Co-Ni SEPARATION IN IX-SX CIRCUIT

A Thesis Submitted to
the Graduate School of Engineering and Science of
İzmir Institute Technology
in Partial Fulfillment of the Requirements for the degree of

MASTER OF SCIENCE

in Chemical Engineering

by
Ayşe Merve CEYHAN

December 2023
İzmir

We approve the thesis of **Ayşe Merve CEYHAN**

Examining Committee Members:

Prof. Dr. Mehmet POLAT
Chemical Engineering Department, Izmir Institute of Technology

Prof. Dr. Ekrem ÖZDEMİR
Chemical Engineering Department, Izmir Institute of Technology

Prof. Dr. Erol KAYA
Mining Engineering Department, Dokuz Eylül University

12 December 2023

Prof. Dr. Mehmet POLAT
Supervisor, Chemical Engineering Department,
Izmir Institute of Technology

Prof. Dr. Aysun Sofuoğlu
Head of the Department of
Chemical Engineering

Prof. Dr. Mehtap EANES
Dean of the Graduate School
of Engineering and Sciences

ACKNOWLEDGMENTS

I am deeply grateful to Cengiz Holding, Eti Gübre, for entrusting me with this thrilling master’s thesis project and the opportunity to contribute to their R&D department through experimental work.

I sincerely express my gratitude to my manager, Carlos ALVAREZ NOVAL, for his invaluable guidance, unwavering support, and enlightening discussions.

I would like to express my gratitude to my advisor Prof. Dr. Mehmet POLAT, for his guidance, comments, suggestions, and support.

I would also like to thank the members of the thesis committee, Prof. Dr. Erol KAYA and Prof. Dr. Ekrem ÖZDEMİR for their valuable and guiding comments and suggestions.

Additionally, I appreciate the contributions of the Quality Laboratory team, especially Cemal ÖZTÜRK and Ismail Burak BAGUÇ, for their help and feedback regarding ICP-OES.

Finally, I extend my heartfelt appreciation to my family and friends for their unwavering support throughout the writing process.

ABSTRACT

Co-Ni SEPARATION IN IX-SX CIRCUIT

Eti Gübre stands out as the sole facility capable of reclaiming multiple metals from chalcopyrite flotation tails in Turkey. While the overall performance of the process has been deemed satisfactory, the cobalt and nickel products have yet to meet commodity standards.

The objective of this project is to ascertain the feasibility of using a series of hydrometallurgical techniques, namely, solvent extraction and ion exchange resin technologies, for attaining premium-quality cobalt and nickel products from a compound comprising cobalt, nickel, and other assorted elements.

Extracting cobalt and nickel selectively from impurities, reaching over 95% recovery in a solution containing various elements and steep concentration differences, presents a considerable challenge. Moreover, accomplishing this within an already operational process adds another layer of complexity, demanding alignment with the existing process's stability.

The strategy involved selectively separating and refining cobalt and nickel from the sulfate solution through solvent extraction (SX) methods and employing the Ion Exchange (IX) method for further purification.

ÖZET

IX VE SX DEVRELERİNDE Co-Ni AYRIMI

Eti Gübre, Türkiye'de kalkopirit flotasyon atığından birden fazla metali geri kazanabilen tek tesistir. Sürecin genel performansı tatmin edici sayılırken, kobalt ve nikel ürünleri henüz emtia standartlarını karşılamadı.

Bu projenin amacı, kobalt, nikel ve diğer çeşitli elementlerden oluşan bir bileşikten birinci kalite kobalt ve nikel ürünleri elde etmek için solvent ekstraksiyon ve iyon değişim reçinesi teknolojileri gibi bir dizi hidrometalurjik tekniğin kullanılmasının fizibilitesini tespit etmektir.

Kobalt ve nikelin safsızlıklardan seçici olarak ektrakte edilmesi, çeşitli elementler ve dik konsantrasyon farklılıkları içeren bir çözeltide %95'in üzerinde geri kazanıma ulaşılması önemli bir zorluk teşkil etmektedir. Üstelik bunu halihazırdaki bir operasyonel bir süreç içerisinde gerçekleştirmek, mevcut sürecin istikrarıyla uyum sağlanmasını gerektiren başka bir karmaşıklık katmanı daha ekler.

Strateji, solvent ekstraksiyonu (SX) yöntemi yoluyla kobalt ve nikelin sülfat çözeltisinden seçici olarak ayrılmasını ve rafine edilmesini ve daha fazla saflaştırma için İyon Değişimi (İX) yönteminin kullanılmasını içermektedir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Cengiz Holding utilizes pyrite tailings obtained from the flotation plant in Kure, Kastamonu. This plant processes complex copper ore as its primary feed material. The pyrite tailings contain around %48-50 sulfur, hence also called pyrite or sulfur concentrate, are transported to the Eti Gübre Plant in Mardin, Turkey, where they serve as the feed material for a sulfuric acid plant, resulting in the production of 98% pure sulfuric acid. Subsequently, this sulfuric acid is utilized as a central component in the phosphate fertilizer plant's primary manufacturing process.

The spent solids, known as calcine, retrieved from the sulfuric acid plant, contain substantial quantities of cobalt (Co) and nickel (Ni). These metals are targeted for recovery in a hydrometallurgical metal recycling facility due to their significant economic value, particularly in applications involving corrosion resistance and rechargeable batteries. Eti Gübre aims to maximize the production of these metals by initially oxidizing a vast amount of metal content from the ore through a hydrometallurgical process. This process involves pressurized leaching using sulfuric acid, followed by subsequent separation and purification stages. There are plans to process black mass, which holds a high concentration of cobalt and nickel. The leaching solution comprises copper (Cu), zinc (Zn), Co, and Ni, alongside primary impurities such as iron (Fe), calcium (Ca), magnesium (Mg), and manganese (Mn).

Separating cobalt from nickel in sulfate-based solutions poses a challenge due to their similar chemical responses in hydrometallurgical processes, such as dissolution and precipitation behavior. The collective experience has shown that Co and Ni solutions can be selectively cleaned using solvent extraction employing Di (2-ethylhexyl) Phosphoric Acid and further purified by ion exchange using proper resin recipes.

1.1. Aim of Project

The possibility of capturing the cobalt and nickel losses from the Solvent Extraction (SX) circuit of the existing hydrometallurgy plant in Eti Gübre and producing a pure $CoSO_4.XH_2O$ and $NiSO_4.XH_2O$ from ammonium/sulfate-base leach solution using this separation and purification method will be studied and investigated in this thesis study.

The project aimed to recover cobalt and nickel from the leach solutions through a two-stage solvent extraction step using Bis (2,4,4 Trimethylpentyl) Phosphinic Acid and Di (2-ethylhexyl) Phosphoric Acid followed by an ion exchange step employing different groups of IX resins. Analysis of products was carried out using ICP-OES and XRD techniques. The theoretical calculations of the requisite separation stages and identifying optimal resin choices have been carried out using the analysis results. Additionally, the study explored the feasibility of producing high-quality battery-grade products through crystallization methods.

1.2. Scope

Following an extensive review of the literature, the experimental phase of the project was planned to be carried out in four distinct phases:

i. Batch separation and purification tests with the raffinate solution using SX and IX under different conditions (pH, acid concentration, BV, and temperature) for obtaining maximum cobalt and nickel recovery. This part has been carried out at a laboratory scale in the Eti Gübre’s R&D facility.

ii. Drawing McCabe-Thiele diagrams based on the results from (i) to ascertain design parameters and the requisite stage number for solvent extraction. This information will be applied in simulating a continuous multistage countercurrent solvent extraction.

iii. Constructing isotherm graphics using the resin results to obtain essential process parameters, such as bed volume (BV), pH, and temperature.

iv. Carrying out crystallization tests for obtaining good-quality battery-grade battery grade $CoSO_4.XH_2O$ and $NiSO_4.XH_2O$ products.

1.3. Cengiz Holding Eti Gübre Metal Recycling and Integrated Fertilizer Plant

Eti Bakir A.S. Mazıdağı Phosphate Facility is a Metal Recovery and Integrated Fertilizer plant located 90 km from Diyarbakır and 65 km from Mardin. The facilities were included within the Cengiz Holding corporate structure in 2011. In Eti Bakır A.Ş Mazıdağı Plant, A total of 250.000 tons of concentrated phosphate and 650.000 tons of sulfuric acid are produced annually as feed material for processing in the phosphoric acid production plant. Also, the 150,000 tons of phosphoric acid and 75,000 tons of liquid ammonia from the Phosphoric Acid and Ammonia Plants are also fed to the Fertilizer Plant which produces 108,336 tons of DAP (18-46-0) fertilizer (Figure 1).

The pyrite raw material utilized by the sulfuric acid plant (SAP) is sourced from the tailings of the copper flotation plant of Cengiz Holding in Kure, Kastamonu, Turkey. Due to its richness in sulfur and its role as the feedstock for the sulfuric acid plant, these pyrite tailings are also referred to as sulfur or pyrite concentrate. The pyrite concentrate is introduced into the Sulfuric Acid Plant. The primary outputs of the SAP plant include 98% pure sulfuric acid and the heat generated by exothermic reactions. This heat is converted into steam, which, in turn, is used to produce electricity in the power plant. Additionally, low-pressure steam is employed in various stages of the process. The sulfuric acid (H_2SO_4) is directed to the Phosphoric Acid Plant (PAP), where it contributes to the leaching process of phosphate rocks obtained from the adjacent phosphate mine, resulting in the production of phosphoric acid (H_3PO_4). The ammonia, produced from natural gas, is combined with phosphoric acid to manufacture phosphate fertilizers in the Fertilizer Plant.

The waste material generated by the sulfuric acid plant is called calcine. It is a mixture of solid oxides formed by roasting the pyrite ore during the process of generating SO_2. The calcine consists of 63.0% Fe, 0.75% Co, 0.65% Cu, 0.45% Zn, and 0.05% Ni, and some additional impurities. The calcine is treated in the Metal Recovery Plant to yield

2.000 tons of copper cathode, 2.500 tons of zinc carbonate, and 11.500 tons of cobalt carbonate.

The hydrometallurgical plant depicted in Figure 2 is used to recover valuable metals from calcine using high pressure acid leaching process (HPAL). The process is composed of a leaching step (under pressure) using sulfuric acid, followed by a purification and separation step. The simplified general flow diagram of the hydrometallurgical processes involved in the Metal Recycling Plant Eti Gübre is given in Figure 2.

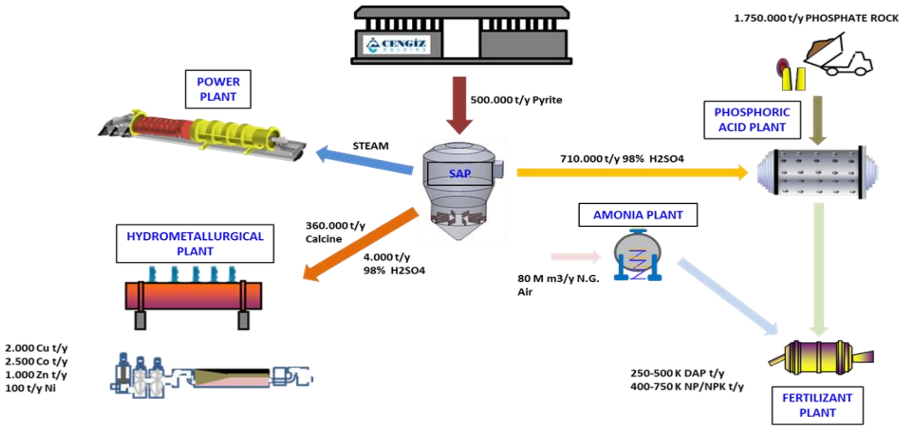


Figure 1. The general flow diagram of the Eti Gübre Metal Recycling and Integrated Fertilizer Plant.

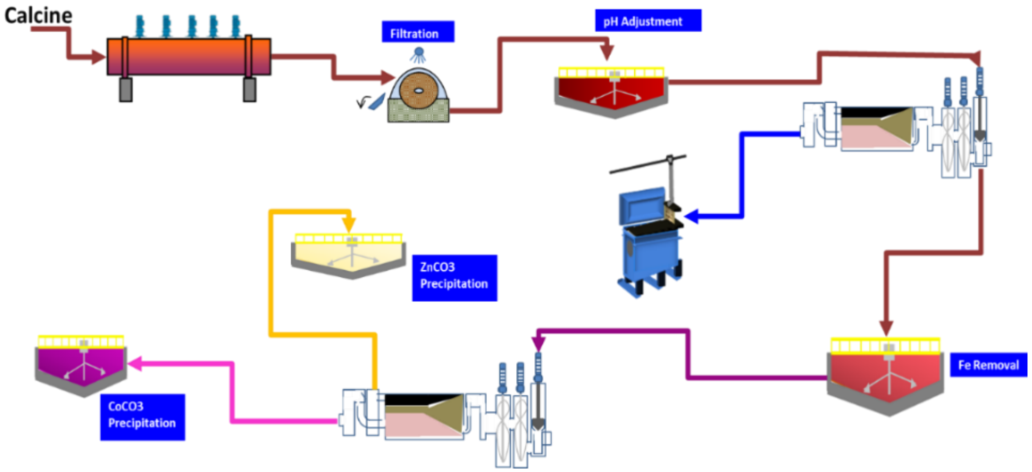


Figure 2. General flow diagram of hydrometallurgical plant.

The Plant contains three main and one supportive process which are Autoclave, Cu SX, Co/Zn SX, and Iron removal. The calcine feed reacts in the Autoclave in the presence of oxygen and sulfuric acid under high pressure and temperature. The process which simultaneously oxidizes and dissolves the calcined material is called high-pressure acid leaching. The sludge from the autoclave is sent to the filtration unit for solid-liquid separation. The solid phase is called “Hematite” due to the high amount of hematite iron which is the dominant phase produced from pyrite under high pressures and temperatures. The liquid phase is sent to the pH adjustment unit to prepare it for the Cu separation stage in the CuSX process where copper is recovered by counter-current continuous solvent extraction using LIX 984N, a brand of organic extractant primarily used in hydrometallurgy for solvent extraction processes. LIX 984N-C belongs to a class of extractants known as hydroxy oximes and is utilized for its selective extraction properties, aiding in the separation and purification of metals from aqueous solutions. The eluate from the Cu separation stage is sent to the electrowinning process to recover cathodic copper.

The residual solution from the copper separation is sent to the Fe Removal process to prepare the solution for the Co-Zn Solvent Extraction Process. The high concentrations of iron in the solution cause cobalt loss and poisoning of the organic phase. The iron-stripped solution is sent to a solvent extraction stage operating under counter-current conditions where it is extracted using Bis (2,4,4 Trimethylpentyl) Phosphinic Acid for selective Co and Zn separation. The cobalt which is initially separated from the solution is sent to the precipitation step to precipitate in carbonate form. The same procedure is applied to zinc remaining in solution to produce $ZnCO_3$.

CHAPTER 2

BACKGROUND

2.1. Ion Exchange (IX) Process

Although the phenomenon of ion exchange has been observed since the mid-19th century, its practical importance was not immediately recognized, and it was not until the 1920s that natural or synthetic ion exchangers became widely known. half of the century. By then, many relatively pure minerals exhibiting alteration properties had been discovered or synthesized, such as zeolites and clays. Despite these exchangers are still widely used in water treatment, they are unstable in acidic and alkaline solutions and can only be used satisfactorily under near-neutral conditions. Therefore, these aluminosilicates are of little importance for the analytical separation of metal ions. However, a breakthrough came in 1934 with the discovery that some high-molecular-weight synthetic organic polymers containing numerous ionic functional groups as integral parts could be used as ion exchangers. (Johann Korkisch and York Toronto 1969).

Ion exchange has started to be widely applied in precious metal ion chemical separation technology. This has led to the widespread use of various ion exchange resins, which are indispensable in many fields of the chemical industry. Since precious elements exist in nature in small quantities and their natural raw materials are constantly depleted, physicochemical methods for recovering them from secondary sources are of particular importance. Anode sludges from exhaust gas reformers, chemical catalysts, dental alloys, copper, and nickel electrorefining, and refinery wastewater and effluent containing traces of precious metals. It is worth noting that these wastes are usually treated pyro- and hydrometallurgical. The recovery of precious metals from such raw materials requires an individual approach to each material and the application of selective removal methods. (Hubicki et al. 2015).

These synthetic ion exchangers can exhibit cation or anion exchange properties and are now known as "cation exchange resins" or "anion exchange resins." Ion exchangers generally consist of a positively or negatively charged matrix (fixed ions) and counterions that compensate for this charge. For resin-based ion exchangers, the matrix consists of highly polymerized cross-linked hydrocarbons containing ionizable groups of the types listed in Table 1.

Ion exchangers are polymeric substances, typically solid, and can be either organic or inorganic. They are insoluble in water and many other solvents, capable of exchanging their active ions with active ions of the surrounding electrolyte. In the industry, these resins usually take the form of porous small beans, granules, or membranes. The behavior of these exchangers is fundamentally determined by the number and nature of their functional groups, as well as the composition of the matrix.

Table 1. Ion extracted properties dependence of the functional group.

TYPE OF ION EXTRACTED	MEDIA pH	MATRIX	FUNCTIONAL GROUP
Cationic	Weak Acid	Styrene, DVB, Polyacryl, Acrylic, Poliacrylate, divinyl benzene….	Amino phosphoric acid, Iminodiacetic acid, Iminodiacetate, Thioronium, Thiurea, Phosphonic acid, Sulfonic acid, Thiol, Complex amine, N-methylglucamine, Impregnated with extractants, tributyl amine, aminoacetc acid, triethylamine….
Cationic	Strong Acid		
Cationic	Weak Basic		
Cationic	Strong Basic		
Anionic	Weak Acid		
Anionic	Strong Acid		
Anionic	Weak Basic		
Anionic	Strong Basic		

The swelling properties of the resin are significantly influenced by the number of hydrophilic groups and the cross-linking of the matrix. These factors determine the mobility of the ions, affecting the exchange rate and other kinetic properties. The composition of the matrix is crucial in terms of the chemical and thermal stability of the exchange resin. (Hubicki et al. 2015; Kilislioğlu 2015). Figure 3 below shows the basic working principles of a resin below.

Figure 3. The basic working process of an ionic resin.

Ion exchange (IX) is an alternative process application that uses little to no volatile organic solvents, needs limited impurity metal removal before or after separation, is operational over a wide pH range, and has better selectivity in some multi-metal systems. The advantages of using IX resins instead of solvent extraction (SX) or precipitation are listed below.

- Ease of use and reusability
- Selectivity
- Small footprint
- Can be fully automated, requiring minimal operator intervention, in short, small OPEX and CAPEX.
- Health and safety — reduced risk of fire compared with SX.
- Compared to precipitation, IX is effective in reducing impurity levels to very low concentrations, while minimizing the need for co-extraction of valuable metals and subsequent bulk recycling streams
- Low reagent loss compared with SX.

Removing impurities to very low levels (typically less than 2 mg/L), Ion exchange (IX) resins are widely used, although some industries require levels as low as parts per billion. Currently, commercially available IX resins have a limited ability to attack some impurities from concentrated cobalt and nickel streams. There are organic solvents available that can fill this gap. The combination of suitable organic solvent functionality and the engineering advantages of IX resins provides an attractive option for the industry. Table 2 provides an overview of typical reagents used to attack specific impurities. (Van Deventer, n.d.; Lister et al. 2021).

Table 2. Impurity removal by available ion exchange and solvent extraction reagents.

Metals	Ion Exchange Resins	Organic Solvents	
	Functional Group	Functional Group	Commercial Products
Cu/Zn from Co/Ni	Aminomethyl Phosphonic	D2EHPA (Di(2-ethylhexyl) phosphoric Acid)	Ionquest 220
	Iminodiacetic Acid	None	-
Ni from Co	Bispicolyl Amine	Carboxylic Acid	Versatic 10
	Hydroxypropylpicolyl Amine	None	
Co from Ni	-	None	Bis (2,4,4 Trimethylpentyl) Phosphinic Acid, Ionquest 290

The IX process Involves three main steps: sorption (adsorption/absorption), elution, and washing (regeneration or reconditioning). Figure 4 illustrates the simulation of the basic ion exchange process.

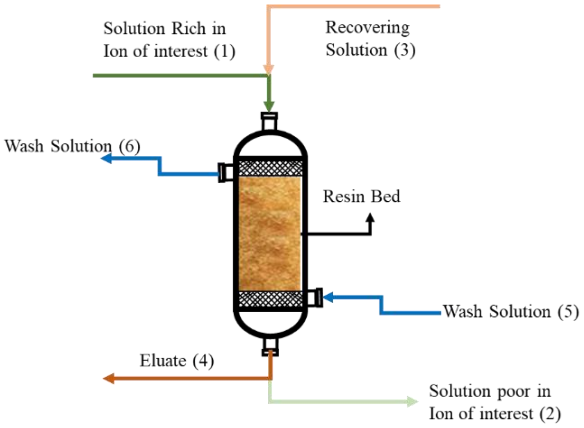


Figure 4. A generalized schematic view of a typical ion exchange process.

In Figure 4, the feeding solution, raffinate solution, recovery feed solution, eluate solution, washing solution, and wash filtrate solution are represented with numbers from 1 to 6 in a general ion exchange process, respectively.

Sorption

In this step, the metal-rich leached liquid solution is introduced into the resin column. Depending on the resin's functional group and metal selectivity, the desired metal(s) or undesired metal(s) are removed from the feed solution. The solution, poor in the ion of interest, is referred to as the raffinate solution and is removed from the column.

An example of this process is the exchange of hydrogen ions of a strongly acid cation exchange resin, for example, Dowex 50, for potassium ions. (Johann Korkisch and York Toronto 1969).

$$R_S SO_3^- H^+ + K^+ \leftrightarrow R_S SO_3^- K^+ + H^+$$

Where, R_s is the resin matrix.

Elution

Ion exchange is a reversible process, and the elution step is the reverse part of this process. An equilibrium is eventually set and the adsorbed or absorbed metal in the resin is removed by recovering the solution which is generally the acidic or basic solution. This recovery solution is decided according to the properties of resins. The output solution is called eluate which involves the desired or undesired metals.

Washing (Regeneration/Reconditioning)

The resins typically need to be washed between cycles and depending on the nature of the feed and eluate solution, they may be washed before introducing any other solutions into the system. The most common wash solution is water, but in cases involving organic solutions, any solvent that doesn't damage the resin matrix or functional group can be used. Depending on the application, resins must be periodically regenerated or reconditioned with a specific solution to maintain optimal performance.

Selectivity determines the efficiency of the process in which the resin is used to recover ions from dilute solutions and the subsequent ease of removal of the ions from the resin. Selectivity is of fundamental importance in all ion exchange resin applications.

This equilibrium distribution of ions between an ion exchange resin and the solution depends on many factors listed below.

- The nature of the exchanging ions (Extraction/Elution kinetic)
- The nature of the ion exchange resin (Extraction/Elution efficiency)
- The nature of the solution (pH, metal concentration)
- Loading capacity
- Temperature

Selectivity decreases with an increase in the concentration of the feed solutions and the temperature. (Van Deventer, n.d.).

The description of ion exchange equilibria can be explained by distribution coefficients and separation factors, which are used in both theoretical and practical contexts. (Johann Korkisch and York Toronto 1969).

The distribution coefficient of an element is defined by the following equation.

$$K_d = \frac{C_1(\text{g resin})}{C_2(\text{ml solution})}$$

C_1: amount of metal ion sorbed on 1 g of the dry resin

C_2: amount of metal ion which remains in 1 ml of solution after the equilibrium

The separation factor is defined as the ratio of the distribution coefficients of two different elements. This ratio serves as a measure of the separability of two elements through ion exchange. For a successful separation, this ratio must deviate from unity. The separation factor can be calculated using the following equation.

$$\alpha = \frac{K_{d_a}}{K_{d_b}}$$

Where, a and b represent the two pairs of elements.

2.2. Solvent Extraction (SX) Process

Solvent extraction is one of the most useful separation methods that is used for selective removal, recovery of metal ions from aqueous solution, purification, and concentration of the metal in hydrometallurgy. This method is interesting for the recovery of a wide range of metals from the base solutions. The separation process is continuously improving with new equipment and extractant development. The advantages of the solvent extraction process are listed below.

- Simple and rapid
- Solvents are easily recoverable to use again in the circuit.
- Solvents are stable components.
- They are transparent to ultraviolent, so it is easy to release metals moving from the aqueous to the organic phase.
- They are as selective as possible.

In solvent extraction, there are two immiscible liquid phases which are the aqueous phase, containing the metal of interest, and the organic phase which can extract the metal ion of interest. The organic phase contains specific organic molecules known as extractants or reagents. These extractants are designed to have an affinity for metal ions. When in contact with the aqueous phase, the extractant molecules selectivity bond with the target metal ions, forming a complex. The general basic flow of solvent extraction is demonstrated in Figure 5.

