

Lappeenranta-Lahti University of Technology LUT  
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**Ion exchange in hydrometallurgical recycling of Li-ion battery metals: production of Li-Ni-Co mixture**

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## **ABSTRACT**

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Use of Li-ion batteries (LIB) in hand-held devices and electric vehicles has skyrocketed in the last decade. 37% of the whole rechargeable battery market is LIBs. Recovery of these metals, mainly located in battery's cathode, anode or electrolyte material is mainly accomplished with combination of pyro- and hydrometallurgical processes. In this thesis recycling of these valuable materials were studied. Focus was on ion exchange separation of impurity metals from battery leach liquor containing 15 g/l Co, 4.6 g/l Li and 1-2 g/l Al, Cu, Fe, Mn and Ni.

Breakthrough experiments were conducted in differing feed pH and temperatures to four resins. Lewatit TP260 chelating resin with aminophosphonic acid functional group proved to be the most promising, being able to remove Al, iron, Cu and Mn in pH of 1,8 and temperature of 60 °C. With this process two bed volumes (BV) was treated before bed need to be eluted. Part of iron and Al could not be removed from the resin with 2 M sulfuric acid elution thus blocking the active sites on the resin before the next loading step. Elution of the TP260 resin was therefore studied as a two-step process. With the use of 2 M sulfuric acid and 0.4 M potassium oxalate bed was successfully regenerated.

Two possible process paths emerged during research. All impurities can be removed with Aminophosphonic chelating resin with two eluents. On the other hand, impurity metals can be fractionated and separated from each other by using multiple resins. First removing iron, then Cu and lastly Mn and Al.

# TIIVISTELMÄ

Lappeenrannan-Lahden Teknillinen yliopisto LUT

School of Engineering Science

Chemical and Process Engineering

Arttu Kaukinen

## **Ioninvaihto hydrometallurgisessa Li-ioniakkumetallien kierrätyksessä: Li-Ni-Co seoksen valmistus**

Diplomityö

2019

78 (+9) sivua, 31 (+9) kuvaa, 17 taulukkoa ja liite

Työn tarkastaja: Prof. Tuomo Sainio

D.Sc. Sami Virolainen

Hakusanat: Litium, Litiumioniakku, ioninvaihto, kierrätys, koboltti, aminometyyli fosfaatti happo

Litiumioniakkujen käyttö mobiililaitteissa ja sähköautoissa on räjähtänyt viimeisen vuosikymmenen aikana. 37% ladattavien akkujen markkinoista on litiumioniakkuja. Näiden metallien talteenotossa, joita löytyy pääasiassa akun katodi-, anodi- ja elektrolyyttimateriaaleista, käytetään hydro- ja pyrometallurgisia prosesseja. Tässä diplomityössä tutkittiin näiden arvokkaiden metallien talteenottoa ioninvaihdolla liuotetusta akkujätteestä, jonka metallipitoisuudet ovat 15 g/l Co, 4.6 g/l Li ja 1-2 g/l Al, Cu, Fe, Mn sekä Ni.

Läpäisykokeita tehtiin erilaisissa pH ja lämpötilaolosuhteissa neljällä eri ioninvaihtohartsilla. Lewatit TP260 gelatoiva hartsin aminometyylifosfonaatihappo funktionaalilla ryhmällä osoittautui lupaavimmaksi. Alumiinin, raudan, kuparin ja mangaanin poistaminen onnistui kyseisellä hartsilla 1,8 pH:ssa ja 60 °C lämpötilassa. Kaksi pettilavuutta syöttöä voitiin käsitellä, kunnes hartsin vaati eluointia. 2 M rikkihappoliuoksella ei kaikkea rautaa ja alumiinia saatu eluoitua hartsista ja tämä heikensi peräkkäisten erotusten kapasiteettiä. TP260 hartsin eluointia tutkittiin tämän takia kaksivaiheisena prosessina. 2 M rikkihapolla ja 0,4 M kaliumoksalaaatilla hartsin petti eluoitui lähes täysin.

Tutkimuksessa löytyi kaksi mahdollista prosessia. Kaikki metallit voidaan poistaa aminometyylifosfonaatihartsilla ja kahdella eluoinnilla. Toisaalta epäpuhtausmetallit voidaan poistaa yksi kerrallaan ja samalla erottaa toisistaan käyttämällä useampaa hartsia. Ensin erotetaan rauta sitten kupari ja viimeisenä mangaani ja alumiini.

## **FOREWORD**

This Master's Thesis was produced in Department of Chemical Engineering at Lappeenranta-Lahti University of Technology LUT's School of Engineering Sciences between March and November in 2019. This thesis was done as a part of Business Finland's project BATCircle.

Thank you to Tuomo Sainio for this position in his research group. I greatly appreciate this opportunity and the help and vision received from him. I would like to bring my greatest gratitude for my instructor Sami Virolainen for superb guidance and help during the making of this thesis.

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Rock on!

Lappeenranta, 9<sup>th</sup> of December 2019.

Arttu Kaukinen

## LIST OF SYMBOLS AND ABBREVIATIONS

AMPA	Aminomethylphosphonic acid
APA	Aminophosphonic acid
BV	Bed volume
CIX	Continuous ion exchange
EV	Electric vehicle
ICP-MS	Inductively coupled plasma – mass spectrometer
IDA	Iminodiacetic acid
IX	Ion exchange
LC	Liquid chromatography
LIB	Li-ion battery
NaEDTA	Disodium ethylenediaminetetraacetate
PMC	Mass centre of peak
SAC	Strong cation exchanger
SHE	Standard hydrogen electrode
USD	US dollar
WAC	Weak cation exchange

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## 1. INTRODUCTION

Hand-held electronic devices have been part of the modern lifestyle for more than two decades. Myriad of devices use rechargeable batteries to enable mobile and flexible usage. Li-ion batteries (LIB) are used in most electronic devices currently and they have replaced nearly all other battery types in hand-held devices. This can be seen in sales figures and in 2008 over three million LIB were sold (Georgi-Maschler et al., 2012). Heelan et al (2016) state that LIB market was over 20 billion USD in 2016. They also present approximation of the landfilled LIBs to be around 95% out of all made LIBs. (Heelan et al., 2016) LIBs contains many valuable metals and raw materials that make third of the unit cost of the LIB. (Georgi-Maschler et al., 2012). It is also noteworthy that legislation concerning LIBs recycling is getting tighter and forcing companies to think what to do with the LIBs at the end of their life. (The European parliament and the council of the European Union, 2006)

Studies show that variety of different approaches are taken what comes to the capture of the valuable metals from various sources. Hydro-, and pyrometallurgical methods are often used to recover valuable metals as described by Joulié et al. (2014) but pyrometallurgy has many notable downsides like high energy consumption and hazardous emissions and hydrometallurgy products salts as a side product (Joulié et al., 2014). Ion exchange is an essential separation technology used in hydrometallurgical processes.

In this Master's Thesis, ion exchange process for recycling valuable metals from Li-ion batteries is examined with extensive review to LIB recycling. In this work impurity removal with stationary ion exchanger phase is focused. Especially four major impurity metals Al, Cu, Fe and Mn are studied. Multiple different ion exchange process configurations and materials are investigated to purify synthetic Li-ion battery leach liquor. Regeneration of the used resins are researched in this thesis as well. In this way actual long-term viability of the ion exchange process is verified.

## 2. RECYCLING OF LI-ION BATTERIES

Demand for LIBs has been increasing drastically in last decade. (Heelan et al., 2016; Kang et al., 2010; Porvali et al., 2019). Fast development of electric vehicles and mobile phones are driving the cost of buying these devices down, making them affordable to all. In year 2015 2.72 million electric vehicles were sold making automotive industry over 5 billion USD market for LIBs. By the 2025 this number is estimated to be 25 billion USD. (Heelan et al., 2016) In the year 2017 LIB represented approximately 37 percent of total rechargeable battery market worldwide and they are fast replacing other technologies (Swain, 2017). Mobile devices and large-scale grid energy storage possibilities create even larger demand for the LIB raw materials. This increase makes efficient and economically viable process for recycling the batteries reaching the end of their lifecycle a necessity. (Porvali et al., 2019) Market growth does not limit itself only to electric vehicles. European Union has estimated the monetary value of LIB market to be from 38 to 122 billion USD in 2025 as described in Figure 1 (Steen et al., 2017). Prices of metals used in LIBs gives good incentive for recycling of the batteries. Especially price of cobalt is increasing and at 21.11.2019 being at 35 USD per kg (LME, 2019).

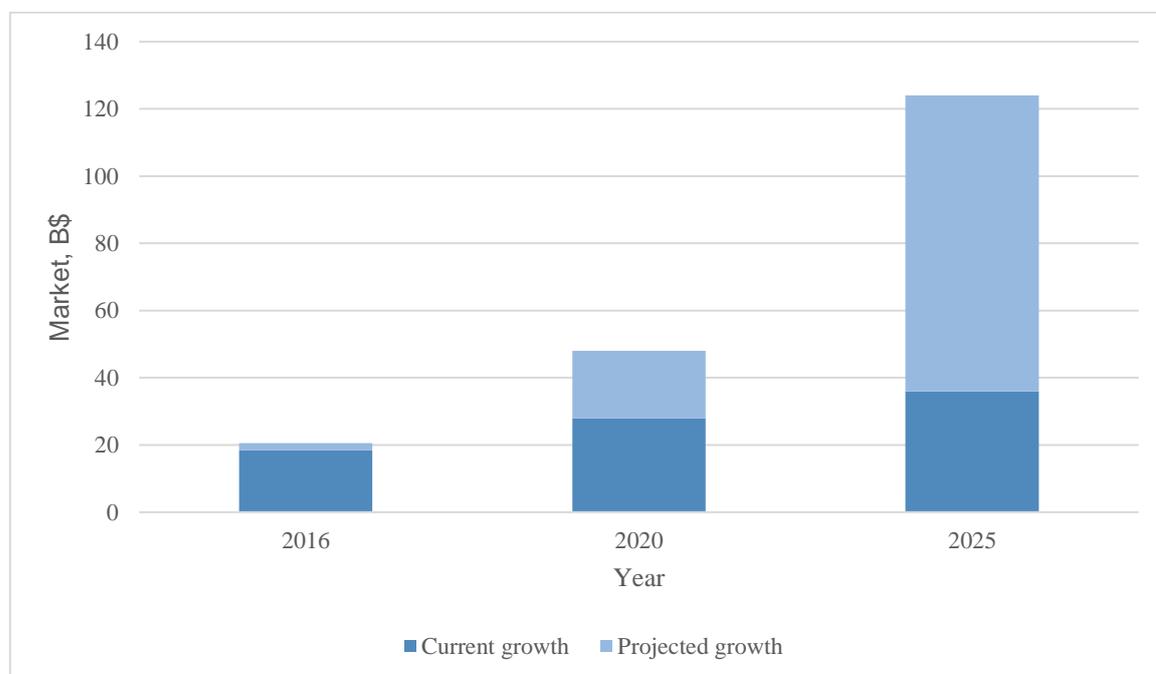


Figure 1 Global LIB market forecast in monetary values (Steen et al., 2017)

Lifecycle of the LIB is relatively short normally being around 2 years (Contestabile et al., 2001). This means that the lag between production and recycling is relatively short. This fact creates a need to constantly evolve the recycling process to meet the change of battery chemistries inside the LIBs. Or on the other hand to develop single process with the capability of treating battery waste with many different compositions. What makes battery recycling process design difficult is that it is most cost effective to just grind the batteries to black mass and that is why all battery leach liquors can have highly varied compositions and metal proportions.

## 2.1 Chemical and physical composition

According to Heelan et al. (2016) Li-ion batteries consist of four parts. They are cathode, anode, electrolyte and separator. Electrodes can be broken down further to active material, conductive carbon additive, current collector and polymeric binder. Figure 2 presents the structure of LIB (Heelan et al., 2016). LIB metal content is conversed on greater detail later in this chapter.

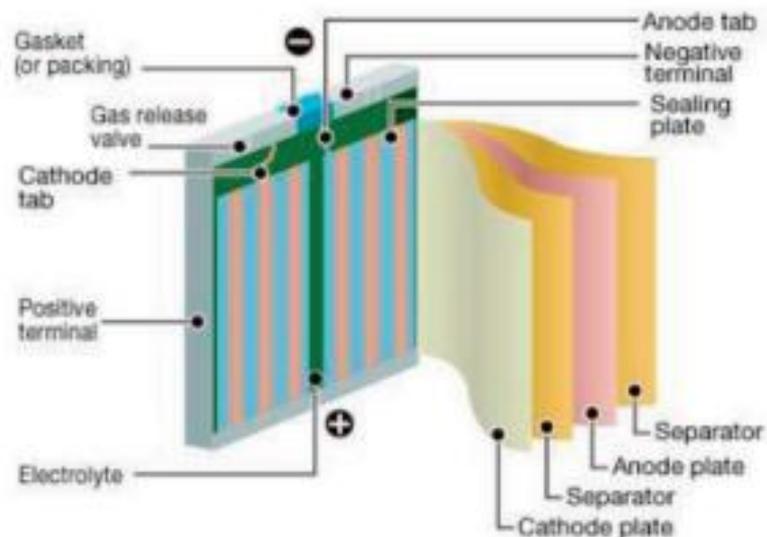


Figure 2 Structure of the LIB (Shin et al., 2015)

Battery chemistry has evolved during the years. Today most of the lead-based batteries are replaced with Li-ion batteries. Even in LIBs cathode/anode materials evolve and change between different aged and model batteries. Heelan et al (2016) describes in their study that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{LiCo(III)O}_2$ ,  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ ,  $\text{LiFePO}_4$  and  $\text{LiMn}_2\text{O}_4$  are widely used materials for cathode and anode (Heelan et al., 2016). These materials contain the most valuable materials to be recycled in the LIB. Especially Co has high market price and since 2016 the price of Co as skyrocketed (Li et al., 2018). Only some metals used in LIBs hold real value. Bulk of the profit from LIB recycling comes from nickel, Co and Li as Figure 3 presents. Cu can be considered as a product as well when recycling LIBs, but it should not require intensive and costly separation.

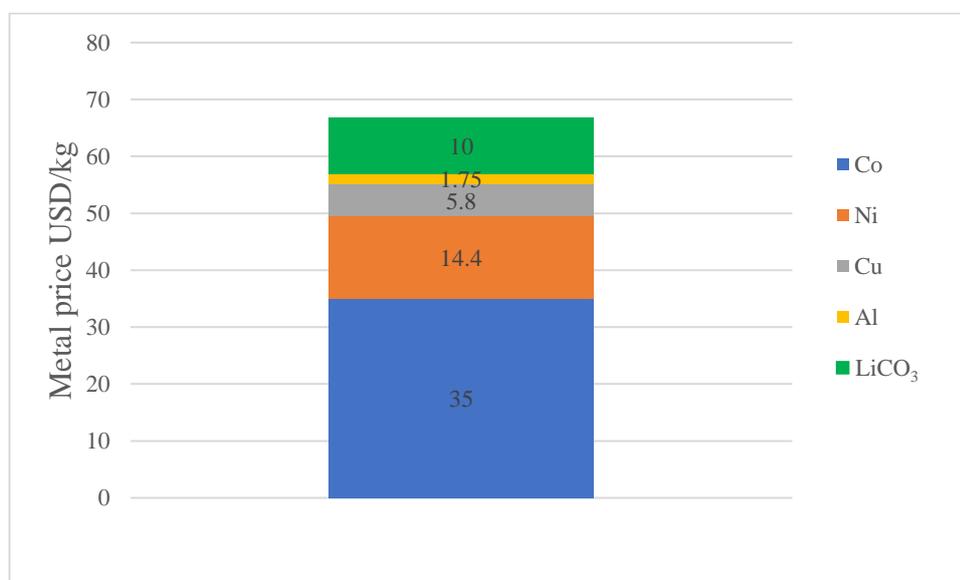


Figure 3 Prices of LIB metals as of 21.11.2019 (prices from (LME, 2019))

LIBs contain other materials that are not that valuable and can even interfere with recycling of the valuable metals.  $\text{LiPF}_6$  is used as an electrolyte inside the battery cell (Heelan et al., 2016). This poses some issues for recycling process in the leaching phase. When Li is separated from said compound, fluorine is free to form hydrofluoric acid (HF) with free  $\text{H}^+$  protons in the acidic leaching solution. HF is highly corrosive and hazardous to health. It is so corrosive in fact that it cannot be stored in metal or glass containers (Seastar Chemicals Inc, 2011). Binders and separators of battery cells are often organic polymers. Polyvinylidene

difluoride, carbomethyl cellulose and styrene butadiene rubber are used in binder material and porous polyolefin membranes are the most widely used separator between cathode and anode.

## **2.2 Present LIB recycling**

Due to the vast amount of different battery chemistries LIB waste is extremely heterogeneous. This causes issues with the recycling process, especially in hydrometallurgy. Presence of different metal ions and organic compounds such as plastics and polymers make recycling LIBs challenging. It is difficult to sort the batteries to different chemistries by visual examination focusing on one type of battery chemistry unfruitful in design of a real industrial process (Porvali et al., 2019). The fact that is the varying raw material, demands universal process capable to handle wide variance in the raw material solution.

Before LIBs can be treated, they need to be pretreated. This is often done with mechanical methods like grinding. Two mostly used methods for recycling of LIBs are hydro- and pyrometallurgical processes. Other methods exist but they are either novel processes or combinations of these processes (Georgi-Maschler et al., 2012; Li et al., 2018). Often times processing of LIBs is integrated to already established large-scale processes that are dedicated to metals separation from other sources. This increases the economic viability of the recycling (Georgi-Maschler et al., 2012).

Good example of pyrometallurgy in LIB recycling is Inmetco process. It was originally developed for NiCd, NiMH and Li-ion batteries. Process produces iron-based alloy and recovers Ni and cobalt. For not being dedicated to LIB recycling Li is not focused and it is lost during the process (Georgi-Maschler et al., 2012). Inmetco process flowsheet is presented in Figure 4. Other example of pyrometallurgical process for LIBs is Sony's process with two steps. First batteries are incinerated in 1000°C to burn all flammable materials and then followed by Co extraction (Li et al., 2018). Hydrometallurgical recovery of metals is used industrially only by few companies. Retrieval, Recupyl, GEM and Brunp have been reported to recycle LIBs solely with hydrometallurgy industrially. Umicore has implemented combination of hydro- and pyrometallurgy into their recycling process. In this process no pretreatment of LIBs are required (Georgi-Maschler et al., 2012; Li et al., 2018). In Umicore process, pyrometallurgy is used to burn organic parts of the battery (plastics and

graphite) to form metal slag that contains Ni, Cu, Co and Fe. Slag is then leached with sulfuric acid and then solvent extraction is used to fractionate metals. Weakness of this process is that Li is lost during the process (Meshram et al., 2014). Umicore process flowsheet is presented in Figure 4. Pretreatment of LIBs is not necessary in either of the Umicore or Inmetco processes.

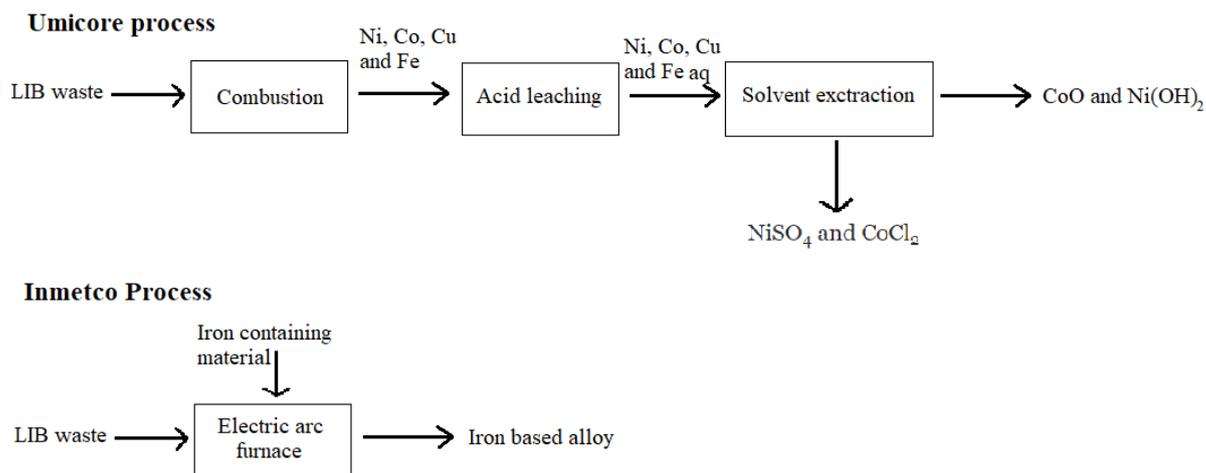


Figure 4 Flowsheets of Umicore and Inmetco processes (drawn according to (Meshram et al., 2014; Georgi-Maschler et al., 2012))

Li et al. (2018) describes that most of the current LIB recycling research is done in hydrometallurgical methods. Chemical precipitation (Contestabile et al., 2001; Dorella and Mansur, 2007), solvent extraction (Chen et al., 2011; Flett, 2004; Kang et al., 2010; Pranolo et al., 2010) and ion exchange (Flett, 2004) are researched widely. This can be seen in wide variety of different laboratory scale methods discovered. Hydrometallurgical methods offer high-purity products but have difficulties to scale up to industrial scale. This has caused pyrometallurgical processes to dominate the industrial-scale LIB recycling even though the higher pollution and energy costs (Li et al., 2018).

It should be noted that with hydrometallurgical processes, pre-treatment of LIBs is necessary to achieve better efficiency. This often means separating cathode material from other LIB scrap with mechanical processes. It should also be noted that in hydrometallurgy first process step often needs to be acid leaching of the metal scrap. Pyrometallurgy can somewhat avoid this pretreating by having increased temperatures to burn off the organic

compounds. Some pretreatment is applied to these processes as well for safety and convenience. LIBs need to be uncharged as well before any recycling can safely be done.

Increasing awareness towards climate change has also produced other competing method for metals recycling from batteries. This concerns high capacity electric vehicle (EV) batteries. In EVs battery capacity needs to be on point. In the case of worn out EV LIBs they still can be used as an energy storage. This idea has arisen from the need of electric grid wide power banks. By using LIBs that have lost most of their power density, can be integrated to power grid and they can be used to balance out deviating production of renewable energy sources. This can over double the life cycle of EV battery. This technology is not ready and needs lot more research before it could be implemented in large scales (Li et al., 2018). This does not mean that recycling processes for LIBs are not needed anymore. Even though LIBs in EV take longer to reach the recycling phase, they end up there eventually and, in the meantime, there are myriad of other sources of LIBs that are unfit for grid power storages.

