, 40 and 50 °C, respectively. 2 M Na_2CO_3 was used as a reagent to form insoluble compounds and simultaneously increase the pH value. It should be noted that excess of sodium carbonate was added to leaching liquor. The Na_2CO_3 decomposes as sodium and carbonate ion (CO_3^{2-}) (Eq. 32). Carbonate ions react with water according to Eq. 33 (Joesten, et al., 2007). The carbonate ions, which are not participating in ongoing reactions increase the pH value. Alternatively, NaOH could have been used for pH adjustment followed by Na_2CO_3 addition to precipitate compounds. The precipitation of Li, Co, Mn, Ni and Cu were investigated.

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-} \tag{32}$$

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \tag{33}$$

The assumed reactions of metal ions and carbonate ions are presented in Eq. 34 - 37.

$$Cu^{2+} + CO_3^{2-} \rightarrow CuCO_3 \tag{34}$$

$$Mn^{2+} + CO_3^{2-} \rightarrow MnCO_3 \tag{35}$$

$$Ni^{2+} + CO_3^{2-} \rightarrow NiCO_3 \tag{36}$$

$$Co^{2+} + CO_3^{2-} \rightarrow CoCO_3 \tag{37}$$

In order to recover Li_2CO_3 as pure product high precipitation efficiency of Co, Mn and Ni was a priority. However, a minimum loss of Li was the main objective. Unfavorable co-precipitation of Li as Li_2CO_3 is presented in Eq. 38.

$$2Li^+ + CO_3^{2-} \rightarrow Li_2CO_3 \tag{38}$$

In all temperatures, the unfavorable co-precipitation of Li_2CO_3 remains insignificant regardless of the pH value. At temperatures 40 and 50°C the precipitation efficiency of Li_2CO_3 was negative according to results. It can be assumed that no precipitation occurs or the amount was extremely small.
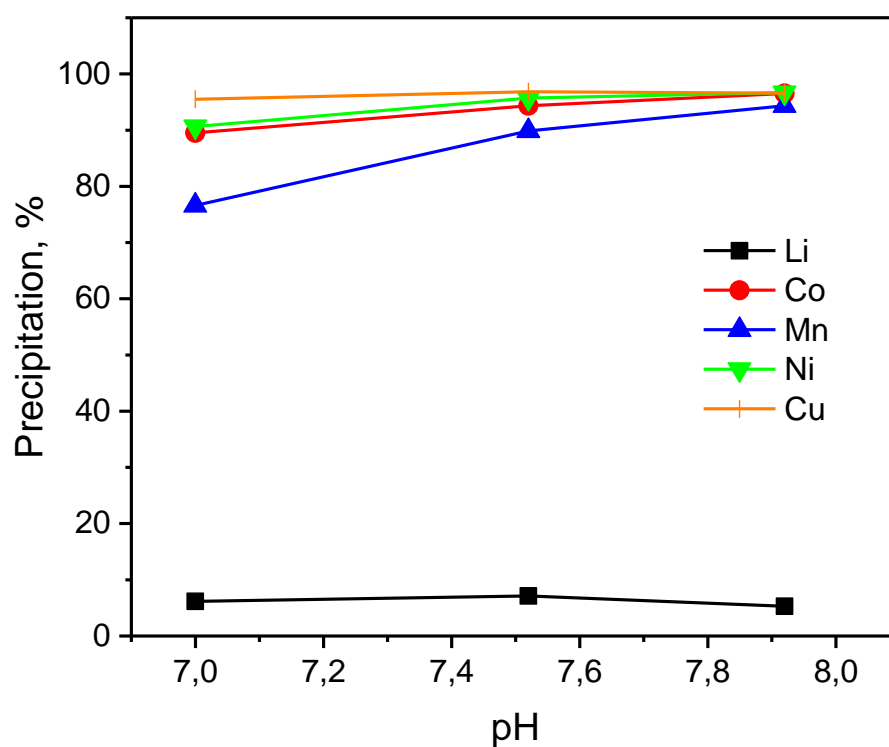
Figure 24. Precipitation efficiency (%) and pH dependency at 30 °C using 2 M Na₂CO₃ (Sample K3X2, K3Y2 and K3Z2, see Appendix D: Table D4).
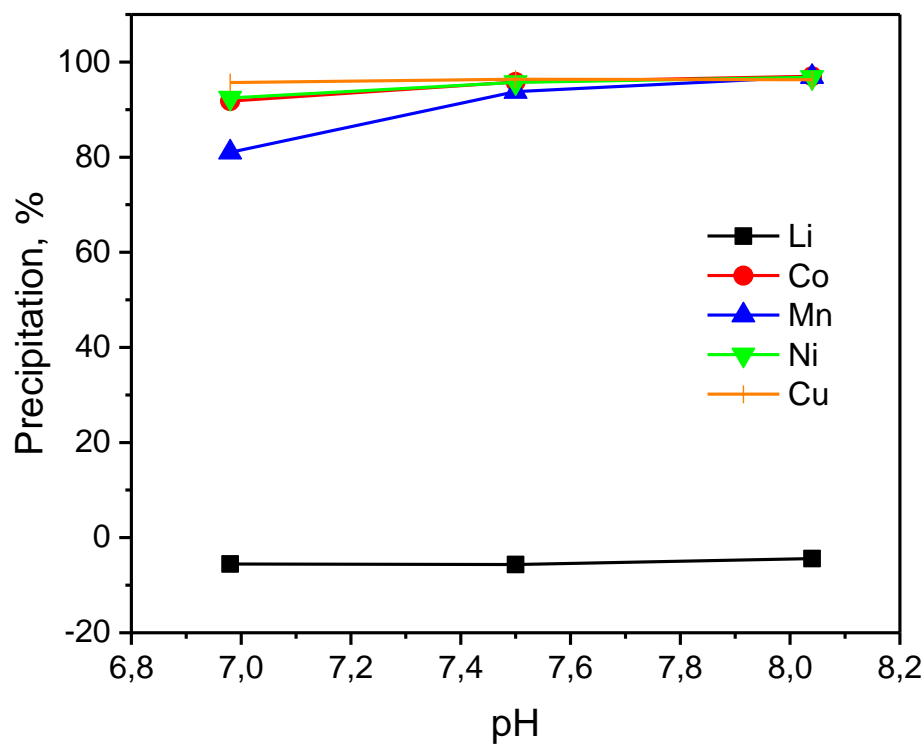
Figure 25. Precipitation efficiency (%) and pH dependency at 40 °C using 2 M Na₂CO₃ (Sample K4X1, K4Y1 and K4Z1, see Appendix D: Table D4).
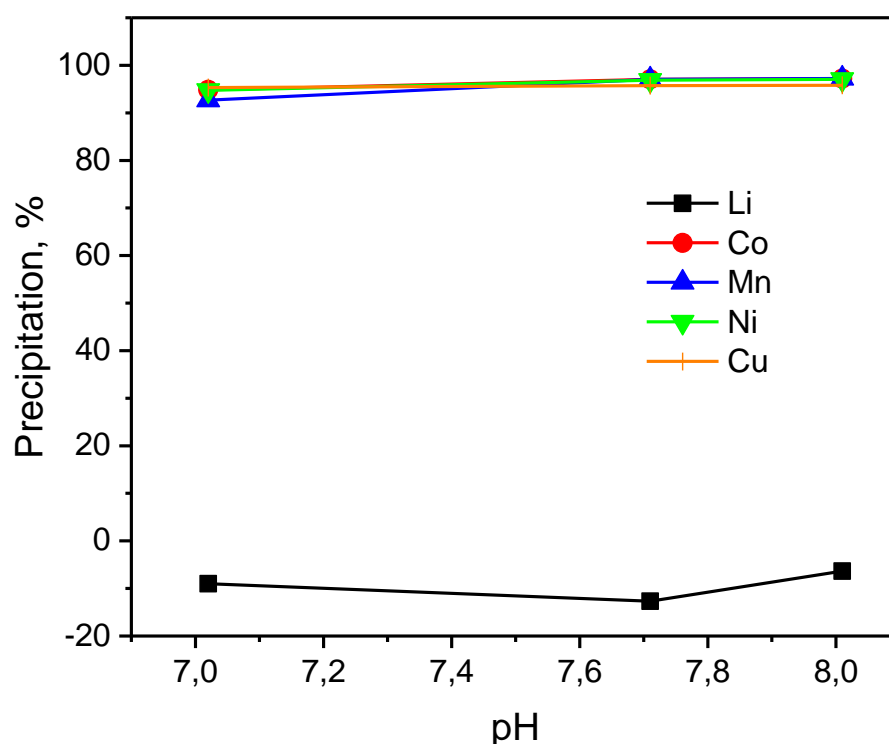
Figure 26. Precipitation efficiency (%) and pH dependency at 50 °C using 2 M Na₂CO₃ (Sample K5X1, K5Y1 and K5Z1, see Appendix D: Table D4).

The pH values during carbonate precipitation experiments were studied. In Table 16 the pH values observed during experiment are presented. Precise adjustment of the pH values was acknowledged to be achievable as metals reacted relatively fast in forming carbonate compounds. At 50 °C the increase in pH from 7.5 to 7.71 was due to fast addition of too much reagent. In repetitive experiments the fluctuation between final pH_e values was well within the limits of normal experimental error. In repetitive experiments the fluctuation between pH_e values were minor.

Table 16. Summary of pH values during carbonate precipitation experiments (see Appendix D: Table D2).

Temperature (°C)	Target pH	pH_i	Assumed pH_e	pH difference
30	7.0	6.99	7.00	0.01
	7.5	7.54	7.52	-0.02
	8.0	8.01	7.92	-0.09
40	7.0	6.98	6.98	0
	7.5	7.5	7.5	0
	8.0	8	8.04	0.04

50	7.0	7.01	7.02	0.01
	7.5	7.52	7.71	0.19
	8.0	8.00	8.01	0.01

Optimal process parameters for the carbonate precipitation step were $T = 50\ °C$ and $pH = 8$. Metal concentrations of PLS3 are presented in Table 17.

Table 17. Metal concentrations after optimal 2 M Na$_2$CO$_3$ precipitation at 50 °C when pH was adjusted to 8.0.

Metal concentration (mg/l)	Li	Co	Ni	Mn	Cu	Al	Fe
	1119	9.4	4.5	4.9	1.3	0.3	0.9

In Table 18 the obtained carbonate precipitate (m = 3.84 g) was analyzed and the metal content is presented as mg/g.

Table 18. Analyses of the precipitate (m = 3.84 g) obtained from the carbonate precipitation step.

ppm (mg/g)	Li	Co	Ni	Mn	Cu	Al	Fe
	1.9	161.6	40.2	47.6	6.5	6.2	0.2

Two similar PLS3 solutions were prepared separately and mixed together. After mixing, the solution was analyzed and metal concentrations (mg/l) are presented in Table 19. The leach liquor contained mainly Li (1199 mg/l) and small amount of Co (6.78 mg/l) as impurity. The concentrations of other metals were low. The amount of Na ions in the PLS3 before precipitation of Li$_2$CO$_3$ was calculated to be approximately 1.9 mol/l (see Appendix E: Table E9).

Table 19. Analyses of metal concentrations after purification and carbonate precipitation steps from remaining leach liquor.

Metal concentration (mg/l)	Li	Co	Ni	Mn	Cu	Al	Fe
	1199	6.78	1.23	0.92	0.63	0.30	0.85

In purity calculations, it was assumed that all the metals form assumed compounds and the all of the detected metal amount participates in the formation of the compound. In carbonate precipitation Co, Ni and Mn form carbonate compounds (Eq. 35 - 37). The purity of Co, Ni, Mn –precipitate was calculated to be relatively low, 51%. The obtained Co, Ni, Mn -precipitate is presented in Figure 27.

