

**OPTIMISATION OF ORGANIC PHASE PRE-
NEUTRALISATION STAGE IN PURIFICATION
STUDIES WITH SOLVENT EXTRACTION FOR
MHP (MIXED HYDROXIDE PRECIPITATE)
PRODUCED FROM GÖRDES LATERITE ORE
AND INVESTIGATION OF ITS EFFECT ON
EXTRACTION**

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**by
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I dedicate this thesis to my lovely little daughter Nil KAYA and my husband Ahmet KAYA.

ABSTRACT

OPTIMISATION OF ORGANIC PHASE PRE-NEUTRALISATION STAGE IN PURIFICATION STUDIES WITH SOLVENT EXTRACTION FOR MHP (MIXED HYDROXIDE PRECIPITATE) PRODUCED FROM GÖRDES LATERITE ORE AND INVESTIGATION OF ITS EFFECT ON EXTRACTION

Intermediate products such as MHP (Mixed Hydroxide Precipitate) are processed by solvent extraction, which is a continuous process in the industry for obtaining final products such as nickel metal or nickel sulphate. Nickel is used essentially in the stainless steel industry and cobalt is used in superalloys. Both metals are used in lithium-ion battery technologies, especially electric vehicles. A preliminary stage of the solvent extraction process is called pre-neutralisation. It is based on partial neutralisation of the acidic organic reactant to prevent pH fluctuations in extraction due to the H^+ ions release aqueous phase, and it provides an exchange mechanism to enable loading of the metals to the organic phase. This thesis study aims to optimise the organic phase pre-neutralisation percent in further purification treatment of MHP leach solution (PLS-Pregnant Leach Solution) from Gördes nickel laterites and investigate its effect on extraction by D2EHPA and Cyanex 272 organic reactants. NaOH and Na_2CO_3 solutions were used in pre-neutralisation with 35%, 40% and 45% in D2EHPA and 30%, 35% and 40% in Cyanex 272. The optimum pre-neutralisation results were found as 35% for D2EHPA and 30% for Cyanex 272.

ÖZET

GÖRDES LATERİT CEVHERİNDEN ÜRETİLEN MHP(KARIŞIK HİDROKSİT ÇÖKELEĞİ) ÜRÜNÜNÜN SOLVENT EKSTRAKSİYON İLE SAFLAŞTIRMA ÇALIŞMALARINDA ORGANİK FAZ PRE-NÖTRALİZASYON OPTİMİZASYONU VE EKTRAKSİYONA ETKİSİNİN İNCELENMESİ

MHP (Karışık Hidroksit Çökeleği) gibi ara ürünler, nikel veya nikel sülfat gibi nihai ürün üretimlerinde endüstride sürekli bir proses olan solvent ekstraksiyon yöntemi ile işlenmektedir. Nikel temel olarak paslanmaz çelik üretiminde, kobalt ise süper alaşım üretimlerinde kullanılmaktadır. Her iki metal, özellikle elektrikli araçlarda, lityum iyon batarya teknolojilerinde kullanılmaktadır. Solvent ekstraksiyon proses ön adımlarından biri olan ve pre-nötralizasyon olarak adlandırılan bu işlem, ekstraksiyon sırasında H^+ salınımı kaynaklı pH dalgalanmalarını önlemek için asidik organik reaktifin kısmi olarak nötralize edilmesine dayanmakta ve organik faza metal yüklenmesini kolaylaştırmaktadır. Bu tez çalışmasında, Gördes nikel lateritlerinden üretilen MHP'nin işlenmesi ile elde edilen çözeltinin saflaştırılmasında, organik fazın pre-nötralizasyonunun optimizasyonu ve ekstraksiyona etkisinin incelenmesi hedeflenmiş olup D2EHPA ve Cyanex 272 organik reaktif olarak kullanılmıştır. Kimyasal ajan olarak NaOH ve Na_2CO_3 çözeltileri ile D2EHPA'da %35, %40 ve %45; Cyanex 272'de %30, %35 ve %40 pre-nötralizasyon yapılmıştır. Optimum sonuç olarak pre-nötralizasyonda D2EHPA için %35, Cyanex 272 için %30 olarak bulunmuştur.

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LIST OF ABBREVIATIONS

HPAL	High Pressure Acid Leach
PLS	Pregnant Leach Solution
MHP	Mixed Hydroxide Precipitate
SX	Solvent Extraction
A/O	Aqueous/Organic Phase Volume Ratio
Aq	Aqueous Solution Phase
Org	Organic Phase
rpm	Revolutions per Minute

CHAPTER 1

INTRODUCTION

1.1.Motivation

Nickel is one of the main inputs of stainless steel production and is used in various industries such as aerospace, automotive, alloy and battery. The usage of portable electronic devices such as mobile phones, computers, and smart applications like smart houses and electric vehicles increases the energy requirements of the world. Depending on air pollution, global warming and climate change, humanity tends to environmentally friendly vehicles. For that reason, by increasing the use of electric vehicles in the world, energy consumption increased substantially. At this point, the storage of energy becomes an important issue. Nickel demand is increasing with the growth of the battery industry.^{1,2} The sulphate form of the nickel ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) is responsible for the specific energy and capacity in lithium-ion batteries.³

Cobalt is used in superalloys, hard facing and other alloys, catalysts, paints, electrolysis, batteries, and similar industries. Especially, the sulphate form of the cobalt ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) is used in lithium-ion batteries because it is responsible for the battery's structural stability and cycle life.³

Mixed Hydroxide Precipitate (MHP) is an intermediate product containing nickel and cobalt in hydroxide form produced from the lateritic nickel ore by the hydrometallurgical process.⁴ Final products of the MHP; metallic nickel, metallic cobalt, nickel sulphate, and cobalt sulphate are produced by processing this material with the solvent extraction method. Processing the MHP brings additional operational expenditure (OPEX), and this additive cost is too important by making the process feasible or not. Pre-neutralisation is an essential and necessary stage because it directly affects the extraction of the target metals and provides smooth pH control in the extraction steps. In addition to that, it can affect and increase the metal extraction depending on the neutralization percent. Contribution of the pre-neutralization stage to the OPEX can be in a role that makes the process feasible or not due to the economy. In addition, reagents

used in this stage can cause problems in the overall solvent extraction circuit. Processes run correctly or shut down unfavourably in industrial plants using various chemical reagents depending on their properties.

In this thesis, the pre-neutralisation step is examined for the solvent extraction process. The pregnant leach solution is produced from MHP intermediate material, which is produced from Gördes nickel laterite ore. NaOH and Na₂CO₃ are used as neutralising chemicals in pre-neutralisation step. The aim is to determine the optimum pre-neutralisation percent for metal extraction and determine their effects on extraction efficiency.

CHAPTER 2

LITERATURE REVIEW

2.1. Nickel Ores and Processing Methods

Nickel ores generally exist in nature in two forms. These are sulphides, and oxides forms. Approximately 70% of the world reserves are oxide type lateritic ores. The rest of the ores, approximately 30%, are sulphide type. Lateritic ores are used for 40% of nickel production in metal form. As shown in Figure 2.1, lateritic ores are generally preferred for ferronickel due to their usage in steelmaking. Primary nickel and its matte are also produced from laterite ores. Sulphide types are generally used to produce high purity nickel metal. Lateritic ores consist of saprolite, limonite and smectite layers. Due to their different mineralogy and composition, they are processed by using different extraction methods. Saprolite ores with a relatively low content of iron are smelted. Ores with high iron content are leached, and the final product is obtained via refining.⁵

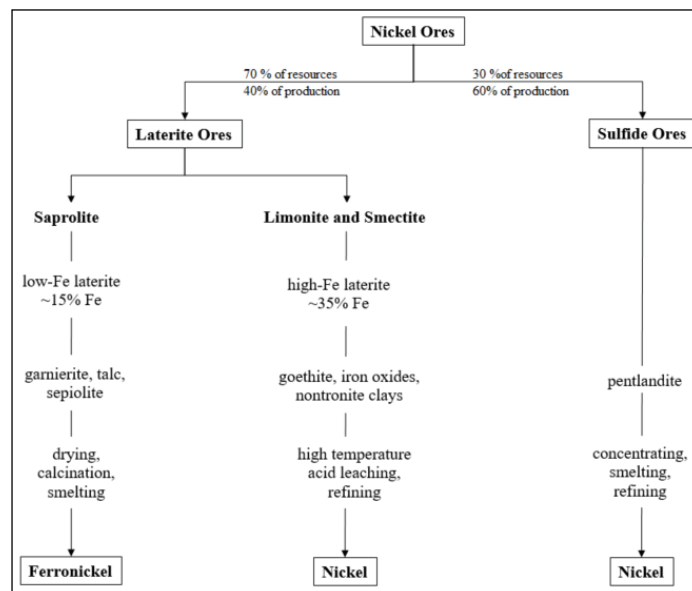


Figure 2. 1. Extraction of nickel from different types of ores
(Source: Crundwell, 2011)⁵

2.1.1. Sulphide Nickel Ores and Processing

Typical sulphide ores include a range between 1.5 wt. % and 3wt. % nickel and 0.05%-0.1% cobalt are generally found in Canada and northern Siberia. The basic nickel mineral in the sulphide ore is pentlandite, $(Ni,Fe)_9S_8$. Pyrrhotite (Fe_8S_9) and chalcopyrite ($CuFeS_2$) minerals are accompanying pentlandite. Metal rich matte is produced from sulphide ores by concentrating, smelting, and converting. Matte is leached by different chemical reagents (like chlorine gas in chlorine or sulphuric acid solutions). After the leaching process, solvent extraction is used for nickel and cobalt separation. Nickel rich and cobalt rich solutions are treated in an electrowinning cell or a hydrogen reduction process is applied to produce high purity nickel and cobalt metals.⁵

Table 2. 1. Concentration change in sulphide ore process⁵

Metal	In Mined Ore (wt.%)	After Concentration (wt. %)	After Smelting and Converting (wt. %)
Nickel	1.5-2.5	10-20	40-70
Cobalt	0.05-0.1	0.3-0.8	0.5-2

The schematic production flowsheet for sulphide ores is seen in Figure 2.2. The main process steps are crushing and grinding ore until to obtain particle size as 50 μm , concentrate production by the flotation, drying, flash smelting or electric furnace melting at 1350 °C temperature, producing matte, converting molten low-Fe sulphide matte (40% Ni content) and production nickel and cobalt via hydrometallurgy or pyrometallurgical processes. In addition to that, depending on the ore content, copper, platinum group metals, gold and silver metals are produced by this method.

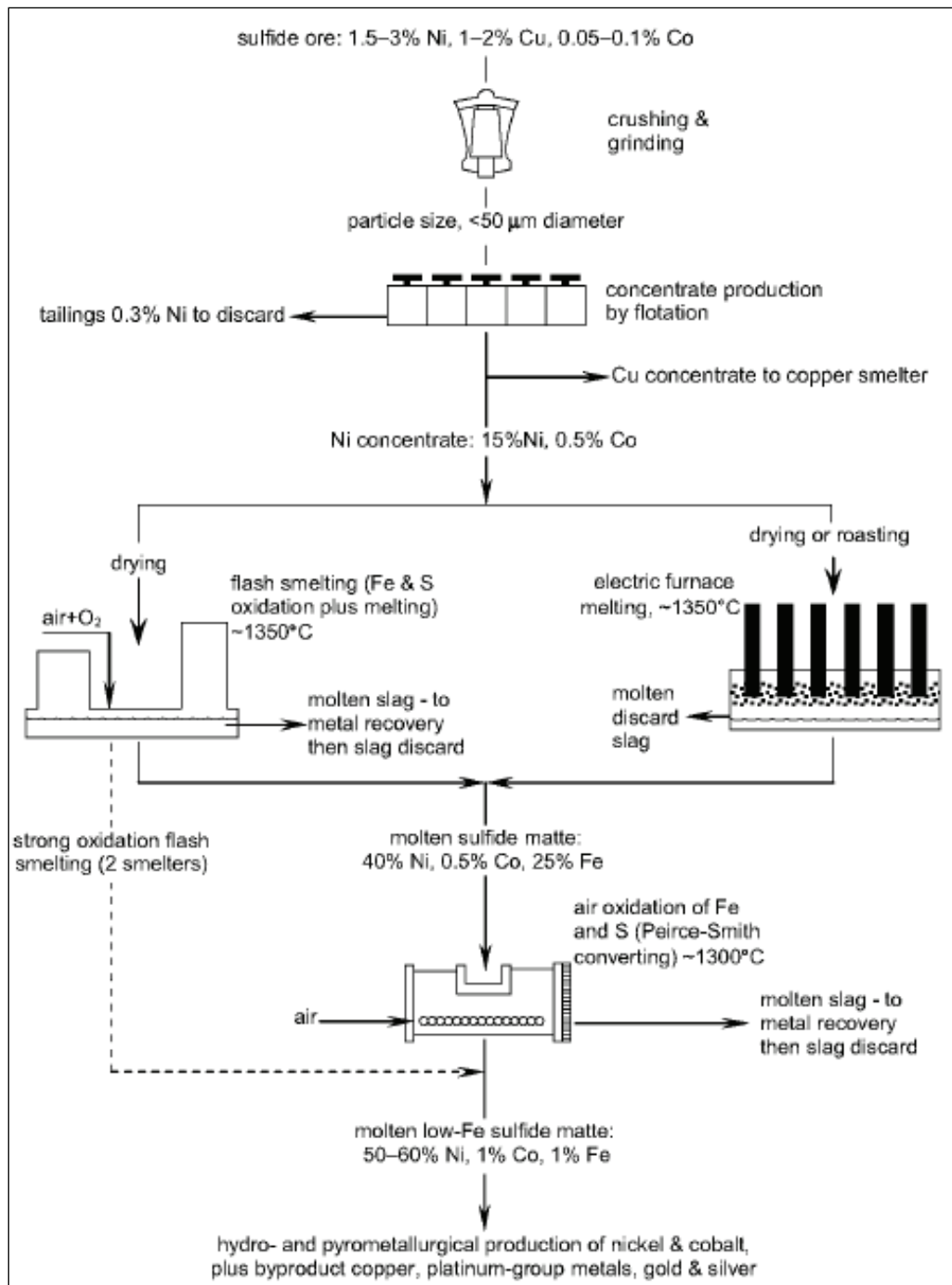


Figure 2. 2. Flowsheet of sulphide ore processing (Source: Crundwell, 2011)⁵

2.1.2. Oxide (Lateritic) Nickel Ores and Processes

Laterite ore is generally mined when the nickel grade is greater than 1.3% Ni and 0.1% Co and generally found in Cuba, Philippines, Australia and Indonesia.

Laterite ores mainly occur in tropical climates and are mined by surface-mining (open pit) due to their presence near the surface. These complex types of ores are formed via tectonic forces and ocean floor's alterations due to the weather conditions. These alterations caused various complex minerals formation. Typically, different nickel containing layers are illustrated with additional, as shown in Figure 2.3.

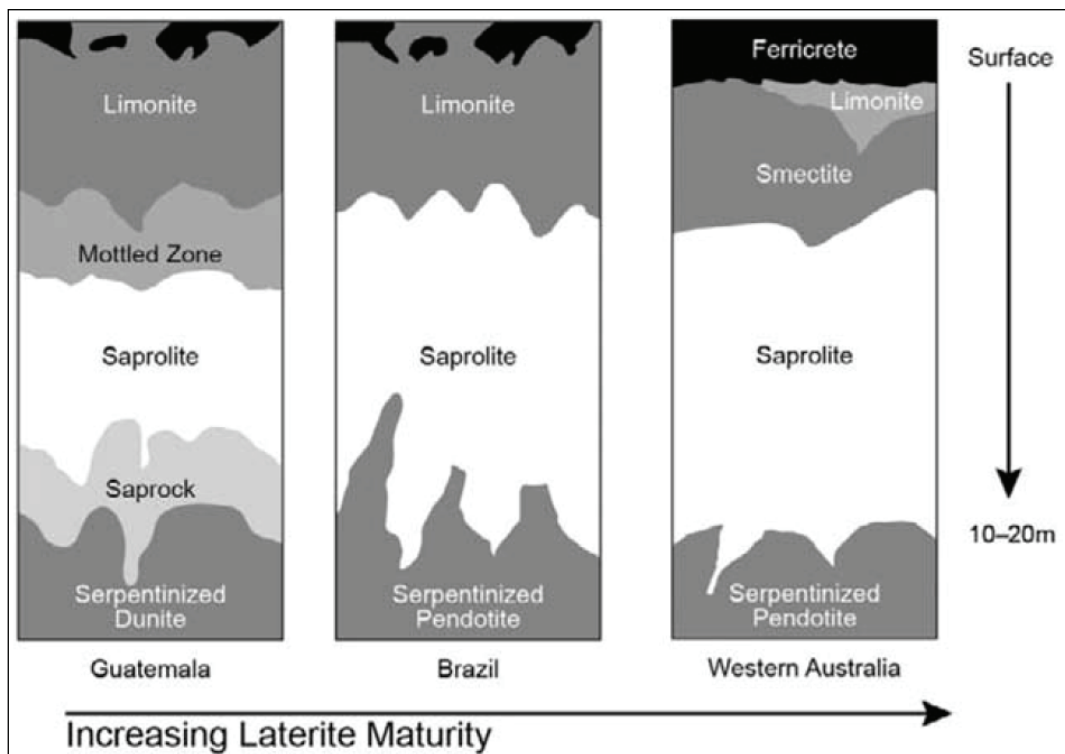


Figure 2. 3. Profiles of lateritic ores with different climatic region and maturity (Source: Crundwell, 2011)⁵

Three layers of the nickel bearing ores are limonite, smectite, and saprolite. Generally, limonitic smectite layers occur close to the surface. The saprolite layer forms below between limonite and smectite. Also, it is possible to observe other altered layers. The mottled and ferricrete layers are well known as altered layers.

The limonite layer contains high iron. In addition to that, it contains low MgO. The limonite layer is known as hydrated iron oxide, $(\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O})$. In this mineral, nickel takes the place of iron, and is termed as goethite and its generic formula is $(\text{Fe},\text{Ni})\text{OOH}$.

The smectite clay layer is also found in related ore. Nontronite is a well-known example of it.

The saprolite layer includes low iron and high MgO and is found below the limonite layer. Saprolite layer is not affected as much as limonite layer because of weathering or altered chemically due to its presence further from the surface. $Mg_3Si_2O_5(OH)_4$ is a kind of hydroxysilicates are found in the saprolite layer. In chemical reactions, $(Mg[Ni,Co])_3Si_2O_5(OH)_4$ generic formula is used for garnierite minerals. An idealized profile of lateritic deposit is shown in Figure 2.4.