## **2.3 LIB leach liquor properties**

Chemical properties of leach liquor chemical properties are important in order to design efficient separation processes for the metals. Oxidation states of these metals can vary and cause them act differently in separation process including ion exchange. It is presumed that LIB waste is leached into acid after mechanical grind. This is usual pretreatment before metal separation for battery waste. In this thesis only the sulfuric acid leaching is considered.

### **2.3.1 Chemical composition**

Leaching of the LIBs has been studied decently in recent years. Chemical composition of the leachate depends highly on the type of LIBs leached. Different leach liquors can be achieved also with leaching only certain parts of the LIB for example only cathode leach has much more desired metals than whole battery leach. Porvali et al. has studied LIB leaching in hydrochloric acid. In the study leach liquor was analyzed and metal composition of the liquor was discovered.

*Table 1 Metal concentrations mg/l in the LIB leach liquor according to different sources*

Metal	(Porvali et al., 2019) HCl	(Chen et al., 2015a) H <sub>2</sub> SO <sub>4</sub>	(Chen et al., 2015b) H <sub>2</sub> SO <sub>4</sub>
Al	1519	-	-
Co	16817	6450	7180
Cu	2145	-	1780
Fe	741	590	1960
Li	2548	1600	1490
Mn	2146	6310	5680
Ni	1996	6890	4290

Other compositions for LIB leachate are presented by Chen et al. (2015a) (2015b). Both were acquired from the cathode materials by reductive leaching with sulfuric acid. These compositions do not include Al and no redox potentials are provided.

Metals that are worth to extract from the liquor are cobalt, Ni and Li. Other metals are considered to be impurities. Cu however might be an exception due having decent concentration in the leach liquor and having somewhat high price. If Cu can be separated from other impurities with relative ease, it can be handled as a product rather than impurity. It has value of 2,68 USD per pound as of in October 21. 2019 (Macrotrends, 2019).

### **2.3.2 Redox potential and pH**

Knowing the redox potential for the leachate is essential to understand in what oxidation state the metals are. The redox potential determines for example will Fe ions be Fe(II) or Fe(III) oxidation state. Redox potentials of the different leach liquors can be found from Table 2.

*Table 2 Redox potentials of the LIB leach liquor according to literature*

Acid	Redox potential, mV vs. SHE	Reference
H <sub>2</sub> SO <sub>4</sub> / C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	967 717-287	(Peng et al., 2018)
HCl	842-1273	(Porvali et al., 2019)
H <sub>2</sub> SO <sub>4</sub>	>1097	(Meshram et al., 2018)
H <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O <sub>2</sub>	777	
H <sub>2</sub> SO <sub>4</sub> /NaHSO <sub>3</sub>	597	

Based of the redox potentials seen in Table 2 it can be assumed that most of the Fe is in the Fe(III) for in the liquor. Change between Fe(II) and Fe(III) occurs at 771 mV vs. SHE electrode and measured redox potentials are above it in most cases (Schweitzer and Pesterfield, 2010). Another quality of the leach liquor that affects the oxidations states and also otherwise the composition of the solution is pH. Leach liquor pH is low and can be as low as 0.17 according to Kang et al. (Kang et al., 2010). This is along the lines with F. Mendes and A. Martins measurements of 0.5-0.7 pH (Mendes and Martins, 2005). Effect of low pH is also important to take into account when choosing resins for ion exchange. PH can change selectivities and absorption capacities of ion exchange resins.

Co is in oxidation state II in lower than 1500 mV redox potential versus the SHE in pH 2 solution. This state of Co is easier to solubilize under the standard leaching conditions. Leaching of the Co (III) would require redox potential of +1,84 V (Meshram et al., 2015). Redox potential of the leach liquor is just above the line of Fe (III) oxidation state. Most of the Fe is going to be Fe (III) form but some Fe (II) might still remain in the liquor. This needs to be considered when designing the process.

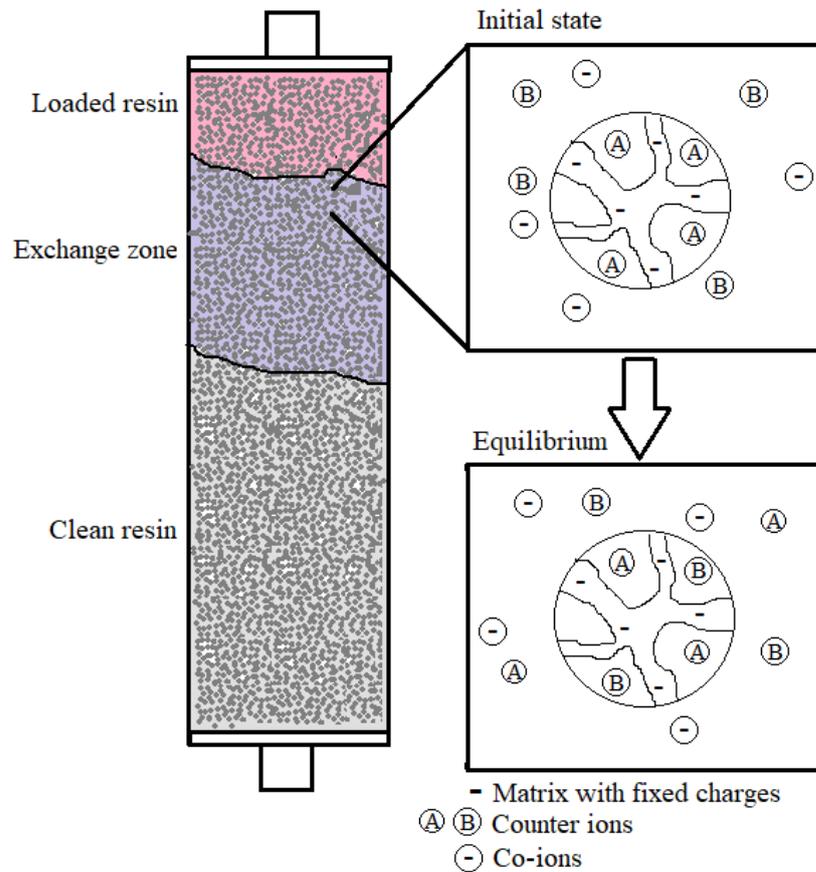
### **3. ION EXCHANGE IN METAL SEPARATION**

Ion exchange as technology has been gaining interest in many industries in last few decades (Inamuddin and Luqman, 2012). In the field of metal separation ion exchange is used widely and applications can be found from wastewater treatment to hydrometallurgy.

#### **3.1 Basic principle and important properties of ion exchange materials**

Korkisch (1989) states that ion exchange has been known as a phenomenon for over a century but practical uses for ion exchange were discovered in early 20<sup>th</sup> century. Ion exchange has applications in many different fields of chemistry, mainly in separation of complex ionic mixtures. (Korkisch, 1989). Ion exchange process is stoichiometric reversible reaction that occurs between ions in aqueous phase and ions in solid phase as described in Figure 5. Ions between electrolyte solution and solid ion exchange material needs to be similarly charged. Ion exchangers preference of one ion over another is caused by several factors (Helfferich, 1962; Nasef and Ujang, 2012):

1. Valence and size of the counter ion affecting electrostatic interactions.
2. Equivalent volume and participation to complex formation with co-ion.
3. Polarizability and strength of the interactions with matrix or fixed ionic groups.
4. Pore structure of the ion exchanger as it might block larger ions from attaching to active site inside the resin particle.



*Figure 5 Basic principle of ion exchange in column process (drawn according to (Helfferich, 1962; Nasef and Ujang, 2012; Ramkumar and Mukherjee, 2012))*

The property of the ion exchange resin to be able to differentiate between different counter ions is called selectivity (Nasef and Ujang, 2012). There is a good understanding of the ion exchange selectivity in the practical level but researchers have been struggling to find fundamental unifying theory to represent all the different behaviors of different ion exchangers (Small, 1989). In this thesis selectivity of the resin is one of the defining characteristics for deciding the best ion exchanger for different stages of the LIB recycling process. With the knowledge of selectivity in different process conditions different materials can be used in series to remove impurity metals and capture valuable metal ions from the solution. In this Thesis selectivity is discussed through comparing dynamic capacities of the ion exchange resins.

Other important property of the ion exchange material for the process design purposes is exchange capacity. According to Nasef and Ujang (2012) exchange capacity is defined as

the number of counter ion equivalents adsorbed to fixed amount of IX material. There are several different capacities that can be determined for the material but in this work dynamic exchange capacity is used meaning equivalents of counter ions per volume of packed bed in water (Nasef and Ujang, 2012). In this multi metal system that LIB leach liquor is, theoretical capacities are difficult to determine beforehand and breakthrough experiments are needed. From the breakthrough experiments breakthrough curves can be drawn and with numerical integration method presented in part 7.1, dynamic bed capacities can be determined and different ion exchange resins can be compared.

Other factors that impact the separation capabilities are pH and temperature. Lopes et al. (2012) states that pH is one of the most important properties to take into account when designing ion exchange processes. Metal uptake properties of resins may be impacted directly by pH of the aqueous solution. PH also affects the aqueous chemistry namely functional groups protonation and deprotonation properties. Temperature changes alter the transport properties and equilibrium, hence having an effect to capacity of the ion exchanger. Severity of this phenomenon depends on the structure and functional groups of the ion exchanger (Lopes et al., 2012).

### **3.2 Applications**

There are different ion exchange materials that can be used depending on the desired separation task. Ion exchange resins are mostly used in column and batch type process and membrane or sheet type materials are used in plate or frame module processes. (Nasef and Ujang, 2012) Other typical materials used as ion exchangers are zeolites and clay. In this work ion exchange resins are studied as ion exchange (IX) material.

Borrini et al. (2012) have filed a patent for ion exchange process for LIB battery recycling. In the process there are leaching step and two ion exchange steps. In both of the ion exchange steps sulfonic cation exchange resin is used to fractionate the feed to three fractions. First fraction contains Li second Ni, Co, Mn and third Al. Fraction containing Mn is treated further with separation of Mn from Co and Ni. First elution is gradient elution and it is carried out with sulfuric acid with increasing concentration from 0,8 M to 4 M. Second steps elution is carried out with organic reagent diethylenetriaminepentaacetic acid (DTPA) to remove Co and Ni from the resin. This is followed by sulfuric acid elution with concentration of 4 M. It

is also stated that closing the maximum capacity of the resin, selectivity decreases and after 40 percent, separation is no longer sufficient. (Borrini et al., 2012).

Ion exchange has been used industrially for Co electrolyte purification. Sole et al. describe in their article about pilot plant results at Luilu plant in Democratic Republic of Congo. They portray commercial design for ion exchange process used in Co plant. They concluded that ion exchange can be successfully used to remove traces of Cu and zinc from Co electrolyte solution. This pilot process consists of two different fixed-bed phases. Cu is removed first with IDA resin and then zinc with AMPA resin. (Jurrius and Sole, 2016) Feed solution has some similarities with LIB leach as well. Co concentration is 17 000 mg/l and Mn concentration 3350 mg/l. Whereas this electrolyte solution is lacking in nickel, Al and Fe content. (Jurrius et al., 2014)

Sainio and Suppala describe a process for purifying Co containing feed solution in ore processing plant. Described process is continuous counter-current ion exchange process. Simulated moving bed (SMB) configuration is used where fixed beds act like counter current material. This is achieved by adjusting feed, extract and raffinate points at certain intervals against the flow of eluent inside the columns. They state that pH of the eluent should be high enough to enable impurity metal absorption but avoid Co absorption. Co concentrations in electrolyte solution surpass the amounts found in LIB leach liquors as they may vary from 10 g/l to 100 g/l while LIB leach liquor has less than 20 g/l. It is described that Lewatit TP-260 AMPA resin is used in the invention as ion exchange material and sulfuric acid as a eluent with concentration below 2.25 M. (Sainio and Suppala, 2015)

### **3.3 Ion exchange resins**

Ion exchange resins are class of ion exchangers that have polymeric matrix that house functional ionic groups. They are insoluble and carry exchangeable cations or anions and fixed charges on the matrix. This polymeric matrix consists of three-dimensional usually hydrocarbon chains that are crosslinked in order to achieve the insolubility. Liquid phase that houses the resin affects resin by swelling or shrinking it, depending on the phase's composition. (Heinonen, 2013) Nasef and Ujang (2012) states that ion exchange resins are most commonly used ion exchange material (Nasef and Ujang, 2012). Ion exchange resins have many different functionalities. Functional group in ion exchange resins define what

ions can be captured with them. Functional groups are attached to resin polymer matrix. According to Nasef and Ujang (2012), resins are divided to strong and weak resins as well as anion and cation exchangers by their functional ionic groups (Nasef and Ujang, 2012). Weak resins can only be used in certain pH, but strong resins are functional regardless of pH. This is due the fact that weak resins functional groups are ionized under only specific pH range causing it not to function outside of it. (Helfferich, 1962)

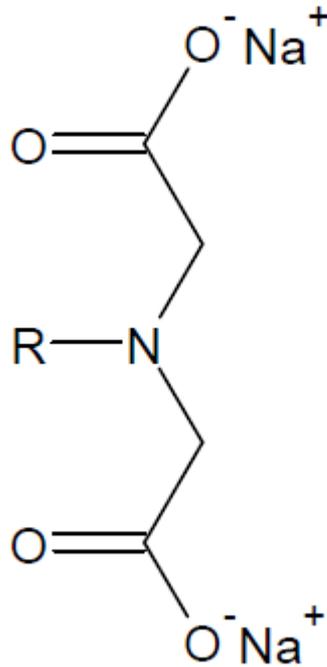
For IX resin to be ideal for industrial use it needs to have certain properties. It should have high chemical and physical stability and decent degree of cross-linking. Other important properties are fast and lasting ion exchange kinetics and capacity with similar particle size. Selectivity suitable for the separation of species needed is also important factor to consider. Physical and chemical properties of the resin define its performance as ion exchanger. (Nasef and Ujang, 2012) For this Thesis, selectivity and capacity are selected to be the main design parameters for selecting appropriate IX resins.

### 3.3.1 Chelating resins

Chelating resins are ion exchange resins that attach the metal ion with multiple interactions. Mechanism of ion exchange is more complicated with chelating resins than it is with regular cation/anion exchangers. Chelating resins binds counter ions with electrostatic and coordinate interactions. This makes them especially potential to transition metals. They have high selectivity towards some metal ions. Stability of the different metal complexes formed by the resin is affected by pH. This makes chelating resins useful in the metals separation, especially for selective sorption of single metal from multi metal solutions. (Nasef and Ujang, 2012) Fe and Al can be difficult to elute out of the chelating resins however because of this. Chelating resins are more compared to other types of IX resins. Metals attach to the resin as Equation 1 presents.

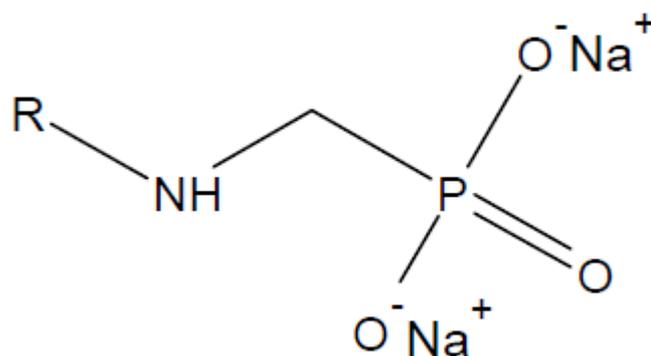


Ion exchange reaction is presented to acid form resins. This is because all resins used in the experimental part are transferred to the acid form as well before use. In experimental part of the Thesis two chelating ion exchange resins are used. Functionalities of these resins are as follows: Aminomethylphosphonic acid for Lewatit TP260 and iminodiacetic acid for Purolite S-930. Structure of these different resins are presented in Figure 6 and Figure 7.



*Figure 6 Molecular structure of iminodiacetic acid functional group in Na<sup>+</sup> form*

Iminodiacetic acid resin (IDA) have three bonding sites, two in the carboxylic oxygen and one in imino nitrogen atom. IDA forms moderately soluble and kinetically labile complexes, hence ensuring the reversible sorption. (Nasef and Ujang, 2012) Zainol and Nicol states in their study of laterite leach tailings that Fe and Al are strongly absorbed by IDA (Zainol and Nicol, 2009). This presents possibilities for the use of IDA resin for impurity removal from LIB leach liquor. However, chelating resins have tendency to hold on to these two metals strongly. If it is discovered that they cannot be eluted from the resin, viability for using this resin in industrial processes diminishes greatly. As stated earlier chelating resins are expensive and single time use is not economically feasible.

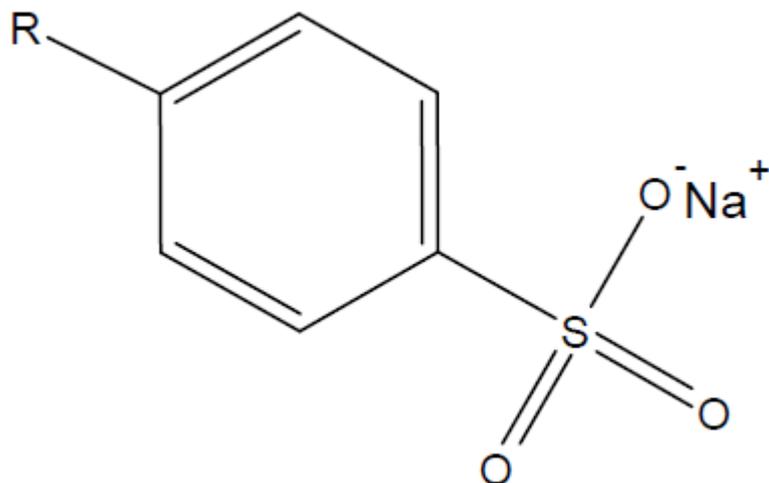


*Figure 7 Molecular structure of aminomethylphosphonic acid functional group in Na<sup>+</sup> form*

Aminomethylphosphonic acid resins (AMPA) have showed increased selectivity to toxic heavy metals. This resin can function under acidic conditions as low as 1 pH and it has three ligand atoms. These are the phosphonic acid groups as a bonding sites and one nitrogen atom as a coordination site. AMPA has shown high selectivity between 2<sup>+</sup> transition metals and alkaline earth group. Altogether AMPA is more versatile than IDA and has had success in metal recovery from complex solutions. (Nasef and Ujang, 2012) AMPA resin has been used in Co electrolyte purification. As the patent from Sainio and Suppala describes, it was used in counter current simulated moving bed continuous ion exchange (CIX) process. With AMPA resin concentrated Co solution was enriched and separated from cadmium (Cd), magnesium (Mg), Mn and lead (Pb). (Sainio and Suppala, 2015)

### **3.3.2 Strong cation exchange resin**

Cation exchangers in general are ion exchangers that can change cations. In strong cation exchange resin the functional group has strong acid in it. In this case the strong acid is sulfonic acid that is one of the most common functional group in strong cation exchangers. In sulfonic acid there is one active atom in ion exchange that is the oxygen atom bind to sulphur with sigma bond as Figure 8 describes.



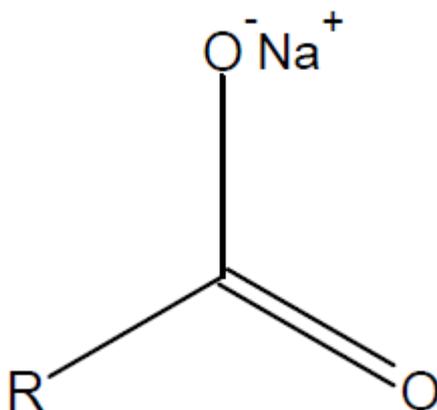
*Figure 8 Molecular structure of sulfonic acid functional group in Na<sup>+</sup> form*

Reaction of metal ions exchanged into resin is presented in Equation 2. This reaction is presented in acid form as it is used in the experimental part of this thesis.



### **3.3.3 Weak cation exchange resin**

Weak cation exchanger differs from the strong cation exchanger with the functional group being weak acid instead of strong one. Structure of the carboxylic acid functional group is presented in Figure 9.



*Figure 9 Molecular structure of carboxylic acid functional group in Na<sup>+</sup> form*

Reaction of metal ions exchanged into resin is presented in Equation 3. This reaction is presented in acid form as it is used in the experimental part of this thesis.



### **3.4 Resin comparison**

For experimental section of the Thesis, resins need to be selected. Important factors for the purpose of metals capture from LIB leach liquor are selectivity, capacity and that the resin is functional in low pH. Through literature survey twelve resins in total were discovered to show promise for the purpose of separating LIB metals. Resins and their properties are compiled to the Table 3. One of these resins is novel resin produced by Li et al. Likewise one resin was discovered to have capabilities for Co and Ni separation.

Table 3 Ion exchange resins for LIB recycling found in literature survey and corresponding properties

Resin	NDC-984	Dowex M4195	Amberlite IRC 748	PUROLITE S-930	TP 207 MonoPlus	PUROLITE S-950	TP 260
<b>Functional group</b>	Poly-amine	Bispicolyl-amine	IDA	IDA	IDA	APA	AMPA
<b>Selectivity</b>	Ni(II) >Co(II)	Cu>Ni>Fe(III)>Co (pH=2)	Fe(III)>Cu>Ni>Co >Fe(II)>Mn	Cu>>Ni>Co(III)> Fe(II)>Mn	Cu>Ni>Fe(II)>Mn pH=acidic	Fe(III)>Cu>Al(III) >Ni>Co(II)	Fe(III)Cu>Ni >Co(II)
<b>Exchange capacity,</b>	-	1.04 eq/l	1.35 eq/l	1.57 eq/l	2.0 eq/l	1.3 eq/l	2.4 eq/l
<b>Other notable properties</b>	Novel resin	Works on pH <2	pH 2 only capable to remove Fe(III), Cu and Hg	Cu removal	Cu removal	Cu, Ca, Mg removal	Works on low pH
<b>Reference</b>	(Li et al., 2012)	(Chiu and Chen, 2017; Flett, 2004)	(Chiu and Chen, 2017)	(Siqueira et al., 2011)	(Jurrius et al., 2014; Zainol and Nicol, 2009)	(Fisher and Treadgold, 2008)	(LanXess, 2011; Sainio and Suppala, 2015)

<b>Resin</b>	Purolite NRW100	Trilite CMP28	Trilite SCRB	Amberlite IRN77	Amberlite IR 120
<b>Functional group</b>	SO <sub>3</sub> H	SO <sub>3</sub> H	SO <sub>3</sub> H	SO <sub>3</sub> H	SO <sub>3</sub> H
<b>Selectivity</b>	-	-	-	Cr>Ni Co	Cr> Ni
<b>Exchange capacity,</b>	1.8 eq/l	2.2 eq/l	2.0 eq/l	1.90 eq/l	1.8 eq/l
<b>Other notable properties</b>	-	-	-	Can absorb Ni and Co but Cr interferes	Gel type resin, can remove Al from cobalt
<b>Reference</b>	(Juang and Wang, 2003)	(Won et al., 2016)	(Won et al., 2016)	(Rengaraj et al., 2002)	(Lemaire et al., 2014)

As per the literature survey, three functionalities are dominant for the impurity removal from LIB leachate. Chelating resins with IDA or APA/AMPA functional groups and sulfonic acid strong cation exchanger. Bis-picolylamine resin has been used before and has shown great promise in the Co and Ni separation (Flett, 2004). Resin NDC-984 could be used as well in the Ni Co separation, but it is a novel resin and hence was inaccessible for this thesis at timeframe available.