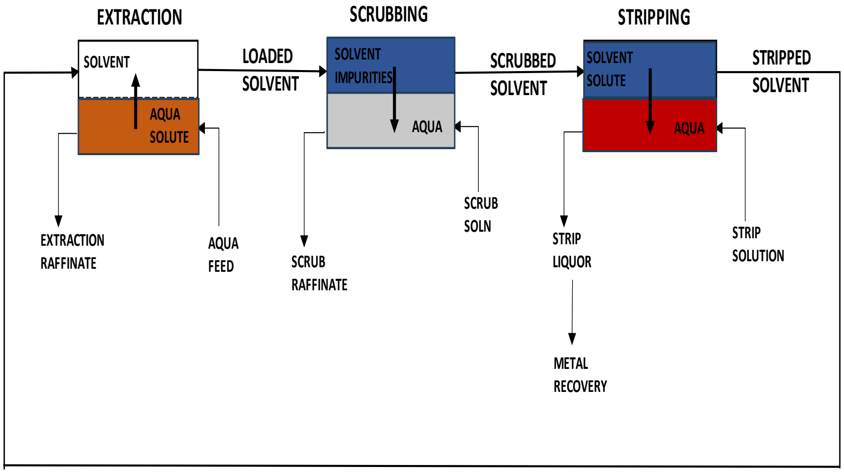


Figure 5. Conventional solvent extraction process.

The metal-bearing aqueous feed solution of interest is extracted from the aqueous phase to the organic phase through an extraction mechanism. The loaded organic phase is then scrubbed with a suitable aqueous solution to remove a small amount of co-extracted impurities. During the scrubbing stage, the pH is adjusted by introducing a new solution, prompting the stripping of most impurities or the targeted impurities for removal. This solution is then reintroduced to the extraction area where the metals are extracted, establishing a stable metal recirculation between the extraction and stripping stages. Although this recirculation increases the total amount of metals in the solution, it maintains a mass balance between the inlet and outlet metals, ensuring optimal quality in the solution reported to stripping. The solution then proceeds to subsequent processes such as electrowinning, precipitation, and crystallization (Shibata, 1991). The operational steps of the solvent extraction process are described more thoroughly below.

Extraction

In this circuit, the aqueous phase and organic phase are mixed by the agitator to facilitate the binding of metal ions to the extractant, allowing them to separate. The resulting aqueous phase, referred to as barren or raffinate, is produced along with the loaded organic phase. The loaded organic phase continues to the stripping circuit, while the raffinate is recycled back to the solvent extraction (SX) feed for further treatment.

Stripping

The metals loaded organic are back-extracted into the aqueous phase by reverse chemical reaction with a suitable solution. The product is called strip liquor or raffinate containing highly concentrated pure metals. The organic is called barren organic and is fed back to the extraction step for use again.

Scrubbing

If the loaded organic phase contains impurities before the stripping step, it undergoes scrubbing to remove all metal impurities. This is achieved by treating it with a fresh scrub solution or recycled strip liquor.

In the chemical consideration of the solvent extraction process, three different extraction mechanisms exist cation extraction, anion extraction, and solvation extraction. However, this thesis will focus on and explain in detail the cation extraction mechanism.

In cation extraction, acidic hydrogen from the acidic extractant is exchanged with the metal ions from the aqueous solution. This extraction mechanism is a pH-dependent equilibrium process, and the simple reaction mechanism is described below.

$$Me^{+2}(aq) + 2RH(org) \leftrightarrow MeR_2(o) + 2H^+(aq)$$

In the formula, Me and R represent metal ions and the functional groups of the extractant.

This enrichment in the phase reactions is dependent on many parameters which are listed below.

- pH
- Metal concentration
- Reagent concentration in the organic
- Reaction temperature

- Reaction time
- Dilute concentration in organic

These parameters affect some essential principles of the solvent extraction process, such as distribution coefficient, extraction percentage, and separation factor.

The distribution ratio (D) of solute concentration between the two phases is expressed as follows when the reaction reaches equilibrium. (Olushola et al. 2013).

$$D = \frac{[\mathrm{Me}]_{\mathrm{org}}}{[\mathrm{Me}]_{\mathrm{aq}}}$$

Where $[\mathrm{Me}]_{\mathrm{org}}$ and $[\mathrm{Me}]_{\mathrm{aq}}$ represent the concentration of the solute metal in the organic and aqueous phases, respectively. The meaning of the high distribution value is that which is the preferred extraction situation, a high amount of metal is extracted into Where $[\mathrm{Me}]_{\mathrm{org}}$ and $[\mathrm{Me}]_{\mathrm{aq}}$ represent the concentration of the solute metal in the organic and aqueous phases, respectively. The meaning of the high distribution value is that which is the preferred extraction situation, a high amount of metal is extracted. (Kihlblom, n.d.)

$$D' = \frac{[\mathrm{Me}]_{\mathrm{aq}}}{[\mathrm{Me}]_{\mathrm{org}}}$$

The percentage of extracted metal (%E) could be calculated as below when the aqueous/Organic (A:O) ratio is equal to 1.

$$\%E = \frac{D}{D+1} \text{ x } 100$$

The high value of D>1 shows the characterization of strong extraction but the small value of D<1 shows the weak extraction characterization.

The ratio of the two extracted metals' distribution coefficient is defined by the separation factor α, the following equation.

$$\alpha = \frac{D_i}{D_j}$$

Where i and j represent different metal components. A high difference between different components means a high value of separation factor and good separation. Due to a big difference between the two components' distribution coefficients, solvent extraction is a suitable separation process for separating and purifying metals.(Kihlblom, n.d.).

The chemical equilibrium between the two phases, the kinetics, selectivity, and ratios between metals in the same phase and even between phases, etc., are complex due to the huge amount of internal recirculation, and the stable internal recirculation of metals that can happen between stages or even inside the different units of one of the stages.

We can operate with a pH range of 3 to 5 during the cobalt extraction step and maintain a pH range of 3.2 to 1.4 in a cobalt stripping circuit to separate it from zinc. In this stage, cobalt is stripped in all circuits, while zinc is stripped at a pH below 2.5; above this value, zinc is extracted.

This makes it challenging to develop software capable of simulating the process with meaningful data output. Most of the world's leading companies in the solvent extraction (SX) sector rely on empirical data, which involves statistical analysis of information gathered over decades from numerous plants. This data is supplemented by specific laboratory work tailored to this scenario.

2.3. Cobalt and Nickel Separation in Sulphate Solution by IX

Battery manufacturers require very high-purity raw materials. This requires suppliers to develop innovative purification methods and meet strict demands. Before product recovery by crystallization or electrowinning methods, most impurities in the liquid must be removed to less than 5 mg/L.

Precipitation methods for impurity removal are commonly included in most flowsheets, but ensuring the removal of impurities to sufficiently low levels is challenging without co-precipitation of the precious metal. To minimize losses of precious metals, precipitation is typically carried out to partially remove impurities. Additional impurity removal is accomplished through more intricate methods, such as ion exchange or solvent extraction.

Cobalt and nickel are often found together in nature. These two elements appear next to each other on the periodic table with cobalt, which has an atomic number of 27, and nickel, which has an atomic number of 28. Thus, they have very similar characteristics, making it difficult to separate them.

Separation of low nickel values from more concentrated cobalt solution can be achieved using bis polyamine or hydroxypropyl polyamine resins as listed in Table 3; but currently available. (Sole 2018).

There are no commercial IX resins that can remove low levels of cobalt from nickel concentrate liquids. The best-chosen organic solvents are di(2-ethylhexyl) phosphoric acid and bis(2,4,4-trimethylpentyl) phosphinic acid. This reagent separates approximately two pH units between cobalt and nickel, as shown in Figure 6 and Figure 7.

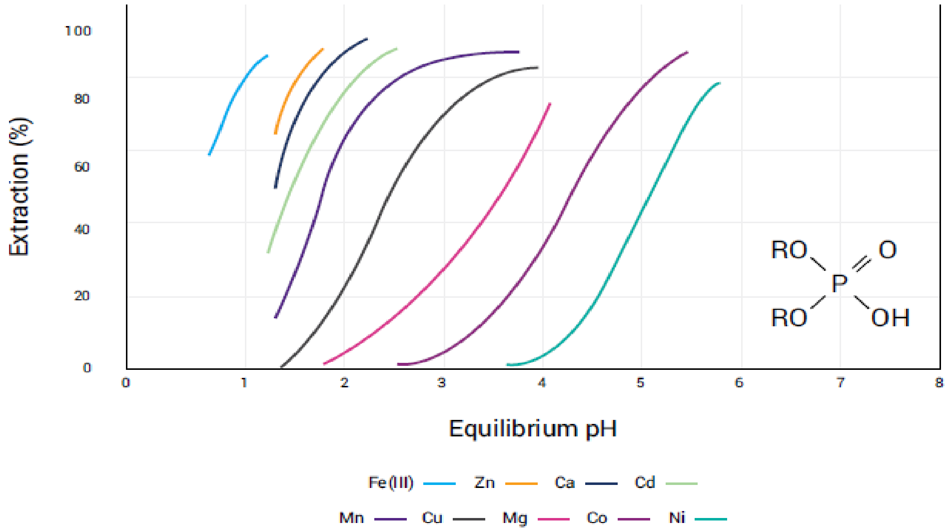


Figure 6. Selectivity order of base metal cations extraction by Di (2 ethylhexyl) phosphoric acid (D2EHPA). (Van Deventer, n.d.).

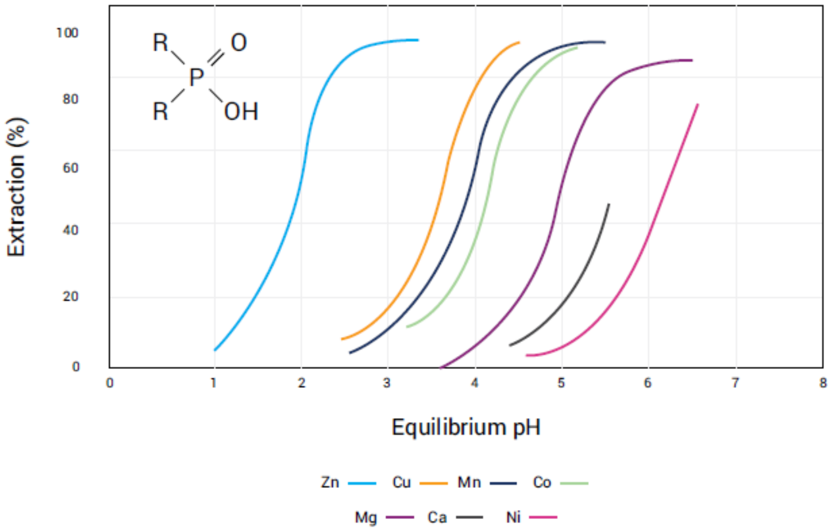


Figure 7. Selectivity order of base metal cations extraction by bis-(2,4,4 trimethyl-pentyl) phosphinic acid (Cyanex 272).(Van Deventer, n.d.).

Table 3. The respective selectivity sequences for selected metal cations.

Strong-acid cation exchanger	Selected Metals
Iminodiacetic-acid resins	$Fe^{+3} > Cu > VO > UO_2 > Pb > Ni > Zn \sim Co \sim Cd > Fe^{+2} > Mn > Ca > Mg > Sr > Ba$
Aminophosphonic-acid resins:	$Fe^{+3} > Pb > Cu > Zn \sim Al > Mg > Ca > Cd > Ni > Co > Sr > Ba$
Bispicolyl Amine resins	$Cu > Ni > UO_2 > Fe^{+3} > Zn > Co > Cd > Fe^{+2}$.
D2EHPA-impregnated resin:	$Fe^{+3} > Zn > Cd > Ca > Mn > Cu > Fe^{+2} > Co > Ni$
Cyanex 272-impregnated resin:	$Fe^{+3} > Zn > Al > Cu > Mn > Co > Mg > Ca > Ni$

2.4. Cobalt and Nickel Separation in Sulphate Solution

The selective separation and recovery of cobalt from nickel have always been challenging due to their adjacent positions in the transition metal series in the periodic table, resulting in similar aqueous chemical behavior. Both cobalt and nickel are preferentially present as divalent hexahydrate ions in a dilute aqueous solution, but the water exchange rate in cobalt ions is significantly higher than that in nickel ions. As a result, complex ion formation generally occurs more readily in divalent cobalt than in nickel. Additionally, despite the nearly identical redox potentials of the Co and Ni pairs, the trivalent cobalt ion is much less unstable and is formed preferentially over nickel.

Cobalt in the divalent state shows a marked tendency to form a tetrahedral configuration under more concentrated electrolyte conditions, rather than the hexagonal configuration of size-coordinated species. These general differences help form the basis of the various separation processes currently used or proposed for cobalt-nickel separation in hydrometallurgy. Traditional processes rely on a form of selective precipitation and can be described as cumbersome and expensive because of that today, this problem has been largely solved by the development of solvent extraction techniques using various extractants. (Kihlblom, n.d.; Douglas Flett 2004).

Solvent extraction of sulphate-based solution involves two different phases; One of them is a metal access solution (aqueous phase), and the other is a liquid sterile organic.

The aqueous phase consists of Cobalt and Nickel, and the organic phase consists of extractants.

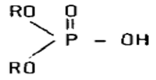
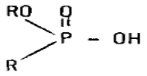
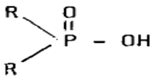
The aim is to extract cobalt from the organic phase and leave nickel in the aqueous phase. After the extraction of cobalt, the cobalt-loaded organic and aqueous phases can be separated from each other by their gravitational differences, and this separation can be thought of as an oil-water mixture. The aqueous phase is called raffinate solution and consists of mostly nickel. The loaded organic is sent to the stripping stage to strip extracted cobalt with a suitable aqueous solution, generally sulfuric acid. The stripped solution is enriched with cobalt, while the barren organic feedback to the extraction circuit. Separated cobalt and nickel solution is sent further process to proceed.

The easy control of the system and to determine extraction and stripping in the separation process, the selectivity of separation must be known. Some parameters affect the selectivity of cobalt separation from nickel in a sulfate solution when using an organophosphorus compound.

- Temperature
- pH
- Acid type
- Co concentration
- Diluent
- Modifier

In this thesis, organophosphorus compound groups are used to separate cobalt-nickel. The groups consist of phosphoric, phosphonic, and phosphinic acid.

Table 4. The structure of compounds and their commercial names.

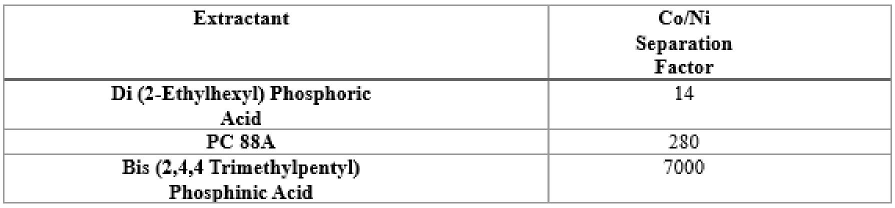
Phosphoric		2-Ethylhexyl (D2EHPA)
Phosphonic		2-Ethylhexyl (PC 88A)
Phosphinic		2,4,4 Trimethylphenyl (CYANEX 272)

The main difference between the compounds is the way the hydrocarbon group ® is attached to the phosphorus atom. In some cases, these structural differences have a significant impact on reagent selectivity. Therefore, in the separation of cobalt-nickel, selectivity increases in order.

$$\text{phosphoric} < \text{phosphonic} < \text{phosphinic acids}$$

This is evidenced by some comparative shake-out experiments by Rickelton and his friends, the results shown below. The increase in the selectivity factor can be explained by the changing nature of the cobalt complex. In other words, the hydrated octahedral complex changes into the anhydrous tetrahedral complex. (Rickelton, Flett, and West 1984; Kihlblom, n.d.).

Table 5. Separation factors of different extractant.



Extractant	**Co/Ni Separation Factor**
Di (2-Ethylhexyl) Phosphoric Acid	14
PC 88A	280
Bis (2,4,4 Trimethylpentyl) Phosphinic Acid	7000

pH controlling is an important parameter to obtain specified process requirements in the cation exchange reaction. Its meaning is that if the equilibrium concentration of the two metal ions is substantially different at a specific pH value, selective extraction is possible. Figure 8 shows the cobalt and nickel recovering from synthetic leach liquor at different pH with three organophosphorus compounds.

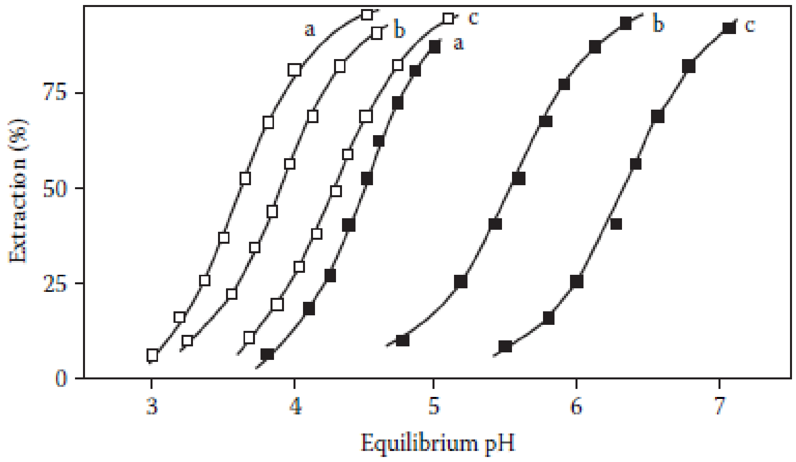


Figure 8. The pH dependence of Co (□) /Ni (□) extraction by three different organophosphorus compounds (a= phosphoric acid; b=phosphonic acid; C=phosphinic acid). (Sole 2008).

The extraction reactions are,

$$Co^{2+}_{(aq)} + 2H_2A_{2(org)} \rightarrow CoA_2.H_2A_{2(org)} + 2H^{+}_{(aq)}$$

$$Ni^{2+}_{(aq)} + 3H_2A_{2(org)} + H_2O \rightarrow NiA_2.H_2A_2.H_2O_{(org)} + 2H^{+}_{(aq)}$$

Cobalt can be selectively mined over nickel because the organic phase favors the formation of tetrahedrally coordinated cobalt species over octahedrally coordinated nickel species. Additionally, cobalt complexes are hydrophobic, while nickel complexes may contain one or two coordinated water molecules in their inner spheres, making them more hydrophilic.(Sole 2008).

While solvent extraction is effective in extracting cobalt, it also extracts some impurities. Therefore, a purification process is applied after solvent extraction to obtain a pure nickel and cobalt sulfate solution. The extraction of organophosphorus acids from base metal ions by pH difference is illustrated in Figure 9, 10, and 11. (Sole 2008). The summary of the graphs can be shown in the table.

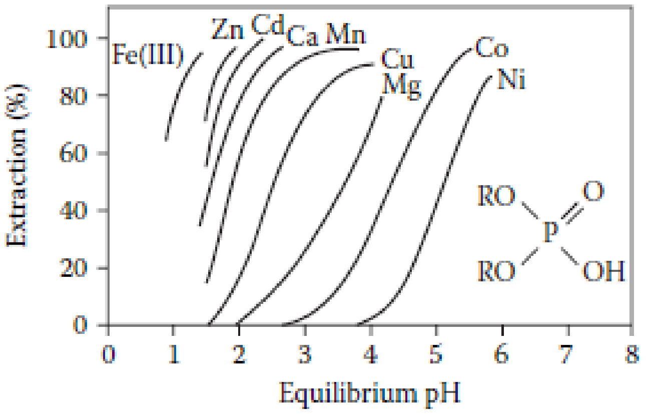


Figure 9. Different metal ion extraction (%) with D2EHPA vs pH.(Sole 2008).

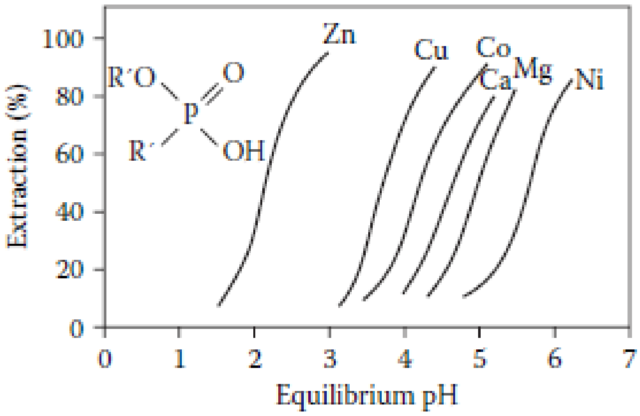


Figure 10. Different metal ion extraction (%) with PC 88A vs pH.(Sole 2008).

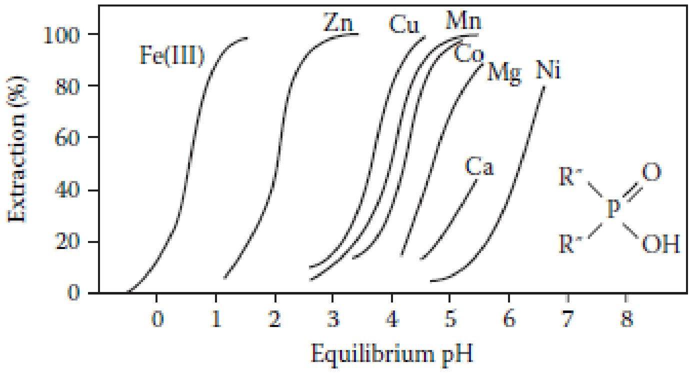
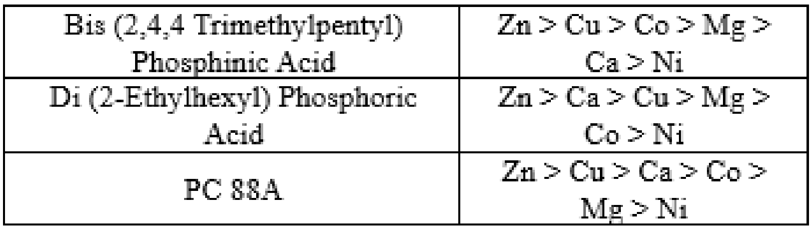


Figure 11. Different metal ion extraction (%) with CYANEX 272 vs pH.(Sole 2008).

Table 6. Summary of extractants’ metal selectivity series.



Bis (2,4,4 Trimethylpentyl) Phosphinic Acid	Zn > Cu > Co > Mg > Ca > Ni
Di (2-Ethylhexyl) Phosphoric Acid	Zn > Ca > Cu > Mg > Co > Ni
PC 88A	Zn > Cu > Ca > Co > Mg > Ni

Bis (2,4,4 Trimethylpentyl) Phosphinic Acid is unique in that it is the only acid of the three organophosphates in question that extracts cobalt instead of calcium. This feature minimizes or eliminates solvent losses associated with calcium extraction and subsequent gypsum crumb precipitation. (Rickelton, Flett, and West 1984).

There are other families of compounds that are used for extremely specific purposes in hydrometallurgy which are versatic acids, amines, TBT, or DBT for example. However, sometimes these compounds are mixed with the phosphor derivates acids as modifiers to increase the selectivity of a specific metal in a specific process. There are more but it is present in the market and is anecdotic.

Extractants are organic complexes that facilitate reversible ion exchange between two liquids under specific parameters. Typically, these extractants are dissolved in a diluent to improve viscosity and establish fluid dynamics equilibrium within the system, especially when loaded with elements. Both aromatic and aliphatic solvents can be used for diluting extractants, and the choice is usually based on economic and safety considerations rather than performance. Generally, while aromatic solvents may offer slightly better performance, they also introduce more operational inconveniences in facilities.

CHAPTER 3

METHODS AND METHODOLOGY

3.1. Materials

The feed solution employed in the test work carried out in this thesis came from the Eti Gübre CoZn SX circuit. Figure 13 illustrates the actual process of CoZn SX in our facilities. In this circuit, the E4 raffinate solution is used to separate CoNi from the circuit by the first resin process. This SX raffinate solution contains cobalt and nickel with impurities which are calcium, magnesium, manganese, aluminum, cadmium, etc.

Other impurities iron, aluminum, cadmium, copper, and zinc were removed beforehand by precipitation, sodium diisobutil ditiofosfinate, copper SX, and electrowinning process, and CoZn SX, respectively. The calcine was leached in high-pressure leaching and the precipitation, aerophine, copper, and cobalt/zinc removing process of metals mentioned had been performed at Eti Gübre facilities.

In this thesis, there are five steps to obtain a good battery grade $CoSO_4$. XH_2O and $NiSO_4$.XH_2O products.

- CoNi recovery from the CoZn SX circuit with LSC710.
- Co/Ni separation with Cyanex 272
- Cleaning of both sulfate solution
- $CoSO_4$ Cleaning with D2EHPA
- $NiSO_4$ Cleaning with D2EHPA
- Purification of both solution
    - $CoSO_4$ Cleaning with Puromet MTX 7010
    - $NiSO_4$ Cleaning with Puromet MTX 7010
- Crystallization of Metal hydrate solution
    - $CoSO_4$. XH_2O

- $NiSO_4 . XH_2O$

For the CoNi recovery part, MTS 9300, provided from Purolite, LWT TP MonoPlus 220, provided from Lanxess, LSC 710 and LSC 772, provided from SunResin, were used as ion exchange resins and their performance compared.