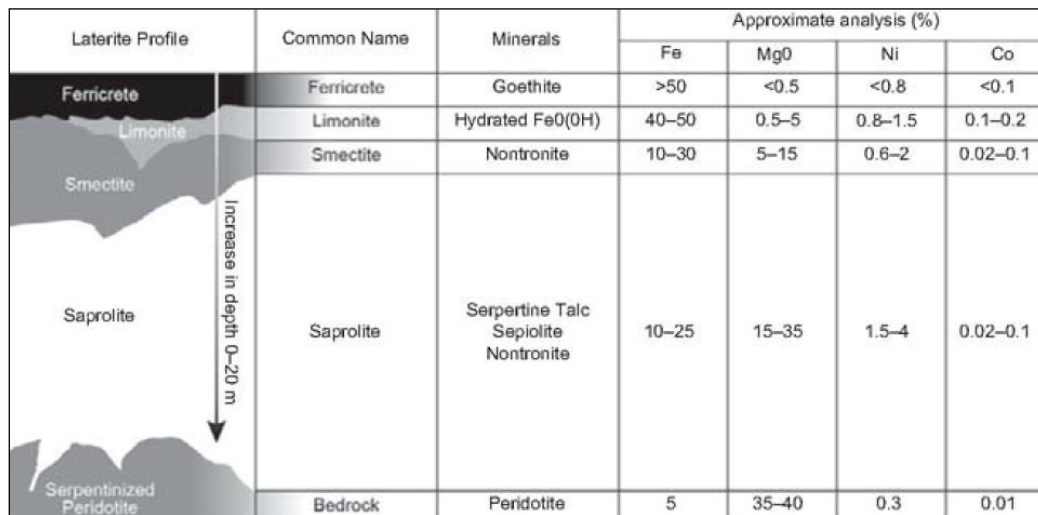


Figure 2. 4. Idealized profile of lateritic ore deposit
(Source: Crundwell, 2011)⁵

Depending on the ore body layers, different extraction methods are applied. There are two fundamental methods for laterite ores. The first one is smelting and the production of ferronickel. The second one is leaching (hydrometallurgy) and refining for metal. Limonite and smectite ores processing are not economical by smelting due to the presence of high amount of iron content and high moisture content of these ores. If goethite bearing limonite ores are leached at high temperature, 40% iron content of these ores precipitates as hematite or jarosite. In addition to that, the low MgO content of limonite (approximately 3%) consumes a low amount of sulphuric acid. Similarly, saprolite ore processing is not economical by leaching due to the presence of high amount of MgO content. Because MgO (approximately 20%) consumes a large amount of sulphuric acid if it is used in the leaching process.^{5,6}

Saprolite ores are smelted for ferronickel production and used in the stainless steel industry and ferrous alloys. Typically, ferronickel contains 30 wt. % nickel and 70 wt. %

iron. Cobalt is also found in small amounts in ferronickel, but it is not economical for end-users. The ferronickel production diagram is shown in Figure 2.5.⁵

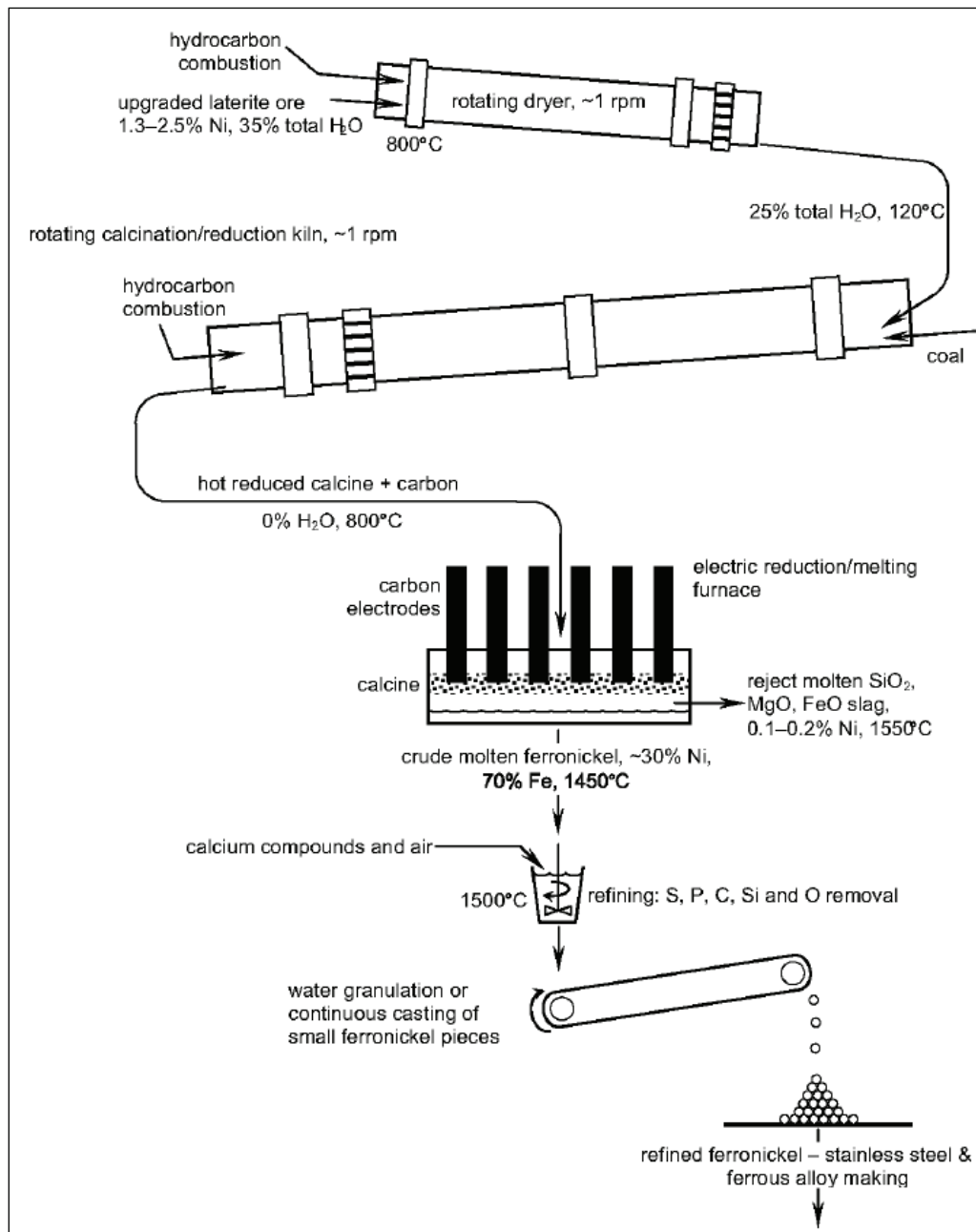


Figure 2. 5. Ferronickel production flowsheet
(Source: Crundwell, 2011)⁵

When the pyrometallurgical methods are not economical, the hydrometallurgical methods are preferred for nickel extraction and these processes are Caron process, High

Pressure Acid Leach (HPAL) process and Atmospheric Leach process (in-situ, heap or column, or dump).^{6,7,8}

In the Caron process, nickel ore is processed by drying, milling, calcination and reducing selectively at 700 °C to metallic form, respectively. After that, the semi-product obtained is leached at low temperature (25-45 °C) at pH=10 with ammonia-ammonium carbonate content solution to produce ammine complexes, such as nickel (II) ammine and cobalt(II) ammine. Ammonia is stripped, and nickel carbonate is produced by precipitation. Then, the solvent extraction method or sulphide precipitation is done for purification and recovery. Initially, it was commercialised at Nicaro, Cuba, in 1942. Nowadays, this method is not preferred because of its disadvantages.⁶

Atmospheric Pressure Acid Leach is divided into 3 sub-groups: in-situ leach, heap and dump leach, agitation leach, and vat leach. Generally, two processes are prominent, which are heap leach and agitation leach. In a heap leach, dilute sulphuric acid is used for extraction. 4-5 m height heaps are formed, and leach solution is pumped to the top of the heap, and percolates to the bottom. Compared to the HPAL process, heap leach requires extensive leach times, such as several months. Heap leach is not selective for a nickel. Fe, and Mg can create problems in this method.⁶

Agitation leach is performed under atmospheric pressure in tanks by sulphuric acid.⁹ Limonite and saprolite ores are processed after heating to 105 °C. It is not a selective process, and a huge amount of iron is co-leached with other metals.¹⁰ Acid consumption is approximately 800-1000 kg/ton dry ore.⁶

HPAL process is one of the most common methods used and commercialised process.¹¹ Lateritic ore is leached under high pressure and high temperature with sulphuric acid. Initially, it was commercialised at Mao Bay in Cuba in 1959. After this plant was constructed and commissioned such as Cawse Plant, Bulong Plant, Murrin Murrin Plant, and Ravensthorpe Plants in western Australia; Coral Bay Plant, and Taganito Plant in Philippines; Goro Plant in New Caledonia; Ambatovy Plant in Madagascar; Weda Bay Plant in Indonesia; Ramu Plant in Papua New Guinea). After these projects, Meta Nikel Plant in Turkey were constructed, and commissioned.⁶ In addition to that, new HPAL plants are under construction in Indonesia.³

Limonite ores are leached with sulphuric acid at high pressure and temperature, such as 250 °C and 40 bars. After leaching, the metal bearing solution is purified by precipitating with MgO. Then, the precipitated material is leached, and separated into

nickel and cobalt by solvent extraction. Finally, the electrowinning or hydrogen reduction method is used to obtain high purity nickel as 99.9%.

The iron concentration of the obtained pregnant leach solution (PLS) of HPAL is lower than that of atmospheric leach solutions, and sulphuric acid consumption is lower than that of atmospheric leach. Typical acid consumption is approximately 300 kg/ton dry ore.^{5,6}

The first capital expenditure of HPAL is expensive. Illustrated HPAL Plant flow sheet is detailed by showing autoclave, tanks, streams and thickeners in Figure 2.6.⁵

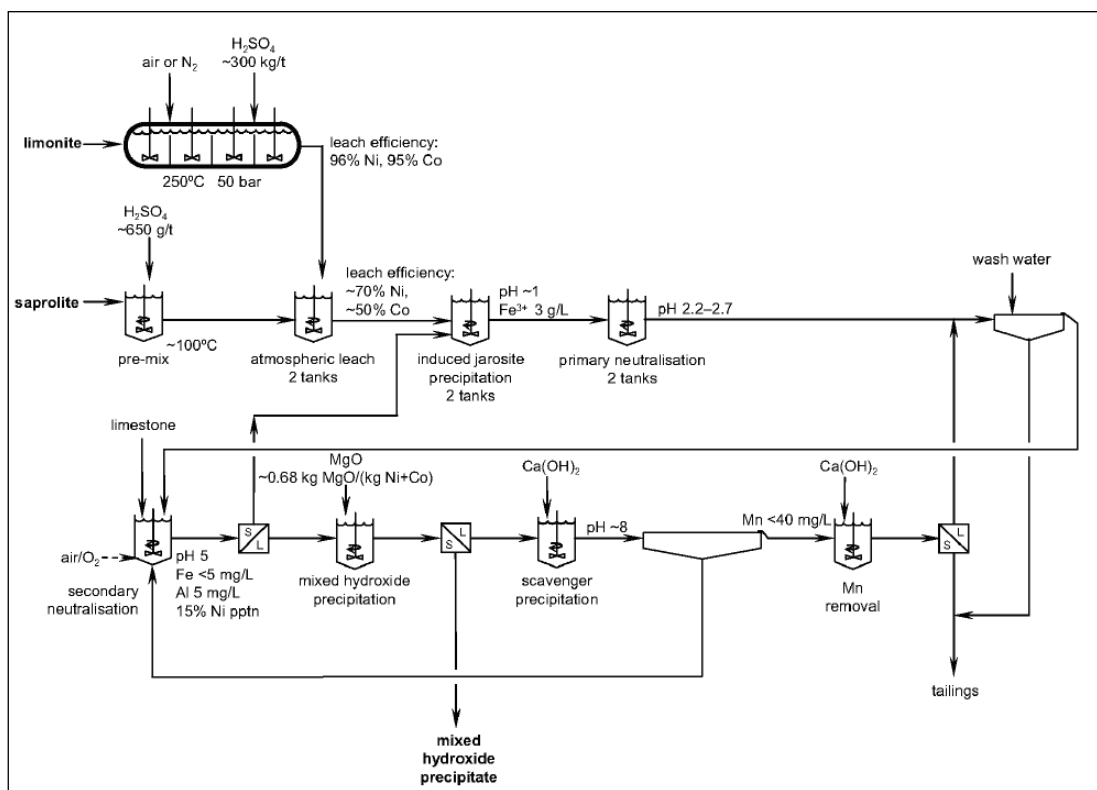


Figure 2. 6. Flowsheet of HPAL process for MHP product
(Source: Crundwell, 2011)⁵

Similarly, MSP (Mixed Sulphide Precipitate) intermediate product is produced from the pregnant leach solution by precipitating Ni and Co with H₂S gas and has a higher nickel content of approximately 55%.⁴ MSP flowsheet and nickel production are illustrated in Figure 2.7.

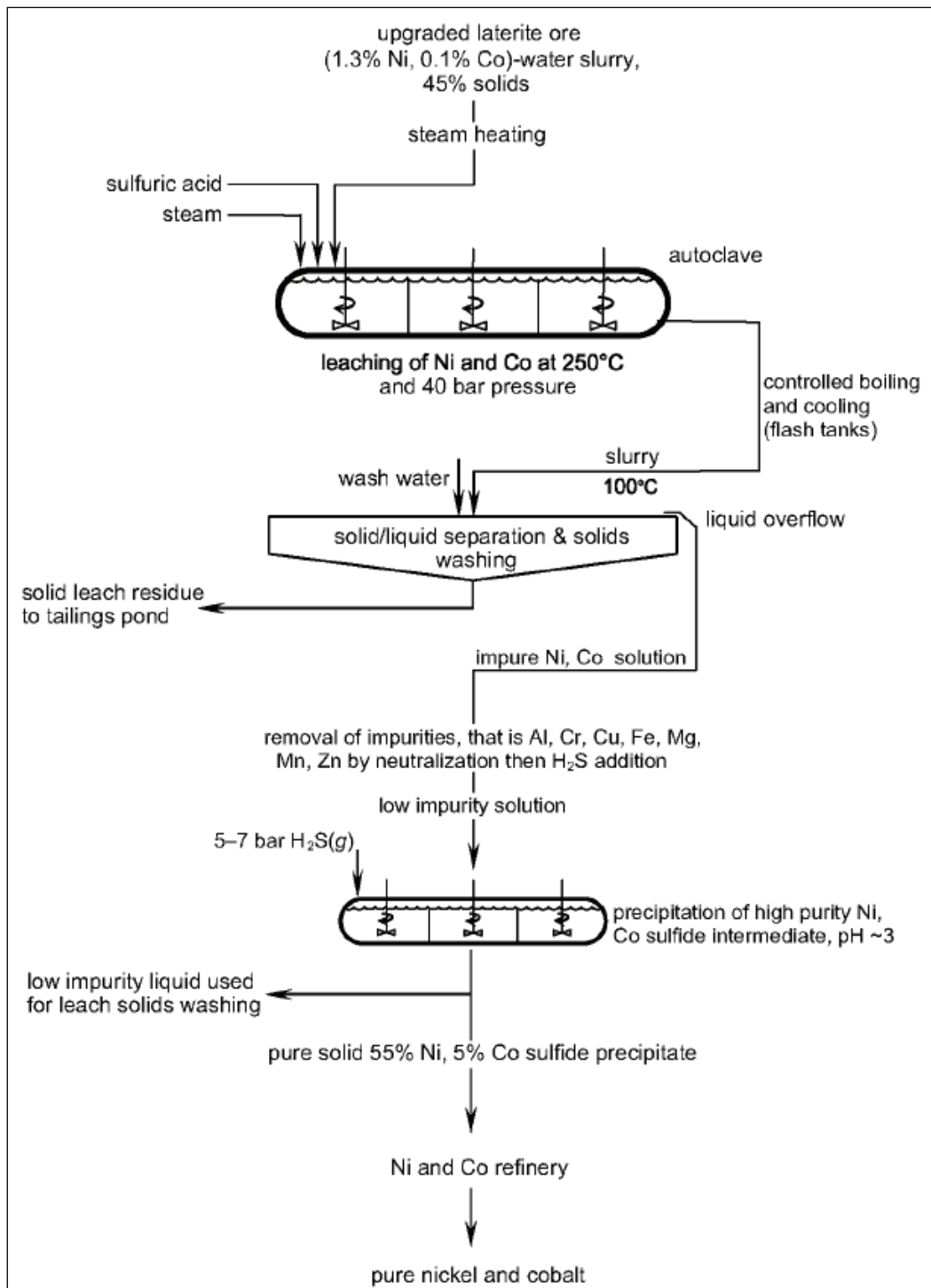


Figure 2. 7. Flowsheet of HPAL process for MSP product
(Source: Crundwell, 2011)⁵

In Gördes lateritic ore deposits, limonite (having mostly goethite mineral) and smectite (nontronite mineral) are present and seen in Figure 2.8. For that reason, the nickel

production method used is HPAL. Gördes process plant's flowsheet is given in Figure 2.9. MHP intermediate product is produced from limonite and nontronite ores.