Selectivities and exchange capacities of the resins provide sufficient information to decide which resins should be selected given that they function in lower pH. Selectivity of the resin is affected mostly by the ionic group of the resin and by the pore size of the resin (Helfferich, 1962). All resins that share the same functional group have usually similar selectivity order. This is not surprising because pore size can influence selectivity, but it often does not. Fe (III), Al and Cu ions are strongly favored by the chelating resins. This is in line with the Nasef and Ujang who state that chelating resins are particularly effective in capturing transition metals (Nasef and Ujang, 2012).

For the experimental part AMPA and IDA resins were selected with sulfonic acid and carboxylic acid resins. Strong and weak cation exchangers were selected merely as a reference to justify the use of more expensive chelating resins. Selected chelating resins were Lewatit TP260 and Purolite S-930.

## **4. ION EXCHANGE CHROMATOGRAPHY IN METAL SEPARATION**

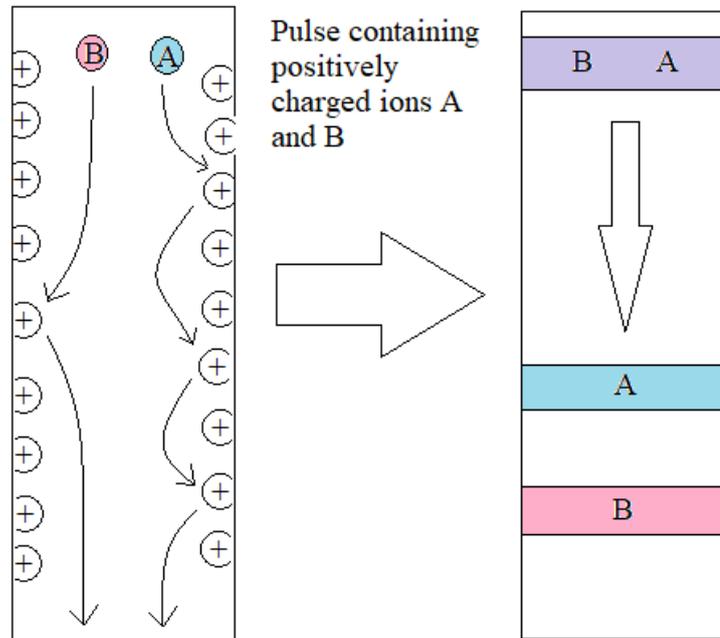
Ion exchange chromatography falls under the liquid chromatography (LC) (Small, 1989). It is used as an analytical tool in biochemistry and medicine (Walton, 1976). As a separation method ion exchange chromatography is mainly used in food, fine chemicals, pharmaceutical and petrochemical industries as a CIX SMB process. Hydrometallurgical applications have also been discovered for SMB type operation (Sainio and Suppala, 2015; Virolainen et al., 2014).

### **4.1 Basic principle**

In liquid chromatography stationary phase is confined by column or capillary. Stationary phase can be any solid absorbent but in the special case of ion exchange chromatography it is ion exchange material. Inside the stationary phase, void space exists through which mobile phase is pumped. In the case of LC mobile phase is liquid. Separation of different species in the liquid phase are driven by the unequal partition of these solutes between phases. It relies on the different passing times through the chromatograph to enable the fractionation. Reasons for this diffusion of solutes to different phases can be identified to be thermodynamics and chemistry (Small, 1989).

In the case of ion exchange chromatography ion exchange capabilities of the stationary phase provide new factor that differentiates solutes in liquid phase to different continuous phases. Ionic solutes react with the ion exchanger continuously on their way through the column. This is possible due the reversible nature of ion exchange reaction and eluent that is capable to replace the solutes ions in the resin. In ion exchange chromatography it is preferable that resin does not capture the target ions but just slightly affect their retention time through the ion exchange bed. This is described in Figure 10. (Gjerde and Fritz, 1987) This is achieved with eluent strong enough to reverse the IX reaction between ions and resin but weak enough not to prevent the reaction totally. In principle ions get captured into resin multiple times during their pass through the column and the number of times that the metal ion react with the resin determines what the retention time is for the specific ion. In Figure 10, ion A is reacting more with the IX material and the retention time is increased when compared to ion B. This provides opportunity to collect concentrated solutions of A and B from the outlet of

the column. Modern ion exchangers used in chromatography have mostly low capacities because of the lack of intent to actually capture the metal ions but merely just slow them down. (Small, 1989)



*Figure 10 Basic principle of separation in ion exchange chromatography (drawn according to (Small 1989; Walton 1976))*

Ever so slight differences in ion exchange resin polymer structure exists providing the void space and this makes it possible to perform wide array of chromatographic separations. In modern liquid chromatography affinity differences do not need to be large to facilitate effective separation. It is also notable that the line between ion exchange and non-ion exchange chromatography is getting obscure. Precision comes from the fact that resin beads are small and uniform in size, forming narrow bands through the bed. Ion exchange resins can be used in chromatography as regular adsorbents with their ability to swell and so affect the penetration of other molecules (Walton, 1976).

## 4.2 Effect of changing ligands

It is possible to affect ion exchange equilibrium in the IC with complexation of metal ions by neutral or anionic ligands. With using complexing agents, it is possible to change metals ion exchange behavior. Mainly the charge of the complex and affinity towards the ion exchanger can be affected with ligands. The stability of the ligand also plays important role. If stability of the complex formed is low more ligand needs to be introduced to the external phase. From these factors the most important factor is the change of charge that the complexation causes. Anionic ligand can change metal ions charge from cationic all the way to anionic. The total charge of complex formed comes from the charges of the metal ion and the ligand as well as from number of ligands attached. (Small, 1989)

Different ligands forming complexes with metal ions are inorganic ions like  $\text{CO}_3^{2-}$  or  $\text{CN}^-$  and multidentate organic ions like EDTA and oxalate. This division to simple inorganic ligands and chelating organic ligands is widely accepted. Cu and Co can form stable cyanide complexes applicable to IC environment and transition metals form strong complexes with multidentate chelating ligands. (Small, 1989) This has similarity to the chelating resins because the reaction the metal ion undergoes with complexing agent is the same regardless whether the ligand is attached to polymer structure like resin or just as a free molecule in moving phase. Ligand forming complexes can be used in IX as well to partially elute resin bed. Elution of difficult to elute metals like Fe (III) can also be achieved with ligand forming complexes.

## **5. PRELIMINARY CONSIDERATIONS FOR ION EXCHANGE PROCESS DESIGN IN LIB RECYCLING**

Recycling process of metals from LIB leachate with ion exchange has two clear challenges to overcome. LIB leach liquor contains multiple impurities that interfere with valuable metal separation. These impurity metals need to be removed or captured before recovery of more valuable metals can be attempted. After leach liquor has only the more valuable metals Co, Ni and Li, the real challenge is separating Ni from Co as Li is still present in the solution.

In this chapter important literature concerning process design is reviewed. On the basis of this literature, process routes for ion exchange process are presented. Impurity removal is straight forward design task. when actual selectivities of the resins to LIB leachate metals are discovered. Co/Ni/Li containing raffinate needs more careful considerations. Ni/Co separation has been achieved with ion exchange but Li in the solution can cause problems. Impurity removal is addressed briefly, and Co/Ni separation is discoursed in more detail.

### **5.1 Impurity removal**

Primary impurity metals in LIB leach liquor are Al, Cu, Fe and Mn (Porvali et al., 2019). Can impurity metals be separated efficiently with ion exchange? As revealed in Table 3, removal of Al, Cu and Fe (III) with ion exchange is easy. Most resin prefer these metals over more valuable product metals of Co, Ni and Li. The problem is manganese. Selectivities of chelating resins seem to prefer Co and Ni over Mn (Jurrius et al., 2014).

Other issue that might be faced in especially Fe and Al elution is that chelating resins might cling strongly to these metals. This means that they cannot be removed easily from the resin phase with regular eluents. If this is the case, alternative eluents for resin regeneration should be investigated to enable continuous operations without changing the resin bed.

### **5.2 Ni and Co separation**

Ni Co separation efficiently is very arduous task as stated in article by L. Rostato et al. These two metals have similar chemical properties. (Rosato et al., 1984) According to Inamuddin and Luqman counter ions having similar charge and ionic radii, the ion exchange materials

selectivity stemming from these properties of the material, is not differentiating enough to achieve good separation. This can be avoided with the use of appropriate complexing agent. When added to aqueous phase, selectivity can be attained through differences in the complexes formed by these metals. (Inamuddin and Luqman, 2012) In complex formation it needs to be kept in mind, as stated by Flett (2004), that other metals can interfere with Co complex formation. Chloride can be used to separate Co and nickel. Co forms  $\text{CoCl}_3$  and  $\text{CoCl}_4$  with chloride which Ni does not. This process can be interfered by other chloro-complex forming ions such as ferric iron, Cu and zinc. (Flett, 2004)

Difficulties in the separation of Co and Ni is caused by very similar properties of Co and Ni ions. As can be seen from Table 4 atomic radius and electronegativity of these two metals are really close each other. Co can be found in higher oxidation state Co(III) but this form of Co has negligible water solubility and so ion exchange separation in aqueous solution as studied in this Thesis does not concern it.

*Table 4 Properties relevant for hydrometallurgy of Co and Ni*

	<b>Electronegativity</b>	<b>Atomic radius, pm</b>	<b>Oxidation states</b>	<b>Valence electrons</b>
Ni	1.91	124	+2	2, 1
Co	1.88	125	+2, +3	2

Complex forming ion exchangers have found to have separating capabilities for these two metals as stated by Flett in his review article (Flett, 2004). These chelating resins capture other metals over the targeted Co and nickel, so it is necessary to remove the impurities first from the leach liquor and then capture Co and Ni from solution containing mostly Co, Ni and Li. For this separation Bis-picolylamine resin Dowex M4195 has been found functional by Flett as well as Chiu and Chen (Chiu and Chen, 2017; Flett, 2004). Manufacturer of Dowex M4195 resin also states on the product sheet that it is especially made for Cu, Co and Ni processing. They also describe that the resin is already being commercially used to purify Co electrolyte solutions from Ni traces (Dow Chemical Company, 2019).

Rosato et al. discovered in their research about Ni and Co separation that it is possible to fractionate these metals with split elution from the loaded resin Dowex M 4195.

Fractionation was achieved by first eluting the resin with 25 g/l sulfuric acid solution with the flowrate of 15-16 BV/h for 4 BV and then using 50 g/l sulfuric acid with flowrate of 2.0-2.5 BV/h for 12 BV. With this method in the first phase around 80 percent of Co with 15 percent of Ni would be eluted and in the second phase rest of the Co would be eluted with 84 percent of nickel. Loaded resin had metals concentrations of 13-15 g/l for Co and 16-18 g/l for nickel. (Rosato et al., 1984) Concept of split elution was also proved in Co electrolyte purification by K. Sole et al. (Jurrius and Sole, 2016).

Rosato et al. operated under slightly differing conditions that of LIB leach liquor. In their study the solution had Co/Ni ratios between 12 to 50 and according to Table 1 LIB leach liquor has conventionally the ratio of 8.4. The study also concludes that the higher the Co/Ni ratio is the better from the ion exchange separation point of view. Separating Co and Ni this way in LIB recycling is a possibility but it needs to be kept in mind that multicolumn operation is needed to fully separate these metals from each other. Also, this separation was done in bi-metal system. In the case of LIBs most likely Li persist in the solution as well and its effects to the process is unknown. Because of this all the Co and Ni needs to be preferably captured from the leachate together.

Co electrolyte purification can be used as a reference for this process. However, it should be kept in mind that in Co electrolyte treatment Co concentrations can reach multiple times the levels of which are present in LIB recycling. Sainio and Suppala states that methods used in electrolyte treatment are focused in the purification of the Co solution rather than capturing the Co out of it. This is because in high Co concentrations the bis-picolylamine resin presented before is not functional and separation does not happen. (Sainio and Suppala, 2015)..

There is a possibility to capture  $\text{Li}^+$  from the Li, Co and Ni solution. Hui and Chitrakar et al. have reported that ion exchanger material of  $\text{H}_2\text{TiO}_3$  is capable to recover  $\text{Li}^+$  (Hui, 2000; R. Chitrakar et al., 2014). From lithium hydroxide solution with Li concentration being 694 mg/l 39,8 mg/g equilibrium adsorptive capacity was reached. Recovery rate of Li was reported being 98,86 %. (SHI et al., 2013)

### 5.3 Alternative ion exchange process routes

First possible option to set up the ion exchange process for LIB leachate is to remove all impurities with aminomethylphosphonic resin and then separate Ni from Co with bis-picolylamine resin. As can be seen from the Figure 11 only two steps are required for the separation. This possibility depends on if the AMPA resin can capture all impurity metals.

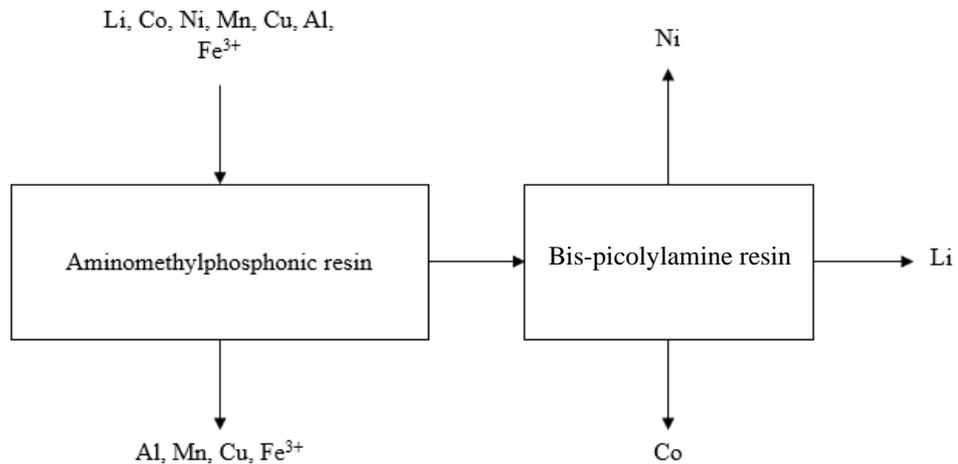


Figure 11 Process possibility with two ion exchange steps

This simple process might have issues with resin filling up quickly due only having one impurity removal step and making all metals to be attached to same resin. Regeneration of the AMPA can prove difficult especially when Fe is concerned. With Cu ending up with all other impurity metals, the economic viability of the Cu capture should be considered. Especially if more than one process step is required. In product metal separation chromatographic separation or selective elution with different eluents could be implemented.

Second possibility for process is like the first one but Li is removed before Ni and Co separation. For Co/Ni separation split elution can be used as described by Rosato et al. (1984) and as presented in Figure 12.

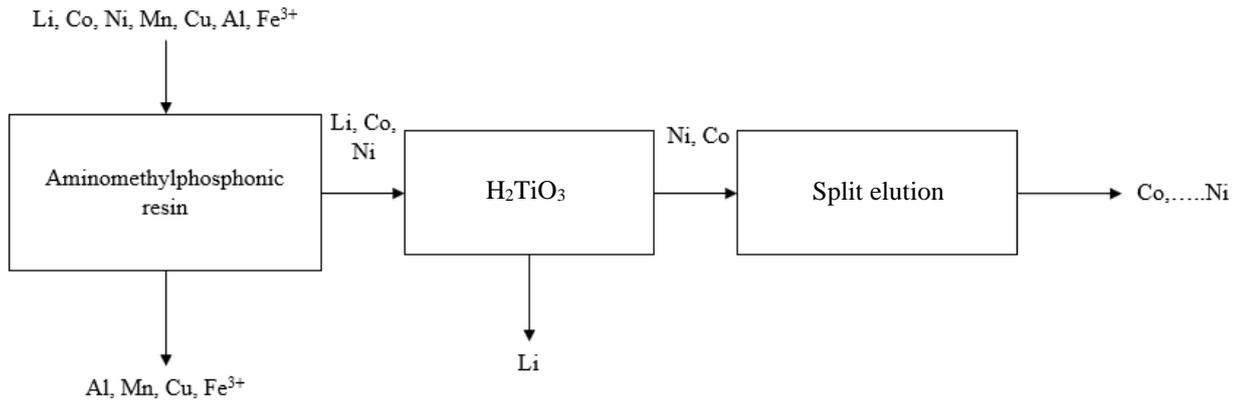


Figure 12 Process possibility with Li removal before Co and Ni separation

Li removal before Co and Ni separation is necessary to enable the split elution.  $\text{H}_2\text{TiO}_3$  is novel ion exchanger that is not available commercially. This makes this process setup unlikely to have significance before this ion exchange material is studied further.

Third process setup again shares similar impurity removal step with previous possibilities but here it is assumed that Li is removed from raffinate before Co/Ni separation. Also, it is assumed that split or chromatographic elution yielding sufficient separation. This means that Co and Ni need to be captured separately (Figure 13). Ni can be captured with bis-picolylamine resin and IDA resin can be used to recover cobalt.

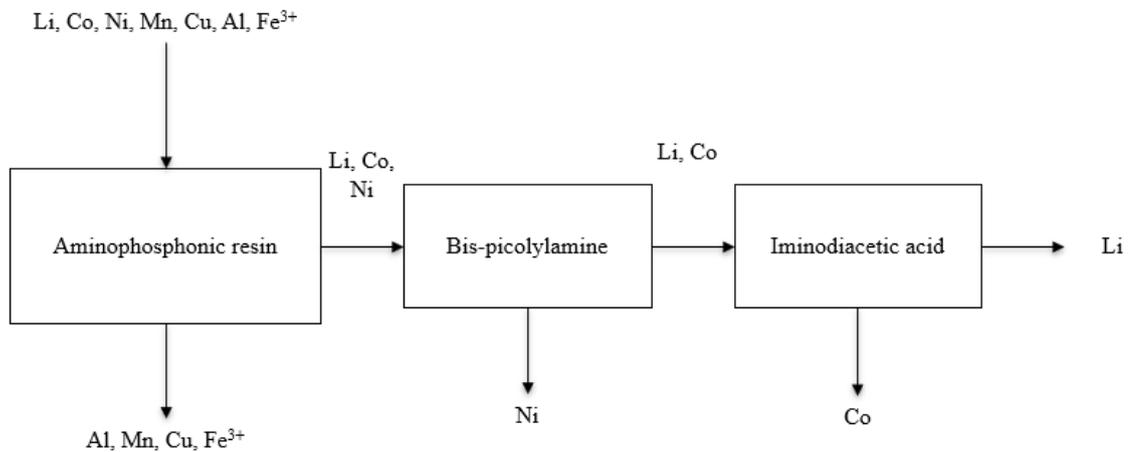
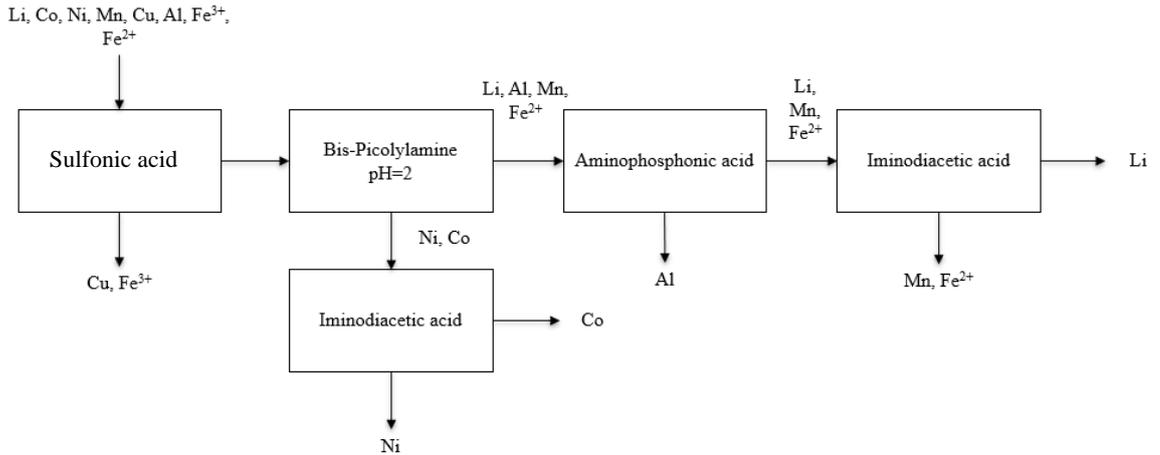


Figure 13 Process possibility with separate steps to remove Ni and Co from Li

Lastly in the undesirable scenario that none of the processes described so far result in the good separation. This scenario assumes that Fe is captured by AMPA resin so that it cannot be eluted from the resin. This means that Fe(III) is required to remove before the use of AMPA resin. It is also assumed that there might be traces of Fe(II). In Figure 14 process with multiple steps for impurity removal is presented.



*Figure 14 Process possibility for worst case scenario with Fe (II) present and AMPA elution difficulties*

From these processes the first one is the preferable. Simple separation step for all impurities and one step separation for the Co and Ni separation. If it proves to be impossible to do this process in two steps, then more steps are added but the goal is to keep amount of unit operations as low as possible to increase the economic viability of the final design.

## **6. MATERIALS AND METHODS**

Goal for the experimental part was to study the possibility of ion exchange process for recovering cobalt, Ni and Li from synthetic LIB waste. Impurity removal was focused in this experimental study. Four different ion exchange resins were studied in impurity removal. Multicycle experiments were conducted with two different elution phases. Different eluents were researched for regeneration of the resin and multicycle experiments with selected resin were done to confirm the possibility for continuous operation. All ion exchange experiments were conducted in glass columns. Metal concentrations of samples were analyzed with Agilent technologies 7900 ICP-MS.