For the Co/Ni separation part, the organic feed Cyanex 272, provided by Solvay, was used as an extractant.

For the $CoSO_4$ and $NiSO_4$ cleaning part, the organic feed is provided by Solvay, and was used as an extractant.

For the purification step of these sulfate solutions, we will use different functional groups from different suppliers and commercial brands, all of this will be explained in detail in the IX resins part.

NaOH (Merck) and H_2SO_4 (Merck) were the reagents to regulate the solution pH and H_2SO_4 was the stripping solution used.

ShellSol D-60, provided by Shell Chemical LP was used as diluent for organic feed.

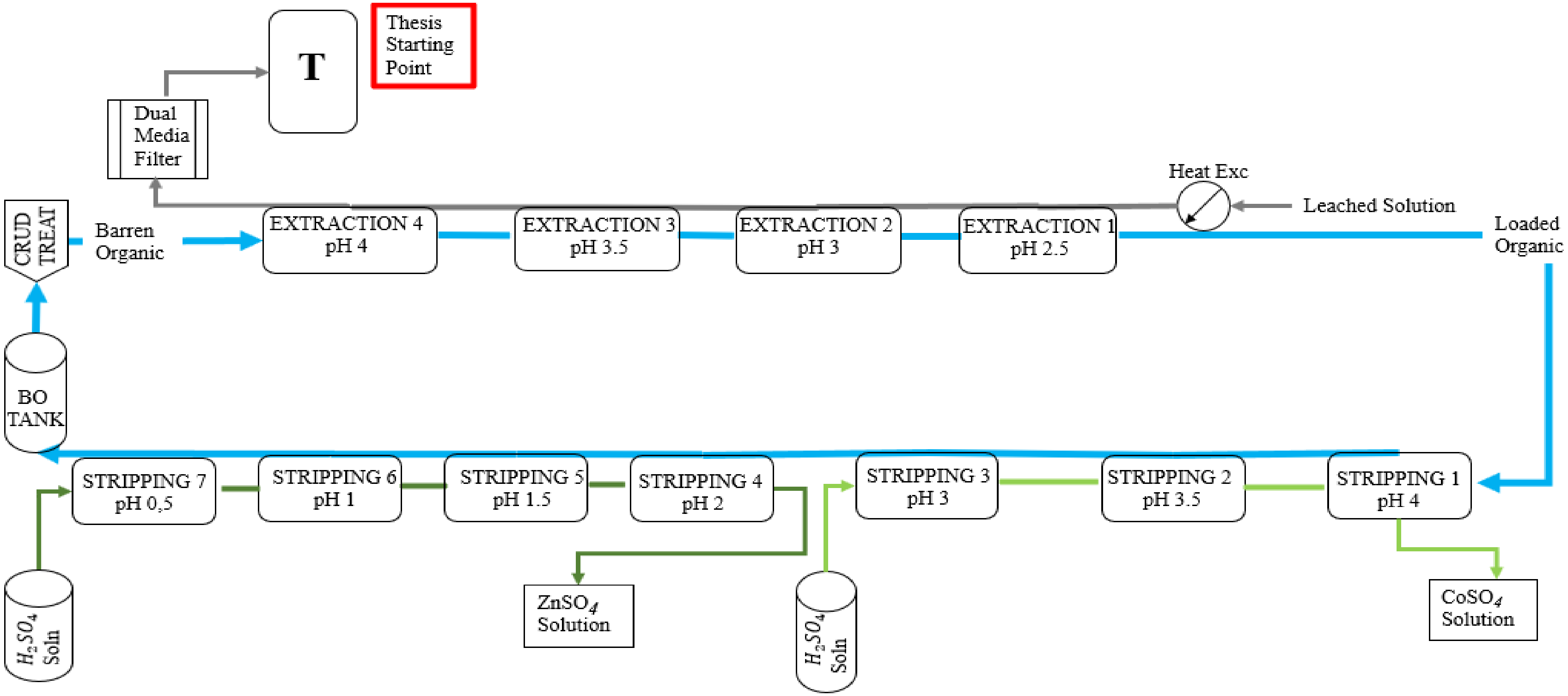


Figure 12. Eti Gübre CoZn SX Circuit.

3.2. Experimental Procedure

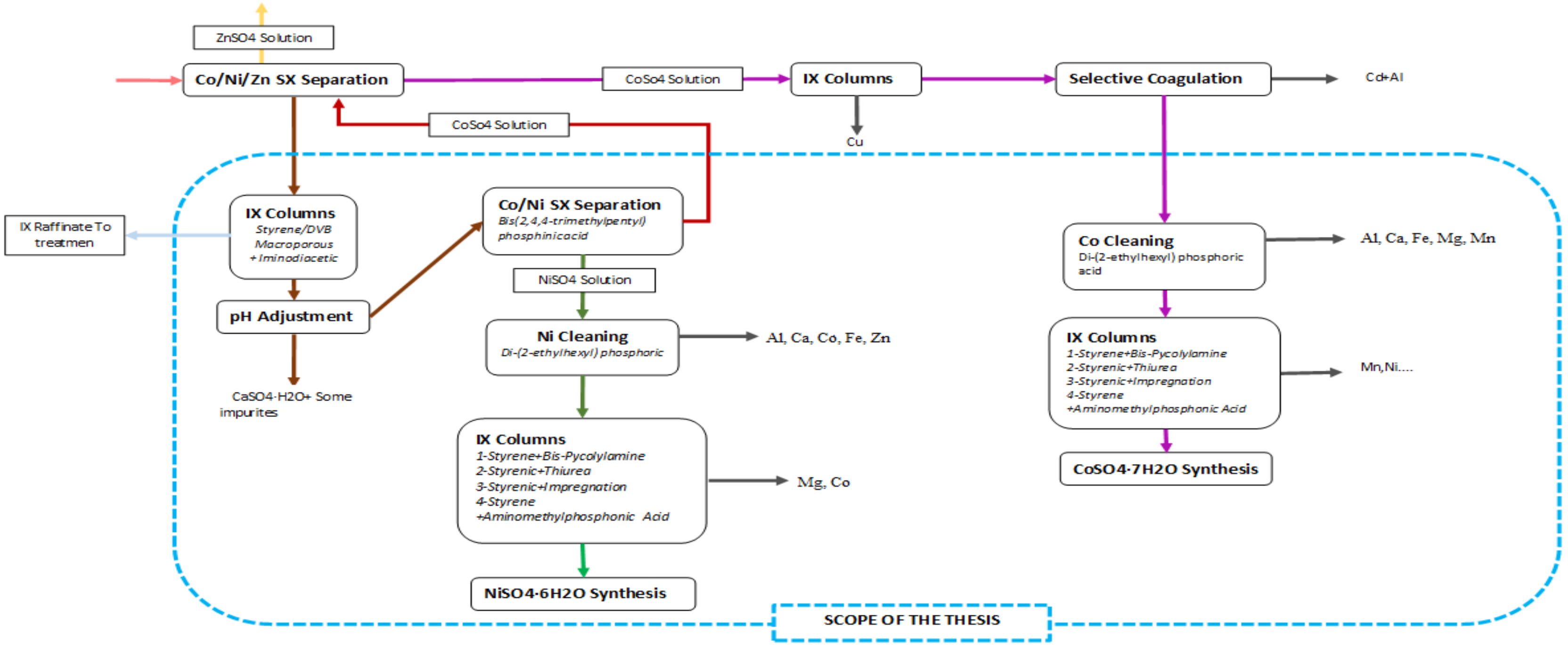


Figure 13. Proposed process flowsheet of the thesis.

The proposed process flowsheet under the scope of the thesis is illustrated in Figure 13 inside the blue broken lines. All the process steps performed as part of the thesis project are explained separately in the paragraphs below.

3.2.1. CoNiZn Separation from SX circuit Raffinate

The separation of CoNi together from the CoNiZn raffinate solution from the SX circuit in our process, in this thesis we tried two different resins groups are chelating resins which consist of iminodiacetic acid, iminodiacetate, and bis-polyamine and impregnate resin consist of Bis-(2,4,4-trimethylpentyl) phosphinic acid. These resins are listed respectively, below. (Ion Exchange Chelating Resin SEPLITE® LSC710-Seplite, n.d.; LEWATIT® MonoPlus TP 220, n.d.; Macroporous Polystyrene Resin SEPLITE® LSC772- Seplite, n.d.; PurometTM MTS9300, n.d.).

- Puromet MTS9300 (Purolite)
- SEPLITE LSC710 (SunResin)
- Lewatit MonoPlus TP 220 (Lanxess)
- SEPLITE LSC772 (SunResin)

The ion exchange batch experimental design for this part of the project is illustrated and presented in the flowsheet below, Figure 14.

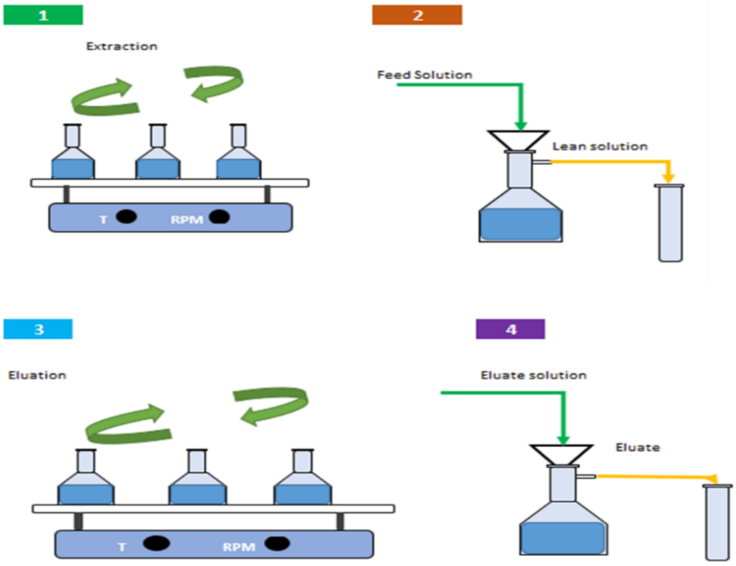


Figure 14. A batch experimental flowsheet of the overall ion exchange design.

Extraction;

i. Erlenmeyer is fed with the decided amount of resin.
ii. The solution is also added into the Erlenmeyer.
iii. Conditions adjusted. (pH, Temperature, Bed Volume, BV,), in the results and discussion part, they will explain in detail.

Filtration;

i. Under the vacuum filter, the loaded resin is separated from the solution.
ii. Taking sample for analysis.

Elution;

i. The separated loaded resin is added into the Erlenmeyer.
ii. The eluate solution is also added to the Erlenmeyer. (20% H_2SO_4).

After the elution part, filtration is repeated to separate the eluate solution and barren resin. Taking samples from the eluate for analysis. In our experiment, the desired metals come with an eluate solution.

Regeneration;

i. The barren resin is washed with pure water and reconditioned for reuse in the circuit.

3.2.1.1. Effect of bed volume and pH on Load Capacity and Selectivity of CoNi vs Mg and Ca

All experiments were continued under the conditions listed below.

- Raffinate Solution from SX circuit
- Resin
- H_2SO_4 140 g/L, (Merck Code :1.1208)
- Distilled water
- Room Temperature & Atmospheric Pressure
- Batch System

Before testing started, the resin where conditioned to perform as best as possible following the recommendations of the suppliers.

In an Erlenmeyer flask (250 to 2000mL), the required amount of resin was added to the raffinate solution (with the raffinate pH adjusted beforehand). The Erlenmeyer was then placed on a mixing table for the necessary time for metal extraction. After extraction, the solution and the loaded resin were separated using vacuum filtration, and a sample of the solution was taken for analysis. The resin was returned to the Erlenmeyer, and an elution solution was added. Elution took place on the mixing table, and after the reaction, the same procedure was followed: filtration, solution sampling, and preparation of the resin for the next batch.

The solutions were analyzed by an ICP-OS in our quality control laboratory.

The raffinate solution used was always the same and the temperature was kept constant at 25 degrees Celsius.

The parameters that were changed to find the best performance parameters,

- pH
- Bed Volume
- Time of extraction
- Time of elution

After researching academic works and finding that it was feasible despite differing conditions in the range of impurities (1), (2), (3), (4), and (5), we decided to contact several resin suppliers. Following discussions with them, we tested four different resins from three different suppliers. The properties of these four resins (Resins 1-4) are summarized in Table 7.

Table 7. Summary of the properties of the resins used in the experiments.

No	Resin	Functional Group	Ionic Form
1	MTS 9300	iminodiacetic acid	Na+
2	LWT 220 TP	iminodiacetate	H+
3	LSC 710	bis-polyamine	Na+
4	LSC 772	Bis-(2,4,4-trimethylpenthyl) phosphinic acid	H+

The pH of the solutions was adjusted with NaOH (33%) according to the recommendations of the suppliers. The maximum load capacity of the resins in CoNi, and the selectivity of CoNi separation on Ca and Mg recovery were checked. Resin load capacity is similar between resins but the selectivity of metals especially in the case of Mg is very different. Also, in most scenarios, the Ca recovery is meager. The details of the experiments will be discussed in the Results and Discussion part.

All samples were analyzed using ICP-OES and mass balance equations were used to calculate the concentrations in the resin extraction and elution phases. Process efficiency is calculated through the percentage of Co and Ni extracted and the separation factor between Ca and Mg metal ions. ($\alpha_1 = D_{Co}/D_{Ca};$ $\alpha_2 = D_{Co}/D_{Mg};$ $\alpha_3 = D_{Ni}/D_{Ca};$ $\alpha_4 = D_{Co}/D_{Mg})$. The calculation of elution efficiency, reverse distribution coefficient, D^1, was calculated.

The best condition was decided after each test was made such as pH optimization, selectivity, and loading capacity. Temperature and reaction time were kept constant. The starting parameters were decided according to resin suppliers' recommendations. NaOH and H_2SO_4 were used for pH adjustment reagents. The experiment conditions and results details will be given in the Results and Discussion part.

3.2.2. Co/Ni Separation by Phosphinic Acid Base Extractant (Bis (2,4,4 Trimethylpentyl) Phosphinic Acid)

To separate cobalt and nickel from the IX elution solution, solvent extraction technologies were chosen, in concert with phosphinic extractant (Bis (2,4,4 Trimethylpentyl) phosphinic acid) as extractant. The laboratory experiment was completed by each test. An illustration of the solvent extraction procedure for this project is presented in Figure 15.

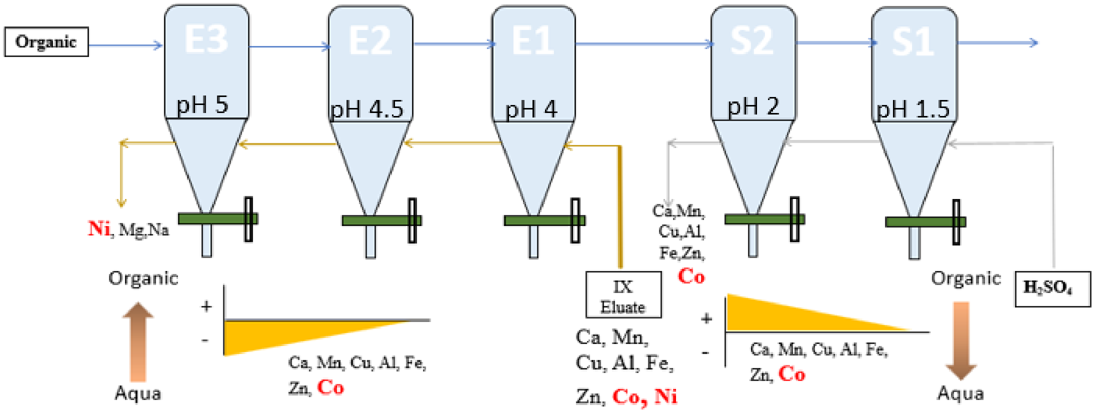


Figure 15. A flowsheet of the experimental solvent extraction design of Co/Ni separation.

The experimental procedure consists of an extraction part, where cobalt is extracted from the sulfate mix solution with the help of an extractant, followed by stripping is carried out to strip cobalt from the loaded organic back to the aqueous phase. The aqueous and organic phases are analyzed using ICP-OES and a mass balance equation was used to calculate the concentrations in the organic phase and aqueous phase. Process efficiency, for the extraction and stripping part, was calculated in the percentage of Co and Ni extracted/stripped and the separation factor between these metal ions.

For extraction;

$$\mathbf{D} = \frac{[\mathrm{Co}]_{\mathrm{org}}}{[\mathrm{Co}]_{\mathrm{aq}}}$$

For stripping;

$$\mathbf{D^1} = \frac{[\mathbf{Co}]_{\mathbf{aq}}}{[\mathbf{Co}]_{\mathbf{org}}}$$

Separation factor between these metal ions;

$$\boldsymbol{\alpha} = \frac{\mathbf{D_{Co}}}{\mathbf{D_{Ni}}}$$

In the experiment, firstly to obtain the best pH condition for the extraction isotherm analyses were done. The result obtained from the isotherm part of the experiment was used in the Mc-Cabe Thiele analysis part to obtain the best O:A ratio and the optimum extraction steps number. A detailed description of the different steps of the experiment will be mentioned in the Results and Discussion part. During the experiment, temperature and contact time were kept constant, temperature was kept constant at 38°C and time was 5 min, respectively. They were decided by the recommendation of the extractant supplier companies. Figure 8 has already shown in the Solvent Extraction process explanation part, the pH effect on the selectivity of Co/Ni. The pH was adjusted continually using 33% NaOH solution and the stripping solution was 20% H_2SO_4 solution.

Table 8 and Table 9 summarize the conditions of the isotherm experiment and Mc-Cabe Thiele analysis, respectively.

After the separation of cobalt and nickel from each other the stripped aqueous solution is rich in cobalt sulfate, and the raffinate solution is rich in nickel sulfate. According to the results of this study, the optimum pH was selected to separate the cobalt and nickel for the Mc-Cabe Thiele diagram.

Table 8. The constant organic/aqua ratios tested at the different pH for CoNi separation.

SAMPLE NAME	pH	Extractant (%)	Ratio O/A	Organic (mL)	Aqua (mL)
CoNi SX Test 1	1	20%	2	300	150
CoNi SX Test 2	1.3	20%	2	290	145
CoNi SX Test 3	1.6	20%	2	280	140
CoNi SX Test 4	1.9	20%	2	270	135
CoNi SX Test 5	2.3	20%	2	260	130
CoNi SX Test 6	2.6	20%	2	250	125
CoNi SX Test 7	2.9	20%	2	240	120
CoNi SX Test 8	3.3	20%	2	230	115
CoNi SX Test 9	3.6	20%	2	220	110
CoNi SX Test 10	3.9	20%	2	210	105
CoNi SX Test 11	4.3	20%	2	200	100
CoNi SX Test 12	4.6	20%	2	190	95
CoNi SX Test 13	4.9	20%	2	180	90
CoNi SX Test 14	5.3	20%	2	170	85
CoNi SX Test 15	5.6	20%	2	160	80
CoNi SX Test 16	5.9	20%	2	150	75
CoNi SX Test 17	6.3	20%	2	140	70

Table 9. The different organic to aqua ratios tested at pH 5.0.

EXP PH	Test No	O/A	Aqua Feed (ml)	Organic Feed (ml)
pH 5	Test1	0.1	500	50
	Test 2	0.2	250	50
	Test 3	0.5	100	50
	Test 4	1	50	50
	Test 5	2	25	50
	Test 6	5	10	50

The residual solutions of both experiments after the Bis (2,4,4 Trimethylpentyl) Phosphinic Acid process under the optimum conditions were used for the next steps of the project.

3.2.3 $CoSO_4$ Cleaning by Phosphoric Acid Base Extractant (Di (2-Ethylhexyl) Phosphoric Acid)

The separated $CoSO_4$ solution from the Co/Ni Sulphate mix solution has some impurities. In the previous section, we mentioned the phosphoric acid base extractant. It is not effective in separating cobalt and nickel from each other, but it has a significant effect on the removal of impurities in our solution. The laboratory experimental procedure is illustrated in Figure 16.

There are two main process steps in this experiment which are extraction and stripping. In the extraction part, the aim is to extract impurities such as Ca, Cd, Fe, Na, Mg, and Mn in the aqueous solution. Later, the organic is fed back to be reused in the circuit. The raffinate solution is the output of the extraction phase is the product, is the clean cobalt solution, but Fe and Mn are not removed completely with the help of a Phosphoric acid extractant. The aqueous and organic phases are analyzed using ICP-OES and a mass balance equation was used to calculate the concentrations in the organic phase and aqueous phase. The efficiency of the process, for the extraction and stripping part, was calculated in the percentage of impurities, using the same equation in the previous solvent extraction part. The raffinate solution was collected and stored for the next purification process.

During the solvent extraction process, reaction temperature and contact time are kept constant, temperature is 38°C and time is 5 min, respectively. They were decided by the recommendation of the extractant supplier companies. The pH was adjusted continually using 33% NaOH solution and the stripping solution was 20% H_2SO_4 solution.

Firstly, to obtain the best pH condition for the extraction isotherm analyses were done in the different pH, and the working range is determined from the isotherm graphic of di (2-ethylhexyl) phosphoric acid. The result obtained from the isotherm part of the experiment was used in the Mc-Cabe Thiele analysis part to obtain the best O:A ratio and the optimum extraction steps number. Table 10 and Table 11 summarize the isotherm and Mc-Cabe Thiele experiment conditions.

Table 10. The constant organic/aqua ratios tested at the different pH for $CoSO_4$ cleaning.

SAMPLE NAME	pH	Extractant (%)	Ratio O/A	Organic (mL)	Aqua (mL)
Co SX Test 1	1	20%	1	200	200
Co SX Test 2	1.3	20%	1	190	190
Co SX Test 3	1.6	20%	1	180	180
Co SX Test 4	1.9	20%	1	170	170
Co SX Test 5	2.3	20%	1	160	160
Co SX Test 6	2.6	20%	1	150	150
Co SX Test 7	2.9	20%	1	140	140
Co SX Test 8	3.3	20%	1	130	130
Co SX Test 9	3.6	20%	1	120	120
Co SX Test 10	3.9	20%	1	110	110
Co SX Test 11	4.3	20%	1	100	100
Co SX Test 12	4.6	20%	1	90	90

Table 11. The different organic to aqua ratios were tested at pH 2.2.

EXP PH	Test No	O/A	Aqua Feed (ml)	Organic Feed (ml)
2.2	Test 1	0.1	500	50
	Test 2	0.2	250	50
	Test 3	0.5	100	50
	Test 4	1	50	50
	Test 5	2	25	50
	Test 6	5	10	50

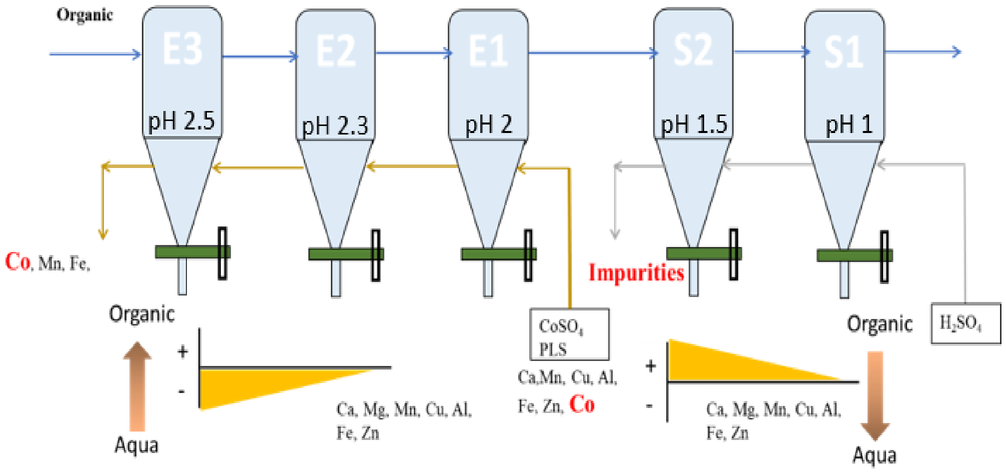


Figure 16. A flowsheet of the experimental solvent extraction design of $CoSO_4$ cleaning.

A detailed description of the different steps of the experiment will be mentioned in the results and discussion part.

3.2.4. $NiSO_4$ Cleaning by Phosphoric Acid Base Extractant (Di (2-ethylhexyl) phosphoric acid)

The $NiSO_4$ solution from the Co/Ni separation part was used in this step to obtain a clean $NiSO_4$ solution by Phosphoric Acid-base extractant in the solvent extraction process. An illustration of the experimental procedure is shown in Figure 17.

