PRESSURE LEACHING OF SİVRİHİSAR-YUNUSEMRE NICKEL LATERITES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF APPLIED AND NATURAL SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

BERK SEÇEN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
METALLURGICAL AND MATERIALS ENGINEERING

JULY 2011

Approval of the thesis:

PRESSURE LEACHING OF SİVRİHİSAR-YUNUSEMRE NICKEL LATERITES

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ABSTRACT

PRESSURE LEACHING OF SiVRiHiSAR-YUNUSEMRE NICKEL LATERITES

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July 2011, 119 pages

The aim of this thesis study was to extract nickel and cobalt from Sivrihisar limonitic nickel laterite ore by high pressure acid leaching (HPAL) method under most economical operating parameters. Optimizing the conditions to yield a saleable quality mixed hydroxide product from the pregnant leach solution (PLS) was also investigated.

To extract high amounts of nickel and cobalt from the laterite matrix; leaching duration, leaching temperature and sulfuric acid/ore ratio were studied at fixed conditions of -850 μ limonitic ore particle size and 40% solids concentration. The Sivrihisar limonitic nickel laterite ore was found to be readily leachable. It was found that 95.4% of Ni and 91.5% of Co were extracted at the optimized conditions of $235^{o}C$, 0.23 acid/ore ratio in 60 minutes. The real pregnant leach solution produced at the optimized conditions of HPAL was purified in two iron removal stages under the determined optimum conditions. Nearly all of the Al and Cr were removed from the PLS in the two stages of iron removal. Then, nickel and cobalt were taken out

from the PLS in the form of mixed hydroxide precipitates (MHP) in two stages. A MHP 1 product containing 33.41 wt.% Ni, 2.93 wt.% Co was obtained with a Mn contamination of 3.69 wt.% at the optimized conditions of pH=7, 50°C and 60 minutes. The MHP 1 product was also contaminated with Fe (2.83 wt.%) since it could not be completely removed from the PLS without the critical losses of nickel and cobalt during the two iron removal stages.

Keywords: High pressure acid leaching, nickel-cobalt mixed hydroxide, precipitation, laterite.

ÖZ

YUNUSEMRE-SİVRİHİSAR LATERİTİK NİKEL CEVHERİNİN BASINÇ ALTINDA LİÇİ

Seçen, Berk

Yüksek Lisans, Metalurji ve Malzeme Mühendisliği Bölümü

Tez Yöneticisi: Prof. Dr. Yavuz A. Topkaya

Temmuz 2011, 119 sayfa

Bu tez çalışmasının amacı nikel ve kobalt içeren limonitik tipteki Sivrihisar lateritik cevherinin basınç altında liç edilerek en ekonomik çalışma parametrelerinin belirlenmesidir. Metalle yüklü çözeltiden belirlenen optimum şartlarda satılabilir kalitede hidroksit karışımı üretimi ayrıca araştırılmıştır.

Lateritin iç yapısında bulunan nikel ve kobaltın yüksek miktarlarda kazanılabilmesi için -850 µ tane boyutu ve %40 katı oranı sabit parametreleri altında liç süresi, liç sıcaklığı ve eklenen sülfürik asit/cevher oranı üzerine araştırmalar yapılmıştır. Elde edilen bulgulara göre Sivrihisar limonitinin kolayca liç edilebildiği görülmüştür. Belirlenen optimum şartlar olan $235^{o}C$ sıcaklık, 0,23 asit/cevher oranı ve 60 dk liç süresinde nikelin %95,4'ü ve kobaltın %91,5'i cevherden kazanılmıştır. Bu koşullar altında elde edilen metalle yüklü çözelti, iki aşamalı demir arıtma işlemine tabi tutulmuştur. Bu süreçte Al ve Cr'un neredeyse tümü metalle yüklü çözeltiden uzaklaştırılmıştır. Nikel ve kobalt, elde edilen çözeltiden iki aşamalı nikel-kobalt

hidroksit çökeleği çöktürme işlemiyle alınmıştır. İçerisinde %3,69 Mn safsızlığı bulunan ve %33,41 Ni, %2,93 Co içeren MHP 1 çökeleği pH=7, 50°C ve 60 dk altında üretilebilmiştir. İki aşamalı demir arıtma işlemleri sırasında yüksek nikel ve kobalt kaybı oluşması nedeniyle metalle yüklü çözeltiden tamamen uzaklaştıralamayan Fe de, MHP 1 üründe %2,83 oranında safsızlık yaratmıştır.

Anahtar Kelimeler: Yüksek basınçta asit liçi, nikel-kobalt hidroksit, çöktürme laterit.

To my dear family;

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

Nickel is a demanded metal for many industries including ferrous and nonferrous metal productions, aerospace and military applications, battery and coinage productions or coating practices. Nickel demand is increasing annually such that the world primary nickel consumption was 1.24 Mt in 2009 and 1.47 Mt in 2010 and an increase in usage to 1.54 Mt is expected by the end of 2011 [1].

In the past (1950), the production of nickel was primarily achieved from sulfide type nickel reserves (90%) due to their high nickel content. The decrease in the availabilty of sulfide reserves moved the trend to utilize lateritic nickel ores. The fact of vast majority of nickel on the earth's crust exists in lateritic type nickel reserves (72%), the easiness of mining (open-pit mining) and co-existence of valuable metal cobalt in laterites create the advantage for lateritic nickel ores over sulfide ores with advancing processesing techniques (e.g., high pressure acid leaching) [2].

Laterites are formed by distinct layers which have to be treated separately due to differences in composition, mineralogy etc. From the ground to the deeper levels, an iron cap is followed by limonite layer. At regions where the water flow is restricted a nontronite layer is found next and at deeper levels the laterite profile is ended with saprolite layer.

Although pyrometallurgical routes are also applicable for saprolite layer to yield a ferronickel product via smelting, a hydrometallurgical process of high pressure acid leaching (HPAL) is gaining interest to extract nickel and cobalt from the laterite matrix. Limonite layer which is mainly formed by goethite and hematite minerals is preferably treated in this process due to its low content of acid comsuming elements

(e.g., Mg, Ca). The acid consumption of the HPAL process is considerably low compared to other hydrometallurgical methods such as heap leaching or agitative leaching since regeneration of acid is favorable due to hematite precipitation at high temperatures.

The pregnant leach solution (PLS) obtained at the end of high pressure acid leaching is further processed to yield a saleable quality mixed hydroxide product (MHP) or mixed sulfide product (MSP). Solvent extraction techniques are also applicable to directly utilize PLS for pure nickel or cobalt [3].

Although mixed sulfide precipitation method provides better selectivity than the mixed hydroxide precipitation, MHP process is the preferred alternative process since it does not require the use of toxic gas (H_2S) as in the case of MSP process [4].

The aim of this study was to extract nickel and cobalt from Sivrihisar limonitic nickel laterite ore by high pressure acid leaching (HPAL) method at the most economical operating parameters. Optimizing the conditions to yield a saleable quality mixed hydroxide product from the pregnant leach solution (PLS) were also investigated.

CHAPTER 2

LITERATURE SURVEY

2.1 Nickel Deposits

The earth's crust contains nickel in the forms of sulfides and oxides. Although nickel sulfides contain only 28% of the total nickel resource on land, 58% of the total nickel production is achieved from the sulfide resources that are being depleted [2]. Today, low grade oxide reserves became more important to be utilized due to depletion of sulfide reserves and many processing techniques are being developed to process oxide nickel reserves with the aim of high nickel and minor amount of co-existing valuable metal recoveries (e.g., Co, Sc).

2.1.1 Sulfide Nickel Ores

Nickel containing sulfide minerals have been formed from magma during cooling period. These reserves are generally below the surface level that the mining operations require high cost. Furthermore, the mining cost is still increasing since the residual ore reserves at the mines are becoming located at deeper levels from the ground.

The depletion of sulfide reserves beside oxide reserves for years is related to the content of nickel element in sulfide minerals, which is very much higher than in oxide minerals. Pentlandite, millerite, heazlewoodite are some examples of nickel containing sulfide minerals. Among them, pentlandite is the most common one with its 34.33% nickel content [5].

2.1.2 Oxide Nickel Ores

Majority of nickel reserves exist on land in oxide form and these reserves are called "laterite" due to layer formation. Mining of laterite deposits is simpler than sulfide nickel deposits since laterites are close to the ground and thus, open pit mining techniques are available. Generally, a laterite profile has a thickness of 20 to 150 m with different thicknesses of layers at different deposits [6].

The formation of nickel laterites is dependent on the weathering of igneous rocks existing at the earth's surface. The magnesium-rich igneous rocks contain iron, calcium, aluminum, silica, nickel, cobalt and the solubility of the related minerals results in mobilization of these elements within the laterite profile [7]. For instance, the soluble minerals move to the deeper levels of the laterite within the solution and re-precipitate at deeper levels, whereas insoluble minerals stay at the higher levels. The climate, chemical environment, humidity and weathering periodicity are some of the factors effective on leaching activity that determine the thickness of each laterite layer and also determine the concentration of the layers. The differences in solubility of minerals result in non-homogenous mineral distribution. This leads to the classification of laterite layers according to their differences in composition, mineralogy, etc.

A typical laterite profile is shown in Figure 1 [8]. At the top of the profile, nearly pure hematite containing layer is found. This purity means that hematite is very insoluble mineral compared to the other co-existing minerals under those environmental conditions. This "iron capping" does not contain nickel in a significant amount (Ni<1.0%) [6]. The following layer is called limonite which is mainly formed by goethite (FeOOH). Generally limonite contains approximately 1.4% Ni, over 40% Fe and 0.15% Co with considerably low content of acid consuming elements such as Mg [9]. Nickel concentration increases with the increase in depth. Limonite layer is followed by a transition zone in some reserves where the water flow is diminished. This transition zone is called nontronite zone which is mainly formed by smectite clays with nickel content between 1.5 to 2.4%. The next layer "saprolite" is low in moisture and considerably rich in Ni (up to 3%). Saprolite is mainly formed by magnesium silicates [6].

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SCHEMATIC LATERITE PROFILE	COMMON NAME	APPROXIMATE ANALYSIS (%)				EXTRACTION PROCESS
		Ni	Co	Fe	MgO	
	RED LIMONITE	<0.8	<0.1	>50	<0.5	
	YELLOW LIMONITE	0.8 to 1.5	0.1 to 0.2	40 to 50	0.5 to 5	ACID LEACH / CARON PROCESS
	TRANSITION	1.5 to 2	0.02 to 0.1	25 to 40	5 to 15	SMELTING
	SAPROLITE/ GARNIERITE/ SERPENTINE	1.8 to 3		10 to 25	15 to 35	
	FRESH ROCK	0.3	0.01	5	35 to 45	
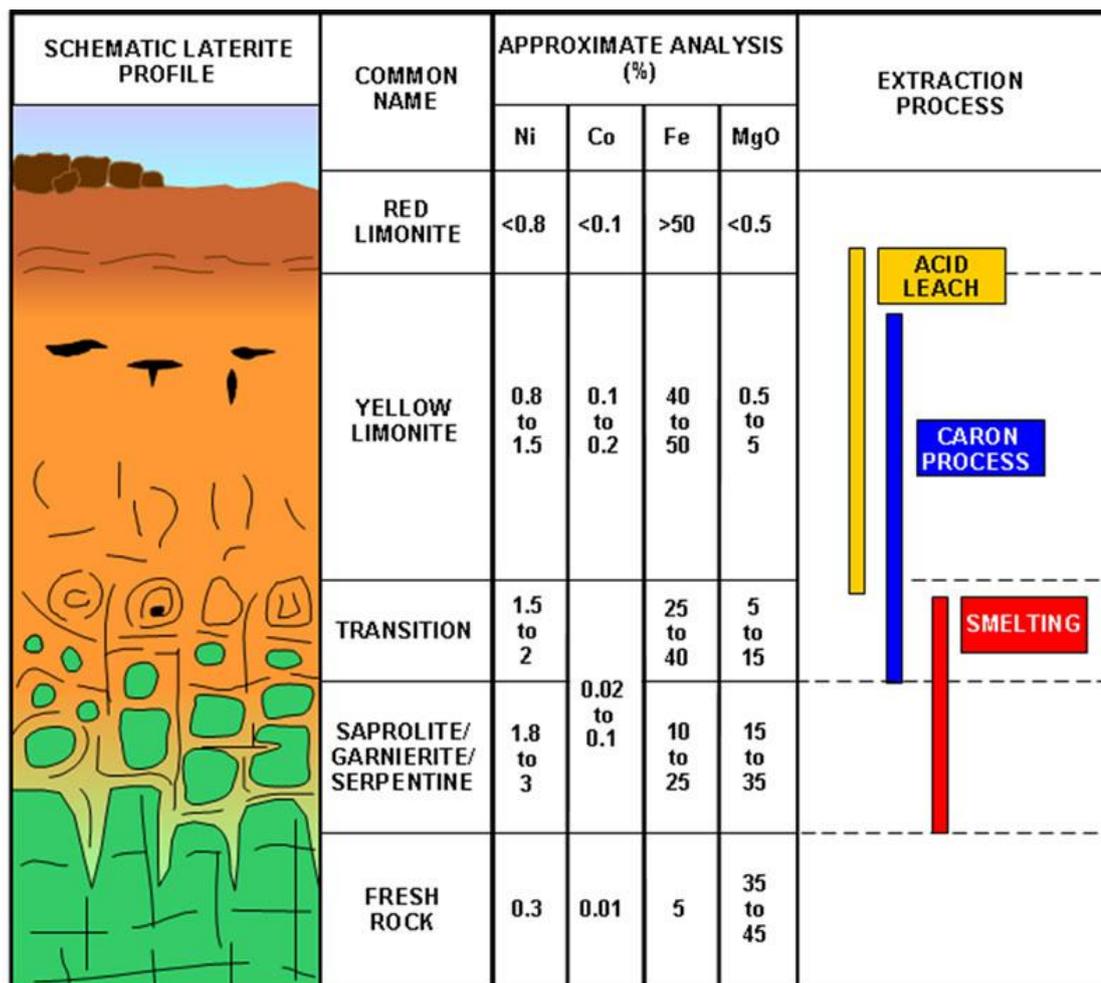
Figure 1. A typical laterite profile.

Magnesium content is critical for hydrometallurgical processes since it is a very acid consuming element. Limonites with their low Mg content are treated preferably by hydrometallurgical routes such as high pressure acid leaching (HPAL), atmospheric acid leaching (AL), etc. Saprolitic layers are suitable for production of ferronickel by pyrometallurgical processes with the advantage of their high nickel and magnesium contents.

Nickel laterites do not have discrete nickel minerals and physical concentration techniques are not applicable to these reserves. Instead of existing as a mineral, nickel and cobalt substitute in the crystal structures of goethite, hematite and other host minerals. The substantial capacity, defect sites in host mineral lattices determine the incorporation of nickel and cobalt within the lattices. Hematite has a lower capacity for this substitution whereas serpentine and nontronite have higher

capacities compared to most common limonite mineral "goethite". There is also a correspondence between cobalt and manganese in manganese minerals (e.g., lithiophorite and asbolane) [9].

The world nickel production has an increasing interest to utilize limonites by high pressure acid leaching (HPAL) in titanium autoclaves after this technique was used at Moa Bay, Cuba in 1959. This process uses the advantages of high temperature hydrolysis reaction of ferric iron to form filterable ferric oxide with regeneration of acid [10]. Murrin Murrin, Cawse, Bulong and Ravensthorpe are the important companies of Australia operating at the moment or that have operated in the past with HPAL technology [2]. 80% of nickel laterite resources on the world exist at the Western Australia region [9]. Turkey has laterite deposits at Gördes, Çaldağ in Manisa and at Sivrihisar in Eskişehir. META Nickel and Cobalt Company of Turkey has been working on building a HPAL plant to utilize the reserves at Gördes. In their future plans, there is also a possibility of utilizing Sivrihisar reserves either for ferronickel or mixed Ni-Co hydroxide (MHP) production.

2.2 Processing of Nickel Laterites

2.2.1 Pyrometallurgical Routes

Oxide nickel resources, especially high magnesia and silica containing layers of laterite profile are suitable to be processed with pyrometallurgical routes. Saprolite layer of laterite profile is preferably utilized with pyrometallurgy techniques. The product is either a ferronickel or a matte. Ferronickel product which has a good market in steel production industry has come out with the aim of minimizing the Fe/Ni ratio in the ore. This is achieved by applying calcination and pre-reduction at 850-1000°C, then smelting is carried out at 1500-1600°C to separate nickel/iron containing phase from silica-magnesia slag [11]. Blast furnaces, rotary kilns and electric arc furnaces are possible to use for ferronickel smelting. Sulfide matte is the second option for a pyrometallurgical product. In this case, a sulphur source is necessary to form a nickel/iron sulfide matte. Generally, gypsum ($CaSO_4.2H_2O$) is the sulfiding agent which is used in the matte production [5].

2.2.2 Hydrometallurgical Routes

Hydrometallurgical technics are appropriately applied to nickel ores in which the valuable metal concentration is low in the reserve. Hydrometallurgy is a process based on leaching of the ore or concentrate with the aid of a leaching agent (i.e., acid). Generally, the metal that is desired to be extracted is aimed to be taken into leach solution selectively than it is utilized to form a product. As compared to pyrometallurgical routes, hydrometallurgy does not require high capital costs as in the case of atmospheric leaching (AL). But the extraction rate is not high for this process and needs longer durations to yield a product. High extraction rates are obtainable with hydrometallurgy if high pressure acid leaching is preferably used. But the capital cost is much higher than atmospheric leaching since acid resistant titanium autoclaves, steam heaters and thickeners are needed to be constructed.

2.2.2.1 Atmospheric Leaching

Leaching of laterites under atmospheric conditions is one of the two basic approaches to extract nickel from the host mineral matrix. Leaching at atmospheric conditions is a non-selective process, so all minerals are leached in a greater or lesser extent [10]. The pregnant leach solution (PLS) is contaminated highly by the metals existing in laterite profile. Since the hydrolysis reaction of ferric iron is not possible at the temperatures where atmospheric pressure is conducted, the regeneration of sulfuric acid is not achieved and this results in high acid consumption. Another drawback of atmospheric acid leaching can be encountered in the stage of purification of PLS. Highly contaminated PLS is going to consume relatively high amounts of reactives in the purification step with the formation of high amount of waste product.

Atmospheric leaching process equipment is relatively simple and their maintenance is low. By conducting the leach at temperatures around $95^{o}C$ rather than at high pressure acid leaching temperatures (e.g., $250^{o}C$), the reaction kinetics become slower and this results in high residence time (10-12 hours to achieve >90% nickel extraction) [12].

2.2.2.2 High Pressure Acid Leaching (HPAL)

In the leaching processes; the percent extraction of valuable metals, the consumption of the leaching reagent, impurity level of the leach solution and the required time for the process are some of the factors important on the selection of the process. Atmospheric acid leaching of nickel laterites requires significant amounts of acid in a long leaching period and impure PLS is obtained at the end of leaching. High pressure acid leaching is a relatively selective process on nickel and cobalt over iron and aluminum since at the high temperatures hydrolysis reactions of iron and aluminum take place with the regeneration of acid.

High pressure acid leaching for nickel laterites was firstly started to be used in an operation at Moa Bay (Cuba) in 1959. The large reserves of limonite in Cuba contain about 70% of goethite with no discrete minerals of nickel and cobalt. These metals are mainly associated with goethite. The ore ground to below 0.8 mm is thickened to about 45% solids before feeding it to leach circuit. Leaching is carried out at $246^{o}C$ in five independent trains, each having four Pachuca type vertical reactors connected in series. The overall retention time is less than two hours. The reactors are made of carbon steel bricks and slurry together with sulfuric acid injection pipes are made of titanium. Leach slurry is cooled and is sent to counter-current-decantation (CCD) thickening before neutralization and purification step. Scale formation is the main operating problem at Moa Bay that a thickness of 75 to 100 mm scale is forming in a period of three to four months [13].

After successful operation at Moa Bay, many high pressure acid leaching plants have been built and operated around the world with the modernization of the system. Today, instead of vertical autoclaves, horizontal acid resistant autoclaves are being used. Ravensthorpe, Coral Bay, Verhelmo, Goro, Ramu are some examples of finished or continuing projects. Turkish company META is also planning to construct the first HPAL plant at Manisa-Gördes in a few years [14].

Generally, limonite zone of a laterite profile is treated in this process due to its low content of high acid consuming element magnesium. Laterites have different characteristics at different locations and this leads to changes in operating procedure.

High pressure acid leaching process flow-sheet is given in Figure 2. Beside limonite, in some cases where the grade of nickel is low, saprolitic zone is also mixed with limonite to increase the content of nickel and cobalt in the ore or concentrate. In this process, the laterite coming from the mine is ground and mixed with water to form a slurry. It is concentrated in the slurry mixer in the range of 25-40% solids loading [9] before being heated. Solid loading strongly depends on the rheology of the laterite. Clay minerals such as smectite are possibly associated with laterites and they affect the rheological characteristics of the slurry. Pumps where the slurry is fed to autoclave or thickeners have certain pumping capacity and solid loading is determined after a complete rheological characterization of laterite. The thickened slurry is fed to preheating unit before feeding it to the autoclave. At the Moa Bay plant where this process was initially used, slurry is preheated by low pressure steam to between 70 and 80°C [13]. Today's HPAL autoclaves are horizontally placed instead of vertical Pachuca types and agitation is accomplished at every compartment of the autoclave. Sulfuric acid is fed to autoclave together with slurry where temperature is between 240-270°C. At this high temperature, the reaction kinetics is fast. The acid dissolves certain metals which are extracted from the solid and transferred into the liquid solution. To prevent the liquid from boiling at these temperatures, the operation is being taken place under high pressure (35-55 atm.). The solid residue after leaching is mainly in the form of hematite due to hydrolysis reaction and liquid solution (PLS) contains dissolved metals such as nickel and cobalt together with iron, magnesium, aluminum, chromium, zinc, copper, etc. The slurry is then cooled and depressurized. This operation generates steam which is recycled and re-used in slurry heating circuit before slurry injection into the autoclave.
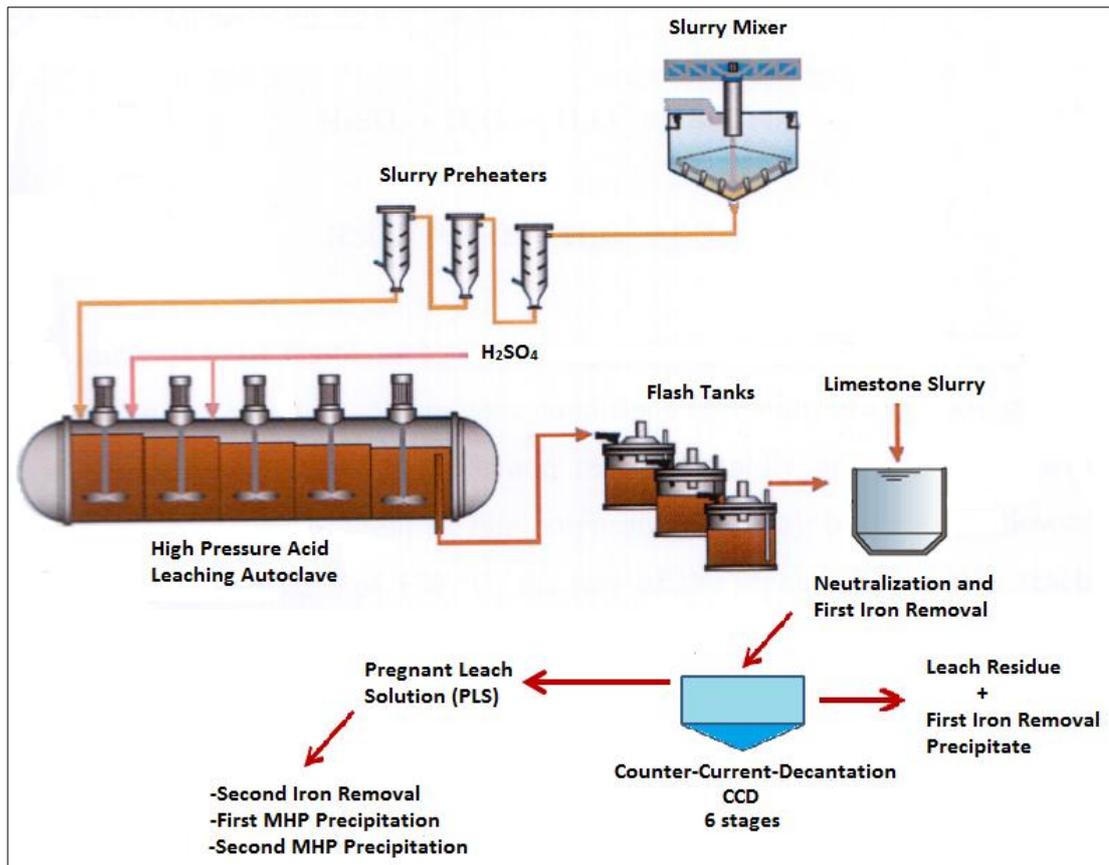
Figure 2. High pressure acid leaching process flow-sheet.

The cooled slurry passes through a decantation circuit usually after neutralization and its main function is to separate liquid and solid and also to wash the solid residues. In continuous-counter-current decantation (CCD), the solids settle at the base and they are collected at the underflow, while the liquid loaded with metal ions is collected at the overflow [15]. The operating principle of counter-current-decantation is presented in Figure 3. Solids are neutralized by lime addition and become environmentally safe before being pumped to tailings dam. Liquid solution loaded with metal ions is sent to neutralization and purification units.
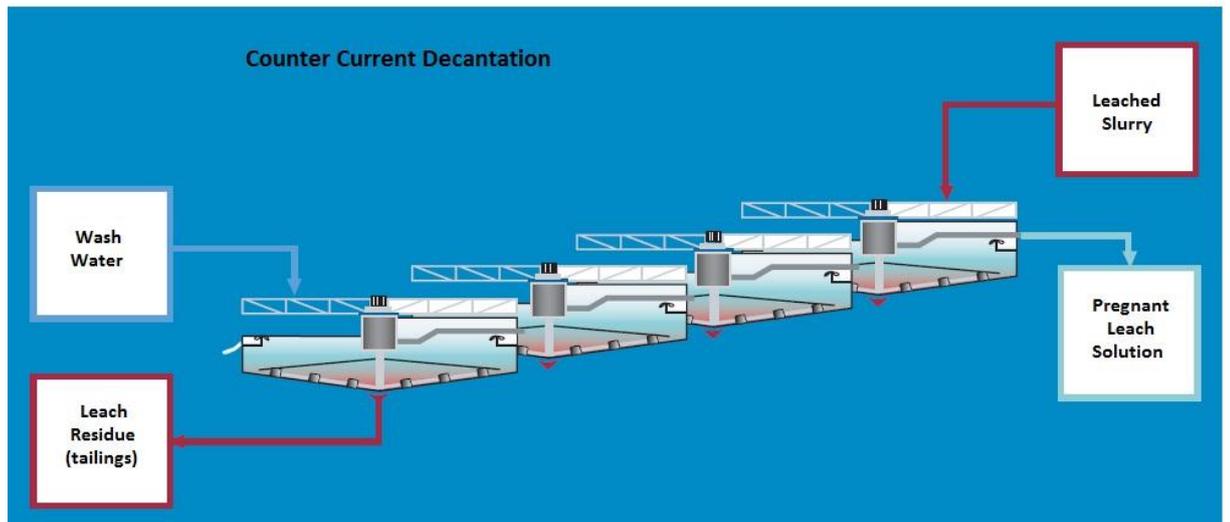
Figure 3. Counter-current-decantation working principle.

2.3 Effect of Processing Conditions on HPAL Process

2.3.1 Effect of Ore Grind

The research by Chou et al. (1977) indicated no effect of grinding of lateritic ores on neither the rate of reaction nor the extraction of nickel. This study was based on the Moa Bay limonite and different limonites can show different characteristics depending on the mineralogy [16]. The research by Kaya et al. (2011) reported a slight increase in the extraction of nickel by grinding the Gördes limonite ore below 74 μ [8]. A relatively low extraction of nickel was believed to be due to lack of liberation of hematite host mineral. By grinding the ore, the liberation of nickel containing hematite from its matrix and better solid-liquid contact have been achieved.

Grinding the ore before being fed into the autoclave has an effect on the impurity ratio of liquid solution (PLS) obtained after leaching. Nickel/impurity ratio increases, suggesting that finer ore particles increases the rate of precipitation reactions of iron and aluminum [9].

2.3.2 Effect of Acid/Ore Ratio

The required amount of sulfuric acid mainly depends on the magnesium content of the lateritic nickel ore or concentrate. As previously mentioned, limonite is poor in Mg whereas saprolite is rich in Mg, thus increases the acid demand for a similar nickel extraction [17, 18].

The HPAL plants of Cawse, Murrin Murrin, Coral Bay, Bulong use or used 0.2-0.6 acid/ore (kg/kg) ratio or acid concentration as a plant operation parameter [9].

Residual acid in the range of 30-50 g/L is required for efficient nickel and cobalt extractions [9].

Using lower acid concentrations decreases the nickel and cobalt extractions while decreasing the ultimate extractions. As previously mentioned about the Moa Bay plant, the major problem of settling is improved with higher acid additions. However, high residual acid concentrations inhibits the precipitation reactions of iron and aluminum, thus impurity concentration of PLS increases [16, 19].

2.3.3 Effect of Solids Concentration

Krause et al. (1998) indicated an insignificant effect of ore concentration on nickel and cobalt extractions between 25-40% solids loading. Production rate is going to be higher in the case of working with high ore input. It is desired to utilize higher amount of ore feed in a similar duration of leaching. However, higher solids loading affects the dissolution of higher amount of impurity elements into leach solution [19].

2.3.4 Effect of Temperature

A temperature range of 240-270°C is appropriate for high nickel and cobalt extractions in HPAL. Increasing the temperature up to 270°C results in the same ultimate nickel extraction while the initial extraction rate of Ni is increased [16]. Operating the leaching process around 300°C is not possible since the nickel extraction is decreased due to formation of nickel-magnesium sulfates. Da Silva et al.

(1992) reported that nickel losses could be attributed to nickel-magnesium sulfates for leaching temperatures in excess of $270^{o}C$ where the precipitation of these sulfates is thermodynamically possible [20]. Higher temperatures have a positive effect on nickel/impurity ratio of PLS since the rate of hematite and alunite precipitation reactions increase together with increases in nickel and cobalt extractions [6, 21].

2.4 Chemistry of the Pressure Acid Leaching of Nickel Laterites

Pressure acid leaching is conducted by sulfuric acid which is favorably ionized at ambient temperatures according to following reaction:

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$
Rx. 1

Sulfuric acid is a polyprotic acid and second dissociation also takes place according to Rx.2:

$$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$$
Rx. 2
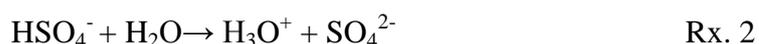
Hydration reaction of sulfuric acid is rapid at ambient temperatures and second dissociation reaction may be ignored. However, the extent of second dissociation of sulfuric acid in the forward reaction in $HSO_4^- = H^+ + SO_4^{2-}$ decreases with increasing temperature so that for temperatures in excess of 150°C, sulfuric acid behaves as a monoprotic acid [19].

For minerals to be dissolved by sulfuric acid, a specific hydrogen ion activity should be supplied to the solution. Since at higher temperatures, hydrogen ion activity decreases due to decreasing rate of second dissociation reaction, an excess amount of sulfuric acid should be supplied to maintain specific hydrogen activity for the dissolution of laterites at high temperatures.

The amount of free acid in the leach solution is expressed by Rx.3:

$$[H_2SO_4]_{free} = [SO_4^{2-}]_{total} - [SO_4^{2-}]_{bound}$$
Rx. 3

where $[SO_4^{2-}]_{total}$ is the total sulfate in solution at the end of the reaction and $[SO_4^{2-}]_{bound}$ is amount of sulfate in dissolved metal salts.

In the following chapters the dissolution of minerals and following precipitation mechanisms will be discussed in detail.

