HIGH PRESSURE ACID LEACHING OF TURKISH LATERITES

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

BY

ŞERİF KAYA

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

JANUARY 2011

Approval of the thesis:

HIGH PRESSURE ACID LEACHING OF TURKISH LATERITES

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ABSTRACT

HIGH PRESSURE ACID LEACHING OF TURKISH LATERITES

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January 2011, 91 pages

The aim of this thesis study was to investigate and find the most cost effective way of extracting nickel and cobalt into the pregnant leach solution (PLS) from Gördes lateritic nickel and cobalt ore by means of sulphuric acid leaching under high temperature and high pressure conditions.

The high pressure acid leach (HPAL) experiments were conducted with nontronitic and limonitic types of Gördes lateritic nickel ore, respectively. Leaching experiments of nontronite ore have shown that almost all of the nickel and cobalt contained in the nontronitic ore were easily extracted into the (PLS). Therefore, the rest of the experiments were concentrated on difficult to leach limonitic sample when compared with the nontronitic one, and higher nickel and cobalt extractions were aimed to be obtained. By taking economic and technical considerations into account, the basic (HPAL) process parameters for the limonitic sample were optimized as; leaching at 255 °C with a particle size of 100% -850 μ with 0.30 sulphuric acid to ore weight ratio in 1 hour of leaching duration. The experiments were conducted with 30% solids ratio and it was found that 87.3% of nickel and 88.8% of cobalt present in the

limonitic ore could be extracted into the pregnant leach solution. Nevertheless, these results were found to be below the desired values. Therefore, the possible reasons of this behavior were investigated and the presence of hematite mineral in the limonitic ore was found to be the most probable one. Therefore, in order to dissolve the nickel and cobalt present in the hematite mineral, the additions of HCl, ferrous ions, cuprous ions and sulphur were tried, respectively and they were found to be beneficial in order to increase the degree of nickel and cobalt extractions.

Keywords: Hydrometallurgy, Laterite, Leaching, Nickel, Cobalt.

ÖZ

TÜRK LATERİTLERİNİN YÜKSEK BASINÇ ALTINDA ASİT LİÇİ

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Tez Yöneticisi: Prof. Dr. Yavuz A. Topkaya

Ocak 2011, 91 sayfa

Bu tez çalışmasının amacı yüksek sıcaklık ve basınç koşulları altında sülfürik asit liç yöntemi kullanılarak lateritik tipteki Gördes nikel ve kobalt cevherinden nikel ve kobaltın metalle yüklü liç çözeltisine alınmasının en ekonomik yolunun araştırılması ve bulunmasıdır.

Yüksek basınç altında asit liç deneyleri, sırasıyla nontronitik ve limonitik tipteki lateritik Gördes nikel cevheri kullanılarak yapılmıştır. Nontronitik tipteki cevherle yapılan deneyler bu cevherdeki nikel ve kobaltın hemen hemen tümünün kolay bir şekilde metalle yüklü liç çözeltisine alınabileceğini göstermiştir. Bu nedenle; geri kalan deneyler, nontronitle karşılaştırıldığında liç edilmesi daha zor olan limonitik cevher üzerine yoğunlaştırılmış ve daha fazla nikel ve kobaltın kazanımı amaçlanmıştır. Teknik ve ekonomik etkenler göz önünde bulundurularak limonitik tipteki örnek için temel yüksek basınç asit liç parametreleri; liç işleminin 255 °C' de 100% -850 µ tane boyutuyla 0.30 sülfürik asit-cevher ağırlık oranı kullanılarak 1 saat sürede gerçekleşmesi şeklinde optimize edilmiştir. Deneyler %30 katı oranı kullanılarak gerçekleştirilmiş olup limonitik cevherde bulunan nikelin % 87,3' ünün

ve kobaltın % 88,8' inin metalle yüklü liç çözeltisine alınabileceği bulunmuştur. Ancak, bu sonuçların istenilen değerlerin altında olduğu belirlenmiştir. Bu nedenle, gözlenen bu davranışın muhtemel nedenleri araştırılmış ve hematit mineralinin cevherdeki varlığı en muhtemel neden olarak tespit edilmiştir. Limonitik nikel cevherindeki hematit minerali içerisinde bulunan nikel ve kobaltın kazanılması için sırasıyla HCl, iki değerlikli demir, tek değerlikli bakır ve kükürt eklentileri denenmiş, ve bu eklentilerin nikel ve kobalt ekstraksiyonlarının artırılmasında faydalı oldukları bulunmuştur.

Anahtar Kelimeler: Hidrometalurji, Laterit, Liç Etme, Nikel, Kobalt.

To my dear parents and especially to my sister Şeyda Kaya,

ACKNOWLEDGEMENTS

First of all, I would like to express my sincere appreciation and gratitude to my supervisor dear Prof. Dr. Yavuz A. Topkaya for his invaluable supervision, kind support, endless patience and continuous guidance in preparation of this thesis.

I must express my special thanks to my roommate Berk Seçen for his valuable suggestions and comments. I would also like to thank to my brothers Onur Gölbaşı and Şenol Reçber for their infinite motivation.

META Nikel ve Kobalt A.Ş. and Kerime Güney are gratefully acknowledged for their support during the chemical analyses of the experimental samples.

I also present my special thanks to the examining committee members for serving on the M.Sc. thesis committee.

Finally, I feel indebted to my family and my wonderful sister Şeyda whose encouragement, support and existence helped me to accomplish this study.

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CHAPTER 1

INTRODUCTION

Ferrous and non-ferrous alloying industries, petro-chemical works, aerospace applications, nickel based catalysts and battery production, military applications, coinage and coating practices are some of the most common areas of nickel utilization in industry which constitute a huge demand for this metal throughout the world. When the tendency of this metal demand is investigated from 1950 to 2009, it is clearly seen that the need for nickel has inflated from under 200 ktpa to over 1300 ktpa, and this dramatic increase is growing at an average rate of 4% per annum [1, 2].

Until recently, this huge demand of nickel has been supplied mostly from the sulphide based nickel reserves, however, this trend is changing towards the more abundant, accounting for about 70% of the world total nickel reserves, lateritic type nickel resources due to technical, economical and environmental reasons [3]. As an example, besides the predominance of lateritic deposits over sulphides, their easier mining by simple open-pit mining methods, unlike extremely expensive sulphide underground mining, makes their utilization more preferable. Finally, significant amount of cobalt contained in laterites makes them more competitive in nickel industry.

According to the annual historical data of nickel production from sulphides and laterites, less than 10% of nickel was produced from lateritic sources in 1950. However, this ratio has increased up to 42% in 2003, and also expected to rise up to 51% by 2012 [4, 5].

1

In the light of this current historical data and changing trend towards the lateritic type nickel deposits; technically, economically and environmentally feasible processing techniques are gaining more and more importance day by day which forces the experimental studies to be concentrated on this area.

Understanding the history of formation of a mineral deposit is very critical in establishing a possible processing route for that value. Typically, lateritic nickel ores vary widely in their chemical composition and mineralogical structure when their history of formation is considered. Depending on their lateritization history, different lateritic profiles may form on a single deposit having different mineralogical formations and distribution. The zones in a typical lateritic ore are classified and named as limonitic, transition (nontronitic) or saprolitic according to its mineral content [6]. Naturally, the response of a specific ore to a metallurgical treatment depends on the chemical composition and mineralogical characteristics of that ore. Due to the complex nature of lateritic ores, three different metallurgical extraction processes are applied, namely pyrometallurgical, hydrometallurgical and 'Caron Process'. Roughly speaking, the energy intensive pyrometallurgical method generally uses the ferro-nickel production route or matte smelting process in order to recover mostly the nickel contained in the saprolitic part of the lateritic ore. However, hydrometallurgical methods generally exploit the highly selective dissolution feature of both nickel and cobalt in the limonitic and nontronitic part of the laterite ore in sulphuric acid media. Whereas, Caron process uses the pyrometallurgical and hydrometallurgical methods together in order to obtain the metallic values [7].

In this study, the response of limonitic and nontronitic profiles of a typical laterite ore from Manisa/Gördes region of Turkey to sulphuric acid was investigated under the high temperature and high pressure conditions by means of hydrometallurgical techniques, and the most cost effective process parameters were determined in order to add value to this deposit.

CHAPTER 2

LITERATURE SURVEY

2.1 Nickel Ores and Their Mineralogy

Although most geological scientists agree upon the iron-nickel core theory of the earth's very heavy core containing from about 5 per cent to over 50 per cent nickel, nickel does not occur abundantly in the earth's crust. When compared with the other elements forming the earth's crust, it makes up just 0.008 per cent by weight of the whole and ranks the twenty-fourth in quantity among the others [8, 9].

Since nickel does not occur natively, it is found in some discrete nickel minerals or in the crystal lattice of other minerals in the form of a solid solution within that crystalline formation. When the distribution of nickel is investigated globally, it is realized that nickel is mostly associated with iron and magnesium and less with silicon and aluminum. Since there is a considerable similarity between atomic dimensions of the divalent cations of iron, magnesium and nickel, it may be a good indication that nickel may substitute for another to a limited extent without distorting the lattice of that crystal. Depending upon this behavior of nickel, nickel-bearing minerals are accumulated in some specific locations of the crust and form the economic, exploitable nickel deposits. Among them sulphide and oxide type nickel-bearing deposits economically constitute the most important nickel reserves throughout the world. In Figure 2.1 and Table 2.1, the distribution of world nickel laterite resources, common nickel-bearing minerals and their associated nickel contents are presented, respectively.
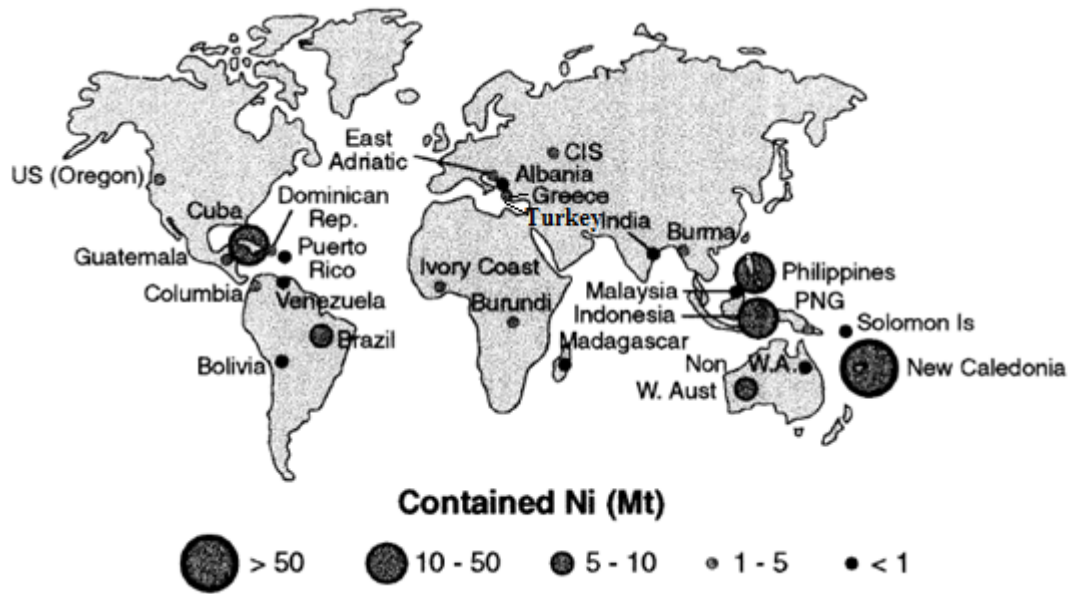
Figure 2.1 World distribution of nickel laterite resources (by country) [10].

Table 2.1 Common lateritic minerals [8, 9].

Mineral Type	Ideal Formula	%Ni	Color
Sulfides			
Pentlandite	$(Ni,Fe)_9S_8$	34.22	Bronze-Yellow
Millerite	NiS	64.67	Brass-Yellow
Heazlewoodite	Ni_3S_2	73.30	Bronze-Yellow
Polydymite	Ni_3S_4	57.86	Steel-Gray
Violarite	Ni_2FeS_4	38.94	Violet-Gray
Siegenite	$(Co,Ni)_3S_4$	28.89	Steel-Gray
Arsenides			
Niccolite or nickeline	$NiAs$	43.92	Copper-Red
Maucherite	$Ni_{11}As_8$	51.85	Platinum-Gray
Rammelsbergite	$NiAs_2$	28.15	Tin-White
Gersdorffite	$NiAsS$	35.42	Steel-Gray
Antimonides			
Breithauptite	$NiSb$	32.53	
Arsenates			
Annabergite	$Ni_3As_2O_8.8H_2O$	29.40	Apple-Green
Silicates and Oxides			
Garnierite	$(Ni,Mg)_6Si_4O_{10}(OH)_8$	≤47%	Green-Gray
Nickeliferous limonite	$(Fe,Ni)O(OH).nH_2O$	0.8-1.5%	Yellow-Brown

2.1.1 Sulfide Nickel Ores

Sulfide type nickel ores typically contain 0.4-2.0% nickel, 0.2-2.0% copper, 10-30% iron, 5-20% sulphur and the rest are silica, magnesia, alumina, and calcium oxide [8]. Pentlandite $(Fe,Ni)_9S_8$ is the main ore mineral in these type of deposits. Other common minerals are pyrrhotite $(Fe_{1-x}S)$, chalcopyrite $(CuFeS_2)$, pyrite (FeS_2), magnetite (Fe_3O_4), ilmenite $(FeTiO_3)$ and iron-rich chromite $(FeCr_2O_4)$. Hopefully, besides the nickel value of this type ores, various precious by-products like copper, platinum group metals, cobalt, gold and silver can also be profited during nickel production. In Table 2.2, the distribution of common magmatic sulfide nickel deposits are tabulated. From the table, it is evident that Canada and Russia have the dominant nickel sulfide reserves in the world [11]. Similar to mineral reserves, Canada and Russia also share the leadership of nickel production from sulfide based nickel resources.

When the formation mechanism of these deposits are investigated in detail, the close relationship between the sulfide nickel ores and magmatic type rocks gives an idea that these ores have formed by the segregation of an immiscible sulphide-rich liquid from an ultrabasic magma, but the exact mechanism of the process is still debatable [12].

Table 2.2 World magmatic sulfide nickel resources (by contained Ni) [11].

Country	Magmatic Sulfides (Mt)	% of World Total Magmatic Sulfides
Australia	13	12.8
Africa	19	18.3
Canada	28	28.1
Russia	28	27.2
USA	8	7.9
China	6	5.4
Asia & Europe	1	0.2
Total	101	100

2.1.2 Lateritic (Oxide) Nickel Ores

Lateritization is a natural, mechanically aided chemical weathering and enrichment process of nickel containing rocks in certain profiles of the parent bedrock in thousands or even millions of years. Lateritic profiles are often observed on tropical or at least sub-tropical climates due to the faster kinetics of chemical reactions by the help of higher temperatures, moisture content and acidity. According to the formation theories of lateritic deposits, olivine $(Fe,Mg)_2SiO_4$ containing up to 0.3% nickel is the primary nickel-bearing mineral in the peridoditic bedrock due to the close similarity among the cationic radius's of Fe^{2+}, Mg^{2+}, and Ni^{2+}. Together with nickel, some amount of cobalt may also exist in the bed due to the similar reason. In some cases the peridoditic rock containing valuable metals nickel and cobalt may have already been altered to mineral serpentine $Mg_3Si_2O_5(OH)_4$ by the removal of iron and leaving a hydrous magnesium silicate structure prior to exposure to the extensive weathering. Thus, olivine and/or serpentine are decomposed into soluble cations of iron, magnesium, nickel, cobalt and sub-microscopic colloidal silica under the effect of high rain fall, atmosphere in acidic character (CO_2, SO_2), expansion/contraction, vegetable matter and biological activity on the so called region. While the soluble species percolating down to the depths of the profile, precipitation of iron in solution takes place and this precipitate forms the minerals of goethite $FeO(OH)$, and hematite Fe_2O_3 close to the ore surface due to preferential oxidation of iron in solution. In contrast to iron, other cations permeate deeper under the effect of gravity as long as they retain their acidic character. However, neutralization of the solution by other minerals weakens the acidic character and solubility; thus, remaining solution precipitates as hydrous silicates.

Due to weathering history, topography, climate characteristics, parent rock composition and, different solubility and mobility of the soluble cations, complete enrichment of nickel in a particular region is never attained. Some of the dissolved nickel remain in the upper layer and enriched within the ferrous minerals through removal of magnesium and silicon and forms nickeliferrous zone. This type of zone mainly consists of ferric oxide minerals and called limonitic zone of the complete

profile. The nickel in this zone mainly associated with goethite FeO(OH), other minerals are hematite α-Fe_2O_3, maghemite γ-Fe_2O_3, and magnetite Fe_3O_4 the distribution of which varies from deposit to deposit [13].

On the other hand, at the deeper profiles, the iron and nickel separation becomes more prominent in silicate minerals due to removal of most of the iron at the higher profiles by precipitation. After iron removal, the remaining nickel rich portion is bonded to hydrous magnesium silicates. In this type of zone formation, the dominant mineral phase is the mineral serpentine $Mg_3Si_2O_5(OH)_4$, and the profile is named as saprolite zone or serpentine ore.

Additionally, in some regions cationic exchange between Mg^{2+} and Ni^{2+} takes place and a new phase called Garnierite $(Ni,Mg)_3Si_2O_5(OH)_4$ forms in veins and pockets of the ore. Since X-ray and other data suggest that this new phase includes several minerals, the term garnierite is omitted from mineral handbooks and it is regarded as a mineral mixture [14].

In addition to limonitic and saprolitic zones in a typical laterite ore, a possible transition layer may also exist between these two layers as a result of environmental factors. In arid areas where the circulation of water is restricted, nontronite $Na_{0.3}Fe_2(Si,Al)_4O_{10}(OH)_2 \cdot n(H_2O)$ (iron rich smectite) and quartz (SiO_2) form a layer called 'nontronite zone' [15].

In summary, lateritic profiles may be illustrated schematically similar to Figure 2.2 and their typical chemical compositions can also be summarized as given below. Meanwhile, minor differences reported by different researchers in the chemical composition of the different lateritic profiles might be worth mentioning for clarity.

(i). upper overburden: (Ni < 1%),
(ii). limonite layer: (SiO_2~6%, MgO~3%, Ni~1.4%, Co~0.15%, and Fe > 40%),
(iii). transition layer: (1.5 to 2.4% Ni),
(iv). saprolite layer: (SiO_2~38%, MgO~25%, Ni~2.4%, Co~0.05%, and Fe < 15%),
(v). lower base rock layer [15].