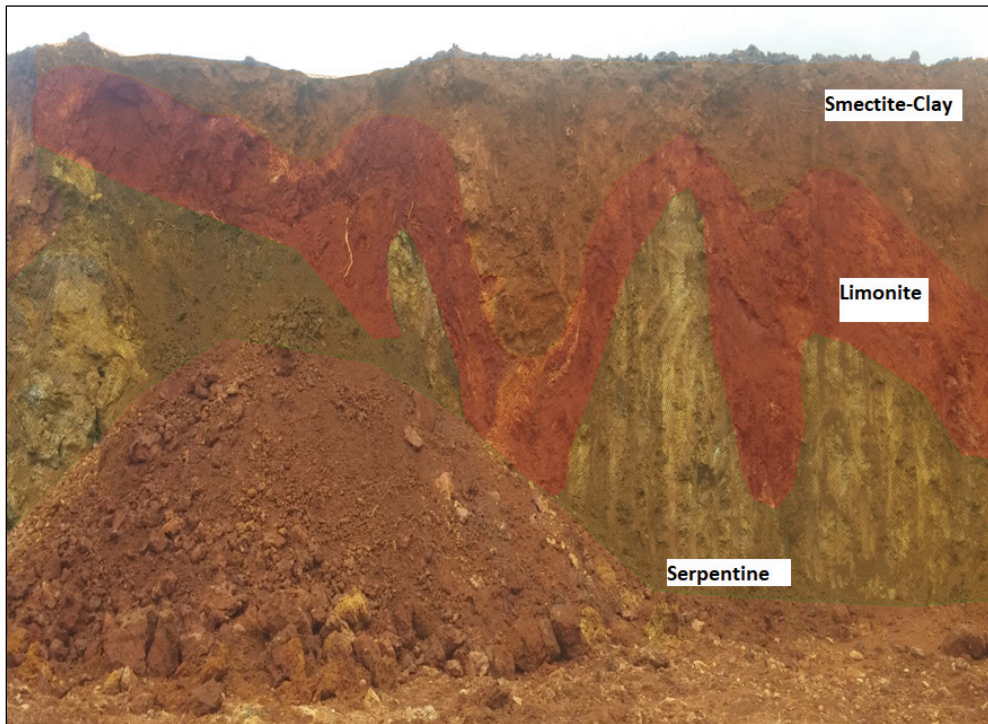


Figure 2. 8. Gördes deposit formation - laterite ore

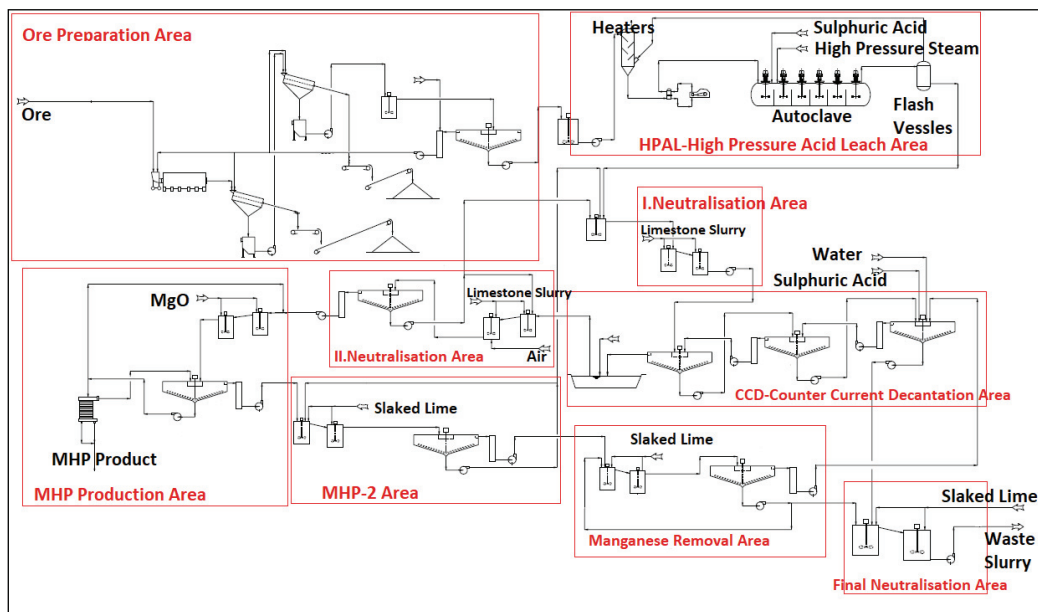


Figure 2. 9. Gördes HPAL Plant process flow sheet

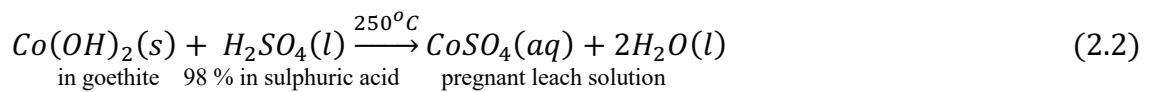
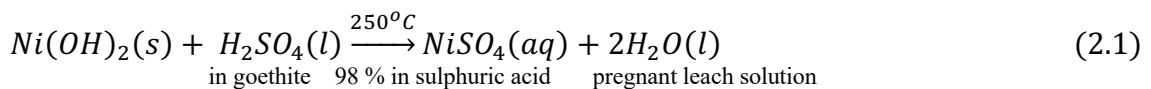
In the Gördes plant, the run-of-mine ore is screened and sized until to specific size such as 750 µm or below and slurried with water and thickened approximately to 38-40% mass percent solids. High solid/liquid interfacial area is provided by small particle sizes in leaching.⁵

Typical leach feed composition is given in Table 1.2⁵, but in Gördes deposit, it changes in the mining area zone by zone.

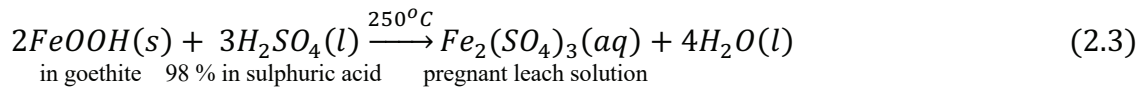
Table 2. 2. Typical leach feed composition of HPAL process⁵

Element	Feed (wt. %)	Main Minerals
Nickel	1.2-1.4	Goethite (Fe[Ni,Co]OOH)
Cobalt	0.08-0.14	Goethite (Fe[Ni,Co]OOH)
Iron	30-50	Goethite (Fe[Ni,Co]OOH)
Silicon	4-20	Lizardite(Mg ₃ Si ₂ O ₅ (OH) ₄), quartz (SiO ₂), talc(Mg ₃ Si ₄ O ₁₀ (OH) ₂)
Magnesium	0.5-4	Lizardite, talc
Aluminium	2-5	Gibbsite (Al(OH) ₃)
Chromium	1-2	Spinel ((Cr,Al,MgFe) ₃ O ₄)
Manganese	0.5-1	Oxide and oxyhydrate
Zinc	Up to 0.05	-
Copper	Up to 0.05	-

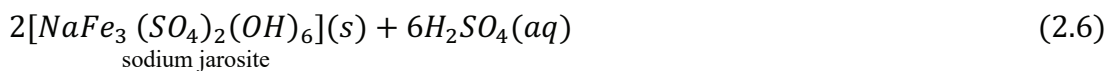
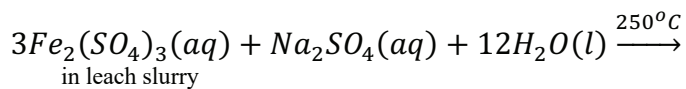
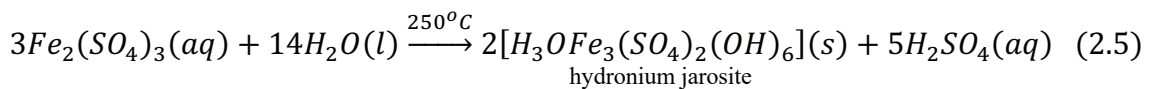
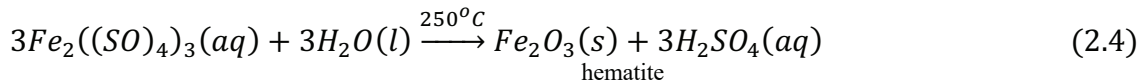
The slurry, which is fed to the HPAL area is heated up in three stages until 200 °C with saturated steam, which is taken from the related three flash tanks and pumped to the autoclave to leach the metals present in the ore. High pressure saturated steam and 98% concentrated sulphuric acid are fed to the autoclave from the first compartment. In the autoclave, Fe, Al, Cr, Ni, Co, Cu, Mn, Zn, Ca, Mg metals and some rare earth are leached in acidic media at 250 °C and transferred from solid phase to aqueous phase as seen in Reaction 1.1 and 1.2 for nickel and cobalt.



Depending on the leaching reaction mechanism, large amount of iron in goethite mineral dissolves rapidly as seen below with Reaction (1.3)⁵



At high temperatures rapidly hydrolysed Fe precipitates as hematite or jarosite in the autoclave and stays in solid phase as seen in Reaction 2.4, 2.5 and Reaction 2.6.



After the autoclave (40-50 atm pressure), acidic leach slurry is transferred to flash vessels. The pressure is decreased to the atmospheric condition in three stages. The flashed steam is sent to heaters to heat the fresh slurry which is coming to the HPAL area.

One of the physical-chemical processes which are applied after HPAL is precipitation. In the precipitation process, the soluble metals transfer from liquid phase to solid phase by converting soluble metals to insoluble salt forms by adding alkaline reagents and increased pH.¹² After the leaching process area, the rest of the process depends on purification by increasing pH with a reagent and solid/liquid separation. Process purification steps base on the metal hydroxides precipitation diagram are seen in Figure 2.10.

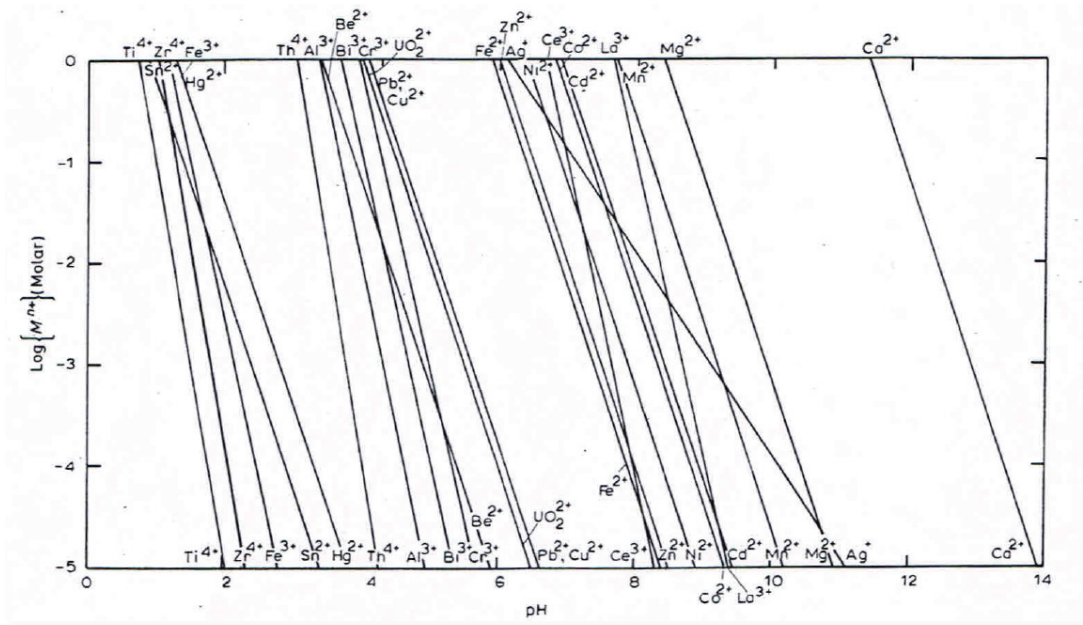


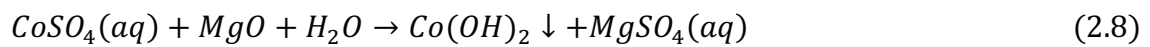
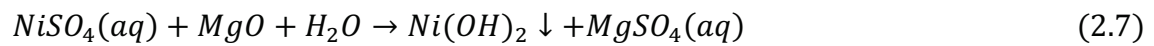
Figure 2. 10. Hydroxide precipitation diagram, 25 °C
(Source: Monhemius, 1977)¹³

For that reason, the slurry coming from the flash tanks is neutralised with CaCO_3 – limestone slurry in the primary neutralisation area by increasing pH to about 3. Most of the Fe and Al are precipitated and transferred from the aqueous phase to the solid phase. A partially neutralised slurry is sent to CCD (Counter Current Decantation) process area for dewatering or solid/liquid separation. In the CCD area, the liquid, which is called pregnant leach solution (PLS), is collected in a pond or a tank and thickened as well as washed solids from the CCD are sent to the final neutralisation area for tailing storage and waste disposal. Then, the accumulated PLS is treated with limestone slurry in the secondary neutralisation area, and the pH value is increased to about 5. So, before the nickel precipitation in MHP production area; Fe, Al, Cu, Zn, Cr are being precipitated as much as possible and at the same time little amount of Ni and Co precipitated with the increase of pH. After the completion of secondary neutralisation, the precipitated solids and PLS are separated by using thickeners. The precipitated solids are transferred to recycle leach tank to gain a specific amount of precipitated nickel and cobalt. After that, in the next step, the purified and Ni concentrated solution is processed by fresh MgO in nickel precipitation tanks which are illustrated in Figure 2.11. So, the bulk of the Ni and Co precipitate and minor amounts of Fe, Al, Zn, Cu, Mn, Cr metals co-precipitate by increasing pH value from 5 to 7.5.



Figure 2. 11. MHP precipitation tank in Gördes HPAL Plant

Nickel and cobalt precipitation reactions are given below:



The obtained precipitate is dewatered in a thickener and sent to filter press. So, MHP intermediate product is produced in a cake form with approximately 50% moisture content, as illustrated in Figure 2.12.



Figure 2. 12. MHP product as cake form

Intermediate products are sold cheaper than final products or it can be said that because of the added value of final products, profits are much more than intermediate

products. For that reason, intermediate products are processed with various chemical methods in order to produce a final product like pure metal, metal sulphate, and carbonate forms, etc.¹⁴ For intermediate products treatment to purify them and produce in the desired material form, the solvent extraction process is the most favoured method since the solvent extraction process is mature and robust.

2.2. MHP Material and Its Characterization

MHP is one of the intermediate products, which includes mainly nickel and cobalt, produced from the PLS by hydrometallurgical processing of a laterite ore. MHP process was first developed as an alternative to MSP (mixed sulphide precipitate) by California Nickel to eliminate undesirable, and costly H₂S precipitation.¹⁵ MHP is leached in ammonia or dilute sulphuric acid before solvent extraction or electrowinning. MHP process was used at Cawse in the past and Ravensthorpe industrial processing plant located in Western Australia is using it at the moment.¹⁶ Currently, the other two companies using the MHP process are Meta Nikel Kobalt in Turkey and Ramu in Papua New Guinea. New plants planning to use the MHP process are under construction in Indonesia.³

As explained above, MHP intermediate product is produced from lateritic ores. In MHP intermediate product, metals are found in the hydroxide form. A typical MHP chemical content is given in Table 2.3.

Table 2. 3. Generic chemical composition data for MHP intermediate product¹⁷

Component	Weight (wt.%)
Nickel	30-39
Cobalt	2-5
Zinc	1-4
Copper	1-4
Manganese	4-9
Magnesium	3-5
Iron	<0.5
Aluminium	0.5
Sulphur	3-5
Moisture	35-45

As seen from Table 1.3, nickel concentration range is between 30-39%, and cobalt concentration range is between 2-5% in MHP product. As seen from the MHP product's XRD pattern, nickel is present as $\text{Ni}(\text{OH})_2$. In addition to that, Mg content of the MHP product is due to unreacted MgO particles and its concentration in MHP changes in a range between 3-5%.¹⁸

In Figure 2.13, the essential mineralogical phases of the MHP are seen as $\text{Ni}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$. The essential peak of XRD, which is $\text{Mg}(\text{OH})_2$ is sharp, and its intensity is high regarding comparison between $\text{Ni}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ peak. This difference is due to the degree of crystallinity of the two main phases. In other words, $\text{Ni}(\text{OH})_2$ crystallinity is poor and has no well-developed crystals.¹⁸

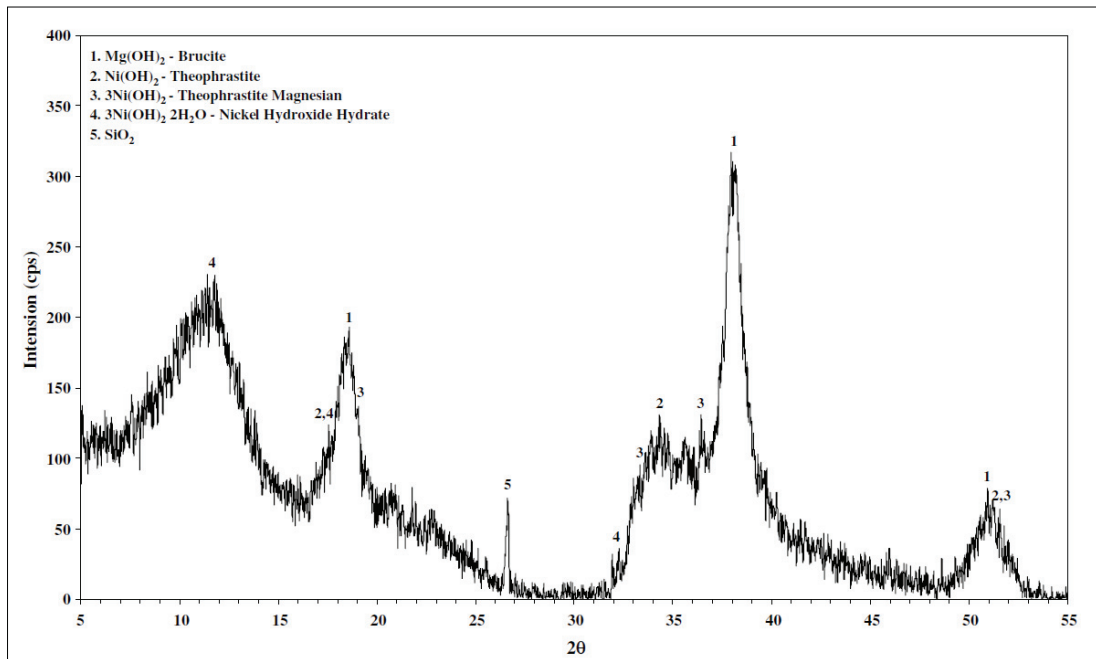


Figure 2. 13. An XRD pattern of the MHP intermediate
(Source: Oustadakis, 2006)¹⁸

Nickel is precipitated with MgO, and MgO particles behave as seed in PLS. Typical MHP material's particle size distribution is seen in Figure 2.14.

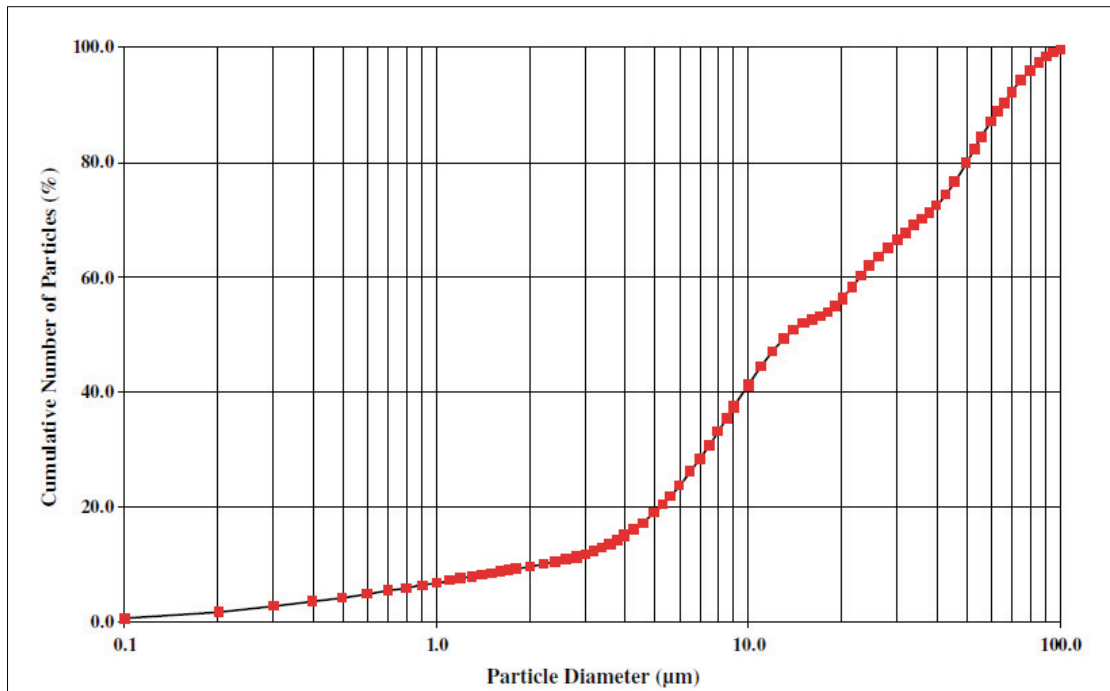


Figure 2. 14. Particle size distribution of the MHP intermediate
(Source: Oustadakis, 2006)¹⁸

It is seen from Figure 2.15 that 50 % of the MHP is below 14 µm, and 100% of the product is below 95 µm.