2.4.1 Iron Chemistry

As explained in the previous sections, limonite layer of a laterite profile is preferentially utilized in the high pressure acid leaching since it contains low amount of acid consuming elements. This layer is mainly composed of iron minerals such as goethite and hematite. Maghemite and magnetite minerals have been also observed in a Chinese laterite [22]. Since nickel has no discrete minerals and due to the fact that this metal substitutes in crystal structure of iron containing minerals, complete dissolution of these iron phases is quite important for full liberation of nickel. Cobalt also substitutes in iron containing minerals but also it is associated with manganese minerals [9].

Dissolution of iron containing minerals consumes significant quantities of acid according to following reaction related to goethite mineral:

$$2\ FeOOH + 3\ H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 4\ H_2O \qquad \text{Rx. 4}$$
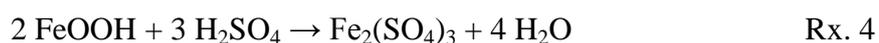
Nontronite is a high magnesium containing mineral but iron can also substitute for magnesium in this mineral structure. This mineral is generally found in a specific layer between limonite and saprolite in dryer climates where mobility of metals is restricted [2]. The layers of a laterite are not definitely separated since the earthquakes cause mixing of them throughout the time. So it is quite possible to observe minerals of other layers in limonite layer. The dissolution of nontronite is given in Rx.5. The chemical formula for nontronite is given for the iron substituted mineral:

$$Fe_2Si_4O_{10}(OH)_2 + 3\ H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 4\ SiO_2 + 4\ H_2O \qquad \text{Rx. 5}$$

As mentioned previously, the dissolution of iron minerals require significant amount of acid for the case of leaching at ambient temperatures. At higher temperatures for the case of high pressure acid leaching, iron sulfate hydrolyses to hematite with the regeneration of acid [23]. This precipitation mechanism lowers the acid demand for a similar extraction of nickel and cobalt. In some cases where the limonite or the water used contains sodium salts, natrojarosite precipitates in a similar way. Acid is

regenerated but for the formation of jarosite a greater loss of acid is expected than for the formation of hematite. The reactions for the hematite and natrojarosite precipitations are given in below reactions:

$$Fe_2(SO_4)_3 + 2\ H_2O \rightarrow 2\ Fe(OH)SO_4 + H_2SO_4 \qquad \text{Rx. 6}$$

$$2\ Fe(OH)SO_4 + H_2O \rightarrow Fe_2O_3 + 2\ H_2SO_4 \qquad \text{Rx. 7}$$
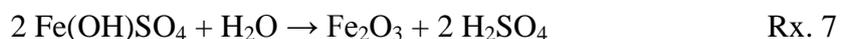
Overall reaction for hematite precipitation:

$$Fe_2(SO_4)_3 + 3\ H_2O \rightarrow Fe_2O_3 + 3\ H_2SO_4 \qquad \text{Rx. 8}$$

For natrojarosite precipitation:

$$3\ Fe_2(SO_4)_3 + 12\ H_2O + Na_2SO_4 \rightarrow 2\ NaFe_3(SO_4)_2(OH)_6 + 6\ H_2SO_4 \qquad \text{Rx. 9}$$
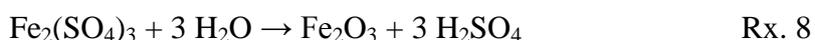
The degree of iron hydrolysis is quite important since filterability is increased with increased amount of hematite precipitation. Natrojarosite formation results in increased amount of solid disposal after leaching. In Western Australia where saline water is used for leaching, the formation of natrojarosite is observed due to the presence of sodium containing salts [9, 24]. Leaching in saline water also results in amorphous silica formation. Muir et al. (2006) indicated that nickel and aluminum are adsorbed in amorphous silica and results in nickel losses [24].

The type of precipitation product is affected from the acidity of the leach solution. If the acidity is high, basic ferric sulfate becomes the stable product (Rx. 6). At the Moa Bay plant, it was reported that ferric sulfate is precipitated in the first autoclave vessel where high acidity exists [23]. Chou et al. (1977) reported that Fe^{3+} in solution reacts to hematite via a sulfate intermediate, which is favored early during the reaction when solution acidity is high. Hematite formation is favored in low acidity and it is the preferred product due to its good filterability and high amount acid regeneration throughout the reaction [16].

Increasing temperature and adding sulfate salts of Zn, Mg or Na increase the maximum acid level at which hematite forms. These salts decrease the free acid levels due to the formation of bisulfate-sulfate buffer, thus an increase in acid level below which hematite formation is observed [9].

Iron concentration in the pregnant leach solution is another important issue for high pressure acid leaching method since the pregnant leach solution is going to be purified in the following stages. The removal of impurities such as Fe, Al, Cr is affected with the concentration of impurities in the leach solution. It is very desirable to have low amount of iron ions and also other impurities in the pregnant leach solution to make purification steps easier.

Iron concentration increases in PLS in the first few minutes of leaching at high temperatures, then decreases to an equilibrium value [25]. Sudden increase in concentration of iron is due to dissolution of respective iron minerals such as goethite and hematite. During this dissolution incorporated nickel and cobalt are released from the host mineral. The decrease in iron concentration with digestion duration is consistent with goethite dissolution-hematite precipitation mechanism. Study of Papangelakis et al. (1996) also indicated that hematite precipitates very rapidly and it is believed to be formed through a homogenous nucleation mechanism due to very high supersaturation. Hematite seeds increase the rate of transformation since the requirement for nuclei formation is satisfied [23].

Equilibrium iron concentration is higher for lower digestion temperatures and for less dense slurries. Since the amount of solids decreases for less denser slurries, secondary nucleation on previously formed crystals or on growing hematite particles does not play as significant role as in denser slurries [25].

In limonites Fe^{2+} may also exist possibly coming from serpentine mineral $(Fe, Mg)_3Si_2O_5(OH)_4$. In that case ferrous ion replaces magnesium which has similar ionic radii. Fe^{2+} containing leach solutions are not desired if mixed hydroxide precipitation method is going to be used for the purification in the further steps. Fe^{2+}

is not selectively precipitated over Ni and Co in the MHP process and it contaminates the product. After dissolution of serpentine mineral, some portion of dissolved Fe^{2+} is oxidized to Fe^{3+} due to the favorable conditions in the autoclave [21]. Remaining Fe^{2+} contributes to significant acid consumption and also it would result in increased downstream costs. Injecting oxygen into the autoclave creates an adequate oxidative environment so that most of the iron in the form Fe^{2+} can be precipitated as hematite together with reduction in acid consumption [26].

Iron containing phases play an important role in the high pressure acid leaching. Complete characterization of the ore is very important since each lateritic nickel ore is different mineralogically and chemically. Iron chemistry is going to be discussed further in terms of the effect of acidity, temperature, residence time in the results and discussion part.

2.4.2 Aluminum Chemistry

Gibbsite [$Al(OH)_3$] and boehmite ($AlOOH$) are the common aluminum minerals associated with laterite deposits. Solid solution of aluminum within goethite matrix is also possible to be observed [27]. The most common aluminum bearing mineral gibbsite transforms into boehmite at temperatures above $135^{o}C$ according to Rx.10 [28]:

$$Al(OH)_3 \rightarrow AlOOH + H_2O \qquad \text{Rx. 10}$$

The temperature in the high pressure acid leaching is enough for this transformation to take place and nearly all of the gibbsite transforms into boehmite. When the sulfuric acid is fed to the titanium autoclave, acid attacks boehmite according to reaction in Rx.11:

$$AlOOH + 3\,H^+ \rightarrow Al^{3+} + 2\,H_2O \qquad \text{Rx. 11}$$

The concentration of aluminum in the leach solution increases with increases in digestion duration. During precipitation of iron, aluminum also precipitates as alunite or other stable phases and the regeneration of acid is observed.

The form of stable phase is sensitive to the temperature of digestion and also depends on the concentration of acid in the leach solution. At temperatures below $250^{o}C$, alunite is the stable phase. Alunite formation is given in Rx.12:

$$6\ Al^{3+} + 4\ SO_4{}^{2-} + 14\ H_2O \rightarrow 2\ H_3O.Al_3(SO_4)_2(OH)_6 + 10\ H^+ \quad T < 250^{o}C \quad \text{Rx. 12}$$

Basic aluminum sulfate formation is also thermodynamically possible at temperatures above $280^{o}C$. This reaction also regenerates acid according to Rx.13:

$$Al^{3+} + SO_4{}^{2-} + H_2O \rightarrow Al(OH)SO_4 + H^+ \quad T > 280^{o}C \qquad \text{Rx. 13}$$
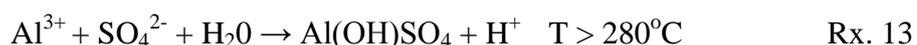
Acid concentration is also effective on the stability of aluminum phases. Formation of $Al(OH)SO_4$ can also occur at leaching temperatures lower than $280^{o}C$ if the acidity is high [29].

As a last comment for aluminum, it can be said that alunite precipitates are responsible for Ni and Co losses since these valuable metal ions incorporate into alunite structure [30].

2.4.3 Magnesium Chemistry

Dissolution and subsequent precipitation mechanisms play a significant role for high pressure acid leaching in terms of decreasing the acid demand since acid is regenerated at the end of reaction. It is important for purity level of solution since impurity ions of iron and aluminum are removed from leach solution as a result of stable precipitate formation. Such a mechanism is not possible for magnesium and nearly all of the dissolved magnesium stays in the PLS. So, the dissolution of magnesium minerals accounts for unrecoverable acid consumption.

Generally limonitic nickel laterites do not contain high fractions of magnesium (approximately 1.5% Mg) but in some cases for increasing the nickel content of the feed, the limonitic laterite is mixed with richer transitional (nontronite) or saprolitic layers. To increase the concentration of Ni in the ore feed in such a way results in an increase in magnesium content and as expected an increase in acid consumption occurs. Limonites have a nickel grade between 1.0 to 1.4%. Nickel grades of transitional ore may be 1.5% or higher. The decision should be made after carrying a detailed economic analysis that increased nickel content can disable the increased amount of acid costs. Study by Marshall et al. (2004) indicated that after blending a transitional layer into limonite, magnesium content was increased from 0.9 to 2.7%. This increase in magnesium content resulted in an increase in acid demand from 0.22 to 0.33 acid/ore (kg/kg). This corresponded to a 50% increase in acid requirements [31].

As indicated in the previous sections, a free acid level of 30 g/L to 50 g/L is necessary in the final PLS for high nickel and cobalt extractions. When the limonite and nontronite are blended, 30 g/L is not sufficient as before blending and extractions of nickel and cobalt drop dramatically for a similar acid addition. In order to achieve high nickel and cobalt extractions higher amount of free acid is required (i.e., 50 g/L) [31]. This amount of free acid will definitely increase limestone demand in the neutralization stage after HPAL process.

Although the magnesium extractions are variable according to different deposits, it is reported that 50-60% of the magnesium dissolves in the pressure acid leaching [9]. Extraction of not all of the magnesium in the ore is desirable since magnesium silicates also give rise to soluble silica after leaching, besides increasing the acid consumption [32]. Dissolution of magnesium containing clays is given in the below reaction:

$$Mg_3Si_2O_5(OH)_4 + 3\ H_2SO_4 \rightarrow 3\ MgSO_4 + 2\ SiO_2 + 5\ H_2O \qquad \text{Rx. 14}$$

A study by Marshall et al. investigated the magnesium solubility at $270^{o}C$ as a function of acidity. The paper indicated that the higher the acidity, the higher was the equilibrium concentration of magnesium in PLS [31]. At $270^{o}C$; for 30 g/L of free acid, magnesium equilibrium value was stated to be 7 g/L while for 50 g/L free acid, it was 11 g/L. If the magnesium content in the ore is very high that dissolved magnesium (10-12 g/L) exceeds the critical equilibrium value, then it precipitates as a simple sulfate according to below reaction:

$$Mg^{2+} + SO_4^{2-} + H_2O \leftrightarrow MgSO_4.H_2O \qquad\qquad Rx. 15$$

This reaction is not quite possible unless the leach solution is loaded with high magnesium amounts. In limonitic/saprolitic blends the magnesium concentration may reach to a value which is higher than the equilibrium value of magnesium. This can lead to precipitation of magnesium sulfates. Another issue about magnesium is that Mg is not present in the solution as a simple ion or a neutral sulfate complex ($MgSO_4$ aq). It is predicted to be in the form of sulfate-bisulfate complex or a basic sulfate-bisulfate complex according to a model proposed [21, 33]. In that case, this form decreases the available H^+ and also the acidity at a fixed temperature.

2.4.4 Manganese/ Nickel/Cobalt Chemistry:

As it is mentioned in the previous sections nickel and cobalt have no discrete minerals in the laterites. They are substituted in the iron-containing mineral structures and when the host minerals are dissolved by sulfuric acid attack, nickel and cobalt are liberated into the solution. Cobalt is mainly associated with the manganese minerals such as lithiophorite $(Al,Li)MnO_2(OH)_2$ or asbolane $(Co, Ni)_{1-y}(MnO_2)_{2-x}(OH)_{2-2y2+x}.n(H_2O)$ [34]. Cobalt and manganese are found together in laterites and they have similar dissolution characteristics [35]. Manganese minerals are not easily leached and they require a reducing agent to be completely leached. Low cobalt extraction in some laterites may arise due to high amount of manganese mineral content in the ore that is not leached completely. But there is also a possibility that minerals like clay type, supply ions that plays a reducing agent role.

For example high cobalt and manganese recoveries are obtained from nontronite ores, since reduction of the Mn (IV) in lithiophorite with Fe(II) coming from clays results in dissolution of Mn (II) and cobalt [36]. Addition of other reducing agents may create difficulties in terms of Fe^{2+} concentration in the leach solution. The reducing agent may reduce Fe^{3+} coming from main mineral goethite to Fe^{2+} and thus amount of hematite precipitation may be lower, acid consumption may increase and settling characteristics may be negatively affected. Furthermore, as previously mentioned Fe^{2+} in the solution creates difficulties for the process involving an intermediate hydroxide or direct solvent extraction of the acid leach solution [37].

Manganese minerals extraction in the autoclave environment is not complete and it accounts for 50-60% of extraction. The manganese present in a laterite ore solubilizes as sulfate [38]. These extraction values are highly sensitive to ore type that New Caledonian, Murrin Murrin or Moa Bay ores can show different characteristics [19, 36, 39].

Although nickel and cobalt do not have their own minerals in laterites, the hypothetical reactions are given below to illustrate the dissolution phenomena:

$$NiO + 2\,H^+ \rightarrow Ni^{2+} + H_2O \qquad\qquad \text{Rx. 16}$$

$$CoO + 2\,H^+ \rightarrow Co^{2+} + H_2O \qquad\qquad \text{Rx. 17}$$

Da Silva et al. (1992) reported that free acid is necessary for high nickel and cobalt extractions. If residual acidity in the PLS is not satisfied, nickel and cobalt precipitate as their respective monohydrate $MeSO_4.H_2O$ salts (where Me is Ni or Co) [20].

2.5 Downstream Applications of Pregnant Leach Solution

After the limonite is attacked by acid, the minerals are dissolved and the pregnant leach solution (PLS) is loaded with impurity ions such as iron, aluminum and chromium together with dissolved nickel and cobalt. This acidic solution is needed to be utilized for neutralization, purification and precipitation of an intermediate product as in the case of mixed hydroxide precipitation method (MHP). This

intermediate product is further re-leached in ammonia solution and electrowinning is applied after solvent extraction for pure Ni and Co products.

Downstream processing of laterite leach solutions has some options to recover nickel and cobalt from this solution. These are:

- Direct Solvent Extraction (DSX)
- Ion Exchange (IX) and Resin-In-Pulp (RIP)
- Molecular Recognition Technology (MRT)
- Mixed Sulfide Precipitation (MSP)
- Mixed Hydroxide Precipitation (MHP)

2.5.1 Mixed Sulfide Precipitation (MSP)

Among these options MSP method is the oldest method to refine and recover Ni and Co from pregnant leach solution. This method was firstly commercialized at the Moa Bay plant in Cuba about 50 years ago [13]. Coral Bay, Murrin Murrin plants are also reported to be utilizing MSP method. This method is highly selective for nickel and cobalt over impurities of iron, aluminum, chromium and manganese. This fact eliminates the necessity of removal of these impurity elements prior to intermediate product precipitation. General flow-sheet of MSP process is presented in Figure 4 [3].

In the MSP process, the leach solution loaded with metal ions is sent to reduction stage after a CCD wash and H_2S is used for the reduction. At this stage copper is selectively precipitated while ferric iron and hexavalent chromium are reduced to ferrous iron and trivalent chromium. In the neutralization stage limestone is added to adjust the pH of the solution to achieve the optimum conditions for nickel and cobalt precipitation. Then, the solution is sent to sulfide precipitation units at which 55-61 wt.% Ni containing intermediate product is precipitated [3]. MSP product generally contains the impurities of zinc and copper since their precipitation characteristics in H_2S media is similar to nickel and cobalt. The intermediate product is further refined for pure product at the refineries.
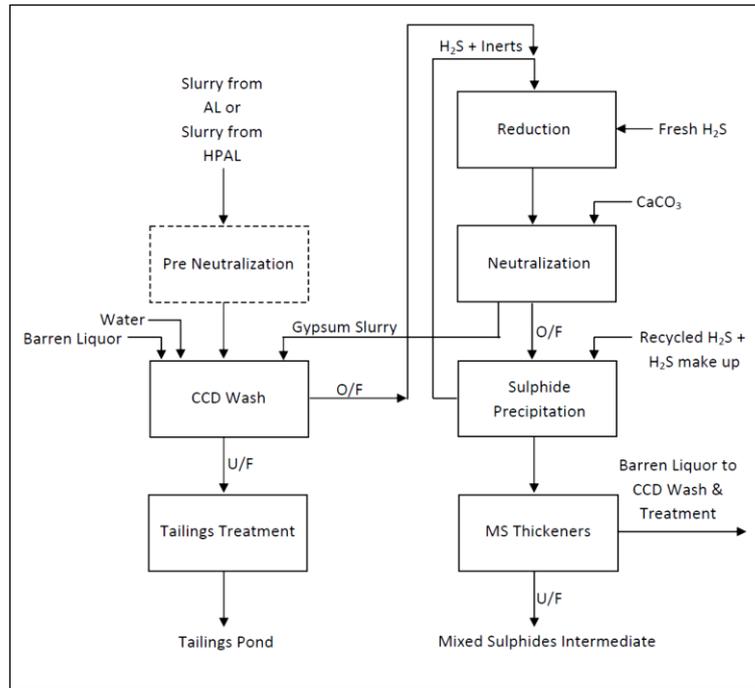
Figure 4. Mixed sulfide precipitation (MSP) process general circuit.

2.5.2 Direct Solvent Extraction

Direct solvent extraction is another commercialized method to recover nickel and cobalt from pregnant leach solution. This process was firstly operated at the Bulong circuits. The general flow-sheet of the DSX method is presented in Figure 5 [40].

In the DSX circuit, the pregnant leach solution is exposed to an organic reagent (Cyanex 272) to separate cobalt from nickel. Copper, zinc, manganese, magnesium are also separated together with cobalt. By sulfide precipitation Co is removed from the strip liquor in the solid form together with Cu and Zn while Mn and Mg are separated. The filtrate of sulfide mixture is sent to cobalt refinery at which Co cathode is obtained. The separated Ni containing solution also contains some impurities of Mg and Ca. These contaminants are separated from the solution by use of D2EHPA, and then nickel is electrowon.
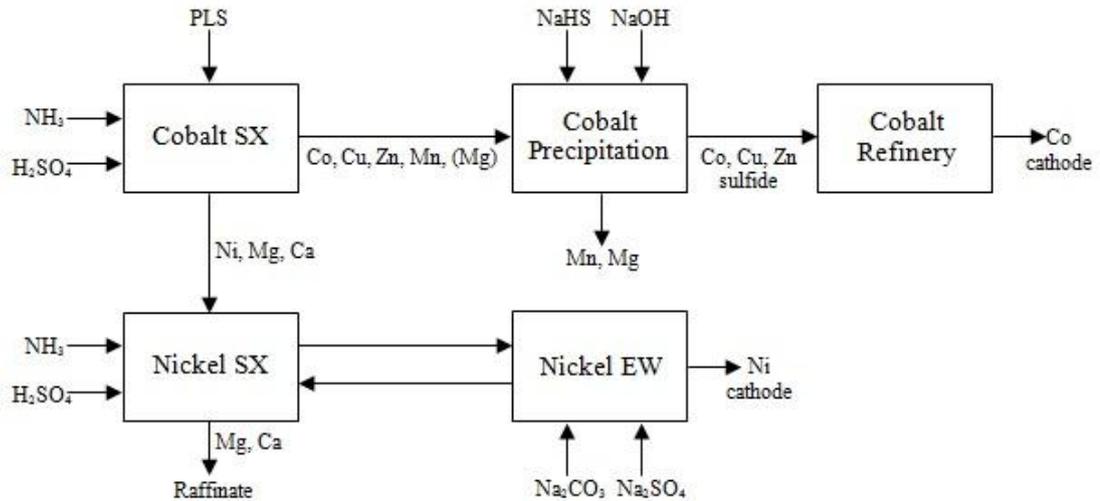
Figure 5. Direct solvent extraction flow-sheet.

2.5.3 Mixed Hydroxide Precipitation

Mixed hydroxide precipitation is another option to recover nickel and cobalt from the pregnant leach solution. This method has a low selectivity over manganese but it is relatively inexpensive compared to other downstream options. At the end of the process an intermediate product of nickel and cobalt which named MHP is obtained, and then it is further processed to produce a nickel compound or pure nickel. Neutralization, iron removal, Ni and Co precipitation and manganese removal steps are the critical stages of this process. These steps will be explained in the following pages. Commercially, this process was utilized at Cawse and is being used at Ravensthorpe plants (Western Australia). Besides these operations, there are some important efforts around the world to devise MHP projects which will come into operation in the near future. Vermelho in Brazil, Ramu in Papua New Guinea and Young, Mount Margaret in Western Australia are planning to integrate MHP circuit as a downstream application. As indicated in the previous pages, Turkish company META Nickel and Cobalt Company is planning to operate a high pressure acid leaching plant to utilize the laterite reserves at Gördes, Manisa. This plant is also going to use MHP technology for downstream applications. An intermediate product of nickel-cobalt hydroxide is going to be obtained at the end of the process [41].

General flow-sheet of the mixed hydroxide precipitation method used in downstream processing of pregnant leach solution coming from high pressure acid leaching units is given in Figure 6 [41].

Figure 6. Process flow-sheet of HPAL and MHP applications.

Mixed hydroxide precipitation method starts with the neutralization of upstream solution and it is necessary to purify the solution prior to precipitation of nickel and cobalt product. This is critical since contamination of impurity elements of Fe, Al and Cr is possible due to favorable conditions. A reactive of alkaline reagent is used during this process to increase the pH of the solution. The pH increase results in the decrease in the solubility of metallic constituent and this favors precipitation mechanism. At this point, investigating the precipitation diagrams of Monhemius is

helpful to understand the route of process. Mixed hydroxide precipitation selectivity diagram is given in Figure 7 [42].
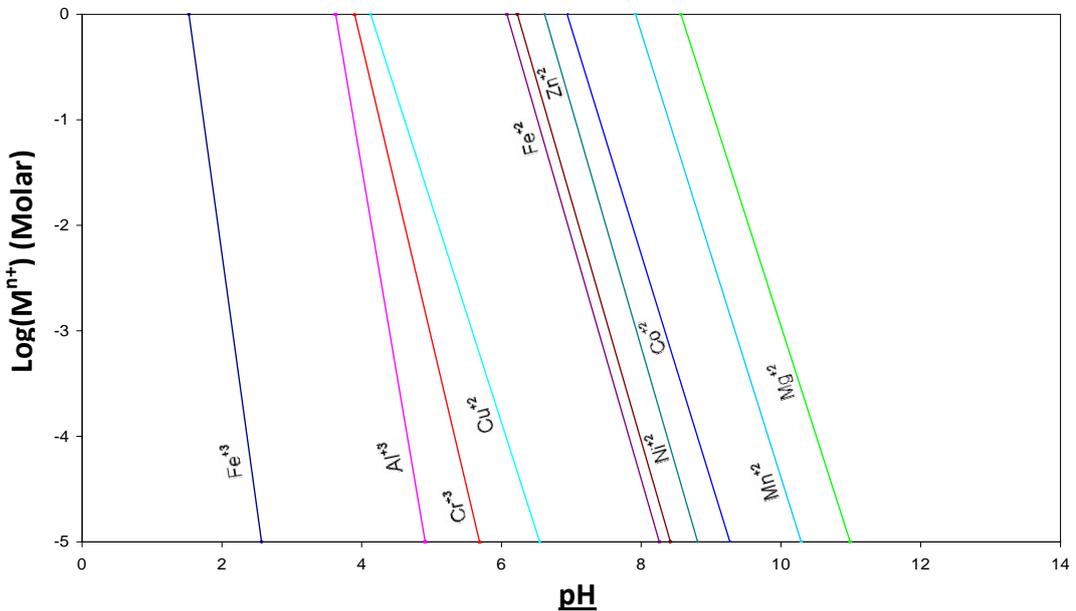
Figure 7. Mixed hydroxide precipitation selectivity graph (25°C, 1 atm.).

The diagram shows the stability of ions or their respective hydroxide precipitates at a given pH. The lines indicate the affinity of the metals to precipitate as hydroxides. To the left of the lines, metal ions are stable in the solution and when the line is passed to the right, the metals are precipitated. The leach solution obtained after high pressure acid leaching has a free acidity generally between 30 to 50 g/L. At the start of the MHP process, the solution is at the left side of Fe^{3+} line. As indicated previously, the pregnant leach solution contains significant amount of impurities and these impurities must be eliminated before precipitating the nickel and cobalt. Fe^{3+}, Al^{3+}, Cr^{3+} stability lines are not very close to Ni^{2+} and Co^{2+} lines. This makes the removal of these impurities possible prior to nickel and cobalt hydroxide precipitation. Removal of these impurities generally takes place in two stages to control the loss of nickel and cobalt. Most of the iron, together with some aluminum and chromium are precipitated around pH=2.5 with minimal loss of nickel and cobalt. Then, the second stage removal of iron is applied around pH=4.5 with the aim of removal of all iron, aluminum and chromium. At this stage, nickel and cobalt are co-precipitated in some amount and the precipitate is sent to recycle leaching to

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recover the lost nickel and cobalt. At this point it should be mentioned that the mass of second iron removal precipitate is very much less than the mass of precipitate formed at the first stage of iron removal. If the leach solution contains Fe^{2+}, ferrous iron will definitely contaminate the product since its stability line is very close to nickel and cobalt. In other words, Fe^{2+} ions precipitate together with nickel and cobalt in MHP process. This problematic behavior must be overcome in the leaching stage so that Fe^{2+} in the leach solution must be oxidized to Fe^{3+}. According to Loveday (2008) the use of oxygen during the high pressure acid leaching or after flashing of the autoclave reported to be the solution of this problematic issue [26]. Fe^{2+} is oxidized to Fe^{3+} under an oxidative environment. Similar contamination behavior was also observed for zinc. Fortunately, zinc is present in very small quantities in nickel laterites.

During the pH increase throughout the process, Mn^{2+} and Mg^{2+} precipitate after nickel and cobalt precipitation as it is also seen in the MHP selectivity graph. But the deportment of these metals especially Mn^{2+} is also possible during the pH increase. Manganese contamination is also critical that it brings out the necessity of precipitation of the MHP product to be taking place in two stages. During the first precipitation, nickel and cobalt precipitation over manganese precipitation should be selective so that at a considerably lower pH, Mn deportment is minimized.

In hydrometallurgical processes, precipitation is a physical-chemical process. The aim is to convert the soluble metals and inorganics to relatively limited soluble metal and inorganic precipitates. This is achieved by lowering the solubility of the metal in solution by increasing the pH of the solution [43]. A representative precipitation reaction for nickel precipitated by lime as alkaline reagent is given in Rx 18.

$$Ni^{2+} + Ca(OH)_2 \rightarrow Ca^{2+} + Ni(OH)_2(s) \qquad\qquad Rx.\ 18$$

When the desired metal or metals are wanted to be removed from the solution, the precipitated solids are filtered out of the solution and the concentrations of these metals are lowered in the solution. Oustadakis et al. (2006) has reported that maintaining the correct pH range throughout the reaction and giving sufficient time

for settling of precipitates is critical for physical-chemical processes [43]. Furthermore, since these reactions require a reactive agent, the addition of the reagent creates the driving force of the reaction. But the reagent should be added in sufficient amount not to create sudden increase in the pH of the solution. Then, the deportment of impurities or loss of valuable metals which require higher pH values are also precipitated.

Controlling the supersaturation is a critical issue for this process since MHP precipitation is not a very selective process. The main difficulties are the impurity uptake and settling characteristics. When the intermediate product of MHP contains impurities, these contaminants create difficulties in subsequent refining applications. For example, the very troublesome contaminant aluminum when allowed to report to intermediate product as low as 0.5%, the dissolution of nickel and cobalt is reduced in the following ammonia leaching by 10-30%. This is believed to be due to creation of an amorphous and gelatinous aluminum oxide precipitate which covers some portion of nickel and cobalt precipitates [3]. Iron is also reported to reduce the extraction of nickel and cobalt as aluminum if the ammonia re-leaching is to be used for the refining of the MHP product [41, 44]. As a consequence, if aluminum and iron are not lowered in the MHP product to desired levels, the nickel and cobalt become insoluble to some degree. Unfortunately, the recovery of these lost valuable metals is impossible. So, the removal of iron, aluminum and chromium from the upstream solution is very critical prior to mixed hydroxide product precipitation.

The kind of neutralizing agent is an important factor affecting the precipitation mechanism. Lime, magnesium hydroxide, caustic or a blend of these alkaline compounds may be the sources of hydroxide ions for precipitation of metal hydroxides. These reagents have some advantages and disadvantages that must be considered before the choice. Sodium hydroxide may create the precipitates in very fine or slimy shape which causes difficulties in settling and filtering. Washing of filter cake is also difficult due to fine particle size. The use of calcium hydroxide has also disadvantage of formation of insoluble calcium sulfate precipitate [43, 44]. Lime and magnesium hydroxide also lead to the possibility of breaking metal complexes that may be present in the wastewater stream. The use of lime may be the most

economic choice in terms of cost of the reagent but Ca^{2+} penetration into the solution causes a secondary precipitate formation such as gypsum ($CaSO_4.2H_2O$) or bassanite ($CaSO_4.5H_2O$). Nickel and cobalt precipitates are gelatinous and have bad filtering characteristics. Although use of Ca containing reagents improves filterability of precipitates due to highly crystalline structure of gypsum, the MHP product is contaminated by calcium sulfate precipitates [45].

Improving settling characteristics of mixed hydroxide precipitates is quite important to produce a superior product. According to Sist and Demopoulos (2003), controlling supersaturation helps to generate well-grown crystalline particles. The precipitates formed by homogenous nucleation due to very high supersaturation have undesirable properties such as bad morphology. Homogenous nucleation results in badly formed crystals, which possess slow settling rates, low solids density and high impurity uptake. The nucleation must be achieved heterogeneously and this can be achieved by providing seed substrates for the precipitation. But if supersaturation is badly controlled, homogenous nucleation may still be effective and the effect of seed may be diminished. By providing the seed, precipitation takes place on to the seed heterogeneously. This results in particle growth and the reduction of the formation of fine colloidal-like precipitates [4]. Nickel and cobalt hydroxide precipitate can be used as a seed material and the substrate can eliminate the induction period for homogenous nucleation in which creation of solid precipitate is necessary for this case. By accelerated reaction kinetics, more filterable precipitates can be achieved by using the seed material [43].