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	
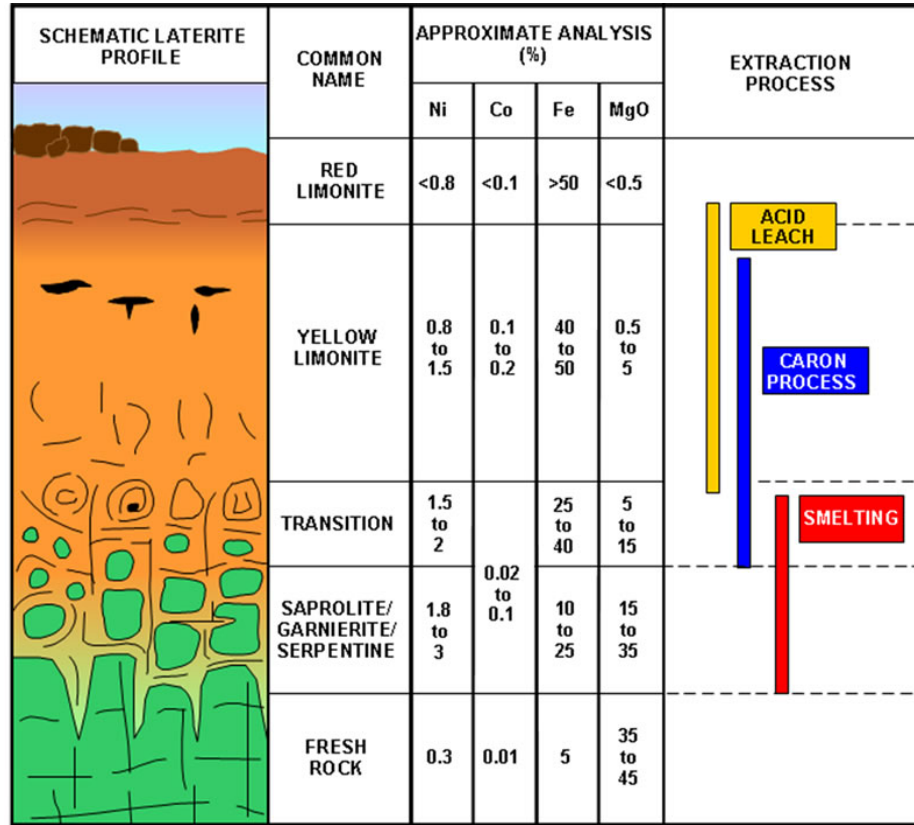
Figure 2.2 Schematic View of a Laterite Profile [16].

For the sake of completeness, it will be complementary to mention about the distribution of lateritic nickel resources throughout the world. According to the data for the year 2008 taken from the British Geological Survey and given in Table 2.3, most of the lateritic nickel deposits are concentrated in New Caledonia, Australia, Africa, Philippines and Indonesia. Among them lateritic deposits of Turkey belong to the sub-class of Asia & Europe, and in fact constitute a minor amount of the world total [11]. The lateritic deposits of Turkey are mainly located on the western part of the country. Specifically; Manisa/Çaldağ, Manisa/Gördes, Uşak/Banaz, and Eskişehir/Yunusemre deposits are the most important lateritic nickel resources of Turkey. Currently, in Manisa/Çaldağ European Nickel PLC (Sardes Nickel) has completed a laterite heap leaching demonstration plant and proved its technical viability for further investment [17]. On the other hand, META Nikel ve Kobalt A.Ş. is planning to construct a pressure acid leaching plant for the processing of

Manisa/Gördes lateritic nickel/cobalt ore. Meantime, the same company is also researching on a suitable hydrometallurgical or pyrometallurgical processing technique for its Eskişehir/Yunusemre deposit. This current situation in Turkey suggests that production of nickel from lateritic sources will be a hot topic in the near future of the country. On the other hand; besides lateritic sources, sulfide type nickel deposits have also been reported in Bursa/Yapköydere, Bitlis/Pancarlı, Bolu/Mudurnu-Akçaalan, and Sivas/Divriği [18]. However; for the time being, these deposits do not seem to be as competitive as their lateritic counterparts.

Table 2.3 World nickel laterite resources (by contained Ni) [11].

Country	Lateritic Resource (Mt)	% of World Total Laterites
New Caledonia	37	22.9
Australia	21	13.1
Africa	13	8.1
Philippines	28	17.4
Indonesia	25	15.8
Central & S. America	17	10.6
Caribbean	11	6.9
Asia & Europe	5	3.3
Other Australasia	3	2.0
Total	161	100

Table 2.4 Nickel resources of Turkey (by ore reserve) [17-19].

Region	Proven Reserve (t)	Probable Reserve (t)	Possible Reserve (t)
Manisa - Çaldağ	33,200,000	37,900,000	-
Manisa - Gördes	32,000,000	40,000,000	70-80,000,000
Eskişehir-Yunusemre	10,000,000	86,625,000	231,000,000
Uşak-Banaz	-	11,601,500	30,937,500
Bursa - Yapköydere	-	82,000	81,000
Bitlis - Pancarlı	-	-	15,500

2.2 Nickel Production Methods from Lateritic (oxide) Ores

2.2.1 Pyrometallurgical Processes

Since nickel grade in a typical laterite ore cannot be increased by conventional mineral beneficiation techniques due to existence of nickel in the crystal lattice of different minerals, various alternative methods were devised, and among them pyrometallurgy is the one which utilizes high temperatures to extract nickel by reduction and smelting of the so called ore. Preferentially, high silica and magnesia containing saprolitic profiles of lateritic nickel ores can be processed by pyrometallurgical techniques by either smelting to ferro-nickel product, or smelting to iron/nickel sulphide matte due to good slag forming ability of this type of ores. Within this scope, a simple flow sheet for smelting processes is given in Figure 2.3 and brief details of these two distinct processes will be given in the following sections.
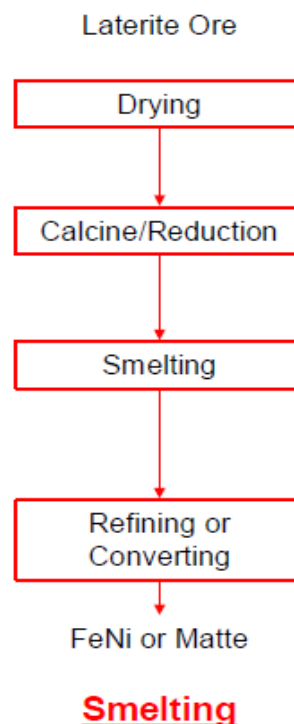
Figure 2.3 Simple flowchart for pyrometallurgical processes.

2.2.1.1 Smelting to Ferro-Nickel

The demand for nickel alloy steels in industry forced the arrival and development of ferro-nickel smelting processes in a number of countries throughout the world. Depending on the availability of energy sources, reducing agents and also energy costs of the operating region, different operating procedures and different furnaces for reduction and smelting were designed. For example, smelting for metal can be achieved in several ways, i.e. in blast furnaces, rotary kilns, and most often, in electric arc furnaces [9]. However in all, the main aim is to form and separate the molten iron/nickel metallic phase from the molten mixture of 'iron oxide-silica-magnesia slag' in order to obtain a crude iron/nickel product.

In industrial practice; generally, first the appropriate nickel ore is dried and calcined, and then the calcination product is exposed to pre-reduction step in solid state at 850-1000 °C in a reducing atmosphere especially coal as being the reductant. In detail; for high carbon ferro-nickel production, the general criterion for the ore is '% Ni to be >2.2% and iron/nickel ratio is to be 5-6'. Similarly, for low carbon ferro-nickel production, the general criterion is '% Ni to be >1.5% and iron/nickel ratio is to be 6-12 together with high silica content' [1]. When the fundamental ore preparation and pre-reduction stages are completed, then smelting operation takes place between 1500-1600 °C in order to form and separate the two distinct liquid phases [15]. Thus, the primary low grade nickel grade ore is enriched and gained an economic value. However, as in the case of production of steel from the blast furnace pig iron, the smelted crude ferro-nickel product contains some impurities like sulphur, carbon, phosphorus, silicon and oxygen. In order to minimize the impurity levels and increase nickel/iron ratio by sacrificing iron, further refining steps may be employed by suitable refining techniques [8], the details of which will not be considered here.

2.1.1.2 Matte Smelting

As in the case of copper production by matte smelting, lateritic (oxide) nickel ores may also be used for the production of nickel by taking the advantage of affinity of nickel to sulphur. In order to exploit this natural tendency of nickel to sulphur, a sulphur bearing material is to be supplied into the furnace charge before smelting. Therefore; as a sulfiding agent, most commonly hydrated calcium sulfate ($CaSO_4.2H_2O$), also called 'gypsum', is added into the furnace charge containing the ore, coke, and limestone. In this process, the ore to be charged into the furnace is preferentially chosen with iron/nickel ratio of >6 and SiO_2/MgO ratio of 1.8-2.2 [1]. As a result of the reduction reactions in the smelting furnace, iron and nickel oxides are reduced gradually, and intentionally added calcium sulfate is reduced to calcium sulfide (CaS). Then, the reduced CaS and iron, nickel oxides react to form an iron-nickel matte and calcium oxide, which then enters into the slag. Finally, at the end of the smelting process, an iron-nickel matte phase and an 'iron-calcium-magnesium-silicate slag' are obtained. After smelting, the resultant matte liberated from the unwanted gangue minerals mainly contains iron, nickel, and sulphur. In order to get rid of the iron present within the matte, smelting product is charged into converters and by blowing with air iron is preferentially oxidized to iron oxide. Then preferentially oxidized iron is collected with the help of silica added into the charge by forming an iron-silicate slag. Converting procedure is continued until all the iron is preferentially removed from the matte. After converting process, mainly nickel and sulphur containing converter product is obtained which is ground and then roasted to nickel oxide in order to eliminate the sulphur within the output. After sulphur elimination by forming nickel oxide from the resultant product, nickel oxide is reduction-melted to its metallic form in electric arc furnaces under a reducing atmosphere and metallic nickel containing little iron, sulphur, and carbon impurities is obtained [8, 9]. Furthermore, this final product may further be refined if required by means of suitable electro-refining techniques, the details of which will not be discussed here.

2.2.2 Caron Process

As an alternative to pyrometallurgical and hydrometallurgical nickel laterite processing, Professor M. H. Caron has combined these two methods and developed a new reduction roast-ammonia ammonium carbonate leaching process in 1920, and he patented his finding in 1924. However, the first commercial production of nickel by this technique was done in 1959 in a plant at Nicaro, Cuba [8, 20].

Due to the very complex nature of lateritic nickel deposits, selectively extracting the nickel from the ore provides a great economic advantage during production. Therefore, selectivity is provided in ammonia-ammonium carbonate leaching process by means of changing the chemical character of the ore prior to leaching. This prior treatment is accomplished by first selectively reducing the nickel to its metallic state in a reducing atmosphere, and then selectively leaching it in an ammoniacal solution. In Figure 2.4, a simple flow sheet for the Caron Process is given in summary:
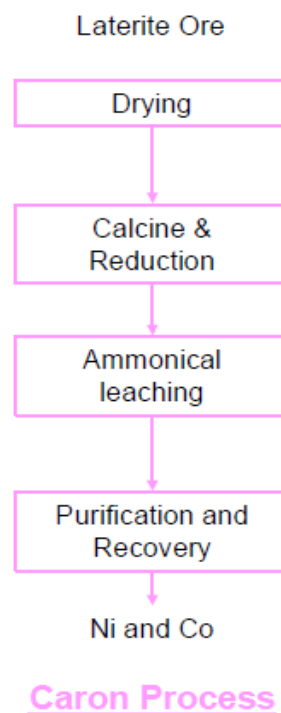
Figure 2.4 Simple flowchart for Caron Process.

During this procedure cobalt is also reduced and selectively leached together with the nickel in the lateritic ore, and they are collected together in the resultant pregnant leach solution as dissolved metal cations. In order to obtain nickel and cobalt present in the ammonia-ammonium carbonate leach liquor, the solution is boiled, and nickel-cobalt is obtained as a basic carbonate precipitate. The basic nickel-cobalt carbonate mixture may then be calcined to a nickel-cobalt oxide product, or can be refined to nickel powder or cathode for further electro-refining purposes [8].

2.2.3 Hydrometallurgical Processes

Environmental concerns and process economics are the main factors that make a metallurgical process to be preferred among other alternatives. When the valuation of lateritic sources is in question, the advent of hydrometallurgical methods as an alternative to pyrometallurgical ones provides lots of advantages over the latter. Since, when a typical lateritic nickel ore is investigated, it is realized that it can hold commonly 25 to 30% of free moisture, although it can contain even 40% or more depending on the topography of the mine site and seasonal weather conditions [21]. In addition to this physically present free moisture, even chemically bonded water may be present in some specific minerals forming the lateritic ore. Because of the high quantity of water present in these lateritic deposits, too much energy is required in order to heat up and evaporate the water during drying and calcining before smelting the ore with pyrometallurgical techniques.

Additionally, due to the huge energy demands during these high temperature processes, lots of environmental concerns also come into question. Since, huge amounts of waste gases give harm to environment during these drying, reducing and smelting processes. Whereas, hydrometallurgical approach through nickel production from lateritic nickel sources at least diminishes these concerns to a certain extent and provides an alternative processing route for nickel laterites. In fact, in common practice normal operation temperatures of hydrometallurgical processes are in the

temperature range of 25-250 ℃ which is very low as compared to the energy intensive pyrometallurgical processes [22].

Finally; the recovery of precious cobalt metal, present in the crystal lattice of some specific minerals similar to nickel, provides extra credit and helps the overall process economics to overweigh towards the hydrometallurgical routes.

According to the above mentioned criteria, atmospheric and high pressure acid leaching processes are the two major process alternatives named under the hydrometallurgical processing techniques, and used widely in the treatment of low-grade metallic ores. In the case of production of nickel from low-grade lateritic nickel ores, technical grade sulphuric acid (H_2SO_4) is the most widespread chemical reagent used both in experimental and production facilities. Therefore; in the following sections, the details of these processes will be discussed only by considering the sulphuric acid leaching case for lateritic nickel deposits in terms of the leaching agent used during the dissolution process.

2.2.3.1 Atmospheric Leaching

Dissolving and getting metallic value of a specific ore into a liquid solution at relatively low temperatures up to 105 °C and at normal atmospheric pressure (1 atm) via the help of either an organic or an inorganic acid is called as atmospheric leaching (AL).

In detail, the general definition of atmospheric leaching leaves its name into several specific processes depending on the type of leaching of the so called ore. These processes are generally called as; in-situ, heap or column in laboratory scale, dump, agitation and vat leaching while normal atmospheric pressure is in question during leaching. Among them, heap and agitation leaching are industrially the most important process types for laterites and it will be more appropriate to only deal with their technical details.

Heap leaching extraction technique for nickel laterites was originally invented and patented primarily by Professor Lina Agatzini-Leonardou in the early 1990's at 'The Laboratory of Metallurgy of the National Technical University of Athens [23, 24]. This novel leaching technique called 'HELLAS' (HEap Leach LAteriteS) is applied and proved to be applicable to low-grade Greek laterites which are similar to the Turkish laterites [25]. Similarly, an invention was patented by Duyvesteyn et al., but then the patent was acquired by Australian mining company BHP Billiton [26]. As an example, European Nickel PLC (Sardes Nickel) has constructed three trial leach pads and a precipitation plant onsite as a pilot plant to test the viability of the project at Çaldağ located in Turkey between 2004 and 2005. In this study more than 75% of the nickel in the laterite heap was extracted into the sulphuric acid leach solution which technically proved the process for the lateritic nickel deposit of Çaldağ [17, 27-29].

Thus, these similar studies have shown that sulphuric acid heap leaching of low-grade, low clay content limonitic nickel laterites in the Balkans and Turkey can be done technically in order to recover the metallic values of the deposit. On the other hand, equatorial laterites having higher clay content are less amenable to heap leach process basically due to higher cost of sulphuric acid consumption [27, 28].

In heap leaching practice of nickel laterites, the ore is crushed and piled up into heaps of several meters in height onto special impermeable membranes, and it is exposed to acidic solution from top of the heap. While the acidic solution percolates down to the bottom of the heap, it intakes the dissolved metallic cations into solution and this solution is then collected in a special pond in order to recover the dissolved nickel and cobalt cations from this pregnant leach solution (PLS). However, the recovery of desired metals, such as nickel and cobalt, from the leach solution is much more complex and problematic. Since, the conditions during heap leaching do not provide selective leaching of nickel and cobalt only; instead, acidic solution also leaches other metals like iron, aluminum, manganese and magnesium from their

minerals, which requires various stages of difficult impurity removal processes mainly by selective precipitation of these impurity elements.

After the solution purification stages mainly by controlling the temperature and pH of the process, finally nickel or nickel and cobalt together are precipitated to a saleable intermediate product. Depending on the precipitate composition or precipitation technique, the intermediate product may be called nickel hydroxide precipitates (NHP), mixed metal hydroxide precipitates (MHP), or mixed sulphide precipitates (MSP). Later, these intermediate products may also be further processed into a final metallic nickel and/or cobalt product by suitable metallurgical techniques.

The second most important atmospheric leaching technique called agitation leaching (AL) primarily aims to decrease the leaching durations by either mechanically or pneumatically agitating the leaching system. In this method, also the feed size of the ore is generally finer than the case as in the heap leaching practice which further increases the leaching kinetics and provides a faster leaching operation. In practice, suitably ground ore is slurried with water and fed to the agitated leaching system and exposed to acidic attack of sulphuric acid which is the most commonly used chemical reagent in case of nickel laterite leaching. In addition to finer feed size and turbulent flow conditions within the leaching system, higher leaching temperatures up to the boiling temperature of water in normal atmospheric pressure may also be applied during leaching which further facilitates the leaching kinetics.

As an illustrative example for the heap and agitation leaching processes of lateritic nickel ores in terms of leaching durations, two different studies conducted by Köse [30], and Büyükakıncı [31] may be a good reference to compare these two processes. According to the conducted studies, 83% of nickel contained in the nontronitic type laterite ore obtained from Gördes/Manisa, could only be extracted into the pregnant leach solution by atmospheric column leaching in 3 months duration [30]. On the other hand, 96% of the nickel present in the same ore could be extracted after 24 hours of leaching with sulphuric acid at 95 °C [31].