Figure 27. The obtained Co, Ni, Mn -precipitate from optimal carbonate precipitation.

6.4   Precipitation of Li₂CO₃

The raw material solution before Li crystallization was the mixture of two PLS3 solutions. The analyses of one PLS3 is presented in Table 19. First the PLS1 was purified with 2 M NaOH at 50 °C until pH was 5. The obtained PLS2 from purification was used in carbonate precipitation where 2 M Na_2CO_3 was added until pH was 8 at 50 °C. The obtained PLS3 was mixed with second PLS3 solution. Finally, Li ions were attempted to be crystallized as Li_2CO_3 compound by adding stoichiometric amount 1:1.2 ($[Li^+]:[CO_3^{2-}]$) of saturated Na_2CO_3 to remaining liquor at 50 °C. See detailed calculations in Appendix E Tables E10-E12. Figure 28 of the obtained powder materials, supposedly Li_2CO_3.
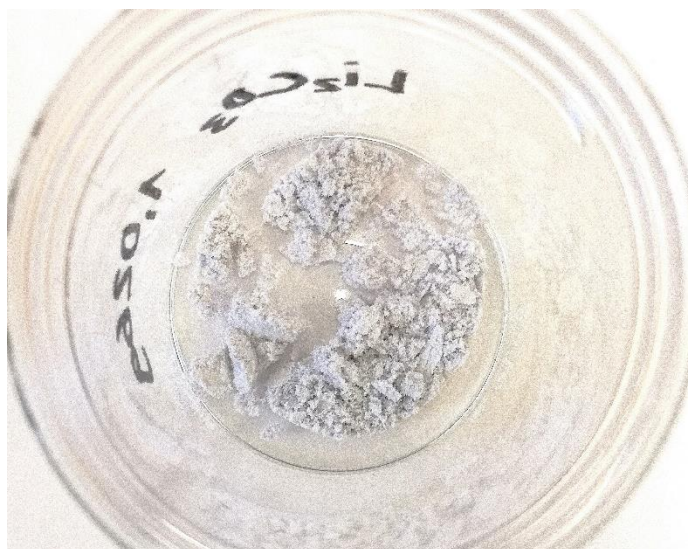
Figure 28. The obtained Li₂CO₃ powder.

Extensive chemical analyses of assumed Li_2CO_3 precipitate were carried out. Metal contents (mg/g) are presented in Table 20. The recovery percentage Li_2CO_3 can be calculated from the Li concentration before precipitation (Table 19) and Li wt.% after recovery (Table 20). Recovery percentage of Li_2CO_3 at 50 °C was 59%. Purity of the obtained Li_2CO_3 precipitate was calculated to be 95.3% according to metal analyses in Table 20. It was assumed that all the detected Li participated in the formation of Li_2CO_3.

Table 20. Analyses of Li₂CO₃ precipitate obtained from Li recovery process step. Metal fractions are presented as ppm (mg/g). The metals in focus are bolded.

Metal	ppm (mg/g)
Al	**0.09**
As	<0.02
B	0.03
Ba	0.02
Ca	0.1
Cd	<0.01
Co	**0.74**
Cr	<0.1
Cu	**0.03**
Fe	**0.06**
K	0.02
Li	**179**

Mg	0.96
Mn	**0.06**
Mo	<0.02
Na	14.5
Ni	**0.06**
P	<0.02
Pb	0.01
S	0.03
Sb	<0.02
Se	<0.02
Sn	0.04
Ti	<0.01
V	<0.02

XRD analysis of the obtained Li_2CO_3 showed that the powder contained Zabuyelite, which has the same chemical formula as lithium carbonate. In literature, XRD pattern of Li salt in the precipitation step of lithium carbonate has indicated Zabuyelite. Figure 29 and Figure 30 show that the positions, shape and ratio of spikes match.
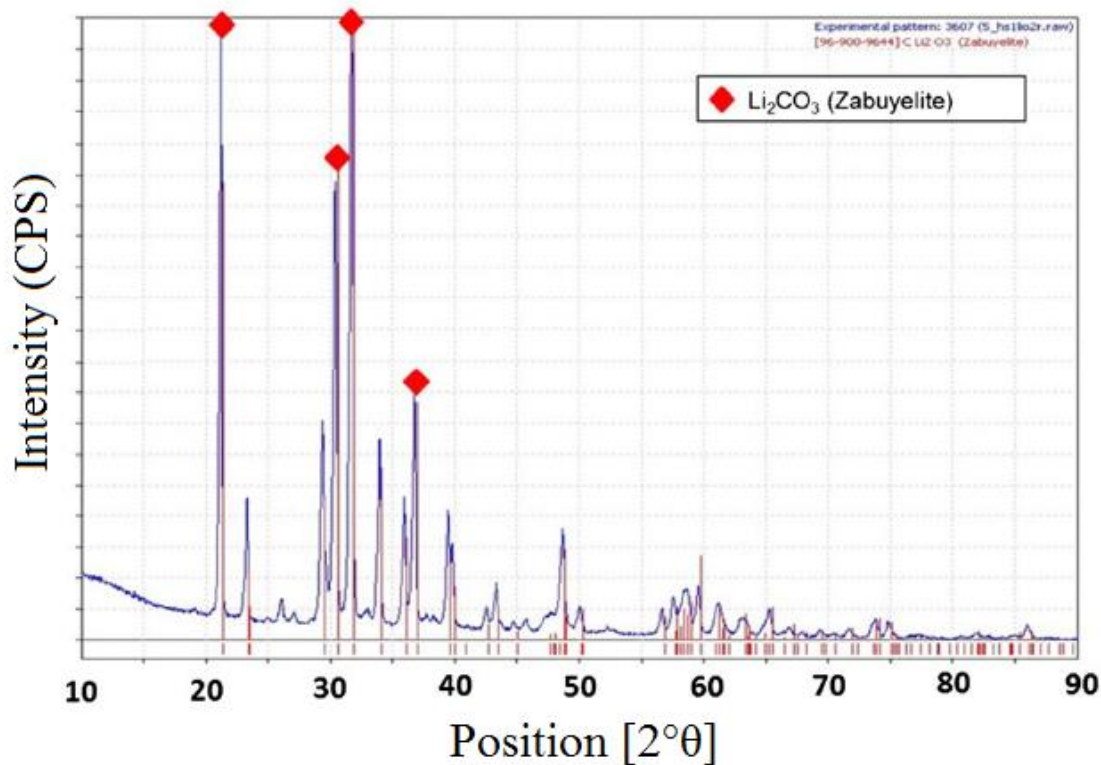
Figure 29. XRD of Li₂CO₃ (Wang & Friedrich, 2015).
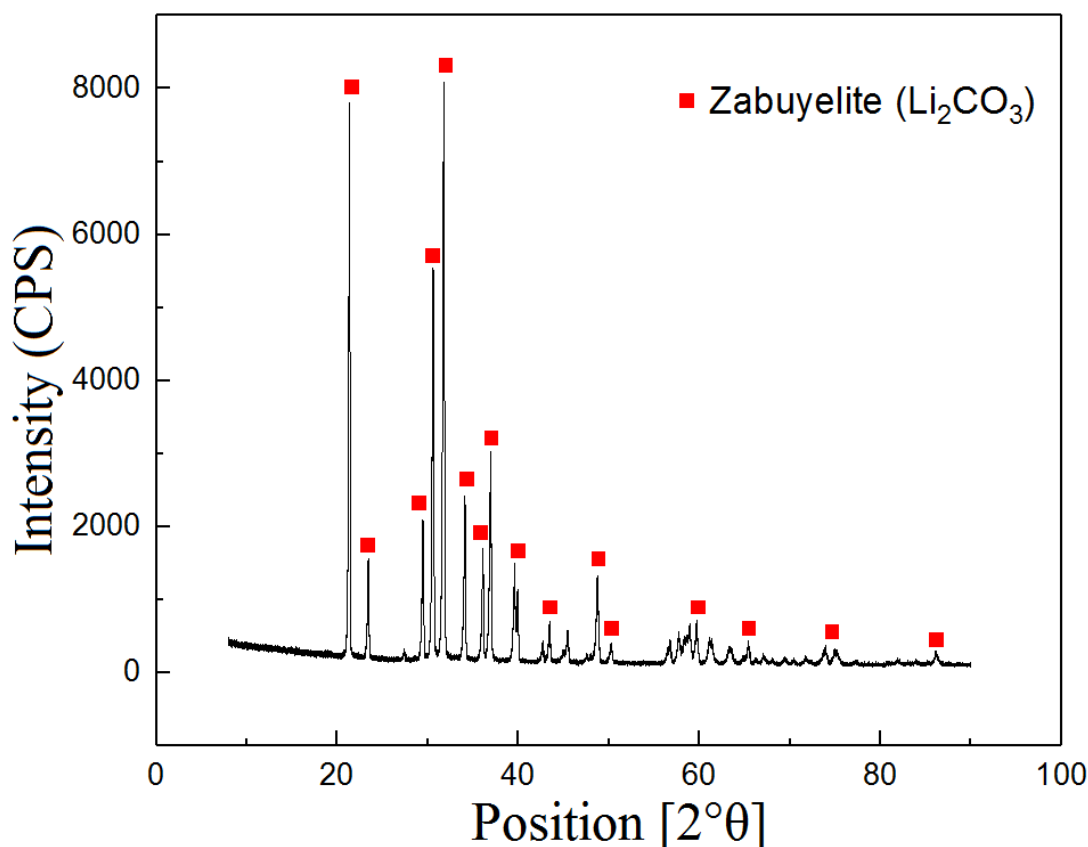
Figure 30. XRD analysis of the obtained Li₂CO₃ powder.

See Section 5.1 for general information about XRD, parameters and analysis methods used in scrap analysis. In the analysis of Li_2CO_3 powder, the scan area was 8 - 90 [2°θ] and rate 2.1 [2°θ]/per min.