### **6.1 Raw materials**

#### **6.1.1 Synthetic solution**

Experiments were started with synthetic LIB solution based on research by Porvali et. al. All the metals used were in sulphate form and they were leached into 1 M sulfuric acid solution. Because of LIB waste has many other impurities than the major ones that are discussed here technical grade substances can be used to create synthetic solution. These other impurities are in such a small quantities that they can be ignored. Synthetic solution was prepared into plastic tank and all compounds were weighted in. Compounds used and their properties can be found in Table 5 with the concentrations in the synthetic solution. Product metal purity was determined to be 75 % in the synthetic leach liquor before any purifying.

*Table 5 Synthetic solution composition and used chemicals*

<b>Substance</b>	<b>Manufacturer</b>	<b>Concentration (according to measured masses), mg/l</b>	<b>Purity, %</b>
$\text{Al}_2\text{O}_3 \cdot 12\text{S}_3, 18\text{H}_2\text{O}$	PROLABO	1360	>95
$\text{CoO}_4\text{S}, 7\text{H}_2\text{O}$	Alfa Aesar	15176	98
$\text{Cu(II)O}_4\text{S}$	VWR Chemicals	1965	99
$\text{Fe(III)}_2(\text{SO}_4)_3, x\text{H}_2\text{O}$	Alfa Aesar	1335	>95
$\text{Li}_2\text{SO}_4, \text{H}_2\text{O}$	Alfa Aesar	4587	99
$\text{MnSO}_4, \text{H}_2\text{O}$	Alfa Aesar	2295	99
$\text{NiSO}_4, 6\text{H}_2\text{O}$	SIGMA-ALDRICH	1800	99
$\text{H}_2\text{SO}_4$	Merck	98079	95-97

Redox potential measurements were performed with Mettler Toledo FiveGo handheld device with LE510 Ag/AgCl electrode. Initial redox potential of the synthetic solution was 538 mV against Ag/AgCl electrode. Redox potential measurements were continued throughout the experimental study. As the Table 6 shows, redox potential of the solution did not oscillate during the two months of measurements. This proves that synthetic leach liquor does not decay, and it can be used in later experiments.

*Table 6 Redox potential of the synthetic leach liquor at different dates*

Date	Redox potential, mV
9.4.	538
18.4.	521
23.4.	522
13.5.	522
3.6.	533

In the experiments, effect of pH was studied and hence pH needed to be adjusted between original pH of -0,04 and pH 3. This was done with solid NaOH pellets and 1M NaOH solution. While adding the nuggets into the leach liquor, pH was monitored with pH meter and proper mixing was ensured. Precipitation of Fe occurred around pH 2. This affected the experiments greatly because of the physical properties of formed Fe(OH)<sub>3</sub>. Fe(OH)<sub>3</sub> particle size is very small and it forms sludge like solid that clogs the HPLC pump used. It is safe to say that observed precipitate is Fe(OH)<sub>3</sub>. This is because redox potential being close to the limit where only Fe(III) exists according to Eh-pH diagram of Fe. Boundary between these two oxidation states is 771 mV vs. SHE in pH 2 and below. Past pH 2 boundary for Fe(OH)<sub>3</sub> to exist decreases linearly reaching 0 mV pH 6. This is implied by the color of the precipitate as well. Fe (III) forms brown sludge-like precipitate and as Figure 15 shows precipitate found in pH adjusted liquor looks exactly that.



*Figure 15 Synthetic leach liquor, pH adjusted to 3 with NaOH, and Fe(OH)<sub>3</sub> precipitate*

Removal of the Fe(OH)<sub>3</sub> precipitate was difficult for it not getting separated with filtration but centrifuging the solution worked. When the sludge was removed, most of the Fe in the solution got removed as can be seen from the Figure 16. This removal of Fe(OH)<sub>3</sub> was arduous and demonstrated that pH values of the solution higher than two would be difficult in larger scale. In Figure 17 centrifuged and filtrated leach liquor is portrayed and it can be seen that even after all of this pretreating some phase boundary exists.

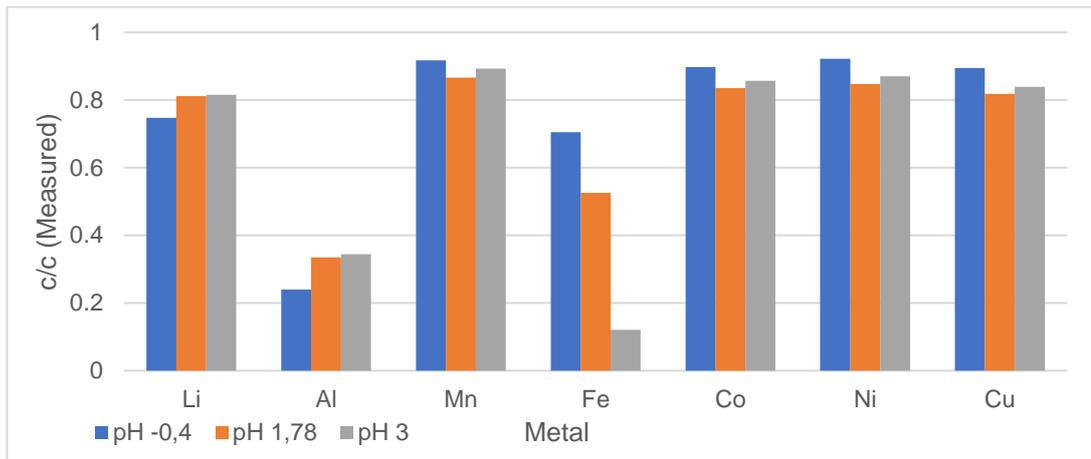


Figure 16 Concentrations of metals in each pH adjusted solution compared to calculated concentrations from the measured masses of metal sulphates.



Figure 17 Centrifuged and filtrated (20  $\mu\text{m}$  syringe filter) synthetic leach liquor with  $\text{Fe}(\text{OH})_3$  phase boundary

Study of the pH adjusted solutions unveiled alongside of the Fe precipitation other significant thing. As shown in the Figure 16 Aluminium sulphate weighted into solution contained significantly less aluminium than stoichiometrically it should have had. It was still possible to be detected with ICP and the amount of aluminium in the leach liquor was low from the beginning, so this discovery does affect the results only marginally. Amount of Co seems to vary greatly but this is most likely due the concentration being significantly over the calibration curve on ICP making analysis inaccurate. Solubility experiment was conducted after participation of Fe was examined.

### 6.1.2 Ion exchange resins

In impurity removal, four resins were studied. Two chelating resins with different functional groups were chosen as per literature review and one strong cation exchanger (SAC) and one weak cation exchanger (WAC) were selected to work as a reference. Properties of these resins used in the experiments are shown in Table 7.

*Table 7 Properties of the ion exchange resins for removal of impurities*

Resin	TP260	S-930	CS12GC	CA16GC
Type	Chelating	Chelating	SAC	WAC
Functional group	Aminophosphonic acid	Iminodiacetic acid	Sulfonic acid	Carbocyclic acid
Bed porosity	0,423	0,430	-	-
Manufacturer	Lewatit	Purolite	Finex	Finex

Void fractions for resin beds were calculated. 5 g/l blue dextran (BD) solution was used for determining empty space in resin beds. Pulse of 4 ml was injected to column in fifteen-minute intervals and it was eluted trough the column with water with the flowrate of 2,011

ml/min. Before this pipevoid of the setup was measured to be 2,2 ml. Breakthrough of the BD pulse was monitored with online UV/Vis analysis. Absorbance data was normalized. Three pulses of BD were injected and center of masses were determined for all three spikes observed in absorbance data from UV/Vis. Average of center of masses in ml were calculated and used in the bed porosity calculations. Center of mass was calculated as equation 4 shows.

$$PMC = \frac{\sum_i A_{N,i}}{\sum_i \left( \frac{A_{N,i}}{V_i - V_p} \right)} \quad (4)$$

Where

$A_N$	Normalized absorbance at temporal point, i
PMC	Center of mass of the peak
$V_p$	Volume of the pipevoid before UV/VIS detector
$V_i$	Volume of eluent fed in the column at temporal point, i

And void fraction was calculated as presented in the equation 5.

$$\Phi = \frac{PMC_{average}}{V_{bed}} = \frac{\frac{1}{3} \sum_{i=1}^3 PMC_i}{h_{bed} \left( \frac{\pi D_{bed}}{2} \right)^2} \quad (5)$$

Where

$\Phi$	Void fraction
$D_{bed}$	Diameter of the resin bed
$h_{bed}$	Height of the resin bed
PMC	Center of mass of the peak

In Table 8 parameters for calculations of void fraction are presented and actual void fraction is shown for TP260 and S-930.

*Table 8*      *Void fractions and required parameters for its determination for chelating resins*

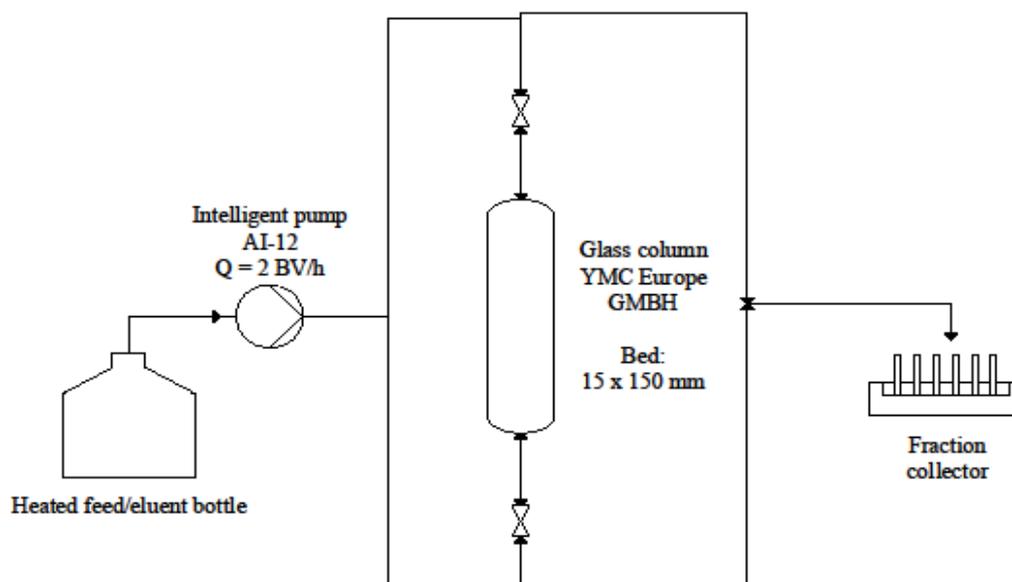
	TP260	S-930
$h_{\text{bed}}$ , cm	15,6	15,1
$V_{\text{pipes}}$ , ml	2,2	2,2
$\text{PMC}_{\text{average}}$	11.672	11.48
$\Phi$	0.423	0.43

All resins were transformed from  $\text{Na}^-$  ion form, which they ship as, to  $\text{H}^+$  form. This was done by first washing the resin with purified water and then pouring 1M HCl and 1M NaOH alternating through the resin. One-liter glass column was used to house the resins. Between each of these steps, resins were washed with purified water. With this procedure, complete ion form change can be achieved. Change was monitored with pH of the outflow. These resins shrink when introduced to 2M sulfuric acid solution and all by different amount. Bed volumes referred in this experimental part are the volumes when resins are packed, and bed is filled with water.

## 6.2 Experimental setup

Ion exchange and chromatographic experiments were performed in Department of Separation and Purification Technology in School of Engineering Sciences at LUT University.

Ion exchange beds were packed with slurry packing method and bed was 1,5 cm in diameter and depending on experiment 14,5 to 16,5 cm long. Glass columns used were manufactured by YMC Europe GMBH. Due the density difference of deionized water and synthetic leach liquor feed into column was from the bottom of it. This made channeling of the feed less of an issue and simultaneously pushed possible air bubbles out of the column. Scheme of experimental setup used in breakthrough experiments is presented in Figure 18. Pipe volumes are larger in this type of setup and full pipe void caused by the system was measured to be 4,5 ml.



*Figure 18 Experimental setup in breakthrough experiments*

All ion exchange experiments consisted of one loading-wash elution-wash cycle. Parameters from these steps are presented in Table 9. In each experiment washing was done with deionized water and elution with 2 M  $\text{H}_2\text{SO}_4$  as eluent. Temperatures were controlled with MGW laud M3 thermostat either to 25 °C or 60 °C. Due the lack of automation flowrate was monitored manually with scale and calculating the change in mass of the eluent or feed solution in set amount of time with the knowledge of the density for eluent or feed. This combined with varying density of the raffinate made early adjustments of the flowrate difficult.

*Table 9 Parameters of different phases in ion exchange experiments*

Phase	Sample time, min	Duration, BV	Flowrate, BV/h
Loading	2	6	2
Wash	20	2	6
Elution	2	3,5	2
Wash	20	2	6

In first multicycle experiment, 24 samples were taken from each loading and elution phase first sample being from minute 4. Temperature was changed in the middle of each feed elution cycle so that feed temperature was 60 °C and elution temperature 25 °C. This was done considering previous experiments showing sharper elution fractions in lower temperature experiments.

Second multicycle experiment with two eluents had different process parameters and procedures when compared to other column experiments. Eluents used were 2 M sulfuric acid and 0,4 M potassium oxalate solutions. Other differing parameters, that are presented in Table 10, were location of the input point into column and volume of the feed of each phase in bed volumes.

*Table 10 Column inputs and volume of each phase in multicycle experiment*

	Cycle 1		Cycle 2		Cycle 3		
	Input	V <sub>f</sub> , BV	Input	V <sub>f</sub> , BV	Input	V <sub>f</sub> , BV	
Load	bottom	2.78	Load	bottom	2.78	bottom	2.78
Wash	top	2.00	wash	top	2.00	top	2.00
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	bottom	2.78	H <sub>2</sub> SO <sub>4</sub>	bottom	2.51	bottom	2.51
H <sub>2</sub> SO <sub>4</sub>	bottom	2.67	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	bottom	2.67	top	2.67
-	-	-	H <sub>2</sub> SO <sub>4</sub>	bottom	0.80	bottom	0.80
Wash	top	2.00	Wash	top	2.00	top	2.00

Parameters were changed because in first cycle precipitation of Cu oxalate was observed. This clogged the pipes from column to sample. This was solved by changing the order of the eluents and adding one more regeneration phase for the resin to change it back from K<sup>-</sup> to

H<sup>+</sup> form. Also in the second cycle channeling was observed and it diminished the elution efficiency. This was solved by changing the direction of the flow inside the column.

Samples from the experiments were analyzed with Agilent Technologies 7900 ICP-MS. For this analysis samples needed to be diluted to 1:10<sup>4</sup> in order to get around the required concentrations for ICP. This was done with two separate 100 times dilution with 1% HCl + 1% HNO<sub>3</sub> matrix acid. In first of these dilutions mass of the sulphate solution was measured in order to determine more accurate dilution factor. This was necessary because of the tendency of the metal sulphate solution not flowing properly into and out of the pipette. With measuring the mass of the sample, this error that was sometimes over 10 % could be eliminated.

## 7. RESULTS

### 7.1 Impurity removal

Ion exchange was studied as a method to remove impurities from LIB leach liquor. Preferably all the impurity ions would be removed with single process step and with one resin. This requires resin to have either good affinity towards capturing impurity ions (Al, Cu, Fe and Mn) or possibility to capture all valuable metal ions (Co, Li and Ni). The behavior was studied with breakthrough and elution curves of metals for different resins. Anode and cathode materials for LIBs need to be as pure as possible and according to European Li 99,5 percent purity is good enough quality to be used in the batteries (European Lithium, 2019). Cutting point for the process was consequently selected to be 99,5 percent purity. Purity demands are of the final products and not for intermediate product, but it was deemed to be proper to have good quality product even in this intermediate state.

Removal efficiency can be determined by calculating dynamic bed capacities for the resins. Dynamic bed capacity can be calculated by numerically integrating the area from theoretical breakthrough point to actual breakthrough as Equation 6 describes. (Virolainen et al., 2018)

$$\frac{m_{abs}}{V_{bed}} = \sum_i \left( c_0 - \frac{1}{2}(c_i + c_{i-1})(V_i + V_{i-1}) \right) - \varepsilon c_0 \quad (6)$$

Where

$c_0$	initial concentration, g/l
$c_i$	concentration at temporal point i, g/l
$V_i$	cumulative volume (in bed volumes) fed at temporal point i, -
$\varepsilon$	void fraction of the resin bed, -
$V_{bed}$	volume of the resin bed, l

Elution curve integrals give some idea how much metals are eluted of the resin. These integrals can be used when combined with dynamic bed capacities and, total metals eluted

from resin can be calculated. Elution curve integral is numerically estimated as equation 7 describes.

$$\sum_i \frac{1}{2} (c_i - c_{i-1})(V_i - V_{i-1}) \quad (7)$$

Where

$c_i$	concentration at temporal point i, g/l
$V_i$	cumulative volume (in bed volumes) fed at temporal point i, -

First resin studied was chelating aminophosphonic resin Lewatit TP260. Resin showed great promise to be used in the impurity metals removal. As shown in Figure 19 and Figure 20 Lewatit TP260 captures all impurity metals from feed and lets all wanted products to flow through. Breakthrough was achieved near one bed volumes of feed. Possible collection of pure enough product metal solution can be done between 1 to 2,9 BVs. All product metals have steep breakthrough curves in all studied temperatures and pressures. In the case of the impurities however the curve is gentle. This can be improved by increasing the temperature inside the column. Increase in temperature also reveals that there is slight difference in breakthroughs of Ni and cobalt. Mn was unaffected by the increase in temperature like other impurity metals. Only slight increase in breakthrough time was observed.

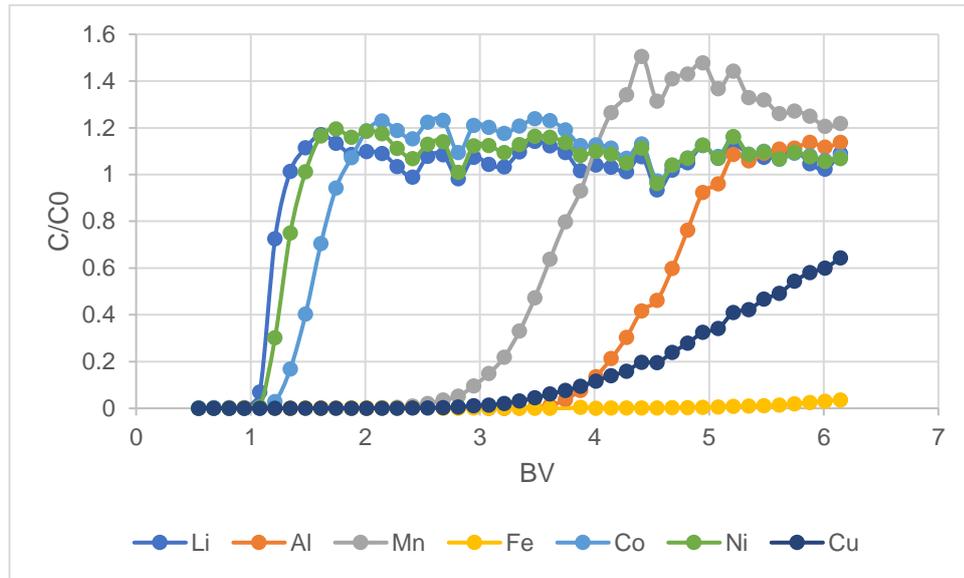


Figure 19 Breakthrough curve of resin TP260 at pH 1,84 and 60°C

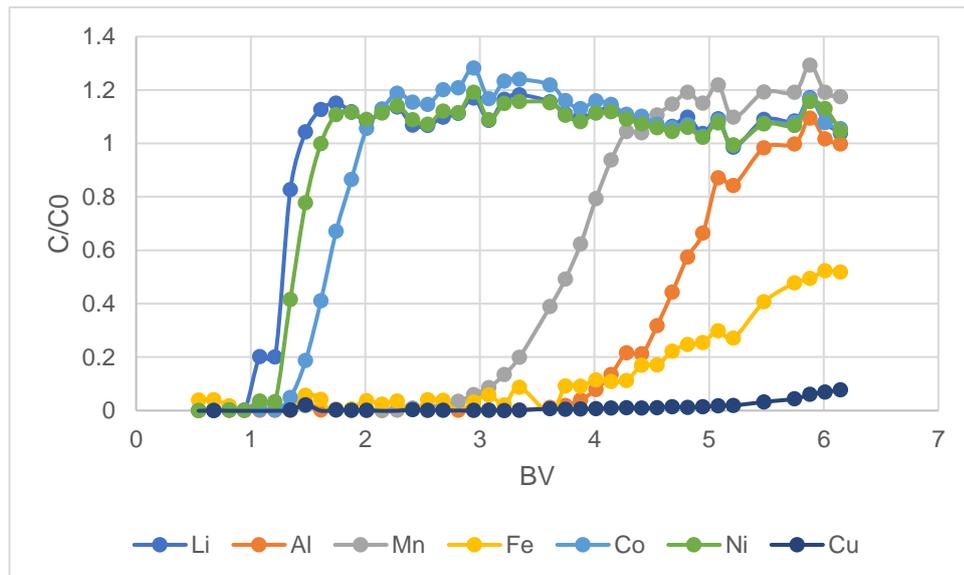


Figure 20 Breakthrough curve of resin TP260 at pH 3 and 60°C

Breakthrough curves in Figure 19 and Figure 20 further confirm that increasing the pH over 2 is not necessary. In low temperature and pH, differences in breakthrough times between metals are smaller and curves are gentle. In both pH 1,84 and pH 3 breakthrough for the products occurred at one bed volume of feed and first impurity metals came through when approximately three bed volumes of feed had been pumped to the column. Over two pH

seems to bring only marginal increase into separation and is hence not worth the trouble. Similar deductions can be drawn from the dynamic bed capacities in the Table 11.

Dynamic bed capacities provide insight into how much feed can be treated before resin need regeneration. This makes it good variable to determine capabilities of different resins in different conditions. In Table 11 comparison between different process conditions are presented with dynamic bed capacities.

*Table 11 Dynamic bed capacities of resin TP260 for different impurity metals in different experimental conditions*

Experimental conditions	Al (Eq/L bed)	Mn (Eq/L bed)	Fe (Eq/L bed)	Cu (Eq/L bed)
60 °C 1,8 pH	0.366643	0.189605	0.124599	0.136333
60 °C 3.0 pH	0.364519	0.196838	0.047725	0.136142
25 °C 3.0 pH	0.243812	0.141846	0.022546	0.086954
25 °C 1,78 pH	0.244294	0.122068	0.084379	0.083361

In higher pH results it is necessary to keep in mind that some of the Fe has been precipitated out of the solution. All dynamic bed capacities are transformed from milligrams to equivalents. From these breakthrough experiments, best resin and experimental conditions were selected to be used in the multi cycle experiment.