In short, several studies have shown that AL may be an alternative processing technique for valuation of low-grade lateritic nickel and cobalt ores. However, as mentioned above, the lateritic ore to be sulphuric acid treatable should satisfy some specific prerequisites for the process to be economically and technically viable. First of all high acid consuming aluminum, magnesium and clay content of the ore should preferably be low in terms of both sulphuric acid consumption and also subsequent removal of these undesired cations from the pregnant leach solution. In fact, the presence of these elements contaminates and deteriorates the solution quality as a result of useless acid consumption. Finally, ore piled into heaps should permit the acidic leach solution to percolate down to the bottom of the heap. Otherwise, the process will be out of operation in a short time.

2.2.3.2 High Pressure Acid Leaching

Throughout the valuation of lateritic nickel deposits as alternative nickel sources, technology and processing techniques were also developed parallel to the needs of the industry and customers. While examining the previous hydrometallurgical extraction techniques, atmospheric leaching, it was pointed out that although they emerged by claiming various benefits over pyrometallurgical techniques, they have still some shortcomings waiting to be solved urgently.

At this point; high pressure acid leaching of the lateritic nickel sources instead of normal atmospheric leaching process came on the scene by proposing more selective leaching and faster leaching kinetics.

When the industrial development of PAL process is considered together with the technical details of the process, the first commercial PAL plant was built at Moa Bay located in Cuba by 'The U. S. Freeport Minerals Company' in 1959 [32]. For a long time period, Moa Bay PAL facility remained the only commercial plant in the world. In Moa laterite process, leaching under high temperature and pressure is carried out in vertical acid resistant lead and brick lined reaction vessels called 'pachuca tanks'.

However, in 1998 a new era started in PAL technology by the construction of three Western Australian PAL plants since Moa Bay. These plants were designed to carry out leaching in modern, horizontal titanium lined reactors called autoclaves rather than vertically placed pachuca tanks as in the case of Moa. The construction of three PAL plants in Western Australia with improved processing techniques encouraged several new PAL projects to be initiated throughout the world. Among them; Ravensthorpe (Western Australia), Coral Bay (Philippines), Taganito (Philippines), Verhelmo (Brazil), Weda Bay (Indonesia), Ambatovy (Madagascar), Goro (New Caledonia), Ramu (Papua New Guinea), Gladson Pacific (Queensland), and finally META-Gördes Project (Turkey) may be given as important PAL projects throughout the world in order to show the future trends of nickel supply from PAL plants and projects [33].

In the application of PAL process in industrial practice, especially, high iron and low magnesium containing limonitic part of a typical lateritic ore is preferred and treated with sulphuric acid for 60 to 90 minutes in a titanium autoclave under a temperature and pressure range of 240-270 °C, and 35-55 atm, respectively. In some cases, depending on the state of the ore mineralogy, proper amounts of limonitic and saprolitic ore blends may also be mixed and used as the feed material for the autoclave. Since, saprolite zone of the deposit contains higher nickel despite consuming more acid due to high magnesium content, by means of proper blending the nickel yield of the process can be upgraded with acceptable extra acid consumption. Therefore; depending on the state of the feed material to be whether limonitic or limonitic/saprolitic mixture, 0.2 to 0.5 acid to ore weight ratios are used during leaching these ores under high temperature and high pressure conditions [3].

In Figure 2.5, a simple PAL operation is illustrated schematically. In this figure, only the important steps in extracting the nickel and cobalt value into acidic leach solution have been exemplified and the downstream processing has not been specified in detail. According to the scheme, PAL feed is slurried to a solids concentration of around 40 to 45% before preheating. However, this ratio is too much dependent on

the rheological characteristics of the ore to be fed into the leaching system. For example, the presence of nontronitic ore in the limonitic sample may limit the slurry concentration to 25-30% due to its hydrophilic nature [15]. Therefore, the rheology of the laterite ore is very important in PAL processing. After suitably adjusting the slurry concentration of the ore, the feed is preheated before exposing to pressure leaching. Finally, preheated slurry is fed into the autoclave and the ore is leached under high temperature and pressure in order to dissolve nickel and cobalt with minimum impurity concentration in the pregnant leach solution.
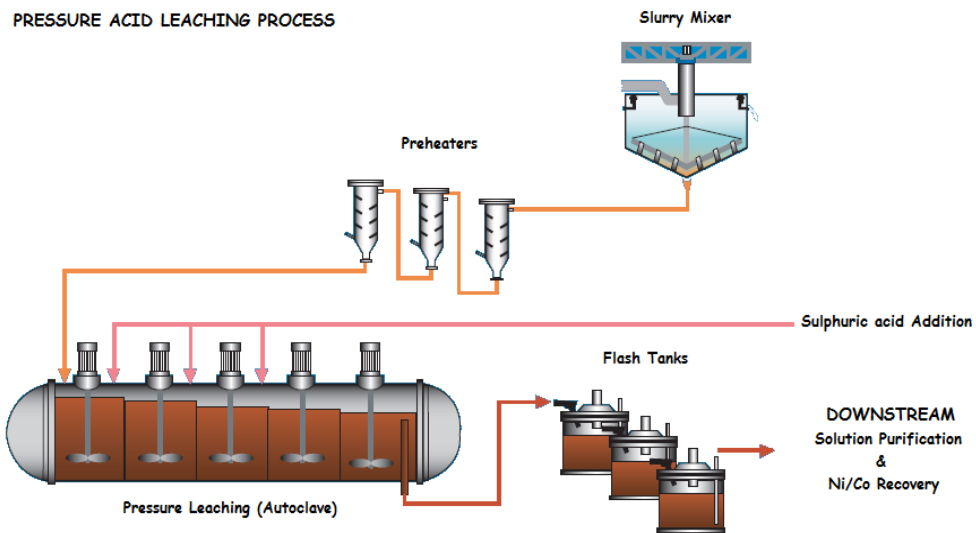
Figure 2.5 Schematic representation of a simple PAL operation [34].

The advantage of the pressure leach process over atmospheric leaching is that iron and to a certain extent aluminum, by dissolving first and then reprecipitating (thermal hydrolysis) at higher temperatures, provide selectivity and low acid consumption for nickel and cobalt to be extracted into the leach solution. To be more specific, Chou et al. stated that as a result of thermal hydrolysis of iron and aluminum cations, Ni/(Fe+Al) ratio in the pregnant leach solution rises from 0.03-0.04 to 3-4 resulting nearly 100-150 times increase in the liquor nickel concentration with respect to total

iron and aluminum impurity concentration which provides a significant simplicity during the following downstream processes [35]. Similarly, Georgiou and Papangelakis reported that by increasing the temperature of the process from 230 °C to 270 °C, the above mentioned ratio increases after 1 hour of leaching due to increase of the iron and aluminum precipitation rates as hematite and alunite, respectively [36].

2.2.3.2.1 Chemistry of High Pressure Acid Leaching

Sulphuric acid is a polyprotic acid and its ionization in aqueous solutions may be expressed according to the following chemical reactions:

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^- \tag{2.1}$$

$$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-} \tag{2.2}$$
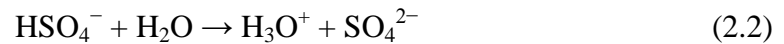
For the minerals to be dissolved by acids, a specific hydrogen ion activity should be maintained in the solution. At ambient conditions hydration reaction of sulphuric acid is thermodynamically favorable and reaction rapidly goes into completion. Therefore, stepwise dissociation of this polyprotic acid may be ignored. However, for temperatures in excess of 150 °C, the rate of the second dissociation reaction decreases seriously and sulphuric acid behaves as a monoprotic acid [37]. Therefore, at higher temperatures an excess amount of sulphuric acid calculated from the stoichiometry of full dissociation should be supplied to provide the specific hydrogen ion activity for the dissolution reactions of lateritic minerals. In the following parts, the details of dissolution and precipitation reactions of the common minerals with sulphuric acid will be discussed and explained.

Chemistry of Iron:

As explained in the previous sections, the presence of iron in a typical laterite ore is associated with mainly goethite, hematite or nontronite minerals. When the literature is examined, the illustration of iron chemistry is limited to mainly accounting for the chemical reactions between sulphuric acid and goethite due to similar reactions with other iron minerals. Therefore, only goethite dissolution reaction has been presented here to provide coherence with the data on literature for iron chemistry.

Specifically, nickel within goethite (FeOOH), is basically locked in the crystal structure of the mineral, thus first the crystal lattice of the goethite should be decomposed by the action of acid and then consumed acid should be regenerated for process economics after liberation of the nickel within the lattice. Iron dissolution reaction and corresponding nickel liberation for the mineral goethite can be represented as:

$$2 \text{ FeOOH} + 3 \text{ H}_2\text{SO}_4 \rightarrow 2 \text{ Fe}^{3+} + 3 \text{ SO}_4^{2-} + 4 \text{ H}_2\text{O} \qquad (2.3)$$
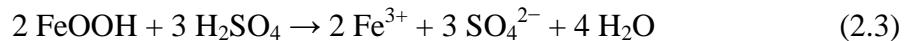
As shown in Reaction 2.3, trivalent iron cation is rapidly solubilized into the acidic solution. Similarly, as proposed by Rubisov et al., divalent iron cation may also be present in the leach solution stemming mostly from the iron present in the mineral serpentine in the following mineral formula $(\text{Fe,Mg})_3\text{Si}_2\text{O}_5(\text{OH})_4$. In this solid solution, Fe^{2+} substitutes for Mg^{2+} in serpentine due to their similar ionic radii. After the dissolution of serpentine, most of the Fe^{2+} in the solution is oxidized to Fe^{3+} due to the prevailing conditions of the reactor [38]. Therefore, generally Fe^{3+} is the dominant oxidation state of iron after the acidic attack. In addition to dissolution reactions, thermally induced iron precipitation reactions come into the picture followed closely after goethite dissolution [39]. According to the data on literature, two different iron precipitation mechanisms were proposed at high temperatures (at least 150 °C) depending on the predominant conditions of the reaction enclosure.

The first mechanism suggests that hematite is directly precipitated from trivalent iron without any extra step as shown in Reaction 2.4:

$$2\ Fe^{3+} + 3\ SO_4^{2-} + 3\ H_2O \rightarrow Fe_2O_3 + 3\ H_2SO_4 \qquad (2.4)$$
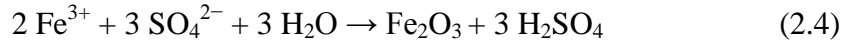
When the iron dissolution and precipitation reaction is examined together, it is realized that the sulphuric acid consumed in the dissolution reaction completely regenerated during the precipitation reaction. Thus, net acid consumption for nickel liberation within the goethite lattice by destructing the crystal lattice and forming stable new iron hematite phase is nil.

However, at higher acid concentrations, iron precipitation mechanism is much more complex. Chou et al. stated that basic ferric sulphate ($FeOHSO_4$) is the first product of trivalent iron precipitation prior to hematite formation when acidity is high [35]. Then, if sufficient time is given or intentionally hematite seed crystals are added in order to accelerate the transformation by eliminating the need for nucleation prior to precipitation, the basic ferric sulphate is hydrolyzed to hematite according to the following chemical reactions:

$$2\ Fe^{3+} + 2\ SO_4^{2-} + 2\ H_2O \rightarrow 2\ FeOHSO_4(s) + 2\ H^+ \qquad (2.5)$$

$$2\ FeOHSO_4 + H_2O \rightarrow Fe_2O_3\ (s) + 2\ SO_4^{2-} + 4\ H^+ \qquad (2.6)$$
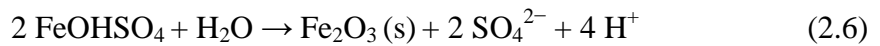
Additionally, some researchers have concentrated on the rate of dissolution-transformation reactions separately, and investigated the effect of E_h on the dissolution or re-precipitation reactions. In their study, Tindall and Muir adjusted the E_h of the solution by adding ferrous ions and they have reported a strong relationship between the E_h of the solution and rate of the iron transformation reactions. According to them, at lower potentials, in the presence of Fe^{2+}, goethite dissolution is faster than hematite precipitation [40].

In short; during pressure acid leaching process, the net reaction for iron transformation reactions can be summarized as $FeSO_4OH$ being the reaction intermediate as given in Reaction 2.7.

$$2 \text{ FeOOH} + 6H^+ \rightarrow 2Fe^{3+} + 4H_2O \rightarrow [FeSO_4OH] \rightarrow Fe_2O_3 + H_2O + 6 H^+ \quad (2.7)$$

And it can be concluded that the concentration of dissolved iron species in the pregnant leach liquor is mainly dependent upon temperature, acidity and E_h of the solution. Therefore, for iron control in the solution, these parameters should be optimized properly.

Chemistry of Aluminum:

Presence of aluminum in a typical ferruginous laterite ore was reported to be associated with some common minerals, namely; gibbsite ($Al(OH)_3$), boehmite ($AlOOH$), and solid solution of aluminum within goethite matrix ($Al_xFe_{1-x}OOH$), respectively [41, 42]. Among them gibbsite is the most common aluminum bearing mineral in the lateritic deposits and, Georgiou and Papangelakis state that it transforms into boehmite during slurry heating at temperatures of 135-155 °C according to Reaction 2.8 [36, 43].

$$Al(OH)_3 \rightarrow AlOOH + H_2O \quad (2.8)$$

Therefore, the dissolution reaction of aluminum bearing minerals in sulphuric acid media is generally represented by Reaction 2.9.

$$AlOOH + 3 H^+ \rightarrow Al^{3+} + 2 H_2O \quad (2.9)$$
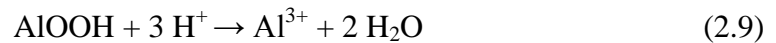
After aluminum is dissolved in the acidic leach solution, it also hydrolyzes and regenerates acid by aluminum precipitation reactions similar to iron. Unlike iron precipitation, aluminum hydrolyzes more slowly and product of the hydrolysis reactions is very sensitive to the ambient conditions. Chou et al. proposed that below

250 ℃, the dominant hydrate form is aluminum 3·4·9 hydrate as given in Reaction 2.10, whereas at temperatures above 280 ℃ tendency of aluminum hydrate precipitate leans to on behalf of aluminum 1·2·1 hydrate product according to Reaction 2.11. Moreover, in addition to higher temperatures above 280 ℃, higher acidity also increases the quantity of 1·2·1 hydrate which causes more acid to bound and lost in the aluminum sulphate precipitate [35].

$$6\ Al^{3+} + 4\ SO_4^{2-} + 14\ H_2O \rightarrow 3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O + 10\ H^+ \qquad (2.10)$$

$$2\ Al^{3+} + 2\ SO_4^{2-} + 2\ H_2O \rightarrow Al_2O_3 \cdot 2SO_3 \cdot H_2O + 2\ H^+ \qquad (2.11)$$
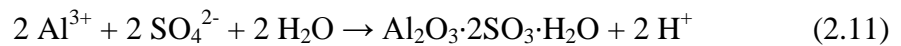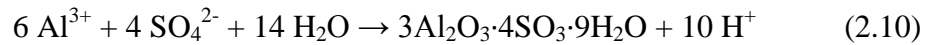
Besides temperature and acidity, quality of process water is also very important for the type of the solid aluminum residue. For example, experience from Bulong PAL plant shows that the presence of sodium cations of saline process water in the plant affects the aluminum precipitation reactions significantly and changes the reaction product towards the formation of sodium jarosite according to Reaction 2.12 [44].

$$6\ Al^{3+} + 9\ SO_4^{2-} + 12\ H_2O + 2\ NaCl \rightarrow 2\ NaAl_3(SO_4)_2(OH)_6 + 2\ HCl + 5\ H_2SO_4$$
$$(2.12)$$
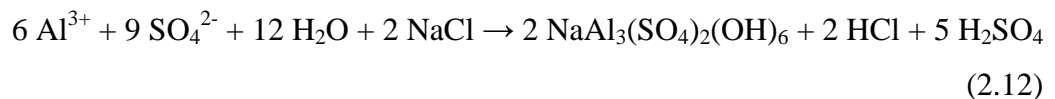
In short; temperature, acidity and water quality (presence of Na cations) are the most important factors effecting the final aluminum concentration and type of residue after the precipitation reactions. Finally; although aluminum precipitation reactions release some portion of the consumed acid into the solution, yet aluminum is still a net acid consumer unlike iron in pressure acid leach process.

Chemistry of Magnesium:

In terms of acid consumption, magnesium content of a lateritic deposit is one of the most important factors during pressure acid leaching. In fact, acid consumed during magnesium dissolution is not regenerated as in the case of iron and aluminum. For limonitic and saprolitic ores, magnesium content of the ore generally changes

between 1 wt. % and 10-20 wt. %, respectively [38]. For these type of ores, it is indicated that typically 50-60% of the magnesium content of the ore is easily extracted into solution as in the form of soluble magnesium sulphates [15]. However, it is also indicated that various extraction results ranging from 40 to 90% magnesium extraction was observed and reported from different industrial PAL plants. Dissolution chemistry of magnesium by sulphuric acid is given in the following chemical reaction:

$$Mg_3Si_2O_5(OH)_4(s) + 6\ H^+ \rightarrow 3\ Mg^{2+} + 2\ SiO_2(s) + 5\ H_2O \qquad (2.13)$$
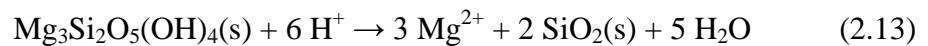
In some special cases when the magnesium concentration is very high in the pregnant leach solution, specifically more than 12 gpl, it is also reported that precipitation of magnesium mono-hydrate sulphate may occur in leaching limonitic/saprolitic blends which causes a different mode of acid consumption [38].

Chemistry of Manganese:

Manganese in lateritic ores is mainly associated with the minerals of lithiophorite $(Al,Li)MnO_2(OH)_2$ or asbolane $(Co,Ni)_{1-y}(MnO_2)_{2-x}(OH)_{2-2y+2x} \cdot n(H_2O)$ [45]. Among them especially asbolane is a very important mineral in terms of its valuable cobalt content. In terms of leachability, these manganese oxyhydroxide minerals are difficult to leach unless a reducing agent is present in the leaching solution which causes a negative effect upon the extraction of cobalt into the pregnant leach solution. Nevertheless, Tindall and Muir have reported that the presence of ferrous cations in nontronitic type limonites triggers the dissolution of manganese and cobalt upon which high manganese and cobalt extraction values are obtained [46]. Finally; in a typical laterite ore, nearly 50-60% of the manganese present in the ore is dissolved in the leach solution as manganese sulphates [15], and of course this value is very dependent on the type of ore and solution conditions.