It is seen from the TGA and DTA in Figure 2.15 that, until 110 °C, moisture water is lost. Until 400 °C heat absorbance is caused by the dihydroxylation reaction of hydroxides and water removal from nickel hydroxide and magnesium hydroxide. The chemical reactions occur as given below.¹⁹



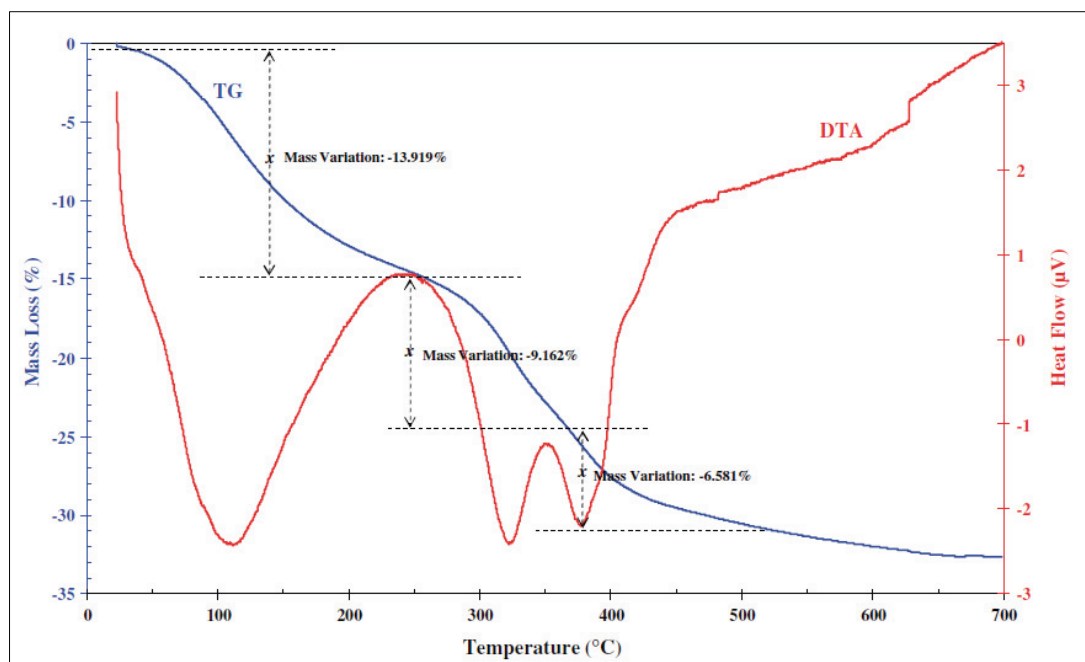


Figure 2. 15. TG and DTA analysis of the MHP intermediate
(Source: Oustadakis, 2006)¹⁸

2.3. Solvent Extraction

Solvent extraction can be described as the distribution of a solute to immiscible liquids. Two liquid phases are the aqueous phase and the organic phase contacted in a vessel. The scientists, engineers, researchers investigate and observe the dynamics and distribution of the solutes in organic and inorganic phases and use it for the industrial separation process for different mixtures.²⁰

The solvent extraction principle is shown in Figure 2.16. There is a vessel which is a separatory funnel containing two immiscible liquid layers. These liquid layers are water and organic solvent. The aqueous phase is denoted as S_{aq} , and the organic solvent is denoted as S_{org} . Generally, organic solvent is lighter than the aqueous phase, but the opposite case is also possible.

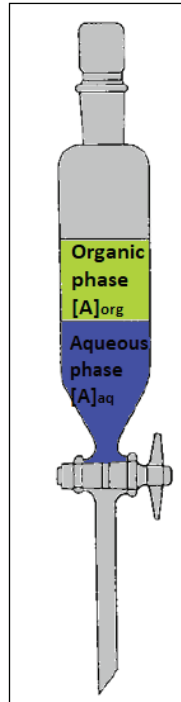


Figure 2. 16. Separatory funnel for solvent extraction
(Source: Rydberg, 2004)²⁰

If a material named A is solute and dissolved in only liquid, this solute A distributes itself between aqueous and organic phases. When the equilibrium is reached, the concentration of A is $[A]_{aq}$ in an aqueous phase. Similarly, the concentration of A is $[A]_{org}$ in the organic phase. The distribution ratio of solute A is expressed as the equation given below (1.11). It is the ratio of the concentration of solute A in the organic phase to the concentration of solute A in the aqueous phase.

$$D = [A]_{org}/[A]_{aq} \quad (2.11)$$

Practically, the percentage extraction or extraction factor is expressed as equation below (2.12) which is preferred in industrial applications since it is more popular.

$$\%E = 100 D/(1 + D) \quad (2.12)$$

D is defined as the distribution ratio for the related component. For example, when D is 1, 50% of the solute A is found in the organic phase, and 50% of the solute A is found in the aqueous phase. The distribution ratio's fundamentals are related to

interactions' between solute and solvent physical chemistry, aqueous complexation, and activity factors of the solutes.

Solvent extraction is a process method preferred in various chemical industries producing pure chemicals like pharmaceuticals, biomedical, heavy organics, metals, and waste purification.

In a solvent extraction system, the organic reagent is dissolved in another organic liquid which is called diluent. The organic solvent is generally used for the whole organic phase to prevent possible confusion.

In the laboratory, tubes, separation funnels, beakers can be used for solvent extraction studies. These are for the tests and experiments. However, in the solvent extraction processing plants, processes are generally run continuously. Thus mixer settlers are used with pumps and agitators for the separation. A mixer, which is also called contactor, is a vessel and has a revolving paddle (agitator). In this section of the equipment, the liquid which is belonging to aqueous or organic is distributed as small droplets in other phases and forms a physical mixture. Later this mixture flows into the settler section of the equipment for the separation, which is a long tank due to the gravity of the phases. Upper flow is a light liquid, which is organic, and lower flow is heavy, which is aqueous. In order to illustrate mixer settler and the general terminology of mixer settler and typical solvent extraction circuit flow sheet are shown in Figure 2.17 and Figure 2.18, respectively.

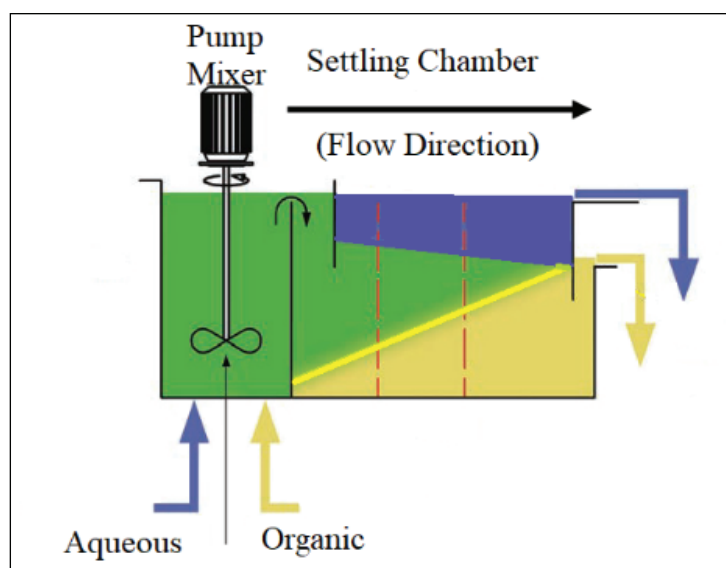


Figure 2. 17. Mixer settler equipment and general terminology
(Source: El-Nadi, 2017)²¹

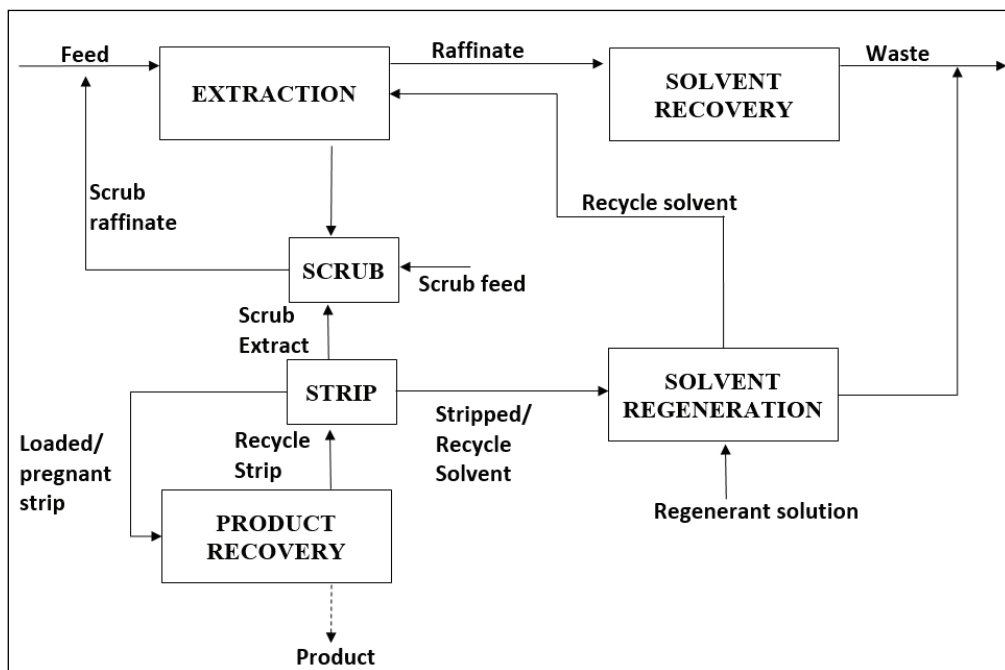


Figure 2. 18. Typical solvent extraction circuit flow sheet
(Source: Rydberg, 2004)²⁰

Generally, the single step extraction stage is not sufficient for the separation. If D value of 100 ($E=99\%$), it means that, after one extraction step, the organic phase is going to obtain 99 parts, and the aqueous part will have a residual part, which is 1. In order to increase extraction, the raffinate, which is an aqueous phase, is contacted in a mixer settler with another amount of organic solvent. 0.99 parts will be transferred to the new organic, and 0.01 part will stay in the aqueous raffinate. Totally, 99.99% extraction will be achieved. (For 2 unit volume organic and 1 unit volume aqueous phase)²⁰

In multi-step extraction, there is more than one stage and there are three different methods of contacting stages or steps. Their names are co-current, cross-current, and counter-current. In the co-current extraction case, both organic and aqueous liquid phases flow together in the same direction. But it is not an efficient choice because in the first stage equilibrium is reached. So, there is no change in the next stage in extraction. In a cross-current case, raffinate is contacted with a fresh and new solvent. Generally, it is used in laboratories with a separatory funnel. But in an industrial case, it is not preferred because of increasing plant size and economics. Counter-current is the best one for industry because of constant volume flow in opposite directions, and this provides the

maximum driving force for metal transfer. Multi-step extraction systems are illustrated in Figure 2.19.

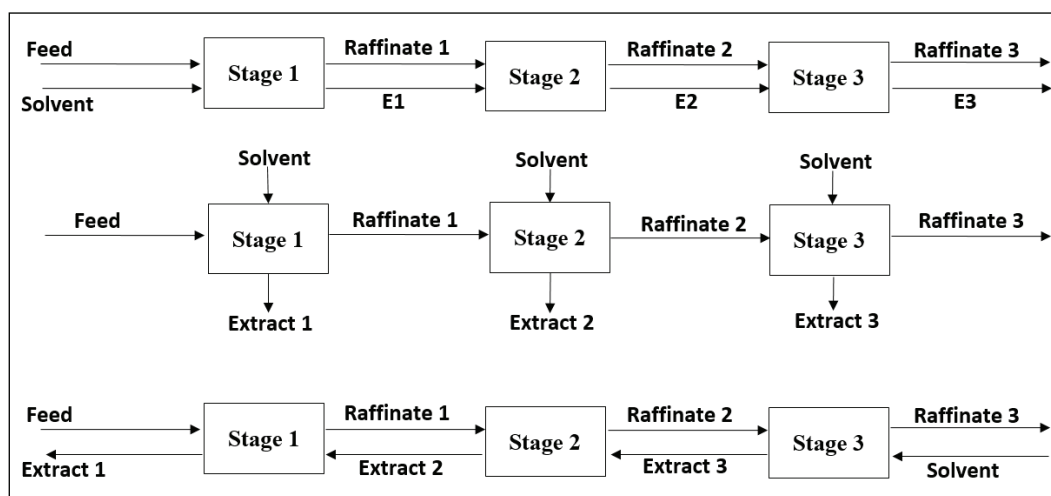
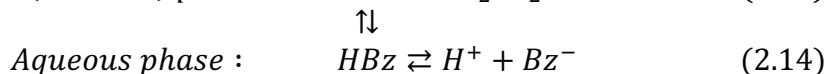
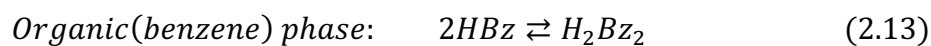


Figure 2. 19. Co-current, cross-current and counter-current arrangement
(Source: Rydberg, 2004)²⁰

In industry, there are different types of extractor equipment. Different types of mixer-settlers, pulsation columns are well-known equipment. It is possible to achieve high purity products like rare earth elements by using different types of reactor in the solvent extraction process.^{22,23}

If the short history of solvent extraction technology is summarized, it is seen that in 1842 Peligot had some pre-explanation with the example of uranyl nitrate. He explained that this component could be separated via recrystallization process from ether, but he did not directly say extraction. After 1870, it was briefly stated that “the ether can even withdraw sublimate (HgCl₂) from aqueous solution”.

The practical usage of solvent extraction to separate and purify the mixtures is expressed by Berthelot and Jungfleisch. They investigated the distribution of the many inorganic and organic chemicals between ether or carbon disulfide and water. In 1872, it was the first time that distribution coefficient term describes the distribution of a solute to organic and aqueous phase depending on the concentration. 20 years later, Nerst showed that different reactions occurred inside each phase. These possible reactions were dimerization in the organic phase and dissociation in the aqueous phase. Benzoic acid (HBz) example is given below. Its reactions are given in Reaction 2.13 for the organic phase and Reaction 2.14 for the aqueous phase, respectively:



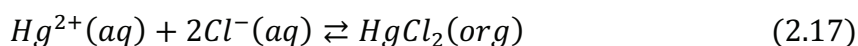
In 1891, Nerst observed that only if the solute has the same molecular weight inside the organic phase as in the aqueous phase, the concentration of the solute will not be dependent on the distribution ratio. It is expressed with simple reaction and validated with the many of the organic and inorganic compounds, which is well known as “Nerst Distribution Law”.

$$K_D = \frac{[HBz]_{org}}{[HBz]_{aq}} \quad (2.15)$$

In solvent extraction, the first parameter is the “measured distribution ratio” and it is already explained by Nerst for the benzoic acid distribution as below:

$$D_{Bz} = \frac{[Bz]_{org,tot}}{[Bz]_{aq,tot}} = \frac{[HBz]_{org} + 2[H_2Bz_2]_{org}}{[HBz]_{aq} + [Bz^-]_{aq}} \quad (2.16)$$

and in 1902, Morse also extended this consideration for metal complexes for divalent mercury between toluene and water at different Hg^{2+} and Cl^- concentrations. The overall reaction can be given as:

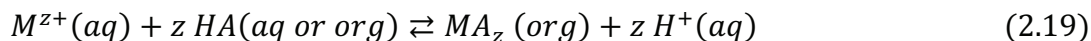


and extraction constant (K_{ex}) is given as,

$$K_{ex} = \frac{[HgCl_2]_{org}}{[Hg^{2+}]_{aq}[Cl^-]_{aq}^2} \quad (2.18)$$

Solvent extraction technology generally was used for the separation of organic substances between 1900 and 1940 years. Desired components generally exist in only one molecular form, and they are called a non-reactive extraction system. In this case, the distribution ratio is the same as the distribution constant. Later, it was found out that many

organic samples, generally weak acids, could be bonded with various metals in the aqueous phase to form a complex in the organic phase. The generic reaction can be given as:



This reaction is an example of reactive extraction. The responsible reagent for the extraction is extractant or organic reactive. When the reaction has occurred, it is possible to show a specific color change which could be identified spectrometrically, and it became a tool for the researchers.

The first industrial usage of solvent extraction was for uranium production, and it was for U.S. Manhattan Project to reprocess irradiated nuclear materials in the decades of 1940. In 1942, the first large scale industrial plant was designed and built for uranium production for a high degree of purity for the nuclear reactor. It was a important discovery for the non-nuclear industry, and solvent extraction became the most famous process for separation and purification for metallurgy and chemistry between the 1950 and 1960. An example of this progress is the leaching of copper ore with sulphuric acid and combining with the solvent extraction process with the organic hydroxyaryloxime dissolved in kerosene. For these similar applications, solvent extraction has progressed, and new terminology was gained by the researchers.²⁰

2.3.1. Solvent Extraction Process Stages

The solvent extraction process consists of three main stages, which are extraction, scrub, and strip. In some cases, there are additional stages, such as the stage for the organic phase. In order to understand each stage's purpose, these are described, and detailed as below.

2.3.1.1. Extraction

In solvent extraction, the feed is an incoming aqueous solution. The aqueous solution (metal bearing) is contacted with the solvent phase (organic contain diluent and organic reactive) and target metals transfer from aqueous phase to organic phase, as extraction occurs. At the end of extraction, the depleted phase is called the raffinate and

enriched phase, which is organic called extract or loaded organic. In extraction, depending on the pH, temperature, and type of organic reactive, the reaction occurs as seen in Equation 1.20. For nickel and cobalt reactions are also is given as Equations 1.21 and 1.22, respectively.