The iminodiacetic resin S-930 differs from the TP260 greatly when it comes to selectivity as can be seen from Figure 21. In studied conditions S-930 showed some selectivity to Cu and Fe in lower pHs. What is interesting however is that this resin seems to have capability of separating Ni from cobalt.

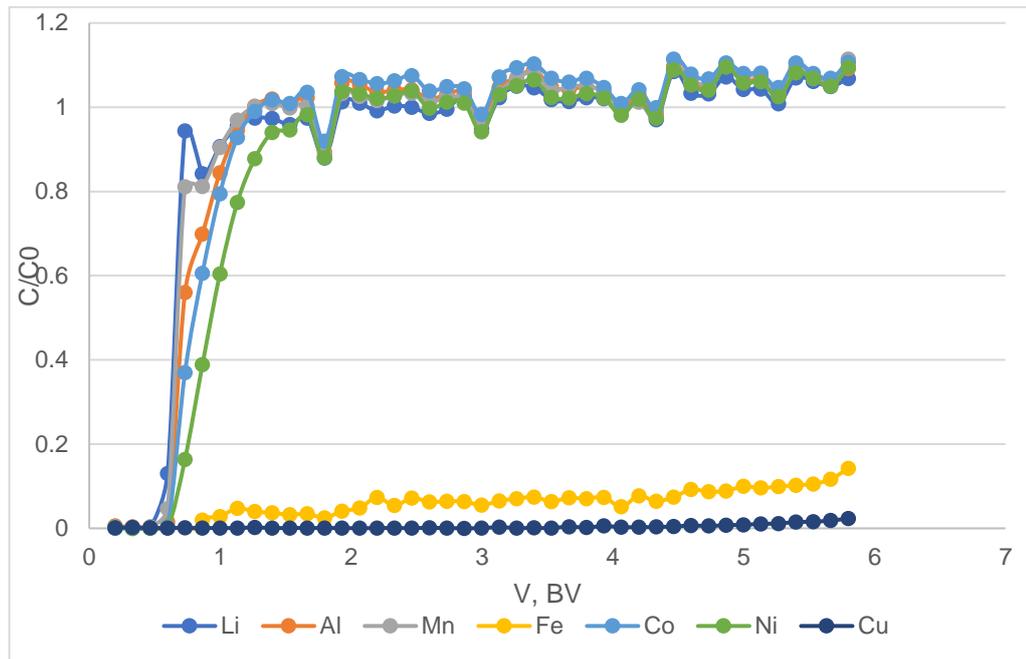


Figure 21 Breakthrough curve of resin S-930 at pH 1,78 and 25 °C

CS12GC strong cation exchange resin with sulphonic acid functionality is not selective towards anything in these pH ranges. This can be seen from the Figure 22 where breakthrough happens simultaneously for all the metals. There was Fe contamination in ICP-MS analysis causing detection limit for Fe to rise. This explains why Fe breakthrough curve does not reach one in  $c/c_0$  axis. To conclude strong cation exchange resin with sulphonic acid functional group cannot be used in the LIB metal recycling.

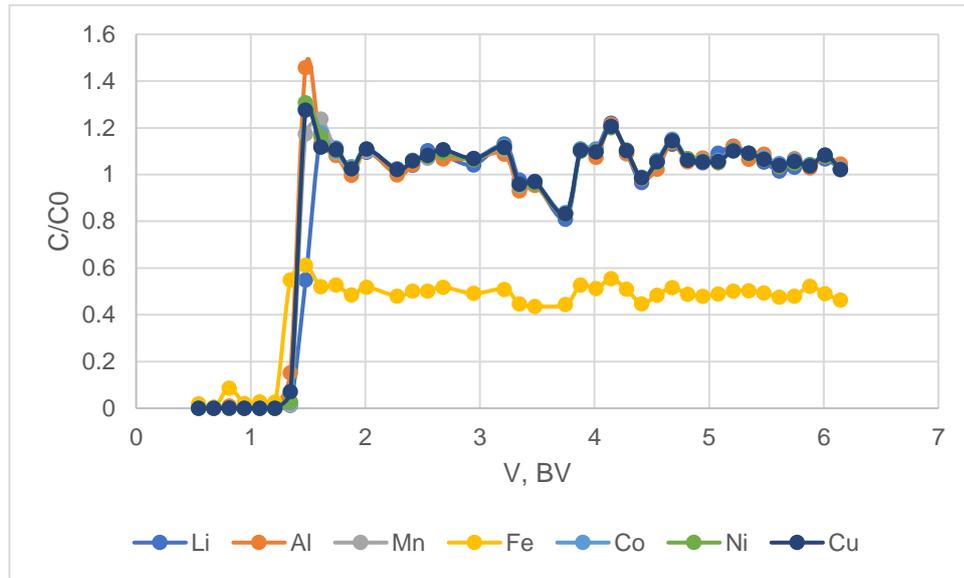


Figure 22 Breakthrough curve of resin CS12GC at pH 3 and 60 °C

Breakthrough curves presented in Figure 23 reveals that CA16GC weak cation exchange resin is selective to only Fe in low pH studied in these experiments. All other metals break through at the same time without being affected by the resin. Separating Fe could be useful trait but it is easily achieved with precipitation as well.

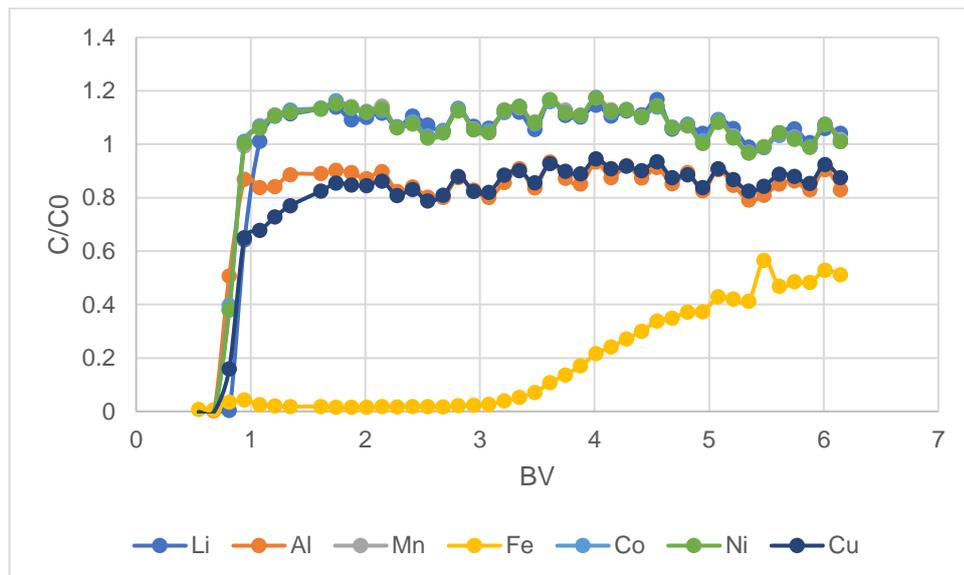
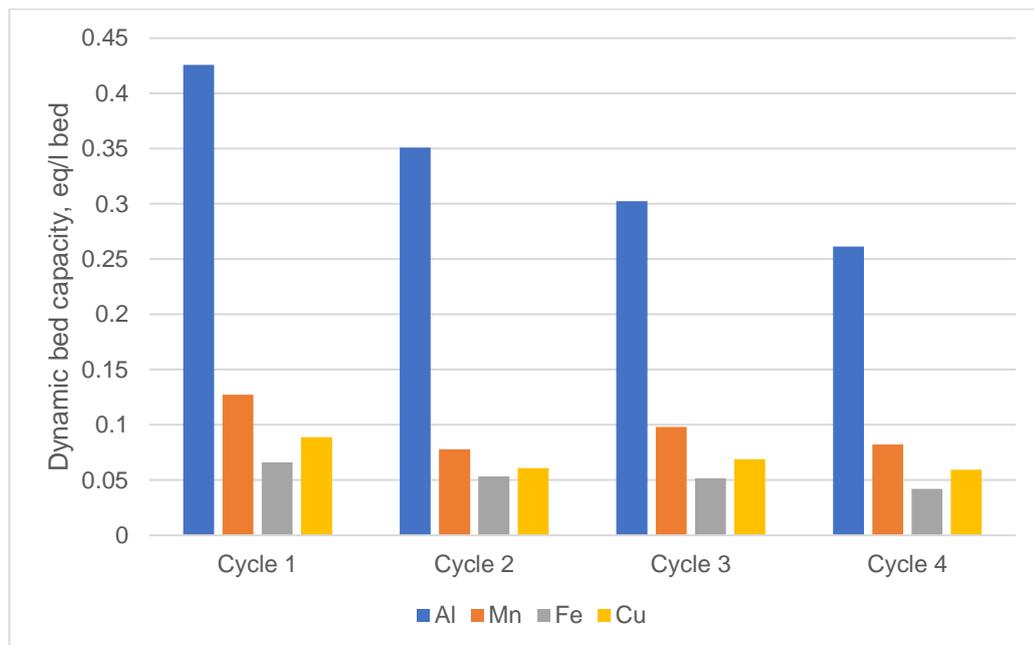


Figure 23 Breakthrough curve of resin CA16GC at pH 3 and 60 °C

From the breakthrough data dynamic bed capacity was calculated for the only metal that attached to the resin being iron. Resin can separate Fe from other metals in the solution with

good capacity. It has similar capacity to TP260 resin, but elution of the Fe is achieved almost fully with just 2 M sulfuric acid. Calculated dynamic bed capacity for Fe was 0.125 and corresponding elution curve integral 0.115. From these two values it was calculated that 91.5% of the Fe was eluted of the resin.

Multicycle experiments were conducted in the best temperature, pH and resin found in the breakthrough experiments. These conditions are pH 1,8 and 60 °C and the resin is TP260 aminophosphonic resin. Four cycles in total were done to get data how resin can be regenerated and can same resin be used multiple times. Dynamic bed capacities were calculated from breakthrough data as previously shown and it revealed that dynamic bed capacity decreased in consequent cycles. This is presented in Figure 24.



*Figure 24 Calculated dynamic bed capacities in each load-elution cycle in multiple cycle experiment*

Similar discovery can be made from purity calculations as the Figure 25 presents. Purity is calculated from comparing concentration of all product metals to impurity metal concentrations combined. It is seen that the purity decreases faster with consequent cycles

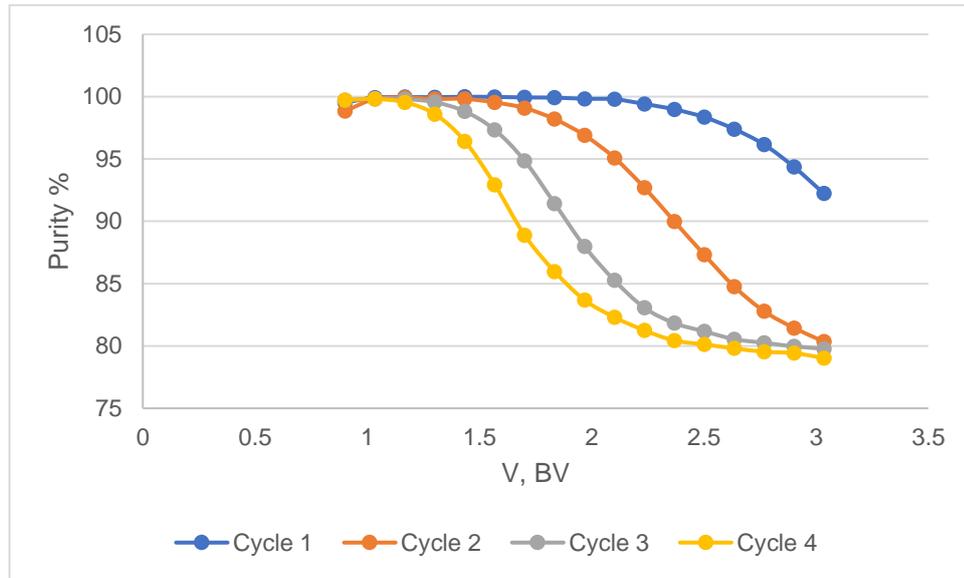


Figure 25 Purity of the raffinate during the multicycle experiment

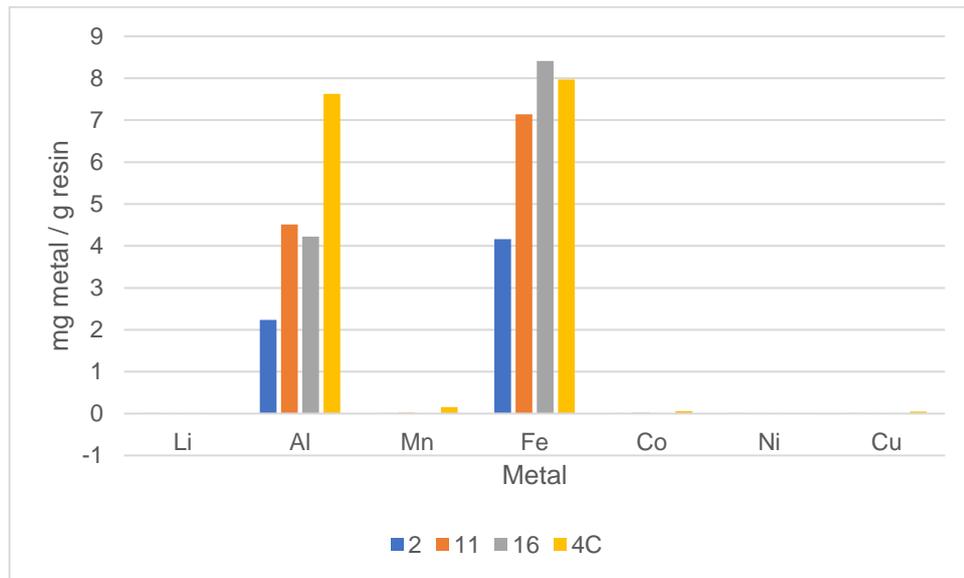
## 7.2 Resin regeneration

From the results of cyclic experiments with TP-260 and calculated breakthrough capacities of elution and breakthrough curves it was clear that not all the metals were eluted from the resin. Because of this used resins were wet digested to determine the amount of metals still in the resin. Resins from Experiments 2, 11, 16 and 4C were selected to be digested. Experimental parameters for the experiments are presented in the Table 12 below.

*Table 12 Parameters of corresponding experiments to wet digested resins*

Experiment	Breakthrough conditions
2	pH 1,78 25 °C
11	pH 1,84 60 °C
16	pH 1,8 60 °C
4C	pH 1,8 60 °C / 25 °C

0,1 grams of damp resin was measured to wet digestion. Excess water was removed from the resin with Büchner funnel. There were three parallel samples per resin and three blank samples were only matrix acid was added. Average of these three analyses were calculated and results are presented in Figure 26. This was done to mitigate the uncertainty of choosing the sample and because wet digestion can sometimes have samples mixing. Wet digestion was carried out in reverse aqua regia 3/1 HNO<sub>3</sub> to HCl as a matrix and the determination was done by ICP-MS.



*Figure 26 Metal content of wet digested resins Lewatit TP 260 at the end of the experiments 2, 11, 16 and multicycle experiment 4C*

As Figure 26 shows, Fe and Al were accumulating in the resin. Fe seems to stay in the resin from the first cycle, but Al accumulates over many cycles. This explains the creeping breakthrough curves. Al and Fe fill the active sites in the resin overtime and while doing so blocking other metals from attaching to the resin. From these experiments it is clear that 2M  $H_2SO_4$  is not sufficient eluent for totally regenerating TP-260 chelating resin. Hence batch elution experiments were conducted with different eluents to find the best for eluting Fe and Al.

For the batch elution experiments, resins from previous experiments were loaded in batch. 70 grams of resin was loaded in 1,5l of the same solution used in breakthrough experiments. Loading time was 24 h during which reactor was constantly mixed sufficiently. After the loading, resin was washed, and excess water was removed with Büchner funnel. Batch elution experiments themselves were done in 50 ml tubes with phase ratio of 2 g resin per 40 ml of eluent. Eluents and concentrations studied can be found from Table 13.

Table 13 Eluents and their concentrations in batch eluent experiments

Eluent	Concentrations, M
Sulfuric acid	1, 2, 4, 6
Nitric acid	1, 2, 4, 6
Hydrochloric acid	1, 2, 4, 6
1M hydrochloric acid + sodium chloride	Saturated, 2, 1, 0.5
Sodium citrate	1.6, 0.8, 0.4, 0.2
Potassium oxalate	0.5, 0.4, 0.3, 0.2
NaEDTA	1.0, 0.5, 0.25, 0.125

In batch elution experiments 2 g of loaded TP-260 resin was measured to the tubes. Resin was damp during the measurements. After this, eluent was added. Tubes were shake for 64 hours. From each tube sample was taken in the end of the experiment. Samples were analyzed with ICP-MS to get metal concentrations of the eluent.

From the ICP data metal concentrations per gram of resin were calculated using Equation 8. Most promising results are shown in Table 14 and Table 15.

$$\frac{m_{metal}, mg}{m_{resin}, g} = \left( c(ppb) \frac{DF * V}{1000} \right) m \quad (8)$$

Where

DF	dilution factor
m	measured mass of the resin
V	eluent volume

*Table 14 Potassium oxalate elution in different concentrations compared to 2 M sulfuric acid elution as per centages*

c(eluent)	Al	Mn	Fe	Cu
0.5	693.1104	82.99684	5442.753	105.3149
0.4	683.8166	64.3798	5350.88	105.3311
0.3	685.0725	34.59597	5142.266	103.5311
0.2	616.6897	7.055993	3662.934	100.8948

*Table 15 NaEDTA elution in different eluent concentrations compared to 2 M sulfuric acid elution as per centages*

c(eluent)	Al	Mn	Fe	Cu
1	71.58331	107.0982	4476.276	102.2423
0.5	46.79219	110.9687	4091.366	106.7568
0.25	33.18118	102.4081	3513.984	102.0445
0.125	22.32099	92.98373	3220.996	100.0859

As the Table 14 suggests, removal of all other metals is better with potassium oxalate, but Mn cannot be removed with this eluent. Similar result can be seen from the Table 15. NaEDTA is unable to detach Al from the resin, but all other metals are removed with great efficiency.

Potassium oxalate was selected for column experiments together with sulfuric acid. Breakthrough experiment was performed in similar conditions to previous experiments. Bed was eluted first with sulfuric acid and then with potassium oxalate. Breakthrough occurred as expected similarly to previous experiments. With using double elution Fe and Al can be also removed from the resin Figure 27. First sulfuric acid removes Mn and Cu and then potassium oxalate removes Fe and Al.

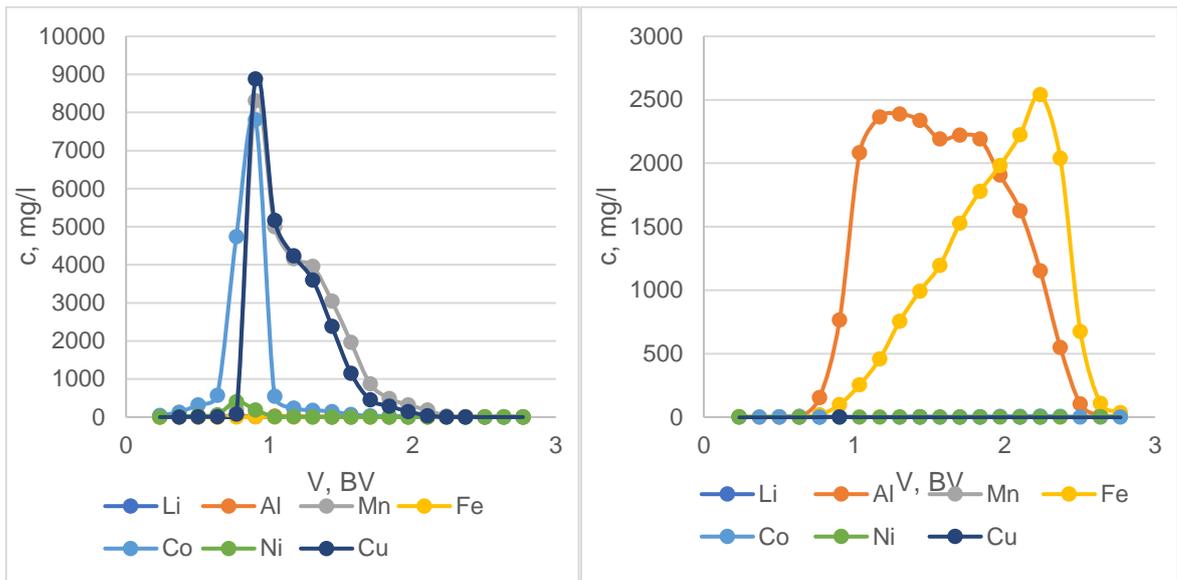


Figure 27 Elution curves of the TP260 resin in 60 °C with 2 M sulfuric acid (left) and 0,4 M potassium oxalate (right)

Cu is especially important to be removed before potassium oxalate elution. Cu oxalate can be formed during the elution and it has really low if any solubility with water 0.0253 g/l at 20 °C (Central Drug House (P) Ltd, n.d.). If Cu oxalate precipitates during elution inside the pipes or column itself it can clog them. Potassium oxalate elution proved to be quite different when compared to sulfuric acid elution curve. In Table 16 dynamic bed capacities for all impurity metals are compared to elution curve integral. Comparison between these two values gives us an idea how much metals are eluted out of resin.

*Table 16 Dynamic bed capacity and elution curve integrals for sulfuric acid and potassium oxalate elutins*

	Dynamic bed capacity (Eq/L bed)	Elution 1 (Eq/L bed)	Elution 2 (Eq/L bed)	% of metal eluted
Al	0.386619	0.003036	0.326916	85.34278
Mn	0.191296	0.138966	0	72.6447
Fe	0.127361	0.000305	0.119424	94.00793
Cu	0.138936	0.110974	0	79.87426

Low numbers in sulfuric acid elution might be due the fact that sampling was done once in 4 minutes. Spikes in sulfuric acid elution were sharp so if the maximum value ended up being somewhere between samples it affects somewhat the surface integrated with numerical integration.

Multicycle experiment was conducted in order to verify that elution with two eluents elutes all metals from the resin. It was decided that three load-elution cycles would give proper understanding of the process performance. Dynamic bed capacities were calculated from each cycle's breakthrough data as before and they were compared to each other (Figure 28).