Chemistry of Nickel and Cobalt:

As explained in the previous sections, the presence of nickel in a typical laterite ore is either associated with high iron (mainly goethite, hematite or nontronite), or high magnesium containing (serpentine) minerals. Similarly, the quantity of cobalt present in the solution is directly attributed to the dissolution of manganese minerals. Since these two metals do not have any discrete nickel or cobalt minerals, the explanations given for iron, magnesium and manganese chemistry will also be valid for nickel and cobalt chemistry. However, if their hypothetical reactions are to be given, the following simple dissolution reactions are usually assumed in high pressure acid leaching process descriptions as being oxides of the so called metals.

$$NiO_{(s)} + 2\,H^+ \rightarrow Ni^{2+} + H_2O \qquad\qquad (2.14)$$

$$CoO_{(s)} + 2\,H^+ \rightarrow Co^{2+} + H_2O \qquad\qquad (2.15)$$

2.2.3.3 Nickel and Cobalt Recovery from the PLS

Up to now, the explanations given are for the dissolution and taking the metallic values of lateritic ore into solution via sulphuric acid either by atmospheric or pressure acid leaching. These chemical operations are generally termed under the general name of 'upstream processes'.

However; in order to obtain a saleable product, the dissolved nickel and cobalt cations should selectively be recovered from the pregnant leach solution (PLS) after the first step of laterite processing. Therefore, these processes are classified under the general name of 'downstream processes' and generally includes; the excess acid neutralization, solution purification like iron, aluminum, chromium and manganese precipitation, as well as nickel-cobalt acquisition either in the form of an intermediate product or in the form of nickel-cobalt cathodes. These above mentioned tasks may be achieved by several methods namely; Direct Solvent

Extraction (DSX), Ion Exchange (IX), Mixed Sulfide Precipitation (MSP), and Mixed Hydroxide Precipitation (MHP), respectively.

There are several factors contributing to the choice of one method among others such as the method of leaching, impurity concentrations, availability of chemical consumables, economics of the final product market, environmental issues, etc. Among them mixed sulfide precipitation (MSP) is the earliest applied recovery technique in PAL technology and it has been in use since the first PAL plant Moa Bay built in 1959. In addition to Moa, Murrin Murrin which was built in 1999 has also preferred (MSP) method for downstream metal recovery. Besides (MSP) method, Bulong, built in 1999, selected a direct solvent extraction (DSX) approach in which nickel and cobalt are extracted sequentially from the pregnant leach solution. Finally, Cawse PAL plant, built in 1999, preferred mixed hydroxide precipitation (MHP) route which also proved commercially to be viable [47]. Alternatively, according to papers on future trends in PAL projects and recently applied patent applications, it is suggested that ion exchange (IX) methods will also be an alternative option in the near future for the treatment of lateritic leach solutions [47-50].

CHAPTER 3

SAMPLE CHARACTERIZATION, EXPERIMENTAL SET-UP AND PROCEDURE

3.1 Sample Description

In this study, the limonitic and nontronitic nickel laterite ore samples of Gördes/Manisa located in the western part of Turkey were used for high pressure sulphuric acid leaching experiments. The samples were originally obtained from 'META Nikel ve Kobalt A.Ş.' in 2007 for atmospheric leaching experiments by Büyükakıncı for his master thesis study [51].

3.2 Characterization of the Samples

In order to determine the general characteristics of the lateritic samples; physical, chemical and mineralogical characterization steps were performed, respectively.

3.2.1 Physical Characterization

Representative limonitic and nontronitic samples of Gördes were 200 kg and 410 kg, respectively with an as received size of -20 mm. Initially, the bulk and solid density measurements were conducted for each lateritic sample by Büyükakıncı, and the results are given in Table 3.1 [51]. Bulk density measurements were done for both as received laterite ore samples (-20 mm) and calculated according to the ratio of ore

weight to ore volume without joggle. A helium pycnometer was used to determine the solid density of the finely ground (-38 µ) limonitic and nontronitic ore samples. In order to check helium pycnometer density measurements of Büyükakıncı, the same samples were analyzed with a bottle pycnometer method and similar results were obtained. According to the results, the pycnometer density of limonitic and nontronitic samples were measured as 3.26 and 2.65 (g/cm^3), respectively which are very coherent with the results obtained previously. After density measurements, the moisture content determinations of the as received ores were accomplished. For this purpose, the ores were subjected to sampling procedure by 'coning and quartering'. The representative limonitic and nontronitic samples obtained were then weighed and dried in a drying oven at 105 °C until the physically present water was removed by evaporation. Moisture contents of the representative limonitic and nontronitic samples are given in Table 3.2 [51].

Table 3.1 Bulk and solid densities of lateritic samples (g/cm^3)

Representative Ore Sample	Limonite	Nontronite
Bulk Density, Wet ore	1.04	0.93
Solid Density, Dry (-38 µ)	3.26	2.64

Table 3.2 Moisture contents of the representative limonitic and nontronitic samples

Representative Ore Sample	Moisture Content (%)
Limonite	23.47
Nontronite	40.10

According to the moisture content determination results, it is very interesting to note that both samples contained high amounts of physically held water in their structures. So, this suggested that it would be a very energy consuming process just in terms of

moisture content, if the pyrometallurgical processing route was to be selected for the treatment of these lateritic ores.

In order to determine the particle size distribution of the limonitic and nontronitic samples, wet screen analysis method was applied to both samples, respectively. During analysis, a simple screening system consisting of a nine-sieve series vibrated by a shaker was used, and tap water was fed on top of this system continuously in order to help the particles to be distributed in each sieve according to their corresponding particle size. The sieves were selected so that the screen aperture sizes decreased by square root of two by starting from 0.710 mm for the coarsest particles and finally ending at 0.045 mm for the smallest particles. After analysis, each sample that has accumulated on the sieve series was dried overnight at 105 °C and their corresponding weight percentages were calculated. Wet screen analysis results for limonitic and nontronitic samples are given in Tables 3.3 and 3.4, respectively.

Table 3.3 Wet screen analysis result of limonitic sample ground to 100% -850 microns

Size (mm)	Weight (%)	Cumulative wt. (%) Oversize	Cumulative wt. (%) Undersize
+0.710	8.08	8.08	91.92
+0.500	6.05	14.12	85.88
+0.355	5.76	19.90	80.10
+0.250	6.84	26.73	73.27
+0.180	4.94	31.67	68.33
+0.125	5.99	37.65	62.35
+0.090	4.96	42.61	57.39
+0.063	4.70	47.31	52.69
+0.045	3.92	51.23	48.77
-0.045	48.77	-	-
Total	100.00	-	-

Table 3.4 Wet screen analysis result of nontronitic sample ground to 100% -850 microns

Size (mm)	Weight (%)	Cumulative wt. (%) Oversize	Cumulative wt. (%) Undersize
+0.710	5.13	5.13	94.87
+0.500	5.53	10.66	89.34
+0.355	6.48	17.14	82.86
+0.250	6.34	23.47	76.53
+0.180	6.03	29.50	70.50
+0.125	6.17	35.67	64.33
+0.090	5.52	41.18	58.82
+0.063	5.24	46.42	53.58
+0.045	4.68	51.09	48.91
-0.045	48.91	-	-
Total	100.00	-	-

3.2.2 Chemical Characterization

For the complete chemical analysis of both limonitic and nontronitic samples, each sample was dried and ground to 100% -38μ and they were analyzed chemically by Inductively Coupled Plasma (ICP) method. The (ICP) results were obtained from ALS Analytical Chemistry and Testing Services in Canada and the corresponding results are presented in Table 3.5.

The most striking result obtained from the chemical and wet screen analysis experiments is that largest fraction of the particles had a size smaller than 0.045 mm. For the limonitic sample 48.77% and for the nontronitic sample 48.91% of the particles were under the size of 0.045 mm. Similar results were obtained in a study conducted by Büyükakıncı for the same ore samples. Büyükakıncı reported that 40-49% of the samples were under the particle size of 0.038 mm, and finer fractions of both samples contained more nickel and cobalt with respect to coarser particles [51]. Another study conducted by Göveli with Gördes limonitic ore, showed that 65.19% of the limonitic sample was under 0.074 mm, and 73.00% of the nickel and 68.28% of the cobalt was distributed in this size fraction [52]. These three studies verified

that both samples contained significant amounts of fine particles and most of the nickel and cobalt were present in the finer size fractions.

Table 3.5 Chemical analysis of limonitic and nontronitic samples

Element/Compound Wt. (%)	Nontronite	Limonite
Fe	15.95	28.70
Ni	1.20	1.28
Co	0.044	0.083
Cr_2O_3	0.99	1.99
MnO	0.34	0.59
As	0.020	0.680
Al_2O_3	4.17	5.83
SiO_2	44.9	28.8
MgO	6.91	2.26
CaO	2.15	1.27
K_2O	<0.122	0.120
TiO_2	0.08	0.13
CuO	0.009	0.039
ZnO	0.025	0.037
PbO	<0.010	<0.011
P_2O_5	0.050	<0.020
S	<0.01	0.43
Loss of Ignition	8.81	8.45

3.2.3 Mineralogical Characterization

In order to determine the type of minerals present in the ore samples, Rigaku D/MAX2200/PC model X-ray Diffractometer with a Cu-Kα X-ray tube working under 40 kV and 40 mA was used during analysis of the limonitic and nontronitic samples. The graphical results of XRD analysis are given in Figures 3.1 and 3.2, respectively.
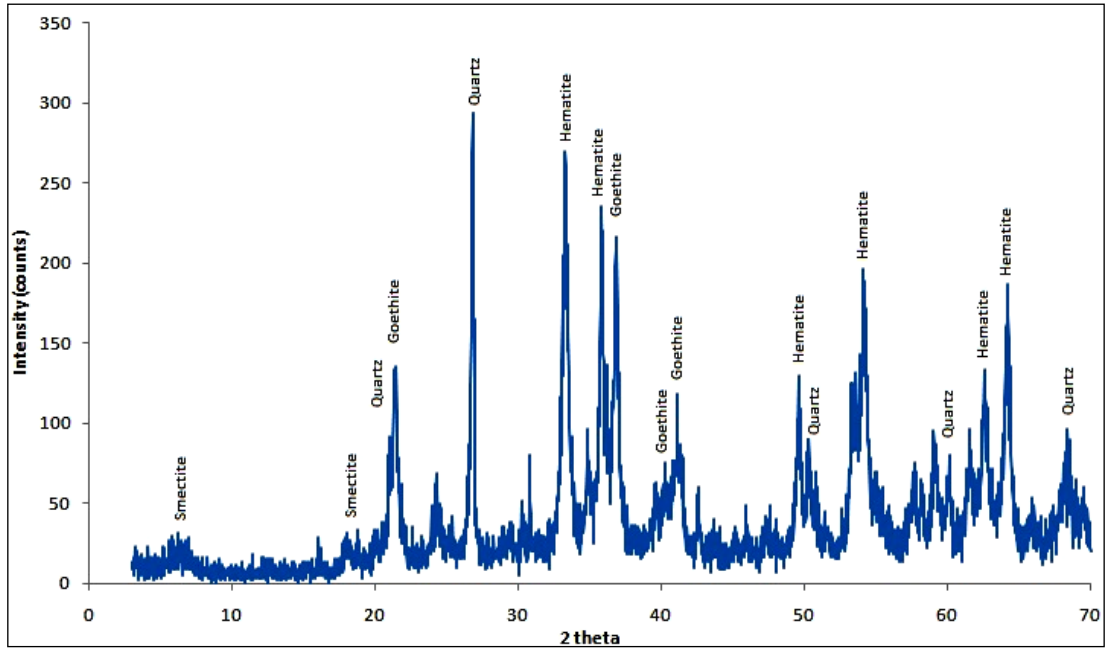
Figure 3.1 XRD pattern of limonitic sample
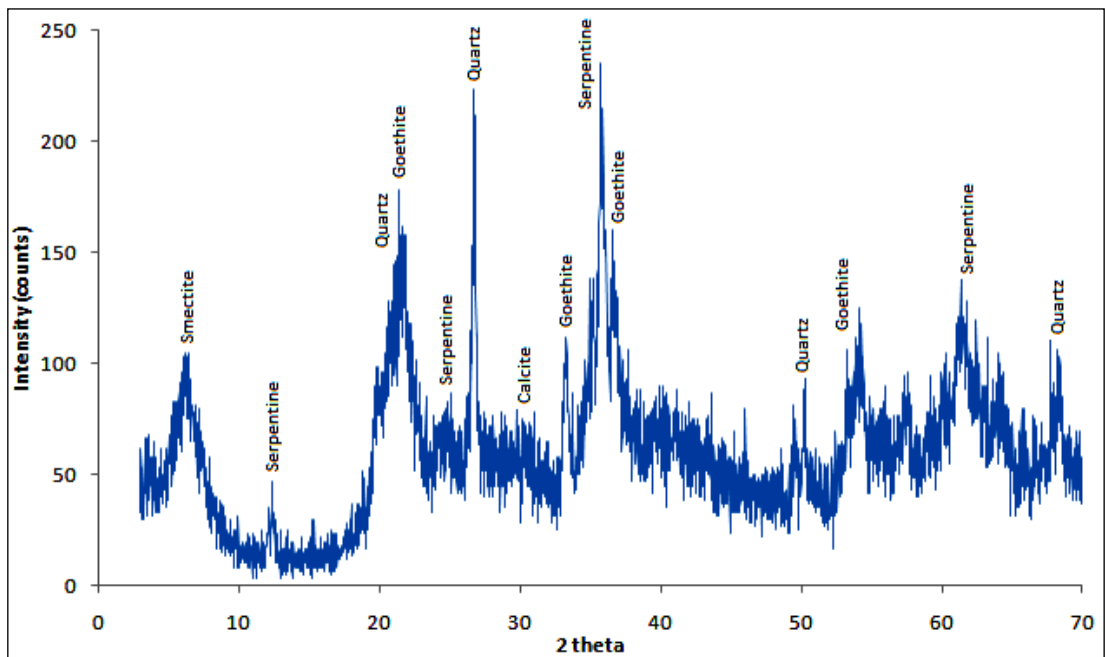
Figure 3.2 XRD pattern of nontronitic sample

By combining the chemical and XRD analysis results for the limonitic sample, it was found that the limonitic sample contained high amounts of quartz (SiO_2), hematite (Fe_2O_3), and goethite (FeOOH) minerals as well as the mineral smectite ($Na_{0.3}Fe_2(Si,Al)_4O_{10}(OH)_2.nH_2O$) as seen in Figure 3.1. Meanwhile, some of the relatively smaller peaks could not be identified.

The same procedure for nontronitic sample has indicated that this sample consisted of high amounts of serpentine ($(Mg,Fe)_3Si_2O_5(OH)_4$), quartz (SiO_2), goethite (FeOOH) and smectite ($Na_{0.3}Fe_2(Si,Al)_4O_{10}(OH)_2.nH_2O$) as well as calcite ($CaCO_3$), as shown in Figure 3.2.

In order to verify the previous analyses, SEM (Scanning Electron Microscopy) studies on both samples by the help of Nova Nanosem 430 in the Department of Metallurgical and Materials Engineering at METU indicated that nickel was mainly present in the crystal lattices of the minerals goethite (FeOOH), hematite (Fe_2O_3), serpentine ($(Mg, Fe)_3Si_2O_5(OH)_4$) and smectite ($Na_{0.3}Fe_2(Si,Al)_4O_{10}(OH)_2.nH_2O$). On the other hand, cobalt was mainly present in the crystal structure of the mineral asbolane $(Co,Ni)_{1-y}(Mn^{4+}O_2)_{2-x}(OH)_{2-2y+2x}.H_2O$. The same results, obtained by a JEOL JSM-6400 scanning electron microscope, were also reported by Büyükakıncı in his master thesis study [51]. Therefore, up to now chemical and mineralogical analysis results seem to be consistent with the ones indicated in the literature.