Loading of an organic phase or reactions in the extraction step is based on metal bonding with organic reactive and releasing H^+ ions into the solution. In order to show hydrogen release, an example of an organic reactant structure, which is D2EHPA, is illustrated in Figure 2.20 (a). In industry, generally D2EHPA organic reactive is used commercially for Zn, Mn, Ca impurity removal stage for nickel and cobalt production. In addition to that, in the nickel and cobalt process, after the impurity removal stage, Cyanex 272 organic reactant is used for nickel and cobalt separation by loading cobalt onto the organic phase, and its chemical structure is illustrated in Figure 2.20 (b).^{24,25}

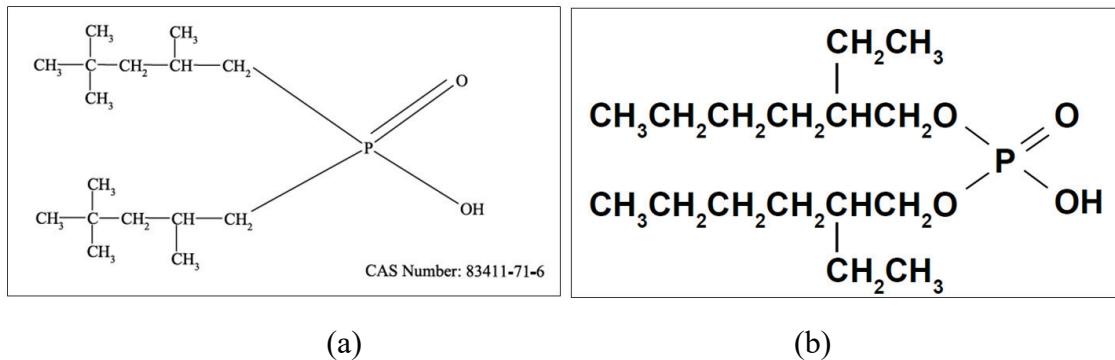


Figure 2. 20. Chemical structure of organic reactants
 (a) D2EHPA (Source: Cytec, 2016)²⁶
 (b) Cyanex 272 (Source: Cytec, 2018)²⁷

When metals are extracted to the organic phase, the extraction process is affected by organic reactive type, solution conditions (pH, temperature), and aqueous phase content. In order to emphasise pH value importance and for the initial start of the

experimentally designing a process for D2EHPA and Cyanex 272 organic reactants % Extraction - pH curves are given in Figure 2.21 and Figure 2.22, respectively.

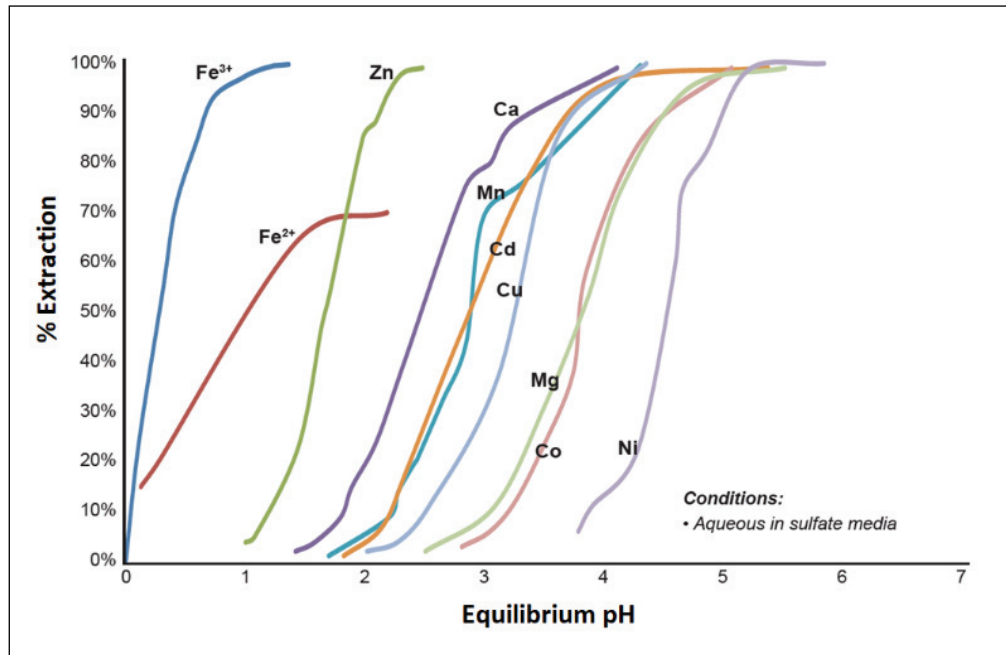


Figure 2. 21. D2EHPA reactive % extraction-pH curve for sulphate media (Source: Cytec, 2016)²⁶

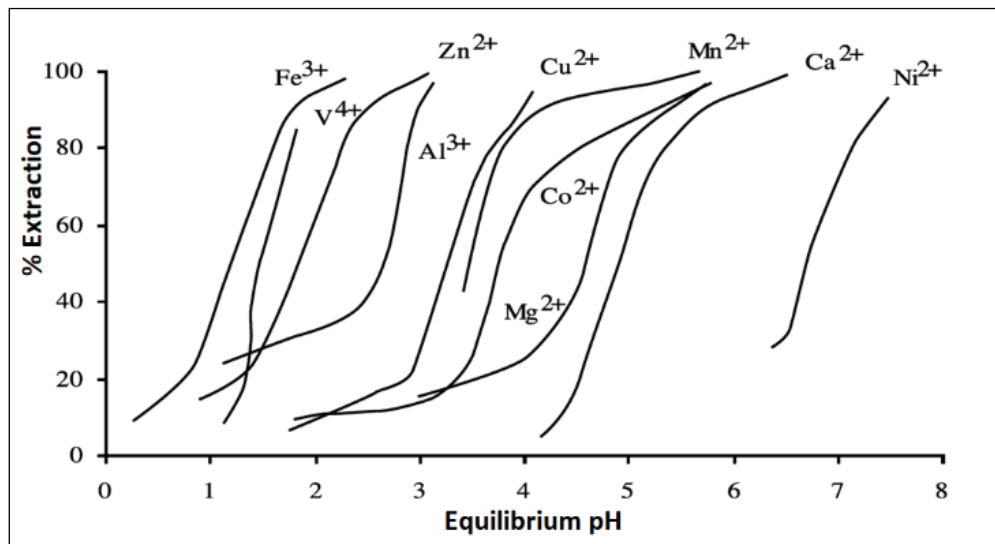


Figure 2. 22. Cyanex 272 reactive % extraction-pH curve for sulphate media (Source: Cytec, 2018)²⁷

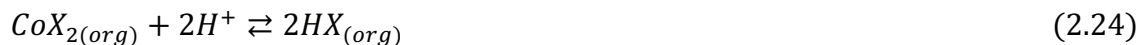
2.3.1.2. Scrubbing

The extraction is specific to solute, but other components or metals can co-extract with the main component. These co-extracted components called impurities and impurities can be removed with an aqueous solution. In the scrub step, the outputs are extracted and scrub raffinate. The scrub raffinate can return to feed solution if it is favoured.²⁰

Co-extracted components or metals with the target metals are generally released into the solution by an acidic scrub wash with decreasing pH value. The purpose of this stage is to make the loaded organic phase contain target metals or components as much as possible. Scrubbing reaction mechanisms are similar to stripping reactions.

2.3.1.3. Stripping

The scrubbed extract is processed via contact with an aqueous solution, and desired component is transferred by stripping to the aqueous phase. The purpose of this stage is to obtain an aqueous solution that contains the target metal or component. The stripped organic may be treated in a regeneration process for the recycling of the organic phase. Strip solution also can be recycled after the desired component is taken. Stripping reactions are exemplified for nickel and cobalt separation cases with Equations 2.23 and 2.24, respectively.



In industry, counter-current arrangement is generally preferred and the whole extraction, scrub, strip, regeneration and pre-neutralisation steps are illustrated in Figure 2.23 below.

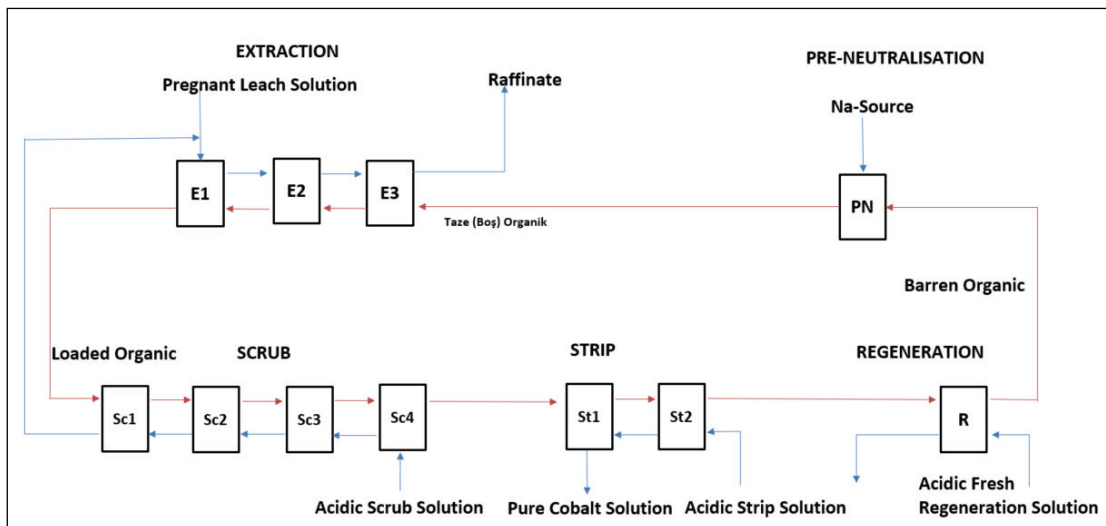


Figure 2. 23. An illustration of the typical solvent extraction process
(Source: Rydberg, 2004)²⁰

2.3.2. Extractant Types and Selection Criteria

Solvents, extractant types, or organic reactivities are classified by various methods such as functional groups, bonding types, etc. In order to have a general viewpoint, in the first case, solvent types are classified into five classes. These are explained as Class 1, 2, 3, 4, and 5 as follows:

Class 1 is liquids that can form a three-dimensional network with strong hydrogen bonds. Example for this type, poly-and amino-alcohols, hydroxy-acids, etc.

Class 2 is liquids that can form hydrogen atoms with donor atoms, but they do not form a three-dimensional network. Example for this type primary alcohols, carboxylic acids, primary and secondary amines, various nitro compounds, liquified ammonia, etc (protic or protogenic substances)

Class 3 is liquids that have donor atom but no active hydrogen atoms. Examples for this type ethers, ketones, aldehydes, esters, tertiary amines (dipolar aprotic samples).

Class 4 is liquids that have active hydrogen atoms but they will not have donor atoms. Example for this type chloroform and some other aliphatic halides.

Class 5 is liquids do not have hydrogen bonds (to form capability) and do not have donor atoms. Examples for these types of hydrocarbons, carbon disulfide, carbon tetrachloride, etc.

After dividing solvents into five groups, it is seen that Class 1 solvents' solubility are very high in water and cannot be used for metal substances. Class 3 are very active solvents, they can react directly with the inorganic substances, and they do not need any additive reagents. Class 4 and 5 groups cannot react directly as Class 3. Although they are used to promote and improve physical properties such as viscosity and density. They are also called diluents.²⁰

In order to have a perspective about chemical reaction tendency or extraction reaction chemistry, in the second case, it is possible to collect extractants under four main groups.

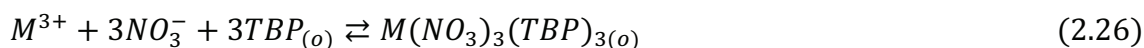
Cationic extractants release protons and exchange cations. In the following equation, M is n valence ion, and HA is a protonated extractant. Some chelating extractants are also in this group.



Carboxylic acids (Versatic 10, Versatic 911), Phosphorous acid (Phosphoric acid such as DEHPA, Phosphonic acid such as P507, PC-88A, Phosphinic acid such as P299, Cyanex 272,301, 302), Aryl sulfonic acids such as Synex 1051, some oximes such as ACORGA and LIX reagents are most common cationic extractants.²⁸

Anionic extractants are used in metal extraction as complexes with strong anionic ligands. Primary amines such as Primene JMT and N1923 and Tertiary amines such as Alamine 336 are belonging to this group of extractant.²⁸

Solvating extractants are used in neutral metal salts and organic solvent complexes. If it is required to give an example of a reaction equation for TBP,



Phosphorous esters, such as TBP, Phosphinic oxides, such as Cyanex 921 (TOPO) and Cyanex 923.²⁸

Coordination extractant based on dissociation and association in order to build coordinated complexes. They are very selective for the ions. So, extraction is limited because of the position of atoms (steric interactions) constraining the molecules. LIX and EDTA reagents are well-known extractants.²⁹

In addition to that, in industry, the most commonly used commercial acidic organic extractants are also given in Table 2.4.

Table 2. 4. Commercial acidic extractants²⁰

Reagent Class	Extractants
Carboxylic Acids	Naphthenic acids
	Versatic Acids
Phosphoric acids	mono-2ethylhexylphosphoric acid
	di-2-ethylhexylphosphoric acid (D2EHPA)
	di-p-octylphenylphosphoric acid (OPPA)
Phosphonic acids	2-ethylhexylphosphonic acid (PC88A)
	mono-2-ethylhexyl ester (P-507)
Phosphinic acids	di-2-ethylhexylphosphinic acid (p-229)
	di-2,4,4-trimethylpentyl-phosphinic acid (Cyanex 272)
Thiophosphorus acids	di-2,4,4-trimethylpentyl-monothiophosphinic acid (Cyanex 302]
	di-2,4,4-trimethylpentyl-dithiophosphinic acid (Cyanex 301)
Sulfonic acid	5,8-dinonylnaphthanesul-phonic acid DNNSA

After the classification of the solvents according to general classification or extraction reaction chemistry, extractant selection criteria are aligned with six sub-titles. These are selectivity, high capacity of extraction, distribution coefficient, and ease of stripping, ease of separation from water, safety – non-toxic, and non-flammable and cost.

Selectivity is the key criteria for a successful extraction. The solvent which is used in the process should have a high affinity for the target metals.

The distribution coefficient is also critical criteria. The distribution coefficient tells metal concentration in the organic phase to the aqueous phase. If the distribution coefficient is high enough, the extraction occurs efficiently.

The high capacity of extraction is a significant concern. Extractant used in the process should have a high capacity to load target metals for optimum separation.

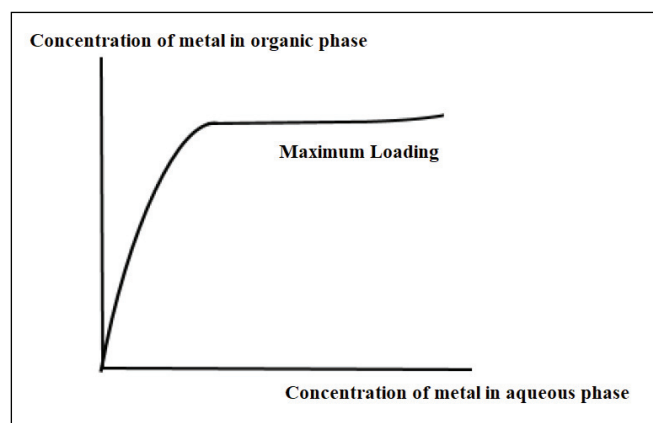


Figure 2. 24. The capacity of the organic extractant³⁰

Ease of stripping of extractant similarly easy regeneration of extractant play important roles in the extraction process.

Ease of separation from water is another important criterion. Used extractants in the process should separate from the water easily and fast for the continuous process. For the health and safety and environment, extractants should be non-toxic and non-flammable.³¹

Similarly, it is possible to consider other criteria such as solvent solubility, the viscosity of the extractant, density of the extractant, chemical stability, recoverability, and possible corrosion tendency. All of these criteria should be evaluated by the researchers and designer for the studies.²⁰

Lastly, the cost issue will be important for the process. Operational expenditure is directly affected by solvent and extractant costs.³⁰

When the researchers decide on separation of some substances or if there is a separate problem occurring in a process, pH of the solution, acidic or basic characters of the substances, additives, availability of the solid in the solution such as suspended solid or colloidal, restrictions, feed and raffinate compositions, toxic components or substances, stabilities of the reagents should be checked and considered.²⁰

When the literature reviewed and commercial applications are checked, it is possible to see that the most favoured extractant for nickel, and cobalt separation is Cyanex 272. But before the separation of the nickel and cobalt, as explained already, MHP material has impurities such as Fe, Al, Mg, Ca, Cr, Mn, Cu, Sc, Zn and some other metals. In order to remove impurities, initially, DEHPA extractant can be used for the

leached MHP liquor. In addition to that, in industry, different extractants are used for nickel and cobalt separation.³²

2.3.3. Additive Reagents

Additive reagents are divided into two groups which are diluents and modifiers.

Diluents are used in solvent extraction with organic reactive or extractant for the proper density and viscosity for the organic phase. In solvent extraction, diluents generally are chosen from hydrocarbons which are aliphatic, aromatic or a mixture of them. It can be considered a carrier for organic reactants such as D2EHPA and Cyanex 272. The most commonly used diluents are given in Table 2.5.³³

Table 2. 5. Most commonly used diluents in industry³³

Diluent	Specific Gravity (20°C)	Boiling Point (°C)
Aromatic Group		
Benzene	0.833	80
Toluene	0.873	110
Xylene	0.870	138
Solvesso 100	0.876	157
Solvesso150	0.931	188
Shellsol D60	0.78-0.81	179-213.9
EXXSOL D80 Fluid	0.798	200-250
Medium Aromatic Group		
Escald 100	0.797	193
Low Aromatic		
Escaid 100	0.816	199
Naptha 140 Flash	0.785	60.5
Aliphatic		
Mineral Spirits	0.785	157
Odorless 360	0.761	177
Aliphatic with Napthenes Group		
Isoparo L	0.767	189
Shell 140	0.79	
Kermac 470 B	0.81	

In the solvent extraction, depending on the processing conditions, sometimes occur some problems such as crud problems or third phase formation. In Figure 2.25, the third phase formation is illustrated. In such cases, solvent extraction does not work properly, and sometimes processes need additive chemicals.