6.5   SX using Na-Cyanex 272

Solvent extraction with saponified Cyanex 272 was performed to purified solution ($T = 50$ °C and *target pH* = 5). Detailed concentrations of the purified solution can be found in Appendix F in Table F1. The separation of Co and Mn from Ni and Li was investigated using 40% Na-Cyanex 272. The target pH was selected to be 5 according to Figure 10 and Figure 11. Additionally, varying O:A ratios (1:1 and 2:1) were investigated. In Figure 31 the extraction efficiencies (%) of investigated metals are presented at O:A 1:1 when average pH_e after extraction was 4.0. In Figure 32 the extraction efficiencies (%) of investigated metals are presented at O:A 2:1 when average pH_e after extraction was 5.3. See Appendix F for detailed calculations.
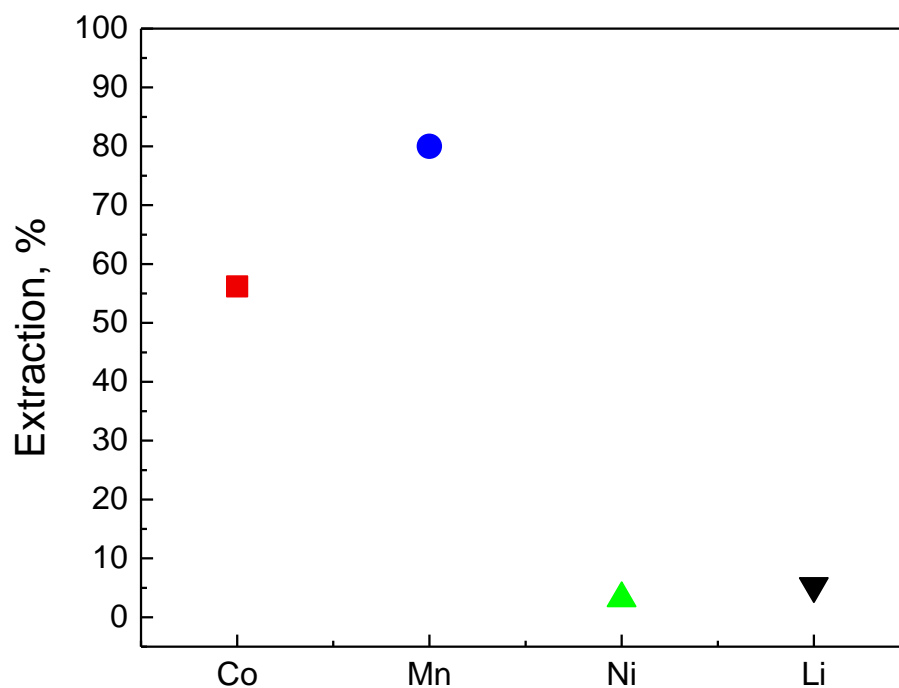
Figure 31. Average extraction efficiencies of Co, Mn, Ni and Li when O:A was 1:1 when average pH$_e$ was 4.0 (Appendix F: Table F4).
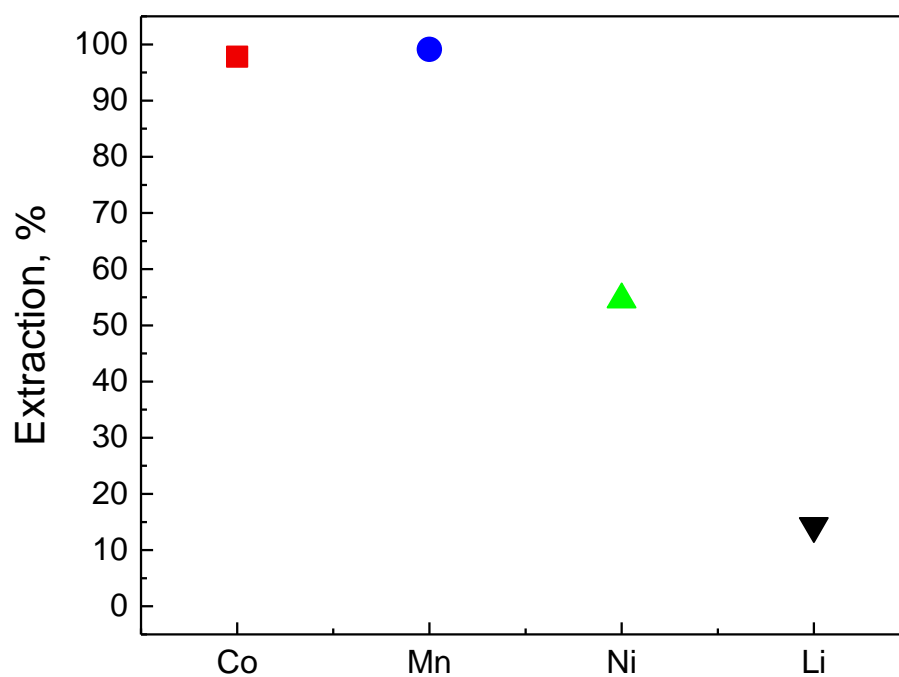
Figure 32. Average extraction efficiencies of Co, Mn, Ni and Li when O:A was 2:1 when average pH$_e$ was 5.3 (Appendix F: Table F4).

At O:A 1:1 the pH$_e$ was low compared to target pH value of 5. Still the results from separation at O:A 1:1 were surprisingly efficient. The extraction efficiencies of Co and Mn were 56% and 80%,

respectively. The co-extraction of Ni (3%) and Li (5%) remained low. However, one extraction stage would not be enough to separate Co and Mn from Ni and Li efficiently with O:A ratio 1:1. Calculated average stripping efficiencies were >90% for all the studied metals (Appendix F: Table F7). Co, Ni and Li stripping efficiencies were above 100% due to error in analyses. Error might have occurred due to inaccurate detection of small concentrations of metals in samples.

At $pH_e = 5.3$ the separation of Co and Mn from Ni and Li could be feasible due to high extraction of Co and Mn (>98%). At O:A 2:1 the target pH was slightly exceeded. Single stage extraction was successful in separation of Co (98%) and Mn (99%) from Ni and Li with O:A ratio 2:1. However, scrubbing is recommended to remove co-extracted Ni (55%) and Li (14%). Average stripping efficiencies were above 90% with all metals. The average stripping of Ni and Li was over 100% due to error in analyses. Detailed stripping calculation are presented in Appendix F in Table F3 and F5-F7.

Optimal condition for Co and Mn separation from Ni and Li was O:A 2:1 when $pH_e = 5.3$, T = 30 °C, contact time 15 min and agitation 400 rpm. Table 21 shows the metal concentrations in aqueous phase after optimal extraction and after stripping.

Table 21. Metal concentrations in aqueous phase after optimal (O:A 2:1) extraction and stripping using Na-Cyanex 272 as extractant (see Appendix F: Tables F2-F7).

Optimal SX experiment for separation of Co and Mn						
Extraction/Stripping	**O:A**	**pH_e**	**Li (mg/l)**	**Co (mg/l)**	**Ni (mg/l)**	**Mn (mg/l)**
Extraction	2:1	5.29	1109	157	373	9
Stripping	2:1	-	124	3273	270	457

7   Discussion

The purpose of this thesis was to investigate the recovery of Li, Co, Ni, Mn Cu, Al and Fe from LIB waste solution using precipitation and SX method. Two reagents (NaOH and Na_2CO_3), temperature and pH dependency were investigated during the precipitation experiments. In SX experiments O:A ratio and pH_e of the system were investigated using Na-Cyanex 272 as an extractant.

7.1   Precipitation experiments

Using precipitation method to remove impurity metals from the original leach liquor lead to unfavorable co-precipitation of Li, Co and Ni. The co-precipitation can be controlled to a certain limit by adjusting the pH precisely, yet loss of valuable metals was unavoidable. In this work it was preferred that the co-precipitation of valuable metals is ≤10% and the purification as efficient as possible. High precipitation efficiency of impurities with minor co-precipitation was achieved as the temperature and pH were optimized. To achieve efficient purification of the leach liquor temperature of 50 °C and pH 5.0 were chosen as optimal parameters. Fe (100%), Al (81%) and Cu (80%) were removed from the leach liquor maintaining the co-precipitation of Li, Co, Ni and Mn under 10%. High impurity removal was preferred over low co-precipitation results in order to obtain more pure products in later process steps. HCl leachate purification efficiencies were similar compared to literature were leaching solution was H_2SO_4.

After impurity removal, the continued hydroxide precipitation was conducted. Co, Ni, Mn and Li hydroxides were precipitated from the leach liquor at pH values 7.5, 8.0 and 8.5 at different temperatures (30, 40 and 50 °C). High precipitation efficiency of Co (mostly over 94%) and Ni (mostly over 97%) was achieved in studied pH range. The selectivity of Mn and Li over Co and Ni was achieved in lower pH values. Increase in the temperature increased the precipitation efficiency of Co, Ni and Mn, yet temperature had no obvious effect on precipitation of Li. Mn precipitation was most affected by the selected range of pH. Selectivity of Mn and Li over Co and Ni was concluded not to be enough considering loss of Mn. Optimal parameters for continued hydroxide precipitation were 50 °C temperature and equilibrium pH of 8.5. The recovery efficiencies of Co, Ni and Mn were 100%, 100% and 79%, respectively. The co-precipitation of Li was negative due to error in analysis. It was noted that in continued hydroxide precipitation 10-20 times less Cu was precipitated compared to carbonate precipitation.

After purification step the Co, Ni, Mn and Li carbonate precipitation was studied in pH values 7.0, 7.5 and 8.0 at different temperatures (30, 40 and 50 °C). High precipitation efficiency of Co, Ni and Mn was achieved in studied pH range. Co, Ni and Mn can be precipitated together as carbonates (over 90%) from the leach liquor while Li remains soluble. The co-precipitation of Li remained under 8% according to the results. Optimal conditions for carbonate precipitation were $T = 50$ °C and *target pH* = 8 when recovery efficiencies of Co, Ni and Mn were 97%.

Reproducibility was tested by repeating precipitation steps in chosen temperature. In the precipitation of hydroxides Li and Mn analyses results were fluctuating. In carbonate precipitation experiments same fluctuation was observed with Li concentrations. The recovery efficiencies were often negative yet it can be concluded that the co-precipitation of Li was as minor as expected. It was acknowledged that concentrated solutions might precipitate in the sampling equipment during analyses and therefore cause error.

During the precipitation experiments it was observed that process time and agitation affect the precipitation process. Shorter process time led to lower recovery rates due to incomplete precipitation reactions. Additionally, it seemed that higher agitation speed led to faster completion of ongoing reactions. The effect of process time and agitation speed were not studied in this work.

Closed system is recommended for future experiments to avoid the evaporation during precipitation in elevated temperature. In this work, the evaporation was estimated with water and acknowledged in recovery calculations (see Appendix). It should be acknowledged that the error in solution sample analyses was exclusively ±3%. Additionally, error caused by pH measurements, sample taking and temperature changes was within normal experimental error. The pH, sample taking and temperature adjustments were well within the limits of normal experimental error, ±0.1 and ±1 °C, respectively.

7.2 Precipitation process

According to results from precipitation experiments a precipitation process was designed and implemented. First impurities (Fe, Al and Cu) were removed with 2 M NaOH at $pH = 5$ and $T = 50$ °C. After filtration, the remaining leach liquor was treated with 2 M Na_2CO_3 to precipitate Co, Ni and Mn carbonates. Optimal parameters were $pH = 8$ and $T = 50$ °C.

After filtration, the leach liquor contains mainly Li. Li concentration was increased by evaporation of leach liquor to 1/3. Remaining solution contained 1199 mg/l of Li. Stoichiometric amount of saturated Na_2CO_3 was added to precipitate Li as Li_2CO_3 when $T = 50$ °C. In literature Li is often

recovered in higher temperature (≈100 °C) and therefore the recovery percentage is high. In this work 15% of Li was recovered due to low recovery temperature. XRD analysis of the Li_2CO_3 precipitate showed one crystal structures of Li_2CO_3, Zabuyelite. XRD analysis showed no impurities. However, the color of the precipitate indicated that small amounts of impurity compounds were present. It was assumed that at least one impurity affecting the color of the compound was $CoCO_3$.

In Section 5.4.4 impurities were suggested to precipitate first before Li_2CO_3 crystallization. Since the recovery efficiency was low due to the low recovery temperature, the obtained purity remained lower as well. The calculated purity of obtained Li_2CO_3 precipitate was 95.3%. Low purity was mainly assumed to be due to insufficient washing of Na. According to the precipitate analyses the amount of Li was 179 mg/g, Na 14.5 mg/g and all other analyzed metals <1 mg/g (Table 20). The purity of Li_2CO_3 could have been higher if all remaining Na would have been successfully washed. In literature 85.3% of Li has been recovered in crystallization process at 50 °C (Section 4.1.5). Higher recovery efficiency of Li was accomplished in this work. However, the obtained Li_2CO_3 precipitate was not furtherly purified in this work thus the purity was lower compared to literature (Section 4.1.5).

The washing of the Li_2CO_3 precipitate with above 50 °C distilled water was challenging. The dissolution of Li_2CO_3 should be avoided and simultaneously the dissolution of impurities should be efficient. Additionally, not all precipitate was recovered from the bottom of the beaker. Some of the precipitate was scraped from the bottom during experiment to avoid major loss of recovered metals.