The logic behind the procedure is the same as the $CoSO_4$ cleaning process. There are two differences between these two processes that are the pH and O:A ratio. Therefore, to obtain the best pH condition for the extraction, the isotherm analyses were done at different pH, and the working range is determined from the isotherm graphic of di (2-ethylhexyl) phosphoric acid, in Figure 9.

The result obtained from the isotherm part of the experiment was used in the Mc-Cabe Thiele analysis part to obtain the best O:A ratio and the optimum extraction steps number. A detailed description of the different steps of the experiment will be mentioned in the Results and Discussion part.

Extraction and stripping are two main steps of this solvent extraction laboratory experiment in this part of the project. In the extraction part, the aim is to extract impurities such as Ca, Cd, Fe, Mg, and Mn in the aqueous solution. Later, the organic is fed back to be reused in the circuit. The raffinate solution is the output of the extraction phase the product, is the clean cobalt solution, but Mg is not removed completely with the help of a Phosphoric acid extractant.

During the solvent extraction process, reaction temperature and contact time are kept constant, temperature is 38°C and time is 5 min, respectively. They were decided by the recommendation of the extractant supplier companies. The pH was adjusted continually using 33% NaOH solution and the stripping solution was 20% H_2SO_4 solution. The experimental conditions were summarized in Table 12 and Table 13.

Table 12. The constant organic/aqua ratios tested at the different pH for $NiSO_4$ cleaning.

SAMPLE NAME	pH	Extractant (%)	Ratio O/A	Organic (mL)	Aqua (mL)
Ni SX Test 1	1	20%	1	200	200
Ni SX Test 2	1.3	20%	1	190	190
Ni SX Test 3	1.6	20%	1	180	180
Ni SX Test 4	1.9	20%	1	170	170
Ni SX Test 5	2.3	20%	1	160	160
Ni SX Test 6	2.6	20%	1	150	150
Ni SX Test 7	2.9	20%	1	140	140
Ni SX Test 8	3.3	20%	1	130	130
Ni SX Test 9	3.6	20%	1	120	120
Ni SX Test 10	3.9	20%	1	110	110
Ni SX Test 11	4.3	20%	1	100	100
Ni SX Test 12	4.6	20%	1	90	90
Ni SX Test 13	4.9	20%	1	80	80
Ni SX Test 14	5.3	20%	1	70	70

Table 13. The different organic to aqua ratios were tested at pH 2.8.

EXP PH	Test No	O/A	Aqua Feed (ml)	Organic Feed (ml)
pH 2.8	Test1	0.1	500	50
	Test 2	0.2	250	50
	Test 3	0.5	100	50
	Test 4	1	50	50
	Test 5	2	25	50
	Test 6	5	10	50

The aqueous and organic phases are analyzed using ICP-OES and amass balance equation was used to calculate the concentrations in the organic phase and aqueous phase. The efficiency of the process, for the extraction and stripping part, was calculated in the percentage of impurities, using the same equation in the previous solvent extraction part. The raffinate solution was collected and stored for the next purification process because to produce the battery-grade product, we need to remove as much as possible most impurities from the last solution.

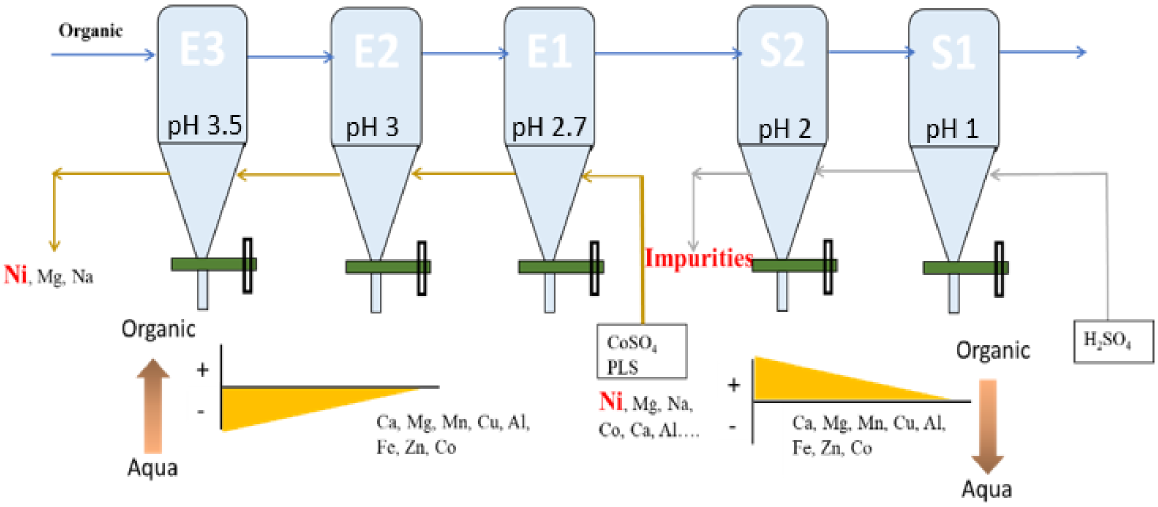


Figure 17. A flowsheet of the experimental solvent extraction design of $NiSO_4$ cleaning.

3.2.5. $CoSO_4$ and $NiSO_4$ Purification by IX Method for Battery Grade Product

In this part of the project, the aim is the purify the cleaned $CoSO_4$ and $NiSO_4$ solution by using different resins in the IX process to obtain the final solution product for the battery grade. There are two different resin groups that were worked in this experiment which are Impregnate resins and chelating resins.

Impregnate resin group consists of two different subtitles which are Di (2-ethylhexyl) phosphoric acid (DEHPA) and Bis (2,4,4-trimethylpenthyl) phosphinic Acid (Cyanex 272). The resins are soaking in suitable solvents/extractant are called solvent-impregnate resins. They are very similar to standard macro-porous resins. The resin pores of the particles contain a liquid extractant and the help of this organic liquid extractant one or more dissolved metal components can be removed from aqueous phase. This is a combination of adsorption, chromatography, and liquid-liquid extraction methods. The density of the impregnate resin is less than the water so that it floats on the aqueous phase. For this reason, during the reaction to avoid the resin moving, strainers can be used at the top and bottom of the reaction vessel. (Van Deventer, n.d.)

In this study we worked; four different solvent-impregnate resins are listed below. (LEWATIT® TP 272, n.d.; LEWATIT® VP OC 1026 - LANXESS, n.d.; PurometTM MTX7010, n.d.; PurometTM MTX8010, n.d.).

1. Bis (2-ethylhexyl) phosphoric Acid (D2EHPA)
    - Puromet MTX7010 (Purolite)
2. Bis (2,4,4-trimethylpenthyl) phosphinic Acid (CYANEX 272)
    - Puromet MTX8010 (Purolite)

The ion exchange experiment with the solvent-impregnate resins is done in the pilot plant of the resin column because of the density problem of the resins. The illustration of the experimental process is shown in Figure 18.

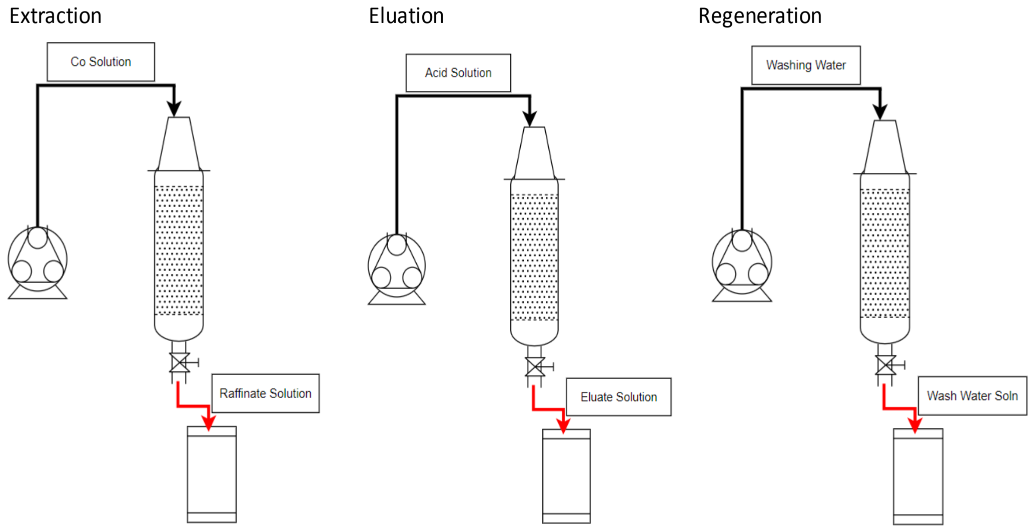


Figure 18. A flowsheet of the experimental ion exchange design of purification step.

Chelating resins are more selective than cationic resins in recovering some metals. Therefore, chelating resin for the recovery of copper, nickel, and cobalt from mining processes and mining waste has been recorded and studied. Chelating resins, including specific, iminodiacetate, bis-picolylamine resins, and aminophosphonic are highly selective for nickel and cobalt. Schematizing resins with the same functional group may have different performances on loading kinetics due to structural differences, functional group density, and degree of cross-linking. (Botelho Junior, Dreisinger, and Espinosa 2019). In this thesis, the listed resin brands below are tried in the iminodiacetate group and bis-picolylamine group. (Ion Exchange Chelating Resin SEPLITE® LSC710 - Seplite, n.d.; LEWATIT® MonoPlus TP 207, n.d.; LEWATIT® MonoPlus TP 208, n.d.; LEWATIT® MonoPlus TP 220, n.d.; PurometTM MTS9500, n.d.; PurometTM MTS9600, n.d.; Special Chelating Resin SEPLITE® LSC495 - Seplite, n.d.).

1. Iminodiacetate Chelating Active Group
    - Lewatit TP 207 (Lanxess)
2. Chelating Bis-picolylamine Groups
    - SEPLITE LSC 495 (SunResin)
3. Chelating Aminophosphonic Groups
    - Puromet MTS 9500 (Purolite)

The experimental procedure of iminodiacetate, bis-picolylamine, and aminophosphonic groups of resins is the batch test design which is illustrated in Figure 14.

3.2.6 Crystallization of $CoSO_4$ and $NiSO_4$ Solutions

The experiments carried out in this project can be divided into two parts. $CoSO_4$ crystallization and $NiSO_4$ crystallization, the experimental equipment set up for both experiments are shown below. This is a batch crystallization process.

Figure 19. The batch crystallization experimental set-up.

<u>Experimental testing steps for $CoSO_4$ are listed below.</u>

1. The $CoSO_4$ solution was heated at 40°C while passing through the graham column.
2. With the jacketed reactor, the reaction temperature was kept constant at 45°C.
3. The mixing was agitated at 600 rpm during the reaction.
4. The solution level was checked periodically to check evaporation.
5. Almost half of the solution has been evaporated. If there is no crystal particle, complete the solution to the initial level. Repeat this step until you notice crystal particles in the solution.
6. Place the seeds into the solution when crystal particles begin to appear.
7. Once you decide you have enough crystals, purge the product from the bottom of the reactor directly to the filter funnel.
8. Wash the wet crystals with ethanol, nearly 150-200 mL, to disperse the solution still on the crystal surfaces.
9. Dry crystals at atmospheric temperature for 3 to 4 hours.
10. If needed, crumble the crystals using a mortar and pestle.

11. Analyze samples using XRD and ICP-OES.

Experimental testing steps for $NiSO_4$ are listed below.

Experimental testing steps for $NiSO_4$ are listed below.

1. The $NiSO_4$ solution was heated at 45°C while passing through the graham column.
2. With the jacketed reactor, the reaction temperature was kept constant at 55°C.
3. The mixing was agitated at 600 rpm during the reaction.
4. The solution level was checked periodically to check evaporation.
5. Almost half of the solution has been evaporated. If there is no crystal particle, complete the solution to the initial level. Repeat this step until you notice crystal particles in the solution.
6. Place the seeds into the solution when crystal particles begin to appear.
7. When adding seeds, decrease the temperature to 25°C.
8. Once you decide you have enough crystals, purge the product from the bottom of the reactor directly to the filter funnel.
9. Wash the wet crystals with ethanol, nearly 150-200 mL, to disperse the solution still on the crystal surfaces.
10. Dry crystals at atmospheric temperature for 3 to 4 hours.
11. If needed, crumble the crystals using a mortar and pestle.
12. Analyze samples using XRD and ICP-OES.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. CoNiZn Separation from SX Circuit Raffinate

The solution we want to recover the metals from is the raffinate solution from the cobalt/zinc solvent extraction stage. This solution has a flow of 40 m3/h and a pH that fluctuates from 4 to 5 most of the time around 4.7 in the process. The feed flow conditions are given in Table 14.

Table 14. CoNiZn Separation process flows conditions.

Steps of Project	**Feeding Flow**	**Ca mg/L**	**Co mg/L**	**Mg mg/L**	**Na mg/L**	**Ni mg/L**	**Zn mg/L**	**pH**
CoNi Recovery (IX)	Raffinate CoNiZn SX (IN)	451.00	55.00	1,867	982.00	48.00	3.00	≈ 1
	CoNi Eluate IX (OUT)	120.00	14,300	4,600	900.00	11,300	46.10	≈ 1
	Lean Raffinate (OUT)	400.00	9.90	2,000	1100.00	0.30	1.30	2.7

Figure 20. Feeding (CoNiZn Raffinate) and output solution (Eluate) of the process.

The first step we took was to check the maximum load of the resins, the concentration of the metals we want to recover is small, and some of the impurities that we want to avoid recovering are in a ratio bigger than 10/1. In these conditions, we want to recover the resins as much as possible to analyze the data, but always prioritize a balance between the metal recovery and the absence of impurities as much as possible.

4.1.1. Resin Capacity

The 4 resins were tested in the next way: Using the pH recommended by the suppliers, we tested in several conditions starting for 5 times the bed volume and multiplying this for 2 each time. When we see that the balance recovery/purity stops increasing, we will find the 2 best results and we will do a test between the best volumes till we to a ratio that we consider optimal. In this stage, to evaluate the performance we decided to take as a main parameter the recovery, the percentage of the metal that will be extracted from the feed solution to the eluate.

For all 4 resins, the recovery of Ni and Co and selectivity against other metals is quite good, especially when we take into consideration the ratios between concentration Mg vs Co and Ni, Ca was an impurity we were concerned about didn't interact with the resin at the test conditions, the analysis of the result show the present of calcium in the eluate but under the detection range. For this reason, we decided to use the minimum value detection range as a value to calculate the recoveries and was included in the table only to show that will not affect the process. The summary of the experimental results is given in Table 15.

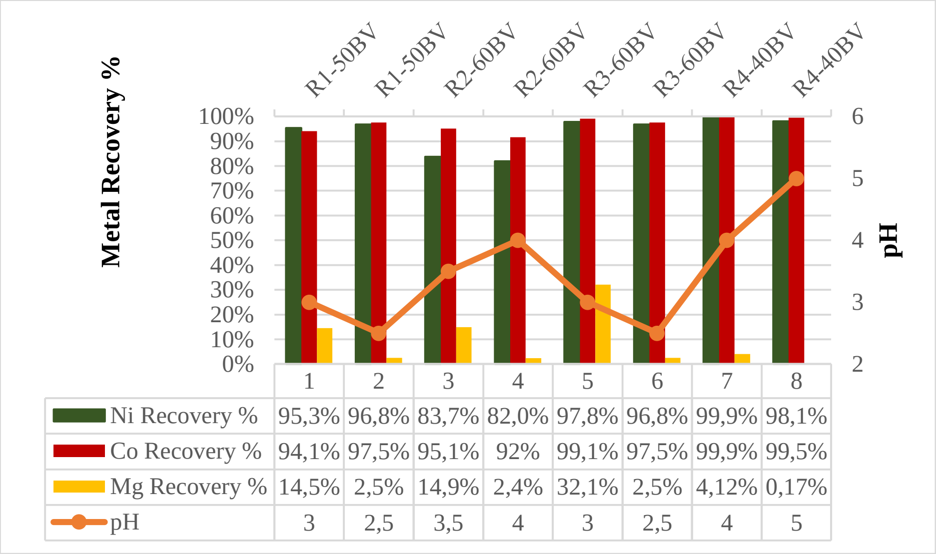
Resins 1 and 3 behave quite similarly, even if the suppliers are different the functional group is the same.

Resin 2 has a slightly higher extraction capacity than any other resin by volume of resin compared in this study but also has the lower selectivity of cobalt and nickel over magnesium.

Resin 4, which uses a similar functional group to the chemical used as an extractant in the solvent extraction where this solution comes from has a higher selectivity over any of them but has the smaller lad capacity of the 4.

4.1.2. Influence of pH in recovery

Most of the ion exchange resins have high susceptibility to pH changes when we talk about the recovery and selectivity of one metal over the other. To check this, we decided to modify the pH of the work recommended by the suppliers to 1 point up and 1 point down. The working methodology was like the previous stage with the difference that we chose the conditions of now the best results changing the pH range. The values for the best conditions were taken from the previous stage. The experimental results are summarized in Table 16. The influence of the pH in the resins was like what the suppliers predicted and recommended, around the pH they recommended with a difference of ±0.5-1. Resin 1 and 2 work better at lower pH.



	1	2	3	4	5	6	7	8
🟩 Ni Recovery %	95,3%	96,8%	83,7%	82,0%	97,8%	96,8%	99,9%	98,1%
🟥 Co Recovery %	94,1%	97,5%	95,1%	92%	99,1%	97,5%	99,9%	99,5%
🟨 Mg Recovery %	14,5%	2,5%	14,9%	2,4%	32,1%	2,5%	4,12%	0,17%
● pH	3	2,5	3,5	4	3	2,5	4	5

Figure 21. Summary and comparison of resin capacity and pH effect on resins.

Resin 1 has its better performance at pH 2.5 where the recovery of cobalt a nickel increases when the extraction of magnesium decreases a 21% when cobalt and nickel recovery increase close to 3.6 and 3 points respectively.

Resin 2 performs better at pH 4 selectivity of magnesium decreased, by 0.1 %, and the recoveries of nickel and cobalt increased by 3.7% and 2.5 % respectively.

Resin 3 has a better performance at pH 3, exactly as the supplier suggested.

Resin 4 works better in a pH of 5 where the recovery of cobalt and nickel is 98.1% and 99.5% respectively, with only 0.17% of the manganese being extracted.

In Figure 21, resin capacity and influence of the pH results of the four different resins are summarized and compared.

Table 15. Summary of resins capacity at constant pH.

Assay time: 4h

Resin	pH	Temperature (°C)	mL Resin	Solution BV	Ni Recovery %	Co Recovery %	Mg Recovery %	Ca Recovery %
1	3	25	25	5	97.4%	97.5%	66.4%	0.01%
1	3	25	25	10	96.5%	98.5%	31.6%	0.01%
1	3	25	25	20	95.3%	94.1%	14.5%	0.01%
1	3	25	25	40	94.3%	93.5%	5.5%	0.01%
1	3	25	25	80	78.5%	68.5%	1.8%	0.01%
1	3	25	25	60	88.7%	91.1%	2.3%	0.01%
1	3	25	25	70	82.3%	84.2%	1.7%	0.01%
1	3	25	25	50	93.2%	93.0%	3.2%	0.01%

Resin	pH	Temperature (°C)	mL Resin	Solution BV	Ni Recovery %	Co Recovery %	Mg Recovery %	Ca Recovery %
2	3.5	25	25	5	85.2%	96.2%	65.8%	0.01%
2	3.5	25	25	10	84.2%	95.7%	32.2%	0.01%
2	3.5	25	25	20	83.7%	95.1%	14.9%	0.01%
2	3.5	25	25	40	79.6%	93.4%	5.4%	0.01%
2	3.5	25	25	80	70.8%	82.5%	1.4%	0.01%
2	3.5	25	25	60	78.3%	89.5%	2.5%	0.01%
2	3.5	25	25	70	79.2%	81.8%	1.9%	0.01%
2	3.5	25	25	50	78.9%	92.3%	3.7%	0.01%

Resin	pH	Temperature (°C)	mL Resin	Solution BV	Ni Recovery %	Co Recovery %	Mg Recovery %	Ca Recovery %
3	3	25	20	5	98.2%	99.5%	65.7%	0.01%
3	3	25	20	10	97.8%	99.1%	32.1%	0.01%
3	3	25	20	20	94.7%	94.9%	14.1%	0.01%
3	3	25	20	40	94.5%	94.7%	4.9%	0.01%
3	3	25	20	80	77.1%	70.3%	1.9%	0.01%
3	3	25	20	60	94.3%	94.7%	1.9%	0.01%
3	3	25	20	70	81.2%	83.5%	1.7%	0.01%
3	3	25	20	50	94.3%	93.8%	3.3%	0.01%

Resin	pH	Temperature (°C)	mL Resin	Solution BV	Ni Recovery %	Co Recovery %	Mg Recovery %	Ca Recovery %
4	4	25	25	5	99.5%	99.6%	58.41%	0.01%
4	4	25	25	10	99.9%	99.9%	27.45%	0.01%
4	4	25	25	20	99.9%	99.9%	11.54%	0.01%
4	4	25	25	40	99.9%	99.9%	4.12%	0.01%
4	4	25	25	80	95.4%	98.2%	0.01%	0.01%
4	4	25	25	160	52.2%	47.2%	0.01%	0.01%
4	4	25	25	120	68.1%	72.2%	0.01%	0.01%
4	4	25	25	100	83.7%	83.8%	0.01%	0.01%
4	4	25	25	90	92.3%	94.1%	0.01%	0.01%

Table 16. Summary of pH effect on metal recovery.

Assay time: 4h

Resin	pH	Temperature (°C)	mL Resin	Solution BV	Ni Recovery %	Co Recovery %	Mg Recovery %	Ca Recovery %
1	2	25	25	50	78%	88%	2%	0.00%
1	2.5	25	25	50	96.8%	97.1%	2.5%	0.00%
1	3	25	25	50	93.2%	93.0%	3.2%	0.01%
1	3.5	25	25	50	84%	79%	3.7%	0.01%
1	4	25	25	50	76.2%	77.2%	3.9%	0.01%

Resin	pH	Temperature (°C)	mL Resin	Solution BV	Ni Recovery %	Co Recovery %	Mg Recovery %	Ca Recovery %
3	2	25	20	60	78%	88%	2%	0.01%
3	2.5	25	20	60	96.3%	98.5%	2.5%	0.01%
3	3	25	20	60	94.3%	93.8%	3.3%	0.01%
3	3.5	25	20	60	84%	79%	3.7%	0.01%
3	4	25	20	60	76.2%	77.2%	3.9%	0.01%

Resin	pH	Temperature (°C)	mL Resin	Solution BV	Ni Recovery %	Co Recovery %	Mg Recovery %	Ca Recovery %
2	2.5	25	25	60	54%	75%	3.1%	0.01%
2	3	25	25	60	82.0%	92%	2.4%	0.01%
2	3.5	25	25	60	78.3%	89.5%	2.5%	0.01%
2	4	25	25	60	77.6%	88.6%	2.6%	0.01%
2	4.5	25	25	60	74%	65%	3.2%	0.01%

Resin	pH	Temperature (°C)	mL Resin	Solution BV	Ni Recovery %	Co Recovery %	Mg Recovery %	Ca Recovery %
4	3	25	25	80	83.3%	89.4%	0.42%	0.01%
4	3.5	25	25	80	87.5%	92.6%	0.37%	0.01%
4	4	25	25	80	95.4%	95.5%	0.01%	0.01%
4	4.5	25	25	80	95.6%	98.4%	0.25%	0.01%
4	5	25	25	80	98.1%	99.5%	0.17%	0.01%

4.2. Co/Ni Separation by Phosphinic Acid Base Extractant (Bis (2,4,4 Trimethylpentyl) Phosphinic Acid)

As explained in the scope of this thesis the aim is to separate Co and Ni from the eluate solution of an existing IX process. After separated $CoSO_4$ solution, is fed back to the beginning of the actual CoZn SX circuit, in this circuit Co will be separated, and then cleaned from impurities to achieve the goal of the works we have explained before. The general proposed process flow diagram is already summarized in Figure 14. $NiSO_4$ solution is sent directly to the cleaning process, just after being separated from $CoSO_4$.

4.2.1. Isotherm Procedure

The first step of the Bis (2,4,4 Trimethylpentyl) Phosphinic Acid procedure is the observation of the pH effect on the Co/Ni separation and defining the best working pH. When separation of Co/Ni some of the impurities also extracting. The feeding solution properties are given in Table 17. The ratio of O/A is 2 and was kept constant with the different pH.

Table 17. CoNi Separation feeding flow composition.