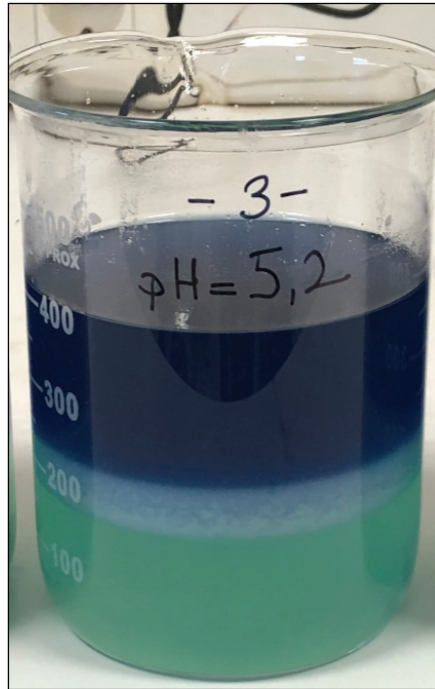


Figure 2. 25. Third phase formation illustration

Modifiers are generally used to prevent third phase and crud formation. In addition to that, modifiers are used to enhance the phase separation in extraction, scrubbing and stripping stages. The most commonly used modifiers are given in Table 2.6.³³

Table 2. 6. Well known modifiers in industry³³

Modifier	Specific Gravity (20 °C)	Flash Point (°C)
2- Ethylhexanol	0.833	85
Isodecanol	0.841	104
Nonylphenol	0.95	140
Tri-n-butyl phosphate	0.973	193

2.4. Pre-neutralisation Application

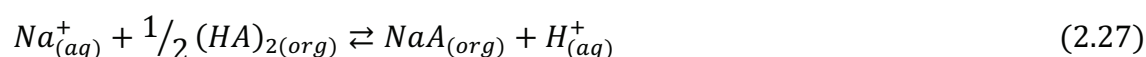
Pre-neutralisation (saponification) is partially neutralising of the acidic characterized organic reactive or extractant. The barren organic phase, which is fed for extraction, is mixed with a sodium source such as NaOH, Na₂CO₃, NaCl, Na₂SO₄, and NaNO₃ in a vessel or industrially in a mixer settler before the extraction step. Hydrogen ion (H⁺) from the organic phase exchanges with sodium (Na⁺) cation. It is preferred because pH control is simplified in the mixer settler within a tight range.²⁴

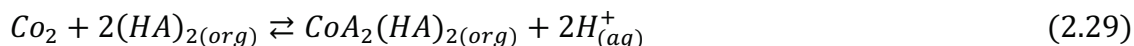
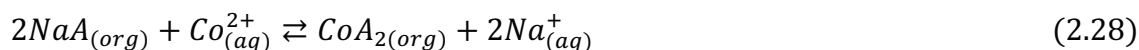
During the metal loading to the organic phase, pH fluctuation occurs because metals that bond with the organic phase causes H⁺ ion release, and pH decreases rapidly, and it must be controlled, otherwise extraction is not achieved as required. Similarly, if pH increases in mixer settler without pre-neutralisation step, high pH value may exhibit increased co-extraction of impurities. As already explained, pH control is very important in solvent extraction because depending on the target metal and organic reactive property, extraction and metal recovery are directly affected. If the pH control is not provided as required, the total metal recovery and efficiency of the refinery unit of the process plant are not sufficient. In addition to that, if pH is not controlled as desired, it is possible that impurity metals cannot be purified, and the final product such as nickel metal, cobalt metal or their sulphate form cannot meet the special specifications.

Pre-neutralisation percent is an important parameter because if it is kept higher than the allowed value for conditioning, it is possible to form a third phase (crud formation) in the mixer settler, and see some viscosity problems.³⁴ In addition to that, organic reagents can be degraded and cannot be used repetitively. In this case, the process is not economical and due to the make-up organic reactive it is possible to bring additional operational costs. On the other hand, if it is kept lower than required, pH cannot be controlled efficiently, and metal extraction stays under a specific level, and similarly efficiency decreases causing economic problems.

Pre-neutralised acidic extractant has additional advantages in case of the presence of an only monomeric form of the extractant. It is also possible that this salt application improves the extraction efficiency.³⁵

For pre-neutralisation step, the reactions are given as below:





An example of the pre-neutralisation of Cyanex 272 is illustrated in Figure 2.1:



Figure 2. 26. Pre-neutralisation of Cyanex 272 with NaOH reagent (Source: Regel-Rosocka, 2016)³⁶

The dimer form of Cyanex 272 is illustrated in Figure 2.2.

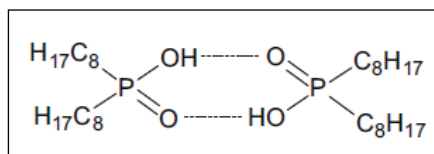


Figure 2. 27. Dimerization of the Cyanex 272 – bis (2,4,4-trimethylpentyl) phosphinic acid (Source: Rydberg, 2004)²⁰

After pre-neutralisation of the organic reactivities such as Cyanex 272; Na-Cyanex 272 itself, both can act as extractants, but their extraction mechanisms show some differences.³⁶

There are some scientific studies about pre-neutralisation in the literature. In a study by Kang for the recovery cobalt in solvent extraction process from a sulphate liquor, it was used to control pH efficiently by pre-neutralisation studies. In pre-neutralisation of the organic reactive, which has acidic character, pre-neutralisation percent was varied in a range between 25% and 75%, and the optimum was found out to be 50%. In addition to that, it was seen that the extraction efficiency had also increased by 50% pre-neutralisation percent.³⁷

In a few studies by Devi, sodium salts of Cyanex 272, D2EHPA, and PC-99 organic reactants were used for Ni (II), Co(II), and Zn(II) extractions from the sulphate solution, and it was found out Na-Cyanex 272 is the best extractant for Co(II) extraction.^{35,38,39,40}

In a study by Reddy, the nickel and cobalt separation from the copper sulphate solution was done Na-Cyanex 272 and Na-D2EHPA, and it was stated that 100% overall metal recovery was achieved.⁴¹

In a study by Magdalena, it is seen that Na-Cyanex 272 extraction percent was higher than Cyanex 272 due to that acidic extractant forming dimers and Na-Cyanex 272 was forming monomers in sulphate media for Co(II) and Zn(II) extraction.³⁶

In another scientific study by Nathsarma, phosphoric, phosphonic, and phosphinic extractants of solvent extraction for Co and Zn were tested and it was stated that pre-neutralisation of the organic reagents improves extraction quality. Increasing the neutralisation percent also enhances the extraction.⁴²

In a thesis study by Eronen, it was stated that pre-neutralisation percent should vary from 30% to 50%. Neutralisation of more than 50% of acidic extractant often requires a phase modifier to prevent third phase formation.⁴³

2.4.1. Pre-neutralisation Reagents

Pre-neutralisation reagents such as NaOH, Na₂CO₃, NaCl, Na₂SO₄, and NaNO₃ are sodium sources. According to the experimental results, it is indicated that NaCl and NaNO₃ influence are not important to extractants. In addition to that, in a research study by Devi, the percentage extraction decreased in D2EHPA, PC-88A, and Cyanex 272 with increasing concentration of Na₂SO₄. For that reason, industrial solvent extraction processing plants generally use NaOH and Na₂CO₃.^{35,44}

CHAPTER 3

EXPERIMENTAL

3.1. Raw Materials and Reagents

MHP, which was produced from Gördes laterite ore, was used as raw material in this research, and the composition of this material is given in Table 3.1. The material has approximately 50% moisture content.

Table 3. 1. MHP intermediate material chemical composition (on dry basis)

Chemical composition of MHP (ppm)												
Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Sc	Zn	Si
5170	5158	21744	1832	803	1497	25584	52876	155	348964	124	4770	1750

MHP slurry was prepared by deionized water, which was supplied as 3 μ S/cm using Merck Millipore with MILLI-Q 8/16 System water purification system.

Concentrated H₂SO₄ was used for nickel and cobalt as leaching reagent, which was supplied by Aurubis.⁴⁵ Specification of the sulphuric acid is given in Table 3.2.

Table 3. 2. Specification of sulphuric acid⁴⁵

Ash Content (ppm)	<50
H ₂ SO ₄ wt. (%)	96.0% +/-0.5%
Fe (ppm)	<25 (typically <15)
Ni (ppm)	<1
Cr (ppm)	<1.5
Mn (ppm)	<0.3
SO ₂ (ppm)	<30
Cl (ppm)	< 2
As (ppm)	<0.2 (typically 0.1)
Pb (ppm)	0.3

pH control reagents and their concentrations are given in Table 3.3.

Table 3. 3. Reagents for pH control

pH Control Reagent	Concentration
NaOH (M)	1
Na ₂ CO ₃ (wt.%)	5
H ₂ SO ₄ (M)	1

D2EHPA (di-ethylhexyl) phosphoric acid was used for impurity removal in single-stage solvent extraction experiments, which was supplied by Solvay. Typical properties for D2EHPA are given in Table 3.4.²⁶

Table 3. 4. Properties of D2EHPA organic reactive²⁶

Parameter	Value
Appearance	Clear colourless
Molecular Weight (g/mol)	322.4
Flash Point (°C)	150
Density, 25 °C (g/cc)	0.974
Viscosity, 0°C (cp)	160

Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid) was used for nickel and cobalt separation in single-stage solvent extraction experiments which was supplied by Solvay. Typical properties for Cyanex 272 are given in Table 3.5.²⁷

Table 3. 5. Properties of Cyanex 272 organic reactive²⁷

Parameter	Value
Appearance	Clear colorless
Molecular Weight (g/mol)	290
Flash Point (°C)	<108
Density, 24 °C (g/cc)	0.920
Viscosity, 25°C (cp)	142

For pre-neutralisation of both acidic extractants (D2EHPA and Cyanex 272), NaOH and Na₂CO₃ of Merck quality reagents were used before extraction experiments.

Kerosene was used as a diluent, which was supplied by ExxonMobil as D80. Typical properties for kerosene D80 are given in Table 3.6.⁴⁶

Table 3. 6. Properties of kerosene⁴⁶

Parameter	Value
Diluent Name	Exxsol TM D80
Molecular Weight (g/mol)	178
Flash Point (°C)	>75
Density 24 °C (g/cc)	0.798
Viscosity, 25°C (cSt)	2.16

3.2. Equipment

In MHP slurry preparation, leaching, neutralisation, pre-neutralisation of organic phase, and extraction, IKA CMAG HS 7 model magnetic stirrer hot plate with a magnetic stirrer was used. For Cyanex 272 experiments, the aqueous phase, which was D2EHPA raffinate, was produced by using IKA model mechanical stirrer. In addition to these, a vacuum line (a vacuum system in the laboratory) was also used for solid-liquid separation. Organic phases were prepared in a 5 L beaker by using a glass graduated cylinder and pre-neutralised in a 500 ml beaker. Similarly, solvent extraction experiments were done in beakers under continuous mixing and aqueous, and organic phases were separated with a separatory funnel.

3.3. MHP Processing and Solvent Extraction Procedure

Experimental studies were carried out in three main steps, which were pre-neutralisation of organic phases with different percent, and extraction experiments with pre-neutralised organic phases after the production of PLS. Initially, D2EHPA experiments were carried out for impurity removal and Cyanex 272 experiments were carried out for nickel and cobalt separation with NaOH and Na₂CO₃.

In the extraction steps, pH was controlled by using NaOH and Na₂CO₃ for increasing pH, and by sulphuric acid for decreasing pH. The order of these experiments is illustrated in Figure 3.1. In this figure, D2EHPA raffinate, which was aqueous phase for Cyanex 272 was already purified by D2EHPA with NaOH at pH 5.5 without pre-neutralisation.

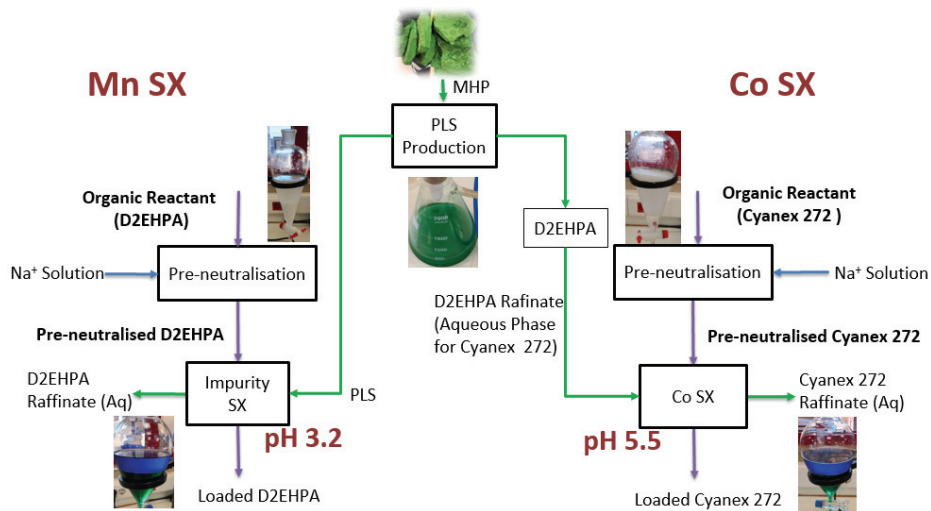


Figure 3. 1. Illustrated experiment plan

3.3.1 MHP Leaching and Organic Phase Preparation

Gördes MHP material slurry was prepared with demineralized water as 20 wt.% and leached for 1 hour with concentrated sulphuric acid at pH approximately 2 and 60 °C temperature. Metals in hydroxide form in the MHP material were leached at atmospheric pressure. Then, the leached slurry was neutralised at pH 3.5 with CaCO₃ slurry with 30 wt.% which was supplied by Gördes Nickel and Cobalt Process Plant. After the leaching and neutralisation stage, the purified leach liquor was obtained for solvent extraction experiments, as illustrated in Figure 3.2. Similar leaching MHP process was already studied in some scientific studies.⁴⁷

PLS was used in D2EHPA experiments, and some amount of PLS was also purified at pH 3.2 to obtain an aqueous phase (D2EHPA raffinate) for Cyanex 272 experiments.

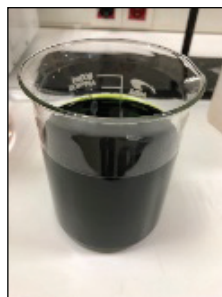


Figure 3. 2. Pregnant Leach Solution (PLS)

According to the PLS chemical composition, D2EHPA and Cyanex 272 organic phases were prepared with the addition of a diluent, which was kerosene D80. Detailed calculations for molarity and further information are given in Appendix A.

D2EHPA organic phases containing 20% D2EHPA were diluted with kerosene as v/v. The molarity of the organic phase was calculated as 0.6 M. The organic phase preparation is given in Table 3.7.

Table 3. 7. D2EHPA organic phase preparation details

Organic Phase - 80% Kerosene + 20% D2EHPA (v/v)					
Extractant	Amount of Extractant (ml)	Diluent	Amount of Diluent (ml)	Total Organic Phase (ml)	Molarity (M)
D2EHPA	1600	Kerosene D80	6400	8000	0.6

Cyanex 272 organic phases containing 13% Cyanex 272 was diluted with kerosene D80 as v/v. The molarity of the organic phase was calculated as 0.4 M. Cyanex 272 organic phase preparation is given in Table 3.8.

Table 3. 8. Cyanex 272 organic phase preparation details

Organic Phase - 87 % Kerosene + 13 % Cyanex 272 (v/v)					
Extractant	Amount of Extractant (ml)	Diluent	Amount of Diluent (ml)	Total Organic Phase (ml)	Molarity (M)
Cyanex 272	520	Kerosene D80	3480	4000	0.4

3.3.2 Pre-neutralisation Step with Different Percent

In each experiment, 200 ml organic phase was taken to a beaker and stirred with the magnetic stirrer at 250 rpm. Depending on the pre-neutralisation percent, 1 M NaOH or 5 wt.% Na₂CO₃ solution was added drop by drop to mixing D2EHPA organic phase in Mn SX and Cyanex 272 organic phase in Co SX. After the addition of final droplet, 5 minutes were allowed for the pre-neutralisation process to be completed. Finally, magnetic stirring was stopped and the organic, and aqueous solution mixture was transferred to a separatory funnel. Phase separation time was measured and recorded. The spent NaOH/Na₂CO₃ solution was separated as waste. The organic phase, which was Na-

D2EHPA or Na-Cyanex 272 volumes, was measured with a measuring cylinder and recorded.

3.3.3 Extraction Experiments

In D2EHPA extraction experiments, pH was kept at the 3.2 range at room temperature because this pH value was known to be the best value favourable for loading impurity metals to organic reactive without loading nickel and cobalt metals. Controlling of pH was provided by the related Na sources. If in the previous pre-neutralisation stage NaOH was used, pH controlling reagent was taken as NaOH. Similarly, if in the previous pre-neutralisation Na_2CO_3 was used, pH controlling reagent was taken as Na_2CO_3 . In addition, in each extraction experiment, the aqueous phase volume to organic phase volume ratio was chosen as one to one (A/O:1/1). After the mixing of organic and aqueous phases in a beaker for 5 minutes at 500 rpm, the agitator was stopped, and it was waited for phase disengagement. Finally, samples were taken both from the aqueous and organic phases.

In Cyanex 272 extraction experiments, pH was kept at 5.5 because this pH value is known to be the best range for selective loading of cobalt to organic reactive without loading nickel. Depending on the phase disengagement, at room temperature and different temperatures such as 25-30 °C, 45-50 °C and 50 °C, experiments were conducted. Controlling of pH was provided by related Na sources. This meant that, if in the previous pre-neutralisation stage NaOH was used, pH controlling reagent was taken as NaOH. Similarly, if in the previous pre-neutralisation Na_2CO_3 was used, pH controlling reagent was taken as Na_2CO_3 . In addition to that, in extraction, the aqueous phase volume to organic phase volume ratio was taken as one to one (A/O:1/1). After mixing organic and aqueous phases in a beaker for 5 minutes, the agitator was stopped and it was waited for phase disengagement. Samples were taken from both aqueous, and organic phases.

3.4. Analytical Methods

For the structural characterization, the phase analysis of MHP material was analysed with the Philips X'Pert Pro instrument(2θ , between 10° and 80° with the scan step; 0.005 °/second). The decomposition behaviour and phase transition points of MHP

were analysed by thermogravimetric analysis (TGA, Perkin Elmer, STA 6000). For this purpose, the MHP sample was heated from 30 °C to 900 °C with a 10 °C.min⁻¹ heating rate in N₂ gas. Nickel and cobalt solutions were analysed by ICP-OES with Agilent 725 (A-G8462AA) model. Particle size distribution was determined by Malvern Master Sizer 3000 model.

CHAPTER 4

RESULT AND DISCUSSION

4.1. Characterization of MHP Material

The phase analysis was conducted with XRD, and the obtained result is shown in Figure 4.1. MHP material was amorphous. According to the peaks obtained from XRD analysis, dominantly nickel hydroxide (N) and the jamborite (J), which is nickel and cobalt hydroxide phase, were found in MHP.