7.3 SX experiments

In SX experiments the 40% saponified Cyanex 272 was successful in recovery of Mn (94%) from PLS2 solution (same solution was used in carbonate precipitation) with O:A was 1:1. Simultaneously 50% of Co was co-extracted, but Ni and Li co-extraction remained low (≤5%). At O:A 2:1 both Co and Mn could be extracted 98% and 99%, respectively. Co-extraction of Ni and Li were 55% and 14%, respectively. Scrubbing of organic from Ni and Li is necessary on future experiments to recover only Mn and Co from leach liquor. Scrubbing was not investigated in this work. Stripping with 2 M H_2SO_4 was efficient (>90% with all studied metals except Li) with contact time of 15 min. It was concluded that predicting the pH_e value in advance was challenging therefore optimal pH_e values should be achieved experimentally.

More experiments in SX are needed to optimize selective recovery of Co, Mn and Ni from leach liquor of LIBs. The effect of saponification rate in the selectivity of metals should be investigated in the future. Optimizing the extraction temperature could lead to better extraction efficiency. Washing of the extractant removes acid residues left from manufacturing and could be beneficial for the saponification process. According to literature, it is recommended to prefer the use of SSX method in the separation of Co and Mn, rather than SX. For further investigations ion exchange or P507 (also known as PC-88A) extractant is suggested for the separation of Ni and Li.

8 Conclusion

The precipitation process was implemented with purification, carbonate precipitation and Li crystallization steps. Fe, Al and Cu were successfully separated from Co, Ni, Mn and Li. In subsequent step the successful carbonate precipitation of Co, Ni and Mn was performed. Same procedures have been successful in literature with H_2SO_4 leach solution (Section 4.1). The obtained precipitate in first step of process was low purity (32%) due to co-precipitation of high concentrated Co and Na. The calculated purity of Co, Mn, Ni -precipitate was also only 51%. The fractions of analyzed impurity metals in Co, Mn, Ni -precipitate were low thus it was concluded that some metals that were not analyzed co-precipitated. The obtained precipitates could potentially be re-leached for conventional separation and/or purified via ion exchange. Obtained product from carbonate precipitation could be potentially used as precursor in battery manufacturing. Additionally, process precipitates could be sent to smelter.

Li is recommended to be recovered at higher temperature than 50 °C and preferably near 100 °C. It was noted that Li_2CO_3 purity (95%) was not battery grade level and further purification of obtained precipitate would be necessary (Section 4.1.5). Ion exchange or lixiviation could be potentially used to remove impurities. Lixiviation has been used in industry in the purification of Li_2CO_3 purification (Section 4.1.5)

According to results from precipitation process experiments, a process flow chart for the recovery of Fe, Al, Cu, Mn, Ni, Co and Li was built (Figure 33). First the powder material of spent LIBs was leached with 4 M HCl (PLS1). In neutralization step the impurities (Fe, Al and Cu) are precipitated at 50 °C with 2 M NaOH. PLS2 from neutralization step was treated with 2 M Na_2CO_3 at 50 °C. Two PLS3 were prepared, mixed and analyzed. Evaporation of PLS3 was carried out at 65 - 70 °C to concentrate the liquor. Li crystallization was performed at 50 °C with saturated Na_2CO_3.

Spent LIBs

4 M HCl → HCl leaching (T = 80 °C)

PLS1 (V = 100 ml)
Concentrations in mg/l: [Li] = 2548, [Co] = 16817, [Ni] = 1996, [Mn] = 2147,
[Fe] = 741, [Al] = 1510 and [Cu] = 2145

2 M NaOH
(V = 127 ml) → Hydroxide precipitation (T = 50 °C and pH = 5) →

Fe, Al, Cu -precipitate (2.53 g)
PPM (mg/g): Li = 4, Co = 100,
Ni = 21, Mn = 7, Cu = 74, Al =
57, Fe = 22

PLS2 (V = 200 ml)
Concentrations in mg/l: [Li] = 1034, [Co] = 5417, [Ni] = 892, [Mn] = 995, [Fe]
= 0.85, [Al] = 100 and [Cu] = 105

2 M Na$_2$CO$_4$
(V = 24 ml) → Carbonate precipitation (T = 50 °C and pH = 8) →

Co, Ni Mn -precipitate (3.84 g)
PPM (mg/g): Li = 2, Co = 162,
Ni = 40, Mn = 48, Cu = 7, Al =
6, Fe = <1

PLS3
Concentration in mg/l: [Li] = 1119, [Co] = 9, [Ni] = 4, [Mn] = 5, [Fe] = 1, [Al]
= 100 and [Cu] = 105

2 x PLS3 prepared and mixed (V = 300 ml)
Concentrations in mg/l: [Li] = 1199, [Co] = 7 [Ni] = 1, [Mn] = 1,
[Fe] = 1, [Al] = 0 and [Cu] = 1

Evaporation (T = 65-70 °C and final volume of liquor =
100 ml)

Saturated Na$_2$CO$_4$
(V = 11 ml) → Li precipitation (T = 50 °C)

1.03 g of powder: Li 179 mg/g, Co 1 mg/g and Na mg/g
Li$_2$CO$_3$ recovery efficiency 59% and purity 95%

Figure 33. Investigated unit processes and resulting flow chart for the recovery of Li$_2$CO$_3$ from spent LIBs via precipitation method. PLS refers to product liquid solution and all concentrations are in mg/l. The precipitate analyses are presented in mg/g.

According to results from SX experiments, a process flow chart for the separation of Co and Mn from Ni and Li was built (Figure 34). PLS1 was purified adding 2 M NaOH. PLS2 was used as solution prior to SX. 40% saponified Cyanex 272 was used as extractant at O:A 2:1. In reality the process will be more complex due to recommended scrubbing stages, possible circulation of effluent to another SX and regeneration of extractant as demonstrated in Figure 9.

PLS1 (V = 100 ml)
Concentrations in mg/l: [Li] = 2548, [Co] = 16817, [Ni] = 1996, [Mn] = 2147,
[Fe] = 741, [Al] = 1510 and [Cu] = 2145

Hydroxide precipitation (T = 50 °C and
pH = 5)

PLS2 (V = 200 ml)
Concentrations in mg/l: [Li] = 1295, [Co] = 6976, [Ni] = 821, [Mn] = 992 and
[Cu] = 113

Aqueous phase PLS2 (V = 10 ml)

Organic (V = 20 ml): 20 vol%
Na-Cyanex 272, 70 vol%
sulfonated kerosene and 10
vol% TBP

SX using 40% saponified Cyanex 272 (T
= 30 °C, O:A = 2:1 and t = 15 min)

Phase separation

Organic Phase
Concentrations in mg/l: [Li] =
186, [Co] = 6820, [Ni] = 26 and
[Mn] = 983

Aqueous Phase
Concentrations in mg/l: [Li] =
1109, [Co] = 157, [Ni] = 373
and [Mn] = 9

Stripping with 2 M H$_2$SO$_4$
(T = 30 °C, organic-to-strip
solution ratio 1:1 and t = 15
min)

Co, Mn -raffinate
Concentrations in mg/l: [Li] =
124, [Co] = 3273, [Ni] = 270
and [Mn] = 457

**Figure 34. Investigated unit processes and resulting flow chart for the separation of Co and Mn
from Ni and Li via SX method. PLS refers to product liquid solution and all concentrations are in
mg/l.**

9 References

Aaltonen, M., 2017. *Hydrometallurgia akkujen kierrätyksessä ,* Pori: Prizztech.

Acker, J., 2016. *ENV Vision - A Recycler's Perspective.* Washington DC, Retriev Technologies.

Al-Thyabat, S., Nakamura, T., Shibata, E. & Iizuka, A., 2013. Adaption of minerals processing operations for lithium-ion (LiBs) and nickel metal hydride (NiMH) batteries recycling: Critical review. *Minerals Engineering,* Volume 45, pp. 4-17.

Biswas, R. & Singha, H., 2007. Solvent extraction of Cu(II) by purified cyanex 272. *Indian Journal of Chemical Technology,* Volume 14, pp. 269-275.

Bi, Y. et al., 2016. Stability of Li2CO3 in cathode of lithium ion battery and its influence on electrochemical performance. *The Royal Society of Chemistry,* Volume 6, pp. 19233-19237.

Castillo, S., Ansart, F., Laberty-Robert, C. & Portal, J., 2002. Advances in the recovering of spent lithium battery compounds. *Journal of Power Sources,* Volume 112, pp. 247-254.

Chagnes, A., 2015a. Fundamentals in Electrochemistry and Hydrometallurgy. In: A. Chagnes & J. Światowska, eds. *Lithium Process Chemistry.* s.l.:Elsevier, pp. 41-80.

Chagnes, A., 2015b. Lithium Battery Technologies: Electrolytes. In: A. Chagnes & J. Światowska, eds. *Lithium Process Chemistry.* s.l.:Elsevier, pp. 167-190.

Chen, L. et al., 2011. Process for the recovery of cobalt oxalate from spent lithium-ion batteries. *Hydrometallurgy,* Volume 108, pp. 80-86.

Chen, X. et al., 2015. Separation and recovery of metal values from leaching liquor of mixed-type of spent lithium-ion batteries. *Separation and Purification Technology,* Volume 144, pp. 197-205.

Christmann, P. et al., 2015. Global Lithium Resources and Sustainability Issues. In: A. Chagnes & S. J, eds. *Lithium Process Chemistry.* France: Elsevier, p. 300.

Cytec Industries Inc., 2008. *Cytec Solvany Group.* [Online] Available at: http://www.cytec.com/products/cyanex-272 [Accessed 2 1 2017].

Dorella, G. & Mansur, M., 2007. A study of the separation of cobalt from spent Li-ion battery residues. *Journal of Power Sources,* Volume 170, pp. 210-215.

Dutrow, B. & Clark, C., 2016. *X-ray Powder Diffraction (XRD).* [Online] Available at: http://serc.carleton.edu/research_education/geochemsheets/techniques/XRD.html [Accessed 14 5 2017].

Ekberg, C. & Petranikova, M., 2015. Lithium Batteries Recycling. In: A. Chagnes & J. Światowska, eds. *Lithium Process Chemistry.* s.l.:Elsevier, pp. 233-267.

EPBA, 2007. *Product information primary and rechargeable batteries.* [Online] Available at: http://www.epbaeurope.net/pub_technicalSupport.html [Accessed 23 September 2016].

Ferreira, D., Prados, L., Majuste, D. & Mansur, M., 2009. Hydrometallurgical separation of aluminium, cobalt, copper and lithium from spent Li-ion batteries. *Journal of Power Sources,* Volume 187, pp. 238-246.

Free, M., 2013. *Hydrometallurgy: Fundamentals and Applications.* 3rd ed. s.l.:Wiley-TMS.

Gaines, L., 2014. The future of automotive lithium-ion battery recycling: Charting a sustainable course. *Sustainable Metals and Technologies,* Volume 1-2, pp. 2-7.

Goonan, T., 2012. *Lithium Use In Batteries,* Reston: USGS.

Granata, G. et al., 2012. Product recovery from Li-ion battery wastes coming from an industrial pre-treatment plant: Lab scale tests and process simulations. *Journal of Power Sources,* Volume 206, pp. 393-401.

Higuchi, A., Ankei, N., Nishihama, S. & Yoshizuka, K., 2016. Selective Recovery of Lithium Cathode Materials of Spent Lithium Ion Battery. *The Journal of Minerals, Metals and Materials,* 68(10), pp. 2624-2631.