Investigation of the thermal behavior of the minerals present in both samples was the last step in the mineralogical characterization study. For this purpose, ore samples were dried and ground to 100% -38μ and subjected to Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA) 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 [51].
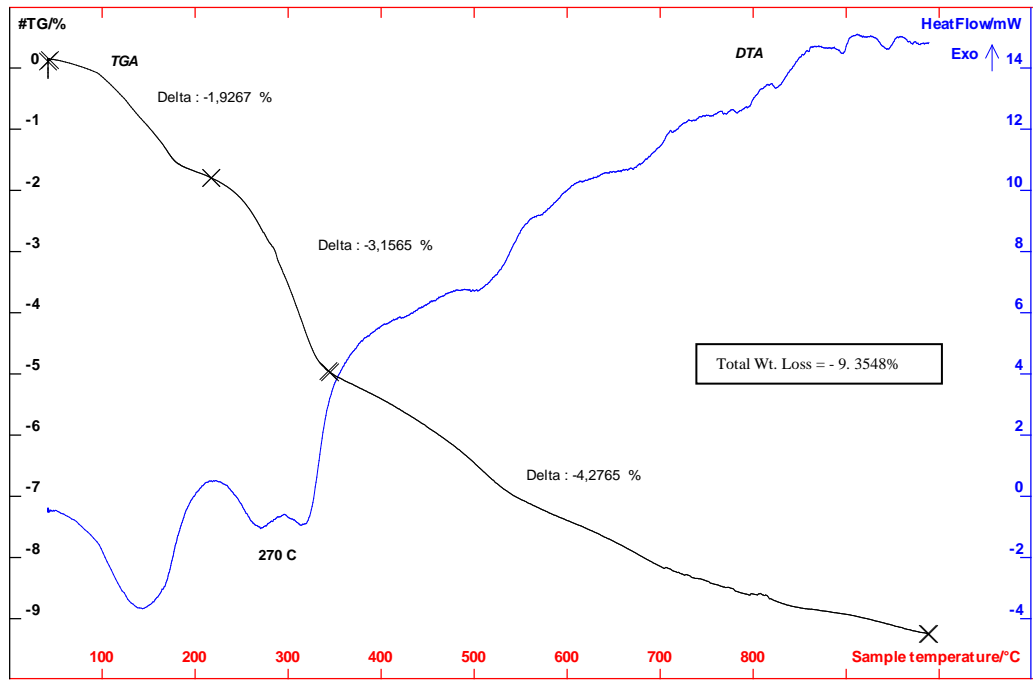
Figure 3.3 DTA/TGA analysis result of limonitic sample
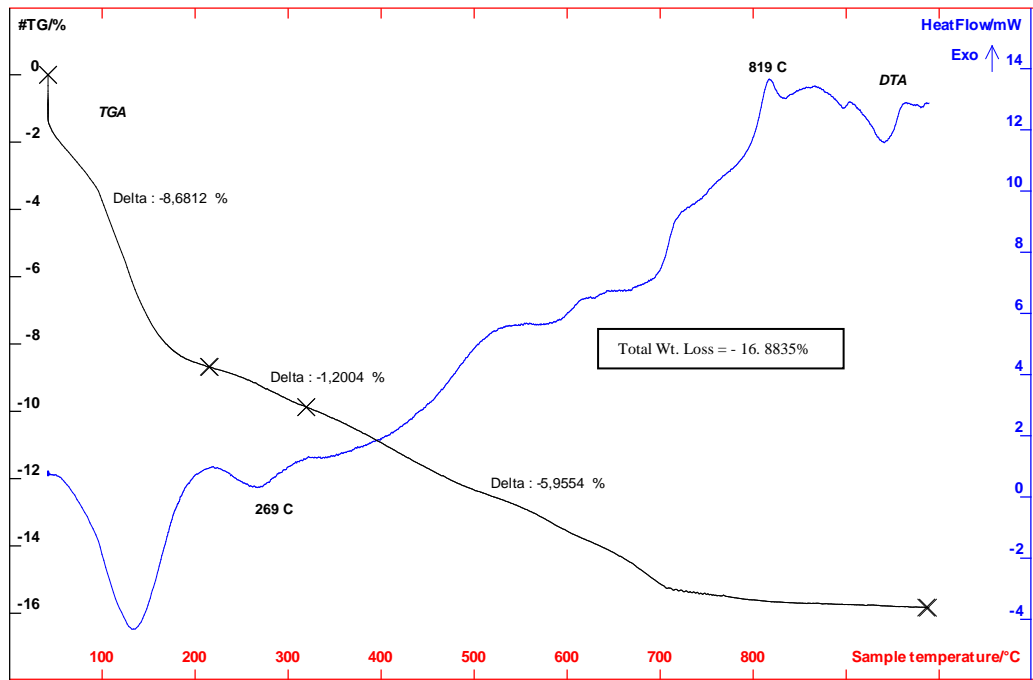
Figure 3.4 DTA/TGA analysis result of nontronitic sample

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When the DTA/TGA analysis results of the limonitic sample were examined in detail, between 100-150 °C there was an endothermic peak corresponding to the removal of both surface and bulk water content of the sample. Similarly, an endothermic peak was observed between 250-280 °C which indicated that goethite underwent a transformation reaction by losing its chemically bound water content according to the following dehydration reaction:

$$FeO(OH).xH_2O \rightarrow FeO(OH) + xH_2O \text{ (Dehydration)} \qquad (3.1)$$

The very close endothermic peak after dehydration reaction between 320-325 °C showed that goethite further transformed to hematite according to the following dehydroxylation reaction:

$$2 FeO(OH) \rightarrow Fe_2O_3 + H_2O \text{ (Dehydroxylation)} \qquad (3.2)$$

Between temperature ranges of 535-545 °C, the small endothermic peak suggested the allotropic transformation of quartz (SiO_2). Furthermore, it is reported that there might be an exothermic peak at around 550 °C for γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ transformation, but it was not obvious in this sample. Moreover, it has been proposed that at around 680 °C an endothermic peak might be observed for α-Fe_2O_3 due to change in magnetic properties of α-Fe_2O_3, but still the analysis result was insufficient to derive this conclusion [53].

When a similar detailed examination was applied to the DTA/TGA analysis results of the nontronitic sample, it was observed that the endothermic peak between 100-150 °C corresponded to the removal of both surface and bulk water content of the nontronitic sample. The next endothermic peak observed in the plot could be attributed to the dehydroxylation reaction of goethite in the nontronitic sample as shown in Reaction 3.2. At around 600 °C, the transformation of quartz (SiO_2) and dehydroxylation of serpentine have been reported [53]. It was also stated that dehydroxylation peak of serpentine is strongly dependent upon the chemical

composition. Therefore, the small endothermic peak at around 550 °C might be attributed to the combined effect of quartz and serpentine together. Finally, it was reported in the thermal analysis reference handbooks that the exothermic peak observed at around 820 °C has belonged to serpentine ($Mg_3Si_2O_5(OH)_4$) forsterite (Mg_2SiO_4) phase transformation according to the chemical reaction given in Reaction 3.3 [53-55]:

$$2\ Mg_3Si_2O_5(OH)_4 \rightarrow 3\ Mg_2SiO_4 + SiO_2 + 4\ H_2O \tag{3.3}$$
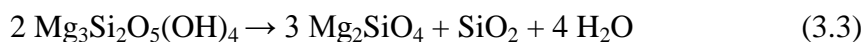
3.3 Experimental Procedure

High pressure acid leaching experiments were conducted in a Parr-4532 model, 2 liter, titanium grade-4 autoclave which was equipped with automatic heating and cooling units, and magnetically driven stirring system. A representative picture of the reactor is given in Figure 3.5.

Figure 3.5 Titanium autoclave and its parts

In order to determine the optimum working conditions, the response of limonitic laterite sample was tested with the following experimental parameters. For the nontronitic laterite sample only the effect of acid amount was investigated.

- Leaching temperature,
- Leaching duration,
- Sulphuric acid/Ore ratio,
- Particle size,
- Heat treatment prior to leaching,
- HCl addition,
- Na_2SO_4 addition,
- $FeSO_4$ addition,
- Cu_2O (Cu^+) addition,
- S addition.

To test the samples, first a slurry of limonitic or nontronitic ore was formed with deionized water according to the predetermined solid/liquid ratio. After the slurry was formed in the autoclave, technical grade sulphuric acid (96-98 wt. %) was added on top of the slurry and the lid of the autoclave was closed carefully in order to prevent any leakage during high pressure leaching operation. At this point, any chemical reagent of high purity to test its effect upon leaching was also added before sealing the autoclave and the system was allowed to heat up to the desired set-point temperature. The start of the reaction defined as zero time was determined when the reactor temperature reached to the set-point and the reaction was left to proceed until the target leaching duration was attained. After the intended leaching duration was completed, the system was allowed to cool down to room temperature approximately in 1 hour by means of water flowing through a titanium cooling coil. In order to perform solid/liquid separation after leaching, the resultant slurry was filtered by the aid of a vacuum pump and Whatman grade-40 filter paper placed on a Buchner funnel. After getting the pregnant leach solution loaded with leached metal cations,

the solid that remained in the Buchner funnel was washed well in order to remove the pregnant leach solution completely. Then, the resultant leach residue was dried overnight at 105 °C in a drying oven for chemical analysis. Leach residues were analyzed chemically with a Niton X-Met 820 X-ray Fluorescence (XRF) analyzer and by Atomic Absorption Spectroscopy (AAS) of META Nikel ve Kobalt A.Ş. Similarly, chemical analyses of the pregnant leach solutions were performed via AAS method in the Chemical Engineering Department of METU. Meanwhile, the resultant pregnant leach solutions were also analyzed for residual acid. Reduction potential or oxidation-reduction potential (ORP) and density measurements were also performed.

During residual free acid determinations, 0.2 molar sodium hydroxide (NaOH) solution was used in order to neutralize the free acid which remained in the pregnant leach solution. In order to suppress the interfering effect of some ions during titration, 280 g/L di-potassium oxalate monohydrate ($K_2C_2O_4.H_2O$) solution was used as a cheating agent during the titration. At the same time pH meter was calibrated to pH 7.0 level by special buffer solutions. The experimentally used titration procedure was as follows; 20 cc of 280 g/L di-potassium oxalate monohydrate solution was diluted with 5 cc of deionized water and the pH of this mixture was measured with pre-calibrated pH meter. Then, 5 cc of pregnant leach solution was added into this mixture and the solution was left to become homogenized by the help of a magnetic stirrer. Finally, this solution was titrated with 0.2 molar sodium hydroxide solution up to the initial pH level. Then, from the amount of sodium hydroxide consumed, residual acid in the pregnant leach solution was determined.

For reduction potential measurements, a Pt-Ag/AgCl electrode (saturated with KCl) was used and measured values were reported according to the Pt-Ag/AgCl reference electrode throughout the presentation of experimental results. If required, the measured values may also be converted into the Standard Hydrogen Electrode (SHE) potential values by the addition of 198 mV.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Pressure Acid Leaching of Nontronitic Sample

Industrial experience and experimental studies suggest that nontronitic type nickel laterite ores are more amenable to sulphuric acid pressure leaching than the limonitic type laterite ore samples. In a paper about the effect of ore type, Whittington et al. verified that finding by comparing the saprolitic, limonitic and nontronitic laterite samples [56]. In the mentioned study; it was stated that serpentine, goethite, and nontronite were the primary nickel bearing minerals in these lateritic ores, respectively. And, rapid nickel extraction from nontronitic samples was suggested to arise from ion exchange of nickel from nontronite, or the presence of rapidly leached, nickel-rich mineral within the nontronitic sample [56]. While keeping this fact in mind; according to the reserve estimation (drilling) studies on the Manisa/Gördes mine site, it was stated that the nontronitic type nickel reserve of Manisa/Gördes deposit comprises only ~30% of the total lateritic formation and the rest is limonitic. Therefore, the pressure acid leaching experiments were decided to be initiated with the easily leachable nontronitic sample.

As a starting point, the operation temperature of Australian Murrin Murrin pressure leaching plant, processing mainly nontronitic type laterite ore was selected as a reference point. In each experiment 150 grams of dry nontronitic laterite sample ground to a particle size of 100% -850 μ was tested with different sulphuric acid additions the amount of which was predicted by a simple stoichiometric calculation

given in Appendix-A based on the chemical analysis result of the nontronitic sample. In Table 4.1, the other parameters kept constant during pressure acid leaching are listed. The results obtained with the addition of different amounts of sulphuric acid per ton of dry nontronitic ore are given in Figure 4.1.

Table 4.1 Pressure acid leach parameters of nontronitic sample

Ore Type:	Nontronite
Leaching Temperature (°C)	255°C
Leaching Duration (min.)	60 min.
Acid/Ore Ratio (wt./wt.)	0.400, 0.425, 0.450, respectively.
Particle Size (µ)	100% -850 µ
Solid/Liquid Ratio (wt./wt.)	0.30 (Excluding the acid amount)
Stirring Speed (rpm)	400 rpm
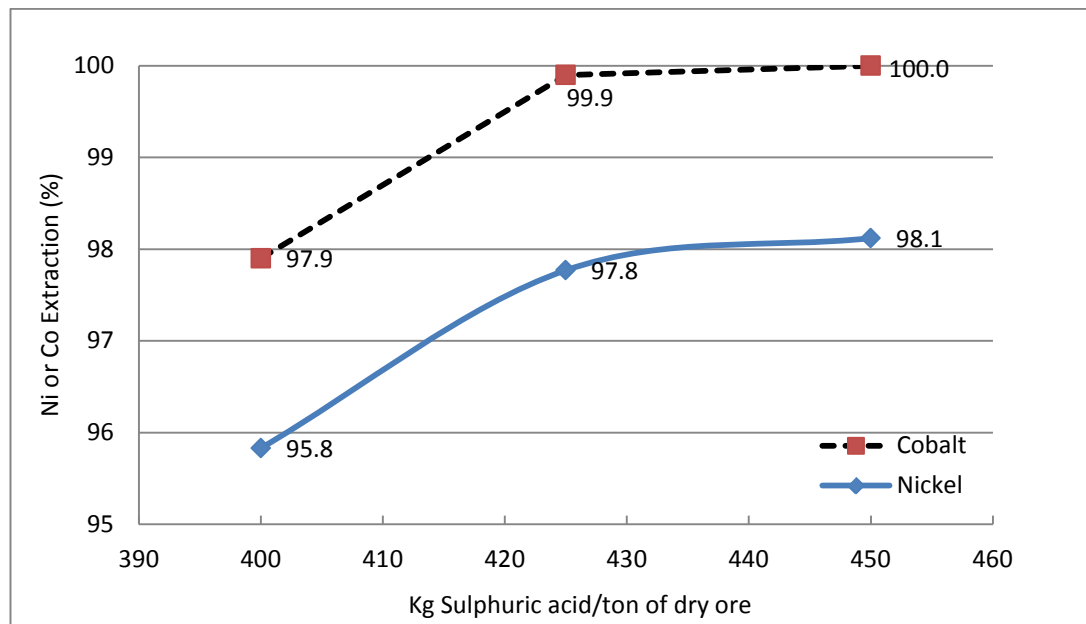
Figure 4.1 Effect of sulphuric acid concentration on nickel and cobalt extractions of nontronitic sample

According to the pressure leach extraction results of nontronitic sample, it is clearly seen that almost all of the nickel and cobalt present in this lateritic ore were extracted easily into the pregnant leach solution which was in close accordance with the data presented previously in the literature and observed in the industry [15]. Therefore, the pressure acid leaching tests for the nontronitic sample were ended due to its higher extractability and lower ratio (~30% of the deposit) in the entire deposit, and further studies were concentrated on plentiful (~70% of the deposit) and difficult to leach limonitic nickel laterite sample.

4.2 Pressure Acid Leaching of Limonitic Sample

In order to test the reproducibility of the experiments and their corresponding analysis results, three consecutive pressure leach tests were repeated with the same parameters in order to make sure that the experimental results were reliable. The experimental conditions were as follows: 255 °C pressure leaching temperature, 60 minutes of leaching duration with 30% solids and 300 kg acid per ton of dry limonitic laterite ore at a particle size of 100% -850 microns with a stirring speed of 400 rpm using 150 grams of dry limonitic laterite ore in each test. During leaching procedure, the gauge pressure of the autoclave was measured to be 44 bar at 255 °C leaching temperature. Calculation of the starting acid addition amount is given in Appendix-A.

Table 4.2 Nickel and cobalt extraction results of identical tests

Test Number	% Nickel Extraction	% Cobalt Extraction
Test-1	87.5	91.6
Test-2	87.1	86.0
Test-3	87.2	88.7

According to the successive experimental results summarized in Table 4.2, the nickel extraction values were found to be very consistent in terms of solid based nickel recovery calculations given in Appendix-B. In detail, these three tests have a mean value of 87.3%, and a standard deviation of 0.17% for nickel extraction results which may be acceptable within the challenge of experimental activity. As compared to nickel, the cobalt extraction values were found to be less reproducible. The three tests performed had an average cobalt extraction value of 88.8% with a standard deviation of 2.3% from the mean.

When the possible reasons of this variable cobalt extraction values were considered in detail, it seemed that the variations have stemmed from the analytical difficulties during the chemical analysis of cobalt leach residues. Since, an unleached limonite sample contained 0.083% cobalt, and after leaching most of the cobalt was taken into the pregnant leach solution. Therefore, the amount of cobalt that remained in the leach residue became more difficult to detect than nickel which in turn caused the aforementioned variations. As a result of these identical tests, the similar extraction values obtained encouraged further pressure acid leach experiments to be done and evaluation of the prospective experimental results was performed within this confidence interval by keeping this experience in mind throughout the experimental study.

4.2.1 Effect of Leaching Temperature upon Nickel and Cobalt Extractions

After the initial tests, the experiments were decided to be performed with the most important pressure acid leaching design parameter chosen as being the temperature. In order to verify this selection as the most important parameter among the others, Figure 4.2 may be helpful during the decision making process.

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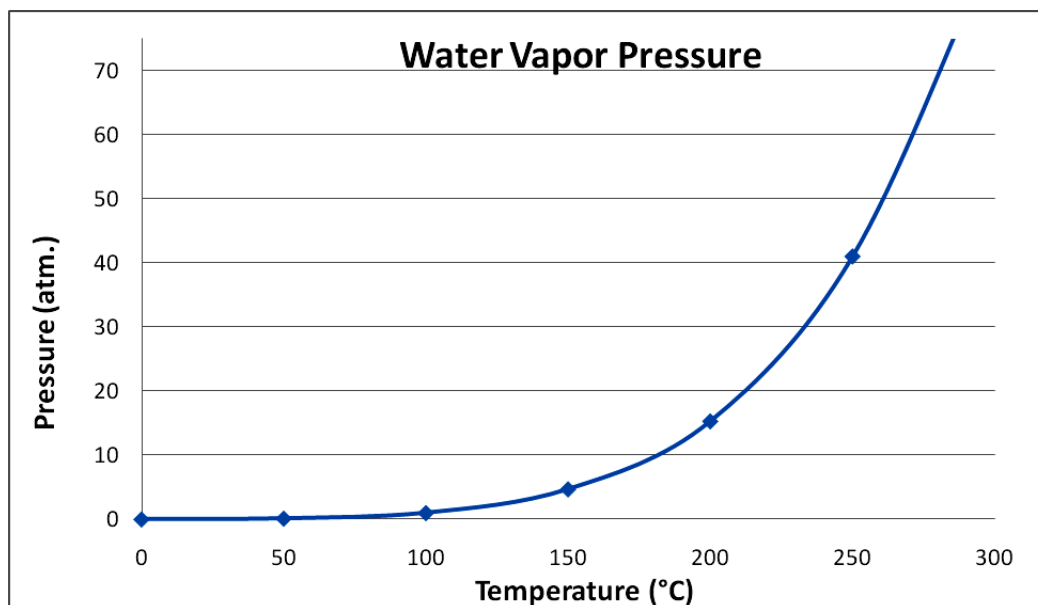
Figure 4.2 Variation in the vapor pressure of water with respect to temperature

As seen from Figure 4.2, the vapor pressure of water increases exponentially especially for temperatures greater than 150 °C which means higher energy requirements for water evaporation and also higher initial equipment costs in order to endure this drastic pressure change. Besides higher initial and operational costs; according to the transmitted reports from industrial experience, working under extreme pressure causes sudden and severe breakdowns during operation and leads to serious problems which increases the overall production costs. Therefore, desired nickel and cobalt extractions during pressure leaching should be attained with the lowest possible operating temperature in order to increase the credibility of the process economics.

In order to reach the above mentioned objectives, six consecutive pressure acid leach tests were conducted with the limonitic sample starting from 245 °C up to 270 °C by a 5 °C increase for each test with the process parameters mentioned in Table 4.3.