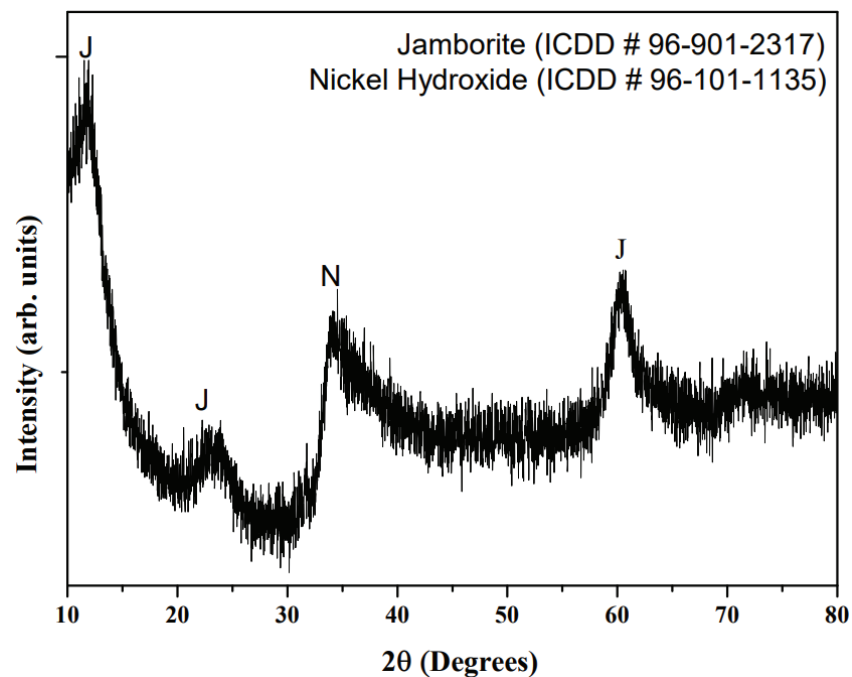


Figure 4. 1. XRD pattern of the MHP material (J: Jamborite, N: Nickel Hydroxide)

According to the thermal analysis data, between 40-140 °C temperature, the weight loss caused by the endothermic reaction was seen due to the physical water evaporation, which was the moisture content of the material. There were not any other endothermic reactions except at a slight endothermic peak of 320 °C.

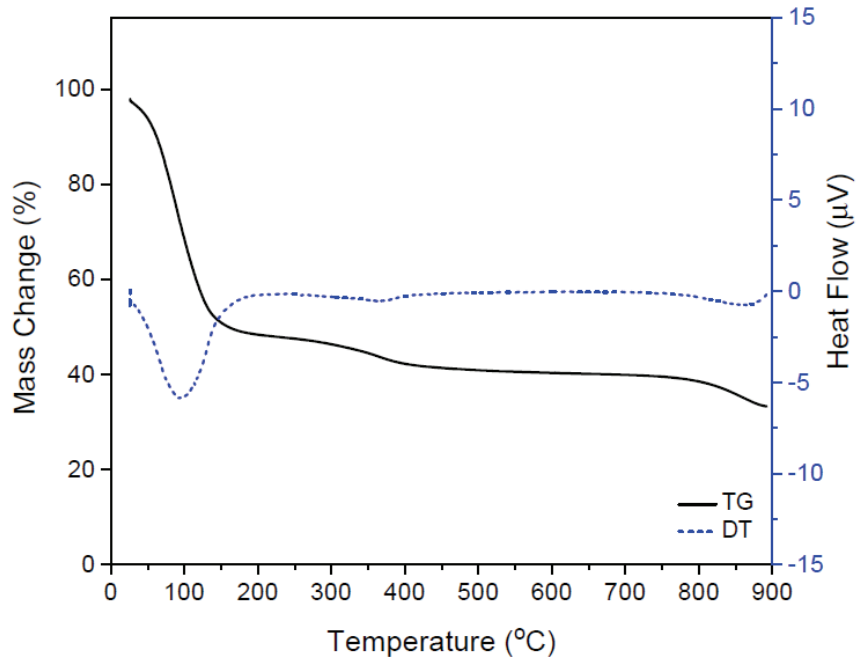


Figure 4. 2. TGA-DTA analysis of the MHP material

The particle size distribution of the MHP material was determined and given in Figure 4.3. According to master sizer analysis, 75% of the material was below 62.7 μm .

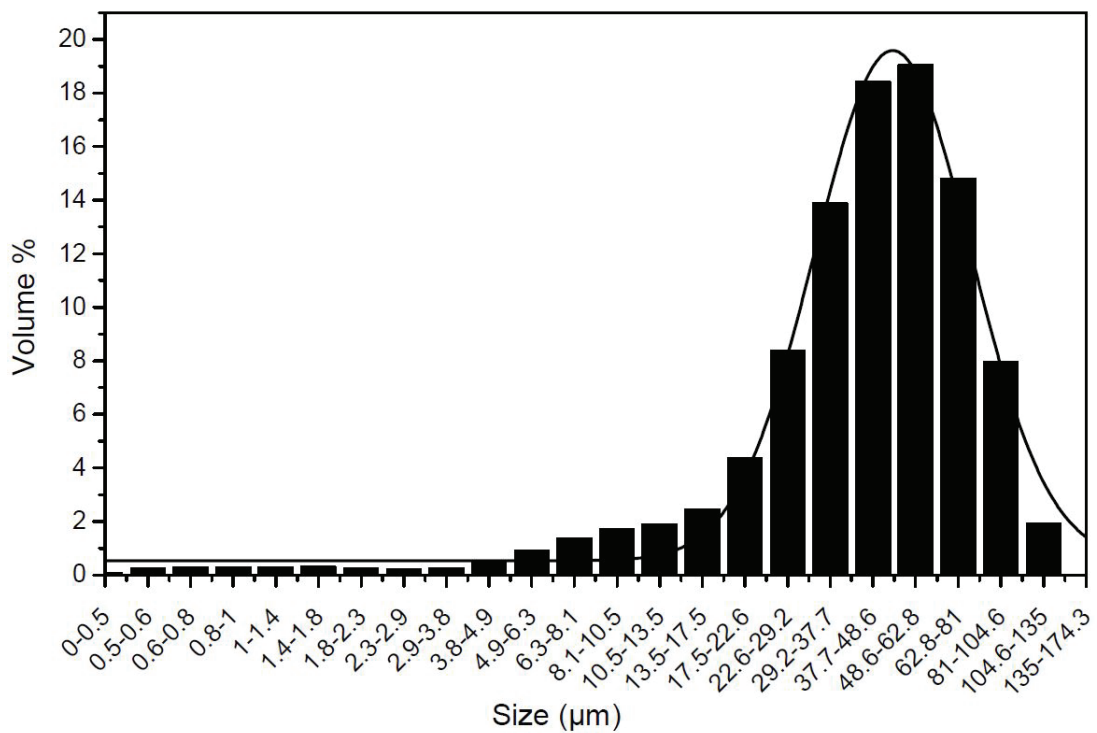


Figure 4. 3. Particle size distribution of the MHP material

4.2. Aqueous and Organic Phase Chemical Compositions

The composition of the PLS produced from MHP material is given in Table 4.1. and the chemical composition of the fresh organic reactant, D2EHPA, is given in Table 4.2. Similarly, D2EHPA raffinate as an aqueous phase in Cyanex 272 tests was also obtained at pH 3.2 without pre-neutralisation is given in Table 4.3. The chemical composition of the fresh organic reactive, Cyanex 272, is given in Table 4.4.

Table 4. 1. Chemical composition of PLS which was used in D2EHPA experiments as an aqueous phase

Chemical composition of PLS (ppm)												
Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Sc	Zn	Si
2	525	6107	141	5	3	6645	6817	33	96838	2	1372	40

Table 4. 2. Chemical composition of D2EHPA organic reactive which was used with PLS for impurity removal

Fresh D2EHPA organic phase composition (ppm)												
Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Sc	Zn	Si
0	5	1	1	0	2	1	1	50	0	1	1	5

Table 4. 3. Chemical composition of aqueous phase (D2EHPA raffinate) which was used in Cyanex 272 experiments (produced without pre-neutralisation, i.e., directly produced at pH 3.2)

Chemical composition of D2EHPA raffinate (ppm)												
Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Sc	Zn	Si
3	80	5151	39	2	2	5601	1926	6331	85548	0	1	37

Table 4. 4. Chemical composition of Cyanex 272 organic reactive which was used with D2EHPA raffinate for nickel-cobalt separation

Fresh Cyanex 272 organic composition (ppm)												
Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Sc	Zn	Si
1	0	0	1	0	3	0	0	0	0	0	0	3

4.3. Pre-neutralisation and Extraction

In D2EHPA experiments, in the beginning, PLS and organic solution were contacted by mixing them as a reference to subsequent experiments without pre-neutralisation. Controlling pH was quite difficult. Sharp pH decrease was seen due to the fast H^+ ion release. Each experiment started with 200 ml D2EHPA organic solution, and pH was controlled by the addition of 1 M NaOH and 1 M H_2SO_4 . After the first reference experiment, pre-neutralisation experiments were started with 40%. In this experiment, gel formation was observed due to the NaOH addition and separation time was approximately 20 minutes which was very long. After the phase separation, the spent NaOH was separated as waste and the pre-neutralised organic phase volume was measured by a measuring cylinder. The organic phase, which was obtained as Na-D2EHPA, and the aqueous phase, which was PLS, were extracted with a ratio of aqueous to organic as 1 to 1 (A/O:1/1). Samples from the raffinate, and aqueous phase were taken for loading efficiency calculation. Then, the same experiment was repeated by slow addition of NaOH as drop by drop and it was observed that there was no gel formation. It was seen that; the rate of addition of the chemical was quite important and in the rest of the experiments chemicals were added to the organic phase using the same method for pre-neutralisation. After the phase separation, extractions were conducted. Both of the aqueous and organic phase samples were taken after phase separation. It was seen that 40% pre-neutralisation was critical because it was possible to see gel formation which meant that, an amount of organic phase had disappeared or dissolved and most probably changed its loading capacity. For that reason, the upper and lower percentages of pre-neutralisation were decided to be tested with the same procedure as 35% and 45%. It was seen that the extraction with 35% pre-neutralisation percent had fast and clear separation. On the other hand, 45% pre-neutralised D2EHPA extraction had a gel and three-phase formation problems.

Experimental data of pre-neutralised D2EHPA with NaOH is given in Table 4.5. Depending on the experiment number, the chemical composition of the raffinate and the elemental extraction percentages are given in Table 4.6 and Table 4.7, respectively. It was seen that if the gel formation was present or phase disengagement was long, the extraction of manganese was decreased, although for 35% pre-neutralisation and zero pre-neutralisation case's extraction results were similar. In terms of pH fluctuation, 35% pre-neutralisation is generally percent was preferred for industrial uses.

Table 4. 5. Experiment data of pre-neutralised D2EHPA with NaOH

Pre-neutralisation of D2EHPA Organic Phase with 1 M NaOH			
No	Pre-neutr. Percent (%)	Separation Duration (min)	Observation
1	0	-	-
2	0	-	-
3	35	8	Fast and clear separation
4	40	20	Gel formation
5	40	10	No gel formation
6	45	-	Gel formation and 3 phase

Table 4. 6. Elemental composition of D2EHPA raffinate obtained from the extraction of PLS and Na-D2EHPA with NaOH

No	Elemental Composition of D2EHPA Raffinate(ppm)									
	Ca	Co	Cr	Cu	Fe	Mg	Mn	Ni	Zn	Si
1	214	5343	111	3	2	5867	4195	85107	9	34
2	203	5184	116	3	2	5791	4138	83743	9	34
3	211	5832	126	3	2	6208	4175	92357	5	36
4	265	5742	126	4	2	6193	4781	91779	9	38
5	288	5838	126	4	2	6276	5002	92798	11	36
6	243	5546	122	3	2	6080	4593	87771	8	37

Table 4. 7. Extraction results of pre-neutralised D2EHPA with NaOH and PLS

No	Pre-neutr. Percent (%)	Elemental Extraction Percent (%)									
		Ca	Co	Cr	Cu	Fe	Mg	Mn	Ni	Zn	Si
1	0	59	13	21	30	26	12	38	12	99	14
2	0	61	15	17	33	31	13	39	14	99	14
3	35	60	5	11	32	44	7	39	5	100	8
4	40	49	6	10	23	30	7	30	5	99	5
5	40	45	4	10	17	31	6	27	4	99	8
6	45	54	9	13	26	41	9	33	9	99	7

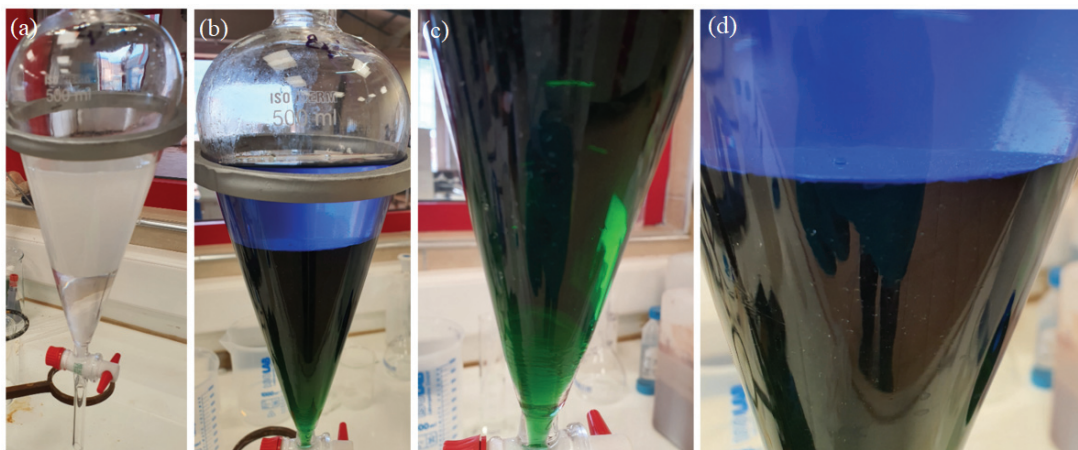


Figure 4. 4. Illustrations of D2EHPA organic phase with NaOH (a) 35% pre-neutralisation (b) phase separation after extraction (c) raffinate phase (d) interface of the organic and raffinate phases



Figure 4. 5. 45 % pre-neutralisation of the D2EHPA organic phase with NaOH (a) three phase formation (middle phase) (b) its appearance one day later

Similar to D2EHPA-NaOH experiments, the same experiments were done with Na_2CO_3 reagent with 35%, 40%, and 45% pre-neutralisation. Experiment data of pre-

neutralised D2EHPA with Na₂CO₃ is given in Table 4.8. Depending on the experiment number, the chemical composition of the raffinate and the elemental extraction percent are given in Table 4.9 and Table 4.10, respectively. 40% pre-neutralisation was critical because gel formation was seen in an experiment which was given in Figure 4.6. The optimum result, which was 35 % pre-neutralisation had clear and fast phase separation.

Table 4. 8. Experiment data of pre-neutralised D2EHPA with Na₂CO₃

Pre-neutralisation of D2EHPA Organic Phase with 5 wt. % Na₂CO₃ Solution			
No	Pre-neutr. Percent (%)	Separation Duration (min)	Observation
7	35	8	Fast and clear separation
8	40	8	Gel formation
9	40	11	No gel formation
10	45	25	Not clear separation
11	45	30	3 phase formation

Table 4. 9. Elemental composition of D2EHPA raffinate obtained from the extraction of PLS and Na-D2EHPA with Na₂CO₃

No	Elemental Composition of D2EHPA Raffinate (ppm)										
	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Zn	Si
7	203	5881	126	3	2	6157	4150	4076	92347	6	37
8	231	5665	126	3	2	6247	4559	4164	91249	8	36
9	167	5515	101	3	1	5110	3518	4243	87984	6	29
10	264	5776	124	4	2	6304	4818	3750	90577	9	37
11	215	5412	118	3	1	5988	4218	4691	88764	6	34

Table 4. 10. Extraction results of pre-neutralised D2EHPA with NaOH and PLS

No	Pre-neutr. Percent (%)	Elemental Extraction Percent (%)									
		Ca	Co	Cr	Cu	Fe	Mg	Mn	Ni	Zn	Si
7	35	61	4	10	32	49	7	39	5	100	6
8	40	56	7	10	27	48	6	33	6	99	8
9	40	68	10	29	41	57	23	48	9	100	28
10	45	50	5	12	18	47	5	29	6	99	8
11	45	59	11	16	29	54	10	38	8	100	14

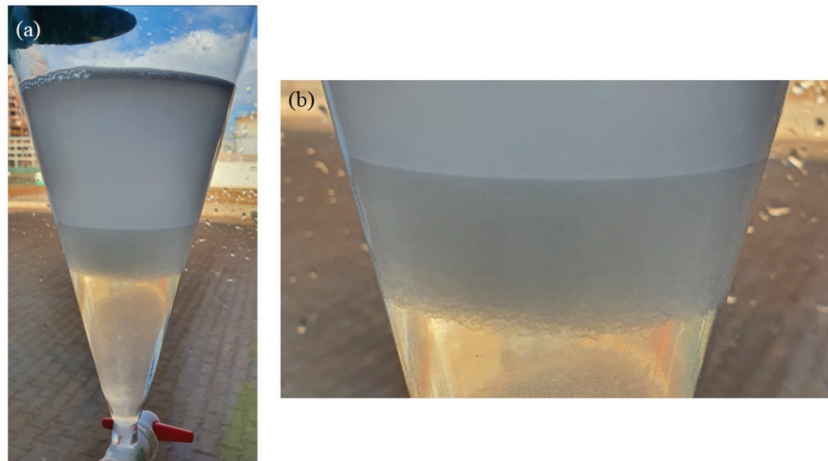


Figure 4. 6. 40% pre-neutralisation of the D2EHPA organic phase with Na_2CO_3 (a) three phase formation (b) crud phase

In Cyanex 272 experiments, in the beginning, PLS is treated by D2EHPA organic solution, and an aqueous phase was prepared for nickel and cobalt separation. The same procedure was applied to Cyanex 272 organic solution with 30%, 35%, and 40% pre-neutralisation. In the experiment, at 35% of the pre-neutralisation the temperature was kept at 20-25 °C, but there was no clear phase separation, and also, it was possible to see some local gel formation in the beaker. After that, the pre-neutralisation process was conducted at 50 °C temperature, and phase separation was clear. For that reason, 30%, 35% and 40% pre-neutralised Cyanex 272 organic solution were used in extraction experiments. In extraction, when the D2EHPA raffinate was added to the organic phase, the temperature was decreased to 25-30 °C. It meant that the extraction was conducted at that temperature. Experimental data of pre-neutralised Cyanex 272 with NaOH is given in Table 4.11. Depending on the experiment number, the chemical composition of the raffinate and the elemental extraction percentages are given in Table 4.12 and Table 4.13, respectively. Since the minimum phase separation period was belonging to 30% pre-neutralisation, additionally, D2EHPA raffinate was also heated up to 50 °C, and the extraction was done. The best results were seen with 30% pre-neutralisation using NaOH as 94% Co extraction efficiency and minimum phase separation duration were obtained.