Mixed Hydroxide Precipitation Process Stages

As indicated in the previous pages, MHP process consists of neutralization and purification stages prior to nickel and cobalt precipitation so as not to contaminate the product with the impurity elements. Figure 6 shows the general flow-sheet of the process and it can be seen that a unit of recycle leach is placed between pressure leach units and neutralization units. Recycle leaching is conducted with the aim of recovering the nickel and cobalt coming from the stages of second iron removal and second MHP precipitation. Each necessary stage of MHP process is explained below:

2.5.3.1 Neutralization (First Iron Removal)

The solution loaded with metal ions coming from high pressure acid leaching units called PLS contains significant amount of free acid (30-50 g/L) which has to be neutralized prior to mixed hydroxide precipitation. At this stage, most of the iron (Fe^{3+}) is removed after the neutralization of the free acid with the addition of limestone ($CaCO_3$). The addition of reactive causes the pH of metal loaded solution to attain 2.5-3.0. When the mixed hydroxide selectivity graph (Figure 7) is observed in detail, Fe^{3+} is expected to be removed from the solution prior to MHP precipitation [3]. Although Cr^{3+} and Al^{3+} stability lines are around pH=4, these metals are also precipitated together to some degree with Fe^{3+}. This is believed to be due to supersaturation of these metals during the pH increase. Gypsum formation is observed as a product of acid neutralization reaction. As a result of limestone reaction with Fe^{3+}, goethite formations is observed. These reactions are given in the below:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \qquad \text{Rx. 19}$$
$$3\,CaCO_3 + Fe_2(SO_4)_3 + 2.5\,H_2O \rightarrow 3\,CaSO_4.0.5H_2O + 2\,FeO(OH) + 3\,CO_2 \quad \text{Rx. 20}$$
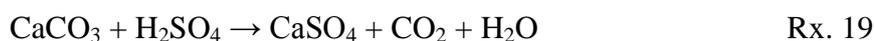
Operating temperature is generally between 70-90°C and at these temperatures slurry viscosity is lowered and reaction kinetics are favored. At ambient temperatures, the reactions are possible but kinetics is slow. The residence time of 90 to 180 minutes is necessary to achieve necessary iron precipitation. Precipitations of some nickel and cobalt also occur at this pH range (2.5-3.0). But the precipitations of nickel and cobalt must be very low not to lose these valuable metals (usually below 0.5 or 1%). The discharge slurry is thickened and soluble nickel and cobalt are recovered by continuous counter-current-decantation (CCD). The solids are separated after washing and they are disposed-off.

2.5.3.2 Second Iron Removal

As the pH increases, the amount of precipitated nickel and cobalt also increases. If the iron removal stage is conducted in a single stage, the loss of nickel and cobalt will be higher since recycle leaching would not be meaningful to operate due to high

amount of solid disposal. By doing the purification in two stages, most of the iron, chromium and some aluminum are precipitated initially at lower pH with the aim of minimal nickel and cobalt precipitation and then at higher pH remaining iron, chromium and aluminum are aimed to be removed. The pH target is generally around 4.4-4.8 with the addition of limestone and it is governed by desired residual impurity concentration in the solution. The residence time is between 60 and 120 minutes at temperatures of 70-90°C [3]. As indicated previously the solids formed at this stage is smaller in mass than the precipitate formed in the neutralization stage and it is recycled to recover the nickel and cobalt. This stage is so critical that it is performed as the last treatment for impurities prior to the mixed hydroxide precipitation. In other words if the impurities of iron, aluminum and chromium in the PLS are not decreased to the desired concentrations at this stage, they will precipitate together with nickel and cobalt and contamination of product will occur. As mentioned before especially the contamination of the product with aluminum creates difficulties in further refining of mixed hydroxide product.

2.5.3.3 Mixed Hydroxide Precipitation

The mixed hydroxide precipitation selectivity graph shows that iron, chromium and aluminum can be removed from the solution before nickel and cobalt precipitation is taking place. From this fact, these impurities have been removed already in two stages of iron removal. But the mixed hydroxide precipitation is not highly selective for nickel and cobalt over manganese since the stability lines of them are close to each other. So it is necessary to precipitate the nickel and cobalt in two stages to control the amount of manganese precipitating together with nickel and cobalt. By this way, it is aimed to reduce the deportment of manganese to the saleable mixed hydroxide product which is called MHP 1. To achieve the limited manganese co-precipitation, pH is adjusted to 7.0-7.5 in order to precipitate the maximum nickel and cobalt achievable while manganese precipitation is limited. The solid product is aimed to be contain <5% of manganese in the composition [3]. The general composition of limonite profile in terms of manganese content in a lateritic ore is also critical due to lack of selectivity of nickel and cobalt over manganese. So this process is better applied to laterites which have high Ni/Mn ratio (usually for ores with Ni/Mn ratio less than 3) [9].

The temperature of MHP precipitation can be in the range of 50-70°C, higher temperatures facilitate faster reaction kinetics but the possibility of manganese precipitation is also increased. Magnesia (MgO) is generally used for pH adjustment for nickel and cobalt precipitation and as a result of this some magnesium reports to the MHP 1 product. It is believed to be due to unreacted magnesium oxide. The reactivity of magnesia is between 0.7 to 0.9 [44]. Therefore, it is necessary to take into consideration that the required amount of magnesia necessary for precipitating the nickel and cobalt will be higher than the theoretical amount required. As a reactive of this stage, instead of magnesia, caustic soda (sodium hydroxide), hydrated lime (calcium hydroxide) or soda ash (sodium carbonate) may also be used. Caustic soda eliminates the Mg contamination of the MHP product due to unreactivity of magnesia and brings higher selectivity for nickel over manganese but it is very expensive. Usage of lime results in the formation of gypsum and causes the product to be contaminated with calcium precipitates. The use of soda ash results in precipitation of carbonates along with hydroxides but the selectivity for nickel over manganese decreases since the solubility of manganese carbonate is lower than that of nickel carbonate [3].

A typical composition range of MHP 1 product is given in Table 1 [3]:

Table 1: Typical MHP 1 composition:

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

2.5.3.4 Second Stage Mixed Hydroxide Precipitation

Due to limitations of manganese incorporation to the mixed hydroxide product (MHP 1), in the first precipitation stage not all of the nickel and cobalt existing in the leach solution are precipitated. Most of the nickel and cobalt is taken out of solution by precipitating over 90% of these metals in this initial stage. The depleted solution usual has about 200 ppm nickel after the first mixed hydroxide precipitation stage. Now to recover the nickel and cobalt which are remaining in the solution, a second mixed hydroxide precipitation step is needed. This stage is also called "scavenger nickel cobalt precipitation" in the literature. At the end of this application the attained product (MHP 2) will not have a saleable quality due to its high content of manganese (10-20% wt.) and it is sent to recycle leaching. So this precipitation stage of nearly all of the nickel and cobalt remaining in the solution must be recovered since there are no further steps to recover these valuable metals. The second MHP precipitation step is expected to lower the nickel and cobalt contents in the solution

to less than 5 ppm levels. To achieve these levels, the pH is adjusted to 7.5-8.0 at about 60-80°C and 60 to 80 minutes of residence time is necessary for the precipitation [3]. Slaked lime is used instead of magnesia since there are no quality limitations at this stage.

2.5.3.5 Manganese Removal

After the second stage of mixed hydroxide precipitation, manganese remains in the pregnant leach solution. When this solution is wanted to be used in the system as system water or wash water, manganese accumulation will occur in the circuit. The accumulation will affect the quality of mixed hydroxide product since it is not desired to be more than 5% Mn in the precipitates. So manganese concentration should be lowered in the solution before recycling it throughout the system. This is achieved around pH 8.5-9.0 at 50-60°C and between 30 and 120 minutes residence time. For some cases air may be introduced to tanks to achieve manganese oxidation.

The saleable product of MHP can be further refined to have nearly pure Ni and Co metals. Applicable processes are:

- Ammonia leach, ammoniacal SX, electrowinning
- Ammonium sulfate leach, cobalt SX, hydrogen reduction
- Acid leach, cobalt SX, electrowinning

As a final comment, if the refinery is far from the MHP plant, the customer may have to deal with high transportation cost due to the high moisture containing (35-45%) nature of MHP product.

CHAPTER 3

SAMPLE CHARACTERIZATION, EXPERIMENTAL SET-UP AND PROCEDURE

3.1 Sample Description

In this thesis study, limonitic nickel laterite sample obtained from Sivrihisar/Eskişehir, located in the central part of Turkey, was used to carry out the high pressure acid leaching and subsequent mixed hydroxide precipitation experiments. The ore sample was obtained via META Nickel and Cobalt Company in December-2009 and the transfer of the sample was done in humidity impermeable barrels.

3.2 Sample Preparation and Physical/Chemical Characterization

As mentioned in the literature part, the characterization of the sample is quite important since the optimum operating parameters for one limonite is not applicable to another since mineralogy, composition, etc. changes. In order to determine the general characteristics; physical, chemical and mineralogical characterization analyses were performed.

The sample obtained from Sivrihisar was received in four humidity impermeable barrels. Two of the four barrels were containing samples from a distinct region (Kara Sivri Tepe) at the mine site and they were limonitic yellow in color. The other two barrels were full of samples from a different excavation (Küçük Sivri Tepe) and they were dark brownish. By considering the fact that a possible future plant will operate with all of the samples having a homogeneous composition, it was decided to mix all

of the samples to form a single composition sample. Each barrel contained about 100 kg of sample and at the end of mixing there were 420 kg of limonitic nickel laterite sample. The crushing, grinding and sampling operations, conducted on the sample can be seen in Figure 8.

Concentration techniques such as flotation or magnetic separation, is not applicable for limonitic nickel laterites since there are no discrete nickel and cobalt minerals in laterites. It was decided to investigate the nickel distribution depending on the particle size to understand whether nickel is richer or poorer in coarser grains. Then, to concentrate the ore it may be possible to discard coarse particles from the sample with a reasonable loss of nickel.

After mixing and homogenizing of all the samples coming from mine site, it was again separated into four parts by coning and quartering method for further operations. One sample was left in a barrel in case of future sample requirement. To investigate the nickel distribution in coarse particles, the run-of-mine ore was decided to be screened from 50 mm and also from 20 mm sieve opening screens. At the end of screening as can be seen in Figure 8 that; +50 mm, -50 mm as well as +20 mm and -20 mm of the ore fractions were separated. Together with the run-of-mine sample, all of the fractions were ground separately by using jaw and roll crushers and finally they were ground to -74 μ for chemical and other analyses.

The screened parts were dried at 105°C for 6 hours to eliminate the physical water. The chemical composition analyses were carried out by META Nickel and Cobalt Company using AAS (atomic absorption spectrophotometer). The results of screening operation in terms of weight of oversize, undersize and their nickel, iron contents and their distributions are given in Table 2.
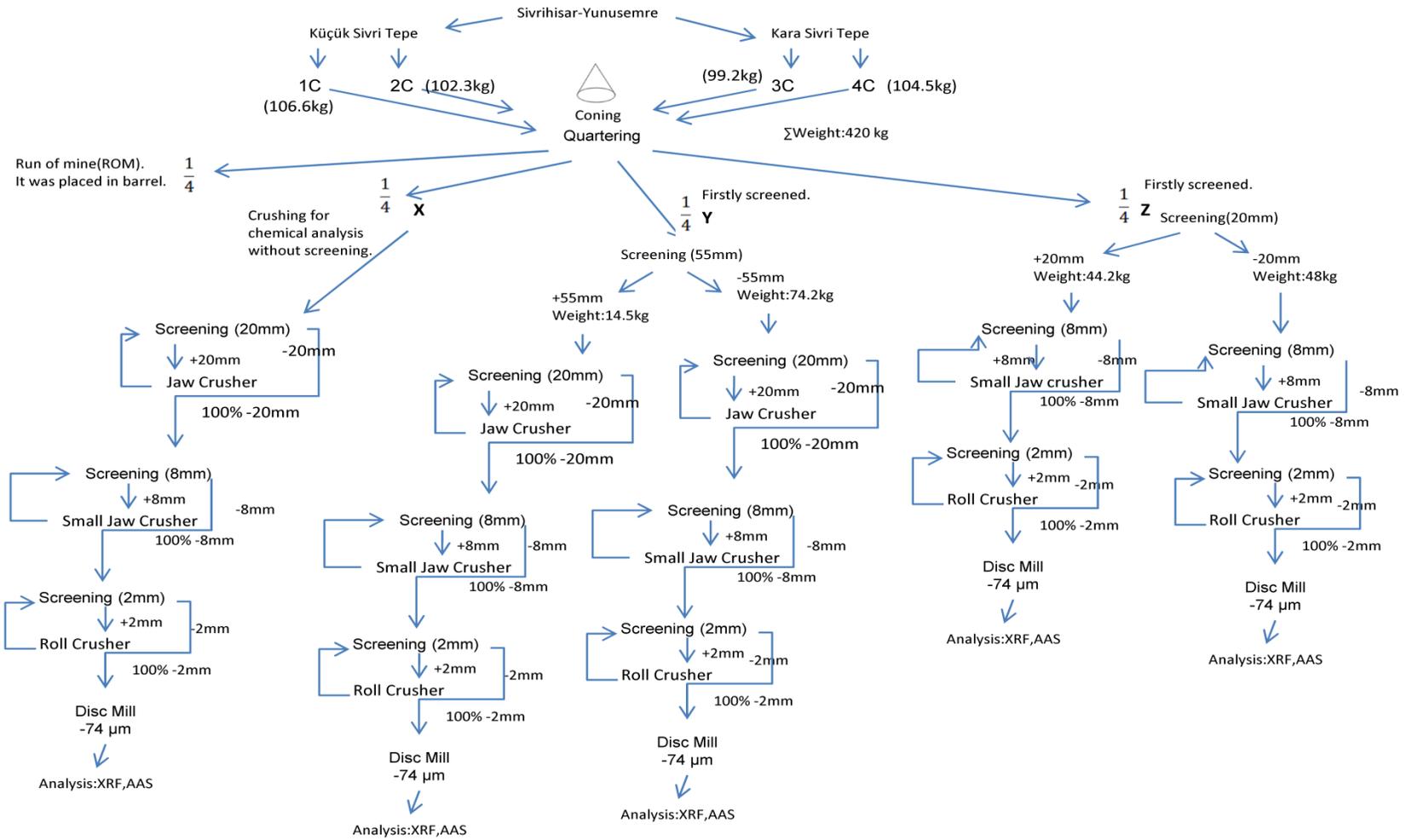
Figure 8. Ore preparation steps conducted on Sivrihisar limonitic nickel laterite.

Table 2. Nickel and Iron distribution after 50 mm and 20 mm screening.

META AAS						Distribution		
	Dry Weight(kg)	%Ni	Weight Ni(kg)	%Fe	Weight Fe(kg)	%Ni	%Fe	Weight %
(+50 mm)	13.54	0.979	0.133	29.074	3.94	11.73	15.37	17.61
(-50 mm)	63.37	1.575	0.998	34.216	21.68	88.27	84.63	82.39
∑	76.91	1.470	1.131	33.311	25.62	100	100	100

META AAS						Distribution		
	Dry Weight(kg)	%Ni	Weight Ni(kg)	%Fe	Weight Fe(kg)	%Ni	%Fe	Weight %
(+20 mm)	40.31	1.312	0.529	35.207	14.19	43.95	50.73	50.02
(-20 mm)	40.27	1.675	0.675	34.232	13.79	56.05	49.27	49.98
∑	80.58	1.493	1.203	34.720	27.98	100	100	100

When the run-of-mine ore was screened from 20 mm opening sieve, it was seen that half of the ore in weight would be discarded with a loss of 44% of nickel. It is not meaningful to discard this amount of ore with a tremendous loss of nickel with the aim of concentrating the sample. Screening from 50 mm screen gave much more positive results for the purpose of concentration. Oversize of 50 mm screening was relatively poor in nickel and also only 17% by weight of the ore accounted for this fraction. In other words, by screening the run-of-mine from 50 mm sieve opening screen, the nickel content was increased in some amount while at the same time small portion of (17% wt.) ore which was rich in quartz was discarded with a loss of 11% of nickel. Coarse grains are believed to contain significant amount of quartz which is not leachable in high pressure acid leaching process. After these findings, it was decided to conduct the experiments by screening the ore coming from the mine site from 50 mm sieve and discarding the oversize. The richness of quartz in the coarse grains and increase in concentration of nickel are also going to be indicated in the full chemical composition analysis in the following pages.

A similar screening operation was also found in the literature which was carried out by Chou et al. (1976) on New Caledonian laterite ore. +6.7mm / -850 μ fraction was removed by screening due to its low nickel and cobalt contents [16].

For the limonites, the existence of nickel in the crystal lattice of iron-containing minerals is also confirmed with the screening results given in Table 2. By separating the undersize from oversize using screening (apparent for 50 mm screening) the nickel content has increased together with the iron content in the undersize. As seen in Table 2, the nickel content has increased from about 0.9% to 1.6% while iron content was increased from about 29% to 34% in 50 mm screen fraction.

After the sample coming from Sivrihisar has reached METU, it was decided to determine the moisture content as soon as possible since the physically present water might evaporate with time. The moisture content was found to be 15.4% as seen in Table 3 after maintaining the run-of-mine portion of the sample in a drying oven at $105^{o}C$ for 6 hours. Coarse fractions moisture content was also determined and it was found that it was much lower than that of the run-of-mine ore. For +50 mm fraction, the moisture content was just 6.6% It should be also mentioned that the moisture content is very sensitive to weather and climate conditions at the time of sampling at the mine site.

Table 3. Moisture content of limonitic sample.

Representative Ore Sample	Moisture Content (wt.%)
Limonite (Run-of-mine)	15.4

In each high pressure acid leaching experiment, a sample of 100% -850μ particle size was decided to be used. To investigate the size distribution in the -850μ sample, wet screen analysis method was decided to be used on the limonitic laterite sample. For this purpose a simple screening system based on Tyler mesh consisting of nine-sieve series was vibrated by a shaker, while tap water was fed on top of this system continuously. A continuous water flow was necessary to help the particles to get distributed in their corresponding particle sizes. The sieves were selected so that sieve opening size was decreasing by square root of two starting from 600 μ for the coarsest particle and finishing at 38 μ for the smallest particle. About 200 grams of sample was used to carry out the test. After the wet screen analysis each screen fraction was dried overnight at $105^{o}C$.

The result of wet screen analysis for the limonite sample is given in Table 4. It can be seen from Table 4 that the sample used in high pressure acid leaching experiments was relatively fine having particles more than about 33% finer than 38 μ.

Table 4. Wet screen analysis result of -850 μ Sivrihisar limonitic sample.

Sieve Opening		Weight (g)	Oversize wt.%	Cumulative Oversize wt.%
+	600 μ	25.14	12.86	12.86
+	425 μ	19.07	9.75	22.61
+	300 μ	16.53	8.45	31.07
+	212 μ	15.97	8.17	39.24
+	150 μ	11.83	6.05	45.29
+	106 μ	11.36	5.81	51.10
+	75 μ	11.04	5.65	56.74
+	53 μ	10.33	5.28	62.03
+	38 μ	9.39	4.80	66.83
-	38 μ	64.85	33.17	100.00
	Σ	195.51	100	

To calculate the expected acid consumption of the sample, a detailed chemical compositional analysis was necessary. Although -50 mm fraction of the sample was chosen to be fed to the titanium autoclave both -50 mm fraction and run-of-mine ore were analyzed chemically by Inductively Coupled Plasma (ICP) method. The ICP analyses were carried out at ALS Analytical Chemistry and Testing Services in Canada and the results are given in Table 5.

As it is explained in the previous pages, the nickel content had increased and reached to 1.405% after screening the ore from 50 mm opening sieve. A significant difference was observed in the quartz content such that after discarding of over 50 mm particles, SiO_2 content decreased from 30.3% to 25.8%. It can be said that the coarser particles were richer in quartz whereas nickel and cobalt were richer in the finer particles.

Table 5. Chemical composition of limonitic sample.

Element/ Compound (wt.%)	Run-of-Mine Limonite	(-50 mm) Limonite
Ni	1.260	1.405
Fe	32.60	33.70
%As	0.03	0.04
%Co	0.082	0.093
%Cr	1.01	1.26
%S	0.01	0.03
%Zn	0.03	0.03
%Cu	0.005	0.006
%SiO$_2$	30.30	25.80
%Al$_2$O$_3$	2.68	3.23
%MgO	1.03	1.29
%CaO	1.69	1.65
%MnO	0.62	0.74
%TiO$_2$	0.06	0.08
%K$_2$O	0.24	0.24
%P$_2$O$_5$	<0.02	0.04

3.2.1 Mineralogical Characterization

Determination of the type of minerals present in the ore sample is significant since the leaching behavior of lateritic nickel ores is very much affected by the mineralogy. Some minerals are suppliers of undesired ions such as (Fe^{2+}) in the case of smectite. If an unsatisfactory extraction value is obtained in the leaching step, the mineralogy investigation results can give the clue for solving this undesired outcome.

In order to determine the type of minerals present in the run-of-mine and -50 mm ore fraction samples, X-Ray diffraction analysis (XRD) were carried out with Rigaku D/MAX2200/PC model X-Ray Diffractometer with a Cu-Kα X-ray tube working under 40 kV and 40 mA. The XRD patterns of both samples are given in Figure 9.
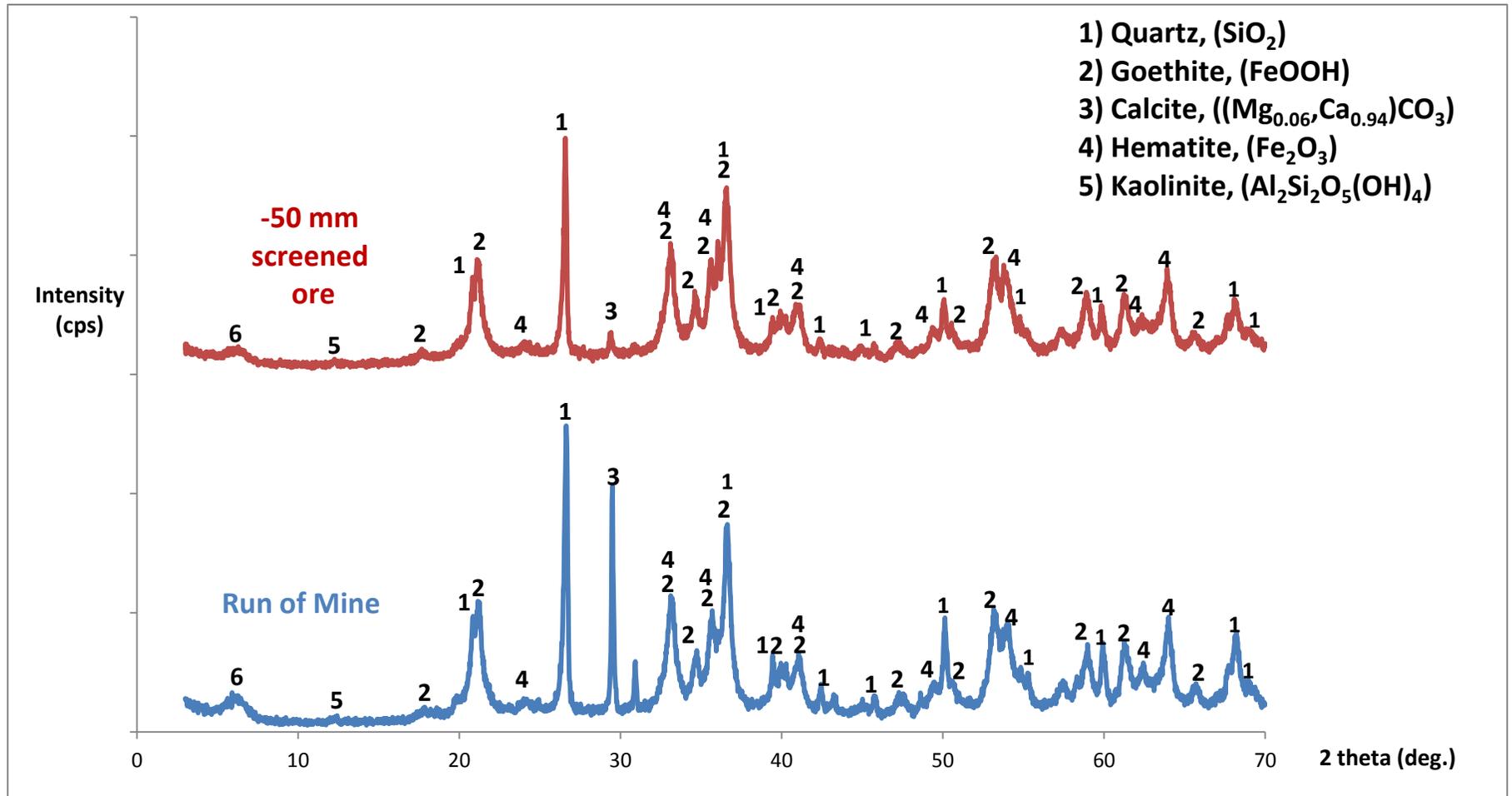
Figure 9. XRD result of run-of-mine and minus 50 mm screen fraction

XRD results indicated that the main peaks were belonging to quartz and goethite. In the literature, it was reported that limonitic nickel laterites contain mainly iron containing minerals [9, 16]. The XRD result of Sivrihisar limonite is consistent with the literature that there were also peaks of hematite together with goethite. As expected, a specific mineral of nickel and cobalt was not observed in the X-ray diffraction analysis since these metals were substituted mainly into crystal structure of iron containing minerals. There were also peaks of calcite, kaolinite and smectite which were observed in the limonite sample. It was already mentioned that the existence of clay minerals is possible in lateritic nickel ores. The smectite mineral has been reported to contain higher amount of nickel than goethite or hematite but when present, it increases the acid demand of leaching process due to its high magnesium content. Minor amount of smectite was believed to exist in the Sivrihisar limonite.

When the Sivrihisar limonitic sample was screened from 50 mm, some amount of poor nickel containing quartz fraction was discarded although it was not very obvious from Figure 9 that some amount of decrease was observed in the peak intensities of quartz mineral by the removal of quartz fraction. By the screening of limonitic sample, a decrease in the peak intensities of calcite was also observed. It was also believed to be discarded in some amount in the coarse fractions.

In order to confirm the results of XRD analysis, Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA) were carried out in the central laboratory of METU. These analyses were conducted with a heating rate of 10°C/min within the temperature range of 35-1000°C in air atmosphere in an alumina crucible [46]. The DTA and TGA results for the run-of-mine and minus 50 mm ore fraction are given in Figures 10 and 11.
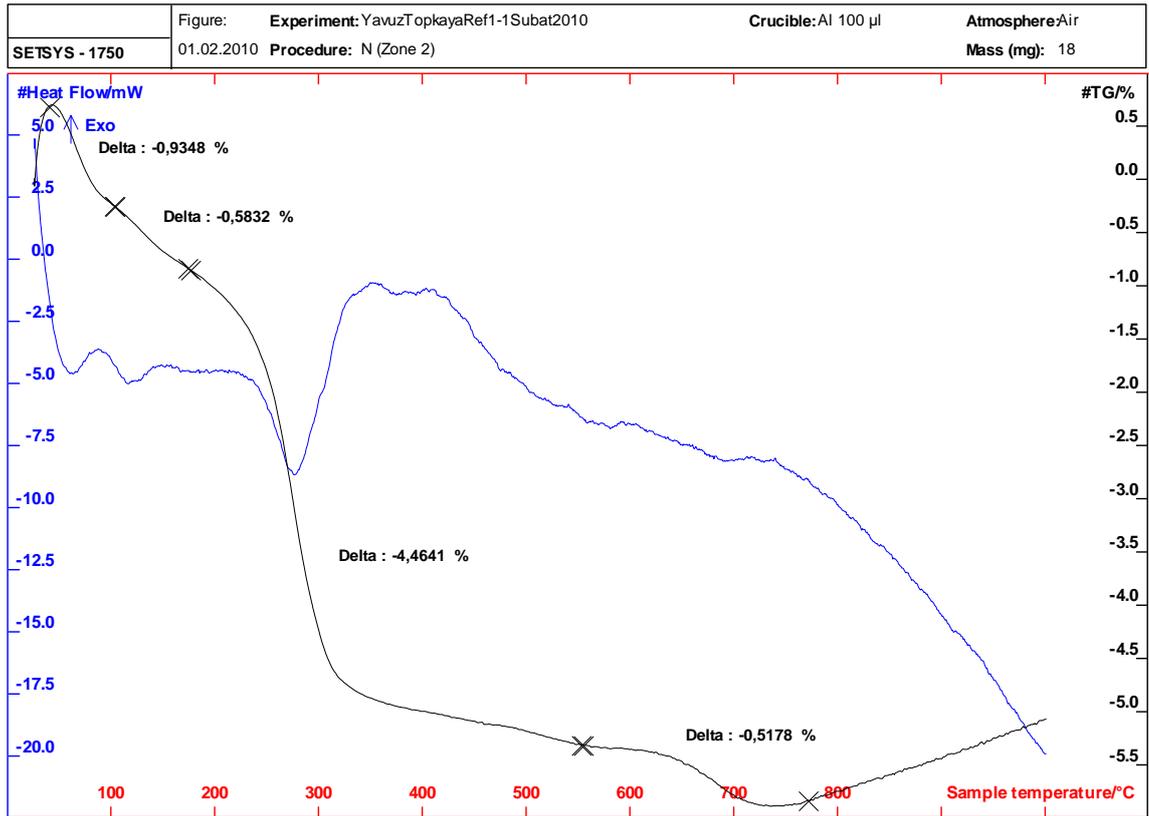
Figure 10. DTA and TGA results of run-of-mine sample.
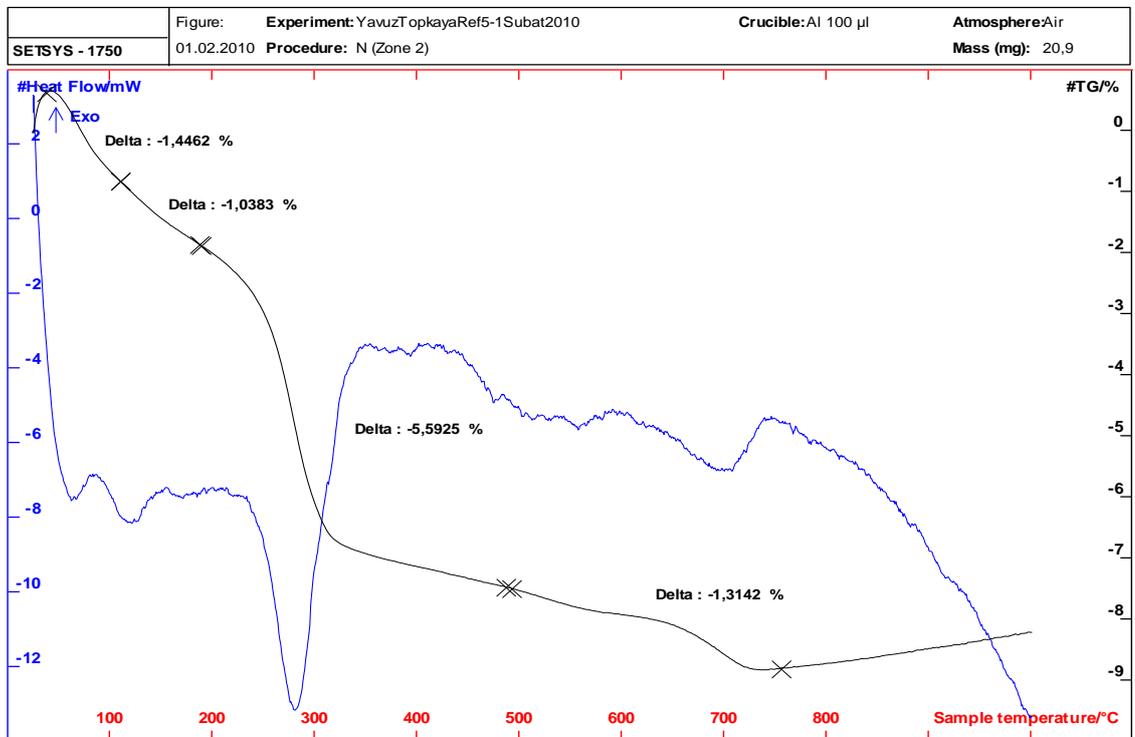
Figure 11. DTA and TGA results of minus 50 mm sample.