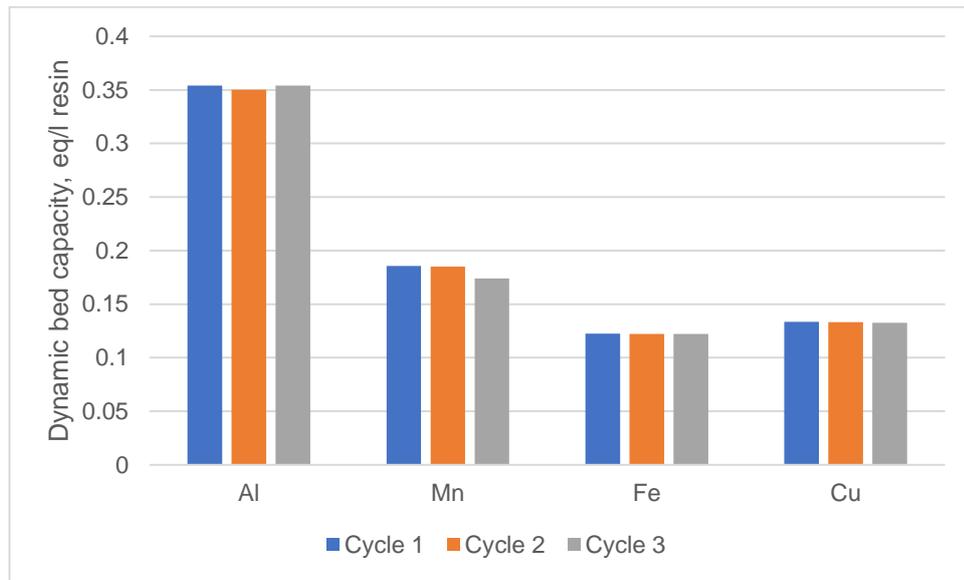


Figure 28 Calculated dynamic bed capacities in each load-elution cycle in multiple cycle experiment with two eluents in 60 °C and 2 BV/h

Cumulative purity of the Co/Ni/Li solution was calculated from the breakthrough data. As Figure 29 shows cumulative purity decreases in consequent cycles. Similar phenomenon was observed in first multicycle experiment with only sulfuric acid as Figure 25 suggest. This time the effect was not as drastic as before and in first two cycles cumulative purity remained above the 99,5.

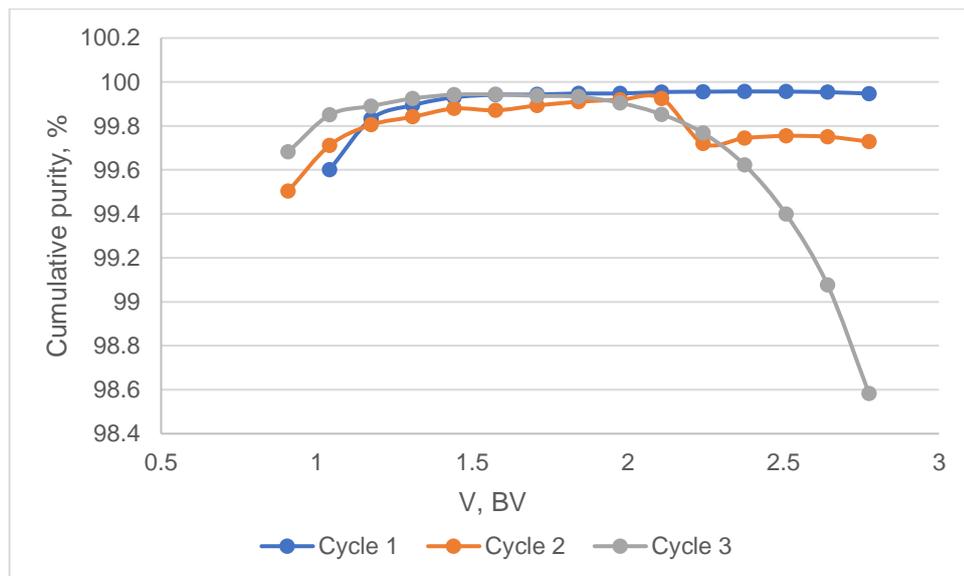


Figure 29 Cumulative purity of the raffinate in multicycle experiment with sulfuric acid and potassium oxalate as eluents

Percentages of metals eluted from resin were calculated from dynamic bed capacities and elution curve integrals. In Table 17 removal rates of impurity metals from the resin are presented. Low amount of Cu removed from the resin in the first cycle is explained because precipitation of Cu oxalate in the sample.

*Table 17 Metals eluted from the resin as calculated from breakthrough and elution curve integrals in percentages*

	Cycle 1	Cycle 2	Cycle 3
Al	100.6983	80.21087	105.4816
Mn	96.5018	71.19962	66.07862
Fe	85.2779	74.61952	140.4997
Cu	36.01105	78.87886	73.8601

From the Table 17 it can be deduced that third cycle was the most successful. Fe and aluminium accumulated from previous two cycles with difficulties, eluted out almost completely. This gave good insight for the practical operation of the process. Differences between eluents needs to be considered when designing direction of flow inside the column. Third cycle was the most successful because direction of flow was always configured so that if column has denser eluent in it, flow is downwards and vice versa. Also sulfuric acid elution is used to first remove Cu that forms precipitate with oxalate. Well insulated pipes are also important part of successful process design if potassium oxalate its used as eluent to prevent the precipitation of metal oxalates.

### **7.3 Ion exchange process design for impurity removal from LIB leachate**

There are two ways the ion exchange process for impurity removal can be arranged. One option is that all metals are separated in different fractions and many resins are used. Namely weak cation exchanger CA16GC for removal of iron, then iminodiacetic acid chelating resin S-930 for Cu and aminophosphonic chelating resin TP260 with double elution using sulfuric acid and potassium oxalate to remove Mn and Al, Mn getting separated from Al due the fact that sulfuric acid cannot remove Al but is fully capable of removing manganese. Flowchart for process described is found from Figure 30. This process enables full recovery of battery metals from waste but coming with the higher cost of having more separation steps. With

this option, less frequent regeneration is needed because all metals are not captured by the same bed.

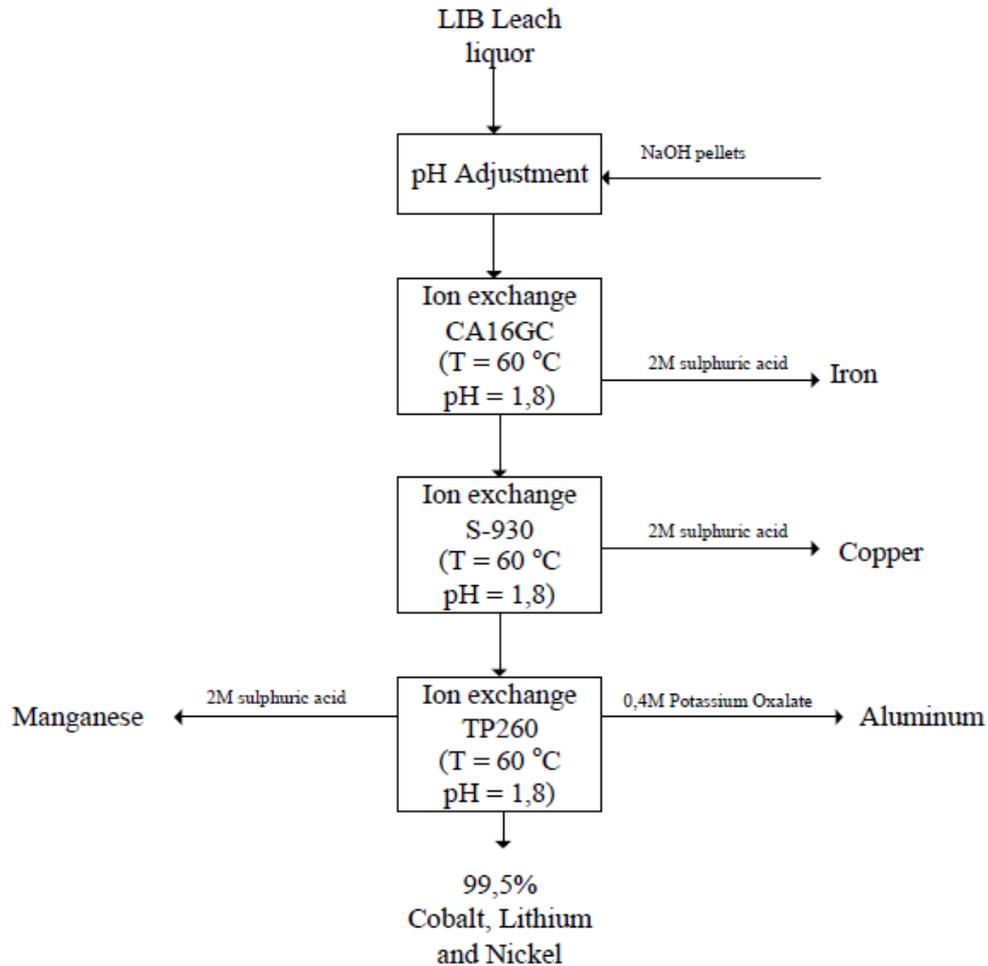


Figure 30 Possible process path for impurity removal with multiple resins

Other possible process path is to remove all impurity metals with single resin. Aminophosphonic resin with double elution can be used to remove all impurities as described in the Figure 31 and it can be regenerated with decent efficiency by using sulfuric acid and potassium oxalate. Only two bed volumes of feed can be treated with this path per regeneration cycle. It is noteworthy that both more valuable metals, Cu and Mn are eluted into same solution. This enables further purification for them, and separation should not take more than one process step now that spoiling Fe and Al are removed. Multicolumn operation can solve the problem of low process capacity. With four columns, loading phase, elution

phases and resin ion form regeneration could all be conducted simultaneously. Loading and elution phases have comparable lengths making automation simple. With this process however it is essential to ensure that potassium oxalate and following metal oxalates will not precipitate inside the process equipment.

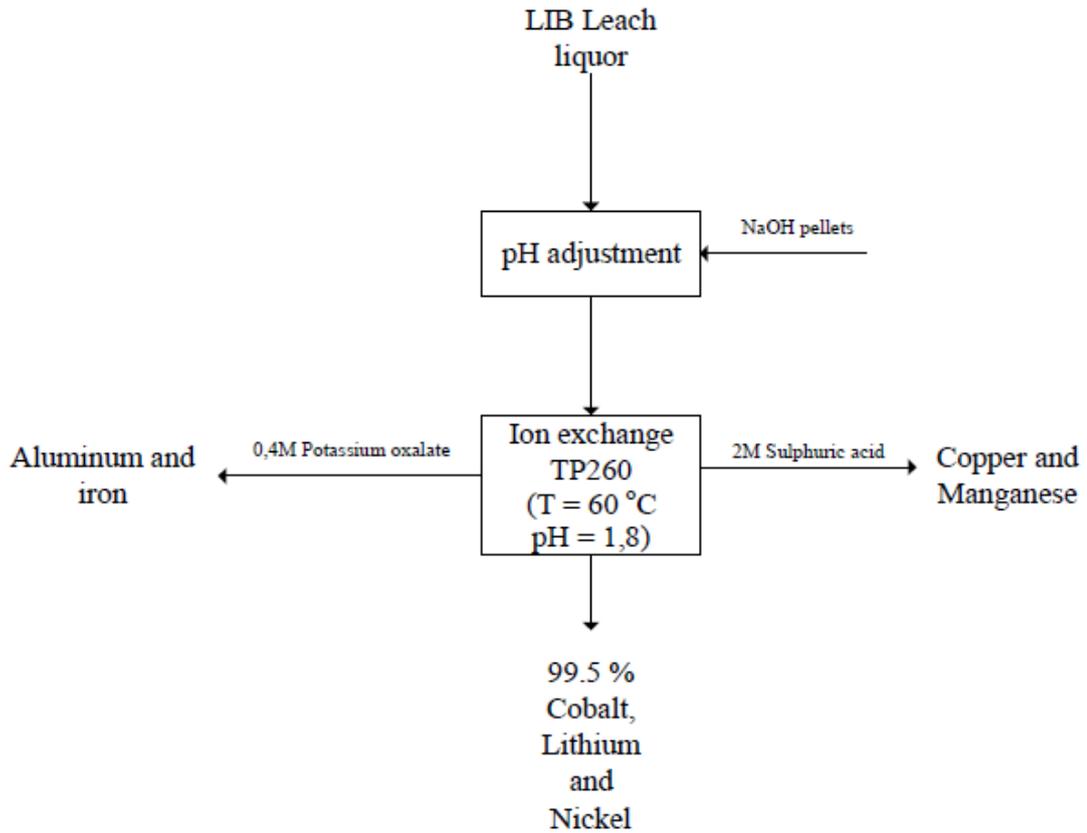


Figure 31 Possible process path of impurity removal with aminomethylphosphonic resin

## 8. DISSCUSSION

The aim of this thesis was to study the possibility of using ion exchange process in LIB recycling. To achieve this, the major impurity metals Fe, Cu, Al and Mn needed to be removed and Ni, Co and Li separated from each other. Four ion exchange resins were studied for the impurity removal. In impurity removal studied parameters were temperature and leach liquors pH. Different eluents were tested to discover best eluent for removing Al and Fe from chelating aminophosphonic resin. Two multicycle experiments were conducted to evaluate the viability of the separations in long term operations.

### 8.1 Impurity removal

From the results, the aminophosphonic resin TP260 works well in the purification of the LIB leach liquor (Table 11). All the unwanted metals were captured with just minor losses of products. There is no need to raise pH over 2 with the resin and formation of the physically difficult  $\text{Fe}(\text{OH})_3$  precipitate is avoided and no difficult solid-liquid separation steps are necessary.

Four resins were studied and only one of them TP260 displayed potency to remove all of impurity metals from the LIB liquor. Best conditions for this separation were high temperature of 60 °C and pH of 1.8 as Table 11 and Figure 19 presented. Higher pH causes Fe to precipitate as  $\text{Fe}(\text{OH})_3$  (Figure 16). This causes clogging of the pumps and is difficult to remove from solution. Lower pH is not favorable for chelating ion exchange resin. Similar deduction can be made from dynamic bed capacities calculated from breakthrough data presented in Table 11. Increasing the temperature from 25 °C to 60 °C increases the dynamic bed capacity of the resin significantly but change of pH to 1,8 to 3 makes no significant impact as Table 11 and Figure 19 and Figure 20 presents. With other ion exchange resins only partial separations were achieved, and some does not work in low pH environments (Figure 21Figure 22Figure 23. Increasing the pH further may increase viability of the other resins but it is preferential to minimize the need for pH adjustment.

This method of recycling the LIB leach liquor has some distinctive advantages over traditional methods of solvent extraction and precipitation. Ion exchange eliminates the need for organic solvents that are prevalent in solvent extraction. Loss of the product metals are

low as well in ion exchange. Something that hinders the viability of the ion exchange processes however is the need for two-step elution. Though, it is known also in solvent extraction that Fe is difficult to elute and some occasional dedicated Fe stripping is needed (Virolainen et al., 2020).

Other resins that proved to have some possibilities for applications in LIB recycling are strong cation exchange resin CA16GC with carbocyclic acid functional group and chelating resin S-930 with iminodiacetic acid functional group. With CA16GC it is possible to remove Fe from the resin (Figure 23). This could be sensible because, as discussed prior, Fe can be eluted from the resin with just sulfuric acid. Chelating resins have tendency to hold Fe and Al tight making resin regeneration difficult. Hence if this resin can be used to remove Fe before chelating resins it can improve efficiency of the process.

S-930 chelating resin with iminodiacetic acid functional group has capability of removing Cu (Figure 21). If Fe is removed beforehand from the leach liquor, Cu can be selectively captured with this resin. Similar pH and temperatures can be used as with TP-260 resin. Cu is valuable metal but in the LIBs there are more valuable metals and intricate processes for Cu capture is not economically viable. However now that it can be selectively captured and purified with only one unit operation it could be worth to make the process more profitable.

Multi cycle experiment provided good information of the process. It was observed that all metals are not eluted from resin with 2 M sulfuric acid as presented in Figure 26. Decrease of the dynamic bed capacity seems to be more severe in the earlier load-elution cycles than in latter ones. Similar deduction can be made from the Figure 25 where purity during experiments drop below 99,5 % earlier but the drop in the volume treated is not linear. Regardless of how much per cycle the dynamic bed capacity drops, need for another eluent is apparent. Used resin was wet digested to discover what causes the capacity decrease. Figure 26 provides insight to what accumulates in the resin. When comparing single used to resin that has been used for multiple load-elution cycles it is revealed that amount of Fe does not grow longer the resin is used but Al accumulates overtime. It was expected that Fe and Al will be the more problematic ions to remove. Chelating resins often have great affinity towards both of these metal ions. Part of the Al and almost no Fe is removed in each cycle.

## 8.2 Resin regeneration

Need for better elution was clear from the results of cyclic experiment and wet digestion of the used resin. In batch elution experiments two eluents proved to be significantly better for eluting Fe off the resin: NaEDTA (Table 15) and potassium oxalate (Table 14). NaEDTA removed all other metals but Al when potassium oxalate removed Al well but left Mn in the resin. All metals were not removed with any eluent meaning that two eluents needed to be used to remove all impurity metals from the resin. Potassium oxalates ability to remove Al and Fe, and the fact that it is more environmentally friendly than NaEDTA makes it superior eluent between these two.

It is apparent though that double elution is necessary for the removal of all impurities (Figure 24). As per previous experiments sulfuric acid elution removes Cu and Mn with decent efficiency from the resin. Hence sulfuric acid paired with potassium oxalate could be the way forward. Concentration of potassium oxalate to be used in the column experiment was decided by examining the Table 14. Removal efficiency compared to 2 M sulfuric acid is affected only minorly by dropping the concentration from 0,5 M oxalic acid concentration to 0,4 M. From 0,4 M to 0,3 M drop in the efficiency is notable and when dropping to 0,2 M especially Fe removal fell almost third from the 0,5 M value. Based on this information 0,4 M potassium oxalate was decided to be used in the column experiments.

Potassium oxalate have few drawbacks when it comes to column operations. It forms oxalate precipitate with metals, and this was observed when oxalate elution was before the sulfuric acid elution. Oxalic acid also has the tendency of precipitating out of the solution in more acidic medium and lower temperatures. Therefore, it is utmost important to keep lines short and well heated and insulated to prevent premature and unwanted precipitation. Another drawback of potassium is that it replaces hydrogen ions in the resin changing it to basic form. However, this is easily mitigated with short regeneration step with other acidic eluent after the potassium oxalate elution. In this case other eluent being sulfuric acid.

Pikes in potassium oxalate elution are wide and different when comparing to sulfuric acid elution. From Figure 27 it can be seen that Fe seems to trickle slowly from the resin. This is not surprising when resins high affinity towards Fe is taken into account. Resin slows down the flow of Fe inside the column making front of concentrated iron. Al on the contrary to Fe

gets released from the resin steadily. These differences are expected between Fe and Al because of the results from the wet digestion (Figure 26). Fe fills sites immediately and is strongly attached to the resin bed when Al accumulates over time and gets released from the bed easier.

As the elution curve in Figure 27 suggest, there is some Co that is attached to the resin in loading phase and it elutes out of the resin in sulfuric acid elution. Elution curve integral reveals that 1983 mg Co per l bed is captured by resin. In this experiment it meant that 51,9 mg of Co was lost during the impurity removal phase. When this is compared to amount of Co passing through the process it can be calculated to be 6,84 percent of all cobalt.

On the contrary to the first multi cycle experiment with two eluents dynamic bed capacities do not decrease significantly over time as the Figure 28 suggest. This means that most of the metals are eluted off the resin. However, Figure 29 tells a different story. Purity drops in the third cycle radically as the loading proceeds. This drop is caused most likely by failed elution in second loading-elution cycle. Channeling was observed during the second cycle and repercussions of this can be seen from the elution curve. Channeling was caused most likely by density difference of the two eluents and the direction of the flow inside the column. It can be presumed however that most of the metals left in the bed after the second elution are eluted in third elution cycle. This conclusion can be drawn from the third elution where over 100 % of certain sorbed metals were eluted from the bed as the Table 17 presents.

Cu and Mn ending up in the same fraction opens a possibility to profit out of them as well. They are more valuable out of the four impurity metals and it might be fruitful to research the possibility of separating and selling them to further increase profit and more completely recycling of the battery metals.

## 9. CONCLUSIONS

Impurity removal from LIB leachate with hydrometallurgical process and traditionally it has been done with the combination of leaching, precipitation and solvent extraction steps. Metals that are low value and hence considered to be impurities are Al, Fe, Mn and Cu. Products are the metals that hold most of the value in LIB waste are Co, Ni and Li. Ion exchange process has been considered for Ni/Co fractionation but not directly for the purification of LIB leachate.

Ion exchange recycling process for the LIB was discovered to be possible. All impurity metals were able to be removed from the synthetic leach liquor with one step. Purity was increased from the original 75% to battery grade 99.5 %. Ion exchange resin proposed for this separation is Lewatit TP260, chelating resin with aminophosphonic acid functional group. Resin captured Fe, Al, Mn and Cu leaving Co, Ni and Li in raffinate. Other resins showed no viable capabilities on their own for the separation. Having only one step, this separation method presents great promise for further development. Relatively low pH combined with lack of need for organic solvents, like in solvent extraction, add up for the viability of this separation. Downside for the suggested ion exchange process is the low capacity of the resin. Effective separation can be achieved only during two bed volumes of feed before the need for elution emerges. Al and Fe can be also difficult to remove from the resin in elution phase.

To elute Fe and Al from the resin, different eluents were tested. Oxalic acid with stoichiometric amount of potassium hydroxide to neutralize the acidity proved to be most potential eluent. With this potassium oxalate Al and Fe could be removed but not manganese.

It is clear from the experiments that ion exchange can be used in the LIB recycling. All impurity metals can be removed with single resin as Figure 31 describes. Even full fractionation of the major impurity metals is possible with the design presented in Figure 30. Both designs have their benefits. Ultimately the profitability comes down to prices of LIB battery metals and if the multi resin path increase the time between elution steps enough to justify the unit operation increase. There is also the possibility of continuous ion exchange process that would make the impact of relatively small capacities of resins not as detrimental for the whole process. Optimization is required to make these processes viable and

competitive options. Especially process conditions of pH and temperature should be studied carefully. Effect of flowrate in different process phases should be studied further. Pilot scale experiments and preliminary economic evaluation should be conducted.

## 10. REFERENCES

Borrini, J., Meyer, D., Fontecave, M., Peneliau, F., (2012). Method for separating metals from batteries containing lithium. EP2532759A1.