Table 4.3 Process parameters used to see the effect of temperature upon nickel and cobalt extractions

Ore Type:	Limonite
Leaching Temperature (°C)	245, 250, 255, 260, 265, 270 °C, respectively.
Leaching Duration (min.)	60 min.
Acid/Ore Ratio (wt./wt.)	0.30
Particle Size (μ)	100% -850 μ
Solid/Liquid Ratio (wt./wt.)	0.30 (Excluding the acid amount)
Stirring Speed (rpm)	400 rpm

In order to see only the effect of temperature upon nickel and cobalt extractions, the other parameters were kept constant and the following results were obtained from these tests which are presented in Figure 4.3.
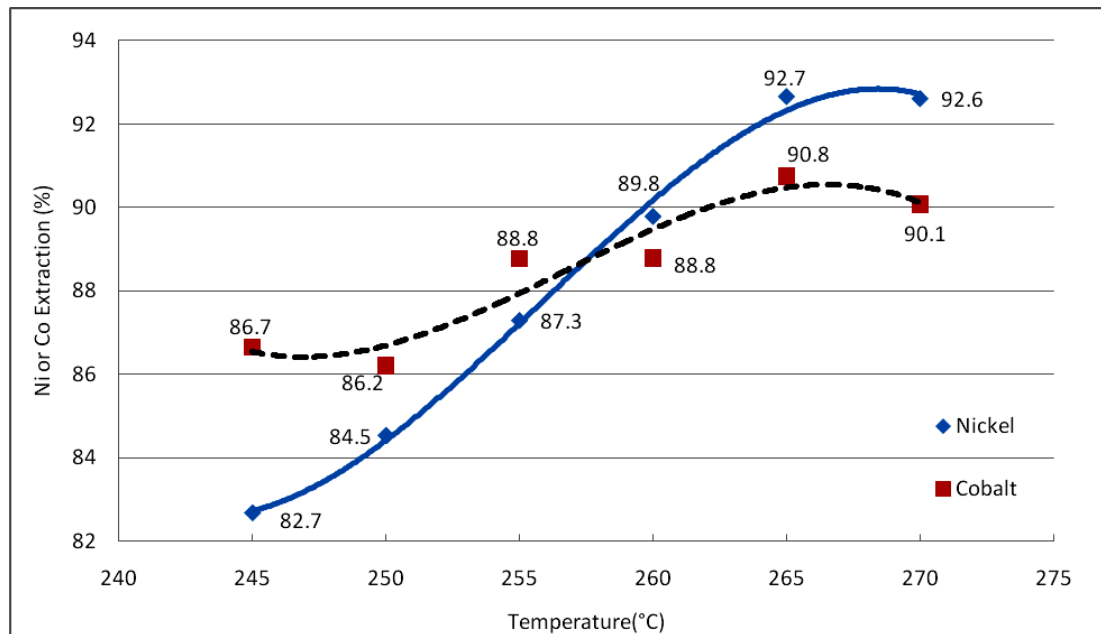
Figure 4.3 Effect of temperature upon degree of nickel and cobalt extractions

According to the extraction behavior of nickel with increasing temperature, it was noticed that there was an increasing trend in the extraction of nickel with the above mentioned process parameters. However, beyond 265 °C this increasing tendency seemed to disappear with further increase in the temperature. Georgiou and Papangelakis reported nearly the same behavior between the temperatures of 230 and 270 °C [36]. Similarly, a study conducted by Chou et al. showed that leaching up to 275 °C increases nickel yield, but leaching conducted at 300 °C leads to a decrease in the degree of nickel extraction [35]. The cause of this behavior was reported in the literature by indicating that in excess of 270 °C, the possibility of nickel-magnesium sulphate $(Mg,Ni)SO_4.H_2O$ co-precipitation increases severely due to lower solubility of magnesium at higher temperatures [15]. This precipitation is generally accompanied with nickel and cobalt losses to the precipitate. It is also reported that as the temperature of pressure leaching goes beyond 280 °C, the possibility of $Fe(OH)SO_4$ (basic iron sulphate) and $Al(OH)SO_4$ (basic aluminum sulphate) formations increase with accompanied acid losses which are not desirable during pressure acid leaching process.

When the extraction behavior of cobalt is in question, it is obvious from Figure 4.3 that cobalt is not as sensitive to increasing process temperatures as nickel and, its tendency loses its intensity in the excess of 265 °C. When this result is compared with the reported data in the literature, it was expressed that almost 80% of the cobalt is rapidly taken into the leach solution possibly due to the presence of cobalt in a readily-leached manganese mineral $((Co,Ni)_{1-y}(MnO_2)_{2-x}(OH)_{2-2y+2x}\cdot n(H_2O))$, asbolane [36]. Georgiou and Papangelakis stated that testing the lateritic ore between the temperatures of 230 and 270 °C had essentially no effect upon the rate of cobalt extraction. Cobalt was leached readily in the first 10 to 20 minutes of leaching, and its dissolution rate slowed down thereafter [57]. Similarly, Chou et al. emphasized the high initial rate of cobalt extraction. Therefore, the extraction behavior of cobalt is generally reported to be less affected by increasing temperature [35]. Other than nickel and cobalt, the extraction behavior of other elements is illustrated in Table 4.4.

Table 4.4 Extraction behavior of other elements with respect to temperature

Temperature °C	Fe (%)	Al (%)	Mg (%)	Mn (%)	As (%)	Cr (%)
245	1.4	29.3	74.0	77.0	2.5	3.5
250	1.7	21.9	98.6	74.9	2.5	2.2
255	1.9	19.8	82.8	78.3	2.7	2.2
260	1.3	18.0	91.1	71.9	2.3	1.5
265	1.0	12.0	91.6	81.6	3.4	2.2
270	1.5	14.5	-	77.8	4.0	1.0

According to Table 4.4, it can be concluded that increasing temperatures above 245 °C affected the extraction of iron in the pregnant leach solution to a limited extend because most of the iron had already been leached and precipitated in the early stages of pressure leaching. However, when this iron extraction result is compared with the low temperature atmospheric leaching processes, it can be said that the solution iron concentration of high pressure leaching is negligible when compared with the former. Therefore, it can be concluded that iron cations in pregnant leach solution cannot stay stable long at the leaching temperatures studied above in the prevailing autoclave conditions.

When the extraction behavior of aluminum is analyzed in detail, the decreasing tendency in the stability of dissolved aluminum cations in the pregnant leach solution draws the attention as a result of increasing leach temperatures. Since, as a result of temperature rise in the pressure leach process, the precipitation rate of iron and aluminum increases in parallel with temperature with inverse solubility of hematite and alunite precipitates. This judgment has also been supported by Georgiou and Papangelakis in such a statement that the increasing leaching temperatures favor increasing nickel and cobalt concentration ratios '[(Ni or Co)/(Fe+Al)]' as a result of the inverse solubility of hematite and alunite in the pregnant leach solution [36].

When the extraction results of magnesium are examined, it seems that it is difficult to make a judgment with these results. Since, the analysis of magnesium is a little bit problematic due to experimental challenges. This was also indicated by Whittington and Muir that the dissolution of magnesium could give a misleading value upon cooling since its chemistry is much more affected by the temperature changes [15].

Fluctuations observed in the extraction behavior of manganese complicate the case so it is difficult to comment on the results. Roughly speaking, about 70-80% of manganese was extracted in the temperature interval stated above. For arsenic, it seems that the increasing leaching temperatures slightly increased the extraction of arsenic in the pregnant leach solution. However, for chromium it was noticed that the extraction of chromium has decreased from 3.5% to 1.0% as a result of temperature rise in the autoclave. This behavior suggests that precipitation of chromium is favored similar to iron and aluminum as a result of higher leaching temperatures.

Finally, the changes in the reduction potential and the free acidity of the solution are tabulated in Table 4.5.

Table 4.5 Reduction potential and free acidity with respect to temperature rise

Temperature (°C)	Reduction Potential (mV)	Free Acidity (gpl)
245	510	41.5
250	497	41.9
255	489	41.2
260	499	42.7
265	451	44.3
270	420	44.9

From tabulated results given in Table 4.5, it's worth saying that the increasing leaching temperatures gave a more reducing character to the final pregnant leach liquor which was verified with the increase in the extend of nickel and cobalt extractions. Since, Tindall and Muir suggested that at low E_h, reduced species (like Fe^{2+}) in the leach solution facilitate the transfer of electrons into the oxide lattice which in turn promotes the breakdown of the oxide lattice by dilute acid [40]. Finally, a slight increase in the residual acid concentration may be related with the increased precipitation behavior of iron, aluminum and chromium. However, it should also be kept in mind that increases in the nickel and cobalt extractions also affected the acid consumption and made the situation more difficult to comment further.

In conclusion, the pressure acid leach experiments conducted at different leaching temperatures showed us that more nickel and cobalt could be extracted into the pregnant leach liquor in just one hour of leaching duration at higher leaching temperatures in the autoclave. However, since higher leaching temperatures mean higher initial investment and operational costs, thus the economically optimum process temperature should be selected whether the extra nickel and cobalt credit compensates the former production expenses. Therefore, for the rest of the tests 255 °C of leaching temperature was selected, and higher nickel and cobalt extractions are intended to be obtained by optimizing the other process parameters effectively.

4.2.2 Effect of Leaching Duration upon Nickel and Cobalt Extractions

In order to see the effect of leaching duration on the degree of nickel and cobalt extractions, five consecutive pressure acid leach tests were conducted in the same manner. The start of the reaction defined as zero time was determined when the reactor temperature reached to 255 °C, and 60, 90, 180, and 360 minutes of leaching durations were defined as proceeding leaching procedure up to the so called time intervals from this reference point. For completeness, other process parameters used during the experiments are given in Table 4.6.

Table 4.6 Process parameters used to see the effect of leaching duration upon nickel and cobalt extractions

Ore Type:	Limonite
Leaching Temperature (°C)	255 °C
Leaching Duration (min.)	0, 60, 90, 180, 360 min., respectively.
Acid/Ore Ratio (wt./wt.)	0.30
Particle Size (μ)	100% -850 μ
Solid/Liquid Ratio (wt./wt.)	0.30 (Excluding the acid amount)
Stirring Speed (rpm)	400 rpm

Corresponding results of the pressure acid leach experiments to see the effect of leaching duration is presented in Figure 4.4.
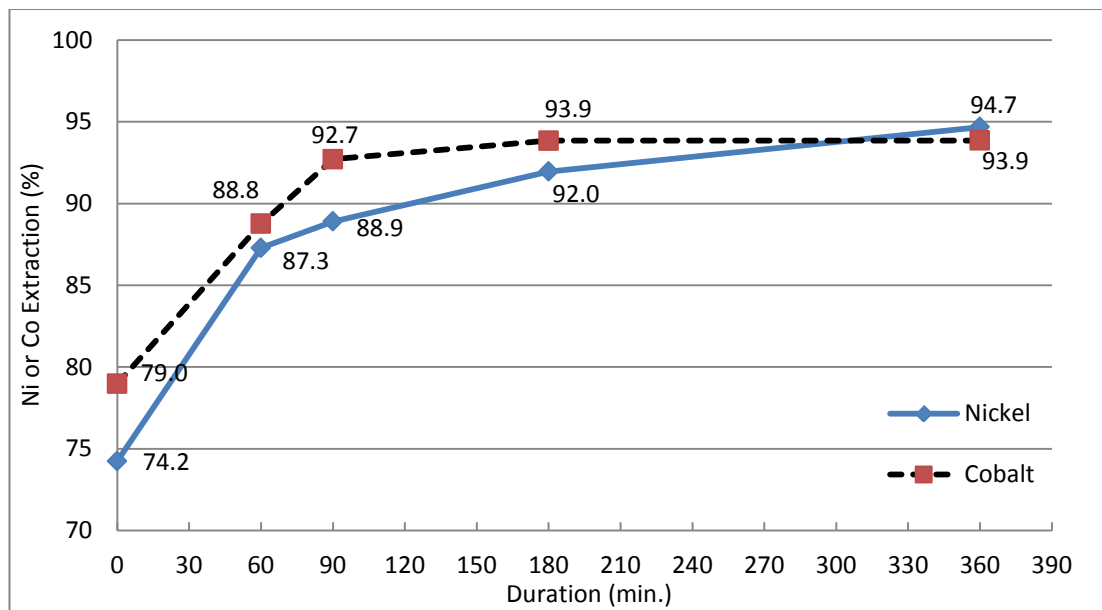
Figure 4.4 Effect of leaching duration upon degree of nickel and cobalt extractions

According to the results obtained from these experiments, it seems that nickel and cobalt behaved nearly in the same manner when the leaching duration was prolonged. The above figure suggests that from the starting point up to 180 minutes of leaching duration, the nickel and cobalt extractions increased as intended. However, although the increasing trend of nickel extraction continued from 180 minutes up to 360 minutes of leaching duration, it seems that this trend finally came to a limiting extraction value of around ~95% which suggested that the further increase in the leaching duration would not be helpful in increasing the degree of nickel and cobalt extractions. Thus, it was thought that together with a problem related with the kinetics of the chemical reactions, also a persistent leaching behavior complicated the process. In other words, these results suggested that there may be very acid resistant refractory minerals present in this limonitic sample which did not let the leaching of nickel and cobalt from the lattice of these minerals. When the mineralogical characterization step is referred again, the presence of hematite mineral within the limonitic sample appeared to be the possible reason of this extraction behavior. This difficulty in the leaching behavior of primary hematite was also reported in the literature by Kui Lui et al. who stated that leaching becomes more difficult among the nickel containing minerals in the following order;

Lizardite>goethite>maghemite>magnetite>hematite>chromite≈ringwoodite [58, 59].

Therefore, this doubt of incomplete extraction of nickel stemming from primary hematite present in the original ore will be kept in mind and examined throughout this study to see whether it is possible to overcome this problem. Other than nickel and cobalt, the extraction behavior of other elements is summarized in Table 4.7.

Table 4.7 Extraction behavior of other elements with respect to leaching duration

Duration (min.)	Fe (%)	Al (%)	Mg (%)	Mn (%)	As (%)	Cr (%)
0	2.4	22.1	78.0	73.6	2.4	5.0
60	1.9	19.8	82.8	78.3	2.7	2.2
180	0.8	8.5	98.2	95.1	2.9	1.3
360	0.8	6.0	92.6	97.8	4.2	1.4

As in the case of the results obtained from the experiments in order to investigate the effect of temperature; the extraction behaviors of iron, aluminum and chromium gave very similar results with respect to leaching duration. Thus, the solution concentrations of these three elements tended to decrease according to the mentioned precipitation reactions given in the chemistry of pressure acid leaching. Therefore, it can be concluded that increasing temperature and prolonged leaching duration were very effective in decreasing the impurity concentrations of the pregnant leach solution in terms of iron, aluminum and chromium. However; in terms of magnesium and manganese, completely opposite situation was observed in such a way that magnesium and manganese extractions in the pregnant leach liquor increased regularly up to 360 minutes of leaching.

Finally, the changes in the reduction potential and the free acidity of the pregnant leach solution are given in Table 4.8.

Table 4.8 Reduction potential and free acidity with respect to leaching duration

Duration (min.)	Reduction Potential (mV)	Free Acidity (gpl)
0	610	42.3
60	489	41.2
90	515	42.1
180	510	44.5
360	460	46.3

According to the results of reduction potential and free acidity measurements given in Table 4.8, an increasing trend in the free acidity was possibly due to increased precipitation reactions which resulted in releasing of consumed acid into the solution. Similarly, a more reducing solution character was observed which may be correlated with the increased nickel and cobalt extractions as a result of enhanced reducing conditions [40].

In conclusion, the pressure acid leach experiments conducted at different leaching durations showed us that more nickel and cobalt could be extracted into the pregnant leach liquor at 255 °C by increasing the duration of leaching in the autoclave. However, as in the case of temperature, there was a limit of this increase possibly due to presence of difficult to leach refractory minerals suspected to be mainly hematite. Therefore, prolonged leaching durations may be helpful in increasing the desired level of nickel and cobalt extractions. However, since prolonged leaching durations decrease the overall capacity of the plant and thus increase the costs, the optimal leaching duration should be selected whether the extra nickel and cobalt credits compensate the former production expenses. Therefore, for the rest of the tests just 60 minutes of leaching duration was selected, and higher nickel and cobalt extractions were intended to be obtained by suitable additives and optimizing other process parameters more effectively.

4.2.3 Effect of Sulphuric Acid/Ore Ratio upon Nickel and Cobalt Extractions

In order to see the effect of sulphuric acid concentration on the degree of nickel and cobalt extractions, four pressure acid leach tests were conducted. In the first experiment 275 kilograms of sulphuric acid per ton of dry limonitic ore was used and acid addition was increased in stages of extra 25 kilograms in the following experiments up to a ratio of 350 kilograms per ton of dry ore.

Other process parameters used during the experiments and their corresponding extraction results to see the effect of sulphuric acid concentration is presented in Table 4.9 and Figure 4.5, respectively.