Huang, Y. et al., 2016. A stepwise recovery of metals from hybrid cathodes of spent Li-ion batteries with leaching-flotation-precipitation process. *Journal of Power Sources,* Volume 325, pp. 555-564.

Joesten, M., Hogg, J. & Castellion, M., 2007. *The World of Chemistry: Essentials.* 4th ed. Belmont: Thomson Learning Inc..

Joulié, M., Laucournet, R. & Billy, E., 2014. Hydrometallurgical process for the recovery of high value metals from spent lithium nickel cobalt aluminium oxide based lithium-ion batteries. *Journal of Power Sources,* Volume 247, pp. 551-555.

JX Nippon Mining & Metals Corporation, 2009. *JX Nippon Mining & Metals.* [Online] Available at: http://www.nmm.jx-group.co.jp/english/news/2009/20090903e.html [Accessed 7 1 2016].

Kang, J. et al., 2010. Preparation of cobalt oxide from concetrated cathode material of spent lithium ion batteries by hydrometallurgical method. *Advanced Powder Technology,* Volume 21, pp. 175-179.

Lemaire, J. et al., 2014. Lithium recovery from aqueous solution by sorption/desorption. *Hydrometallurgy,* Volume 143, pp. 1-11.

Li, L. et al., 2013. Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assesment. *Journal of Power Sources,* Volume 233, pp. 180-189.

Linden, D. & Reddy, T., 1995. *Handbook of Batteries.* Third ed. s.l.:McGraw-Hill.

Liu, F. et al., 2017. Recovery and separation of Ga and Ge from oxalate solution of zinc refinery residues using N235 and TBP. *Article is currently under the review process,* p. 38.

Lorente, B. et al., 2016. Life Cycle and Sustainability. In: *Lithium Process Chemistry.* s.l.:Elsevier, pp. 269-288.

Lowe, M., Tokuoka, S., Trigg, T. & Gereffi, G., 2010. *Lithium-ion Batteries for Electric Vehicles: The U.S. Value Chain,* Durham: Center on Globalization, Governance & Competitiveness Duke University.

Ma, L., Nie, Z., Xi, X. & Han, X., 2013. Cobalt recovery from cobalt-bearing waste in sulphuric and citric acid systems. *Hydrometallurgy,* Volume 136, pp. 1-7.

Mansur, M., 2011. Solvent extraction for metal and water recovery from industrial wastes and effluents. *Revista Escola de Minas,* 64(1).

Meshram, P., Pandey, B. & Mankhand, T., 2015. Hydrometallurgical processing of spent lithium ion batteries (LIBs) in the presence of a reducing agent with emphasis on kinetics of leaching. *Chemical Engineering Journal ,* Volume 281, pp. 418-427.

Morel, H., 2010. *Ultra High Temperature (UHT) technology at Umicore.* s.l., Umicore.

Nan, J. et al., 2006. Recovery of metal values from a mixture of spent lithium-ion batteries and nickel-metal hydride batteries. *Hydrometallurgy,* Volume 84, pp. 75-80.

National Center for Biotechnology Information , 2017. *Homepage.* [Online] Available at: https://pubchem.ncbi.nlm.nih.gov/ [Accessed 21 3 2017].

Nazim, M., Pal, P., Al Shoaibi, A. & Elkamel, A., 2012. Optimization of the Cementation Process for the Removal of Copper in Process Effluent Discharges. *Chemical engineering technology,* 35(10), pp. 1744-1750.

Nguyen, V. et al., 2015. The Separation and Recovery of Nickel and Lithium from the Sulfate Leach Liquor of Spent Lithium Ion Batteries using PC-88A. *Korean Chem. Eng. Res,* 53(2), pp. 137-144.

Noubactep, C., 2013. Relevant Reducing Agents in Remediation Fe0 / H2O Systems. *CLEAN - Soil, Air, Water ,* 41(5), pp. 493-502.

Ordoñez, J., Gago, E. & Girard, A., 2016. Processes and technologies for the recycling and recovery of spent lithium-ion batteries. *Renewable and Sustainable Energy Reviews,* Volume 60, pp. 195-205.

Painuly, A., 2015. Separation and recovery of vanadium from spent vanadium pentaoxide catalyst by Cyanex 272. *Environmental Systems Research,* Volume 4, pp. 1-7.

Peters, R. & Shem, L., 1993. *Separations of heavy metals: Removal from industrial wastewaters and contaminated soil,* Argonne: Argonne National Lab..

Pospiech, B., 2015. Synergistic solvent extraction of Co(II) and Li(I) from aqueous chloride solutions with mixture of Cyanex 272 and TBP. *Physiochemical Problems of Mineral Processing,* 52(1), pp. 353-364.

Pranolo, Y., Zhang, W. & Cheng, C., 2010. Recovery of metals from spent lithium-ion battery leach solutions with mixed solvent extractant system. *Hydrometallurgy,* Volume 102, pp. 37-42.

Saloojee, F. & Lloyd, J., 2015. *Lihtium Battery Recycling Process,* Parklands: Crundwell Management Solutions (PTY) LTD, t/a CM solutions (PTY) LTD.

Sharkey, J. & Lewin, S., 1971. Conditions governing the formation of atacamite and paratacamite. *The American Mineralogist,* Volume 56, pp. 179-192.

Shin, S. et al., 2012. *Method for recovery of cobalt and manganese from spent cobalt-manganese-bromide (cmb) catalyst and method for producing cmb catalyst including the recovery method.* United States of America, Patent No. US 13/211,063.

Shin, S. et al., 2005. Development of a metal recovery process from Li-ion battery wastes. *Hydrometallurgy,* Volume 79, pp. 172-181.

Silem, A. & Boualia, A. M. A., 1990. The effect of raw and sulfonated kerosene-type diluent on the solvent extraction of uranium and co-extractable impurities from solutions. Part 2. Industrial phosphoric acid. *Hydrometallurgy,* Volume 24, pp. 11-17.

SQM, 2014. *Sociedad Quimica y Minera se Chile S.A. Annual Report 2014,* s.l.: SQM.

Srinivas, C. et al., 1994. *Alkaline hydrolysis processes for treatment and disposal of purex solvent waste,* Bombay: Government of India Atomic Energy Commission.

Swain, B., 2017. Recovery and recycling of lithium: A review. *Separation and Purification Technology,* Volume 172, pp. 388-403.

Swain, B., Lee, J., Jeong, J. & Lee, G., 2006. *Separation of cobalt and lithium from mixed sulfate solution using organophosphorous extractant Na-Cyanex 272.* Beijing, ResearchGate.

Światowska, J. & Barboux, P., 2015. Lithium Battery Technologies: From the Electrodes to the Batteries. In: A. Chagnes & J. Światowska, eds. *Lithium Process Chemistry.* s.l.:Elsevier, pp. 125-166.

Takacova, Z., Havlik, T., Kukurugya, F. & Orac, D., 2016. Cobalt and lithium recovery from active mass of spent Li-ion batteries: Theoretical and experimental approach. *Hydrometallurgy,* Volume 163, pp. 9-17.

Tedjar, F. & Foudraz, C., 2004. *Procede de recyclage en melange de piles et batteries a base d'anode en lithium..* France, Patent No. FR 2 868 603.

Thackeray, M., Wolverton, C. & Isaacs, E., 2012. Electrical energy storage for transportation—approaching the limits of, and going beyond, lithium-ion batteries. *Energy & Environment Science,* Issue 5, pp. 7854-7863.

Tran, T. & Luong, V., 2016. Lithium Production Processes. In: A. Chagnes & J. Swiatowska, eds. *Lithium Process Chemistry - Resources, Extraction, Batteries and Recycling.* s.l.:Elsevier, pp. 81-124.

Tunsu, C. & Retegan, T., 2016. Hydrometallurgical Processes for the Recovery of Metals from WEEE. In: *WEEE Recycling.* s.l.:Elsevier, pp. 139-175.

Umicore, 2017. *Precious Metal Refining.* [Online] Available at :http://pmr.umicore.com/en/ [Accessed 2 May 2017].

UNEP, 2011. *Recycling Rates of Metals - A Status Report,* Paris: UNEP.

UNEP, 2013. Metal Recycling - Opportunities, Limits, Infrastructure. In: M. Reuter, et al. eds. s.l.:International Researc Panel, p. 316.

USGS, 2016. *Mineral Commodity Summaries, January 2016,* s.l.: United States Geological Survey.

Wang, H. & Friedrich, B., 2015. Development of Highly Efficient Hydrometallurgical Recycling Process for Automotive Li-Ion Batteries. *Journal of Sustainable Metallurgy,* Issue 1, pp. 168-178.

Wang, H., Vest, M. & Friedrich, B., 2011. *Hydrometallurgical processing of Li-Ion battery scrap from electric vehicles,* Aachen: Institut für Metallurgische Prozesstechnik und Metallrecycling.

Wang, J. et al., 2012. Leaching study of spent Li-ion batteries. *Procedia Environmental Sciences,* Volume 16, pp. 443-450.

Wang, M., Zhang, C. & Zhang, F., 2016. An environmental bening process for cobalt and lithium recovery from spent lithium-ion batteries by mechanochemical approach. *Waste management,* Volume 51, pp. 239-244.

Warner, J., 2015. *Handbook of Lithium-Ion Battery Pack Design - Chemistry, Components, Types and Terminology.* s.l.:Elsevier.

Vliegen, J., 2010. *Battery Recycling.* s.l., Umicore.

Zeng, X. & Li, J., 2014. Innovative application of ionic liquid to separate Al and cathode. *Journal of Hazardous Materials,* Volume 271, pp. 50-56.

Zhang, P. et al., 1998. Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries. *Hydrometallurgy,* Volume 47, pp. 259-271.

Zhao, J. et al., 2011. Synergistic extraction and separation of valuable metals from waste cathodic material of lithium ion batteries using Cyanex272 and PC-88A. *Separation and Purification Technology,* Volume 78, pp. 345-351.

Zhu, P., Chen, Y., Wang, L. & Zhou, M., 2012. Treatment of waste printed circuit board by green solvent using ionic liquid. *Waste Management,* 32(10), pp. 1914-1918.

Zhu, S. et al., 2012. Recovery of Co and Li from spent lithium-ion batteries by combination method of acid leaching and chemical precipitation. *Transactions of Nonferrous Metals Society of China,* Volume 22, pp. 2274-2281.

10 Appendix A

The metal concentrations in the raw material before any experiments are listed in Table 8. Table A1 presents the analyzed metals concentrations after purification experiments using 2 M NaOH. Purification was studied in different temperatures and pH values.

Table A1. Analyzed metal concentrations (mg/l) with temperature (T), target pH and sample name.

Metal concentrations after removal of impurities									
T (°C)	**Target pH**	**Sample**	**Li (mg/l)**	**Co (mg/l)**	**Ni (mg/l)**	**Mn (mg/l)**	**Cu (mg/l)**	**Al (mg/l)**	**Fe (mg/l)**
30	5	A3X2	1070	7269	827	918	401.7	238.2	1.6
30	5.5	A3Y2	1095	6855	762	921	106.5	94.9	1.4
30	6	A3Z2	1043	5914	610	881	40.9	11.3	1.3
40	5	A4X1	1273	7519	855	945	347.7	190.8	1.2
40	5.5	A4Y1	1030	6532	741	897	90.2	54.6	1.2
40	6	A4Z1	1040	5762	546	878	36.7	6.1	1.5
50	5	A5X1	1098	7302	795	903	176.6	129.8	1.2
50	5.5	A5Y1	1121	6644	647	908	55.7	18.0	1.2
50	6	A5Z1	1097	5087	362	888	24.3	<1	1.4
40	5	A4x2	1250	7082	762	927	85.0	87.6	1.6
40	5.5	A4z2	1137	5227	406	993	22.5	6.9	1.1
40	6	A4y2	1187	6308	633	986	43.5	15.6	1.3

Table A2 shows the equilibrium pH values ($\mathrm{pH_e}$), calculated pH difference and added amount of NaOH (ml). The presented pH difference is between initially adjusted pH ($\mathrm{pH_i}$) and equilibrium pH ($\mathrm{pH_e}$) as shown in Eq. A1.

$$\mathrm{pH\ difference} = \mathrm{pH_e value} - \mathrm{pH_i value} \qquad \text{(A1)}$$

Table A2. The equilibrium pH values ($\mathrm{pH_e}$) and NaOH addition (ml). The calculated pH difference between equilibrium and target pH.