Central Drug House (P) Ltd, (2019). *Copper oxalate material safety data sheet*.

Chen, L., Tang, X., Zhang, Yang, Li, L., Zeng, Z., Zhang, Yi, (2011). Process for the recovery of cobalt oxalate from spent lithium-ion batteries. *Hydrometallurgy* 108, pp. 80–86.

Chen, X., Chen, Y., Zhou, T., Liu, D., Hu, H., Fan, S., (2015a). Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries. *Waste Management* 38, pp. 349–356.

Chen, X., Xu, B., Zhou, T., Liu, D., Hu, H., Fan, S., (2015b). Separation and recovery of metal values from leaching liquor of mixed-type of spent lithium-ion batteries. *Separation and Purification Technology* 144, pp. 197–205.

Chiu, K.-L., Chen, W.-S., (2017). Recovery and Separation of Valuable Metals from Cathode Materials of Spent Lithium-Ion Batteries (LIBs) by Ion Exchange. *Science of Advanced Materials; Stevenson Ranch* 9, pp. 2155–2160.

Contestabile, M., Panero, S., Scrosati, B., (2001). A laboratory-scale lithium-ion battery recycling process. *Journal of Power Sources* 92, pp. 65–69.

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

Dow Chemical Company, (2019). *DOWEX M4195*.

European Lithium, (2019). *Lithium. European Lithium*. URL <https://europeanlithium.com/lithium/> (accessed 10.25.19).

Fisher, K., Treadgold, L.G., (2008). *DESIGN CONSIDERATIONS FOR THE COBALT RECOVERY CIRCUIT OF THE KOL (KOV) COPPER/COBALT REFINERY, DRC.*

Flett, D., (2004). Cobalt-Nickel Separation in Hydrometallurgy: a Review. *Chemistry for Sustainable Development* 2004, pp. 81–91.

Schweitzer G., Pesterfield L., (2010). *The Aqueous Chemistry of the Elements.* Oxford university press.

Georgi-Maschler, T., Friedrich, B., Weyhe, R., Heegn, H., Rutz, M., (2012). Development of a recycling process for Li-ion batteries. *Journal of Power Sources* 207, pp. 173–182.

Gjerde, D., Fritz, J., (1987). *Ion Chromatography, 2nd ed, Chromatographic methods.* Dr. Alfred Hüthig Verlag Heidelberg, New York.

Heelan, J., Gratz, E., Zheng, Z., Wang, Q., Chen, M., Apelian, D., Wang, Y., (2016). Current and Prospective Li-Ion Battery Recycling and Recovery Processes. *JOM* 68, pp. 2632–2638.

Heinonen, J., (2013). *Chromatographic Recovery of Chemicals from Acidic Biomass Hydrolysis.* Lappeenranta University of Technology, Lappeenranta.

Helfferich, F., (1962). *Ion Exchange,* McGraw-Hill. McGraw-Hill Book Company, Inc, California.

Hui, Z., (2000). Property of H<sub>2</sub>TiO<sub>3</sub> type ion-exchangers and extraction of lithium from brine of natural gas wells. *Chineze Journal of Applied Chemistry* 17, pp. 307–309.

Inamuddin, Luqman, M. (Eds.), (2012). *Ion-exchange technology. I: Theory and Materials.* Springer, Dordrecht ; New York.

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

Juang, R.-S., Wang, Y.-C., (2003). Use of complexing agents for effective ion-exchange separation of Co(II)/Ni(II) from aqueous solutions. *Water Research* 37, pp. 845–852.

Jurrius, Y., Sole, K., (2016). *PURIFICATION OF A COBALT ELECTROLYTE BY ION-EXCHANGE: PILOT-PLANT RESULTS AND PRELIMINARY COMMERCIAL DESIGN*.

Jurrius, Y., Sole, K.C., Hardwick, E., (2014). Removal of copper and zinc from a cobalt electrolyte by ion exchange at kamoto copper company's lulu plant. *Hydrometallurgy*.

Kang, J., Senanayake, G., Sohn, J., Shin, S.M., (2010). Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272. *Hydrometallurgy* 100, pp. 168–171.

Korkisch, J., (1989). *CRC Handbook of Ion Exchange Resins*, 6th ed. CRC Press, Inc.

LanXess, (2011). *Product information Lewatit-MonoPlus-TP-260*.

Lemaire, J., Svecova, L., Lagallarde, F., Laucournet, R., Thivel, P.-X., (2014). Lithium recovery from aqueous solution by sorption/desorption. *Hydrometallurgy* 143, pp. 1–11.

Li, B., Liu, F., Wang, J., Ling, C., Li, L., Hou, P., Li, A., Bai, Z., (2012). Efficient separation and high selectivity for nickel from cobalt-solution by a novel chelating resin: Batch, column and competition investigation. *Chemical Engineering Journal* 195–196, pp. 31–39.

Li, L., Zhang, X., Li, M., Chen, R., Wu, F., Amine, K., Lu, J., (2018). The Recycling of Spent Lithium-Ion Batteries: a Review of Current Processes and Technologies. *Electrochem. Energ. Rev.* 1, pp. 461–482.

LME, 2019. *London Metal Exchange: Non-ferrous* [WWW Document]. URL <https://www.lme.com/Metals/Non-ferrous#tabIndex=0> (accessed 11.22.19).

Lopes, C.B., Lito, P.F., Cardoso, S.P., Pereira, E., Duarte, A.C., Silva, C.M. (Eds.), (2012). *Metal Recovery, Separation and/or Pre-concentration, in: Ion-Exchange Technology. II: Applications, Ion-Exchange Technology*. Springer, Dordrecht ; New York, pp. 237–323.

Macrotrends, (2019). *Copper Prices - 45 Year Historical Chart* [WWW Document]. URL <https://www.macrotrends.net/1476/copper-prices-historical-chart-data> (accessed 11.19.19).

Mendes, F.D., Martins, A.H., (2005). Recovery of nickel and cobalt from acid leach pulp by ion exchange using chelating resin. *Minerals Engineering* 18, pp. 945–954.

Meshram, P., Pandey, B.D., Mankhand, T.R., (2015). Recovery of valuable metals from cathodic active material of spent lithium ion batteries: Leaching and kinetic aspects. *Waste Management* 45, pp. 306–313.

Meshram, P., Pandey, B.D., Mankhand, T.R., (2014). Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review. *Hydrometallurgy* 150, pp. 192–208.

Nasef, M.M., Ujang, Z., (2012). Introduction to Ion Exchange Process, in: Ion-Exchange Technology. I: Theory and Materials, *Ion Exchange Technology*. Springer, Dordrecht ; New York, pp. 1–41.

Peng, C., Hamuyuni, J., Wilson, B.P., Lundström, M., (2018). Selective reductive leaching of cobalt and lithium from industrially crushed waste Li-ion batteries in sulfuric acid system. *Waste Management* 76, pp. 582–590.

Porvali, A., Aaltonen M., Ojanen S., Velazquez-Martinez O., Eronen E., Liu F., Wilson B. P., Serna-Guerrero R., Lundström M., (2019). Mechanical and hydrometallurgical processes in HCl media for the recycling of valuable metals from Li-ion battery waste. *Resources, Conservation and Recycling* 2019, pp. 257–266.

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

Meshram, P., Abhilash, Pandey, B. H., Mankhand, T., Deveci, H., (2018). Extraction of metals from spent lithium ion batteries - Role of acid, reductant and process intensification in recycling. *Indian Journal of Chemical Technology* 2018, pp. 368–375.

Chitrakar, R., Makita, Y., Ooi, K., Sonoda, A., (2014). *Lithium recovery from salt lake brine by H<sub>2</sub>TiO<sub>3</sub>*. Dalton Trans. 2014, pp. 8933–8939.

Ramkumar, J., Mukherjee, T., (2012). Principles of Ion Exchange Equilibria, in: Ion-Exchange Technology. I: Theory and Materials, *Ion Exchange Technology*. Springer, Dordrecht ; New York, pp. 41–51.

Rengaraj, S., Yeon, K.-H., Kang, S.-Y., Lee, J.-U., Kim, K.-W., Moon, S.-H., 2002. Studies on adsorptive removal of Co(II), Cr(III) and Ni(II) by IRN77 cation-exchange resin. *Journal of Hazardous Materials* 92, pp. 185–198.

Rosato, L., Harris, G.B., Stanley, R.W., (1984). Separation of nickel from cobalt in sulphate medium by ion exchange. *Hydrometallurgy* 13, pp. 33–44.

Sainio, T., Suppala, I., (2015). *Method for Purification of a Cobalt Containing Solution by Continuous Ion Exchange*. United States of America, Patent No. 20150361524.

Seastar Chemicals Inc, (2011). *Hydrofluoric Acid MSDS*.

Shi, X., Zhang, Z., Zhou, D., Zhang, L., Chen, B., Yu, L., (2013). Synthesis of Li<sup>+</sup> adsorbent (H<sub>2</sub>TiO<sub>3</sub>) and its adsorption properties. *Transactions of Nonferrous Metals Society of China* 23, pp. 253–259.

Shin, S., Jung, G., Lee, W.-J., Kang, C., Wang, J., (2015). Recovery Of Electrode Powder From Spent Lithium Ion Batteries (LIBs). *Archives of Metallurgy and Materials* 60, pp. 1145–1149.

Siqueira, P., Silva, C.D., Silva, I.D., (2011). Nickel and cobalt adsorption in an ion exchange resin as an alternative for treating the leached liquor. *Rem-Revista Escola De Minas* 64, pp. 319–326.

Small, H., (1989). *Ion Chromatography, Modern Analytical Chemistry*. Plenum Press, New York and London.

Steen, M., Lebedeva, N., Di Persio, F., Boon-Brett, L., (2017). *EU Competitiveness in Advanced Li-ion Batteries for E-Mobility and Stationary Storage Applications – Opportunities and Actions* (No. EUR 28837 EN). Publications Office of the European Union, Luxembourg.

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

The European parliament and the council of the European Union, (2006). DIRECTIVE 2006/66/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 6 September 2006 on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC. *Official Journal of the European Union*.

Virolainen, S., Holopainen, O., Maliarik, M., Sainio, T., (2018). Ion exchange purification of a silver nitrate electrolyte. *Minerals Engineering* 2019, pp. 175–182.

Virolainen, S., Huhtanen, T., Laitinen, A., Sainio, T., (2020). Two alternative process routes for recovering pure indium from waste liquid crystal display panels. *Journal of Cleaner Production* 243, 118599.

Virolainen, S., Suppala, I., Sainio, T., (2014). Continuous ion exchange for hydrometallurgy: Purification of Ag(I)–NaCl from divalent metals with aminomethylphosphonic resin using counter-current and cross-current operation. *Hydrometallurgy* 142, pp. 84–93.

Walton, H.F., (1976). *Ion-exchange Chromatography, A BENCHMARK*. Dowden, Hutchinson & Ross, Inc.

Won, Y.S., You, H., Lee, M.-G., (2016). Kinetics and Equilibrium Isotherm Studies for the Aqueous Lithium Recovery by Various Type Ion Exchange Resins. *Korean Journal of Materials Research* 26, pp. 498–503.

Zainol, Z., Nicol, M.J., 2(009). Comparative study of chelating ion exchange resins for the recovery of nickel and cobalt from laterite leach tailings. *Hydrometallurgy* 96, pp. 283–287.

APPENDIX A

LEWATIT TP260

Lewatit TP260 resin breakthrough and elution curves with temporal purity curve in pH 1.78 and 25 °C is presented in Figure A 1 and same data in pH 3 is presented in Figure A 2

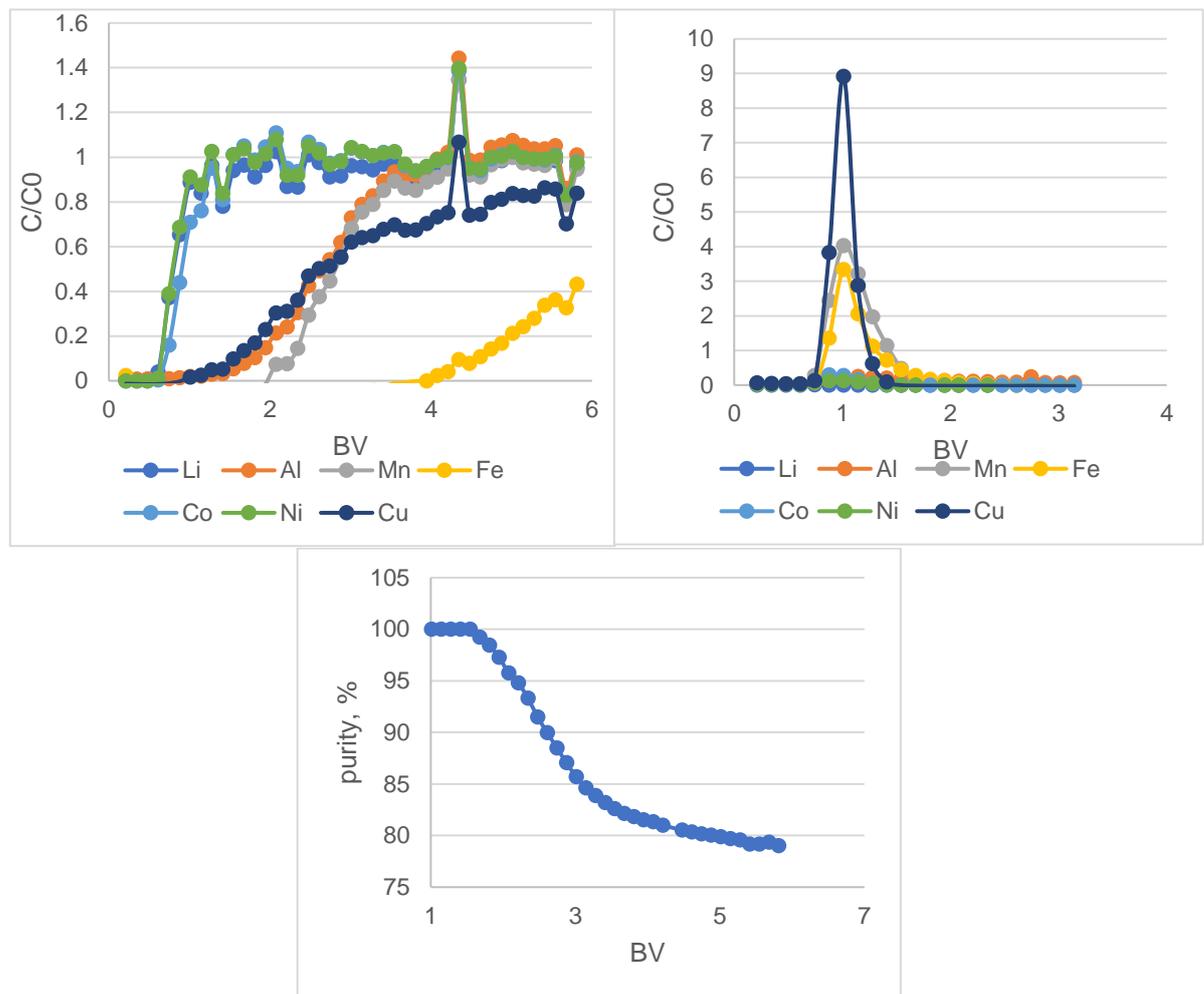


Figure A 1 Lewatit TP260 resin breakthrough and elution curves with temporal purity curve in pH 1.78 and 25 °C

## APPENDIX A

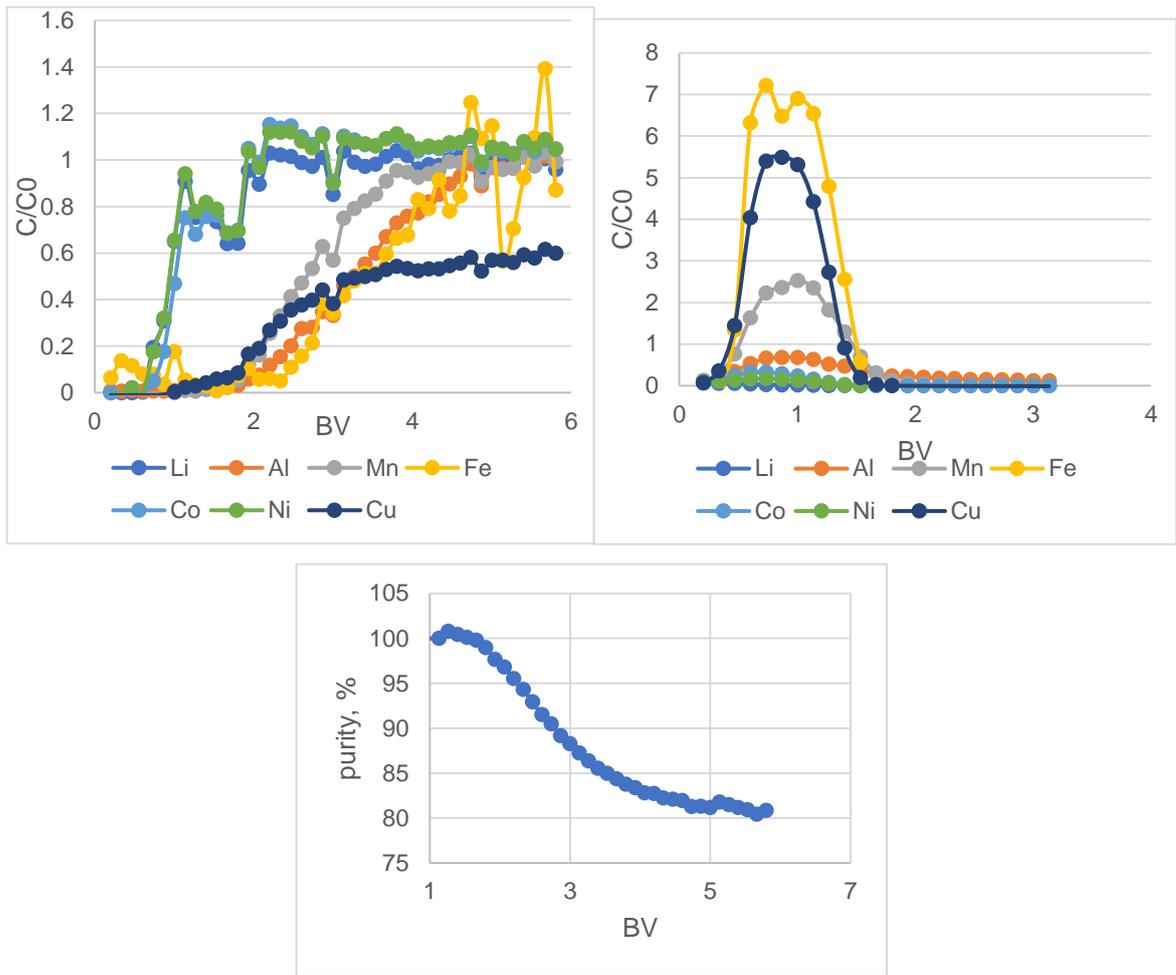
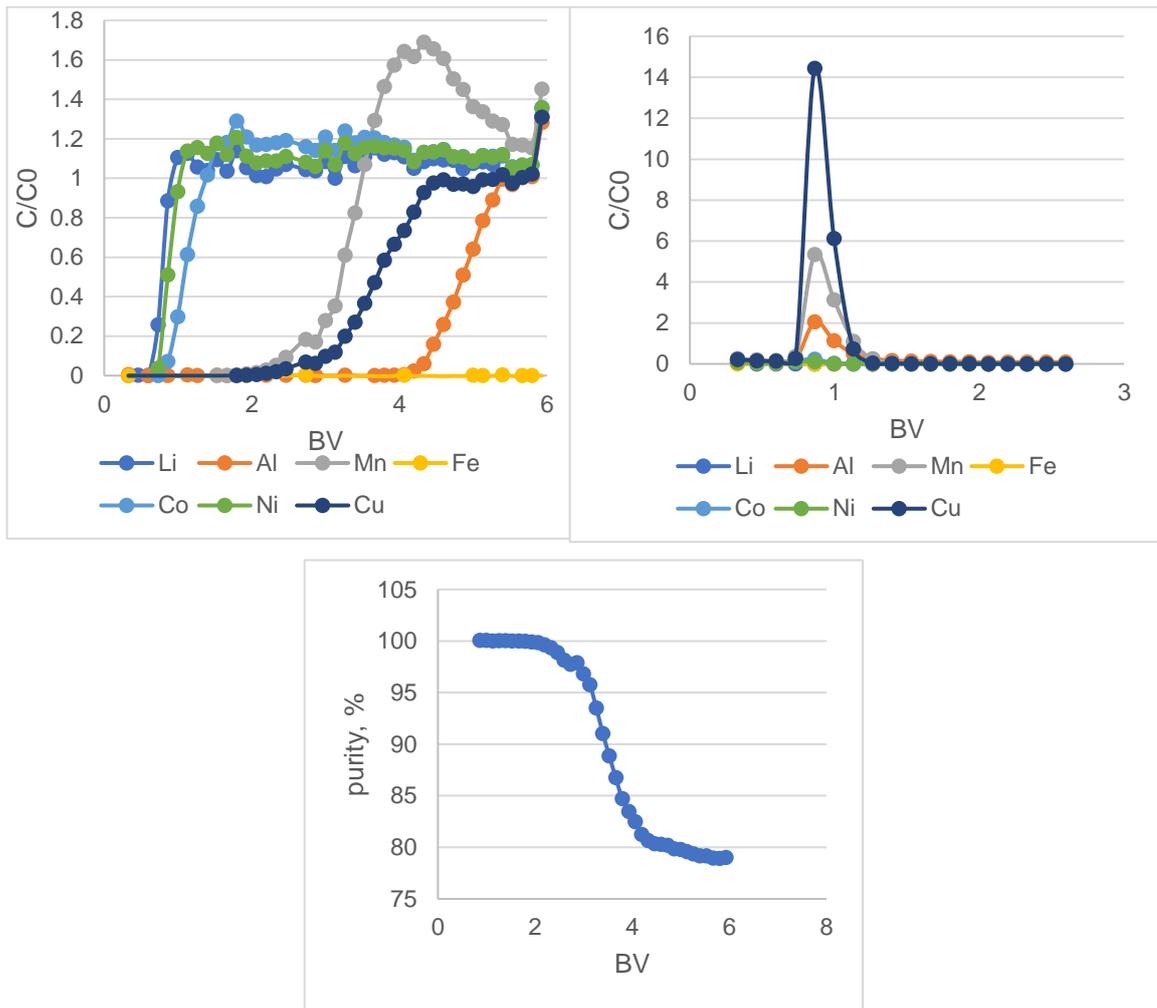


Figure A 2 Lewatit TP260 resin breakthrough and elution curves with temporal purity curve in pH 3 and 25 °C

Experiment was conducted in long 70 cm bed for the Lewatit TP260 resin in pH 1.84 and 60 °C. Results from this experiment prove that length of the column does not significantly affect the results. These results are presented in Figure A 3.