Table 4.9 Process parameters used to see the effect of sulphuric acid concentration upon nickel and cobalt extractions

Ore Type:	Limonite
Leaching Temperature (°C)	255 °C
Leaching Duration (min.)	60
Acid/Ore Ratio (wt./wt.)	0.275, 0.300, 0.325, 0.350, respectively.
Particle Size (μ)	100% -850 μ
Solid/Liquid Ratio (wt./wt.)	0.30 (Excluding the acid amount)
Stirring Speed (rpm)	400 rpm

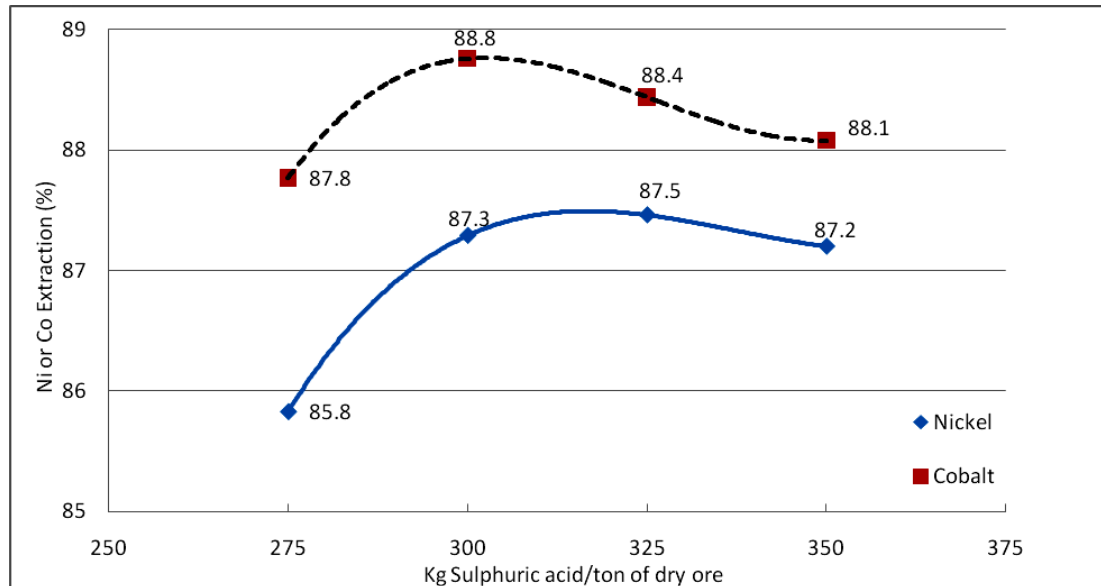**Figure 4.5** Effect of sulphuric acid concentration upon degree of nickel and cobalt extractions

While examining the results of the effect of acid concentration experiments on nickel and cobalt extractions, the amount of residual acid of the pregnant leach liquor after leaching should also be kept in mind in the decision making process. Since it is reported from various testworks that for high nickel and cobalt extractions sufficient

free acid should remain in the pregnant liquor in order to maintain the stability of dissolved species and prevent undesired nickel and cobalt losses [15]. However, while various researchers have reported the positive effect of residual acidity in the pregnant leach liquor, there is also a limiting value in the amount of this residual acid present in the solution. Because during solution purification and metal recovery steps, this residual acid should also be neutralized somehow, most often $CaCO_3$ being the suitable reactant. Therefore the amount of residual acid becomes directly related with the consumption of basic reagent and, in turn it determines the viability of the process economics in terms of rising cost of consumables.

To clarify the above mentioned point, the practical data from various processing plants may help and enlighten this situation. Testwork of Ramu ore at 250 °C suggests that 30 g/L of residual acid was optimal for sufficient nickel and cobalt extractions. Similarly, 30-40 g/L and 40 g/L of free acid were necessary for Bulong and Murrin Murrin ores, respectively. Therefore, for Gördes limonites an amount of 40g/L residual sulphuric acid was targeted for satisfactory results. The actually measured residual acid values are given in Table 4.10.

Table 4.10 Reduction potential and free acidity with respect to acid concentration

Acid Amount (kg/ton dry ore)	Reduction Potential (mV)	Free Acidity (gpl)
275	503	39.2
300	489	41.2
325	497	44.9
350	499	44.5

Therefore, when the nickel and cobalt extraction results in Figure 4.5 and residual acid measurement values in Table 4.10 are evaluated together, 300 kilograms of sulphuric acid addition seemed to be the most appropriate selection among the other

alternatives. Since the extra acid addition did not satisfy the desired increase in the extraction values, on the contrary increased the acid and base consumptions pointlessly. In addition to above mentioned considerations, the leach residue samples were analyzed by XRF method and sulphur content of the leach residue samples were also determined. According to the obtained results, the sample leached with 300 kilograms of sulphuric acid was found to contain 1.89% sulphur, whereas the sample leached with 350 kilograms of sulphuric acid was determined to contain 2.25% sulphur which showed that increased sulphuric acid addition had also increased the sulphur losses in the leach residue pointlessly. Therefore, this finding also showed that 300 kilograms of sulphuric acid addition would give the best result when the overall considerations were taken into account. Other than nickel and cobalt, the extraction behavior of other elements is illustrated in Table 4.11.

Table 4.11 Extraction behavior of other elements with respect to acid concentration

Acid Amount (kg/ton dry ore)	Fe (%)	Al (%)	Mg (%)	Mn (%)	As (%)	Cr (%)
275	1.1	17.8	90.7	79.5	2.6	1.4
300	1.9	19.8	82.8	78.3	2.7	2.2
325	2.1	34.4	73.7	73.3	4.2	2.1
350	3.4	38.8	66.2	71.8	5.6	2.8

When the acid amount of the dissolution reactions was increased excessively, this high acidity unfortunately hindered the acid regeneration (hydrolysis) reactions and led to undesired increases in the impurity concentrations of the solution. This assertion could be verified by considering the increases in the extractions of iron, aluminum, arsenic and maybe chromium. This observation was also reported by Krause et al. in such a way that increases in the residual free acid concentration, increases the extractions of iron, aluminum and chromium in the liquor which is very parallel with the summarized data in Table 4.11 [37].

One more point worth commenting is that the extraction of magnesium decreased continuously as a result of increased sulphuric acid concentration which may be correlated with the possible formation of insoluble magnesium sulphates as a result of the sulphate saturation in the solution.

In conclusion; as a result of discussions made above, 300 kilograms of sulphuric acid addition per ton of dry limonitic ore was found to be the most appropriate amount needed to get the desired nickel and cobalt extractions together with the minimum impurity concentrations and minimum consumption of costly consumables.

4.2.4 Effect of Particle Size upon Nickel and Cobalt Extractions

In order to see the effect of particle size on the degree of nickel and cobalt extractions, five consecutive pressure acid leach tests were conducted. Particle size of the sample was chosen as 100% -2000 μ for the coarsest PAL sample and the particle size was decreased stage wise respectively to 100% -1400 μ, -850 μ, -425 μ and finally to -38 μ for the finest particles. The other process parameters used during the particle size experiments and their corresponding extraction results are given in Table 4.12 and Figure 4.6, respectively.

Table 4.12 Process parameters used to see the effect of particle size upon nickel and cobalt extractions

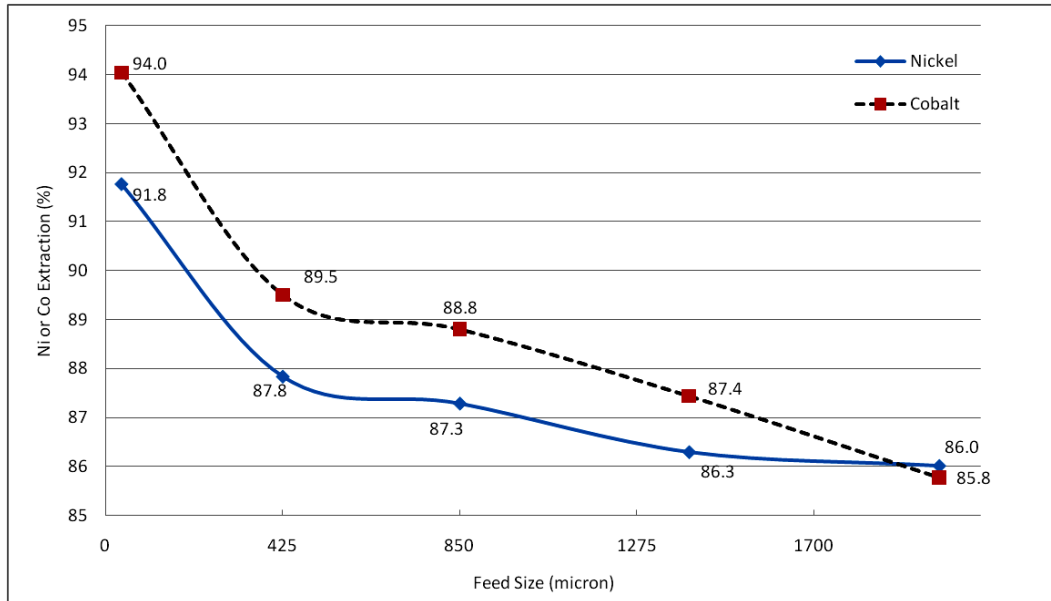| Ore Type:	Limonite
Leaching Temperature (°C)	255 °C
Leaching Duration (min.)	60
Acid/Ore Ratio (wt./wt.)	0.30
Particle Size (μ)	-38 μ, -425 μ, -850 μ, -1400 μ, -2000 μ, respectively.
Solid/Liquid Ratio (wt./wt.)	0.30 (Excluding the acid amount)
Stirring Speed (rpm)	400 rpm

Figure 4.6 Effect of particle size upon degree of nickel and cobalt extractions

The results of particle size experiments given in Figure 4.6 showed that the responses of nickel and cobalt extractions were positive when finer particles were fed into the autoclave. As seen from the mentioned figure, particle size became more important in terms of nickel extraction when the feed size was decreased below 425 μ, and further reduction in the particle size seemed to give more effective results. Similarly, the extraction of cobalt was increased in such a way that as the particle size was reduced from -2000 μ to -425 μ; it gave almost a linear increase in the cobalt extraction. However, this trend became steeper when the size was reduced from -425 μ to -38 μ. In a similar study conducted by Chou et al. to see the effect of particle size on leaching behavior of limonitic samples, no effect of excessive grinding of the ore was reported upon the degree of nickel extraction [35]. This may indicate that most of the nickel contained in that limonitic sample was present in the finer fractions and was already in a leachable form, thus further grinding did not affect the extraction behavior. However, Gördes limonitic sample did not look like to the one stated above. This meant that some coarse grains above 425 μ within the ore sample also contained nickel which needed to be ground further in addition to the finer

fractions. Besides nickel, some researchers specifically reported a better improvement in the extraction behavior of cobalt as a result of finer grinding [15]. This statement can also be verified in Figure 4.6 that further grinding of the limonitic ore below 425 μ led to an exponential increase in the extraction of cobalt into the pregnant leach solution.

In the study of Chou et al., it was also stated that excessive grinding of the ore created extra surface area which in turn provided additional nucleation sites for iron and aluminum precipitation. Therefore, the impurity concentration of pregnant leach solution decreased as a result of over grinding. This trend may also be seen in the leaching results of Gördes limonites. As shown in Table 4.13, the extractions of iron and aluminum tended to decrease as a result of reduction in the feed size which was in parallel with the statement made by Chou et al. [15, 35].

Table 4.13 Extraction behavior of other elements with respect to particle size

Particle Size (μ)	Fe (%)	Al (%)	Mg (%)	Mn (%)	As (%)	Cr (%)
-2000	2.0	34.4	85.9	74.1	3.3	1.9
-1400	1.9	24.0	89.4	77.1	2.0	1.9
-850	1.9	19.8	82.8	78.3	2.7	2.2
-425	1.5	19.5	99.4	74.8	3.0	1.8
-38	1.2	14.7	84.9	86.4	2.4	2.1

When the overall results of particle size experiments are considered to come up with a conclusion, it can be said that grinding was beneficial in terms of higher nickel and cobalt extractions and cleaner solution characteristics for further downstream processing. However, it had a limit due to technical and economic reasons. Since, grinding becomes more difficult and energy consuming when the particle size is reduced excessively. The rheology of the pulp to be fed into the autoclave is also a

very important consideration which should be kept in mind during the final decision making process. Since, rheology and ease of stirring in the autoclave are a function of the feed size, and it becomes very difficult to provide an effective stirring when very coarse particle sized feed is fed into the system. Therefore, in the light of these above mentioned considerations, the limonitic samples ground to 100% -850 μ of particle size were used in the rest of the experiments.

Up to now; the effects of temperature, leaching duration, acid/ore ratio, and particle size upon nickel and cobalt extraction results were investigated and further tests were decided to be performed at 255 °C with 0.30 acid to ore weight ratio with a particle size of 100% -850 μ in 1 hour of leaching duration with 30% solids ratio. When these optimum parameters were used and the leach residue sample was analyzed by XRD and Mastersizer 2000 laser particle size analyzer, the following analysis results given in Figure 4.7 and Table 4.14 were obtained, respectively.
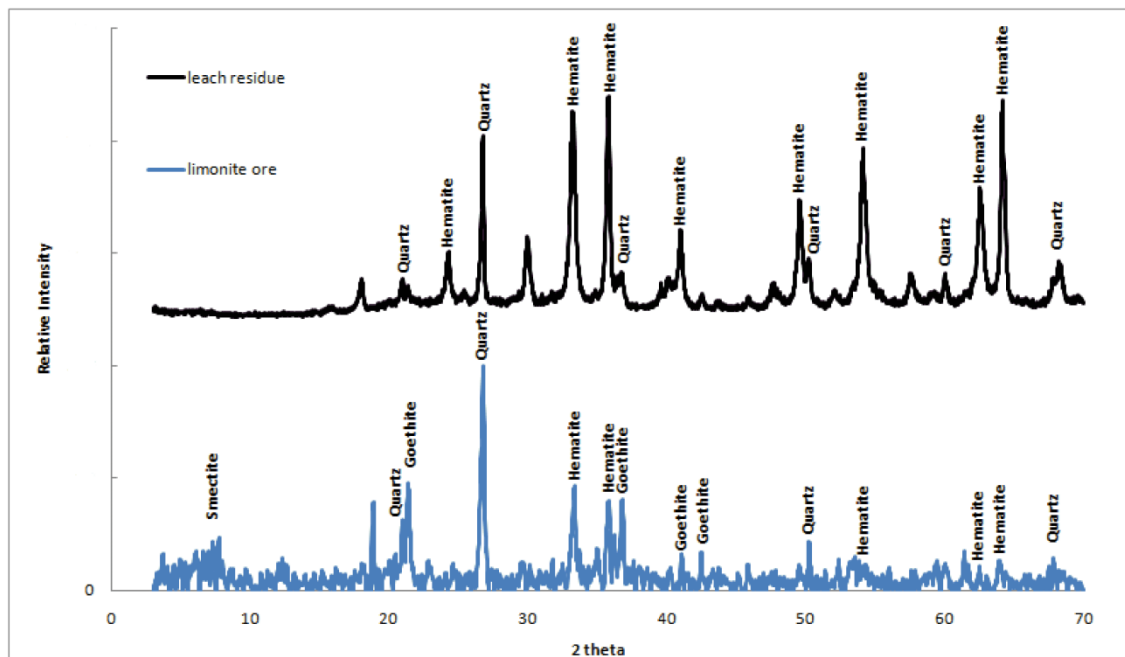

Figure 4.7 XRD result comparison of limonite ore and its leach residue

Table 4.14 Particle size distribution of the leach residue

Size (μ)	Vol. % Undersize	Size (μ)	Vol. % Undersize	Size (μ)	Vol. % Undersize
0.25	0.00	1.78	17.97	11.25	50.72
0.32	0.27	2.00	18.99	14.16	57.84
0.36	0.87	2.24	20.12	15.89	61.47
0.40	1.77	2.52	21.36	17.83	65.12
0.45	2.95	2.83	22.71	22.44	72.38
0.50	4.37	3.17	24.16	25.18	75.98
0.56	5.94	3.56	25.72	28.25	79.54
0.63	7.59	3.99	27.39	31.70	83.02
0.71	9.22	4.48	29.19	39.91	89.59
0.80	10.76	5.02	31.15	44.77	92.51
0.89	12.15	5.64	33.3	50.24	95.07
1.00	13.36	6.33	35.66	56.37	97.14
1.13	14.41	7.10	38.24	63.25	98.68
1.26	15.34	7.96	41.05	70.96	99.61
1.42	16.19	8.93	44.09	79.62	99.97
1.59	17.05	10.02	47.32	89.34	100.00

According to Figure 4.7, the characteristic peaks of smectite and goethite within the limonite ore have disappeared indicating that these minerals were leached out from the original ore sample. After leaching, the intensity of the characteristic hematite peaks increased in the XRD plot of the leach residue verifying that iron had tended to precipitate in the form of secondary hematite. Therefore, it is supposed that nickel present within the primary hematite may constitute to be the main source of the low extraction results experienced with these limonitic samples. Finally, there were no considerable changes in the quartz peaks after leaching showing that quartz had remained almost intact during leaching operation. Some of the relatively smaller peaks in Figure 4.7 could not be identified.

Meanwhile, the particle size analysis result of the leach residue sample has showed that all of the particles had a particle size of less than 89.34 μ and there was no particle smaller than 0.25 μ. Moreover, 80% of the particles had a particle size of less than nearly 30 μ as seen in Table 4.14.

Finally, the analysis result of the pregnant leach solution of the experiment carried out with limonite at the above mentioned optimum conditions is given in Table 4.15. According to Table 4.15, in the final pregnant leach solution 4677 mg/L nickel and 266 mg/L cobalt were analyzed to be present after leaching. Fe, Al, Cr, Mn and Mg were found to be the primary elements contaminating the solution and Fe, Al, Cr should be removed prior to nickel and cobalt precipitation.

One more thing about the solution analysis result is that the concentration of Fe^{2+} was found to be very low when the total iron concentration is considered and most of the iron was present in the form of Fe^{3+}. This result is desirable in terms of iron removal from the pregnant leach solution, because ferrous iron should be oxidized to ferric iron prior to iron precipitation from the solution. Therefore, the iron removal from the pregnant leach solution was expected to be less problematic during the downstream processing of nickel and cobalt production. In addition to the given analysis result of the metal ions, the reduction potential of the pregnant leach solution was measured to be 489 mV and it contained 41.2 gpl of residual sulphuric acid after pressure leaching prior to solution purification.