According to DTA and TGA results an endothermic peak between 100-150°C was detected which was responsible for the removal of physical water which was present in the bulk of the sample. This peak was found to be consistent with the findings of Lopez et al. (2008). In this paper it was stated that this peak corresponds to elimination of water absorbed on minerals [47]. A second deep endothermic peak was observed around 290-300°C which corresponded to goethite-hematite transformation. This peak proved the presence of goethite mineral which was also found in the XRD results. During the goethite to hematite transformation, goethite loses its chemically bonded water according to below reaction:

$$2 \text{ FeO(OH)} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \quad \text{(Dehydroxylation)} \quad\quad\quad \text{Rx.21}$$
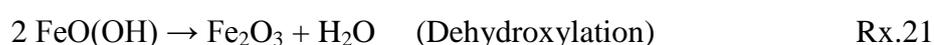
The book of "Thermal Analysis of Minerals" by Todor reports that the removal of hydroxyls takes place from 450 to 700°C for kaolinite type clay minerals [48]. The variation of temperature from one type of kaolinite to another depends on variation of particle size. For instance, the dehydration temperature decreases with decreasing particle size. Also the temperature variation can be explained by the degree of crystallinity of the kaolinite minerals. By considering the behavior in the temperature interval from 450 to 700°C, there was a continuous decrease in mass around these temperatures. A possible clay mineral was believed to exist in Sivrihisar ore since it was losing its chemically bonded CO_2 or H_2O upon heating (kaolinite, smectite) [48, 49].

Around 535-545°C, a small endothermic peak was observed for both samples. In the -50 mm ore fraction, the peak was more apparent. Although the allotrophic form of quartz in the limonite couldn't have been determined from the XRD results, there is a possibility that this peak corresponded to the allotrophic transformation of quartz (SiO_2). The polymorphous transformation of β-quartz into α-quartz occurs at around 573°C ± 40°C [48].

Another endothermic peak was observed around 690-700°C which is apparent in the latter DTA-TGA result. This peak was believed to belong to the decomposition of calcium carbonate. But after further detailed research, a possible presence of montmorillonite [$Al_2(Si_4O_{10})(OH)_2$] mineral in the Sivrihisar limonite has been detected.

This mineral has three specific thermal behaviors but only two of them were observable in the temperature range in which the experiment was conducted. The first one was an expected endothermic effect between 100 and 250°C as a result of the removal of adsorbed water and the second endothermic peak for montmorillonite was observed from 670 to 710°C and it was due to removal hydroxyl groups.

3.3 Experimental Procedure for HPAL Experiments

High pressure acid leaching experiments were conducted in a Parr-4532 model, 2 liter, titanium grade-4 autoclave. The autoclave was equipped with automatic heating and cooling units. It had magnetically driven stirring system. A picture of the system is given in Figure 12.

Figure 12. The autoclave used in HPAL experiments (Titanium-grade 4).

The experimental procedure followed in this study for high pressure acid leaching had some differences with the other studies reported in the literature. As in the industrial practice, sulfuric acid is normally injected to the titanium autoclave at about the leaching temperatures but for this study this was not the case. This system which is present in the METU Hydrometallurgy Laboratory did not have an acid injection system. Installation of autoclave with acid injection system is an expensive investment and also maintenance of the parts which are exposed to very high pressure is quite critical and creates additional costs. If this maintenance could not be supported, working at these high temperature and pressures under sulfuric acid environment could be fatally dangerous. So another procedure was followed such that acid was fed to the autoclave container together with the ore slurry before starting to heat the autoclave to leaching temperature. The effect of this procedure on metal extractions will be discussed in the following paragraphs.

The principal working parameters of the high pressure acid leaching can be given as;

- Leaching temperature
- Leaching duration
- Sulfuric acid concentration or acid/ore ratio

It is not possible to change the pressure of the autoclave without changing the temperature since it is a steam pressure dependent autoclave. The above indicated parameters are the main variables which can yield high nickel and cobalt extractions if the mineralogy of the sample permits leaching reactions. After any undesired situation (i.e., low valuable metal extractions, high impurity levels in PLS, etc.), researchers try to solve the situation by changing operating parameters or adding different reagents (e.g., salts). As it was mentioned in the literature part, the addition of salts and the use of oxidizing or reducing agents have been studied previously.

In this study, the effects of leaching temperature, leaching duration and acid/ore ratio on high pressure acid leaching were investigated and the optimum conditions to reach high nickel and cobalt extractions for Sivrihisar limonite have been tried to be determined. The batch composition used in these experiments is given in Table 6.

Table 6. Typical batch composition of autoclave.

Additives	Weight (g)
Limonite	200
Deionized Water	300
Sulfuric Acid	54

200 grams of limonite was mixed with 300 grams of deionized water to satisfy the predetermined solids concentration of 40% (excluding acid amount). The mixture of ore and water is called slurry. The slurry was fed into the autoclave container and then the technical grade sulfuric acid (96-98 wt.%) was added on top of the slurry according to the theoretical acid consumption calculations. For instance 54 grams of sulfuric acid satisfied the acid to ore ratio of 0.27 for the first experiment. The lid of the autoclave was closed carefully in order to prevent any leakage during the high pressure leaching operation. At this point, it should be also mentioned that the system was equipped with a rupture disc to protect the researcher from sulfuric acid splash in case of any failure. The autoclave container was placed inside the heating furnace after controlling the gaskets and the target temperature was set. When the autoclave reached to the target temperature, the duration of leaching was started to be counted. After the intended leaching duration was completed, the system was cooled back to room temperature via flowing water through a titanium cooling coil. This titanium coil was present inside the autoclave container and cooling of the autoclave to room temperature took approximately 1 hour. After the pressure leaching, the solid and liquid had to be separated. This was achieved by a vacuum pump and a Buchner funnel. The slurry was filtered with Whatman grade-42 filter paper placed on a Buchner funnel. After separating the liquid which was a metal ions loaded solution (PLS) from the solids, the leach residue stayed on the Buchner funnel. Before the chemical compositional analysis, the leach residue had to be washed completely to remove the pregnant leach solution from solid particles. This was performed with deionized water adjusted to pH=2 to prevent ions precipitation during filtration. The resultant leach residue was dried for 6 hours at 105°C before sending to chemical analysis.

Niton X-Met 820 X-ray Fluorescence (XRF) and Atomic Absorption Spectrosphotometer (AAS) of META Nickel and Cobalt Company were used for chemical analysis. Also, the chemical analyses of the pregnant leach (loaded with metal ions) solutions were done at the Chemical Engineering Department of METU with the method of AAS. The free acid in the pregnant leach solution, oxidation-reduction potential and density measurements were also performed after each experiment. For the oxidation-reduction potential measurements, a Pt-Ag/AgCl electrode (saturated with KCl) was used. If required, the measured values may also be converted into the Standard Hydrogen Electrode (SHE) potential values by the addition of 198 mV.

To determine the free acid in the pregnant leach solution, 0.2 molar sodium hydroxide (NaOH) solution was used. While neutralizing the free acid in the leach solution, the determination of consumption of sodium hydroxide was problematic since some ions interfere with the reaction. This was overcome by using 280 g/L di-potassium oxalate monohydrate ($K_2C_2O_4.H_2O$). Before starting the titration, pH meter was also calibrated to pH 7.0 by a buffer solution. During each titration reaction 20 cc of di-potassium oxalate monohydrate solution diluted with 5 cc of deionized water and the pH of this solution was measured. This was noted as target pH that was aimed to be reached with the addition of NaOH after the addition of 5 cc of pregnant leach solution into the prepared solution. During the titration experiments magnetic stirring was also done and the amount of NaOH consumption to reach the target pH was determined. Then, the corresponding free acid amount in the pregnant leach solution was calculated from the amount of NaOH consumption.

3.4 Experimental Procedure for Mixed Hydroxide Precipitation (MHP)

Mixed hydroxide precipitation experiments were done to obtain a saleable quality MHP product by initially removing impurities from the pregnant leach solution, then from the purified PLS the nickel and cobalt were precipitated. This was achieved by increasing the pH of the pregnant solution and controlling the conditions for metals to precipitate as their respective hydroxides (Figure 7).

The increase in pH was achieved by adding different reactives (e.g., limestone, magnesia, slaked lime) at different stages (i.e., neutralization together with first iron removal, second iron removal, first and second Ni and Co precipitation stages).

In the literature, there are some researches on the precipitation of nickel-cobalt hydroxides based on synthetic leach solutions obtained by mixing of the respective metal salts [50]. In this research a real pregnant leach solution obtained by the high pressure acid leaching of Sivrihisar limonitic laterite ore was used. After determining the optimum conditions of HPAL for Sivrihisar limonitic nickel laterite ore which will be discussed in the following chapters, about 3.9 liters of pregnant leach solution was produced at 235°C, 0.23 acid/ore ratio (kg/kg) and at 1 hour of leaching duration. The solid leach residues were also stocked after being washed and dried. The oxidation-reduction potential (ORP) and density of the pregnant leach solution obtained were measured to be 395 mV and 1.13 g/cc.

In the industrial process flow-sheet of HPAL, it can be seen that after pressure leaching of limonitic laterite sample, the pregnant leach solution and the solid leach residue go into neutralization together with first stage of iron removal as a mixture. Then, the separation of the liquid (PLS) and solid (leach residue) phases coming from neutralization tanks take place at the counter-current-decantation (CCD) unit.

At the start of HPAL experiments, 40% of solids concentration (kg/kg) was fed into the autoclave and about 43.5% of solids concentration was obtained after the experiments conducted at the optimum conditions. The pregnant leach solution was then separated from leach residue by vacuum filtration and residual solids were dried in a drying oven. After homogenization of all PLS and all solid residues obtained after each experiment, a slurry having 43.5% of solids concentration (pregnant leach solution / solid leach residue) was formed (i.e., 100 cc of PLS = 113 g and 87 g leach residue) and neutralization together with first stage of iron removal experiments were initiated. The experiments for neutralization together with first iron removal, second iron removal and mixed hydroxide precipitation stages were carried out in 250 or 500 ml glass balloons with 4 necks. A condenser not to lose the feed in the vapour form, a contact thermometer and a pH electrode were placed in the three available necks, while the reagents in the slurry form were added through the feed neck. The experimental set-up is given in Figure 13.

After these experiments, each PLS was filtered through an ashless filter paper (Whatman No 42/110mm diameter) which was placed onto a Buchner funnel with a 1000 ml Pyrex flask. An acid resistant vacuum pump connected to the Pyrex flask was used for filtration purposes. Then, the precipitated solids and the leach residue as in the case of neutralization (together with first stage of iron removal) were washed on the filter paper with de-ionised water and dried at 105°C for 6 hours in a drying oven, while the filtrate was stocked. At the end of each experiment, the filtrate obtained was sent for AAS analysis and the solids were analysed with XRF and AAS units. Precipitation recovery calculations were carried out using the precipitate weights and solution volumes as well as AAS and XRF analyses data of the experiments.
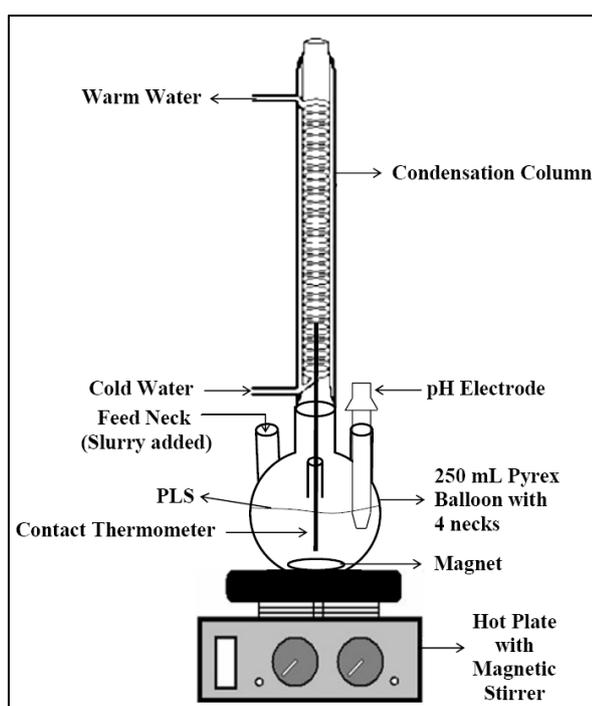
Figure 13. Downstream experimental set-up.

In the neutralization and first iron removal stage, the reactive used for removing most of the iron, aluminum and some chromium was limestone (~14 micron) (Merck 2066). 25% weight / weight limestone slurry was prepared by mixing 25 grams of limestone with 100 cc of de-ionized water. The slurry was fed into 4 necked glass

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balloon through the feed neck drop by drop not to cause the supersaturation of metals. The feeding of limestone slurry to the balloon took about 45-50 minutes. At the fixed conditions of 90^oC and 2 hours of precipitation duration, a pH range from 2.50 to 3.50 was studied. The main operating problem of this stage was the difficulty of stirring the slurry. Since the solid leach residue was also fed to the balloon together with the pregnant leach solution, magnetic stirring was difficult to perform. But using smaller magnets (2-3 cm long) was found to be effective in obtaining sufficient mixing.

After optimizing the conditions for the neutralization and first iron removal stage, a new stock of pregnant leach solution was produced (1.75 L) under the determined optimum conditions. The oxidation-reduction potential (ORP) and density of the pregnant leach solution were measured to be 240 mV and 1.078 g/cc. In the second stage of iron removal, a 12.5% weight / weight limestone slurry was used with the aim of removing the residual iron, aluminum and chromium from the pregnant leach solution. The first set of experiments was done by contacting the pregnant leach solution and limestone ($CaCO_3$) slurry directly. In the process flow-sheet of MHP process, it can be seen that the pregnant leach solution coming from the neutralization stage is being washed by process water (wash water) in the CCD tanks (Figure 6). Dilution by a factor of 1.5 also usually takes place at the CCD units. The wash water comes from the manganese removal stage and it contains significant quantities of magnesium (i.e., 3.5-4 g/L). By considering the magnesium content of process water, the pregnant leach solution obtained after neutralization stage was decided to be diluted with Mg-containing water. To perform these experiments, 33 cc of pregnant leach solution obtained at the optimum conditions of neutralization stage was mixed with 17 cc Mg-containing de-ionized water. 0.6096 g of $MgSO_4.7H_2O$ was intentionally added to 17 cc of de-ionized water to prepare a 3500 ppm magnesium containing solution. A pH range from 4.00 to 4.75, at temperatures of 50, 70, 90^oC and precipitation durations from 1 to 3 hours were studied.

After obtaining the optimum conditions for second iron removal stage, a new stock was produced (0.7 L) under the chosen optimum parameters of precipitation. The first mixed hydroxide precipitation experiments were done by using this solution and a reactive of magnesia (MgO) slurry was used. The magnesia was very fine powder (98-100.5% MgO) of Merck 5862 quality. It was kept away from CO_2 and moisture of air in a sealed container. Magnesia was used freshly as in slurry form by mixing it with de-ionised water with a magnetic stirrer in a beaker at room temperature just before each experiment. In order to prepare the slurry, 0.50 g MgO was added into 50 ml de-ionised water (1% wt./wt. slurry) contained in a beaker. The prepared slurry was slowly added drop by drop in 45-50 minutes with the help of a 5 ml pipette. A pH range from 7.00 to 7.20 was studied at fixed conditions of 50^oC and 1 hour precipitation duration.

For the second mixed hydroxide precipitation experiments, a new stock of solution (0.5 L) was prepared under the optimum conditions mentioned above. Then, the experiments were done in a pH range of 7.50 to 8.00 at the fixed conditions of 60^oC and 1 hour precipitation duration. The procedure was similar to the first mixed hydroxide precipitation experiments except that slaked lime [$Ca(OH)_2$] was used as a reactive instead of magnesia.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 High Pressure Acid Leaching

At the starting point of high pressure acid leaching experiments, it was necessary to calculate the theoretical acid consumption. The demand of acid for Sivrihisar limonitic laterite ore was calculated according to the Sherritt assumption based on its chemical compositional analysis. The theoretical consumption of acid depending on each element is indicated in Table 7.

According the calculations given in Table 7, Fe^{3+} consumes very high amount of acid if iron is leached completely, but percent extraction was assumed to be 5% according to the Sherritt assumption. The assumption was made according to dissolved iron (Fe^{3+}) which is being precipitated at high pressure acid leaching. Similarly, aluminum is also precipitated as alunite and its extraction accounts for 25%. The remaining aluminum (75%) exists in solid form as alunite. Alunite precipitation is not as favorable as hematite precipitation under the high pressure acid leaching conditions. Some elements are assumed to be totally leached under the high pressure acid leaching conditions (i.e., Ni, Co, Mn, Mg, Ca), whereas some elements are not leached or they are just extracted in small quantities. For example, according to XRD results Sivrihisar limonite contains quartz in high amounts, but its leachability is very low (<0.9% extraction).

The beauty of high pressure acid leaching over leaching at atmospheric conditions can also be seen from this table. If the leaching was conducted at ambient temperatures, the precipitation reactions of iron and aluminum would not be taking place and sulfuric acid would not be regenerated. Then, the acid demand for leaching

would be in much higher amounts. For instance, if Sivrihisar limonite was leached at ambient conditions such as in heap leaching or atmospheric leaching at about 95 $^{\circ}$C, the acid consumption would expected to be about 1144 kg per ton of dry ore. The detailed calculation of theoretical acid consumption is given in Appendice A. But in high pressure acid leaching process since the operating temperature is thermodynamically adequate for iron and aluminum dissolution and subsequent precipitation mechanisms, the acid demand decreases to about 271 kg per ton of dry ore. According to these calculations the starting acid to ore ratio was decided to be 0.27 a/o (acid/ore) by weight.

Table 7. Theoretical acid consumption of – 50 mmSivrihisar limonitic laterite ore.

Element	Limonite ALS (Weight percent)	Limonite Sulfuric Acid Consumption (kg) / Ton of Ore	Sherritt Assumption Percent Extraction	Acid Used (kg/ton)
Fe^{3+}	33.7	887.80	5.00	44.39
Fe^{2+}	33.7	591.86	0.00	0.00
Ni	1.405	23.46	100.00	23.46
Al	1.71	93.45	25.00	23.36
Al	1.71	41.53	75.00	31.15
Co	0.093	1.55	100.00	1.55
Mn	0.573	10.23	100.00	10.23
Ca	1.170	28.59	100.00	28.59
Mg	0.777	31.34	100.00	31.34
Cr	1.26	23.79	5.00	1.19
As	0.04	-	0.00	-
Si	12.04	-	<0.90	-
Na	0.04	1.71	0.00	-
Cu	0.006	-	100.00	-
Zn	0.03	0.45	100.00	0.45
Free Acid	-	-	-	75.00
TOTAL ACID CONSUMPTION (KG/TON OF DRY ORE)		**1144**	**-**	**271**

The starting leaching temperature was investigated in the literature and it was found that the industrial plants of Murrin Murrin (255°C), Moa Bay (246°C), Cawse (250°C) and Bulong (250°C) have working temperatures around 255°C [13, 51]. Also in a previous study by Kaya et al. (2011) based on another Turkish nickel laterite ore near Gördes/Manisa, the optimum leaching temperature was found to be 255°C [8]. Considering this survey in the literature, it was decided to leach the limonitic sample initially at 255°C.

4.1.1 Effect of Leaching Duration

The first series of experiments were performed to investigate the leaching duration according to the parameters given in Table 8:

Table 8. Pressure acid leach parameters.

Ore Type	Limonite
Leaching Temperature (^{o}C)	255
Leaching Duration (min.)	0, 60, 90, 120
Acid/Ore Ratio (wt./wt.)	0.27
Particle Size (μ)	100% -850
Solid/Liquid Ratio (wt./wt.)	0.4
Stirring Speed (rpm)	400

As explained in the experimental set-up section, the autoclave in which the pressure leaching experiments were conducted did not have an acid injection system. Acid was fed to the autoclave together with the prepared slurry at the room temperature and the mixture has reached to 255°C as a mixture. So during this heating, the limonite was leached in some amount. To determine the reference point of duration of extraction, the autoclave loaded with the mixture was heated to the planned leaching temperature (255°C) and cooled to room temperature without a waiting period at the leach temperature. To understand how long the limonite was exposed to acid attack while heating, the data was taken in a period of time for revealing the heating curve of the autoclave. Heating curve is given in Figure 14. As seen from Figure 14 that it has taken less than 1 hour to reach 255°C.
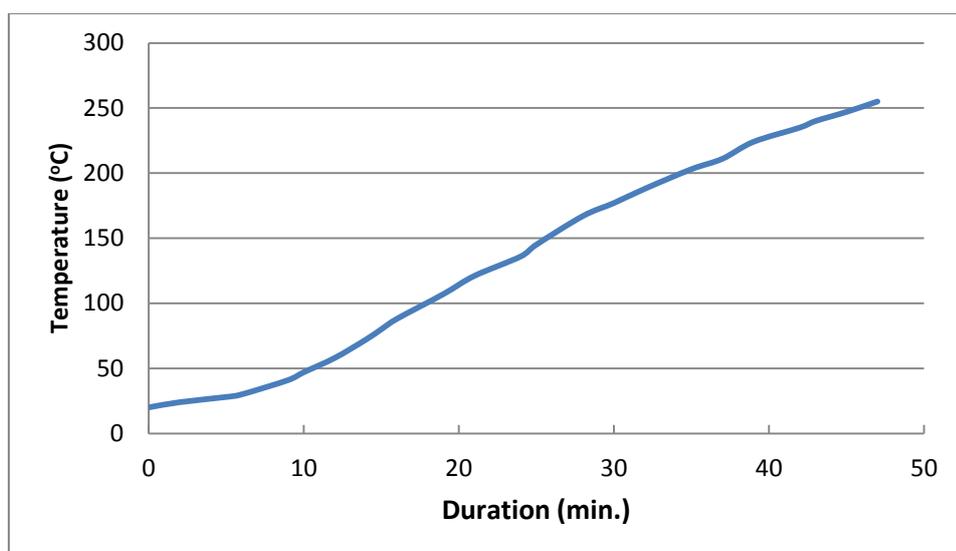
Figure 14. Heating curve of the autoclave.

Effect of leaching duration on nickel and cobalt extractions

At 255°C under acid to ore ratio of 0.27 (kg/kg), the effect of leaching duration on nickel and cobalt extractions is given in Figure 15. The calculation method of metal extractions is given in Appendice B.

At this high temperature (255°C) and under a pressure of 43 atm. the Sivrihisar limonite has showed a reactive characteristic that the nickel and cobalt extractions were found to be very high. Just heating the limonite to 255°C in about 1 hour and subsequent cooling to room temperature also resulted in very high extraction values (85.3% for nickel and 80.9% for cobalt). The digestion duration of 60 minutes at this temperature was found to be sufficient for nickel and cobalt. Extractions reached very high values after 1 hour of leaching duration (97.0% for nickel and 95.2% for cobalt). Further durations of leaching did not create a remarkable difference in the nickel and cobalt extractions at this temperature. A nickel extraction as high as 98.9% was obtained after 120 minutes leaching duration. But 2 hours of leaching is a long digestion duration that is not welcome in the high pressure acid leaching process since long durations limit the production capacity.
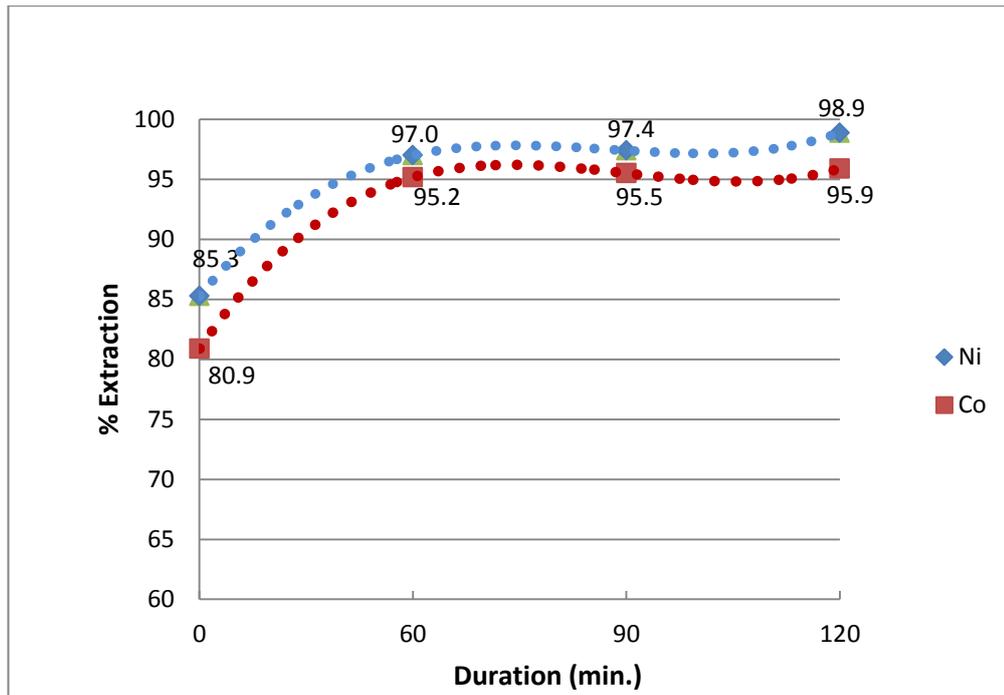
Figure 15. Effect of leaching duration on metal extractions (255°C, 0.27 a/o).

After examining the temperature dependence of limonite leaching which is going to be discussed in the following chapters, the effect of leaching duration at temperatures of 235°C and 220°C was also found to be meaningful to investigate. The results are shown in Figure 16. The effect of leaching duration on nickel extraction was also found to be similar at these temperatures. General behavior of the nickel with increased leaching duration was that, its concentration was increasing from the first minute of leaching up to 1 hour of leaching duration and then reached a near equilibrium value. The increase in nickel concentration in leach solution was believed to be caused by the destruction of host minerals by the acid attack. It was observed that one hour of leaching was adequate to obtain the extractable nickel in the sample since a significant further increase in the nickel extraction was not observed in longer leaching durations. This limonite can be stated to be easily leachable.
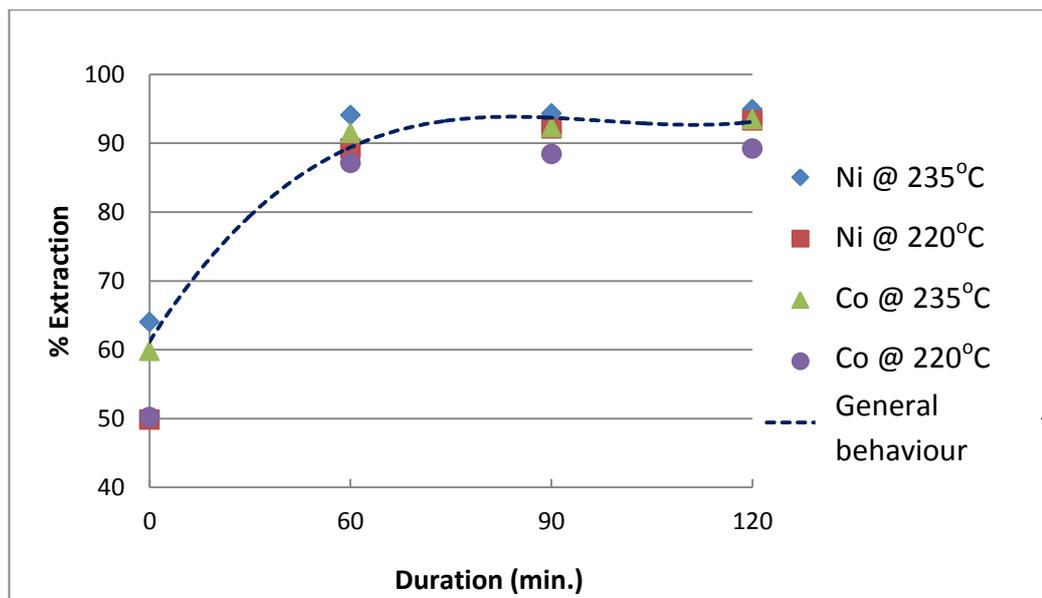
Figure 16. Effect of leaching duration on Ni/Co extractions at 220 and 235°C (0.23 a/o).

Effect of leaching duration on iron extraction:

At 255°C and 0.27 a/o ratio, the iron extraction was found to be decreasing by increasing digestion duration. Papangelakis et al. (1996) reported that the concentration of iron in the solution increases at short digestion times then decreases to an equilibrium value via a goethite dissolution-hematite precipitation mechanism [25]. A similar behavior was observed for leaching of Sivrihisar limonite. The results can be seen in Figure 17. For the first minutes of leaching, main iron minerals of goethite and hematite were dissolved by acid attack and Fe^{3+} ions were loaded into the pregnant leach solution. It can be stated that the highest iron concentration was attained at the first few minutes of leaching. This observation was critical since the host iron mineral matrix was being destroyed; the nickel and cobalt were also going into solution together with iron. Then, the iron concentration in the solution decreased continuously to an equilibrium value while hematite was precipitating. The precipitation of easily filterable hematite in solid form decreased the total extraction of iron to lower values.

Dissolution of iron was reported to be followed by a rapid precipitation in the literature [29]. The iron extraction results were also consistent with this information

in that the rate of decrease in the iron extraction was the highest in the first hour of leaching process.
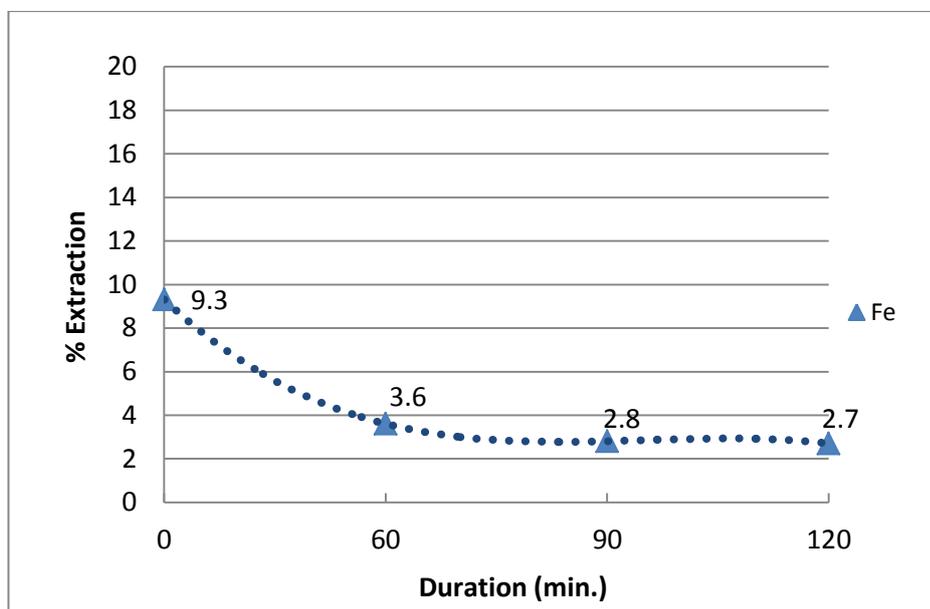
Figure 17. Effect of leaching duration on iron (255°C, 0.27 a/o).

The behavior of iron was also found to be similar at temperatures of 220°C and 235°C. The iron extraction was decreasing to an equilibrium value with increasing leaching duration. But higher equilibrium iron concentrations were attained at lower temperatures since the precipitation mechanism is more favorable at higher temperatures [9, 29].