Steps of Project	***Feeding Flow***	***Al***	***Ca***	***Cd***	***Co***	***Cu***	***Fe***	***Mg***	***Na***	***Ni***	***Zn***
		mg/L	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***
Co/Ni Separation (CYANEX)	*CoNi ELUATE IX (IN)*	2.15	432.9	78.05	6,803	0.95	94.25	1,405	490.15	8,513	2.80

Under the low pH, the Co/Ni selectivity of the organic is low, but the extraction of the impurities was started. The best pH conditions are starting for the separation of cobalt around 5. The complete separation of Co and Ni from each other by Bis (2,4,4 Trimethylpentyl) Phosphinic Acid is not possible but the aim is to extract as much as possible cobalt from the solution with a low amount of nickel. In Table 18, the pH effect on the extraction of the metals in the feeding solution is summarized.

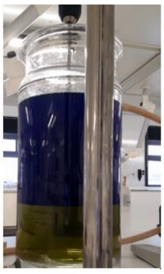


Figure 22. The Bis (2,4,4 Trimethylpentyl) Phosphinic Acid batch experiment simulation. (At the separation of Co/Ni after pH 4.)

After extraction of metals, the organic was stripped with $H2SO_4$ (180 g/L) solution to reuse the circuit again. The stripped solution consists of $CoSO_4$.

Figure 23. Feeding and output solution of process. Eluate, $CoSO_4$, and $NiSO_4$ from left to right.

Table 18. Effect of pH on extraction equilibrium.

pH	Al Extrc	Ca Extrc	Cd Extrc	Co Extrc	Cr Extrc	Cu Extrc	Fe Extrc	Mg Extrc	Ni Extrc	Zn Extrc
	%	%	%	%	%	%	%	%	%	%
1	45%	6%	14%	11%	0%	47%	18%	12%	0%	25%
1.3	48%	9%	18%	14%	0%	57%	25%	16%	0%	29%
1.6	46%	10%	18%	16%	0%	60%	28%	17%	1%	39%
1.9	47%	9%	20%	16%	0%	55%	30%	19%	2%	47%
2.3	65%	12%	21%	17%	0%	61%	31%	20%	5%	71%
2.6	82%	10%	20%	19%	0%	66%	30%	19%	5%	88%
2.9	90%	13%	23%	24%	0%	74%	31%	20%	7%	92%
3.3	100%	18%	30%	33%	0%	80%	34%	26%	8%	94%
3.6	99%	19%	34%	45%	0%	87%	35%	26%	12%	90%
3.9	100%	18%	34%	43%	0%	85%	34%	26%	15%	91%
4.3	100%	23%	47%	60%	0%	90%	36%	30%	21%	94%
4.6	100%	33%	70%	87%	0%	90%	37%	39%	24%	90%
4.9	100%	44%	83%	94%	0%	90%	37%	48%	24%	92%
5.3	100%	65%	95%	99%	0%	85%	40%	77%	26%	89%
5.6	100%	78%	98%	100%	31%	83%	44%	91%	33%	88%
5.9	100%	88%	99%	100%	45%	86%	52%	97%	42%	89%
6.3	100%	91%	100%	100%	46%	84%	61%	98%	52%	86%

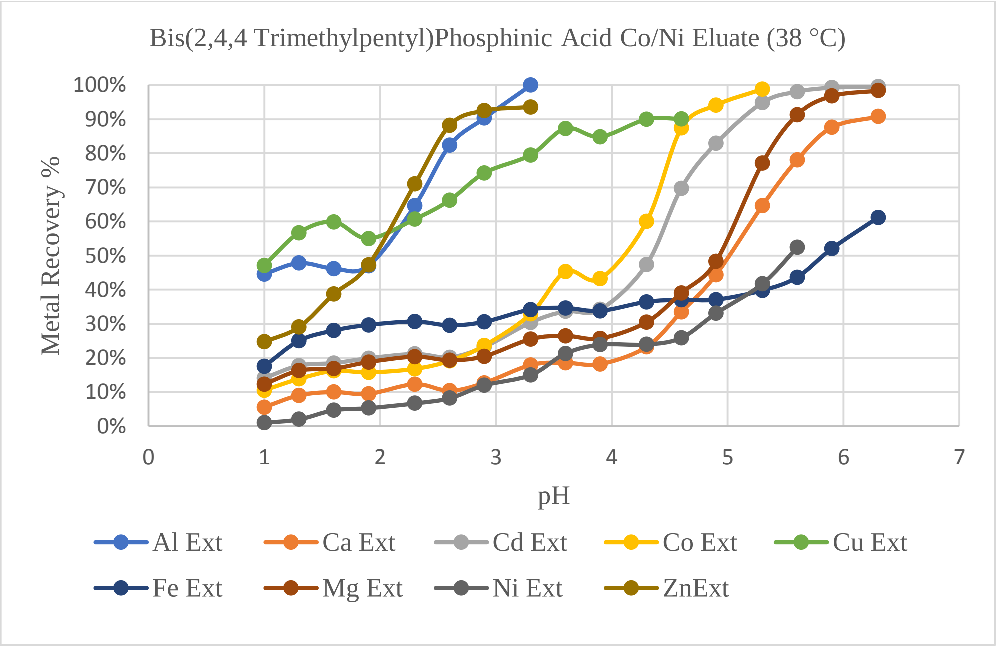


Figure 24. Isotherm diagram of Bis (2,4,4 Trimethylpentyl) Phosphinic Acid.

4.2.2. Mc-Cabe Thiele Procedure

The experimental data from pH 5 gave a polynomial curve. It is possible to calculate the required extraction stages, which was one of the purposes of these tests by the McCabe-Thiele diagram. The feeding flow conditions are shown in Table 19.

Table 19. Feeding flow conditions of Mc-Cabe Thiele diagram.

Steps of Project	***Feeding Flow***	***Al***	***Ca***	***Cd***	***Co***	***Fe***	***Mg***	***Na***	***Ni***	***Zn***
		mg/L	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***
Co/Ni Separation (CYANEX)	*CoNi ELUATE IX (IN)*	2.50	500.9	70.10	8,665	113.20	1,286	400.60	8,705	2.30

All experiments were repeated two times to be sure of the repeatability of the process. The data of the experiment results are summarized in Table 20.

Figure 25 presented below, shows the McCabe- Thiele diagram with an operating line slope of 1 at pH 5. Figure 25 shows that 3 stages were required for solvent extraction operation to reach 2.49 g/L cobalt in the final raffinate. Based on the constructed Isothermal curves, pH 5 is the value chosen for the SX test to build the McCabe- Thiele diagrams, in a batch simulation experiment. The final raffinate solution Co content is high so this means that extracting the maximum amount of cobalt from the solution at only one extraction with a fixed pH is not optimal so the best option is a several-step extraction, where we will gradually increase the pH with each step.

Table 20. The different O/A ratios tested at pH 5.

Co

Test No	**Ratio O/A**	**Organic**		**Aqua**	
		g/L	X_a	g/L	X_b
Test 1	0.1	0.97	**0.13**	6.34	**0.87**
Test 3	0.2	2.17	**0.23**	7.28	**0.77**
Test 5	0.5	3.71	**0.34**	7.12	**0.66**
Test 7	1	4.51	**0.36**	8.05	**0.64**
Test 9	2	10.18	**0.78**	2.94	**0.22**
Test 11	5	7.63	**0.75**	2.49	**0.25**
Test 2	0.1	1.17	**0.17**	5.66	**0.83**
Test 4	0.2	1.73	**0.18**	7.95	**0.82**
Test 6	0.5	3.71	**0.33**	7.43	**0.67**
Test 8	1	4.51	**0.35**	8.25	**0.65**
Test 10	2	10.18	**0.92**	0.94	**0.08**
Test 12	5	7.63	**0.78**	2.15	**0.22**

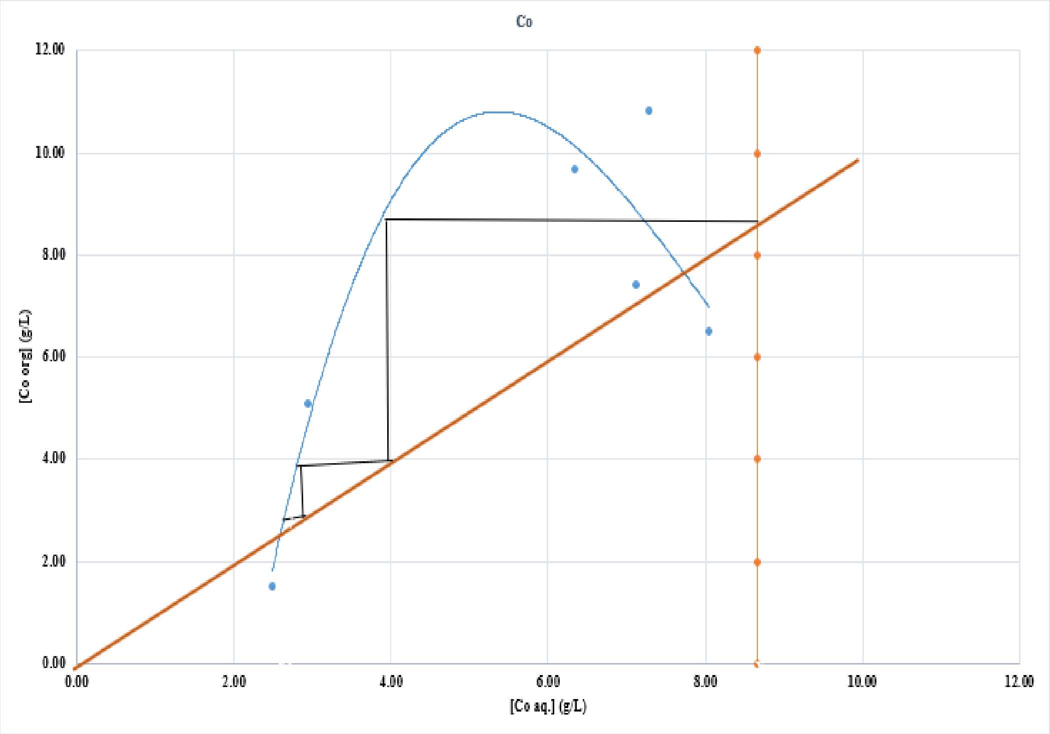


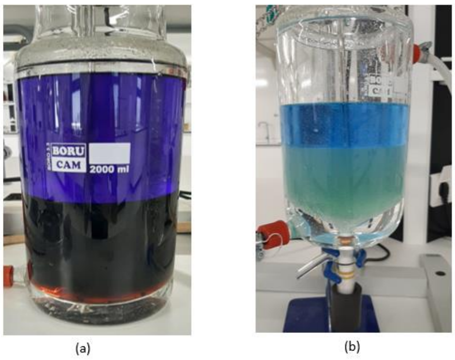
Figure 25. Mc-Cabe Thiele diagram for Co at pH 5.

4.3. $CoSO_4$ & $NiSO_4$ Cleaning by Phosphoric Acid Base Extractant (Di (2-Ethylhexyl) Phosphoric Acid)

This study aims to remove impurities from $CoSO_4$ and $NiSO_4$ solutions. Isotherm diagrams were drawn for both solutions and the best pH was determined to ensure minimum cobalt and nickel loss while removing impurities. The O/A ratio is 1 and is kept constant.

In the actual process at the company field, $CoSO_4$ process feeding comes after the selective coagulation of Cd and Al to remove them, this process is effective and lets us a solution with a concentration of Cd and Al under 2mg/L. Therefore, Al and Cd have already been removed before the solution came here. However, in the laboratory, we didn’t simulate Al and Cd removal before using the $CoSO_4$ solution.

After pH evaluation, a Mc-Cabe Thiele diagram was drawn for each metal to find out how many extraction steps were needed.



(a) (b)

Figure 26. $CoSO_4$ and $NiSO_4$ solution in the cleaning process, through from the left.

4.3.1. Isotherm Procedure of $CoSO_4$ Solution

The biggest issue of the $CoSO_4$ solution is the amount of magnesium, and manganese. There is a slight amount of aluminum, calcium, cadmium, and iron in the solution, shown in Table 21.

Table 21. $CoSO_4$ feeding condition for D2EHPA cleaning process.

Steps of Project	***Feeding Flow***	***Al***	***Ca***	***Cd***	***Co***	***Fe***	***Mg***	***Mn***	***Ni***	***Zn***
		mg/L	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***
$CoSO_4$ Cleaning	*$CoSO_4$ PLS*	17.27	2.33	50.60	87,931	3.10	30.73	1,054.1	0.70	7.63

The pH is around 2-2.5, and nearly all aluminum and calcium were extracted. More than 50% of Fe is removed. Mg and Mn removal are less than the 0ther impurities. If the pH continues to increase around 60% Mn can be removed but with the loss of cobalt. The result of the experiment is summarized in Table 22 and Figure 27.

Table 22. Effect of pH on extraction equilibrium.

pH	Al Extrc %	Ca Extrc %	Cd Extrc %	Co Extrc %	Cu Extrc %	Fe Extrc %	Mg Extrc %	Mn Extrc %
1	60%	99%	3%	5%	47%	67%	3%	3%
1.3	66%	99%	0%	9%	57%	55%	3%	1%
1.6	72%	99%	3%	11%	60%	60%	6%	5%
1.9	85%	100%	11%	12%	55%	61%	7%	18%
2.3	94%	100%	25%	16%	61%	60%	12%	41%
2.6	100%	100%	32%	17%	66%	59%	14%	49%
2.9	99%	100%	43%	18%	74%	60%	13%	62%
3.3	100%	100%	37%	19%	80%	60%	15%	61%
3.6	100%	100%	30%	21%	87%	63%	18%	60%
3.9	99%	99%	26%	22%	85%	63%	17%	59%
4.3	100%	99%	27%	24%	90%	65%	20%	61%
4.6	100%	99%	27%	25%	90%	64%	21%	63%

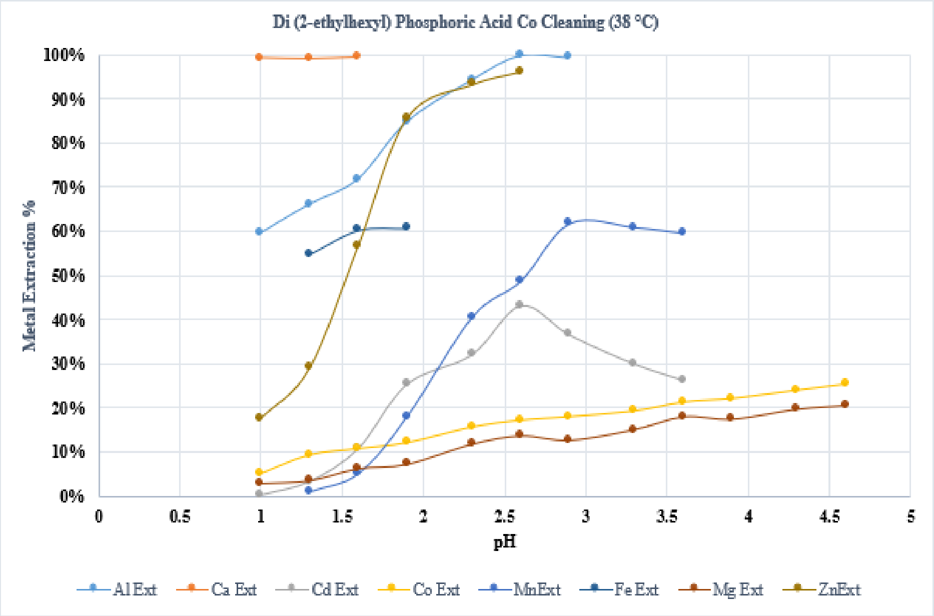


Figure 27. Isotherm diagram of Di (2-ethylhexyl) Phosphoric Acid.

4.3.2. Mc-Cabe Procedure of $CoSO_4$ Solution

This process aims to remove Mg, and Mn in the circuit as much as possible to clean the $CoSO_4$ solution. The feeding solution metal concentrations used for this experiment are given below.

Table 23. $CoSO_4$ feeding solution metal concentration for Mc-Cabe Thiele diagram.

Steps of Project	***Feeding Flow***	***Al mg/L***	***Ca mg/L***	***Cd mg/L***	***Co mg/L***	***Fe mg/L***	***Mg mg/L***	***Mn mg/L***	***Ni mg/L***	***Zn mg/L***
$CoSO_4$ Cleaning	*$CoSO_4$ PLS*	0.60	3.82	49.30	77,333	3.40	35.40	1,054.1	1.00	8.70

In Table 24, experimental results are summarized for the McCabe Thiele diagram to decide the needed stage number. The experiments were repeated two times to check the continuity of the results.

Table 24.The different O/A ratios tested at pH 2.2.

		Mg				Mn			
		Organic		**Aqua**		**Organic**		**Aqua**	
Test No	**Ratio O/A**	mg/L	X_a	mg/L	X_b	mg/L	X_a	mg/L	X_b
Test 1	0.1	1.2	**0.03**	33.1	**0.97**	410.9	**0.30**	975.3	**0.7**
Test 3	0.2	1.6	**0.05**	30.4	**0.95**	370.0	**0.31**	839.9	**0.7**
Test 5	0.5	1.2	**0.04**	29.1	**0.96**	336.0	**0.32**	701.2	**0.7**
Test 7	1	1.1	**0.04**	28.2	**0.96**	270.0	**0.36**	480.3	**0.6**
Test 9	2	0.9	**0.03**	26.0	**0.97**	250.9	**0.50**	247.0	**0.5**
Test 11	5	0.5	**0.02**	22.9	**0.98**	143.2	**0.44**	180.0	**0.6**
Test 2	0.1	1.1	**0.03**	39.1	**0.97**	460.0	**0.39**	941.1	**0.6**
Test 4	0.2	1.3	**0.04**	33.5	**0.96**	590.0	**0.35**	840.1	**0.6**
Test 6	0.5	0.8	**0.03**	29.2	**0.97**	372.0	**0.35**	695.8	**0.7**
Test 8	1	0.5	**0.02**	28.3	**0.98**	265.6	**0.37**	460.0	**0.6**
Test 10	2	0.4	**0.01**	27.6	**0.99**	159.4	**0.36**	285.1	**0.6**
Test 12	5	0.2	**0.01**	22.7	**0.99**	141.4	**0.52**	132.6	**0.5**

According to Figure 28 and Figure 29, it was shown that 2 stages were required for the solvent extraction operation to reach 0.0229 g/L magnesium and 0.18 g/L manganese in the raffinate.

Whereas Mg and Mn remained in the aqueous phase and were co-extracted completely into the organic phase at these experimental conditions. Their recovery results are shown in Table 25. After the di (2-ethyhexyl) phosphoric acid solvent extraction process, the residual amount of metals in the aqueous phase is not enough to produce a good battery-grade product.

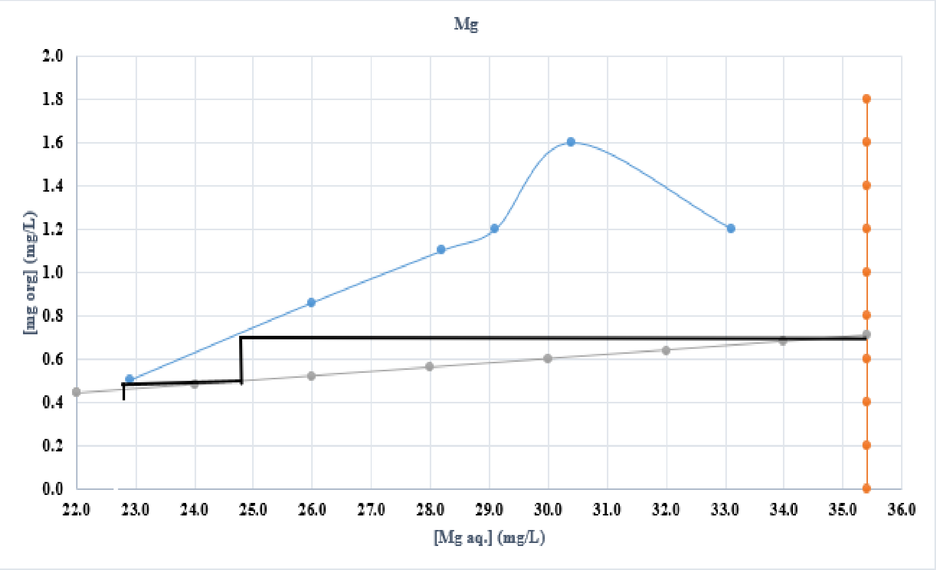


Figure 28. The Mc-Cabe Thiele diagram for Mg at pH 2.2.

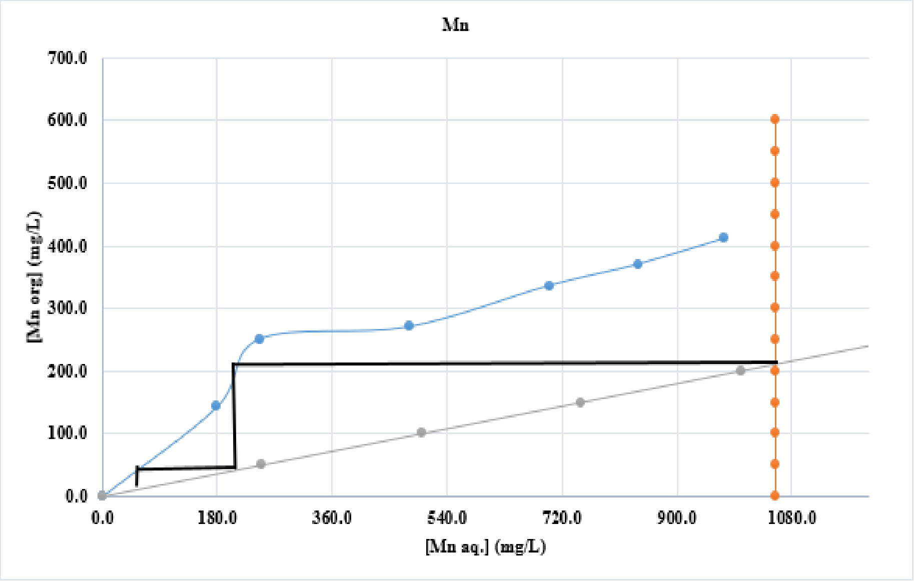


Figure 29. The Mc-Cabe Thiele diagram for Mn at pH 2.2

The ratios of the O/A in the graphics are 0.02 and 0.2 for Mg and Mn, respectively. However, in the batch simulation, experiments were performed at O/A=1 so that for extraction theoretical stages are 2 numbers but probably we will need more due to recirculation.

In other words, a Mc-Cabe Thiele diagram may not be an optimal representation of the required stages for a more complex system, most of the time is used to design the extraction, scrubbing, or stripping of the main metal. Here we are defining the stages necessary to use SX as a cleaning stage, something little out of the ordinary till around 15-20 years ago. Traditionally the way to eliminate impurities was by froth flotation of the solid ore, or selective precipitation where we sacrifice a percentage of the value metal. Due to the current world situation of metallurgical metal where the prices are quite high and the richest and simplest ore is in the best scenario scarce and usually inexistent, the sector deals with complex ores, and the traditional analysis and test methods have been not still optimized enough where many metal ions are present in the solution and the concentration rations are in the hundreds and thousands, between the metal of interest and the impurities.

When deciding on a pH value for the operation, many parameters must be weighed against each other e.g., Mg and Mn recovery, co-extraction of impurities (Co purity), economical aspects, etc. For instance, when operating at around pH 4 a high magnesium and manganese recovery is obtained, but cobalt is also extracted into the organic phase. To avoid this problem, the solvent extraction process should be operated above pH 2.7 instead.

Nevertheless, if three stages were applied by three different pH that is between 2.5 and 2.2 the recovery of Mg and Mn could be increased because the scrubbing process was not examined in the project. Under these conditions removing Mg and Mn in the raffinate also required a new cleaning process. Therefore, the project will continue with the ion exchange process to produce a good battery-grade $CoSO_4$ solution.

Table 25. Metal recoveries from the aqueous phase by different O/A ratios at pH 2.2.

pH 2.2.

Test No	Ratio O/A	Mg	Mn
		%	%
Test 1	0.1	97%	61%
Test 3	0.2	95%	65%
Test 5	0.5	97%	68%
Test 7	1	97%	74%
Test 9	2	98%	76%
Test 11	5	99%	86%
Test 2	0.1	97%	56%
Test 4	0.2	96%	44%
Test 6	0.5	98%	65%
Test 8	1	99%	75%
Test 10	2	99%	85%
Test 12	5	100%	87%

4.3.3. Isotherm Procedure of $NiSO_4$ Solution

The aim is the same as the $CoSO_4$ part. However, the working pH range is different than for the $CoSO_4$ solution, based on the information collected from several sources. (Sainio, Virolainen, and Andrey, n.d.).

Table 26. $NiSO_4$ feeding solution for isotherm graphics.

Steps of Project	***Feeding Flow***	***Al***	***Ca***	***Cd***	***Co***	***Fe***	***Mg***	***Ni***	***Zn***
		mg/L	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***
$NiSO_4$ Cleaning	*$NiSO_4$*	2.13	421.97	81.93	6,860	95.20	1,421.53	8,812.07	2.37

The main impurities are aluminum, calcium, cobalt, iron, magnesium, and zinc in the solution. The impurities extraction is increasing with the increasing of pH but around pH 4, nickel extraction is increasing. The best condition of pH is around 3.5 between 2.6 for cleaning of $NiSO_4$ solution.