Sample	$\mathrm{pH_e}$	$\mathrm{pH_i}$	pH difference	NaOH addition (ml)
A3X2	5.10	5.00	0.10	124.2
A3Y2	5.59	5.56	0.03	128
A3Z2	5.94	6.00	-0.06	131.2
A4X1	5.03	4.97	0.06	129.6

A4Y1	5.41	5.49	-0.08	133.32
A4Z1	5,74	5.99	-0,25	137.8
A5X1	5.06	5.00	0.06	128.65
A5Y1	5.38	5.51	-0.13	132.99
A5Z1	5.79	6.01	-0.22	139.05
A4x2	5.16	5.18	-0.02	127
A4z2	5.47	5.55	-0.08	130
A4y2	5.82	6.03	-0.21	134.2

The dilution of leach liquor was acknowledged in the precipitation experiments. Table 22 presents the calculated metal concentrations after NaOH additions. The metal concentrations were calculated using following Eq A2.

$$C(Me) = \text{original } C(Me) * \frac{\text{Volume before experiment}}{(\text{Volume after reagent addition} - \text{evaporation})} \quad (A2)$$

where C(Me) is metal concentration and evaporation is measured in (ml).

Evaporation was measured to be 1 ml/h when $T = 40 \ °C$ and 2 ml/h when $T = 50 \ °C$. In each experiment where the pH was gradually raised by three steps for example 5.0, 5.5 and 6.0 the process time was approximately 3 h. The process time includes pH adjustment, retention time, sample taking and filtration. If the pH was only adjusted to one specific value, the process time was approximately 1 h.

Table A3. The calculated metal concentrations after 2 M NaOH addition. Temperature (T), target pH and sample name are presented.

Metal concentrations after 2 M NaOH									
T (°C)	Target pH	Sample	Li (mg/l)	Co (mg/l)	Ni (mg/l)	Mn (mg/l)	Cu (mg/l)	Al (mg/l)	Fe (mg/l)
30	5	A3X2	1136.49	7500.89	890.28	957.40	890.28	673.51	330.51
30	5.5	A3Y2	1117.54	7375.88	875.44	941.45	875.44	662.28	325
30	6	A3Z2	1102.08	7273.79	863.32	928.42	863.32	653.11	320.50
40	5	A4X1	1114.61	7356.52	873.14	938.98	873.14	660.54	324.15
40	5.5	A4Y1	1101.49	7269.89	862.86	927.92	862.86	652.76	320.33

40	6	A4Z1	1085.18	7162.27	850.09	914.18	850.09	643.10	315.59
50	5	A5X1	1124.2	7419.81	880.66	947.05	880.65	666.23	326.94
50	5.5	A5Y1	1112.71	7343.99	871.65	937.38	871.65	659.42	323.59
50	6	A5Z1	1093.33	7216.05	856.47	921.05	856.47	647.93	317.96
40	5	A4x2	1127.43	7441.15	883.19	949.78	883.19	668.14	327.88
40	5.5	A4y2	1117.54	7375.88	875.44	941.45	875.44	662.28	325
40	6	A4z2	1102.08	7273.79	863.32	928.42	863.32	653.11	320.50

Table A4 presents the calculated recovery efficiencies (%) for studied metals. Precipitation efficiencies were calculated according to Eq. A3.

$$\% = \left(1 - \left(\frac{\text{analyzed C(Me) after filtration}}{\text{C(Me)after reagent addition}}\right)\right) * 100 \qquad (A3)$$

Table A4. The calculated recovery efficiencies (%) for each metal. Temperature (T), target pH and sample name are presented. Efficiencies in red were interpreted as inaccurate due to error in analyses.

					Recovery efficiencies				
T (°C)	Target pH	Sample	Li (%)	Co (%)	Ni (%)	Mn (%)	Cu (%)	Al (%)	Fe (%)
30	5	A3X2	5.89	3.10	7.06	4.10	58.01	64.63	99.50
30	5.5	A3Y2	2.05	7.07	12.91	2.12	88.68	85.67	99.57
30	6	A3Z2	5.36	18.69	29.38	5.11	95.59	98.28	99.59
40	5	A4X1	-14.19	-2.21	2.07	-0.69	62.94	71.11	99.63
40	5.5	A4Y1	6.53	10.15	14.18	3.35	90.27	91.64	99.63
40	6	A4Z1	4.17	19.56	35.75	4.00	95.98	99.05	99.52
50	5	A5X1	2.29	1.59	9.68	4.64	81.34	80.52	99.63
50	5.5	A5Y1	-0.75	9.53	25.76	3.12	94.06	97.28	99.63
50	6	A5Z1	-0.36	29.50	57.74	3.58	97.36	99.85	99.56
40	5	A4x2	-10.91	4.82	13.67	2.42	91.04	86.89	99.51
40	5.5	A4y2	-1.71	29.13	53.67	-5.52	95.38	97.64	99.61
40	6	A4z2	-7.74	13.28	26.73	-6.23	97.58	98.95	99.60

Appendix B

Results from optimal purification experiments with 2 M NaOH are presented below in Table B1. The samples from optimal purification steps were analyzed 11 times and result were compared. Additionally, average concentrations of metals were calculated.

Table B1. The optimal parameters for purification were $T = 50°C$ and target $pH = 5$. The analyzed metal concentrations after optimal purification experiments are presented.

	Optimal purification ($T = 50\ °C$, target $pH = 5$)						
Sample	**Li (mg/l)**	**Co (mg/l)**	**Ni (mg/l)**	**Mn (mg/l)**	**Cu (mg/l)**	**Al (mg/l)**	**Fe (mg/l)**
A5x1	1098	7302	795	903	176.6	129.8	1.2
EB3xyz2 *	1205	8057	860	958	151.9	113.2	1.5
EB3xyz3 *	1354	7665	1435	1003	135	-	-
EB4xyz1 *	1163	5547	618	678	112.7	172	0.3
EB4xyz2 *	1351	6840	713	992	45.4	-	-
EB5xyz1 *	1230	7276	777	1046	120.6	116.7	1.3
EK3xyz1 *	1139	6908	760	990	83.0	84.4	1.4
EK3xyz2 *	1321	7126	818	951	70.5	-	-
EK4xyz1 *	1206	7111	760	1116	107.3	89.2	1.5
EK5xyz1 *	1194	7600	832	966	108.3	86.8	1.4
P1.1*	1034	5417	892	995	105	100	0.85
Average	1209	6986	842	964	111	111.5	1.2

* EBxxxx were samples prior of continued hydroxide precipitation and EKxxxx were samples prior to carbonate precipitation. P1.1 was sample from precipitation process. Number in between name represents temperature (for example 3 = 30 °C) and the last number is the experiment number. EB3xyz2 is PLS2 prior to B3X2, B3Y2 and B3Z2 experiments.

Table B2 presents the sample name with equilibrium pH value (pH_e), calculated pH difference and added amount of 2 M NaOH (ml). Additionally, average pH_e value and amount of NaOH were calculated.

Table B2. The equilibrium pH values (pH$_e$) and NaOH addition (ml).

Sample	pH$_e$	2 M NaOH addition
A5x1	5.06	128.65
EB3xyz2	4.97	129.50
EB3xyz3	5.07	126.00
EB4xyz1	5.06	128.00
EB4xyz2	5.22	124.14
EB5xyz1	4.98	125.70
EK3xyz1	5.05	127.45
EK3xyz2	5.13	122.05
EK4xyz1	5.00	126.82
EK5xyz1	5.11	126.90
P1.1	5.07	127.00
Average	5.07	126.56

Table B3 presents the calculated metal concentrations after adding 2 M NaOH to leach liquor. Additionally, evaporation during experiments was acknowledged.

Table B3. The calculated metal concentrations after 2 M NaOH addition are presented with sample name.

				Metal concentrations after NaOH addition			
Sample	Li (mg/l)	Co (mg/l)	Ni (mg/l)	Mn (mg/l)	Cu (mg/l)	Al (mg/l)	Fe (mg/l)
A5x1	1124.2	7419.81	880.653	947.0549	946.3931	666.2255	326.9358
EB3xyz2	1120	7392.088	877.3626	943.5165	942.8571	663.7363	325.7143
EB3xyz3	1137.5	7507.589	891.0714	958.2589	957.5893		
EB4xyz1	1127.434	7441.15	883.1858	949.7788	949.115	668.1416	327.8761
EB4xyz2	1147.024	7570.451	898.5325	966.2825	965.6073		
EB5xyz1	1139.025	7517.658	892.2664	959.544	958.8735	675.0112	331.2472
EK3xyz1	1130.184	7459.304	885.3404	952.0958	951.4305	669.7716	328.676
EK3xyz2	1157.919	7642.354	907.0666	975.4601	974.7785		
EK4xyz1	1133.351	7480.206	887.8214	954.7638	954.0966	671.6484	329.597
EK5xyz1	1132.948	7477.546	887.5056	954.4242	953.7572	671.4095	329.4798
P1.1	1132.444	7474.222	887.1111	954	953.3333	671.1111	329.3333

Table B4 presents the calculated recovery efficiencies (%) of metals after purification step. Cu, Al and Fe results were repeated successfully. Li and Mn results showed more divergence. Efficiencies were calculated according to Eq. A3.

Table B4. The recovery efficiencies (%) of metals are presented after purification of the leach liquor. The recovery efficiencies in red were interpreted as inaccurate.

			Recovery efficiencies (%)				
Sample	**Li**	**Co**	**Ni**	**Mn**	**Cu**	**Al**	**Fe**
A5x1	2.287876	1.594249	9.676114	4.639111	81.33968	80.51711	99.63296
EB3xyz2	-7.54464	-8.98923	1.992635	-1.58169	83.88791	82.9381	99.54439
EB3xyz3	-19.033	-2.09669	-61.0421	-4.669	85.9021		
EB4xyz1	-3.1156	25.45024	30.07497	28.58632	88.12283	74.23121	99.9085
EB4xyz2	-17.783	9.648713	20.64839	-2.66149	95.2983		
EB5xyz1	-7.98705	3.209744	12.94977	-9.01845	87.42024	82.70458	99.62046
EK3xyz1	-0.81544	7.396181	14.19798	-3.94542	91.27125	87.40615	99.56297
EK3xyz2	-14.084	6.756479	9.819188	2.507547	92.76759		
EK4xyz1	-6.38362	4.929896	14.42197	-16.9106	88.75711	86.71388	99.55825
EK5xyz1	-5.41526	-1.64191	6.299178	-1.2422	88.64009	87.07614	99.56234
P1.1	8.693093	27.52423	-0.5511	-4.29769	88.98601	85.09934	99.7419
Average	-6.47097	6.707446	5.317	-0.78123	88.39937	83.33581	99.64147
Average when values in red are excluded							
	-0.54772	5.58921	9.939347	3.573329			

Appendix C

After purification precipitation experiments were continued adding 2 M NaOH. The metal concentrations before precipitation of Co, Ni, Mn, Cu and Al are presented in Table B1. Table C1 presents the metals concentrations after 2 M NaOH addition and filtration.