The oxidation-reduction-potential (ORP) of the pregnant leach solution was also determined after each experiment. The results are given in Figure 18. ORP generally increases when the concentration of higher oxidative state of an ion increases in the system (i.e., more Fe^{3+} than Fe^{2+} or more Cr^{+6} than Cr^{3+}) [9]. With the increase in leaching duration, a decrease in oxidation-reduction-potential was observed. Since Fe^{3+} was precipitated favorably at 255°C, higher amount of Fe^{3+} was removed from the pregnant leach solution with increasing leaching duration. The decreasing Fe^{3+} concentration in the liquid phase resulted in a decrease in oxidation-reduction potential of the pregnant leach solution.
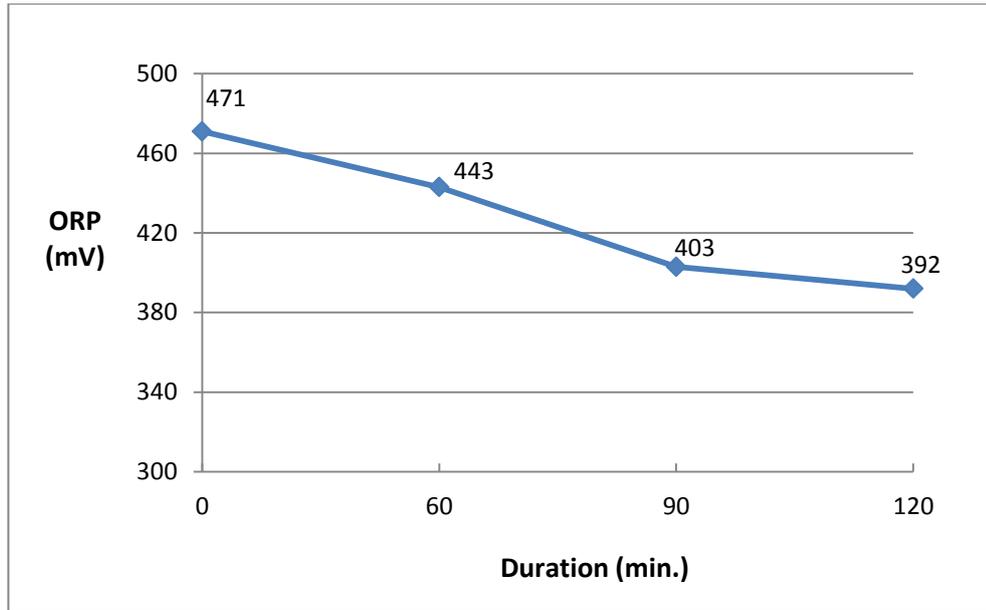
Figure 18. Oxidation-reduction potential (ORP) of PLS (255°C, 0.27 a/o).

After the experiments based on the effect of leaching duration on metal extractions, it was decided to choose the optimum leaching duration as 1 hour. The decision of optimum leaching duration was made with the consideration of maintaining the production rate high with shorter digestion times.

Minimal increases in the extractions of nickel and cobalt were obtained after increasing the leaching duration from 60 minutes to 120 minutes. Furthermore, after 1 hour of leaching duration iron concentration did not reach to its equilibrium value but Figure 16 indicated that most of the iron hydrolysis reaction had taken place in the first hour of leaching and it was very close to the equilibrium.

4.1.2 Effect of Acid/Ore Ratio

As indicated in the literature part, the sulfuric acid consumption is the main operating cost of high pressure acid leaching. It was theoretically calculated that Sivrihisar limonite would consume about 271 kg of sulfuric acid per ton of dry ore according to its chemical composition. The experiments were performed to find the effect of acid concentration on metal extractions by changing acid levels by ±20 kg per ton of dry ore. The temperature was chosen to be 255°C and leaching duration was 1 hour during these experiments. The results are given in Figure 19.

<u>Effect of acid/ore ratio on nickel/cobalt</u>

To extract the nickel and cobalt into the leach solution, the host minerals of these valuable metals must be attacked by acid. Sulfuric acid was the reagent for high pressure acid leaching that plays the role of destruction of host minerals. As expected, when the acid concentration was increased, the chance of a host mineral getting attacked by acid was increased. So, the increased amount of acid addition resulted in increasing amount of nickel and cobalt being leached (Figure 19).
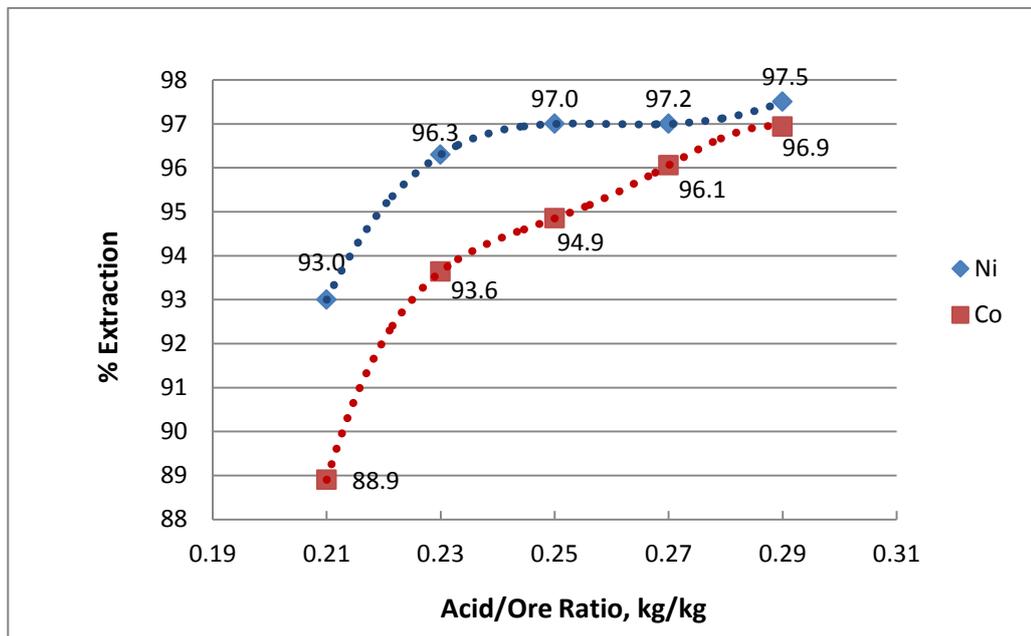
Figure 19. Effect of acid/ore ratio on nickel and cobalt extractions (255°C, 1 hour).

According to Georgiou (1998) using of lower acid to ore ratios reduces both the initial rate and the ultimate extractions of nickel and cobalt [29]. The effect of acid concentration on nickel and cobalt extractions was found to be consistent with the literature [9]. Throughout the experiments, both of these valuable metals were extracted in higher amounts with increased amount of acid supplied to the autoclave. Although the acid supply to the autoclave decreased to lower amounts than the theoretical needed for Sivrihisar limonite (0.27 kg/kg), the extraction of nickel did not decrease to values below a certain value. After decreasing the acid/ore concentration to less than 0.23 (kg/kg) then the extraction of nickel has decreased

sharply. This was believed to be due to insufficient amount of sulfuric acid supply which dissolves the host minerals. Cobalt extraction was found to be more sensitive to acid concentration change than nickel. The host minerals of cobalt (i.e., asbolane) may require more H^+ activity. So an increased amount of acid may facilitate the amount of extraction of Co from this mineral. Higher acid/ore ratios were found to be necessary for the maximum cobalt extraction whereas the nickel extractions stayed at high values in a range of acid/ore ratios of 0.23-0.29 kg/kg.

According to Whittington et al. (2000) there was a strong relationship between the residual free acid and nickel and cobalt extractions. It was also reported that 30-50 g/L sulfuric acid was necessary for sufficient nickel and cobalt dissolution [9]. The experiments conducted at different acid/ore ratios showed that the residual free acids of the leach solutions obtained for Sivrihisar limonite were in the desired free acid range. The results are given in Figure 20.
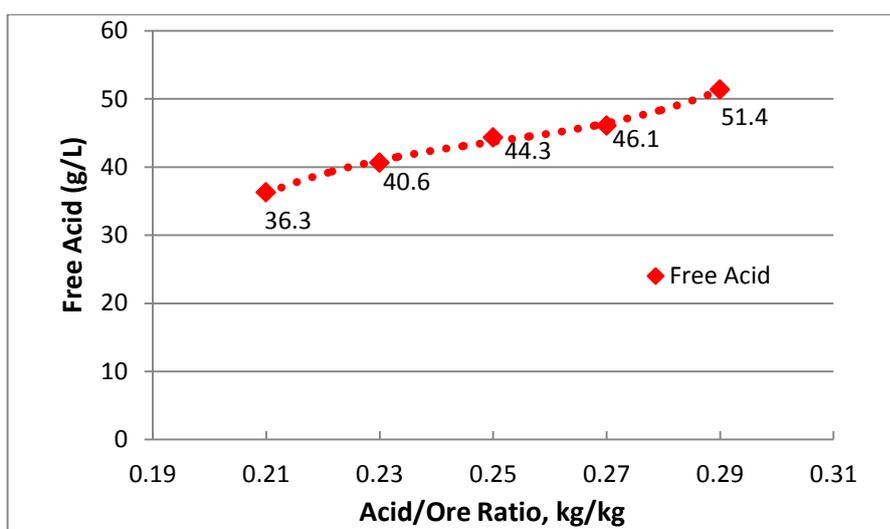
Figure 20. Effect of acid concentration on the residual free acid of leach solution (255°C, 1 hour).

Effect of acid/ore ratio on iron

The increased amount of acid addition had also an increasing effect on iron extractions. The results are given in Figure 21. When the acid concentration was increased, the acidity became higher and this limited the hematite precipitation mechanism of iron. In the literature, it was reported that the acidity level of leach solution determines the stable phase of iron product. After dissolution of the goethite and hematite, the dissolved Fe^{3+} can form by precipitation the preferred product of hematite (Fe_2O_3) at low acidity, whereas basic ferric sulfate [$Fe(OH)SO_4$] is formed at the high acidity levels [23]. It was observed that the addition of higher amounts of sulfuric acid to the titanium autoclave resulted in increases in free acid content of in the pregnant leach solution (Figure 20). By titration the residual acid was determined and it was found that at free acid level as high as 51.4 g/L was reached at an acid to ore ratio of 0.29 kg/kg. It was also apparent that a continuous increase in the residual acid of pregnant leach solution was present as the acid addition was increased at 20 kg intervals.

The shape of Figure 21 indicated that after a certain acidity, hematite precipitation was critically limited and iron stayed in the solution. Then, this created an existence of a breakpoint acidity level such that basic ferric sulfate precipitation was more favorably taking place than hematite precipitation due to high acidity level of pregnant leach solution. The breakpoint acidity level had already been mentioned in the literature that some sulfate salts of Zn, Cu(II), Mg and Na increase the maximum acid level at which hematite forms [23]. If the ore sample contains these salts in the ore composition or if they are intentionally added to the leach container, the effect of high acidity may be diminished to higher acidity levels. In other words, the acidity range of hematite formation may be widened with the existence of these salts in the pregnant leach solution.
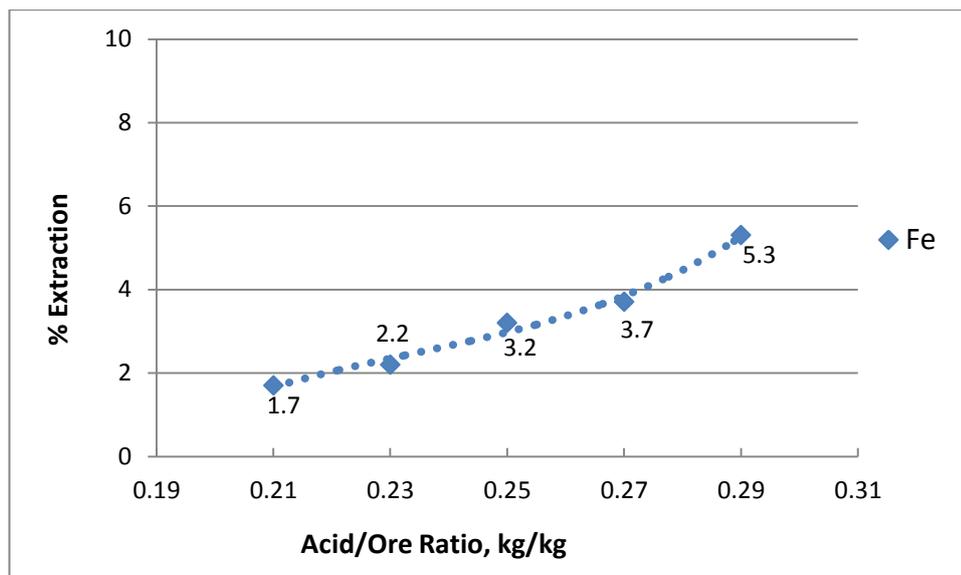
Figure 21. Effect of acid concentration on iron extraction (255°C, 1 hour).

It was already mentioned that the concentration of iron in the leach solution was increased with the increase in acid addition. As a consequence, an increase in the cost of extraction has resulted since acid consumption is the main operating cost of the process. Besides this, the impurity level of the pregnant leach solution was significantly affected. Some minerals may need higher H^+ to be dissolved in the leaching environment. Satisfying this requirement may result in loading of higher amount of impurity elements into the pregnant leach solution. After increasing the acid addition, the change in concentration of impurity ions in the pregnant leach solution is given in Table 9. These experiments were conducted at 255°C and 1 hour leaching duration. As expected, all of iron, aluminum and chromium concentrations in the pregnant leach solution were increased with the increasing acid addition. This is not a desired situation since it creates additional difficulties in the purification stage of HPAL solution. For example, to remove higher amounts of impurities may lead to significant losses of nickel and cobalt during the precipitation of these impurities or higher amount of alkaline reagent will be required to decrease the impurity concentrations to the desired levels. Furthermore, the product quality is determined by the amount of impurities present. Its saleability is decreased if it does not satisfy the desired impurity limits. So, operating the high pressure acid leaching at the optimum acid to ore ratio is so significant in terms of impurities that loading of solution, the amount of reactive used in purification stage and the quality of mixed

hydroxide product are all affected. Care must be taken not to liberate or carry so many impurities to the pregnant leach solution but high nickel and cobalt extractions must be attained at the same time.

Table 9. Chemical analysis of leach solution.

Leach Solution Analysis (AAS)			
	mg/L (ppm)		
Acid to Ore Ratio (kg/kg)	Fe	Al	Cr
0.21	3577	2144	10.0
0.23	5818	2436	17.6
0.25	6403	4535	48.2
0.27	7337	5170	59.1
0.29	10330	5480	71.8

The theoretical acid consumption (0.27 kg/kg) which was calculated prior to start of experiments has led to considerably high impurity (Fe, Al, Cr) loading of the pregnant leach solution. The extent of liberation of aluminum into the pregnant leach solution is given in Figure 22. Aluminum extractions reached over 50% extraction when 0.29 acid/ore ratio was used for leaching. But it was possible to maintain the extraction of aluminum around 20-25% by operating the pressure leaching with low acid to ore ratios. Although the extractions of nickel and especially of cobalt were found to be high at 0.29 acid/ore ratio (Figure 19), the impurity concentration of the solution should be lower to ease the purification and subsequent precipitation applications by decreasing the acid addition. Without decreasing the nickel and cobalt extractions to quite low values, the acid addition was decided to be maintained at the acid/ore ratio of 0.23 kg/kg. At this acid to ore ratio the extractions of nickel and cobalt were found to be 96.3% and 93.6%, respectively. These values were still quite high but the impurity concentrations were lowered more than 45%. In other words selectivity of nickel and cobalt has been increased over iron, aluminum and chromium by lowering the acid addition.
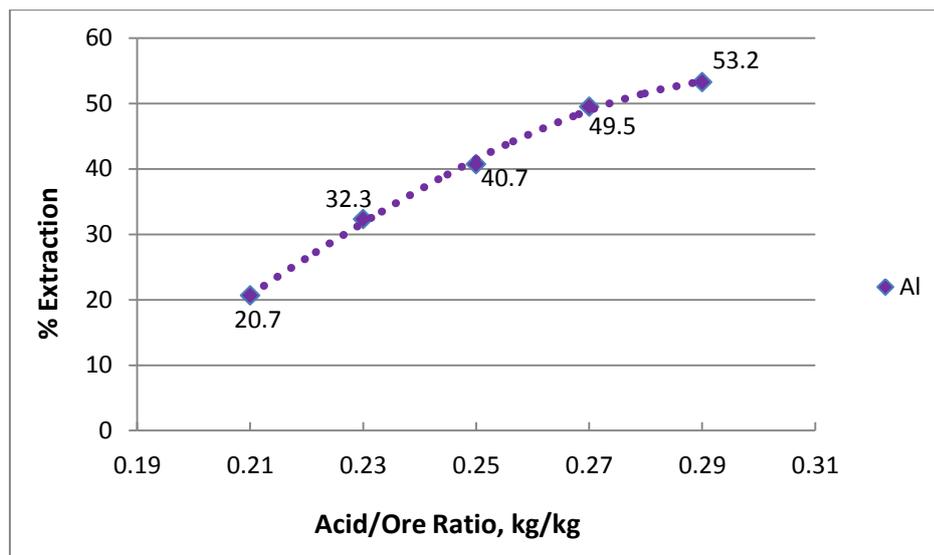
Figure 22. Effect of acid/ore ratio on extraction of aluminum (255°C, 1 hour).

4.1.3 Effect of Temperature

In high pressure acid leaching, temperature of leaching is another significant parameter that it enables mineral dissolutions then subsequent precipitation mechanisms as indicated in the previous chapters. In the first series of experiments, the starting temperature was decided to be 255°C according to the operating plants around the world and laboratory researches previously done. The reactivity and leachability of this limonitic laterite sample was found to be high while studying the effect of digestion duration at 255°C. So, this good characteristic brought in mind that this limonite may have high extraction values of nickel and cobalt at temperatures lower than 255°C. As expected, by lowering the temperature about 10 to 20°C, high nickel and cobalt extractions were still attainable. Then, it was decided to investigate much lower temperatures at which this process might still be applicable. This brought the experiments to a breakpoint temperature at which a sudden decrease in nickel and cobalt extractions was observed. The breakpoint temperature of Sivrihisar limonite based on high pressure acid leaching was found to be between 210 and 220°C. The sudden decrease in metal extractions in this temperature range was believed to be due to incomplete leaching of the host minerals (goethite, hematite). The results of experiments showing nickel and cobalt extractions are presented in Figure 23.
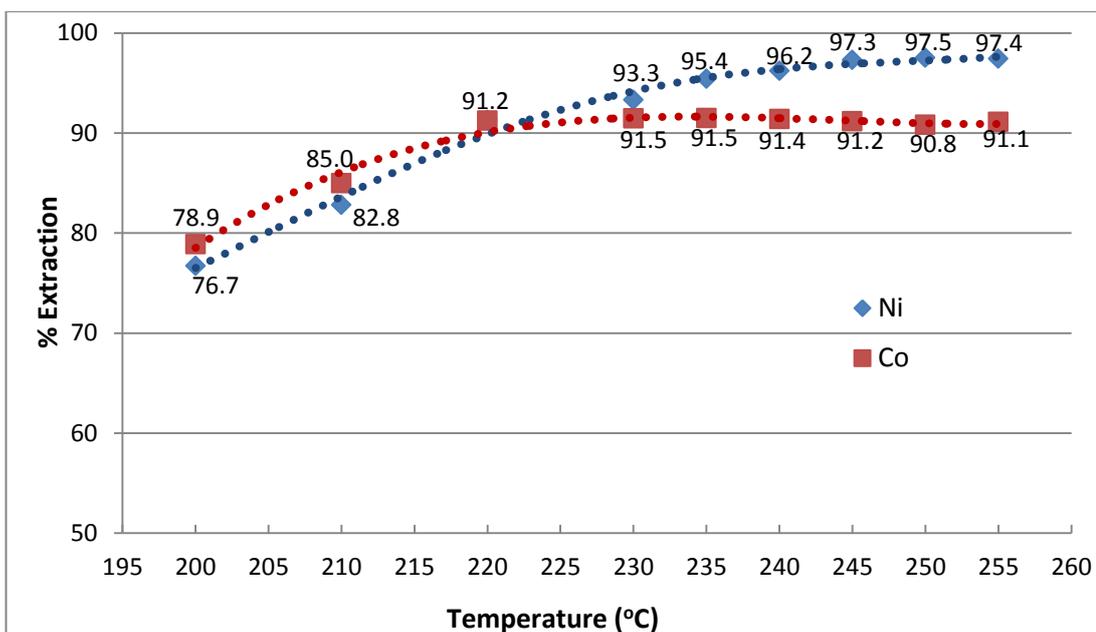
Figure 23. Effect of leaching temperature on Ni/Co extractions (0.23 a/o, 1 hour leaching duration).

According to Figure 23, the nickel extraction was decreasing continuously to lower values from 255°C to about 220°C. Then, the liberation of nickel from the host minerals suddenly decreased at temperatures lower than 220°C. In the literature similar behavior was also found for an Indonesian limonite. Georgiou and Papangelakis (1998) reported that the nickel extraction was increasing with increasing temperature in the range of 230 to 270°C [29]. In the thesis of Kaya based on Gördes/Manisa limonite, it was also reported that the increase in leaching temperature resulted in increasing nickel extraction [8].

The effect of temperature increase on cobalt extractions was found to be minimal for Sivrihisar limonite. This is also consistent with the findings of Georgio et al. (2009). In the temperature range of 230-270°C, the variation of temperature was found to have no essential effect on cobalt dissolution rate based on Soroako, Indonesia limonitic laterite [52]. This mentioned ore was reddish-brown, clay like solid with high humidity content (42-44% water). Valuable information about laterites was given in this paper such that laterite is highly porous material with very fine size pores and a high specific area [52].

The minimal effect of temperature on cobalt extraction values can be explained since the chemical reactions of cobalt containing minerals are faster at high temperatures. The asbolane which is one of the host manganese minerals of cobalt was reported to be readily leachable [9].

Chou et al. (1977) also reported that for rapid leaching of nickel, temperatures approaching 250°C are required. In this paper it was also mentioned that the total extraction of nickel was high for higher leaching temperatures [16]. To investigate the initial leaching behavior of nickel at different temperatures with varying durations, a series of experiments at 220, 235 and 255°C were also performed. The results are given in Figure 24.

The results are consistent with Chou et al. (1977) that at higher temperatures the initial liberation of nickel from the host mineral was higher. Also it was found that at higher temperatures the total nickel extractions were higher [16].
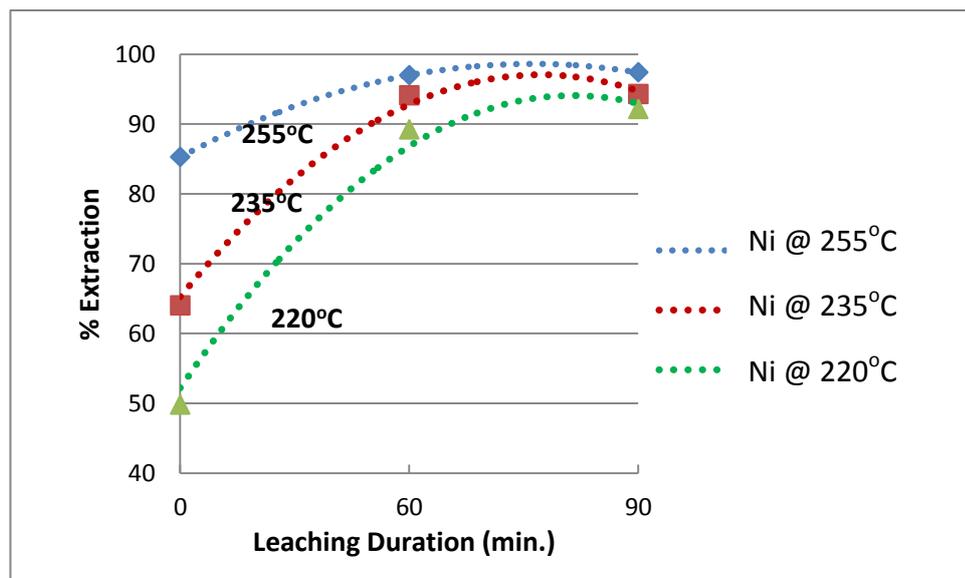
Figure 24. Nickel extractions at 220, 235 and 255°C with varying durations (0.23 a/o).

Effect of leaching temperature on iron:

Throughout the high pressure acid leaching, iron goes through dissolution-precipitation mechanism. To remember this mechanism, the reactions are given in the following equations:

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$$2 \text{ FeOOH(s)} + 3 \text{ H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 4 \text{ H}_2\text{O} \qquad \text{Rx.22}$$

$$\text{Fe}_2(\text{SO}_4)_3 + 3 \text{ H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + 3 \text{ H}_2\text{SO}_4 \qquad \text{Rx.23}$$
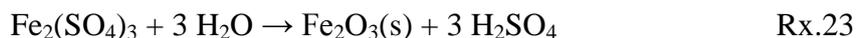
The increase of temperature has a positive effect on the total extraction of iron, since at high temperatures the precipitation of hematite is more favorable [19, 25]. Iron concentration in the PLS decreased at higher temperatures since Fe^{3+} precipitated and transferred from the pregnant leach solution into the filterable solid. The results are given in Figure 25. Not to contaminate the pregnant leach solution with impurity elements of Fe, Al and Cr the highest possible leaching temperature must be preferred to favor the precipitation reactions of hematite and alunite.
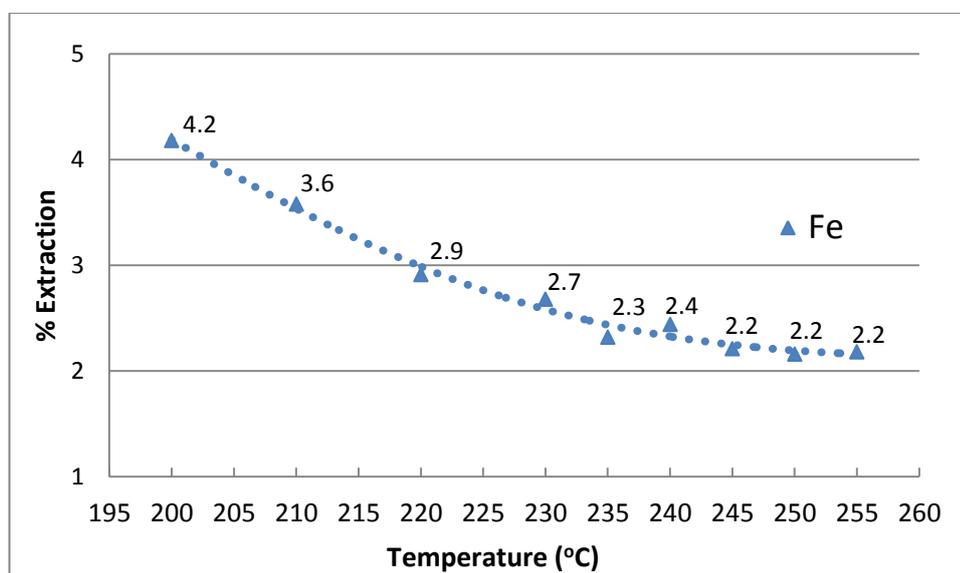
Figure 25. Effect of leaching temperature on iron extractions (0.23 a/o, 1 hour).

The effect of increase in leaching temperature on chromium extractions was also investigated and it was found that chromium had similar behavior like iron. Its concentration in pregnant leach solution decreased with increasing leaching temperature. The results are given in Figure 26. Whittington et al. (2000) stated that chromium present in the leach solutions as Cr^{3+} is oxidized to CrO_4^{2-} [9]. Chromium does not create its discrete precipitate but it is taken away from the pregnant leach solution in the form of alunite in pressure acid leaching. Sobol (1969) reported that CrO_4^{2-} is incorporated into alunite for every two SiO_4^{4-} [30].
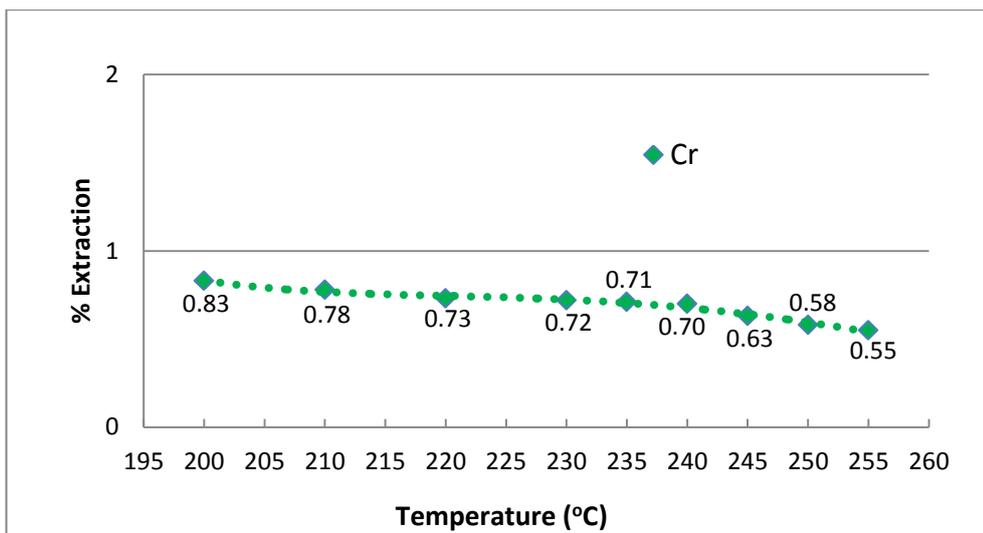
Figure 26. Effect of temperature on chromium extractions (0.23 a/o, 1 hour).

During the precipitation of iron as hematite, sulfuric acid is generated as a result of precipitation mechanism. Since this mechanism is more favorable at higher temperatures, the amount of sulfuric acid generated is higher as a result of conducting leaching at higher temperatures [9, 23]. This situation was also found to be consistent with the Sivrihisar limonite such that the amount of free acid was found to be increasing with increasing temperature. These results are given in Figure 27. For a constant starting acid concentration, the variation of free acid depending on leaching temperature was found to be in the range of 30-50 g/L.
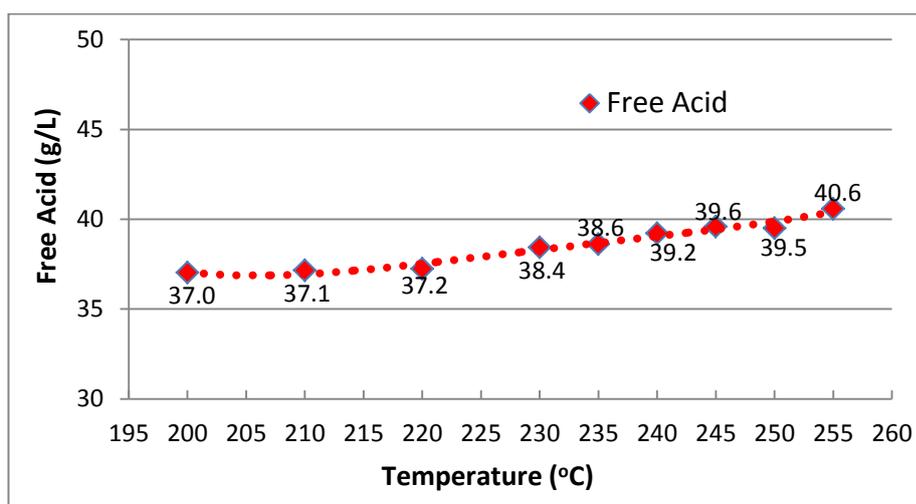
Figure 27. The amount of free acid depending on leaching temperature (0.23 a/o, 1 hour).