The experimental results are presented in Table 27 and the graphic of the data is shown in Figure 30.

Table 27. Effect of pH on extraction equilibrium.

pH	**Al Extrc**	**Ca Extrc**	**Cd Extrc**	**Co Extrc**	**Cu Extrc**	**Fe Extrc**	**Mg Extrc**	**Ni Extrc**	**Zn Extrc**
	%	**%**	**%**	**%**	**%**	**%**	**%**	**%**	**%**
1	56%	99%	15%	20%	61%	24%	16%	4%	10%
1.3	68%	99%	20%	20%	72%	29%	20%	4%	25%
1.6	75%	99%	23%	25%	73%	32%	22%	3%	35%
1.9	96%	70%	36%	34%	74%	35%	27%	3%	58%
2.3	98%	85%	49%	49%	83%	36%	32%	4%	80%
2.6	100%	93%	68%	57%	100%	38%	41%	4%	89%
2.9	99%	97%	77%	64%	74%	39%	47%	4%	81%
3.3	99%	98%	86%	68%	92%	40%	55%	1%	88%
3.6	99%	99%	90%	71%	100%	43%	62%	1%	81%
3.9	99%	99%	92%	76%	100%	45%	67%	1%	81%
4.3	100%	98%	94%	79%	92%	50%	72%	6%	99%
4.6	99%	96%	94%	82%	92%	55%	76%	11%	90%
4.9	99%	95%	94%	85%	78%	59%	79%	13%	20%
5.3	98%	94%	95%	87%	71%	64%	82%	14%	39%

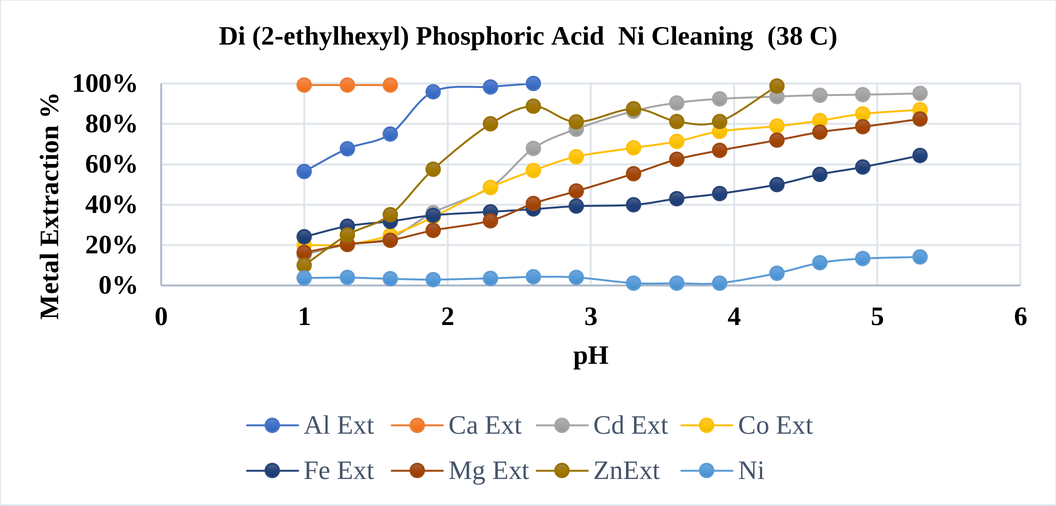


Figure 30. Isotherm diagram of Di (2-ethylhexyl) Phosphoric Acid.

4.3.4. Mc-Cabe Procedure of $NiSO_4$ Solution

The metal contents of process feeding are given in Table 28. The feeding comes from the Co/Ni SX Separation part of the Eti Gübre process, which is shown in Figure 13, in the Experimental section. This process aims to remove Ca, Mg, and Co in the circuit as much as possible to clean the $NiSO_4$ solution. In Table 29, experimental results are summarized for the McCabe Thiele diagram to decide the needed stage number. The experiments were repeated two times to check the continuity of the results.

Table 28. $NiSO_4$ solution metal content for Mc-Cabe Thiele diagram.

Steps of Project	***Feeding Flow***	***Al mg/L***	***Ca mg/L***	***Cd mg/L***	***Co mg/L***	***Fe mg/L***	***Mg mg/L***	***Ni mg/L***	***Zn mg/L***
$NiSO_4$ Cleaning	*$NiSO_4$*	0.20	383.40	8.40	226	76.60	688.50	7,935.30	1.90

According to Figure 31, it was shown that 2 stages were required for solvent extraction operation to reach 0.0019 g/L calcium in the raffinate.

Figure 32, and Figure 33, it was shown that 4 stages were required for solvent extraction operation to reach 0.1277 g/L magnesium and 0.101 g/L cobalt in the raffinate.

Whereas, Mg and Co remained in the aqueous phase and were not co-extracted completely into the organic phase at these experimental conditions. Their recovery results are shown in Table 29. After the Di (2-ethylhexyl) Phosphoric Acid solvent extraction process, the residual amount of Mg and Co in the aqueous phase is not enough to produce a good battery-grade product.

Table 29. The different O/A ratios tested at pH 3.

		Ca				Mg				Co			
	Ratio	**Organic**		**Aqua**		**Organic**		**Aqua**		**Organic**		**Aqua**	
Test No	O/A	mg/L	X_a	mg/L	X_b	mg/L	X_a	mg/L	X_b	mg/L	X_a	mg/L	X_b
Test 1	0.1	920	**0.83**	188	**0.17**	167.8	**0.22**	613	**0.78**	21.0	**0.09**	223.9	**0.91**
Test 3	0.2	1202	**0.93**	85	**0.07**	177.5	**0.27**	474	**0.73**	20.9	**0.11**	171.9	**0.89**
Test 5	0.5	651	**0.97**	20	**0.03**	156.1	**0.29**	375	**0.71**	17.6	**0.10**	150.8	**0.90**
Test 7	1	298	**0.96**	13	**0.04**	125.1	**0.31**	282	**0.69**	15.6	**0.10**	138.2	**0.90**
Test 9	2	162	**0.97**	5	**0.03**	102.4	**0.31**	227	**0.69**	14.1	**0.10**	121.2	**0.90**
Test 11	5	62	**0.97**	2	**0.03**	56.8	**0.31**	128	**0.69**	10.4	**0.09**	101.0	**0.91**
Test 2	0.1	1493	**0.87**	219	**0.13**	147.1	**0.20**	606	**0.80**	19.70	**0.08**	236.7	**0.92**
Test 4	0.2	1021	**0.90**	110	**0.10**	144.0	**0.23**	491	**0.77**	17.90	**0.09**	185.6	**0.91**
Test 6	0.5	546	**0.96**	21	**0.04**	118.2	**0.23**	405	**0.77**	15.70	**0.09**	162.4	**0.91**
Test 8	1	274	**0.97**	9	**0.03**	110.4	**0.25**	340	**0.75**	11.50	**0.07**	143.0	**0.93**
Test 10	2	178	**0.97**	6	**0.03**	110.2	**0.26**	320	**0.74**	9.10	**0.07**	124.3	**0.93**
Test 12	5	63	**0.98**	1	**0.02**	81.5	**0.36**	143	**0.64**	4.70	**0.05**	99.2	**0.95**

The ratios of the O/A in the graphics are 2, 0.25, and 0.1 for Ca, Mn, and Co respectively. However, in the batch simulation, experiments were performed at O/A = 1 so that the extraction stage number choice was 3. In other words, a Mc-Cabe Thiele diagram may not be an optimal representation of the required stages for a more complex system, where many metal ions are present. When deciding on a pH value for the operation, many parameters must be weighed against each other e.g., Mg and Co recovery, co-extraction of impurities (Ni purity), load capacity of the extractant, separation kinetics, economical aspects, etc.

For instance, when operating at around pH 4 a high magnesium and cobalt recovery is obtained, but nickel is also extracted into the organic phase. To avoid this problem, the solvent extraction process should be operated above pH 3.5 instead but under pH 4. Nevertheless, if three stages were applied by three different pH that is between 3.3 and 2.7 the recovery of Mg and Co could be increased because the scrubbing process was not examined in the project. Under these conditions removing Mg and Co in the raffinate also required a new cleaning process. Therefore, the project will continue with the ion exchange process to produce a good battery-grade $NiSO_4$ solution.

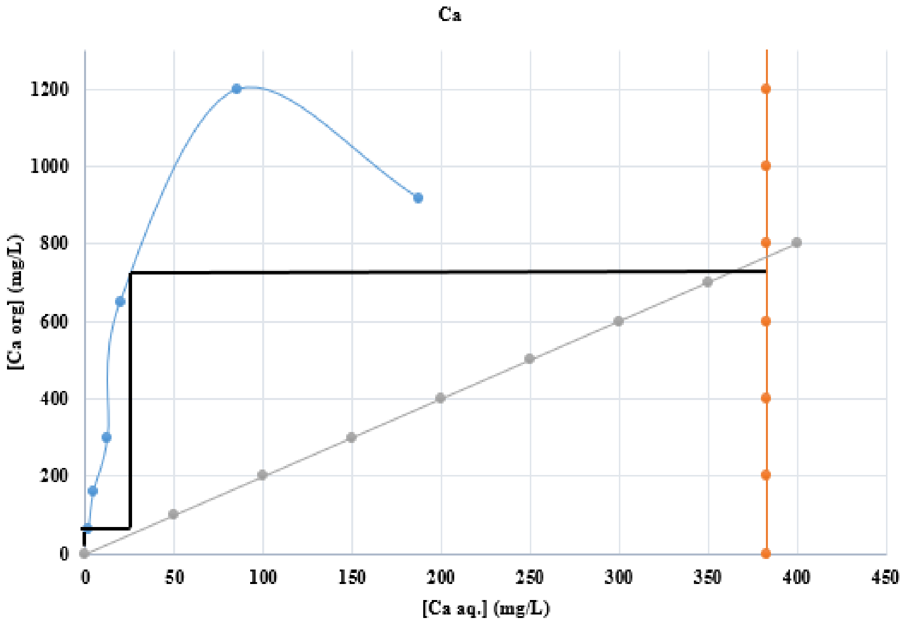


Figure 31. The Mc-Cabe Thiele diagram for Ca at pH 3

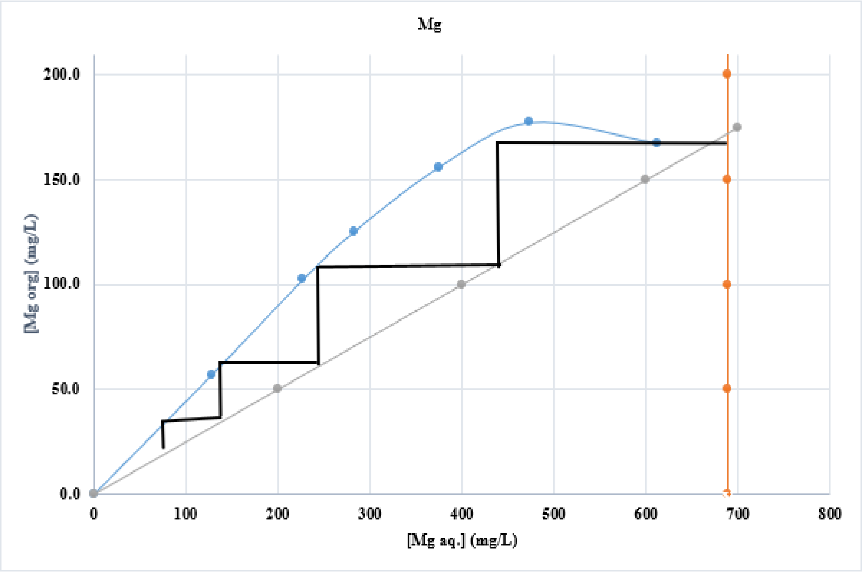


Figure 32. The Mc-Cabe Thiele diagram for Mg at pH 3.

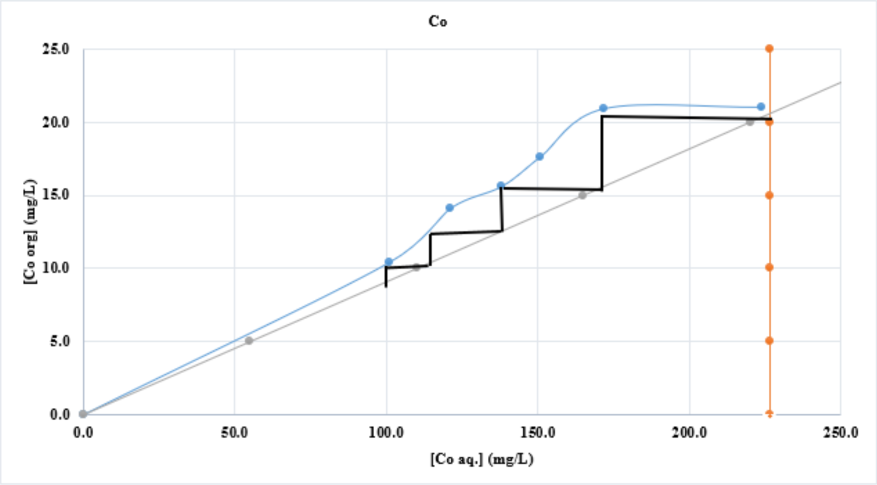


Figure 33. The Mc-Cabe Thiele diagram for Co at pH 3.

Table 30. Metal recoveries from the aqueous phase by different O/A ratios at pH 3.

Test No	**Ratio O/A**	**Ca**	**Mg**	**Co**
		%	%	%
Test 1	0.1	51%	11%	1%
Test 3	0.2	78%	31%	24%
Test 5	0.5	95%	46%	33%
Test 7	1	97%	59%	39%
Test 9	2	99%	67%	46%
Test 11	5	100%	81%	55%
Test 2	0.1	43%	12%	0%
Test 4	0.2	71%	29%	18%
Test 6	0.5	95%	41%	28%
Test 8	1	98%	51%	37%
Test 10	2	98%	53%	45%
Test 12	5	100%	79%	56%

4.4. $CoSO_4$ Purification by IX Method for Battery Grade

The tolerated number of impurities present in the solution to achieve a metallic salt with a purity of 95% or more is small. As has been explained in previous parts of this document, started with a solution where the metals of interest, Co, and Ni, are in ratios of concentration 10, 100 even 1000 times smaller than other of the elements present in the solution. This situation implies that is needed several stages to recover, separate, and improve the quality of the solutions that will be used for crystallization.

The resins we have checked to clean the solution are:

Table 31. The list of chosen resins to clean $CoSO_4$ solution for battery grade product.

Resin Chosen to Clean $CoSO_4$ Solution After D2EHPA Impurities Removal	
Functional Group	Commercial Products
Bis (2-ethylhexyl) phosphoric acid Impregnated	MTX 7010
Imminodiacetate Chelating	LWT 207 TP
Biscopicolamine Chelating	LSC 495
Aminophosphonic Chelating	MTS 9500

IX resin technologies have some advantages against SX and in many scenarios will work better when the ratios between the elements that are needed to separate are huge. That is exactly our scenario.

After checking the information available, we decided to try several functional groups to see which one is the best for use.

Test conditions:

The test was performed in an IX-column system, Figure 18. The columns have a max capacity of 500 mL, and the peristaltic pump allows us to regulate the flow of our necessities in an easy and precise way.

The volume of resin used will be 400 mL of each resin and the amount of solution treated will be 2000 mL or equal to 5 BV. The pH range selected for each resin was chosen based on the information studied and analyzed by the suppliers and on academic research available for this thesis.

Figure 34. Resin experiment with IX column in a continuous process.

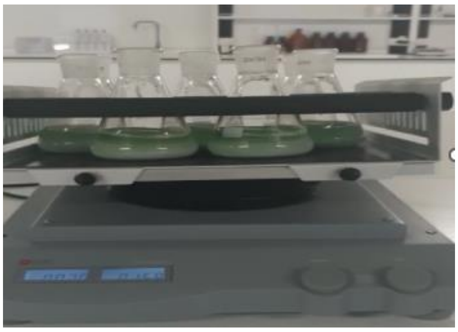


Figure 35. Resin experiment in batch process.

The elements in red, in Table 32, will not be considered in this study due to the low concentration in the solution, they already have the quality needed to achieve the purity aimed. All the resins have been tested with the same solution and all stages were repeated three times to see the repeatability between results.

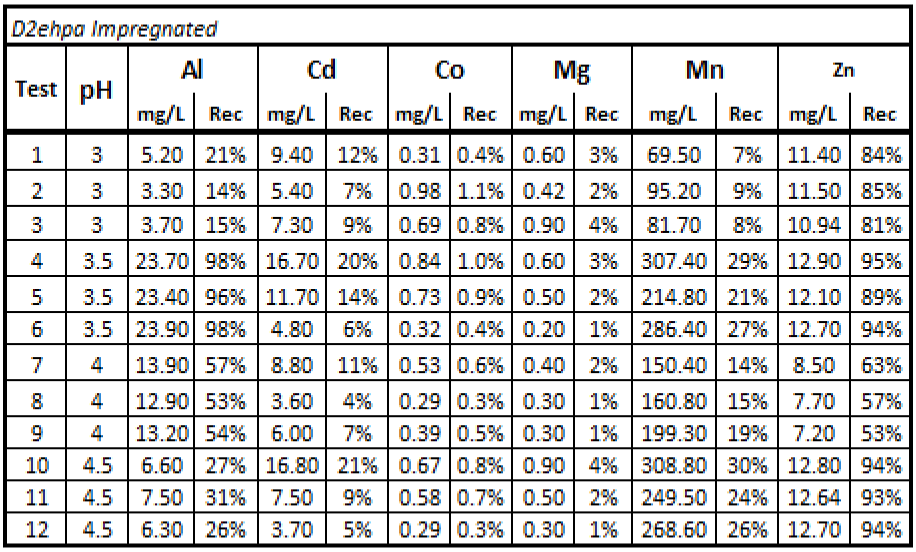
Table 32. Feeding solution metal content for $CoSO_4$ cleaning process by IX method.

$CoSO_4$ After Dehpa	**Al**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Zn**
	mg/L	**mg/L**	**mg/L**	**g/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**g/L**	**mg/L**	**mg/L**	**mg/L**
	24.30	**2.10**	81.60	85.35	**0.05**	**0.00**	**1.95**	**0.00**	20.15	1045	**0.00**	**0.40**	**0.00**	**1.70**

4.4.1. Bis(2-ethylhexyl) phosphoric acid Impregnated, D2EHPA, (MTX 7010)

In Table 33, the recovered total amount of metals from the loaded resin after washing it with H_2SO_4, a 10% acid solution, was shown.

Table 33. The metal ions recover into the resin with different pH.



D2ehpa Impregnated													
Test	pH	Al		Cd		Co		Mg		Mn		Zn	
		mg/L	Rec	mg/L	Rec	mg/L	Rec	mg/L	Rec	mg/L	Rec	mg/L	Rec
1	3	5.20	21%	9.40	12%	0.31	0.4%	0.60	3%	69.50	7%	11.40	84%
2	3	3.30	14%	5.40	7%	0.98	1.1%	0.42	2%	95.20	9%	11.50	85%
3	3	3.70	15%	7.30	9%	0.69	0.8%	0.90	4%	81.70	8%	10.94	81%
4	3.5	23.70	98%	16.70	20%	0.84	1.0%	0.60	3%	307.40	29%	12.90	95%
5	3.5	23.40	96%	11.70	14%	0.73	0.9%	0.50	2%	214.80	21%	12.10	89%
6	3.5	23.90	98%	4.80	6%	0.32	0.4%	0.20	1%	286.40	27%	12.70	94%
7	4	13.90	57%	8.80	11%	0.53	0.6%	0.40	2%	150.40	14%	8.50	63%
8	4	12.90	53%	3.60	4%	0.29	0.3%	0.30	1%	160.80	15%	7.70	57%
9	4	13.20	54%	6.00	7%	0.39	0.5%	0.30	1%	199.30	19%	7.20	53%
10	4.5	6.60	27%	16.80	21%	0.67	0.8%	0.90	4%	308.80	30%	12.80	94%
11	4.5	7.50	31%	7.50	9%	0.58	0.7%	0.50	2%	249.50	24%	12.64	93%
12	4.5	6.30	26%	3.70	5%	0.29	0.3%	0.30	1%	268.60	26%	12.70	94%

The selectivity of each of the metals that we want to recover at different pH to identify the optimal working pH and how it influences the recovery of different metals has been checked. In Figure 36, the comparison of the metal recovery while the changeable pH is summarized.

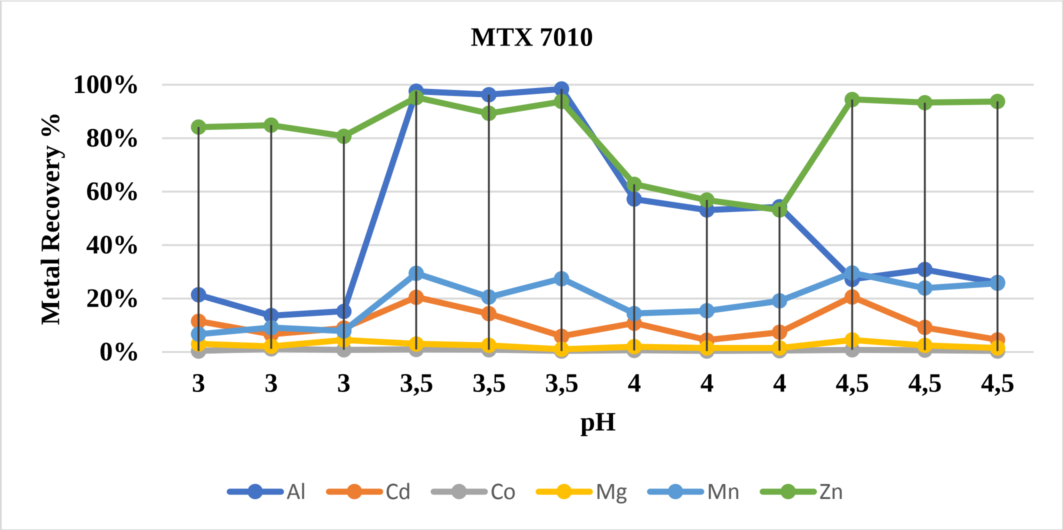


Figure 36. The pH effect on metal selectivity.

The cobalt is not affected, with less than 1% of losses. Everything points out that this is due that if even we have washed the resin in between the extraction step and the elution, there will be always a small amount of the solution “wetting “the matrix of the resins. Also using Bis(2-ethylhexyl) phosphoric acid as the functional group we must assume some small loss of cobalt due to the selectivity of this chemical for cobalt extraction.

According to the results, and as the related documents say, D2EHPA has a high selectivity for Zn and Al from Low pH been removed both of over 90% at pH 3.5.

The decrease of Al removed at pH 4 and 4.5 most probably is due to the trivalent state of the cation in the solution, when we start to extract more metals, the amount of free radicals in the resin active group decreases, and the kinetics becomes slower, with this combination the selectivity of Al is reduced.

The Mg was slightly affected, and the recovery was low, never over 4% in all the ranges of pH analyzed.

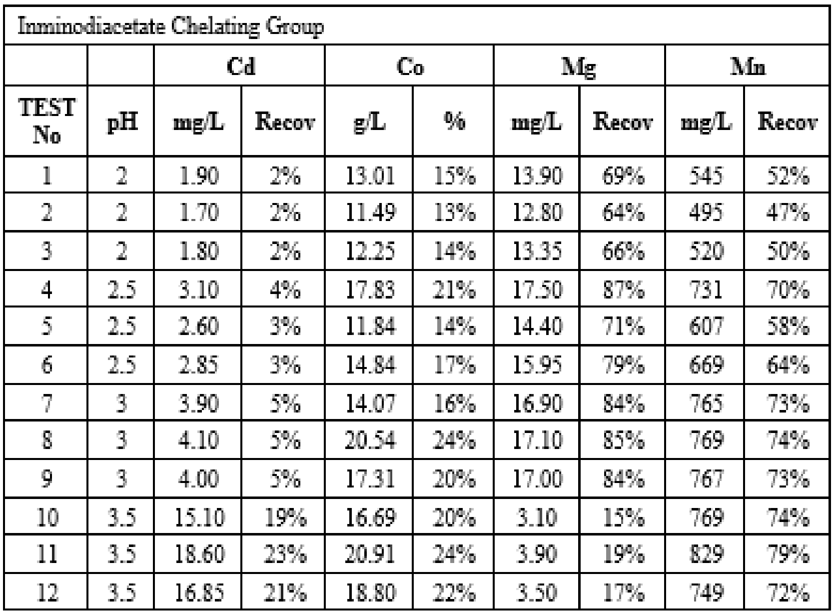
The Mn recoveries are not but are in the range of 20 to 30% at pH 3.5, which even if is not in a step is encouraging and could mean that we will need several stages of the resin in series to achieve the results we desire.