Table C1. Metal concentrations after 2 M NaOH addition at pH 7.5, 8.0 and 8.5 in different temperatures.

T (°C)	Target pH	Sample	Li (mg/l)	Co (mg/l)	Ni (mg/l)	Mn (mg/l)	Cu (mg/l)	Al (mg/l)
30	7.5	B3X2	1037	2497	149	736	20.7	< 2
30	8	B3Y2	860	407	19.5	574	19.1	< 2
30	8.5	B3Z2	913	70.2	2.3	380	17.6	< 2
40	7.5	B4X1	1017	722	31.7	568	22.7	< 2
40	8	B4Y1	911	136	3.5	443	22.1	< 2
40	8.5	B4Z1	1109	25.2	< 0.2	301	20.2	< 2
50	7.5	B5X1	1031	334	10.2	504	23.2	< 2
50	8	B5Y1	946	57.1	2.0	395	20.2	< 2
50	8.5	B5Z1	1183	13.4	< 0.2	198	10.5	< 2
30	8	B3y3	1132	295	13.0	655	17.2	-
40	7.5	B4x2	1219	280	12.3	712	9.9	-
40	8	B4y2	1210	32.6	2.2	451	8.7	-
40	8.5	B4z2	1165	9.9	1.4	210	7.7	-

Table C2 shows the measured pHe values, calculated pH difference and added NaOH amount (ml).

Table C2. The equilibrium pH values (pHe) and NaOH addition (ml). The calculated pH difference between equilibrium and target pH.

Sample	pHe	pHi	pH difference	2 M NaOH addition
B3X2	7.47	7.5	-0.03	16.50
B3Y2	7.99	8.03	-0.04	25.00
B3Z2	8.56	8.66	-0.1	27.03
B4X1	7.52	7.52	0.00	24.00
B4Y1	7.91	8.00	-0.09	27.00
B4Z1	8.44	8.54	-0.1	28.47
B5X1	7.5	7.53	-0.03	24.30
B5Y1	7.97	8.06	-0.09	26.00
B5Z1	8.5	8.49	0.01	27.40

B3y3	7.982	8.01	-0.03			27.20	
B4x2	7.49	7.51	-0.02			21.80	
B4y2	8.19	8.20	-0.01			23.75	
B4z2	8.46	8.57	-0.11			24.45	

Table C3 outlines the calculated metals concentrations after 2 M NaOH addition. Concentrations were calculated according to Eq. A2.

Table C3. The calculated metal concentrations after 2 M NaOH addition are presented with sample name, target pH and temperature.

Metal concentrations after NaOH addition								
T(°C)	Target pH	Sample	Li (mg/l)	Co (mg/l)	Ni (mg/l)	Mn (mg/l)	Cu (mg/l)	Al (mg/l)
30	7.5	B3X2	1112.70	7442.57	794.35	885.39	140.34	104.62
30	8	B3Y2	1070.67	7161.40	764.34	851.95	135.04	100.66
30	8.5	B3Z2	1061.11	7097.50	757.52	844.34	133.83	99.77
40	7.5	B4X1	1042.66	4975.21	553.87	608.32	101.10	154.41
40	8	B4Y1	1033.39	4930.99	548.95	602.91	100.20	153.04
40	8.5	B4Z1	1031.23	4920.71	547.81	601.65	99.99	152.72
50	7.5	B5X1	1101.41	6515.63	695.52	936.72	108.01	104.54
50	8	B5Y1	1102.96	6524.81	696.50	938.03	108.17	104.69
50	8.5	B5Z1	1106.07	6543.24	698.46	940.68	108.47	104.98
30	8.5	B3y3	1185.22	6709.51	1256.12	877.97	118.17	-
40	7.5	B4x2	1229.94	6227.07	649.11	903.11	41.33	-
40	8	B4y2	1212.88	6140.73	640.11	890.59	40.76	-
40	8.5	B4z2	1214.60	6149.4	641.01	891.84	40.82	-

Table C4 outlines the calculated recovery efficiencies (%) of metals. Recovery efficiencies were calculated according to Eq. A3.

Table C4. Calculated metal recovery efficiencies (%).

Recovery efficiencies (%)

T (°C)	Target pH	Sample	Li	Co	Ni	Mn	Cu	Al
30	7.5	B3X2	6.81	66.45	81.25	16.85	85.24	98.09
30	8	B3Y2	19.69	94.32	97.44	32.59	85.84	98.01
30	8.5	B3Z2	14.00	99.01	99.70	55.05	86.86	98.00
40	7.5	B4X1	2.49	85.48	94.28	6.60	77.57	98.70
40	8	B4Y1	11.85	97.24	99.36	26.56	77.95	98.69
40	8.5	B4Z1	-7.55	99.49	99.96	49.99	79.81	98.69
50	7.5	B5X1	6.44	94.87	98.53	46.23	78.48	98.09
50	8	B5Y1	14.28	99.12	99.72	57.87	81.36	98.09
50	8.5	B5Z1	-6.99	99.79	99.97	78.99	90.29	98.09
30	8.5	B3y3	4.46	95.61	98.96	25.36	85.40	-
40	7.5	B4x2	0.90	95.50	98.11	21.14	76.15	-
40	8	B4y2	0.22	99.47	99.65	49.35	78.70	-
40	8.5	B4z2	4.10	99.84	99.78	76.42	81.13	-

Appendix D

After purification, the precipitation experiments were continued adding 2 M Na_2CO_3 to precipitate Co, Ni, Mn and Cu at different temperatures and pH values. Table D1 presents the analyzed metal concentrations after Na_2CO_3 precipitation.

Table D1. Metal concentrations after 2 M Na_2CO_3 addition at pH 7.0, 7.5 and 8.0 in different temperatures.

			2 M Na_2CO_3 precipitation						
T (°C)	Target pH	Sam ple	Li (mg/l)	Co (mg/l)	Ni (mg/l)	Mn (mg/l)	Cu (mg/l)	Al (mg/l)	Fe (mg/l)
30	7	K3x1	1125	694	66.5	214	3.1	-	-
30	7.5	K3y1	1164	190	17.7	94.2	1.1	-	-
30	8	K3z1	1218	77.3	8.6	35.8	1.2	-	-
40	7	K4x1	1155	365	35.3	137	1.6	-	-
40	7.5	K4y1	1153	109	12.6	32.3	1.0	-	-
40	8	K4z1	1137	24.3	4.3	4.0	1.1	-	-
50	7	K5x1	1187	178	20.3	42.2	2.0	-	-
50	7.5	K5y1	1233	20.6	3.7	2.8	1.6	-	-
50	8	K5z1	1170	10.6	2.2	0.9	1.6	-	-
30	7	K3x2	1134	525	51.7	186	1.2	-	-
30	7.5	K3y2	1112	151	13.6	69.6	0.5	-	-
30	8	K3z2	1129	54.3	5.0	26.4	0.5	-	-
50	8	P1.2	1119	9.37	4.48	4.87	1.27	0.29	0.92

Table D2 shows the sample names, measured pH values (pH_e and pH_i), calculated pH difference and added amount of Na_2CO_3. pH difference was calculated according to Eq. A1.

Table D2. The equilibrium pH values (pHe) and NaOH addition (ml). The calculated pH difference between equilibrium and target pH.

Sample	pHe	pHi	pH difference	2 M Na_2CO_3 addition
K3x1	6.98	6.98	0.00	17.60
K3y1	7.48	7.5	-0.02	20.26
K3z1	7.93	7.99	-0.06	21.59
K4x1	6.98	6.98	0.00	19.54
K4y1	7.5	7.50	0.00	21.26
K4z1	8.04	8.00	0.04	22.56
K5x1	7.02	7.01	0.01	20.80
K5y1	7.71	7.52	0.19	21.97

K5z1	8.01	8.00	0.01	22.44
K3x2	7	6.99	0.01	17.45
K3y2	7.52	7.54	-0.02	19.40
K3z2	7.92	8.01	-0.09	20.39
P1.2	8	7.99	0.01	23.55

Table D3 the metal concentrations after Na_2CO_3 addition were calculated. Concentrations were calculated according to Eq. A2.

Table D3. Metal concentrations after Na₂CO₃ addition.

Metal concentrations after Na₂CO₃ addition									
T (°C)	Target pH	Sam ple	Li (mg/l)	Co (mg/l)	Ni (mg/l)	Mn (mg/l)	Cu (mg/l)	Al (mg/l)	Fe (mg/l)
30	7	K3x1	1097.70	6985.59	764.34	888.13	99.58	-	-
30	7.5	K3y1	1084.44	6901.16	755.10	877.39	98.38	-	-
30	8	K3z1	1077.93	6859.74	750.57	872.13	97.79	-	-
40	7	K4x1	1092.971	6411.5	701.52	815.14	91.40	-	-
40	7.5	K4y1	1089.382	6932.64	758.54	881.39	98.83	-	-
40	8	K4z1	1087.903	6923.23	757.52	880.20	98.69	-	-
50	7	K5x1	1086.25	6912.71	756.36	878.86	98.54	-	-
50	7.5	K5y1	1090.606	6940.4	759.40	882.38	98.94	-	-
50	8	K5z1	1098.728	6992.12	765.05	888.96	99.68	-	-
30	7	K3x2	1210.452	6529.46	749.54	871.43	64.60	-	-
30	7.5	K3y2	1199.23	4917.48	809.73	903.46	95.76	-	-
30	8	K3z2	1193.62	6438.65	739.12	859.31	63.70	-	-
50	8	P1.2	929.33	4867.74	801.54	894.32	94.79	89.79	2.04

Table D4 shows the calculated recovery efficiencies (%) of metals. In carbonate precipitation experiments the metal recovery efficiencies were calculated according to Eq. D1. HNO_3 addition to the solution sample needs to be considered in the calculations. Volume of the samples was approximately 11 ml and added HNO_3 volume was 0.3 ml.

$$\% = \left(1 - \left(\frac{\text{analyzed C(Me) after filtration}}{\text{C(Me)after reagent addition}}\right)\right) * 100 * \left(\frac{11}{11.3}\right) \qquad \text{(D1)}$$

Table D4. Calculated recovery efficiencies (%) of metals with target pH and temperature.

			Recovery efficiencies (%)						
T (°C)	Target pH	Sample	Li	Co	Ni	Mn	Cu	Al	Fe
30	7	K3x1	-2.46	87.67	88.88	73.87	94.35	-	-
30	7.5	K3y1	-7.11	94.67	95.06	86.90	96.21	-	-
30	8	K3z1	-12.62	96.25	96.24	93.35	96.17	-	-
40	7	K4x1	-5.55	91.81	92.44	81.01	95.68	-	-
40	7.5	K4y1	-5.65	95.81	95.73	93.78	96.41	-	-
40	8	K4z1	-4.40	97.00	96.79	96.91	96.27	-	-
50	7	K5x1	-9.01	94.83	94.73	92.68	95.34	-	-
50	7.5	K5y1	-12.70	97.06	96.87	97.04	95.73	-	-
50	8	K5z1	-6.35	97.20	97.06	97.25	95.80	-	-
30	7	K3x2	6.17	89.52	90.63	76.59	95.48	-	-
30	7.5	K3y2	7.11	94.36	95.71	89.85	96.82	-	-
30	8	K3z2	5.30	96.52	96.68	94.36	96.58	-	-
50	8	P1.2	-19.88	97.16	96.80	96.81	96.04	97.03	53.31

Appendix E

Precipitation process was developed after optimal parameters were determined. Optimal parameters for Co, Ni, Mn and Cu precipitation were T = 50 °C and adding 2 M Na_2CO_3 until pH_e = 8.0. Table E1 shows the analyses of samples from precipitation process. Sample P1.1 was from step 1 of the process and P1.2 from step 2. P3 was the mixture of two solutions, which were prepared similarly. Mixing was performed after step 2 prior to evaporation and crystallization.