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At the higher leaching temperatures more Fe^{3+} ions were favorably removed from the pregnant leach solution in the form of hematite (solid). At the same time more Al^{3+} liberation into the pregnant leach solution took place since higher temperatures favors dissolution of boehmite. The two different behaviors resulted in the small variations of oxidation-reduction-potential of the pregnant leach solution. The results for oxidation-reduction-potential (ORP) of PLS in a range of leaching temperature are given in Figure 28.
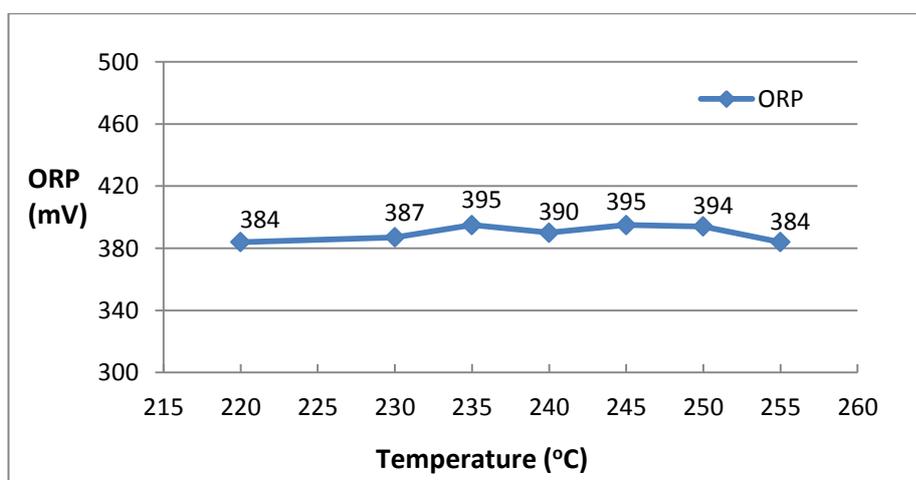
Figure 28. The variation of oxidation-reduction-potential of PLS in a range of leaching temperature (0.23 a/o, 1 hour).

The autoclave of high pressure acid leaching process is a steam dependent unit such that its pressure is dependent on the temperature of the water vapor. The variation of the pressure of the autoclave with the change in temperature of the process is given in Figure 29. The pressure changes exponentially with the variation in temperature and attaining very high pressures at high temperatures. High pressures are preferred for the process since it prevents boiling in the autoclave and enables the sulfuric acid to penetrate into porous limonite ore [9]. For Sivrihisar ore the extractions of nickel and cobalt were found to be very high at relatively lower temperatures. In other words, it did not require such high pressures to be readily leached.

The capital cost of HPAL unit is very high and the construction of acid resistant titanium autoclaves accounts for the biggest investment part of the process. With the increase in pressure/ temperature of the process, the thickness of the titanium clad

steel autoclave wall must be increased to tolerate the pressure inside the vessel [53]. So, considering the capital cost of the process, the optimum temperature of the operation can decreased to lower temperatures if the extraction values of the nickel and cobalt are high enough and impurity concentrations of the solution are in the tolerable ranges.
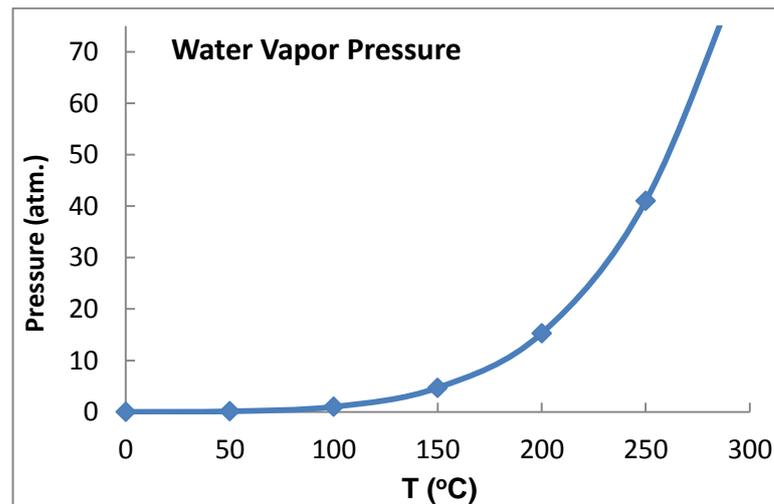
Figure 29. Temperature dependence of steam pressure.

In the literature, the majority of the HPAL operations were reported to be working at temperature of around 255°C. Sivrihisar limonite had also good extraction values at this temperature. But, high pressure leaching tests on the Sivrihisar limonitic laterite ore also indicated that it could be leached effectively at lower temperatures due to very leachable mineral content of it (i.e., goethite). At 235°C the extractions of the nickel and cobalt were found to be also high (95.4% for nickel, 91.5% for cobalt). Considering the investment cost of the titanium autoclave, the optimum temperature was decided to be chosen as 235°C. At 255°C, the pressure was 43 atm. and by lowering the temperature to 235°C the pressure of the process has dropped to 32 atm. The change in pressure was found to be so critical (approx. 25%) that the decrease in the thickness of the titanium autoclave wall is going to result in lowering of investment costs.

4.1.4 Optimum HPAL conditions of Sivrihisar Limonite

With the considerations of high production capacity, lower digestion durations should be preferred. To lower the impurity liberation or carry over to the pregnant leach solution and to lower the operation cost of the process (consumption of sulfuric acid) lower acid/ore ratio should be chosen. Finally, to lower the investment cost of process, the essential wall thickness of the autoclave was desired to be decreased by lowering of the leaching temperature of the process. The optimum conditions for the HPAL processing of Sivrihisar limonite is summarized in Table 10.

Table 10. The experimental and optimum conditions of Sivrihisar laterite.

Parameters	Experimented Conditions	Optimum Conditions
Temperature (^{o}C)	200, 210, 220, 230, 235, 240, 245, 250, 255	235
Pressure (atm.)	18-43	32
Leaching Duration (min.)	0, 30, 60, 90, 120	60
Acid/Ore Ratio (kg/kg)	0.21, 0.23, 0.25, 0.27, 0.29	0.23
Particle Size (μ)	-850	-850
Stirring Speed (rpm)	400	400
Solid/Liquid Ratio (kg/kg)	0.4	0.4

At the optimum conditions, the nickel and cobalt extractions were mentioned previously but, the leaching of other metals is also critical. The extractions of all the metals determined at the optimum conditions are given in Table 11.

Manganese extraction is desired to be low since in the next stage (MHP precipitation) manganese is expected to contaminate the MHP product. But HPAL process is not selective on manganese and its extraction was calculated to be 91.6%. Magnesium was also present in PLS as contaminant. Although, as it was mentioned previously that 50-60% of magnesium was expected to be leached during pressure leaching [9] for Sivrihisar limonite magnesium extractions reached 72.1%.

Table 11. The extraction of metals at the optimum conditions.

Metal	% Extraction
Ni	95.4
Co	91.5
Fe	2.3
Mn	91.6
Cr	0.71
Al	32.3
Mg	72.1

The final composition of the pregnant leach solution obtained under the optimum conditions is presented in Table 12. About 8.7 g/L of nickel was liberated into the pregnant leach solution together with about 0.4 g/L of cobalt. The solution loaded with these valuable metals needs to be purified in order to obtain a pure mixed hydroxide precipitate. It is possible to remove Fe, Al and Cr prior to MHP precipitation but Fe^{2+} precipitates together with Ni/Co during an addition of a reactive and it contaminates the final product. Fortunately, the concentration of Fe^{2+} in PLS was found to be very low. If the Fe^{2+} present in the pregnant leach solution was to be found in higher amounts, an oxidizing environment had to be created to convert Fe^{2+} to Fe^{3+} during the pressure leaching or in the neutralization stage.

Table 12. Composition of the pregnant leach solution obtained at the optimum conditions.

Element	mg/L (ppm)
Ni	8743
Fe^{3+}	6658
Ca	29
Co	448
Zn	109
Cu	30
Mg	4824
Mn	3725
Cr	30
Al	3328
Fe^{2+}	2.2
Free Acid	38600
ORP (mV)	395

In order to characterize the leach residue XRD investigation was performed on this solid which was obtained at the optimum conditions (235°C, 0.23 a/o, 1 hour) of pressure leaching. The XRD result of leach residue is presented in Figure 30 together with that of the original sample for comparison purposes. As expected there were no goethite peaks remaining in the XRD pattern of the leach residue since all of the goethite minerals which were containing also nickel and cobalt had been leached under high pressure. The quartz mineral present as a gangue in Sivrihisar lateritic nickel ore was not readily leached under the high pressure acid leaching conditions, but a limited leaching of quartz and amorphous silica or dissolution of magnesium silicates could lead soluble silica [$Si(OH)_{4(aq)}$] [9]. The unreacted silica remained in the leach residue and silica peaks could be seen in the XRD result. Hematite peaks were present prior to leaching of the sample. It was already mentioned that the existence of other iron minerals is quite possible in the limonitic laterite [22, 29, 54]. Although hematite dissolution is more difficult than that of goethite [8], the high Ni extraction values obtained for Sivrihisar limonite could be interpreted as hematite in this sample was being leached readily. As indicated in the previous chapters, hematite precipitation occurs rapidly after dissolution of iron minerals. XRD result of the Sivrihisar sample was consistent with the literature in that there were high peaks of hematite. Calcite, smectite and kaolinite minerals which existed in the original sample were completely dissolved during the leaching and their peaks have disappeared from the leach residue. Finally, it can be said that hematite was found to be the main phase in the solid leach residue as expected, and unreactive quartz remained in the solid phase. The lack of leaching of the quartz minerals is good for the process since it creates scaling problems. It can also form a silica gel which disrupts the interaction between acid and nickel host minerals [9].
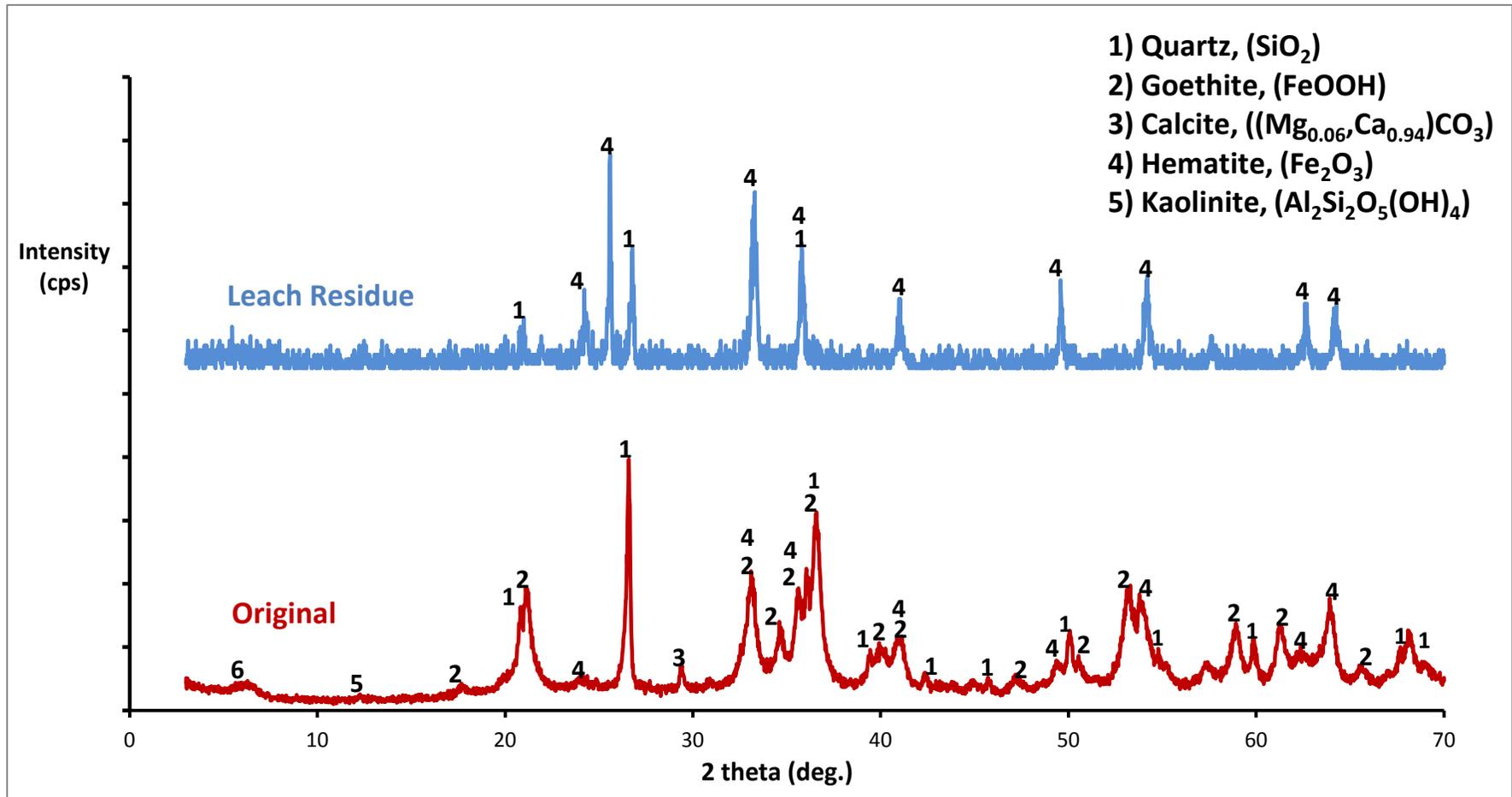
Figure 30. XRD patterns of leach residue and the original ore.

4.2 Neutralization, Purification and Mixed Hydroxide Precipitation Results

As previously mentioned, the purity level of the MHP product is critical in terms of saleability so the pregnant leach solution has to be purified prior to mixed hydroxide precipitation. The purification is achieved by neutralization together with first iron removal and second iron removal stages. It is possible to precipitate iron, aluminum and chromium as their respective hydroxides in the lower pH ranges before nickel and cobalt precipitation takes place (Figure 7). An example of a metal precipitation calculation is given in Appendice B.

4.2.1 Neutralization and First Iron Removal Stage

The pregnant leach solution stock prepared under the stated optimum condition of pressure leaching had a volume of 3.9 L having 38.6 g/L H_2SO_4 was initially needed to be neutralized. At this stage, the aim was also to precipitate most of the iron, aluminum and chromium with minimal losses of nickel and cobalt. In the industrial process flow-sheet of this method, the solid waste product obtained after this stage is sent directly to tailings dam (Figure 6). So, the minimization of nickel and cobalt precipitation at this stage is so critical that there is no further possibility of recovering the lost nickel and cobalt after this stage. In the literature, the optimum conditions were mentioned to be $90^{o}C$ and 120 minutes of residence time [3, 42]. It was decided to optimize the pH of the solution at these fixed conditions which was expected to lead to high precipitation values for iron, aluminum and chromium with minimal losses of nickel and cobalt.

With the addition of limestone slurry (25% wt./wt.) to 4 necked balloon which was containing both the pregnant leach solution (PLS) and autoclave leach residue, a pH range from 2.50 to 3.50 was studied at $90^{o}C$ and 120 minutes precipitation duration. The results are given in Figure 31.

Although Figure 7 indicates that the nickel and cobalt precipitations are expected to occur at pH values around 7.00, but at lower pH values (e.g., pH=2.50) the precipitation of these valuable metals were also taking place. It was indicated that the supersaturation causes metal ions to precipitate as their respective hydroxides.

The absorption was also stated to be the reason of nickel and cobalt losses [4]. With the increase in pH both of the nickel and cobalt losses were found to be increasing for Sivrihisar limonitic laterite sample. At the pH of 3.50, the nickel loss reached to 27.9% while 16.3% of cobalt was being lost at the same time. The high amount of losses of nickel and cobalt are not tolerable at this stage since the treatment of the solid waste is not possible due to its huge mass.
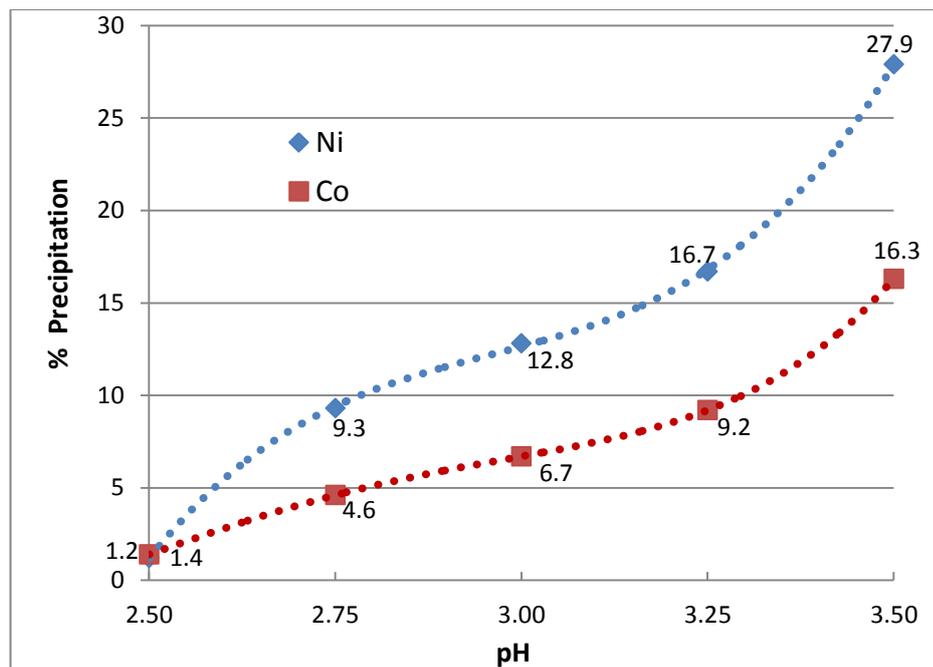
Figure 31. Effect of pH on nickel and cobalt precipitations (90°C in 120 min.).

At this stage (neutralization with first stage of iron removal), the aim was to remove most of the iron, aluminum and chromium. With the increase in pH, the increasing amount of precipitation of these metals occurred. The results are given in Figure 32. Aluminum and chromium precipitations were found to be reaching very high values such that at the pH of 3.50, 100% of chromium and 97.7% of aluminum were precipitated. The effect of increasing pH on iron was found to be less critical when compared to aluminum and chromium. This situation was also consistent with the findings of Agatzini-Leonardou et al. (2001). At lower pH (e.g., 2.50) the initial precipitation of Fe was higher than those of chromium and aluminum. But with the increasing of pH to about 3.50, the chromium and aluminum precipitations increased

abruptly [55]. But with increasing of the pH from 2.50 to 3.50, the increase in iron precipitation was found to be only 6.6%.
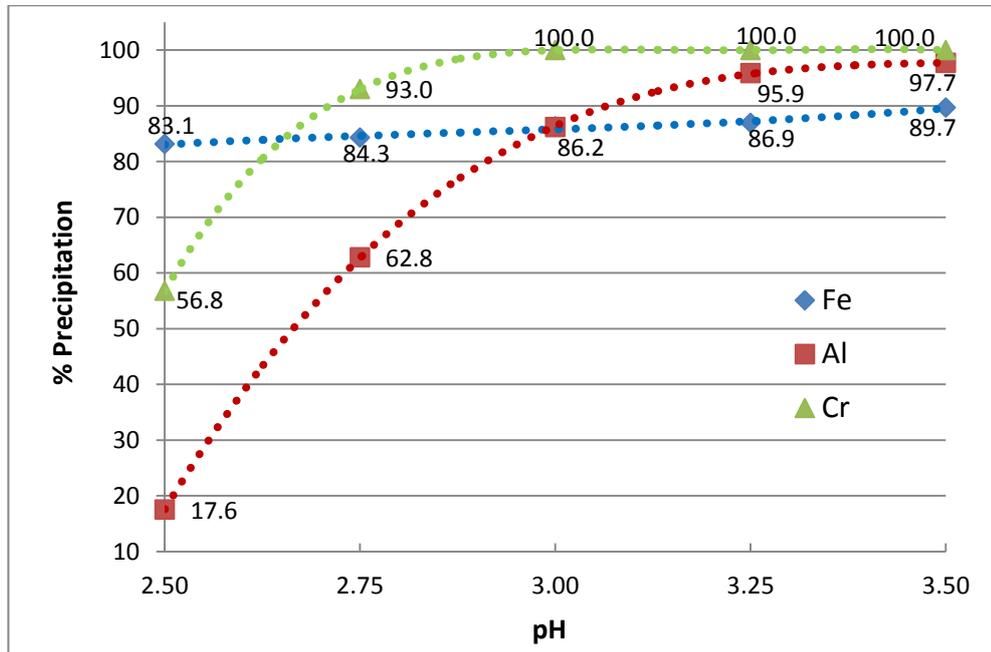
Figure 32. Effect of pH on precipitations of iron, aluminum and chromium (90°C in 120 min.).

Not to transfer copper and zinc to the mixed hydroxide product is also critical in obtaining a high quality product. The effect of pH increase on copper and zinc concentrations of the pregnant leach solution were also investigated. With the pH increase, both of these metals were favorably precipitated as expected, such that most of the copper was removed from the pregnant leach solution. The results are given in Figure 33.
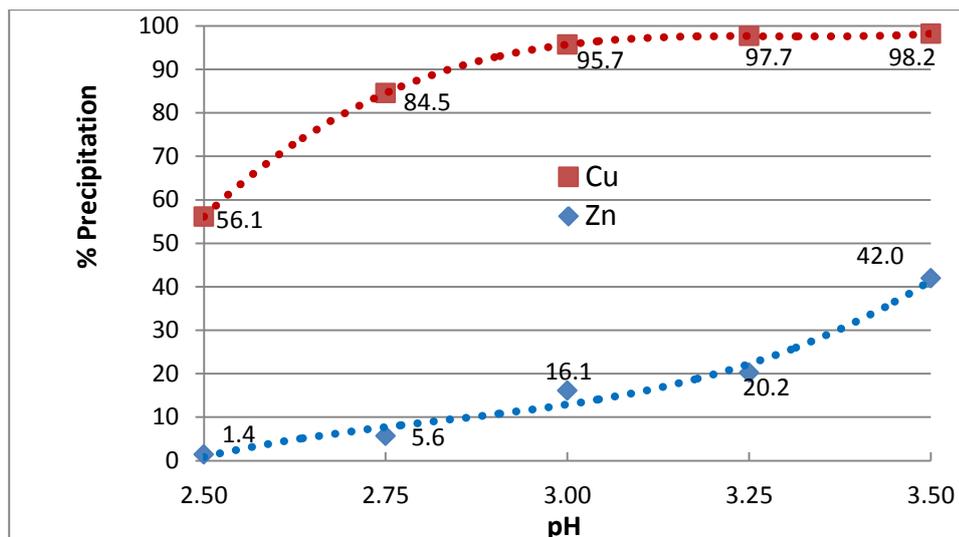
Figure 33. The effect of pH increase on precipitations of copper and zinc (90°C in 120 min.).

By considering the fact that the nickel and cobalt losses could not be recovered after the first stage of iron removal, the optimum pH was decided to be 2.50. At this pH, the nickel and cobalt losses were minimized to 1.2 to 1.4%, respectively. The amount of precipitation of the metals occurring at pH=2.50 at 90°C in 120 minutes are given in Table 13.

Table 13. Chemical composition of PLS after neutralization with first stage of iron removal.

At pH=2.50 90°C, 120 minutes		Chemical Composition of PLS mg/L (ppm)	
		Before Neutralization	After Neutralization
Metal	% Precipitation		
Ni	1.2	8743	7644
Co	1.4	448	391
Fe^{3+}	83.1	6658	998
Al	17.6	3328	2427
Cr	56.8	30	12
Cu	56.1	30	12
Zn	1.4	109	95
Mg	5.2	4824	4049
Mn	4.4	3725	3153
ORP	(mV)	395	340

After the neutralization and first removal of iron stage, the concentration of iron in PLS was decreased from 6658 ppm to 998 ppm with the addition of limestone slurry. The consumption of $CaCO_3$ at this stage was calculated to be 28.6 cc $CaCO_3$ (25 wt./wt.) / 100 cc of PLS (119 kg $CaCO_3$ / 1 ton of dry limonite). The chemical composition of the precipitate obtained at first iron removal stage is given in Table 14.

Table 14. Composition of precipitate obtained at first iron removal stage.

Constituent	wt.%
Ni	0.15
Fe	35.24
Co	0.008
Cr	0.95

The XRD results of the residue obtained after the neutralization with first iron precipitation stage showed the peaks of hematite, quartz and bassanite. By considering the fact that most of the solid in the filtered solids was coming from the pressure leaching circuit, hematite peaks were detected due to hematite precipitation reaction occurring in the pressure acid leaching of the sample. FeOOH which was expected to precipitate were not detected in the XRD pattern. This could be due to the presence of minor amount of FeOOH or being overlapped by other peaks. The observed quartz peaks belonged to unleachable quartz mineral during high pressure acid leaching. The removal of free acid (neutralization) was taking place with the addition of limestone and bassanite formed at the end of reaction given below:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4.0.5H_2O + CO_2 + 0.5\ H_2O \qquad \text{Rx. 24}$$

The observed bubble formation in the feed slurry during the limestone slurry addition was attributed to evolution of CO_2 which occurred as a result of neutralization reaction.
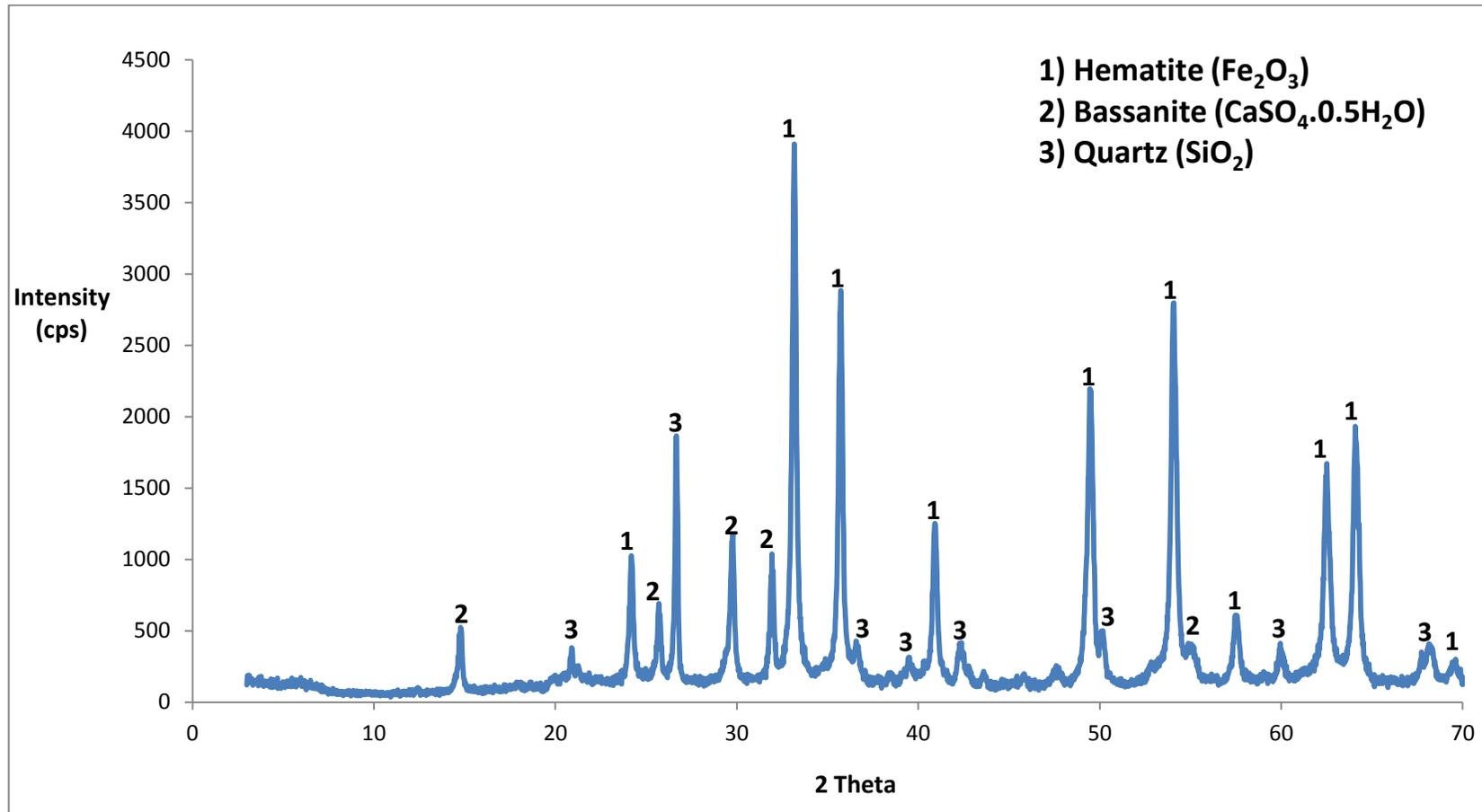
Figure 34. XRD result of the solid residue after neutralization with first stage of iron removal.

4.2.2 Second Iron Removal Stage

Most of the iron (83.1%) in the pregnant leach solution has already been removed at the neutralization and first iron removal stage. At the previous stage the loss of nickel and cobalt was critical since the recycling of the huge mass of solids formed at the first iron removal stage was not economical. At the second stage of iron removal, the aim is to remove the residual iron, aluminum and chromium prior to mixed hydroxide precipitation. Decreasing the impurity concentrations to low levels is necessary since the deportment of these impurities to the MHP precipitate makes the product insoluble in the ammonia solutions (i.e., further processing of MHP) [3]. The quantity of precipitates formed at this stage is typically less than 10% of the solids precipitated in the neutralization and first iron removal. This makes the recycling of the precipitates possible in order to recover the nickel and cobalt lost at the second iron removal stage.

After the determination of the optimum conditions for neutralization and first iron removal stage (pH=2.50, 90°C, 2 hours), a new stock of pregnant leach solution having a volume of 1.75 L was produced at these parameters. In the literature, a pH range from 4.0 to 4.8 is recommended for the second iron removal [3, 56]. The first set of experiments was done to investigate the effect of pH increase on metal precipitations at 70°C and 1 hour duration. The pH of the pregnant solution was increased to the target pH by the addition of 12.5% (wt./wt.) $CaCO_3$ slurry. The precipitation of the impurities of aluminum, chromium and copper from PLS were over 99.5% at pH=4.25 so all of these impurities were removed from the pregnant leach solution at this pH level. The results of experiments based on iron, nickel and cobalt precipitations are given in Figure 35. Iron precipitation was observed to be 98.7% and the total removal of iron took place at pH=4.50. Nickel and cobalt precipitations were also increasing with the increasing pH. Although the nickel and cobalt lost at this stage is going to be recycled to the re-leaching unit, the high extent of nickel and cobalt precipitation makes the process inefficient in terms of productivity. For instance, at pH=4.25 although the precipitation of iron (98.7%) was not satisfactory for a pure MHP product, 30.7% of nickel and 14.3% of cobalt were lost.
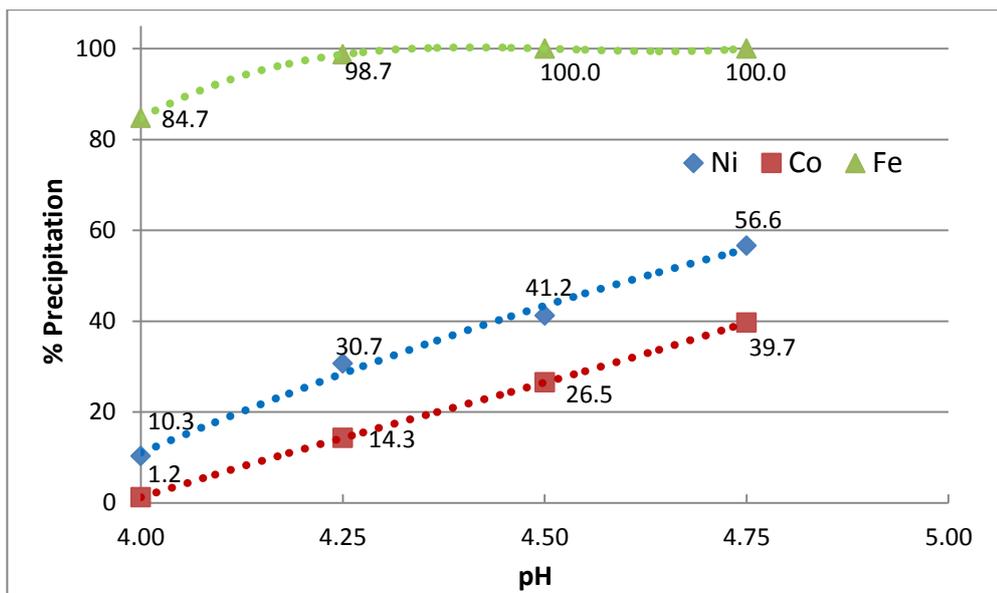
Figure 35. Effect of pH on precipitation of iron, nickel and cobalt (70°C in 1 hour).