The Cd behavior is like the manganese one, this is not a big issue due to the possibility of using several stages in a series or other methods to remove it.

4.4.2. Inminodiacetate Group (LWT 207 TP)

With the Inminodiacetic acid as a functional group, we are aiming to recover and eliminate from the solution the metals we could not recover from the solution with previous, the experimental results of the metal recoveries are summarized in Table 34.

Table 34. The metal ions recover into the resin with different pH.



Inminodiacetate Chelating Group									
		Cd		**Co**		**Mg**		**Mn**	
TEST No	**pH**	**mg/L**	**Recov**	**g/L**	**%**	**mg/L**	**Recov**	**mg/L**	**Recov**
1	2	1.90	2%	13.01	15%	13.90	69%	545	52%
2	2	1.70	2%	11.49	13%	12.80	64%	495	47%
3	2	1.80	2%	12.25	14%	13.35	66%	520	50%
4	2.5	3.10	4%	17.83	21%	17.50	87%	731	70%
5	2.5	2.60	3%	11.84	14%	14.40	71%	607	58%
6	2.5	2.85	3%	14.84	17%	15.95	79%	669	64%
7	3	3.90	5%	14.07	16%	16.90	84%	765	73%
8	3	4.10	5%	20.54	24%	17.10	85%	769	74%
9	3	4.00	5%	17.31	20%	17.00	84%	767	73%
10	3.5	15.10	19%	16.69	20%	3.10	15%	769	74%
11	3.5	18.60	23%	20.91	24%	3.90	19%	829	79%
12	3.5	16.85	21%	18.80	22%	3.50	17%	749	72%

With the Inminoacetic acid group, we can observe that the Mn and Mg extraction is optimal and adequate for our aim at pH 3. The pH control should be restricted due to the strong decrease in the Mg recovery of the resin after pH 3.5.

Cd extraction is still poor with a maximum of 20-23% at pH 3.5 that pH could not be worked due to the decrease of recovery in Mg.

The extraction of Co is constant and high, keeping between 15-25% at the range of pH where the recovery of Mn and Mg is optimal. In Figure 37, the pH effect on the selective recovery of metals is summarized.

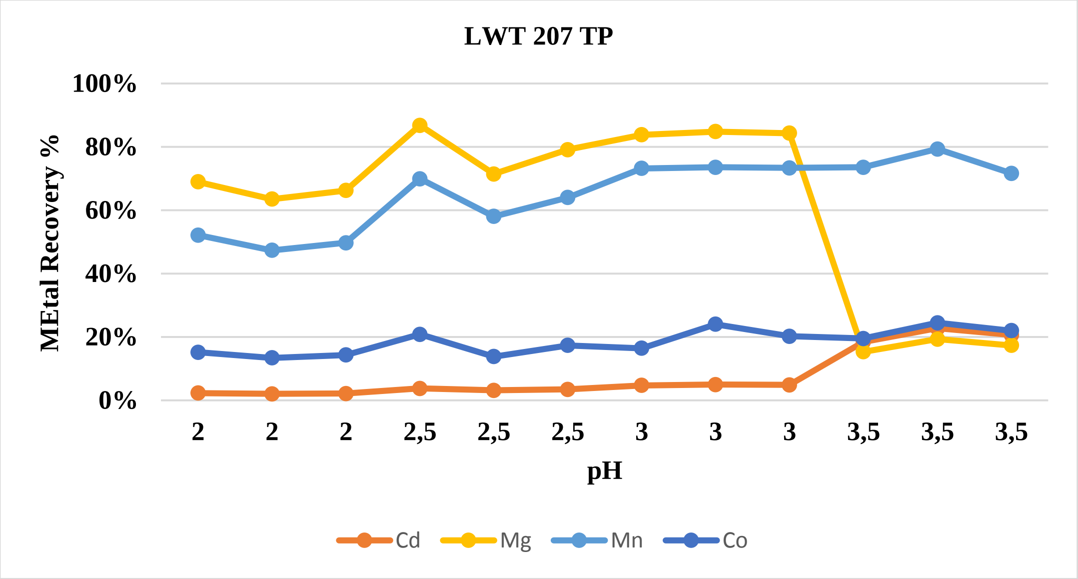


Figure 37. The pH effect on metal selectivity.

4.4.3. Bis-picolylamine Chelating Group (LSC 495)

The overall impurities recovery is low for Cobalt, at higher pH the recoveries are better but not enough to justify a good performance for the solution and product specifications. The metal recovery results and pH effect on the selective metal recovery are summarized in Table 35 and Figure 38, respectively.

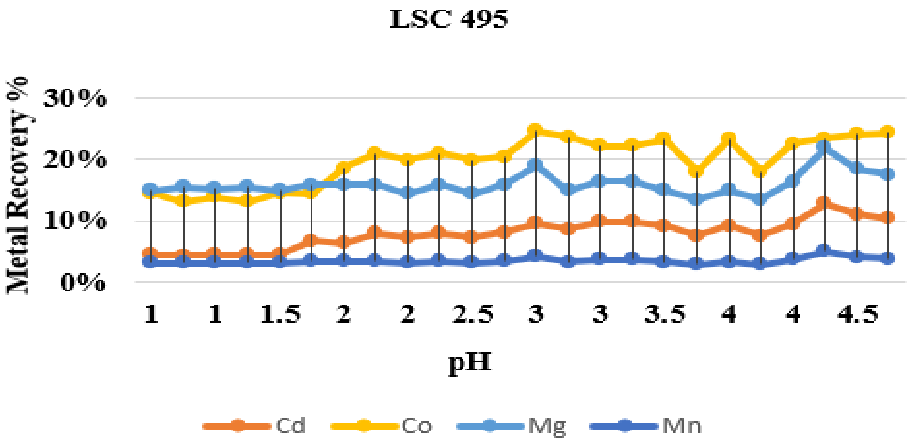
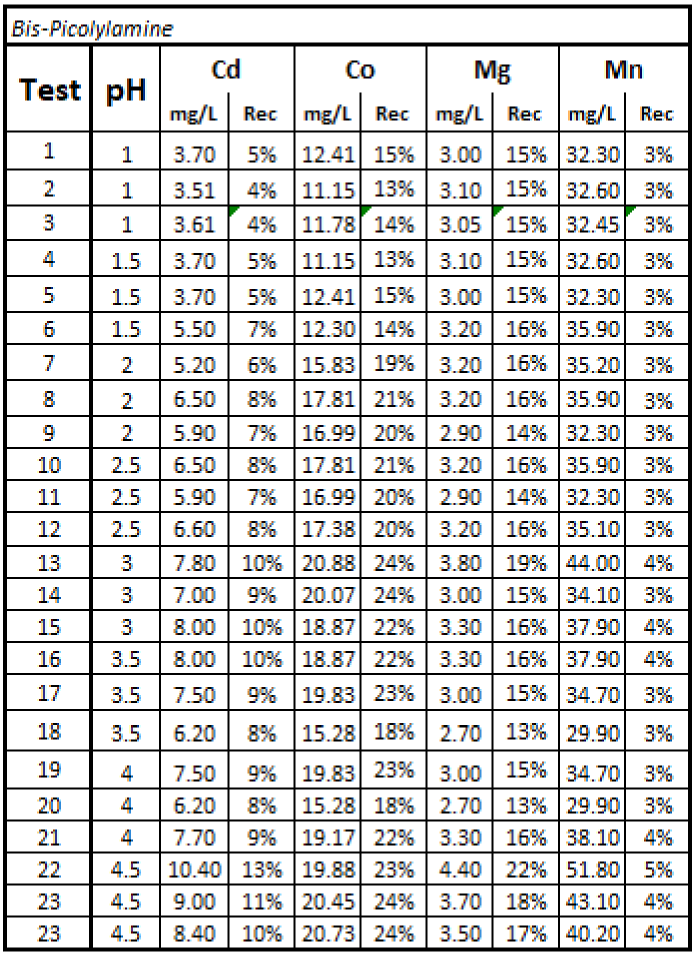


Figure 38. The pH effect on metal selectivity.

Table 35. The metal ions recover into the resin with different pH.

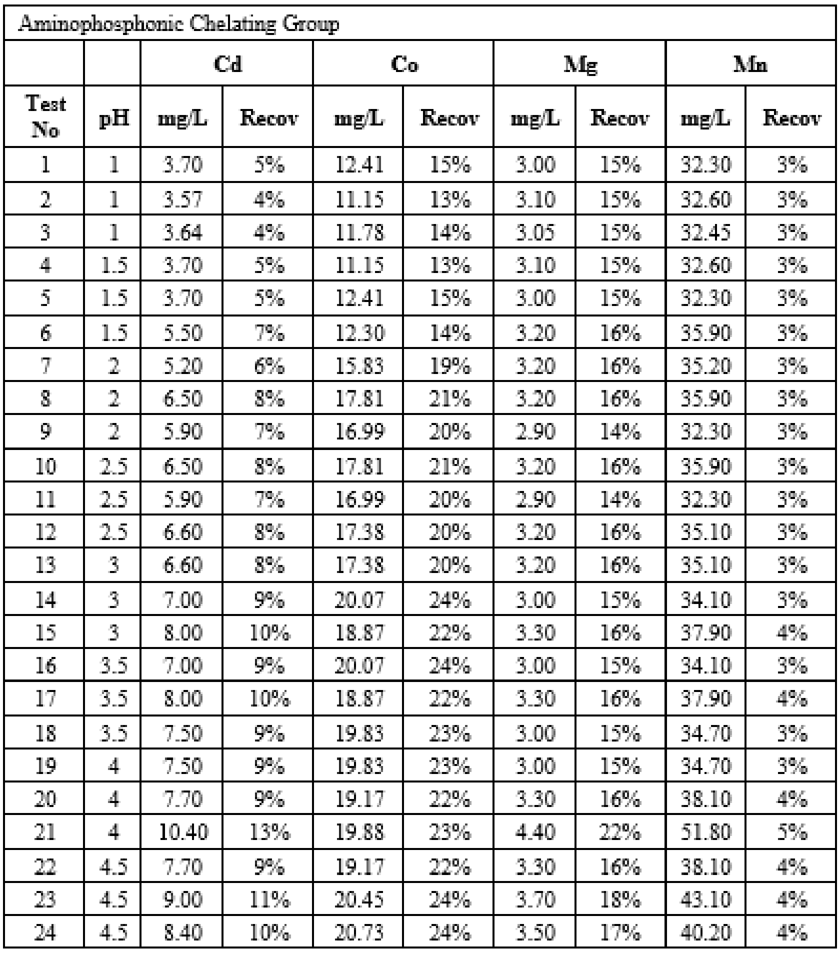


Bis-Picolylamine									
Test	**pH**	**Cd**		**Co**		**Mg**		**Mn**	
		mg/L	Rec	mg/L	Rec	mg/L	Rec	mg/L	Rec
1	1	3.70	5%	12.41	15%	3.00	15%	32.30	3%
2	1	3.51	4%	11.15	13%	3.10	15%	32.60	3%
3	1	3.61	4%	11.78	14%	3.05	15%	32.45	3%
4	1.5	3.70	5%	11.15	13%	3.10	15%	32.60	3%
5	1.5	3.70	5%	12.41	15%	3.00	15%	32.30	3%
6	1.5	5.50	7%	12.30	14%	3.20	16%	35.90	3%
7	2	5.20	6%	15.83	19%	3.20	16%	35.20	3%
8	2	6.50	8%	17.81	21%	3.20	16%	35.90	3%
9	2	5.90	7%	16.99	20%	2.90	14%	32.30	3%
10	2.5	6.50	8%	17.81	21%	3.20	16%	35.90	3%
11	2.5	5.90	7%	16.99	20%	2.90	14%	32.30	3%
12	2.5	6.60	8%	17.38	20%	3.20	16%	35.10	3%
13	3	7.80	10%	20.88	24%	3.80	19%	44.00	4%
14	3	7.00	9%	20.07	24%	3.00	15%	34.10	3%
15	3	8.00	10%	18.87	22%	3.30	16%	37.90	4%
16	3.5	8.00	10%	18.87	22%	3.30	16%	37.90	4%
17	3.5	7.50	9%	19.83	23%	3.00	15%	34.70	3%
18	3.5	6.20	8%	15.28	18%	2.70	13%	29.90	3%
19	4	7.50	9%	19.83	23%	3.00	15%	34.70	3%
20	4	6.20	8%	15.28	18%	2.70	13%	29.90	3%
21	4	7.70	9%	19.17	22%	3.30	16%	38.10	4%
22	4.5	10.40	13%	19.88	23%	4.40	22%	51.80	5%
23	4.5	9.00	11%	20.45	24%	3.70	18%	43.10	4%
23	4.5	8.40	10%	20.73	24%	3.50	17%	40.20	4%

4.4.4. Amino phosphonic Chelating Group (MTS9500)

In truth, this resin has low efficiency for our goals and the recovery of cobalt. The resin has good stability, and the influence of the pH only affects the metal selectivity but not increasing the overall recovery. For this reason, is not resin that could be used in this project. The results of the experiment are summarized in Table 36 and Figure 39.

Table 36. The metal ions recover into the resin with different pH.



Aminophosphonic Chelating Group

		Cd		Co		Mg		Mn	
Test No	pH	mg/L	Recov	mg/L	Recov	mg/L	Recov	mg/L	Recov
1	1	3.70	5%	12.41	15%	3.00	15%	32.30	3%
2	1	3.57	4%	11.15	13%	3.10	15%	32.60	3%
3	1	3.64	4%	11.78	14%	3.05	15%	32.45	3%
4	1.5	3.70	5%	11.15	13%	3.10	15%	32.60	3%
5	1.5	3.70	5%	12.41	15%	3.00	15%	32.30	3%
6	1.5	5.50	7%	12.30	14%	3.20	16%	35.90	3%
7	2	5.20	6%	15.83	19%	3.20	16%	35.20	3%
8	2	6.50	8%	17.81	21%	3.20	16%	35.90	3%
9	2	5.90	7%	16.99	20%	2.90	14%	32.30	3%
10	2.5	6.50	8%	17.81	21%	3.20	16%	35.90	3%
11	2.5	5.90	7%	16.99	20%	2.90	14%	32.30	3%
12	2.5	6.60	8%	17.38	20%	3.20	16%	35.10	3%
13	3	6.60	8%	17.38	20%	3.20	16%	35.10	3%
14	3	7.00	9%	20.07	24%	3.00	15%	34.10	3%
15	3	8.00	10%	18.87	22%	3.30	16%	37.90	4%
16	3.5	7.00	9%	20.07	24%	3.00	15%	34.10	3%
17	3.5	8.00	10%	18.87	22%	3.30	16%	37.90	4%
18	3.5	7.50	9%	19.83	23%	3.00	15%	34.70	3%
19	4	7.50	9%	19.83	23%	3.00	15%	34.70	3%
20	4	7.70	9%	19.17	22%	3.30	16%	38.10	4%
21	4	10.40	13%	19.88	23%	4.40	22%	51.80	5%
22	4.5	7.70	9%	19.17	22%	3.30	16%	38.10	4%
23	4.5	9.00	11%	20.45	24%	3.70	18%	43.10	4%
24	4.5	8.40	10%	20.73	24%	3.50	17%	40.20	4%

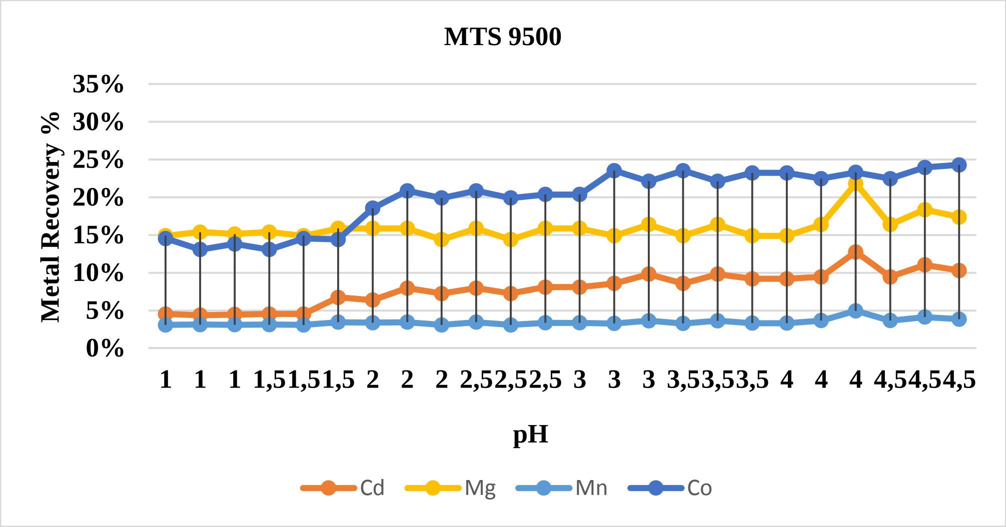


Figure 39. The pH effect on metal selectivity.

4.5. $NiSO_4$ Purification by IX Method for Battery Grade

The market for cathode precursors requires in its products stability in the composition and high purity. Indeed, region by region (Asia/Europe/ America) the market changes, and each company could have different impurities requirements, in addition to this the technology is still quite young and evolution is always present.

The experimental procedure and test conditions applied to cobalt were applied. The same $NiSO_4$ solution was used throughout the experiments and the solution metal content is given in Table 37. The elements in red, in Table 37, will not be considered in this study due to the low concentration in the solution, they already have the quality needed to achieve the purity aimed.

Table 37. Feeding solution metal content for $NiSO_4$ cleaning process by IX method.

	Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
$NiSO_4$ After Dehpa	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	g/L	g/L	mg/L	mg/L
	0.00	118.70	6.30	298.20	0.20	0.00	8.47	54.40	714.70	0.10	8.06	38.19	1.50	0.40

4.5.1. Bis(2-ethylhexyl) phosphoric acid Impregnated, D2EHPA (MTX7010)

The loss of Ni is good under pH 2.5 and acceptable till pH 3.

The recovery of Mg starts at pH 2 with a recovery of slightly over 50% and is excellent at pH 3 to 3.5 with an average of over 90%.

The recovery of Cd starts at pH 1 but becomes early at pH 2 and becomes significant at pH 2.5 with a recovery between 20% to 30%. At pH 3.5 the recovery is over 70% been decent.

Cobalt's recovery started at pH 2 and continued growing fast till pH 3.5 from a recovery of around 15% to over 80% at pH 3.5.

Calcium has an increase of recovery from pH 1 to pH 2.5 then starts to decrease, most probably because with the change of pH, the kinetics of calcium becomes slower, and the resin full load with the other metals. The results of the experiment are summarized in Table 38 and Figure 40.

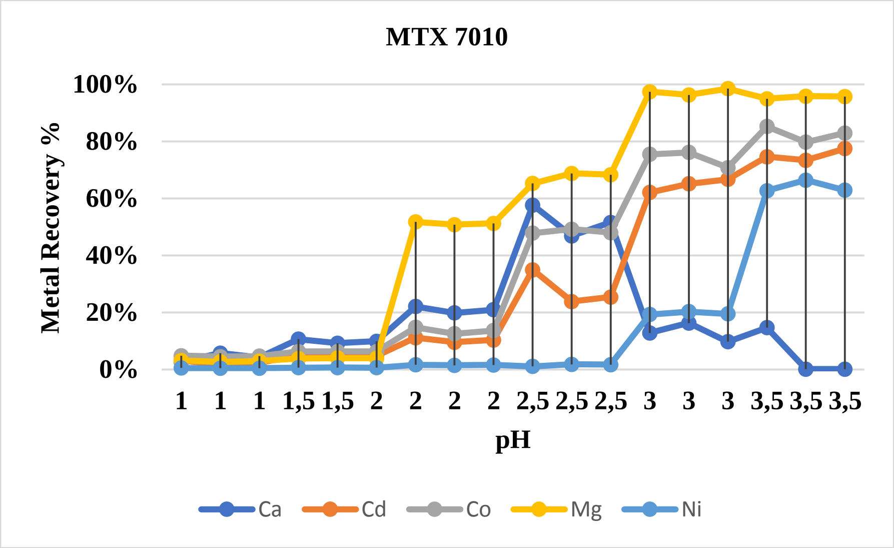
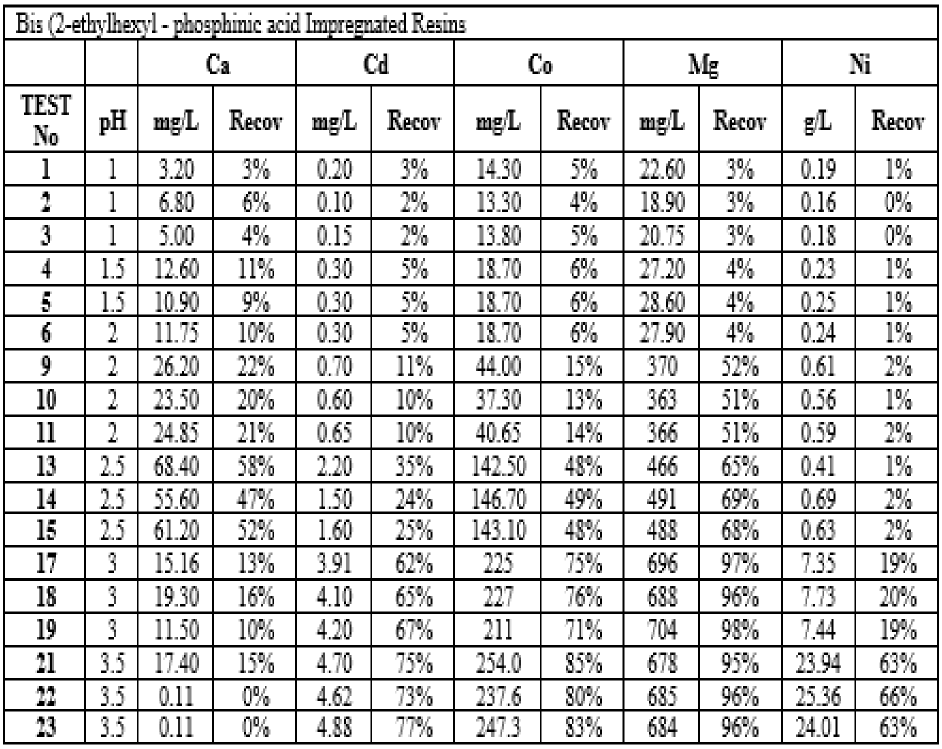


Figure 40. The pH effect on metal selectivity.

Table 38.The metal ions recover into the resin with different pH.



Bis (2-ethylhexyl - phosphinic acid Impregnated Resins											
		Ca		Cd		Co		Mg		Ni	
TEST No	**pH**	**mg/L**	**Recov**	**mg/L**	**Recov**	**mg/L**	**Recov**	**mg/L**	**Recov**	**g/L**	**Recov**
1	1	3.20	3%	0.20	3%	14.30	5%	22.60	3%	0.19	1%
2	1	6.80	6%	0.10	2%	13.30	4%	18.90	3%	0.16	0%
3	1	5.00	4%	0.15	2%	13.80	5%	20.75	3%	0.18	0%
4	1.5	12.60	11%	0.30	5%	18.70	6%	27.20	4%	0.23	1%
5	1.5	10.90	9%	0.30	5%	18.70	6%	28.60	4%	0.25	1%
6	2	11.75	10%	0.30	5%	18.70	6%	27.90	4%	0.24	1%
9	2	26.20	22%	0.70	11%	44.00	15%	370	52%	0.61	2%
10	2	23.50	20%	0.60	10%	37.30	13%	363	51%	0.56	1%
11	2	24.85	21%	0.65	10%	40.65	14%	366	51%	0.59	2%
13	2.5	68.40	58%	2.20	35%	142.50	48%	466	65%	0.41	1%
14	2.5	55.60	47%	1.50	24%	146.70	49%	491	69%	0.69	2%
15	2.5	61.20	52%	1.60	25%	143.10	48%	488	68%	0.63	2%
17	3	15.16	13%	3.91	62%	225	75%	696	97%	7.35	19%
18	3	19.30	16%	4.10	65%	227	76%	688	96%	7.73	20%
19	3	11.50	10%	4.20	67%	211	71%	704	98%	7.44	19%
21	3.5	17.40	15%	4.70	75%	254.0	85%	678	95%	23.94	63%
22	3.5	0.11	0%	4.62	73%	237.6	80%	685	96%	25.36	66%
23	3.5	0.11	0%	4.88	77%	247.3	83%	684	96%	24.01	63%

4.5.2. Bis-picolylamine Chelating Group (LSC 495)

It is highly effective in all pH ranges and at high pH, with increased extraction of all metals including Ni. Losses are too high to be considered a candidate for the process.

Additionally, there is not much difference in selectivity between metals due to pH changes. Therefore, it is not a suitable resin for the aim of this project. The results of the experiment are shown in Table 39 and Figure 41.

Table 39. The metal ions recover into the resin with different pH.