Table E1. Solution samples from optimized precipitation process.

T (°C)	pH_e	Sample	Li (mg/l)	Co (mg/l)	Ni (mg/l)	Mn (mg/l)	Cu (mg/l)	Al (mg/l)	Fe (mg/l)
50	5	P1.1	1034	5417	892	995	105	100	0.85
50	8	P1.2	1119	9.37	4.48	4.87	1.27	0.29	0.92
(P1.1+P2.1)		P3	1199	6.78	1.23	0.92	0.63	0.30	0.85

Table E2 outlines the analyses of the precipitates obtained after step 1 and 2 in the precipitation process. Precipitates were weighed before analyses.

Table E2. Obtained and analyzed precipitates from optimized precipitation process.

	Obtained precipitates								
Sample	Li (mg/g)	Co (mg/g)	Ni (mg/g)	Mn (mg/g)	Cu (mg/g)	Al (mg/g)	Fe (mg/g)	Sum (mg/g)	Weight (g)
Fe, Al, Cu - precipitate	3.7	99.7	20.8	6.7	73.6	56.5	22	283	2.53
Co, Ni, Mn - precipitate	1.9	161.6	40.2	47.6	6.5	6.2	0.2	264.2	3.84

Table E3 shows the molar masses used in the purity calculations.

Table E3. Shows the molar masses used in purity calculations.

Molar mass	g/mol	Molar mass	g/mol
M(OH)	17.008	M(Co)	58.933
M(Fe)	55.845	M(Ni)	58.693
M(Al)	26.982	M(Mn)	54.938

M(Cu)	63.546	$M(CO_3^{2-})$	60.010

Table E4 shows the calculated masses (mg) of assumed compounds in the Fe, Al, Cu -precipitate and the calculated purity (%).

Table E4. Calculated masses of assumed compounds in Fe, Al, Cu -precipitate, the sum of masses and purity of precipitate.

	$m(Fe(OH)_3)$	$m(Al(OH)_3)$	$m(Cu(OH)_3)$	Sum (mg)	Purity (%)
Fe, Al, Cu -precipitate	42.101	163.344	112.998	318.442	31.84

Table E5 shows the calculated masses (mg) of assumed compounds in the Co, Ni, Mn -precipitate and the calculated purity (%).

Table E5. Calculated masses of assumed compounds in Co, Ni, Mn -precipitate, the sum of masses and purity of precipitate.

	$m(Co(CO)_3)$	$m(Co(CO)_3)$	$m(Co(CO)_3)$	Sum (mg)	Purity (%)
Co, Ni, Mn - precipitate	326.153	81.302	99.595	507.050	50.71

Crystallization of Li_2CO_3 was performed adding stoichiometric amount of saturated Na_2CO_3 into a solution where Co, Ni, Mn, Cu, Al and Fe concentrations were as low as possible. Saturated Na_2CO_3 solution was prepared by adding excess amount of Na_2CO_3 to 100 ml of water. The amount of Na_2CO_3 used in crystallization calculations is presented in Table E6.

Table E6. Na_2CO_3 amount used in calculations (T = 25 °C).

Saturated Na_2CO_3 solution		
T25	30.72	g/100 ml (water)
T25	0.3072	g/1 ml (water)

Table E7 shows the recovery temperature, equilibrium pH values and amounts of NaOH additions (ml) in the purification (Step1) of precipitation process.

Table E7. Optimal step 1 parameters and reagent additions. Two similar solutions were produced (P1.1 and P2.1).

Optimal Step1		
Temperature	50	°C
Equilibrium pH (P1.1)	5.07	-
Equilibrium pH (P2.1)	5.12	-
NaOH addition (P1.1)	127.00	ml
NaOH addition (P2.1)	129.94	ml
Sum of NaOH addition	256.94	ml

Table E8 outlines the parameters after optimal 2 M Na_2CO_3 precipitation and prior to evaporation.

Table E8. Parameters in the optimal Step 2 where metals were precipitated using 2 M Na_2CO_3. Two similar solutions were produced (P1.2 and P2.2) and mixed for recovery of Li_2CO_3.

Optimal Step2		
Temperature	50	°C
Equilibrium pH (P1.2)	8.00	-
Equilibrium pH (P2.2)	8.10	-
Na_2CO_3 addition (P1.2)	23.55	ml
Na_2CO_3 addition (P2.2)	22.84	ml
Sum of Na_2CO_3 addition	46.39	ml
Final volume of solutions (P3)	296	ml
Lithium concentration	1199	mg/l

Table E9 outlines the calculations of Na^+ ions amount in the leach liquor before recovery of lithium.

Table E9. The amount (mol/l) of Na^+ ions in the leach liquor before lithium recovery.

Amount of Na ions in leach liquor before lithium recovery		
V(NaOH)	256.94	ml
V(Na_2CO_3)	46.39	ml
2 M NaOH	82.40	g/l
2 M Na_2CO_3	213.04	g/l
m(NaOH	21.17	g
m(Na_2CO_3)	9.88	g
n(NaOH)	0.36	mol

n(Na₂CO₃)	0.09	mol
V(P3)	296	ml
Na⁺ ions	1.86	mol/l

Table E10 outlines the parameters for evaporation before lithium recovery. The goal in evaporation was to increase the concentration of lithium prior to recovery.

Table E10. Evaporation parameters before Li₂CO₃ precipitation.

Evaporation		
Temperature	65-70	°C
Final volume of solution	98.67	ml

Table E11 outlines the parameters and calculations prior to precipitation of Li_2CO_3.

Table E11. Calculations for Li₂CO₃ precipitation.

Precipitation of Li₂CO₃		
Temperature	50	°C
M(Li₂CO₃)	73.9	g/mol
M(Li)	6.94	g/mol
M(Li₂CO₃)/2*M(Li)	5.32	-
Amount of soluble Li⁺	0.31	g/100 ml
Amount of potential Li₂CO₃	1.66	g/100 ml
Solubility of Li₂CO₃ (60 °C)	1	g/100 ml
$n(CO_3^{2-})/n(Li)$	1.2	
n(Li)	0.04	mol
$M(CO_3^{2-})$	60.01	g/mol
$m(CO_3^{2-})$	3.24	g
Addition of saturated Na₂CO₃	10.55	ml

Table E12 shows the calculated recovery efficiency of Li using molar masses from Table E10. Weight of the recovered precipitate was 1.03 g.

Table E12. Lithium recovery efficiency and purity calculations.

Lithium recovery efficiency and purity calculations		
m(Li)	179	mg/g
n(Li)	25.79	mol

$n(CO_3^{2-})$	12.90	mol
$m(CO_3^{2-})$	773.90	mg
$m(Li_2CO_3)$	952.90	mg/g
Li_2CO_3 purity*	95.29	%
True $m(Li_2CO_3)$	981.49	mg
Recovery efficiency	59.04	%

*If all analyzed Li^+ participates in the formation of carbonate compound.

Appendix F

SX was studied as a method for the separation of Co. SX experiments were conducted to purified solution using 40% Na-Cyanex 272 as extractant. Table F1 presents the metal concentrations in the purified aqueous solution prior to SX.

Table F1. Metal concentrations prior to SX.

	Analyzed metals from purified solution				
Sample	**Li (mg/l)**	**Co (mg/l)**	**Ni (mg/l)**	**Mn (mg/l)**	**Cu (mg/l)**
SXPRE	1295	6976	821	992	113.0

Table F2 presents the analyzed metal concentrations of samples after SX experiments. Metal concentrations were analyzed from aqueous phase. Samples with capital letter T in the name were from repeated experiments.

Table F2. Analyzed metals from SX experiments using 40% Na-Cyanex 272 as extractant.

	Analyzed metals from SX experiments					
Sample	**O:A**	**pH$_e$**	**Li (mg/l)**	**Co (mg/l)**	**Ni (mg/l)**	**Mn (mg/l)**
C40ext#1*	1:1	3.95	1276	3300	792	219
C40ext#2*	2:1	5.35	1108	97	347	6.4
C40TE#1*	1:1	4.07	1178	2816	798	177
C40TE#2*	2:1	5.23	1110	216	399	11.5
C40TS#1.1**	1:1	-	58.5	3882	21.4	719
C40TS#2.1**	2:1	-	132	3358	276	469
C40strip#1.1**	1:1	-	68.0	4158	39.1	772
C40strip#2.1**	2:1	-	116	3188	264	445

*Analyzed aqueous solution from extraction

**Analyzed aqueous solution from stripping

Table F3 presents the calculated extraction percentages in SX experiments. Extraction percentages were calculated according to Eq. F1.

$$\left(1 - \left(\frac{c(\text{Me})\text{in aqueous phase after SX}}{c(\text{Me}) \text{ before SX}}\right)\right) * 100 \tag{F1}$$

Table F3. Extraction percentages of investigated metals were calculated.

		Extraction (%)			
Sample	O:A	Li	Co	Ni	Mn
C40ext#1	1:1	1.47	52.70	3.50	77.93
C40ext#2	2:1	14.42	98.61	57.78	99.35
C40TE#1	1:1	9.06	59.64	2.80	82.13
C40TE#2	2:1	14.25	96.90	51.45	98.85

Table F4 presents the calculated average extraction percentages. Average extractions were calculated from Table F3.

Table F4. Experiments were repeated twice and average extraction percentages were calculated.

	Average extraction (%)			
O:A	Li	Co	Ni	Mn
1:1	5,264865	56,17058	3,150895	80,02822
2:1	14,33514	97,75477	54,61381	99,09848

Table F5 shows the calculated metal concentrations in organic phase before stripping.

Table F5. Metal concentrations were calculated before stripping.

		Metal concentrations before stripping			
Sample	O:A	Li (mg/l)	Co (mg/l)	Ni (mg/l)	Mn (mg/l)
C40TS#1.1	1:1	19	3676	29	773
C40TS#2.1	2:1	93	3440	237	493
C40strip#1.1	1:1	117	4161	23	815
C40strip#2.1	2:1	92	3380	211	490

Stripping was performed using 2 M H_2SO_4 when strip to aqueous solution ratio was 1:1. Table F6 shows the calculated stripping efficiencies (%). The values in red were considered as inaccurate due to error in analyses. Stripping efficiencies were calculated according to Eq. F2.

$$\left(\frac{c(Me)\text{after stripping}}{c(Me)\text{ before stripping}} \right) * 100 \qquad (F2)$$

Table F6. Stripping was conducted using 2 M H_2SO_4. The ratio of strip solution and aqueous solution was 1:1.

Stripping efficiencies of metals (%)

Sample	O:A	Li	Co	Ni	Mn
C40TS#1.1	1:1	357.35	113.09	136.16	99.89
C40TS#2.1	2:1	123.84	92.68	111.31	90.17
C40strip#1.1	1:1	49.88	93.31	92.82	88.26
C40strip#2.1	2:1	142.55	99.35	130.55	95.67

In Table F7 the average stripping efficiencies were calculated. Values in red were considered as inaccurate due analyses error.

Table F7. Average stripping efficiencies (%) were calculated from Table F6.

Average stripping efficiency (%)				
O:A	Li	Co	Ni	Mn
1:1	203,6168	103,2038	114,4911	94,07567
2:1	133,1937	96,01613	120,9342	92,9214