To decrease the nickel and cobalt precipitations, i.e., not to lose these metals into second iron removal solids, a series of experiments at different temperatures (e.g., 50, 70, 90°C) were performed for 1 hour duration. The results are given in Figure 36. At lower temperatures, the precipitation of the nickel and cobalt decreased. Similar behaviours were observed at pH=4.00 and pH=4.25. But lowering of the temperature has also resulted in decreasing iron precipitation. The result are consitent with the findings of Köse et al. (2011) [56]. At pH=4.25, by lowering the temperature from 70°C to 50°C, acceptable results were obtained for nickel and cobalt losses but the precipitation of iron decreased by about 15%. This was not a satisfactory result since more than acceptable Fe^{3+} ions had remained in the pregnant leach solution. At higher temperatures the extent of nickel, cobalt and iron precipitations were reported to be increased before. It was possible to remove most of the iron remaining in the pregnant leach solution at pH=4.25 and 90°C, but under these conditions the losses of nickel and cobalt were very high since 44.3% of nickel and 21.7% of cobalt were lost to the second iron precipitate.
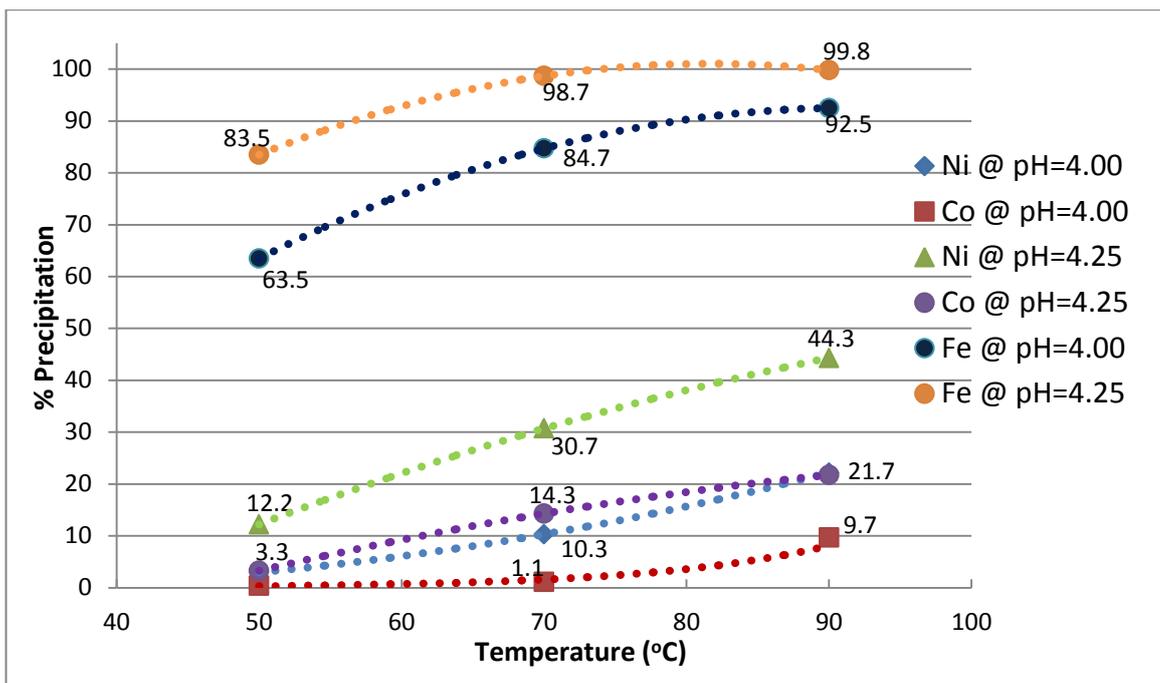
Figure 36. Effect of temperature on precipitation of iron, nickel and cobalt at various pH (in 1 hour).

To investigate the effect of duration on precipitation of metals, at pH=4.25 and 50°C, the experiments were performed for 1, 2 and 3 hours. The results are given in Figure 37. Increasing the duration, the precipitations of the iron, nickel and cobalt were previously reported to be increased. After 3 hours the iron precipitation reached to 97.2% while 29.7% of nickel and 16.7% of cobalt were being co-precipitated.
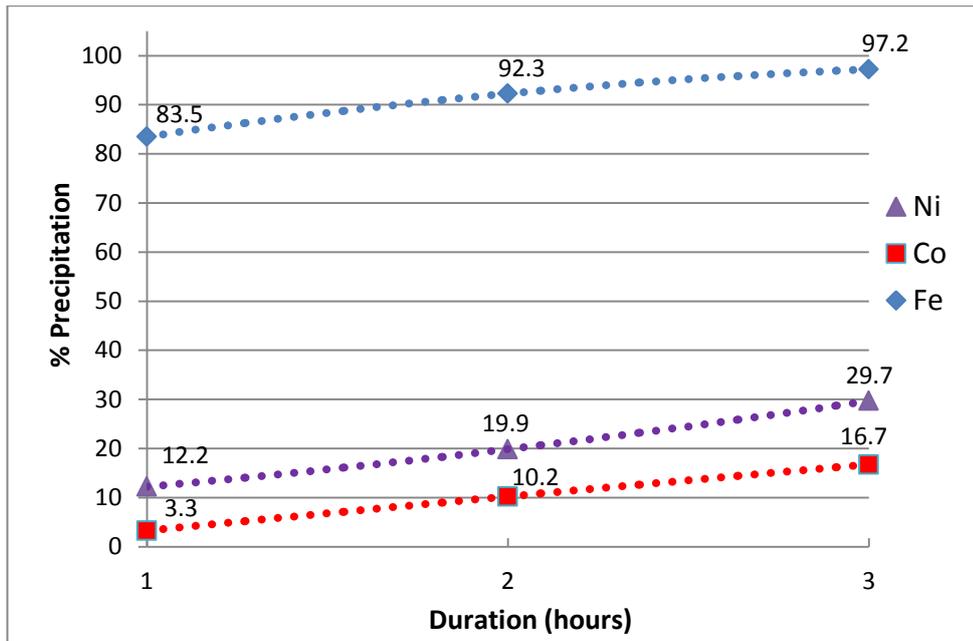
Figure 37. Effect of duration on precipitations of iron, nickel and cobalt (pH=4.25, 50°C).

In the industrial practice, the pregnant leach solution coming from the neutralization and first iron removal stage is sent to counter-current-decantation (CCD) prior to second iron removal stage. At the CCD, dilution of the pregnant leach solution by a factor of 1.5 takes place while washing the solids to remove the nickel and cobalt that may be present on solids. The wash water of CCD is the process water of MHP circuit such that it contains about 3.5 g/L magnesium. So as to make a realistic approach, the pregnant leach solution obtained after the neutralization and first iron removal stage was diluted by a factor of 1.5 with magnesium containing water (containing about 3500 ppm Mg) and second iron removal experiments were continued. The change in chemical composition of the PLS after the dilution is given in Table 15.

Table 15. Chemical composition of PLS before and after dilution.

Chemical Composition of PLS mg/L (ppm)		
Metal	Before Dilution	After Dilution
Ni	7644	4778
Co	391	290
Fe^{3+}	998	812
Al	2427	1558
Cr	12	8
Cu	12	8
Zn	95	63
Mg	4049	3224
Mn	3153	2103

After the preparation of diluted pregnant leach solution, the effect of increase in pH was investigated at $70^{o}C$ and 1 hour duration. The optimum pH value for the highest impurity removals with the minimum nickel and cobalt losses was determined. The results obtained are given in Figure 38. The loss of nickel and cobalt increased with the pH increase as expected. Iron precipitation was not high enough to decrease this impurity to very low levels. This situation is not consistent with the literature findings since about 99% of iron precipitation is expected to take place at pH=4.25 under similar conditions [56]. Ferrous ion (Fe^{2+}) was reported to precipitate at higher pH range but the chemical compositional analysis of pregnant leach solution showed a minor amount of this ion (about 2 ppm). So this problem did not originate from the presence of Fe^{2+}. Further investigation must be done to understand the phenomena behind the impeding or retarding effect on iron precipitation from the PLS of Sivrihisar limonitic laterite ore.
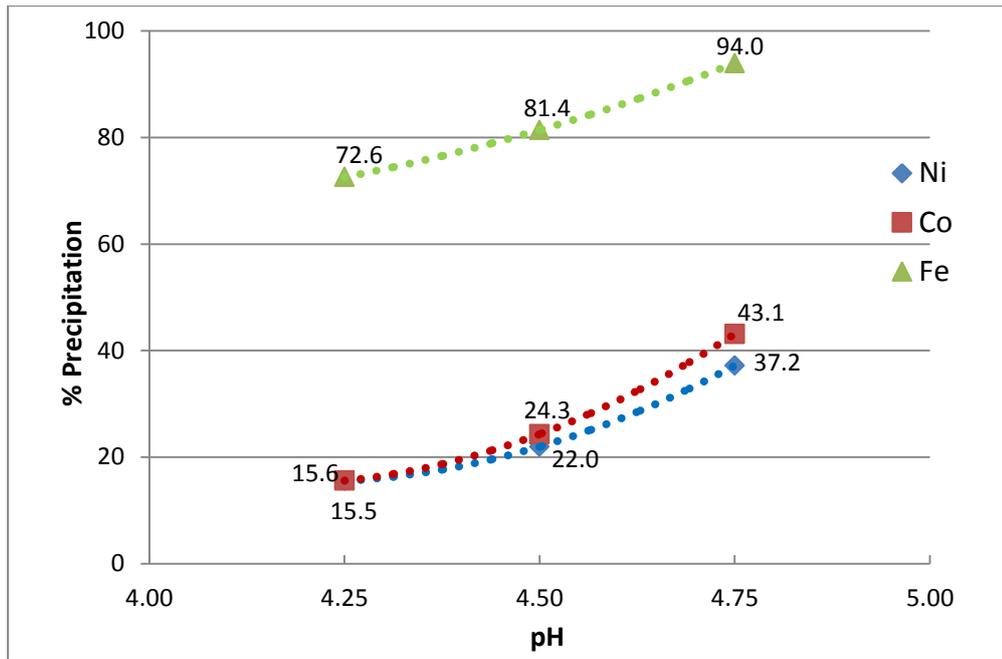
Figure 38. Effect of pH on nickel, cobalt and iron (diluted PLS) (70°C in 1 hour).

The results of the effect of pH increase on other impurity metals (e.g., Al, Zn, Mn, Mg) are given in Figure 39. Nearly all of the aluminum was removed from the solution at this pH interval. Zinc precipitation was reported to be the most sensitive one among these impurities that its precipitation increased by about 40%, reached a level of 97.3% while increasing pH from 4.25 to 4.75. Magnesium and manganese precipitations showed similar characteristics that their precipitations accounted for 19.7% and 15.3% at pH=4.25, respectively.
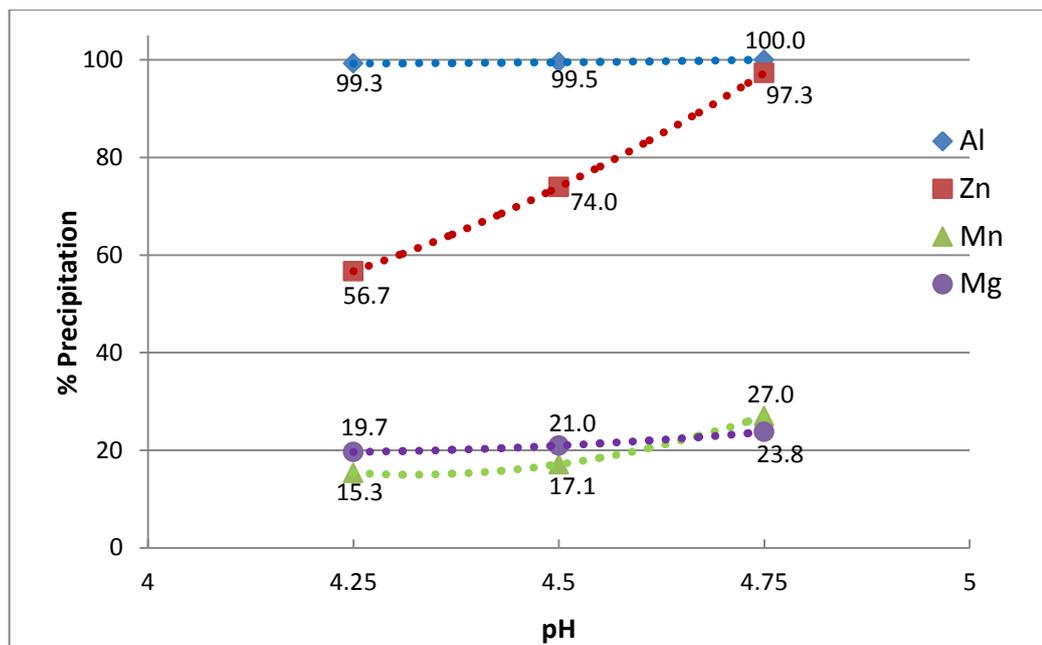
Figure 39. Effect of pH increase on Al, Zn, Mn and Mg precipitations (diluted PLS) (70°C in 1 hour).

After these experiments, it was concluded that waiting for longer precipitation durations did not create a positive result for nickel and cobalt losses. Increasing the temperature increased the iron precipitation but nickel and cobalt losses also increased. Whereas decreasing the temperature decreased nickel and cobalt losses but iron precipitation was insufficient and resulted in pregnant leach solution with high ferric ion (Fe^{3+}) concentration. It was decided to use diluted pregnant leach solution for the mixed hydroxide precipitation stage. The optimum conditions were decided to be pH=4.25, 70°C and 1 hour duration. The consumption of $CaCO_3$ slurry (12.5 wt./wt.) was found to be 3.8 cc/ 33cc of PLS (23.75 kg $CaCO_3$/ 1 ton of dry limonite). At the stated conditions, 15.5% of nickel and 15.6% of cobalt were precipitated. Fortunately, it is possible to recycle the second iron removal solids and gain the nickel and cobalt lost. Only 72.6% of iron was precipitated under the optimum conditions chosen. For Sivrihisar limonite, it was reported that obtaining a pregnant leach solution containing very low concentration of iron (i.e., <10 ppm) was impossible without huge losses of nickel and cobalt to the precipitate. The composition of pregnant leach solution after second iron removal stages is given in Table 16. The composition of the precipitate obtained at this stage is given in Table 17.

Table 16. Composition of PLS after second iron removal.

Element	mg/L (ppm)
Ni	4204
Co	255
Ca	474
Fe^{3+}	232
Zn	29
Cu	2
Mg	2698
Mn	1854
Cr	2
Al	12
ORP (mV)	289

Table 17. Composition of the precipitates obtained at the second iron removal stage.

Constituent	wt.%
Ni	9.69
Fe	15.16
Co	0.46
Cr	0.24

The XRD analysis of second iron removal solids showed the peaks of bassanite due to reactions between metal sulfates and limestone. There were also peaks of unreacted calcite and iron hydroxide.
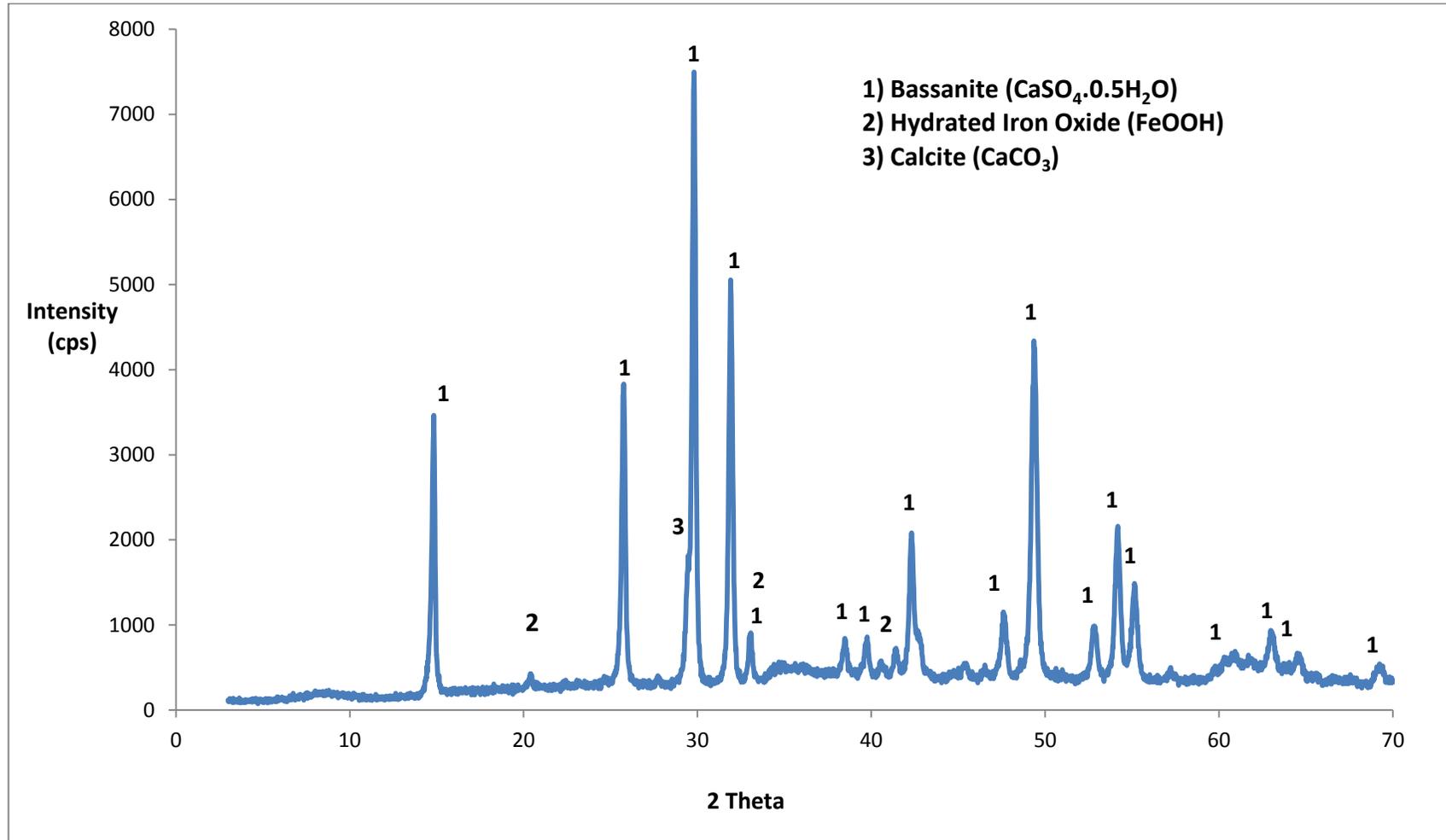
Figure 40. XRD result of the solid obtained after second iron removal stage.

4.2.3 First Mixed Hydroxide Precipitation Stage (MHP 1)

After the neutralization and purification of the pregnant leach solution in two iron removal stages, a new purified stock solution was prepared which had a volume of 0.7 L for the mixed hydroxide precipitation experiments. In the literature, the precipitation temperature of 50^oC in a duration of 1 hour at a pH range around 7 were stated to be the optimum conditions to yield a product containing 30-39% of nickel and 2-5% of cobalt [3, 56]. To have a saleable quality product, the contamination of the product with manganese should be less than 5%. At the mixed hydroxide precipitation experiments, MgO slurry (1% wt./wt.) was used instead of limestone to adjust the pH of the pregnant leach solution in order to precipitate the nickel and cobalt. Using limestone was reported to contaminate the MHP product with calcium precipitates (e.g., bassanite, gypsum) [44]. At 50^oC and 1 hour, the effect of pH on precipitations of nickel, cobalt and manganese was investigated. The results are given in Figure 41. The amount of MgO to be added was initially calculated by assuming that the Ni, Co and Mn would be precipitated according to the stoichiometric reactions given below with 90% MgO efficiency. The aim was to precipitate minimum 90% of Ni and Co with less than 5% Mn in MHP 1 precipitation stage.

$$NiSO_4 + MgO + H_2O \rightarrow MgSO_4 + Ni(OH)_2(s) \qquad \text{Rx.25}$$

$$CoSO_4 + MgO + H_2O \rightarrow MgSO_4 + Co(OH)_2(s) \qquad \text{Rx.26}$$

$$MnSO_4 + MgO + H_2O \rightarrow MgSO_4 + Mn(OH)_2(s) \qquad \text{Rx.27}$$
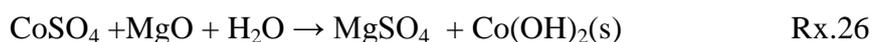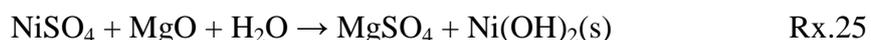
When the calculated amount of MgO was added, a value of pH 7.0 was obtained and the impurities such as iron, zinc, aluminum, copper, chromium remaining in the pregnant solution after the second iron removal stage were almost totally precipitated and contaminated the MHP 1 product. On the other hand, manganese and magnesium were precipitated partially. So the nickel and cobalt were selectively precipitated over manganese at pH around 7.0. At higher pH values (e.g., pH=7.2), the selectivity of nickel and cobalt over manganese decreased since manganese precipitation also became favorable.

To limit the manganese incorporation into mixed hydroxide product, pH=7.0 was decided to be the optimum condition to give the highest acceptable precipitation of nickel and cobalt with the minimum manganese co-precipitation. At the conditions of pH=7.0, 50°C and 1 hour, 93.5% of nickel and 95% of cobalt were precipitated, while manganese precipitation was kept at 22%. The consumption of MgO slurry was calculated to be 15.5 cc MgO (1% wt./wt.) slurry / 50 cc of PLS (5.16 kg MgO / 1 ton of dry limonite) under these conditions.
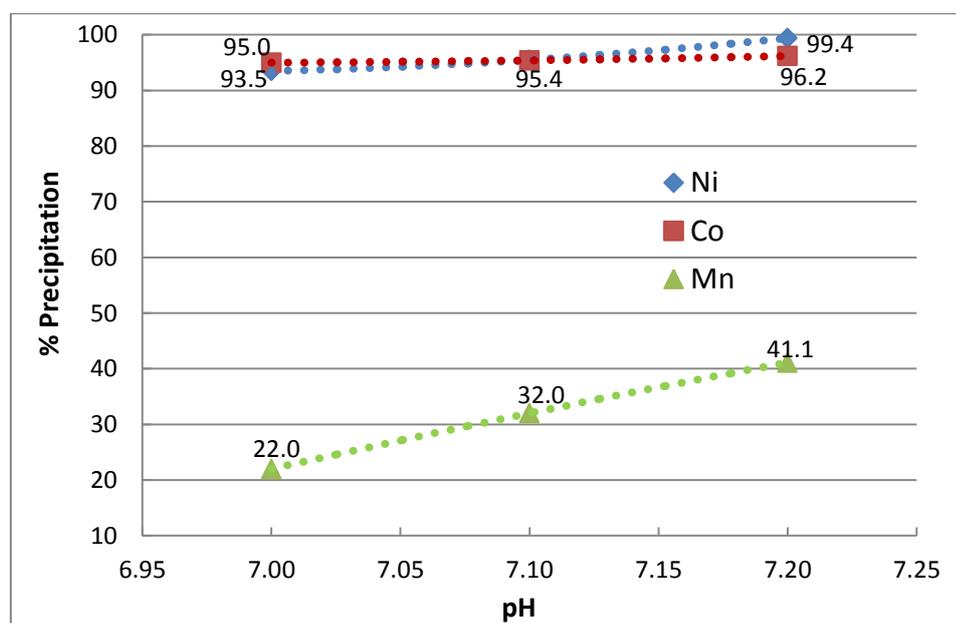
Figure 41. Effect of pH on nickel, cobalt and manganese precipitations (50°C in 1 hour).

The chemical composition of the mixed hydroxide product (MHP 1) obtained at the optimum conditions (pH=7.0, 50°C, 1 hour) is given in Table 18. The obtained MHP contained 33.41% of nickel and 2.93% of cobalt. It was noticed that the impurities of aluminum, chromium and copper did not contaminate the product since they had been already removed in the purification stages. The manganese content of solid precipitate was 3.69% which was below the target value (< 5%) for a saleable quality product [3]. But it was found that the experiments conducted at pH=7.2 could yield a MHP product containing higher manganese content (i.e., 6.08% Mn) with the higher amount of precipitation of Ni and Co. The MHP product obtained at the optimum conditions was also contaminated with 2.83% of Fe. This is not a

welcomed situation since iron reduces the ammonia re-leach extractions of MHP product in further processing [41].

Table 18. Chemical composition of the mixed hydroxide product (MHP 1).

Component	wt.% (dry)
Ni	33.41
Co	2.93
Fe	2.83
Mn	3.69
Ca	0.06
Mg	1.00
Zn	0.39
Cu	0.10
Al	0.50
Cr	0.10

The problem of iron in the MHP 1 product can be overcome with a new suggested approach. According to Vaughan et al. (2011), instead of ammonia leaching an alternative MHP leaching process can eliminate the effect of iron contaminated mixed hydroxide product. The flow-sheet of this selective process is given in Figure 42. In this process a sufficiently strong oxidant is employed with sulfuric acid as leaching media. If sufficient conditions are created cobalt remains insoluble. At pH around 3, the silica, iron, aluminum and most of the manganese also remain insoluble and form the oxide concentrate while nickel is almost completely leached together with magnesium, calcium, copper, sodium and zinc. The strict control of the impurity elements (e.g., Fe, Al) in the MHP product may be minimized with this process [41]. The nickel containing solution is further utilized by typical solvent extraction or ion-exchange techniques prior to nickel electrowinning.
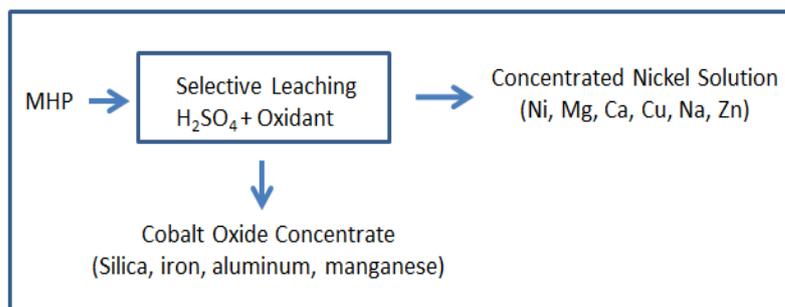
Figure 42. Process flow-sheet of nickel and cobalt separation.

In this reasearch under the optimum conditions determined experimentally, the nickel and cobalt concentrations were lowered in the pregnant leach solution and most of the nickel and cobalt precipitated as their respective hydroxides which is named MHP 1. The concentration of the pregnant leach solution before and after mixed hydroxide precipitation is given in Table 19.

Table 19. Chemical Composition of PLS before and after mixed hydroxide precipitation.

Chemical Composition of PLS, mg/L (ppm)		
Component	After Second Iron Removal (Before MHP)	Afer Mixed Hydroxide Precipitation
Ni	4204	234
Co	255	11
Fe^{3+}	232	2
Al	12	1
Cr	2	0
Cu	2	0
Zn	29	2
Mg	2698	2158
Mn	1854	1247
ORP (mV)	289	157

To characterize the MHP 1 product XRD and DTA and TG analysis were performed. The XRD pattern of MHP 1 product is given in Figure 43. In the XRD pattern of the mixed hydroxide precipitate, the main phase was found to be jamborite $(Ni,Co,Fe)(OH)_2(OH,S,H_2O)$ which is a form of nickel-cobalt hydroxide. In the literature jamborite composition is given as 42-49% of nickel, 1.9% of Co and 0.9% of Fe [57]. Theophrastite $(Ni(OH)_2)$ which is a nickel hydroxide was also found to be present in the obtained mixed hydroxide product. The Pourbaix Diagrams of Ni and Co in H_2O system which indicate the formation of hydroxides at higher pH levels are given at Appendice C. Magnesium hydroxide in the form of brucite $(Mg(OH)_2)$ was another compound found in the MHP product. Presence of magnesium hydroxide was possibly due to unreacted MgO added during the mixed hydroxide precipitation stage [44]. As previously mentioned, manganese co-precipitates with nickel and cobalt in the MHP process. The mineralogical characterization of the obtained MHP product showed the peaks of groutite $(MnO(OH))$ which is a manganese hydroxide compound.
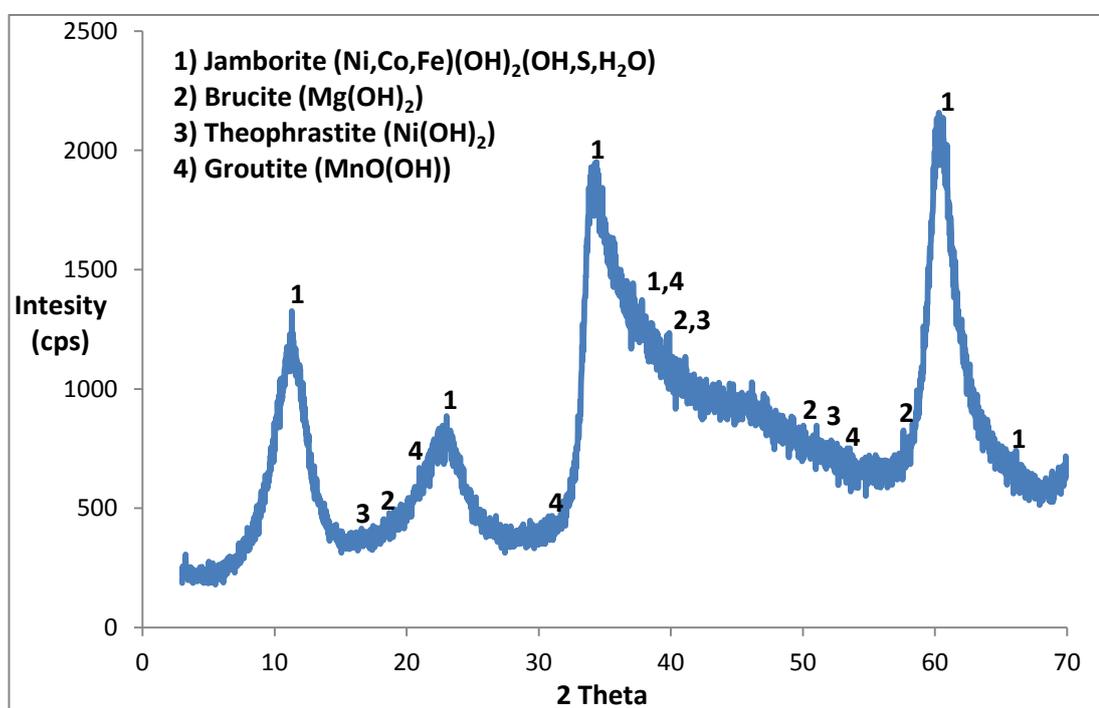
Figure 43. XRD pattern of MHP 1 product.