## APPENDIX A



*Figure A 3 Lewatit TP260 resin breakthrough and elution curves with temporal purity curve in pH 1,84 and 60 °C in experiment conducted in 70 cm long column.*

### **PUROLITE S-930**

Below Purolite S-930 resin breakthrough experiment data from the experiments that were not discussed in the results section of the Thesis are presented in Figure A 4 and Figure A 5

APPENDIX A

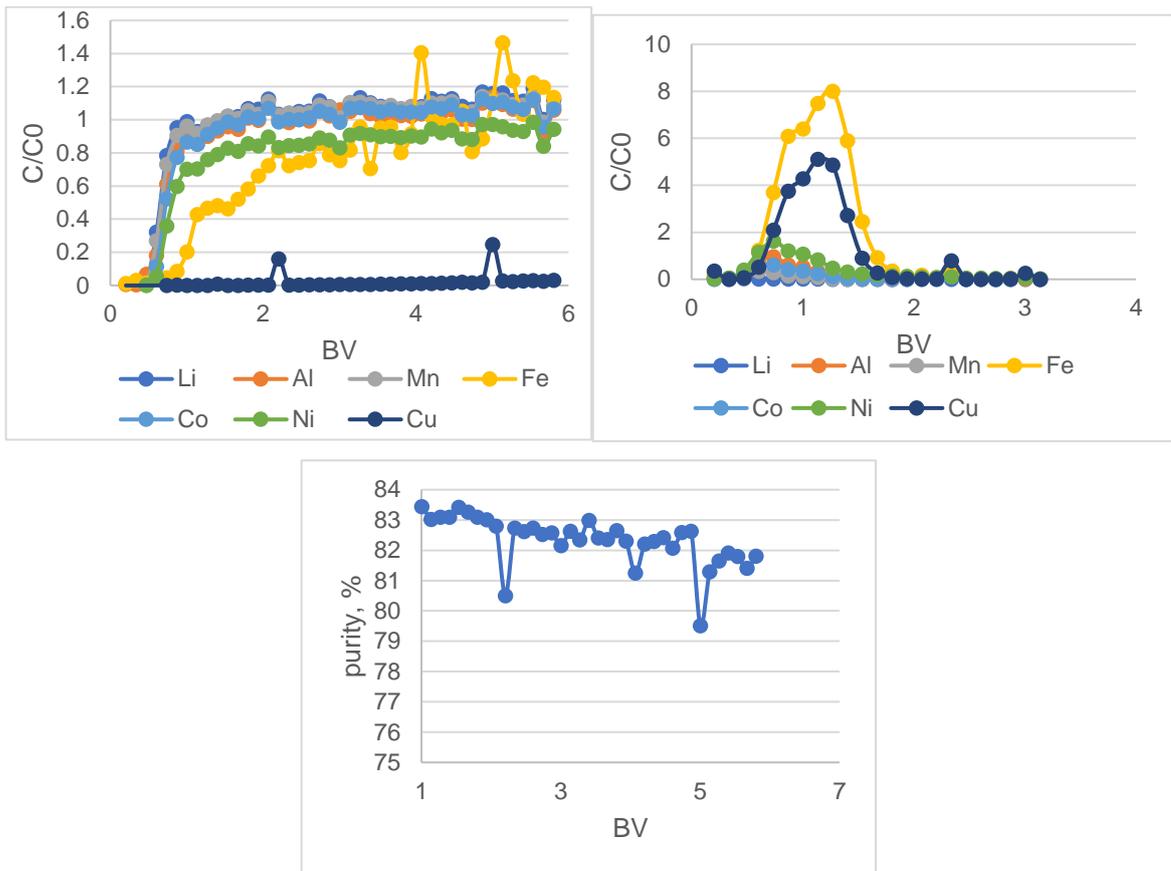


Figure A 4 Purolite S-930 resin breakthrough and elution curves with temporal purity curve in pH 3 and 25 °C

## APPENDIX A

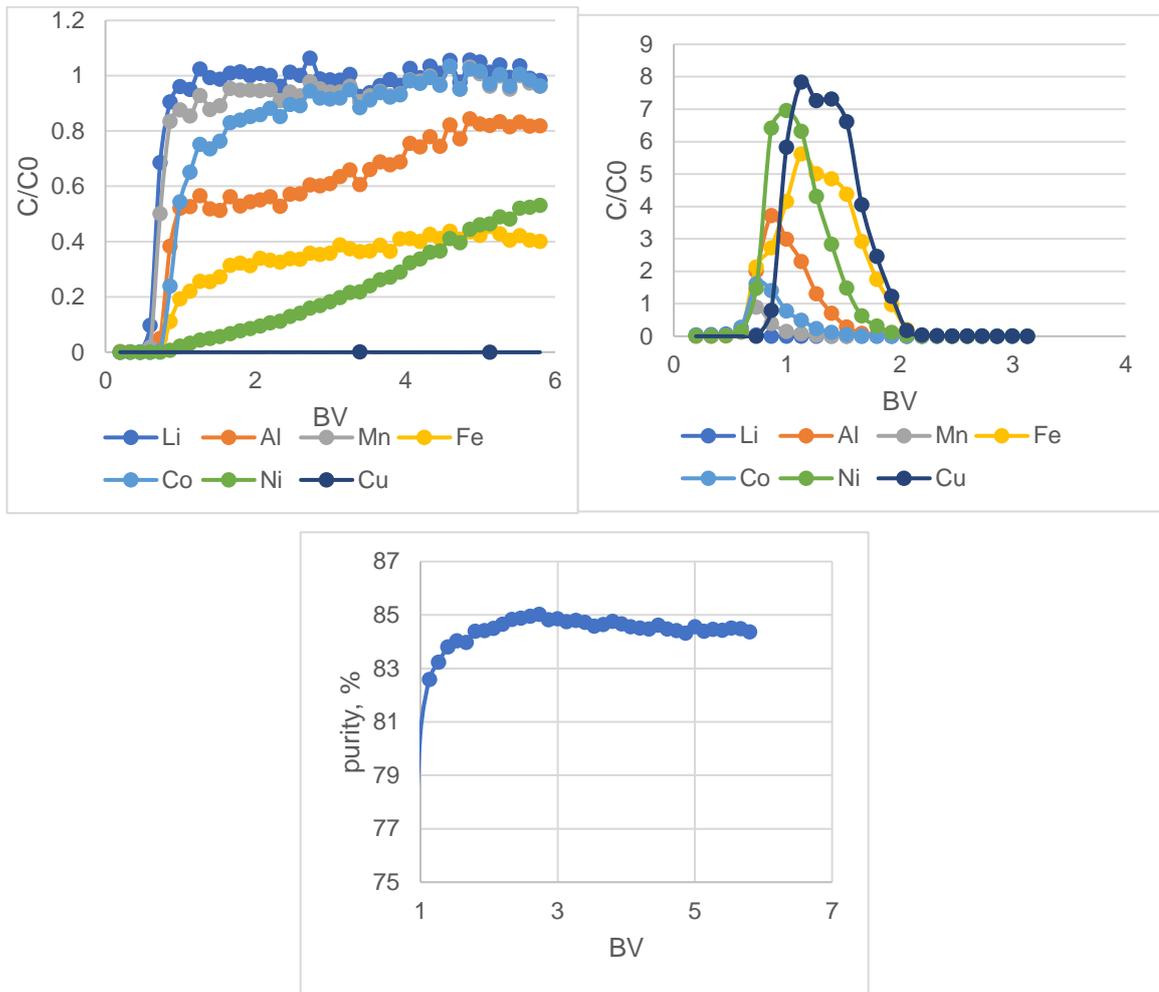


Figure A 5 Purolite S-930 resin breakthrough and elution curves with temporal purity curve in pH 3 and 60 °C

### CS12GC

Below CS12GC resin breakthrough experiment data from the experiments that were not discussed in the results section of the Thesis are presented in Figure A 6 and Figure A 7

APPENDIX A

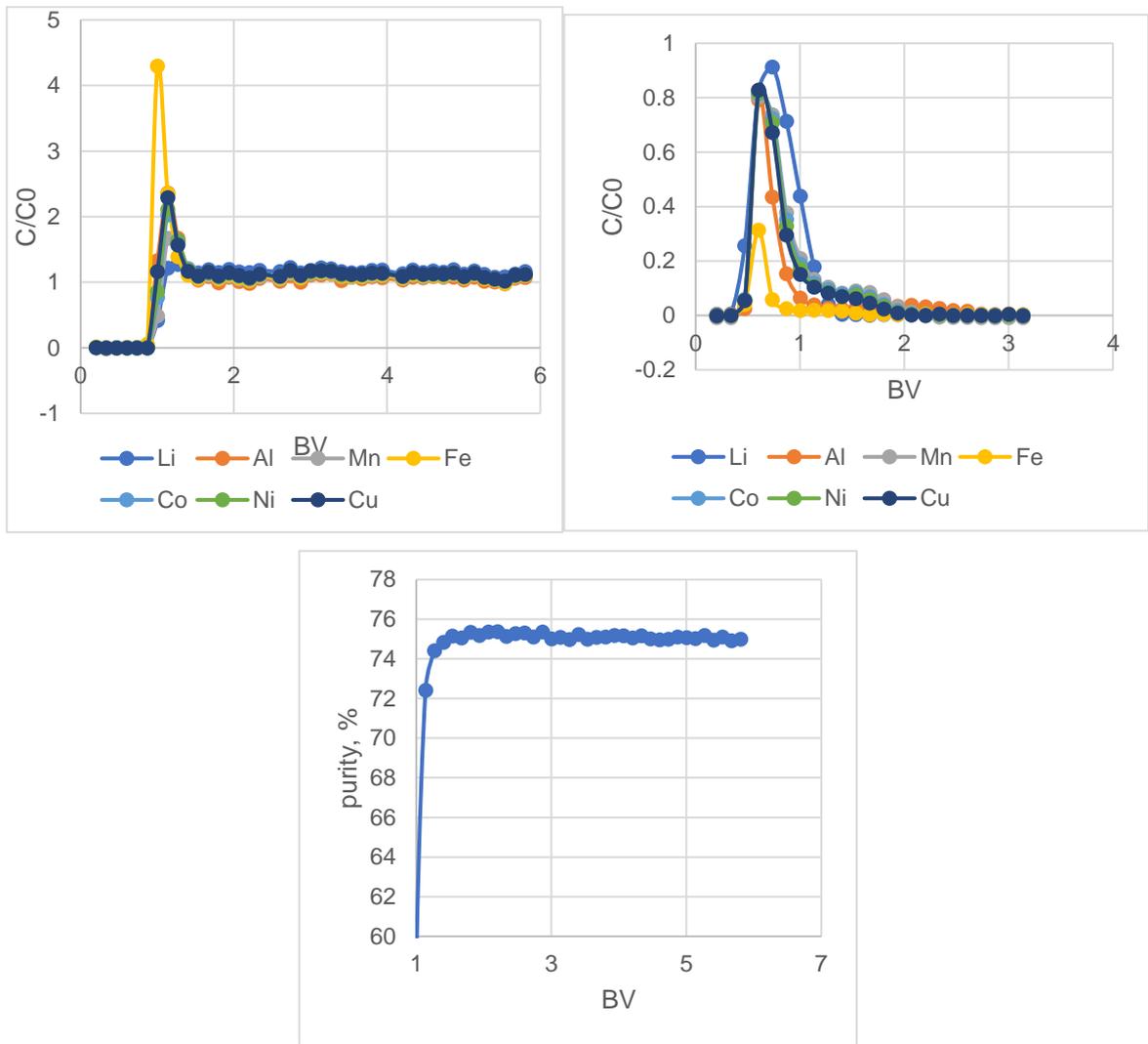


Figure A 6 CS12GC resin breakthrough and elution curves with temporal purity curve in pH 1.84 and 25 °C

## APPENDIX A

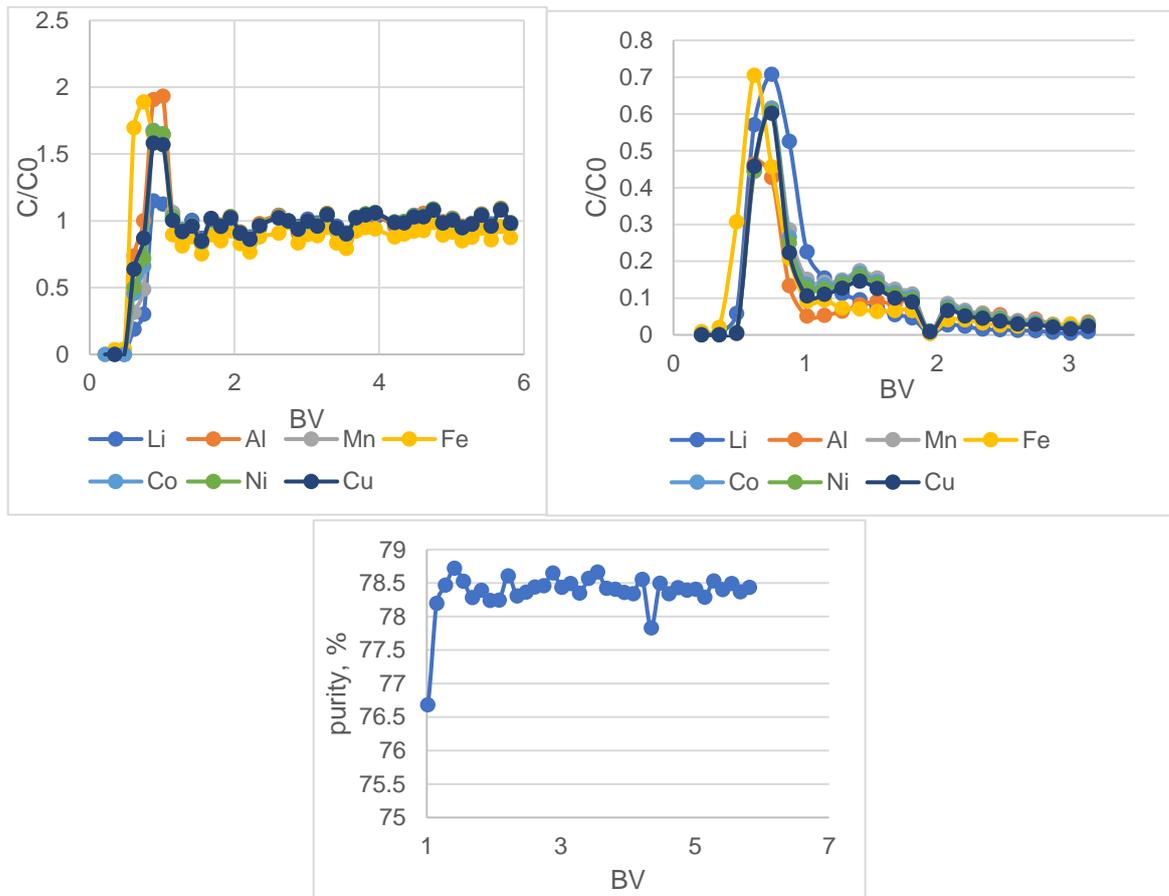


Figure A 7 CS12GC resin breakthrough and elution curves with temporal purity curve in pH 3 and 25 °C

### CA16GC

Below CA16GC resin breakthrough experiment data from the experiments that were not discussed in the results section of the Thesis are presented in Figure A 8 and Figure A 9

APPENDIX A

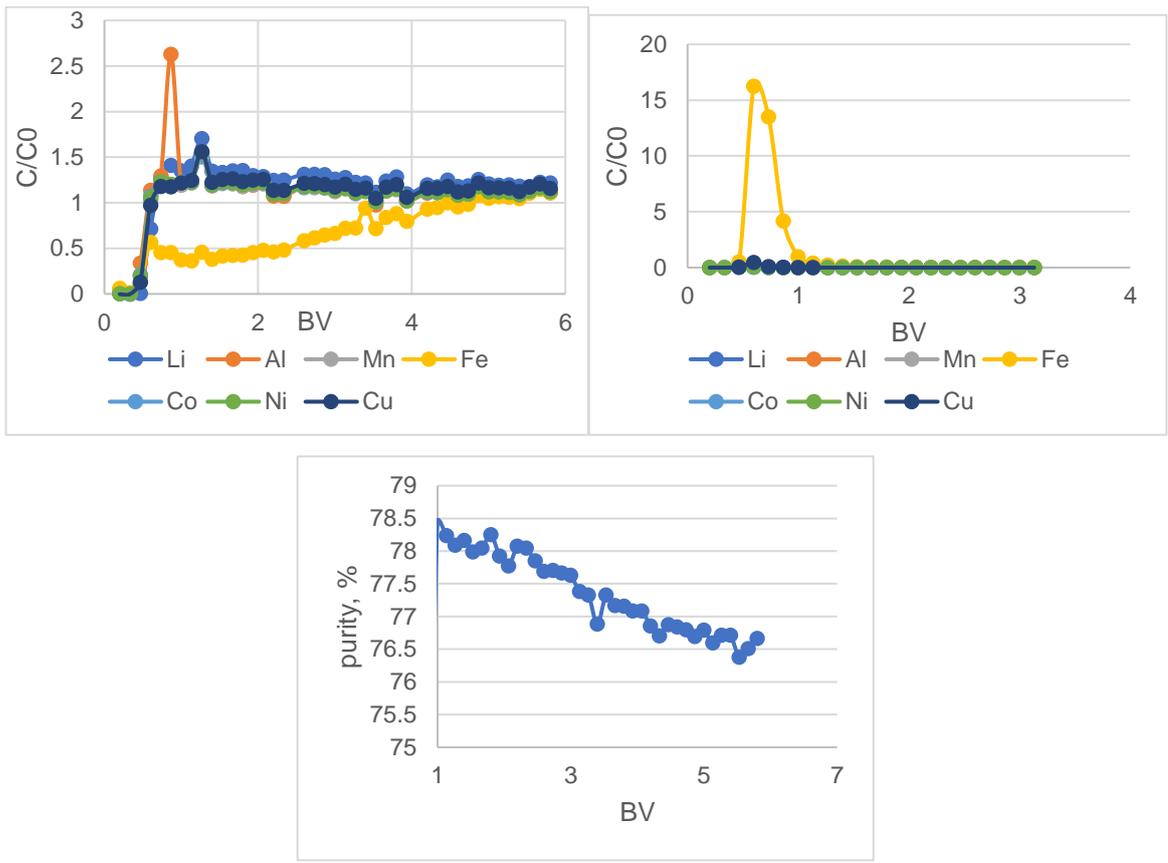


Figure A 8 CS12GC resin breakthrough and elution curves with temporal purity curve in pH 1.8 and 25 °C

APPENDIX A

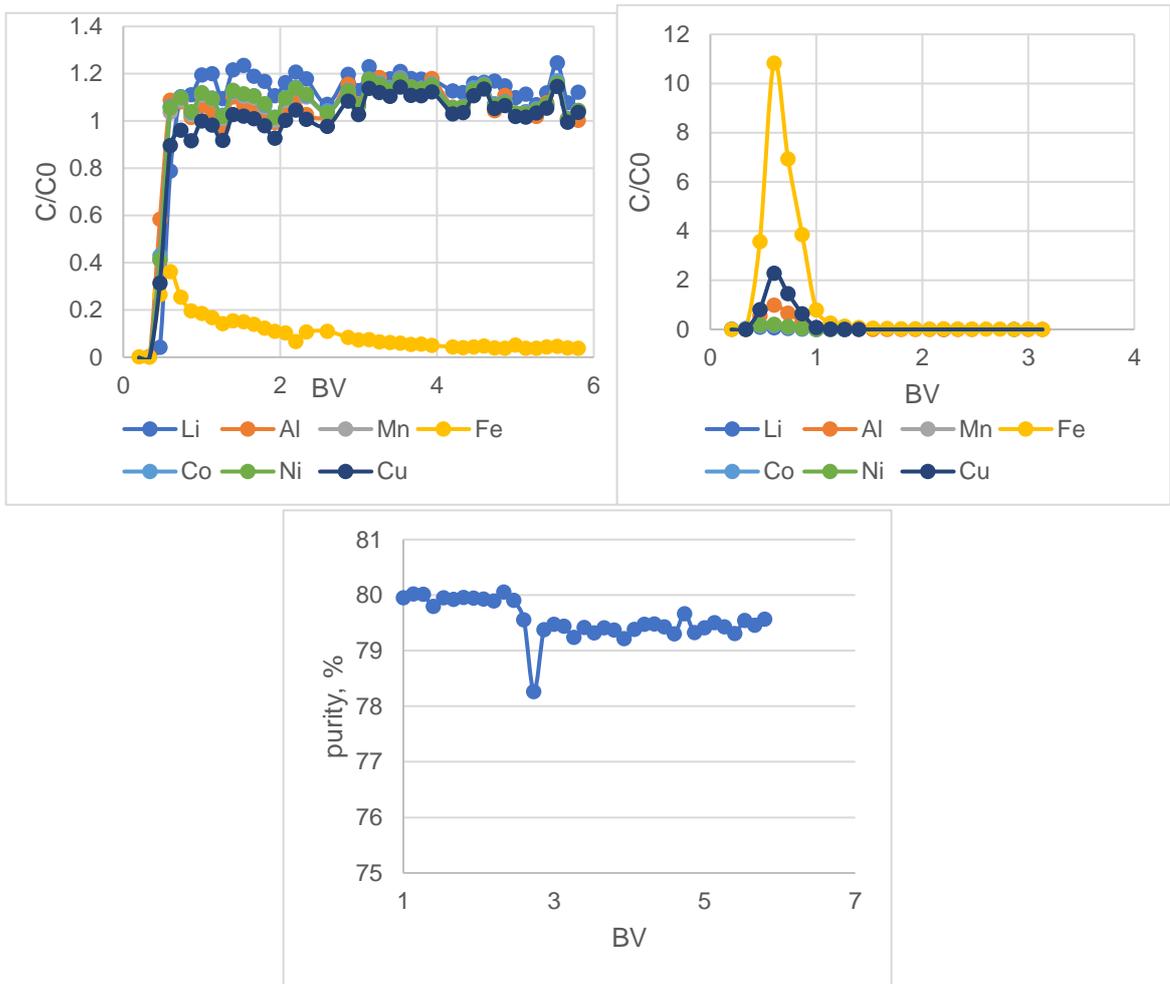


Figure A 9 CS12GC resin breakthrough and elution curves with temporal purity curve in pH 3 and 25 °C