Bis-picolylamine Chelating Group											
		Ca		Cd		Co		Mg		Ni	
TEST No	pH	mg/L	Recov	mg/L	Recov	mg/L	Recov	mg/L	Recov	g/L	Recov
1	1	13.70	12%	0.80	13%	42.00	14%	71.50	10%	6.67	17%
2	1	15.20	13%	1.00	16%	48.90	16%	82.50	12%	7.80	20%
3	1	14.45	12%	0.90	14%	45.45	15%	77.00	11%	7.24	19%
4	1.5	16.80	14%	1.20	19%	49.60	17%	84.20	12%	9.60	25%
5	1.5	21.10	18%	1.40	22%	59.70	20%	105.00	15%	9.69	25%
6	1.5	18.95	16%	1.30	21%	54.65	18%	94.60	13%	9.64	25%
7	2	18.60	16%	1.70	27%	59.60	20%	98.10	14%	11.52	30%
8	2	16.70	14%	1.60	25%	55.30	19%	86.20	12%	11.31	30%
9	2	17.65	15%	1.65	26%	57.45	19%	92.15	13%	11.41	30%
10	2.5	19.70	17%	2.10	33%	64.10	21%	99.50	14%	11.77	31%
11	2.5	19.30	16%	1.80	29%	59.90	20%	93.30	13%	11.08	29%
12	2.5	19.50	16%	1.95	31%	62.00	21%	96.40	13%	11.42	30%
14	3	18.60	16%	2.30	37%	64.50	22%	86.90	12%	9.92	26%
15	3	18.60	16%	2.30	37%	64.50	22%	86.90	12%	9.92	26%
16	3.5	17.40	15%	2.20	35%	58.10	19%	77.20	11%	9.40	25%
17	3.5	17.50	15%	2.10	33%	62.40	21%	80.60	11%	8.96	23%
18	3.5	17.45	15%	2.15	34%	60.25	20%	78.90	11%	9.18	24%
19	4	16.50	14%	2.10	33%	112.80	38%	76.00	11%	8.76	23%
20	4	22.40	19%	2.80	44%	123.70	41%	105.70	15%	10.50	28%
21	4.5	19.30	16%	2.70	43%	102.60	34%	90.80	13%	10.61	28%
22	4.5	19.00	16%	2.60	41%	93.10	31%	83.00	12%	10.22	27%
23	4.5	19.15	16%	2.65	42%	97.85	33%	86.90	12%	10.42	27%

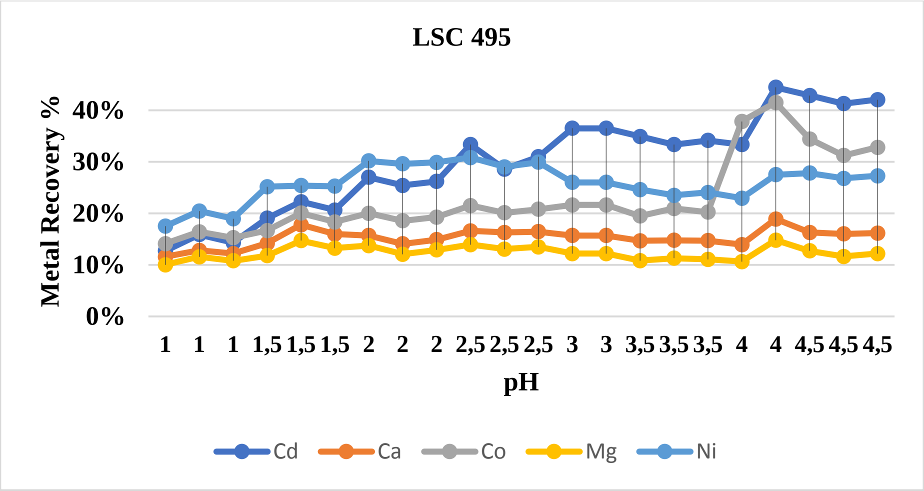


Figure 41. The pH effect on metal selectivity.

4.5.3. Bis(2,2,4 trimethypenthyl) Phosphinic Acid Impregnated, Cyanex 272 (MTX 8010)

It works similarly as it does in the SX form, with the difference that the loading capacity of the Mg gets affected stronger now we start to load the functional group with Ni.

The range of work of pH 4.5 to 5 allowed us to eliminate most of the impurities without losing a famous part of the Ni feed. The metal recovery selectivity by the pH changing and recovery summaries are given in Figure 42 and Table 40.

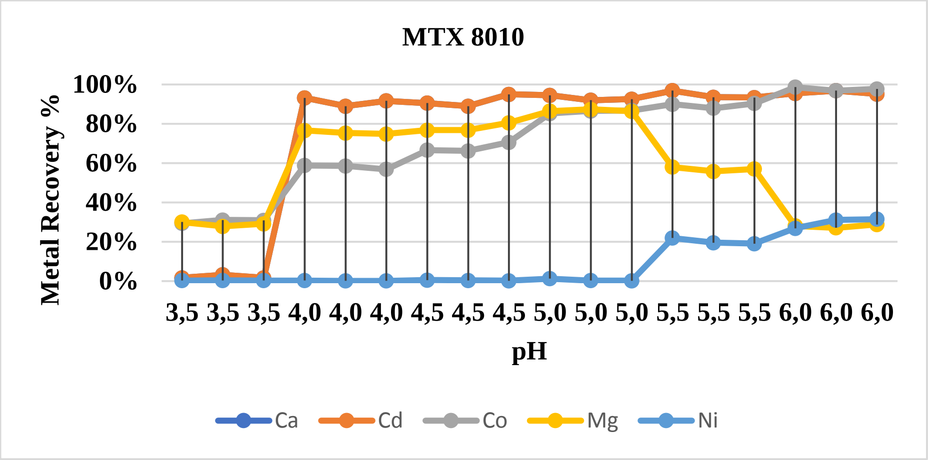
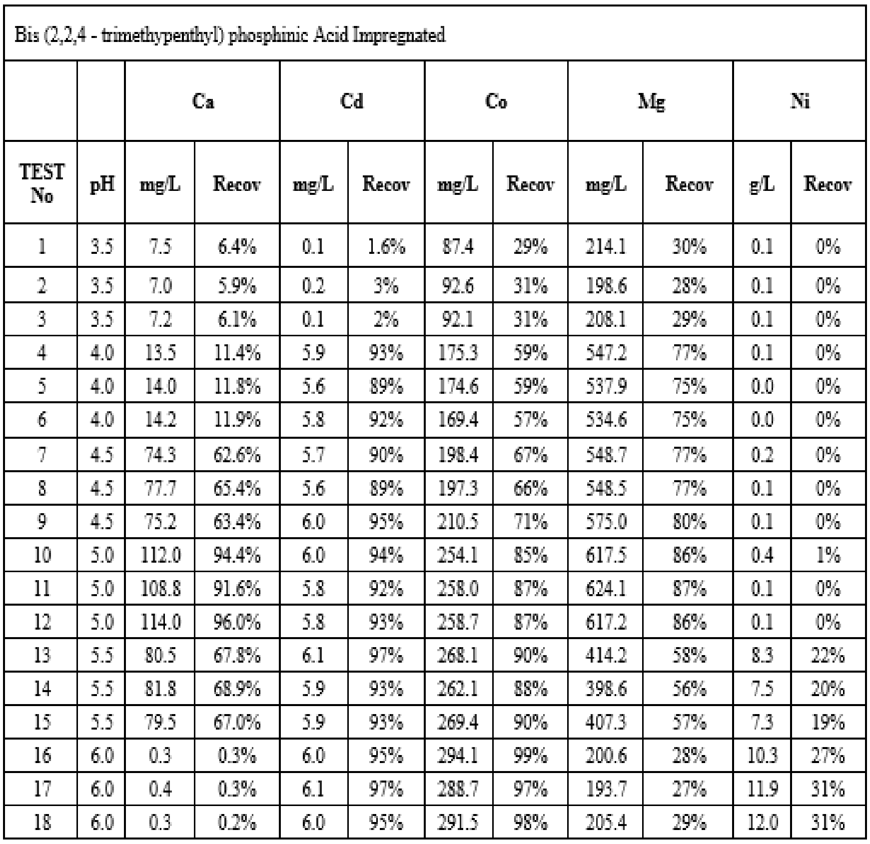


Figure 42. The pH effect on metal selectivity.

Table 40. The metal ions recover into the resin with different pH.



Bis (2,2,4 - trimethypenthyl) phosphinic Acid Impregnated											
		Ca		Cd		Co		Mg		Ni	
TEST No	pH	mg/L	Recov	mg/L	Recov	mg/L	Recov	mg/L	Recov	g/L	Recov
1	3.5	7.5	6.4%	0.1	1.6%	87.4	29%	214.1	30%	0.1	0%
2	3.5	7.0	5.9%	0.2	3%	92.6	31%	198.6	28%	0.1	0%
3	3.5	7.2	6.1%	0.1	2%	92.1	31%	208.1	29%	0.1	0%
4	4.0	13.5	11.4%	5.9	93%	175.3	59%	547.2	77%	0.1	0%
5	4.0	14.0	11.8%	5.6	89%	174.6	59%	537.9	75%	0.0	0%
6	4.0	14.2	11.9%	5.8	92%	169.4	57%	534.6	75%	0.0	0%
7	4.5	74.3	62.6%	5.7	90%	198.4	67%	548.7	77%	0.2	0%
8	4.5	77.7	65.4%	5.6	89%	197.3	66%	548.5	77%	0.1	0%
9	4.5	75.2	63.4%	6.0	95%	210.5	71%	575.0	80%	0.1	0%
10	5.0	112.0	94.4%	6.0	94%	254.1	85%	617.5	86%	0.4	1%
11	5.0	108.8	91.6%	5.8	92%	258.0	87%	624.1	87%	0.1	0%
12	5.0	114.0	96.0%	5.8	93%	258.7	87%	617.2	86%	0.1	0%
13	5.5	80.5	67.8%	6.1	97%	268.1	90%	414.2	58%	8.3	22%
14	5.5	81.8	68.9%	5.9	93%	262.1	88%	398.6	56%	7.5	20%
15	5.5	79.5	67.0%	5.9	93%	269.4	90%	407.3	57%	7.3	19%
16	6.0	0.3	0.3%	6.0	95%	294.1	99%	200.6	28%	10.3	27%
17	6.0	0.4	0.3%	6.1	97%	288.7	97%	193.7	27%	11.9	31%
18	6.0	0.3	0.2%	6.0	95%	291.5	98%	205.4	29%	12.0	31%

4.6. Metal Sulfate Salts Crystallization

This is the last section of this thesis which is named the crystallization process to obtain the metallic salts form the cleaned $CoSO_4$ and $NiSO_4$ solutions in the battery grade quality.

Table 41 and Table 42 are given the metal contents of the feeding solutions for this process.

Table 41. The feeding solution metal contents for crystallization of $CoSO_4$.

Steps of Project	***Feeding Flow***	***Al***	***Ca***	***Cd***	***Co***	***Fe***	***Mg***	***Mn***	***Zn***
		mg/L	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***
Crystallization	*Clean* $CoSO_4$ *Solution*	14.40	3.10	84.40	86,819	66.10	22.20	1,117.4	1.00

Table 42. The feeding solution metal contents for crystallization of $NiSO_4$.

Steps of Project	***Feeding Flow***	***Al***	***Ca***	***Cd***	***Co***	***Fe***	***Mg***	***Ni***	***Zn***
		mg/L	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***	***mg/L***
Crystallization	*Pure* $NiSO_4$ *Solution*	0.80	161.20	2.60	204.20	175.80	605.80	20,791.3	2.30

The crystallization process is applied as mentioned in the experimental procedure part in 3.2.6. After the crystallization, the solid particle was obtained and filtered to separate the residual aqueous solution and solid particles. Solid particles were sent to ICP-OES and XRD analysis to see the metal concentration and define the water molecule amount in the solids.

The solids photographs obtained after the filtration are given Figure 43. Solid $NiSO_4$ color is like a kind of dark green and the $CoSO_4$ color is like pinky.

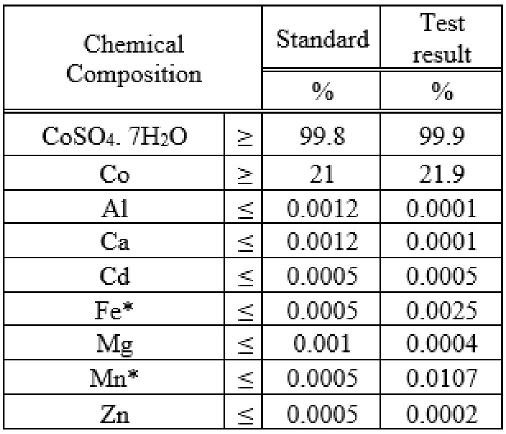
Figure 43. The crystal form of the metal salts after crystallization process.

Their solubility is so low in ethanol as mentioned in the literature, before being sent to analysis we washed both of solids with ethanol to remove the impurities from their surface. (Zhang et al. 2022; Sainio, Virolainen, and Andrey, n.d.).

The market for cathode precursors requires in its products stability in composition and high purity. Even though, due to the nature of most of the ores, the number of impurities allowed changes substantially. Indeed, region by region (Asia/Europe/ America) the market changes, and each company could have different impurities requirements, in addition to this the technology is still quite young and evolution is always present. The most common standards of the industry and our test results comparison are shown in Table 43 and Table 44 for $CoSO_4$ and $NiSO_4$ salts, respectively.

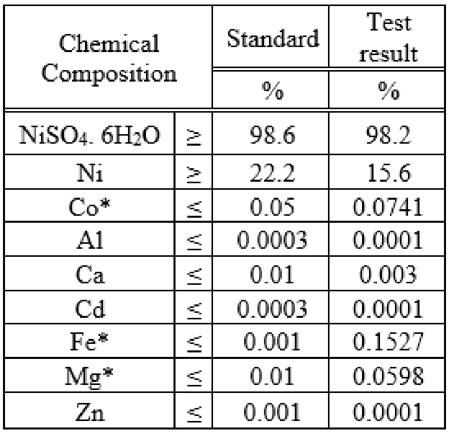
For $CoSO_4.XH_2O$ product, Fe and Mn is out of the standard limit of the battery grade, but any other limitation was obtained, by the ICP-OES technology we have we cannot assure the exact concentration under the limits of detection. In the previous steps of the product obtaining part, especially in Fe removing step of the process, can be increased the reagent consumption, or optimized again. Additionally, it should not be forgotten that ICP-OES analysis equipment has different minimum detection limits for each metal, and at values below this limit can't be exact, therefore is a high probability of error when determining metal concentration. XRD technologies were later used to confirm our suspicions about the Fe and Mn concentration.

Table 43. Comparison of standard of $CoSO_4$. $7H_2O$ and our product.



Chemical Composition		Standard	Test result
		%	%
$CoSO_4$. $7H_2O$	≥	99.8	99.9
Co	≥	21	21.9
Al	≤	0.0012	0.0001
Ca	≤	0.0012	0.0001
Cd	≤	0.0005	0.0005
Fe*	≤	0.0005	0.0025
Mg	≤	0.001	0.0004
Mn*	≤	0.0005	0.0107
Zn	≤	0.0005	0.0002

Table 44. Comparison of standard of $NiSO_4$. $6H_2O$ and our product.



Chemical Composition		Standard	Test result
		%	%
$NiSO_4$. $6H_2O$	≥	98.6	98.2
Ni	≥	22.2	15.6
Co*	≤	0.05	0.0741
Al	≤	0.0003	0.0001
Ca	≤	0.01	0.003
Cd	≤	0.0003	0.0001
Fe*	≤	0.001	0.1527
Mg*	≤	0.01	0.0598
Zn	≤	0.001	0.0001

For $NiSO_4.XH_2O$ products, Co, Fe, and Mg are out of the standard limit of the battery grade, but we are so close to the purity of the based product. In the previous steps of the product obtaining part, especially in Co/Ni separation with CYANEX 272 or $NiSO_4$ cleaning with D2EHPA steps of the process, can be increased the extraction steps, or optimization of the O/A ratio. Additionally, to increase the Ni concentration in the solid, the evaporation steps repetition can be increased because our feeding solution Ni concentration is not high enough.

The XRD analysis of these two metal salts is given below. Figure 44 shows the comparison of the market product and our synthesis product of $CoSO_4.7H_2O$.

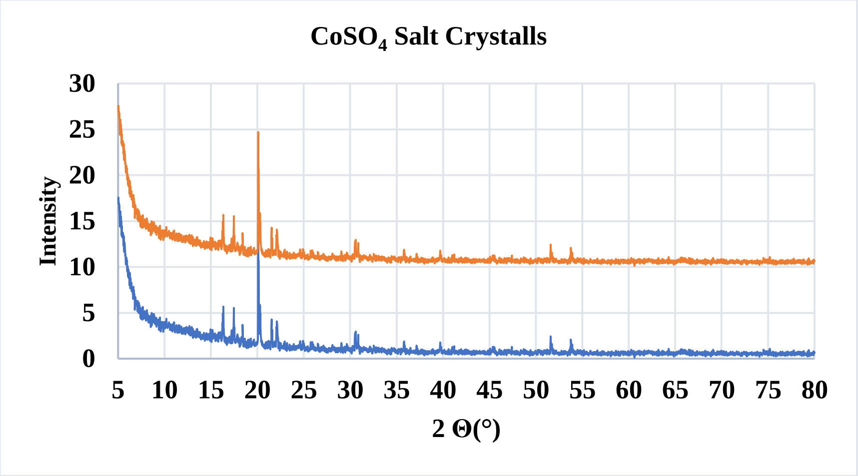


Figure 44. The XRD analysis comparison of market product and synthesis product of $CoSO_4.XH_2O$ crystals.

When the XRD patterns are examined, it is seen that the $CoSO_4.XH_2O$ salt we obtained overlaps with the $CoSO_4.7H_2O$ salt sold in the market. According to the results of ICP-OES and XRD analyses, we can say that it is $CoSO_4.7H_2O$ with high purity and good crystal structure. The white line represents the high-purity product available on the market, and the orange line is the synthesized product.

For $NiSO_4.XH_2O$ salt, the XRD patterns are examined, and it is seen that the $NiSO_4.XH_2O$ salt we obtained did not overlap with the $NiSO_4.6H_2O$ salt sold in the market. The results of ICP-OES already showed us that purity is not enough to produce battery-grade $NiSO_4.6H_2O$ and the XRD analysis again proved this. The white line represents the high-purity product available on the market, and the orange line is the synthesized product. In the future, the optimization and procedure of producing battery grade $NisO_4.6H_2O$ will be continued.

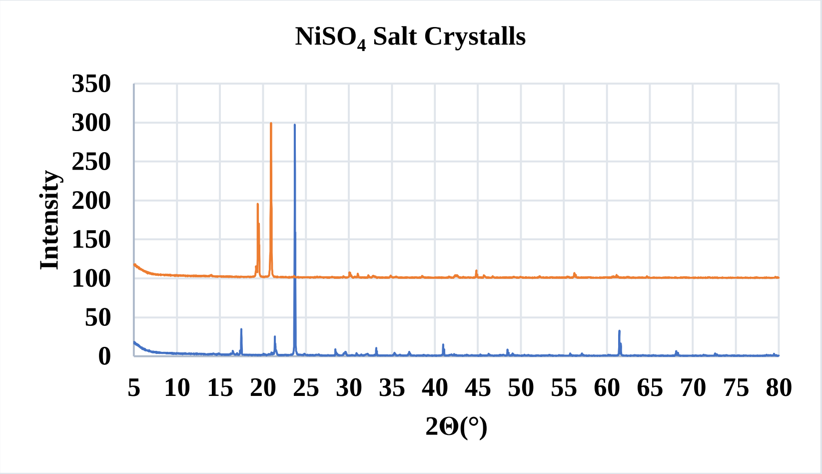


Figure 45. The XRD analysis comparison of market product and synthesis product of $NiSO_4.XH_2O$ crystals.

CHAPTER 5

CONCLUSION

After all these experimental tests, the answers to the questions intended to be answered for all the topics determined for this study are presented below:

Cobalt and Nickel were recovered from the ongoing process of SX by IX process. Sun Resin LSC 710 was chosen, because of working pH is like the feeding solution pH, and Mg recovery is better than other resins.

Cobalt and Nickel were separated from the mixed solution of IX Eluate by the SX method. Cyanex 272 was chosen because of the selectivity effect of Co/Ni.

Cobalt Sulphate solution and Nickel Sulphate solution were cleaned by the SX method. D2EHPA was chosen for its effect on impurities element selectivity.

Cobalt Sulphate solution and Nickel Sulphate solution were purified by the IX method to produce the battery-grade product. For purification of the CoSO4 solution and NiSO4 solution, Bis(2-ethylhexyl) phosphoric acid Impregnated, D2EHPA, (MTX 7010) resin was chosen. In the purification of the cobalt solution, the system was operated at pH 3.5. The observation is that the impurity selectivity is higher than the cobalt selectivity. While removing the impurities, the cobalt loss is less than 1%. However, in the purification of the nickel solution, the system was operated at pH 2.5. The result of the experiment shows that the impurity selectivity is higher than the nickel selectivity. While removing the impurities, the nickel loss is around 1% or 2%.

After applying all these separation, cleaning, and purification processes, the quality of the obtained solutions is over 95%.

The crystallization methods for both solutions were operated, and the production of the crystal was achieved. For Cobalt salt, the battery grade $CoSO_4$. $7H_2O$ was obtained. For Nickel salt, the battery grade $NiSO_4$. XH_2O was not obtained so the purification and the crystallization process optimization are continued to study.

REFERENCES

Botelho Junior, Amilton Barbosa, David B. Dreisinger, and Denise C.R. Espinosa. 2019. “A Review of Nickel, Copper, and Cobalt Recovery by Chelating Ion Exchange Resins from Mining Processes and Mining Tailings.” *Mining, Metallurgy and Exploration* 36 (1): 199–213. https://doi.org/10.1007/S42461-018-0016-8/METRICS.

Deventer, Johanna Van. n.d. “Presenter and Corresponding Author Application of Solvent-Impregnated Resins for Production Of High-Purity Nickel and Cobalt Liquors.”

Douglas Flett. 2004. “Cobalt-Nickel Separation in Hydrometallurgy: A Review.”

Hubicki, Zbigniew, Monika Wawrzkiewicz, Grzegorz Wójcik, Dorota Kolodynska, and Anna Wolowicz. 2015. “Ion Exchange Method for Removal and Separation of Noble Metal Ions.” In *Ion Exchange - Studies and Applications*. InTech. https://doi.org/10.5772/60597.

Johann Korkisch, by, and New York Toronto. 1969. “Modern Methods for The Separation of Rarer Metal Ions Pergamon Press.”

Kihlblom, Caroline. n.d. “Separation of Cobalt and Nickel Using CYANEX 272 for Solvent Extraction In the Presence of Other Contaminates in Sulphate Based Leaching Solution.”

Kilislioğlu, Ayben. 2015. *Ion Exchange - Studies and Applications*. InTech.

Lister, Tedd E, Mark Strauss, Luis A Diaz Aldana, Joshua S McNally, and John R Klaehn. 2021. “Separation of Cobalt, Nickel, and Manganese in Leach Solutions of Waste Lithium-Ion Batteries Using Dowex M4195 Ion Exchange Resin.” http://www.inl.gov.

Olushola, S Ay, a, A Adekola Folahan, A Baba Alafara, J Ximba Bhekumusa, and S Fatoki Olalekan. 2013. “Application of Cyanex Extractant in Cobalt/Nickel Separation Process by Solvent Extraction.” *International Journal of Physical Sciences* 8 (3): 89–97. https://doi.org/10.5897/ijps12.135.

Rickelton, W. A., D. S. Flett, and D. W. West. 1984. “Cobalt-Nickel Separation by Solvent Extraction with Bis(2,4,4 Trimethylpentyl)Phosphinic Acid.” *Solvent Extraction and Ion Exchange* 2 (6): 815–38. https://doi.org/10.1080/07366298408918476.

Sainio, Tuomo, Sami Virolainen, and Bershak Andrey. n.d. “Purification of Nickel Sulfate Solutions Via Solvent Extraction Method Examiners.” Accessed November 3, 2023.

Sole, Kathryn C. 2008. “Solvent Extraction in the Hydrometallurgical Processing and Purification of Metals: Process Design and Selected Applications.” https://www.researchgate.net/publication/281136739.

Sole, Kathryn C. 2018. “The Evolution of Cobalt–Nickel Separation and Purification Technologies: Fifty Years of Solvent Extraction and Ion Exchange.” In , 1167–91. https://doi.org/10.1007/978-3-319-95022-8_95.

Zhang, Jianxin, Arshe Said, Bing Han, and Marjatta Louhi-Kultanen. 2022. “Semi-Batch Evaporative Crystallization and Drying of Cobalt Sulphate Hydrates.” *Hydrometallurgy* 208 (February). https://doi.org/10.1016/j.hydromet.2022.105821.