Table 4. 11. Experiment data of pre-neutralised Cyanex 272 with NaOH and D2EHPA raffinate

Pre-neutralisation of Cyanex 272 Organic Phase with 1 M NaOH					
No	Pre-neutr. Percent (%)	Pre-neutr. Temperature (°C)	Separation Duration (min)	Observation	Extraction Temperature (°C)
12	0	-	-	-	-
13	30	45-50	5	Very fast phase separation	25
14	30	50	5	Very fast phase separation	50
15	35	20-25	30	No clear phase separation	20-25
16	35	20-25	30	Gel formation	20-25
17	35	50	8	Clear separation	25-30
18	40	50	10	Clear separation	25-30

Table 4. 12. Elemental composition of Cyanex raffinate obtained from the extraction of D2EHPA raffinate (obtained at the beginning without pre-neutralised) and Na-Cyanex 272 with NaOH

No	Elemental Composition of Cyanex 272 Raffinate (ppm)							
	Ca	Co	Cr	Mg	Mn	Na	Ni	Si
12	63	1768	31	4394	218	9045	67101	27
13	70	2097	34	4870	259	9682	77414	31
14	61	290	31	2940	42	13221	67306	30
15	72	2947	36	5174	512	8837	78117	33
16	71	2563	34	4918	357	9047	79502	32
17	73	3248	36	5184	568	8506	78469	32
18	71	3073	35	5080	524	8531	76732	33

Table 4. 13. Extraction results of pre-neutralised Cyanex 272 with NaOH and D2EHPA raffinate

No	Pre-neutr. Percent (%)	Elemental Extraction Percent (%)						
		Ca	Co	Cr	Mg	Mn	Ni	Si
12	0	22	66	21	22	89	22	27
13	30	13	59	14	13	87	10	16
14	30	25	94	22	48	98	21	18
15	35	11	43	8	8	73	9	11
16	35	12	50	13	12	81	7	15
17	35	10	37	9	7	71	8	14
18	40	12	40	10	9	73	10	12

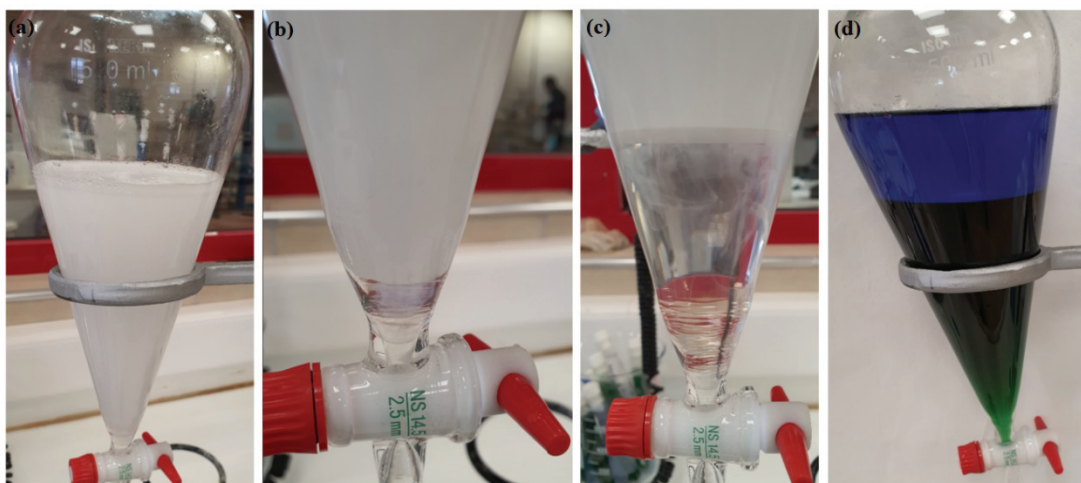


Figure 4. 7. 30% pre-neutralisation of Cyanex 272 with NaOH organic phase and extraction (a) beginning of the phase separation of the organic phase (upper phase), and spent NaOH solution (lower phase) (b) phase separation progress (c) end of the phase separation of the organic phase, and spent NaOH solution (d) organic (upper phase), and raffinate phase(lower) separation after extraction

In Cyanex 272 with Na_2CO_3 experiments, the same procedure was applied. Experimental data of pre-neutralised Cyanex 272 with Na_2CO_3 is given in Table 4.14. Depending on the experiment number, the chemical composition of the raffinate and the elemental extraction percentages are given in Table 4.15 and Table 4.16, respectively. It was seen that 74% of the Co was extracted to the organic phase, which was the highest result obtained in Na_2CO_3 experiments.

Table 4. 14. Experiment data of pre-neutralised Cyanex 272 with Na_2CO_3 and D2EHPA raffinate

Pre-neutralisation of Cyanex 272 Organic Phase with 5 wt. % Na_2CO_3 Solution					
No	Pre-neutr. Percent (%)	Pre-neutr. Temperature ($^{\circ}\text{C}$)	Separation Duration (min)	Observation	Extraction Temperature ($^{\circ}\text{C}$)
19	30	45-50	5	Fast separation	25-30
20	30	50	5	Fast separation	50
21	35	50	12	Slow separation	20-25
22	40	50	30	Gel formation	25-30

Table 4. 15. Elemental composition of Cyanex raffinate obtained from the extraction of D2EHPA raffinate (obtained at the beginning without pre-neutralised) and Na-Cyanex 272 with Na₂CO₃

No	Elemental Composition of D2EHPA Raffinate (ppm)							
	Ca	Co	Cr	Mg	Mn	Na	Ni	Si
19	66	1328	33	4469	161	10702	73772	28
20	68	1322	33	4319	179	11027	73184	29
21	70	1449	33	4597	157	10661	75365	29
22	68	1659	34	4748	203	10451	73840	32

Table 4. 16. Extraction results of pre-neutralised Cyanex 272 extractant with Na₂CO₃ and D2EHPA raffinate

No	Pre-neutr. Percent (%)	Elemental Extraction Percent (%)							
		Ca	Co	Cr	Mg	Mn	Ni	Si	
19	30	18	74	16	20	92	14	26	
20	30	16	74	16	23	91	14	22	
21	35	13	72	15	18	92	12	21	
22	40	15	68	13	15	89	14	13	

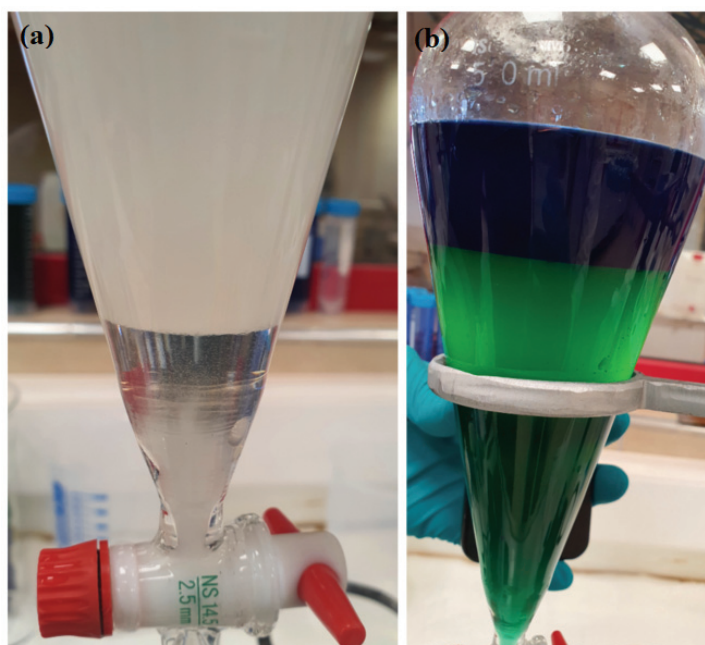


Figure 4. 8. 30% pre-neutralisation of Cyanex 272 with Na₂CO₃ organic phase (a) clear separation image (b) clear phase separation after extraction (pre-neutralisation temperature at 45-50 °C and extraction temperature at 25-30 °C)

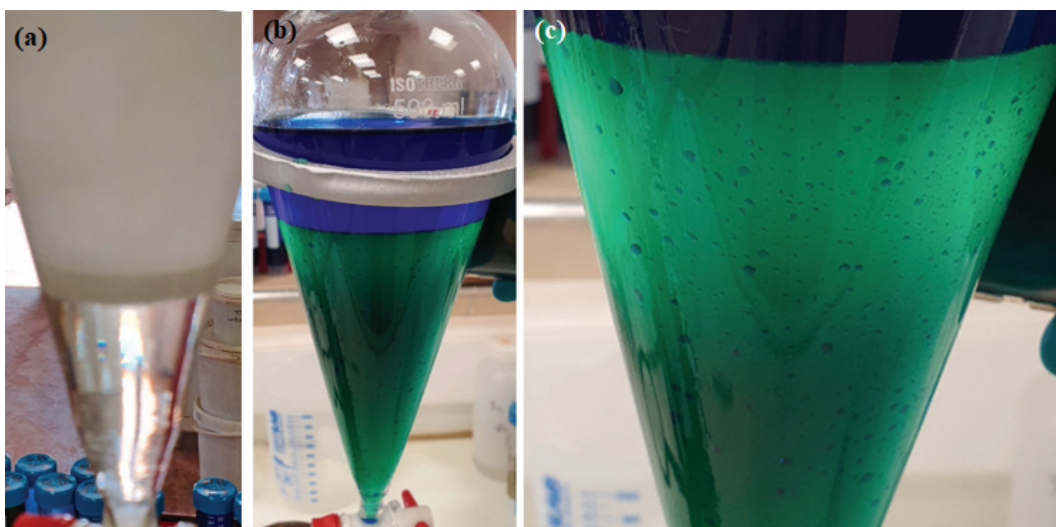


Figure 4. 9. 35% pre-neutralisation of Cyanex 272 with Na_2CO_3 organic phase (a) pre-neutralisation at 50 °C (b) phase separation after extraction at 20-25 °C (c) suspended organic droplets

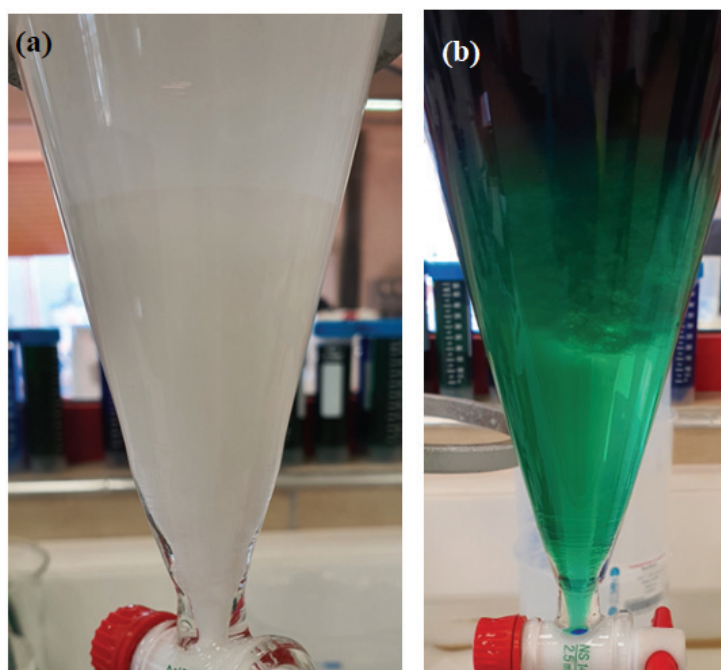


Figure 4. 10. 40% pre-neutralisation of Cyanex 272 with Na_2CO_3 organic phase (a) poor phase separation (b) crud formation at phase interface after extraction (pre-neutralisation at 50 °C and extraction at 25-30 °C)

The best conditions obtained from the experiments were repeated three times for reproducibility check. The chemical composition and elemental extraction efficiency percentages of the D2EHPA are given in Table 4.17 and Table 4.18, respectively.

Table 4. 17. Elemental composition of D2EHPA raffinate of the reproducibility experiments

No	Elemental composition (ppm)										
	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Zn	Si
23	221	5722	31	4	2	6199	4196	4462	92854	7	37
24	203	5690	28	3	1	6127	4141	4414	92818	5	38
25	207	5685	27	3	1	6145	4186	4459	92849	4	39

Table 4. 18. Extraction percent of D2EHPA in reproducibility experiments

No	Elemental Extraction Percent (%)										
	Ca	Co	Cr	Cu	Fe	Mg	Mn	Ni	Zn	Si	
23	58	6	78	23	42	7	38	4	100	7	
24	61	7	80	42	54	8	39	4	100	4	
25	60	7	81	45	58	8	39	4	100	4	

Similarly, the chemical composition and elemental extraction efficiency percent of the Cyanex 272 are given in Table 4.19 and Table 4.20, respectively.

Table 4. 19. Elemental composition of Cyanex 272 raffinate of the reproducibility experiments

No	Elemental Composition (ppm)							
	Ca	Co	Cr	Mg	Mn	Na	Ni	Si
26	55	300	26	2782	51	13190	67212	32
27	71	299	31	2991	53	13253	67381	33
28	69	338	32	2772	48	13232	67330	33

Table 4. 20. Extraction percent of Cyanex 272 in reproducibility experiments

No	Elemental Extraction Percent (%)							
	Ca	Co	Cr	Mg	Mn	Ni	Si	
26	31	94	34	50	97	21	14	
27	11	94	21	47	97	21	11	
28	14	93	18	51	96	21	12	

CHAPTER 5

CONCLUSIONS

Solvent extraction is a typical and mature process for nickel and cobalt. According to industry, D2EHPA and Cyanex 272 organic reactants are well known and best organics nickel and cobalt separation process. One of the process steps of solvent extraction is “pre-neutralisation” stage is examined in this thesis.

Pre-neutralisation process is partially neutralising the acidic characterized organic extractant. The barren organic phase, which is fed for extraction is mixed with a neutralising sodium source such as NaOH and Na₂CO₃ in a vessel or industrially in a mixer settler before the extraction step. Hydrogen ion (H⁺) from the organic phase exchanges with sodium (Na⁺) cation. It is preferred because pH control is simplified without sharp changes.

During the metal loading to the organic phase, pH fluctuation occurs because metals that bond with the organic phase causes H⁺ ion release, and pH decreases rapidly. For that reason, pH must be controlled. Otherwise, extraction is not achieved as required. Similarly, if pH increases in mixer settler without pre-neutralisation step, high pH value may exhibit increased co-extraction of impurities.

In this study, D2EHPA and Cyanex 272 organic reactants were pre-neutralised by NaOH and Na₂CO₃ chemicals, and then the solvent extraction process was conducted with Pregnant Leach Solution (PLS) which was produced from MHP intermediate product from Gördes laterite ore. Initially, MHP was leached by concentrated sulphuric acid with pH=2 and neutralised by CaCO₃ solution with pH=3.5 at 60 °C. PLS was obtained by solid-liquid separation via filtration.

D2EHPA organic solution was prepared as 20 vol.% (0.6 M) and Cyanex 272 organic solution was prepared as 13 vol.% (0.4 M) diluted with kerosene D80. D2EHPA and Cyanex 272 reactants have acidic characters. These organic reactants in organic solution were neutralised partially, which is called as pre-neutralisation process at specific percentages. By doing that, it was aimed to control pH changes smoothly in extraction

stage to prevent sharp pH decrease due to the H⁺ ion release. In addition to that, it is aimed to increase metal extraction efficiency.

In D2EHPA extraction, manganese was major impurity. Firstly, D2EHPA experiments were done for the impurity removal from PLS. In first D2EHPA experiment, PLS and organic solution was directly mixed with 1 to 1 ratio without pre-neutralisation for reference to subsequent experiments. Then, D2EHPA organic solution was pre-neutralised at 35%, 40% and 45% with NaOH chemical, respectively. In terms of impurity extraction (especially Mn), optimum pre-neutralisation was found 35%. In these experiments, highest manganese extraction was found as 39 % with minimum cobalt and nickel extractions as %5 and %5, respectively. In addition to that, the phase separation was seen 8 minutes. In Na₂CO₃ experiments, the highest manganese extraction was found 48% at 40% pre-neutralisation. But the cobalt extraction was 10% and nickel extraction was 9%. These nickel and cobalt loss directly affects metal recovery in industry scale.

Cyanex 272 experiments were done for the nickel and cobalt separation from the purified PLS, which was D2EHPA raffinate. Cyanex experiments were required heating for pre-neutralisation stage and extraction stages. According to this information, Cyanex 272 organic solution was pre-neutralised at 30%, 35%, and 40% with NaOH and Na₂CO₃ chemicals, respectively. The optimum results were obtained when 30% NaOH pre-neutralisation was applied. In this experiment, maximum cobalt extraction was 94% at 50 °C minimum with 5 minutes phase separation time. In Na₂CO₃ experiments, at 30% pre-neutralisation, cobalt extraction was obtained maximum 74%, which was lower than NaOH experiments with 30% pre-neutralisation.

As a result that, the best pre-neutralisation percent was determined in D2EHPA extraction as %35 for maximum extraction efficiency for impurity metal extraction and Cyanex 272 as %30 for nickel and cobalt separation.

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APPENDIX

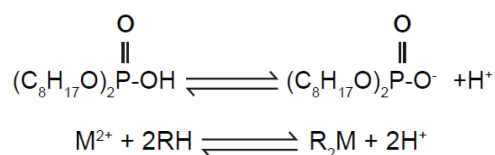
THEORETICAL ORGANIC PHASE CONCENTRATION CALCULATION

- **D2EHPA Organic Concentration Calculation**

PLS Composition is given in Table below. In each experiment 200 ml organic phase was used.

Chemical composition of PLS (ppm)												
Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Sc	Zn	Si
2	525	6107	141	5	3	6645	6817	33	96838	2	1372	40

The total number of moles for Mn, Zn, Cr and Ca were calculated. According to stoichiometric ratio, 1 mole metal bond to 2 moles of organic reactant.



Regarding to this information, the required number of moles for organic reactant were calculated. The total impurity moles were obtained as 0.0321 moles. Minimum required number of D2EHPA moles were calculated as 0.0642 moles. The number of D2EHPA moles of the organic phase solution was prepared with 2 times the number of moles which were 0.1284 moles due to these reasons which were given as below:

- For the extra capacity providing to the minor impurity metals
- The capacity decrease co-extraction of cobalt,
- To improve phase separation consideration (the high viscosity after loading of organic phase disengagement)
- Depending on the ore and MHP composition change (extra impurities)

As a result of that, 0.6 M D2EHPA organic solution was decided to prepare.

- **Cyanex 272 Organic Concentration Calculation**

Chemical composition of D2EHPA raffinate (ppm)												
Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Sc	Zn	Si
3	80	5151	39	2	2	5601	1926	6331	85548	0	1	37

The number of cobalt mole were calculated as 0.0175. The required number of Cyanex 272 reactant were calculated as 0.035 moles. The number of Cyanex 272 moles of the organic phase solution was prepared with 2 times the number of moles which 0.07 moles due to these reasons which were given as below:

- To improve phase separation consideration (the high viscosity after loading of organic phase disengagement)
- Depending on the ore and MHP composition change (extra cobalt content)
- To provide extra capacity for the recycling and recovery lines in industrial cases.

As a result of that, 0.4 M Cyanex 272 was decided to prepare.