DTA and TGA results of the MHP 1 product are given in Figure 44. The removal of hydroxyl (OH) groups from the lattice of MHP 1 is a general identification and determination method for metal hydroxides. The removal of hydroxyls occurs in the form of water molecules and the temperature at which the decomposition takes place is specific to the respective compound [48]. In the DTA and TGA results of the MHP 1 product, the endothermic peaks between 90-140°C were most likely due to the removal of physical water (dehydration). In the literature it is mentioned that dehydration of nickel hydroxide can proceed up to 200°C [58]. From 275 to 350°C endothermic peaks were detected with a critical loss of mass. At this temperature range, dehydroxylation reactions of hydroxides took place and the chemically bonded water was removed from the lattice. A typical dehydroxylation reaction based on nickel hydroxide is given in Rx 28:

$$Ni(OH)_2 \rightarrow NiO + H_2O \text{ (Endothermic)} \qquad \text{Rx. 28}$$

Ramesh (2009) studied X-ray diffraction on thermal decomposition of nickel hydroxide. It was stated that the intensities of nickel hydroxide peaks were decreasing while heating the nickel hydroxide sample and at 350°C, the remaining peaks were only belonged to nickel oxide [58]. But Logvinenko et al. (2011) suggested that the temperature intervals for the decomposition of nickel hydroxide is applicable only for a certain compound. It was stated that the temperature for decomposition of nickel hydroxide is very prolonged (i.e., 327-627°C) [59]. So, in the DTA and TGA results of MHP 1 product, at 350°C the metal hydroxides may not have completed their decompositions. The observed endothermic peaks between 550-600°C were possibly due to decomposition of the nickel hydroxide (e.g., jamborite, theophrastite).
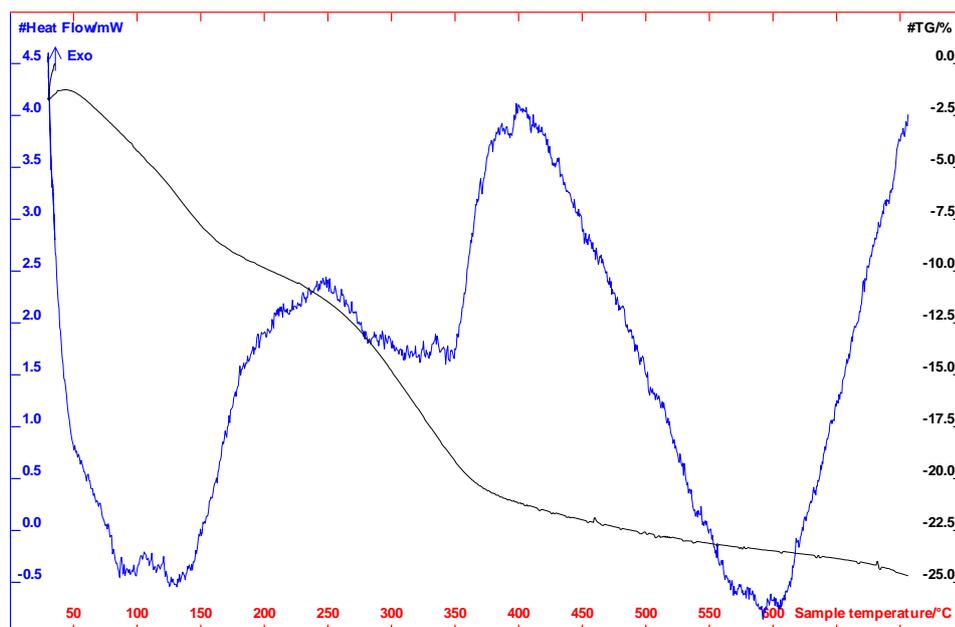
Figure 44. DTA and TGA results of MHP 1 product.

4.2.3 Second Mixed Hydroxide Precipitation Stage (MHP 2)

The nickel and cobalt in the pregnant leach solution were not completely precipitated at pH value of 7.0 in the first mixed hydroxide precipitation stage. This was done in order to control the manganese deportment into the product [3, 44, 56]. The depleted solution obtained after the first mixed hydroxide precipitation stage which had a volume of 0.5 L had still some nickel (234 ppm) and cobalt (11 ppm) which had to be recovered. To achieve this, since the quality of the product (MHP 2) which is going to be obtained at this stage is not as critical as MHP 1 composition wise, a cheaper reagent of slaked lime $[Ca(OH)_2]$ was added to raise the pH of the depleted solution. At $60^{\circ}C$ in 1 hour, the effect of varying pH on the precipitation of nickel and cobalt was investigated. The results are given in Figure 45. The nickel, cobalt and manganese precipitations increased with the increasing pH level such that at pH=7.75 about 97% of the nickel, all of the cobalt and 40.7% of the manganese were precipitated from PLS. The attained product at the second mixed hydroxide precipitation stage was not a saleable quality product due to its high content of manganese (typically 10-20%), so to recover its nickel and cobalt contents, the precipitate should be sent to recycle leaching [3].
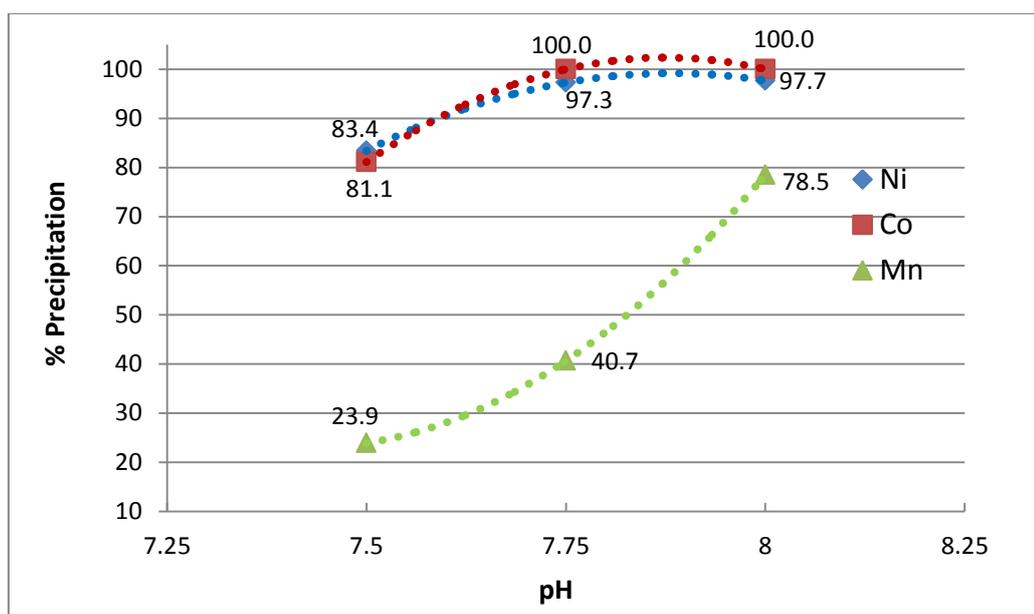
Figure 45. Effect of pH on precipitation of nickel, cobalt and manganese as MHP 2 (60°C in 1 hour).

The optimum pH value for this stage must be decided according to the residual nickel and cobalt that should remain in the purified and precipitated solution. Generally, the terminal concentrations of nickel and cobalt should be less than 5 ppm [3]. The chemical composition of the depleted solution after the experiments conducted at different pH values is given in Table 20. At pH=7.75, the precipitations of nickel (97.3%) and cobalt (100%) were found to be sufficient since the residual concentrations of these metals in the depleted solution remained close to 5 ppm or below. The oxidation-reduction potential (ORP) of the depleted solution was measured to be 149 mV. So, the optimum pH for the second mixed hydroxide precipitation was decided to be pH=7.75 at 60°C in 1 hour. To reach this pH value, the consumption of slaked lime [$Ca(OH)_2$] was calculated to be 5.9 cc (1 wt./wt. $Ca(OH)_2$ slurry) / 50 cc of pregnant leach solution. (1.96 kg $Ca(OH)_2$ / 1 ton of dry limonite).

A higher pH value (e.g., pH=8.00) was not selected since more manganese precipitation took place at this pH and the manganese content of MHP 2 precipitate reached to 40%. Since this precipitate is going to be recycled in the system, the high amount of manganese content of the precipitate can lead to manganese accumulation in the process. So this is not so desirable since manganese content is a quite important criteria for a saleable MHP product. In the product obtained at the optimum conditions (pH=7.75, 60°C and 1 hour), the manganese content accounted for 25.66%. While the nickel and cobalt contents were 13.18% and 0.95%, respectively. The chemical composition of the MHP 2 product is also given in Table 20.

Table 20. Chemical composition of depleted solution and MHP 2 product obtained at different pH values (60°C, 1 hour).

Chemical Composition of the Depleted Solution, mg/L (ppm) or MHP 2 Precipitate (wt. % dry)						
	MHP 2 Precipitate (wt. %)				Depleted Solution (ppm)	
Component	At pH=7.50	**OPTIMUM At pH=7.75**	At pH=8.00	After MHP 1 Precipitation	At pH=7.50	**OPTIMUM At pH=7.75**	At pH=8.00
Ni	11.50	**13.18**	10.21	234	37	**6**	5
Co	0.77	**0.95**	0.75	11	2	**0**	0
Mn	15.44	**25.66**	40.11	1247	912	**698**	248
Mg	0.62	**2.35**	2.04	2158	2065	**2030**	1954
Fe	0.30	**0.12**	0.12	2	0	**0**	0
Zn	0.09	**0.06**	0.04	1	0	**0**	0
Al	0.04	**0.04**	0.03	1	0	**0**	0

CHAPTER 5

CONCLUSIONS

The aim of the study was to extract nickel and cobalt efficiently in an economical way (i.e., with low acid consumption) and then produce a mixed hydroxide precipitate from the pregnant leach solution. With these purposes Sivrihisar limonitic laterite ore was effectively treated and a saleable quality mixed hydroxide product (MHP 1) was obtained. High pressure acid leaching process was used to extract the nickel and cobalt from the matrix of the Sivrihisar limonitic sample. Then, the obtained pregnant leach solution was treated by the mixed hydroxide precipitation method to yield an intermediate product named MHP. The results obtained from the study are summarized below:

- The Sivrihisar limonitic laterite could be concentrated by discarding of over 50 mm particles after screening. The coarse particles were richer in gangue (i.e., quartz) minerals. By this treatment, the nickel content was increased to 1.405 from 1.260 wt.% while SiO_2 content was decreased to 25.80 from 30.30 wt.%. The concentrated sample also had 0.093% of Co, 33.7% of iron, 1.29% of MgO, 1.26% of Cr and 3.23% of Al_2O_3.

- The mineralogical characterization of Sivrihisar limonite showed that nickel was mainly in the crystal structure of goethite. Hematite, quartz, calcite and clay minerals of kaolinite and smectite were also observed. A distinct mineral of nickel or cobalt was not observed to be present in the sample. The nickel content was found to be increasing with increase in iron content. This finding indicated the presence of nickel mainly in the matrix of iron minerals.

- The moisture content of as received Sivrihisar limonitic sample was 15.4 wt.%. The wet screen analysis of concentrated ore ground to -850 μ showed that the sample was very fine and 64.85 wt.% of it was less than -38 μ.

- High pressure acid leaching experiments were conducted at the fixed conditions of 100% -850 μ particle size, 40% of solids concentration, 400 rpm. stirring speed in a 2 L titanium grade-4 autoclave.

- Theoretical acid consumption of the Sivrihisar limonite was calculated as 271 kg of sulfuric acid per 1 ton of dry ore for high pressure acid leaching. If the process had been conducted at lower temperatures (i.e., 95°C for atmospheric leaching), the acid consumption would have been 1144 kg per ton of dry ore.

- The experiments conducted in order to investigate the effect of leaching duration on metal extractions showed that the nickel and cobalt extractions reached to very high amounts (> 90%) in 1 hour. Further durations did not create a remarkable increase in the extraction of these valuable metals. Similar behavior was obtained at temperatures of 220, 235 and 255°C. Sivrihisar limonite was found to be readily leachable. For iron, the increased leaching durations were necessary to decrease its concentration in the PLS. With the increased leaching duration, the ORP of the pregnant leach solution was decreased since more Fe^{3+} ions were removed from the solution in the form of hematite precipitate.

- As the acid concentration increased, more amounts of nickel and cobalt extractions took place in the range of 0.21-0.29 acid/ore ratio. Iron, aluminum and chromium extractions also increased with more acid supply to the autoclave. The impurity concentration of the PLS also increased with the increasing acid concentration. In order to keep the concentration of impurity metals at low levels, 0.23 acid/ore ratio was decided to be the optimum parameter for leaching. At this acid concentration the nickel and cobalt extractions were still high (96.3% for nickel and 93.6% for cobalt at 255°C in 1 hour). The amount of free acids in the pregnant leach solutions were

determined to be between 36.3 to 51.4 g/L in the range of 0.21-0.29 acid/ore ratio.

- With the increase in leaching temperature, the nickel extractions increased while the effect of increasing temperature on the cobalt extractions were found to be minimal in the temperature range of 220-255°C. At temperatures less than 220°C, the extractions of nickel and cobalt dropped sharply. At higher temperatures, the initial extractions and total attained extractions were found to be higher. Iron and chromium extractions decreased and free acid increased with increasing leaching temperature. Due to the fact that pressure determines the thickness of autoclave wall thickness, in order to decrease the capital cost of expensive titanium autoclave, the lowest possible leaching temperature was chosen which also satisfied high nickel and cobalt extractions.

- The optimum conditions were chosen as 235°C, 0.23 acid/ore ratio and 1 hour leaching duration. Under these conditions 95.4% of nickel and 91.5% of cobalt were effectively extracted, giving a PLS concentration of 8743 ppm Ni, 391 ppm Co, 6658 ppm Fe and 38600 ppm free acid. XRD results of the leach residue showed that goethite mineral was totally leached and hematite had precipitated during high pressure leaching.

- For the neutralization and first iron removal stage of PLS, the optimum conditions were found as pH=2.50, 90°C in 2 hours with addition of limestone slurry (25 wt./wt.). The pregnant leach solution and solid residue containing the leach residue and the partially precipitated metals such as Fe, Al, Cr were separated at this stage. Higher pH levels resulted in more unrecoverable nickel and cobalt losses in solid residues. At the optimum conditions, 83.1% of iron was precipitated with 1.2% of nickel and 1.4% of cobalt losses. The consumption of $CaCO_3$ was calculated to be 119 kg $CaCO_3$/1 ton of dry ore.

- In the second iron removal stage, the effects of temperature and duration were studied. At higher temperatures and higher durations, the nickel and cobalt losses increased. The pregnant leach solution was diluted by a factor of 1.5 and the optimum conditions were decided to be pH=4.25, 70°C and 1 hour with the addition of limestone slurry (12.5 wt./wt.). Under these conditions, 99.3% of aluminum, 72.6% of iron precipitated while 15.5% of nickel and 15.6% of cobalt were lost to the precipitate. The PLS after this stage contained 232 ppm Fe, 12 ppm Al and 2 ppm Cr. The consumption of $CaCO_3$ was calculated to be 23.75 kg $CaCO_3$/1 ton of dry ore.

- The optimum condition for a saleable quality MHP product named MHP 1 was determined to be pH=7.0, 50°C and 1 hour with the addition of MgO slurry (1 wt./wt.). At the optimum conditions 93.5% of nickel, 95% of cobalt selectively precipitated over manganese (22%). The content of MHP was determined to be 33.41 wt.% Ni, 2.93 wt.% Co, 2.83 wt.% Fe and 3.68 wt.% Mn. At higher pH values, the manganese content reached to about 6 wt.%, which was higher than the limit (<5%) for a saleable product. The consumption of MgO was calculated to be 5.16 kg MgO/1 ton of dry ore.

- Jamborite, theophrastite, brucite and groutite were observed to be present in the MHP 1 product.

- A second mixed hydroxide named MHP 2 was precipitated in order to recover the nickel and cobalt remaining in the solution. The optimum conditions were chosen to be pH=7.75, 60°C in 1 hour with the addition of slaked lime (1 wt./wt.). The composition of MHP 2 was 13.18 wt.% Ni, 0.95 wt.% Co and 25.66 wt.% Mn. The consumption of $Ca(OH)_2$ was calculated to be 1.96 kg $Ca(OH)_2$/1 ton of dry ore.

- In conclusion, including the losses in the screening stage and assuming full recovery of second iron removal and second mixed hydroxide precipitates in releaching units, about 83% of nickel in Sivrihisar limonitic laterite ore was recovered at the end of research.

Recommendations for Further Study

The main problem encountered in this research was the contamination of the MHP 1 product with iron. Although this situation can be overcome in the refining of MHP stages with new approaches, it is possible to decrease the iron content in the MHP 1 product by upgrading the general process. The source of iron was the limonitic laterite ore. The amount of iron entering the process can be decreased by lowering the solids concentration in the HPAL process to less than 40%. The particle size of the studied limonitic sample was less than 850 μ. Working with finer particle size was reported to increase the leach solution quality (i.e., higher (Ni + Co)/(Fe + Al)). Also leaching at higher temperatures may result in a decreased iron concentration in the pregnant leach solution.

During the purification stage, it is also possible to decrease the iron concentration much more. Partial recycling of second iron removal precipitate as seeds to the second iron removal stage may accelerate the iron precipitation, thus giving a lower concentration of iron in the purified pregnant leach solution. Controlling the supersaturation of metals so that by raising the pH of the solution in a slower manner can also decrease the nickel and cobalt losses at purification stages.

Since the high pressure pumps through which the slurry is fed to the system have a certain capacity, so the rheological characterization of the limonitic laterite sample has to be done before designing a plant.

The solution obtained at the end of the MHP 2 precipitation was depleted in nickel and cobalt. But it contained significant quantities of manganese and magnesium. If the solution is going to be used in the process as wash water in CCD's, the manganese and magnesium have to be removed before recirculating the solution in the system. Otherwise, the accumulation of these impurities in the process will be encountered and the MHP product will be contaminated with manganese and magnesium in higher amounts.

Separation of nickel and cobalt from the obtained MHP 1 has to be investigated in order to obtaine higher value added products.

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EXAMPLE OF THEORETICAL SULPHURIC ACID CONSUMPTION CALCULATION

Theoretical sulphuric acid consumption of metals present in the lateritic ore was performed by assumming all the metals were present in oxide form and 100% of them were extracted into the pregnant leach solution. Corresponding chemical reaction between the ideal metal oxides and H_2SO_4 is given in Equation A.1, where M denotes the metals present in the laterite ore, x and y denote their corresponding stoichiometric values. The theoretical amount of H_2SO_4 required for the complete reaction is given in Equation A.2.

$$M_xO_y + y\,H_2SO_4 = M_x(SO_4)_y + y\,H_2O \tag{A.1}$$

$$H_2SO_4 \text{ consumed (kg / ton of dry ore)} = \left[\frac{M_xO_y\,(\%)}{100} \times \frac{y \times MW_{H_2SO_4}}{x \times MW_M} \times 1000\right] \tag{A.2}$$

Theoretical H_2SO_4 consumption of nickel per ton of dry limonitic ore:

$$NiO + H_2SO_4 = NiSO_4 + H_2O \tag{A.3}$$

$$\left[\frac{1.405}{100} \times \frac{1 \times 98}{58.7} \times 1000\right] = 23.4 \text{ kg } H_2SO_4 \tag{A.4}$$

Theoretical H_2SO_4 consumption of cobalt per ton of dry limonitic ore:

$$CoO + H_2SO_4 = CoSO_4 + H_2O \tag{A.5}$$

$$\left[\frac{0.093}{100} \times \frac{1 \times 98}{58.9} \times 1000\right] = 1.5 \text{ kg } H_2SO_4 \tag{A.6}$$

Theoretical H_2SO_4 consumption of iron (Fe^{3+}) per ton of dry limonitic ore:

$$Fe_2O_3 + 3\,H_2SO_4 = Fe_2(SO_4)_3 + 3\,H_2O \tag{A.7}$$

$$\left[\frac{33.7}{100} \times \frac{3 \times 98}{2 \times 55.8} \times 1000\right] = 887.8 \text{ kg H}_2\text{SO}_4 \tag{A.8}$$

Theoretical H$_2$SO$_4$ consumption of aluminum per ton of dry limonitic ore:

$$Al_2O_3 + 3\ H_2SO_4 = Al_2(SO_4)_3 + 3\ H_2O \tag{A.9}$$
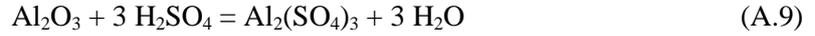
$$\left[\frac{1.71}{100} \times \frac{3 \times 98}{2 \times 26.9} \times 1000\right] = 93.4 \text{ kg H}_2\text{SO}_4 \tag{A.10}$$

Theoretical H$_2$SO$_4$ consumption of manganese per ton of dry limonitic ore:

$$MnO + H_2SO_4 = Mn(SO_4) + H_2O \tag{A.11}$$
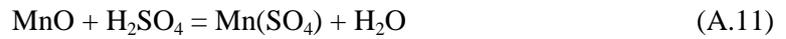
$$\left[\frac{0.573}{100} \times \frac{1 \times 98}{54.9} \times 1000\right] = 10.2 \text{ kg H}_2\text{SO}_4 \tag{A.12}$$

Theoretical H$_2$SO$_4$ consumption of magnesium per ton of dry limonitic ore:

$$MgO + H_2SO_4 = Mg(SO_4) + H_2O \tag{A.13}$$
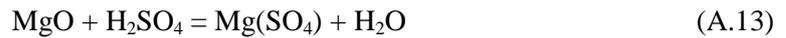
$$\left[\frac{0.777}{100} \times \frac{1 \times 98}{24.3} \times 1000\right] = 31.3 \text{ kg H}_2\text{SO}_4 \tag{A.14}$$

Theoretical H$_2$SO$_4$ consumption of calcium per ton of dry limonitic ore:

$$CaO + H_2SO_4 = Ca(SO_4) + H_2O \tag{A.15}$$

$$\left[\frac{1.17}{100} \times \frac{1 \times 98}{40.1} \times 1000\right] = 28.6 \text{ kg H}_2\text{SO}_4 \tag{A.16}$$

With the similar calculations, when all of the metals in the laterite composition were considered to be totally extracted, it was found that 1144 kg of H$_2$SO$_4$ is required per for ton of dry limonite. But in high pressure acid leaching conditions, not all of the metals are 100% extracted (e.g., Fe, Al). According to the Sherritt assumptions, the theoretical acid consumption of Sivrihisar limonite was found to be 271 kg per ton of dry ore including free acid [19].

APPENDICE B

EXAMPLE OF METAL EXTRACTION OR PRECIPITATION CALCULATIONS

The chemical analysis of original limonite sample and leach residues obtained at the end of leaching were performed according to the AAS analysis results of the leach residue done by META Nickel and Cobalt Company. The extraction of nickel and cobalt was found according to Equation B.1 given below:

$$\% \text{ Extraction of Ni or Co} = [1 - \frac{\text{Residue wt. * \% Ni or Co in Residue}}{\text{Ore wt. * \% Ni or Co in the ore}}]*100 \qquad (B.1)$$

Examples of metal extraction calculations for the nickel and cobalt are given in Equations B.2 and B.3, respectively, according to the experimental data given in Table 21.

Table 21. Experimental data obtained at 255°C, 0.27 acid/ore ratio, 120 min.

Limonite Ore and Corresponding Leach Residue Data	Nickel	Cobalt
Residue Weight (g)	172.41	172.41
Weight % Ni or Co in the Residue	0.020	0.004
Ore weight (g)	200	200
Weight % Ni or Co in the Ore	1.520	0.086

$$\% \text{ Extraction of Ni} = [1 - \frac{172.41 * 0.02}{200 * 1.520}]*100 = 98.9 \qquad (B.2)$$

$$\% \text{ Extraction of Co} = [1 - \frac{172.41 * 0.005}{200 * 0.086}]*100 = 95.9 \qquad (B.3)$$

Besides nickel and cobalt, the extraction calculations of the other elements were performed according to the AAS analysis results of the pregnant leach solution done by the Chemical Engineering Department of METU after pressure leaching. The extraction calculation of the other metals was found according to Equation B.4 given below:

$$\% \text{ Metal Extraction} = \left[\frac{\text{Preg Volume}(cc) * \text{ppm Metal}\left(\frac{mg}{liter}\right)*10^{-4}}{\text{Ore Weight} * \% \text{ Metal in the ore}} \right] * 100 \quad (B.4)$$

Examples of metal extraction calculations for iron and chromium are given in Equations B.5 and B.6, respectively, according to the experimental data given in Table B.2. Metal extraction percentages of the other elements can be found similar to iron and chromium.

Table 22. Experimental data obtained at 235^{0}C, 0.23 acid/ore ratio, 60 min.

Limonite Ore and Corresponding Pregnant Leach Solution Data	Iron	Chromium
Preg. Volume (cc)	329.6	329.6
Fe or Cr in the Preg. (ppm)	4017	19.68
Ore weight (g)	200	200
Weight % Fe or % Al in the Ore	33.70	1.26

$$\text{\% Extraction of Fe} = \left[\frac{329.6 * 4017 * 10^{-4}}{200 * 33.70} *100 \right] = 1.96 \qquad (B.5)$$

$$\text{\% Extraction of Cr} = \left[\frac{329.6 * 19.68 * 10^{-4}}{200 * 1.26} *100 \right] = 0.26 \qquad (B.6)$$

The precipitation of metals during iron removal and mixed hydroxide precipitation stages were calculated based on compositional analysis of pregnant leach solution according to given equation B.6. Experimental data of mixed hydroxide precipitation performed at pH=7.1, 50°C in 60 min is given in Table 23 to make an illustrative Ni precipitation calculation.

% Precipitation of Ni =

$$= \left[\frac{(\text{Initial PLS Volume} * \text{initial Ni conc.}) - (\text{Final PLS Volume} * \text{final Ni conc.})}{(\text{Initial PLS Volume(cc)} * \text{ppm Ni initial})} \right] * 100 \qquad (B.7)$$

Table 23. Experimental data obtained at pH=7.1, 50°C and 60 min.

Limonite Ore and Corresponding Pregnant Leach Solution Data	Ni
Initial PLS volume (cc)	50
Initial Ni concentration (ppm)	4204
Final PLS volume (cc)	60
Final Ni concentration (ppm)	19.5

$$\% \text{ Precipitation of Ni} = \left[\frac{(50 \times 4204)-(60 \times 19.5)}{(50 \times 4204)} \right] * 100 = 99.5$$

POURBAIX DIAGRAMS OF NICKEL AND COBALT

The Pourbaix diagrams of Ni and Co in H_2O system as given in Figures 46 and 47 indicated that Ni^{2+} and Co^{2+} were the stable form of ions throughout the high pressure acid leaching (at low pH). With the increase in pH, the stable forms $Ni(OH)_2$ and $Co(OH)_2$ were formed at higher pH values [60].
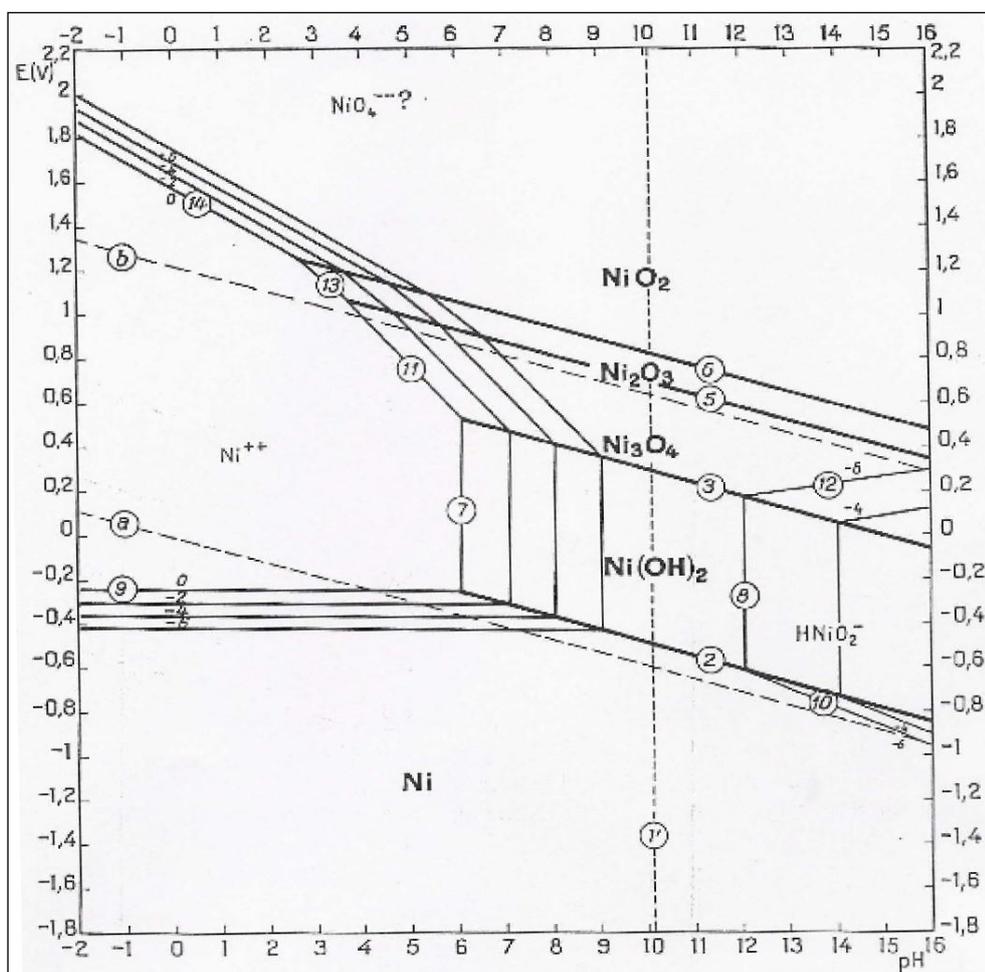
Figure 46. Pourbaix diagram for Ni-H_2O system at 25°C.
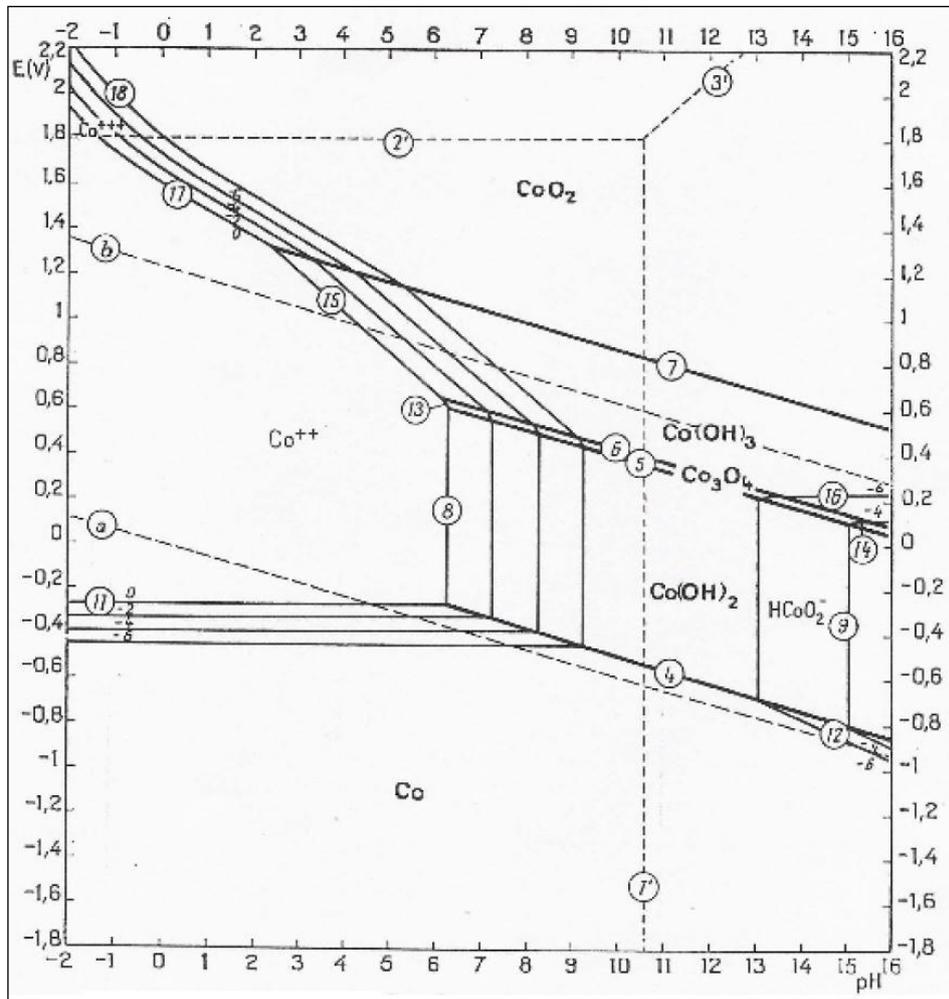
Figure 47. Pourbaix diagram for Co-H₂O system at 25°C.