Table 4.15 Pregnant leach solution analysis of experiment carried out with limonite at the optimum combination

Ni (mg/L)	Co (mg/L)	Al (mg/L)	Mn (mg/L)	Mg (mg/L)	As (mg/L)	Cr (mg/L)	Fe^{2+} (mg/L)	Fe_{total} (mg/L)
4677	266	2620	1364	4754	98	123	0.2	2296

4.2.5 Effect of Prior Heat Treatment upon Nickel and Cobalt Extractions

The experimental results evaluated up to now suggest that there is a problem that hinders the ease of extraction of the desired metallic values. Since, when the data from various plants were examined, it was seen that generally more than 95% of the nickel and cobalt contained in various ores could easily be extracted when basic pressure leach parameters such as 60 to 90 minutes of leaching duration at about

63

255 °C with a feed particle size of less than 1 mm were being used during operation. However, when the Gördes limonite is considered, it was a bit more difficult to reach previously mentioned extraction results with the same basic parameters. Therefore, as mentioned in the argument made on the effect of leaching duration, it is supposed that nickel present within the hematite mineral may constitute to be the main source of this problem experienced with these limonitic samples. In order to verify this prediction, the limonitic sample was heated to 350 °C in order to transform all of the goethite to hematite present in the ore. Selection of heat treatment temperature was made based on the thermal analysis result of limonitic sample given in Figure 3.3 in the mineralogical characterization part of the samples. As easily seen in Figure 3.3, at around 270 °C goethite present in the limonitic sample transformed into hematite according to the dehydroxylation reaction of goethite given in Reaction 3.2. However, in order to be on the safe side, the heat treatment temperature was chosen as being 350 °C. The nickel and cobalt extraction results obtained after pressure leaching for the heat treated limonitic ore are given in Figure 4.8 together with those of the original ore obtained under the same experimental conditions for comparison purposes.
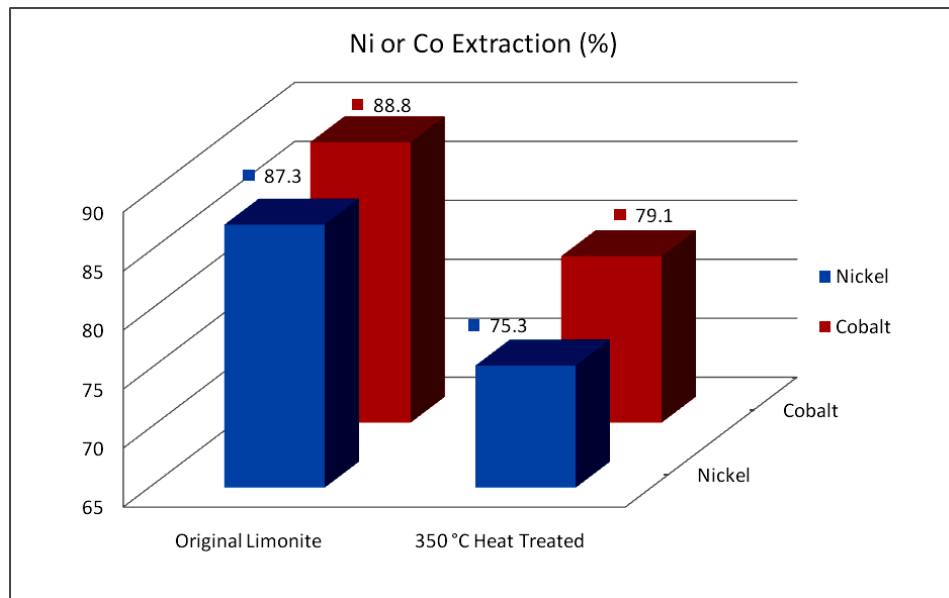

Figure 4.8 Effect of prior heat treatment upon degree of nickel and cobalt extractions

It is obvious from Figure 4.8 that upon transforming the goethite to hematite by suitable heat treatment, there was about 10% decrease in the extraction percent's of nickel and cobalt which means that it is more difficult to leach and obtain nickel from hematite when compared with goethite. Therefore, in the following steps of this study, this difficulty was tried to be overcome by making various additions to the leaching environment.

4.2.6 Effect of HCl Addition upon Nickel and Cobalt Extractions

Addition of hydrochloric acid together with sulphuric was the first alternative tried in order to improve the extraction behavior of valuable metals by the help of more vigorous leaching conditions. For this purpose 5 and 10 grams of HCl (37 wt. %), corresponding to 33.33 and 66.67 kilograms HCl per ton of dry limonitic ore were added initially into the leach solution having the constant leach parameters tabulated in Table 4.16. The results obtained are given in Figure 4.9.

Table 4.16 Process parameters used to see the effect of HCl addition upon nickel and cobalt extractions

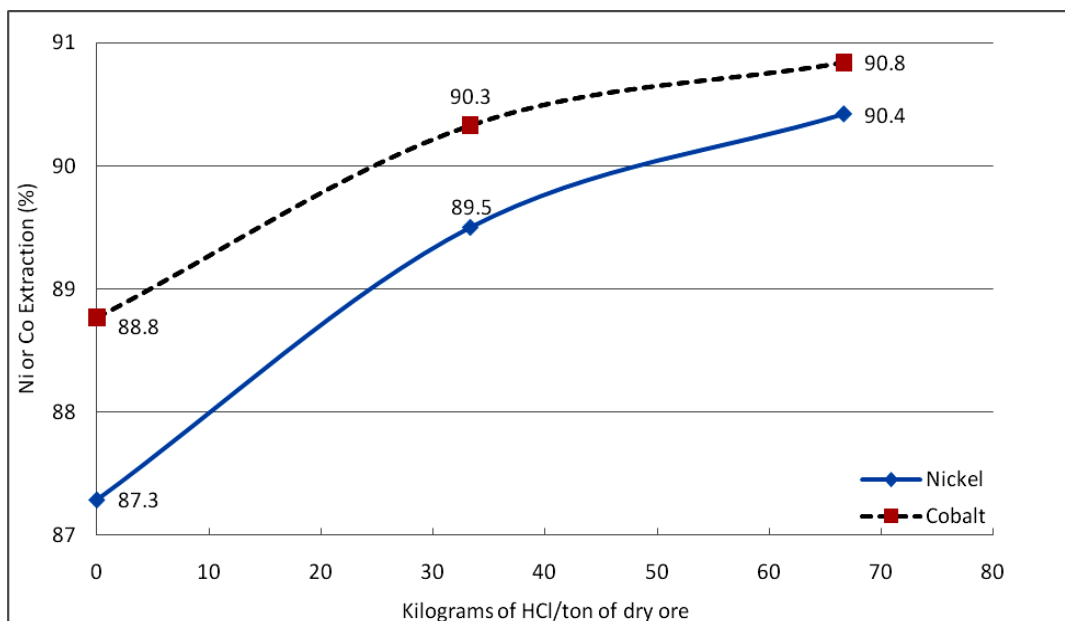| Ore Type:	Limonite
Leaching Temperature (°C)	255 °C
Leaching Duration (min.)	60
Acid/Ore Ratio (wt./wt.)	0.30 with HCl addition
Particle Size (μ)	-850 μ
Solid/Liquid Ratio (wt./wt.)	0.30 (Excluding the acid amount)
Stirring Speed (rpm)	400 rpm

Figure 4.9 Effect of HCl addition upon degree of nickel and cobalt extractions

When the results of hydrochloric acid addition experiments were evaluated, the results were satisfactory just in terms of increasing the nickel and cobalt extractions. However, extremely corrosive behavior of the acidic mixture resulted in undesired damage of the leaching equipment. As a result of severe acidic attack, a few rupture plates of the autoclave have exploded during the period of acid mixture testing and this phenomenon led to the decision of further tests to be terminated. Thus, the overall conclusion was that HCl addition into the autoclave together with H_2SO_4 might be an alternative in order to enhance the extraction behavior of nickel and cobalt from the refractory minerals of limonitic laterite ore. However, the autoclave should specially be designed in order to endure the severe corrosive leaching conditions under consideration. Besides the nickel and cobalt, slight increases in the extractions of iron, aluminum, arsenic and chromium were observed similar to nickel and cobalt. However, there was no considerable change in the extractions of manganese and magnesium. In conclusion, since there is no study and data present about the effect of this additive in the literature, more detailed investigation should be performed in order to understand the changes after the addition.

4.2.7 Effect of Na₂SO₄ Addition upon Nickel and Cobalt Extractions

In order to see the effect of Na_2SO_4 addition on the degree of nickel and cobalt extractions, two pressure acid leach tests were conducted with the additions of 12.5 gpl and 25 gpl of Na_2SO_4 to the autoclave, respectively. The parameters kept constant during the experiments are given in Table 4.17 and the corresponding results obtained are given in Figure 4.10.

Table 4.17 Process parameters used to see the effect of Na_2SO_4 addition upon nickel and cobalt extractions

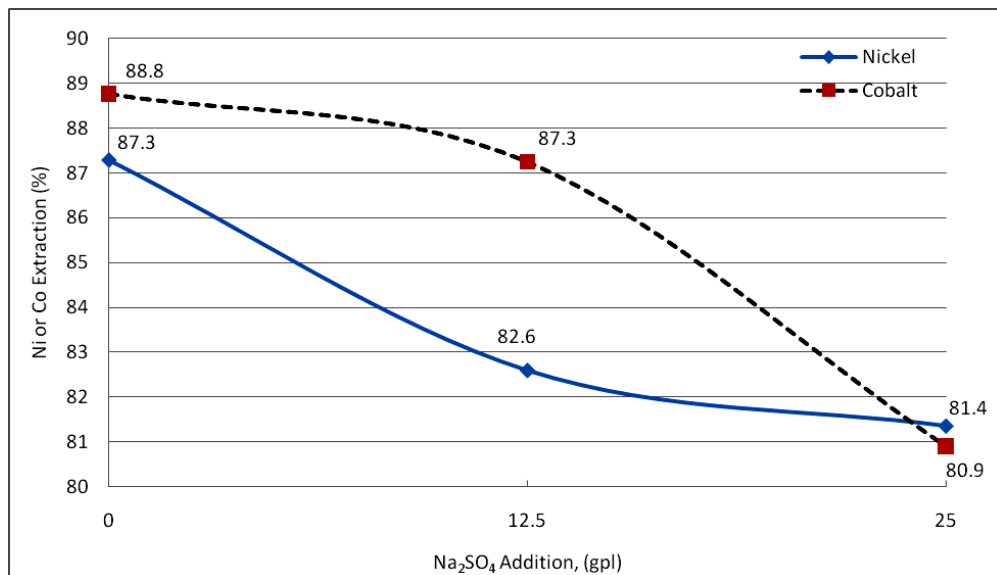|	
Ore Type:	Limonite
Leaching Temperature (°C)	255 °C
Leaching Duration (min.)	60
Acid/Ore Ratio (wt./wt.)	0.30
Particle Size (µ)	100% -850 µ
Solid/Liquid Ratio (wt./wt.)	0.30 (Excluding the acid amount)
Stirring Speed (rpm)	400 rpm

Figure 4.10 Effect of Na_2SO_4 addition upon degree of nickel and cobalt extractions
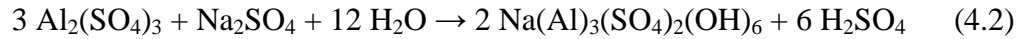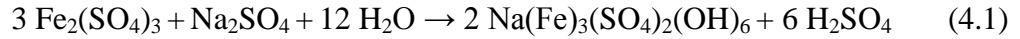
Although some studies report the beneficial effects of Na_2SO_4 addition, the experimental results of Gördes limonite were unsatisfactory due to the observed decrease in the degree of nickel and cobalt extractions. However, the contribution of Na_2SO_4 in changing the solution impurity concentrations and residue mineralogy could not be ignored. Since, when the extractions of Fe, Al, Mn, Mg, and Cr in the pregnant leach solution were considered, the effective decreases in their amounts easily draws ones attention as seen in Table 4.18. The reason in the decrease of these ions is explained by the increased stability of natroalunite and/or natrojarosite and their precipitation as a result of sodium ions present in the solution [60].

Table 4.18 Extraction behavior of other elements with Na_2SO_4 addition

Na_2SO_4	Fe (%)	Al (%)	Mg (%)	Mn (%)	As (%)	Cr (%)
No addition	1.9	19.8	82.8	78.3	2.7	2.2
12.5 gpl Na_2SO_4	1.3	3.3	81.7	72.8	2.8	1.0
25 gpl Na_2SO_4	0.8	2.0	67.2	69.9	3.2	0.3

When the possible causes of this behavior were investigated, it may be said that the sudden decrease in the nickel and cobalt extractions may have resulted from the difficulty faced during filtration of the leach residue. Since, after the addition of Na_2SO_4, the leach residue showed a colloidal behavior which has inhibited the effective washing and separation of the pregnant leach solution from the leach residue. In addition to colloidal nature of the residue, the amount of residual acid continuously decreased from 41.2 gpl to 37.8 and 33.9, respectively as a result of increases in the Na_2SO_4 concentration in the solution. This behavior was explained by Sobol in such a way that the reduction in free acidity may hydrolyze the silicic acid to colloidal silica which in turn complicates the solid-liquid separation process [15, 61].

The decrease in residual acid and the formation of natroalunite and/or natrojarosite were explained and formulated according to the chemical reactions given below [60]:

$$3\ Fe_2(SO_4)_3 + Na_2SO_4 + 12\ H_2O \rightarrow 2\ Na(Fe)_3(SO_4)_2(OH)_6 + 6\ H_2SO_4 \qquad (4.1)$$

$$3\ Al_2(SO_4)_3 + Na_2SO_4 + 12\ H_2O \rightarrow 2\ Na(Al)_3(SO_4)_2(OH)_6 + 6\ H_2SO_4 \qquad (4.2)$$

Finally, Sobol stated that Ni, Co or Mn may substitute into alunite/jarosite structure, thus, this may be the reason of low nickel and cobalt extraction values [15, 61]. In conclusion; although Na_2SO_4 served very effectively for solution purification purposes, it seemed that this additive would not solve the problem of low extraction results due to the challenges faced during pressure leaching and filtration which complicated the overall process. Therefore, further tests were terminated.

4.2.8 Effect of FeSO₄ Addition upon Nickel and Cobalt Extractions

Various researchers have already reported the positive effect of the presence of reducing species in the pregnant leach solution during pressure acid leaching of lateritic nickel resources. Therefore; in this part of the study, the effect of divalent iron addition to the leach solution was investigated in order to enhance the nickel and cobalt extraction values. For this purpose, 5 and 10 grams of $FeSO_4$, corresponding to 14.3 and 28.6 gpl of iron sulphate in solution, were added into the leach solution and the corresponding changes after the addition were observed. During these experiments the other constant process parameters and corresponding experimental results are given in Table 4.19 and Figure 4.11, respectively.

Table 4.19 Process parameters used to see the effect of FeSO₄ addition upon nickel and cobalt extractions

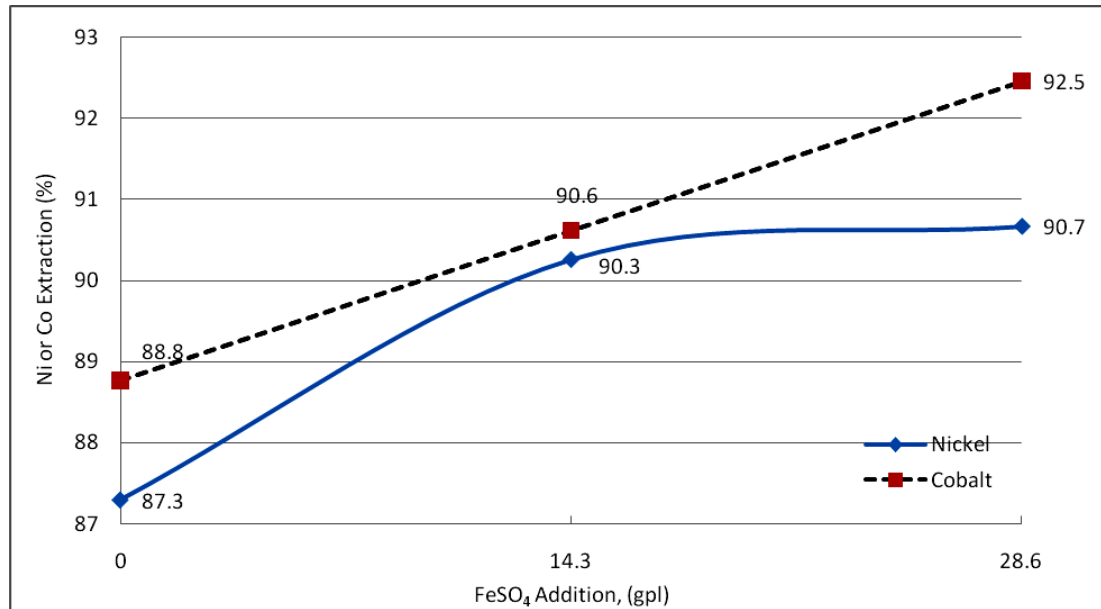| Ore Type:	Limonite
Leaching Temperature (°C)	255 °C
Leaching Duration (min.)	60
Acid/Ore Ratio (wt./wt.)	0.30
Particle Size (μ)	100% -850 μ
Solid/Liquid Ratio (wt./wt.)	0.30 (Excluding the acid amount)
Stirring Speed (rpm)	400 rpm

Figure 4.11 Effect of FeSO₄ addition upon degree of nickel and cobalt extractions

As stated in the literature, the addition of divalent iron led to a drastic fall in the reduction potential of the leach solution. To be more specific; the reduction potential of pregnant leach solution has decreased from 489 mV to 366 and 344 mV, respectively after the FeSO₄ additions and this reducing solution characteristics has led to the desired increase in the nickel and cobalt extraction values. This behavior

was explained by Tindall and Muir in such a way that the presence of divalent iron species facilitates bond breakage and aids iron oxide dissolution via electron transfer in the leach solution and thus increases the extraction of valuable metals from goethite and hematite matrix [40].

Table 4.20 Extraction behavior of other elements with $FeSO_4$ addition

$FeSO_4$	Fe (%)	Al (%)	Mg (%)	Mn (%)	As (%)	Cr (%)
No addition	1.9	19.8	82.8	78.3	2.7	2.2
14.3 gpl $FeSO_4$	6.2	28.5	81.0	80.7	4.7	1.9
28.6 gpl $FeSO_4$	12.0	28.6	65.5	75.7	4.9	1.3

Other than nickel and cobalt, the overall extraction results of other elements are given in Table 4.20. As seen from the table, the amount of iron present in the leach solution has increased due to iron sulphate addition as expected. Before ferrous ion addition, most of the iron in the solution was in the form of ferric ion, however after this addition the amount of ferrous ion was naturally increased which is the drawback of this addition during downstream processes. Moreover, more reducing solution characteristics of the leach liquor have also led to the increases in the extractions of aluminum and arsenic in the pregnant leach solution. However, there was a decreasing tendency in the extractions of magnesium and chromium as opposed to the others. In conclusion; besides the negative effect of ferrous ions during the downstream solution purification processes, this addition was effective in enhancing the extraction behaviors of nickel and cobalt upon changing the solution characteristics in a more reducing manner in terms of its reduction potential.

4.2.9 Effect of Cu₂O Addition upon Nickel and Cobalt Extractions

After obtaining somewhat encouraging results from the $FeSO_4$ addition experiments, further tests to see the positive effect of reducing solution characteristics were attempted with the addition of cuprous ions (Cu^+) into the leach solution. For this purpose, Merck grade Cu_2O as chemical reagent was used in order to provide 1, 2 and 3 gpl of initial cuprous ions concentration in the leach solution as a catalyst to favor the dissolution of hematite mineral.

The catalytic mechanism of cuprous ions is correlated with the ease of electron transfer between Cu^+ and iron species. According to the proposed data in the literature, the dissolution of iron species in the presence of cuprous ions is catalyzed according to the following electrochemical reaction and meanwhile nickel present within crystal lattice of iron minerals is predicted to be liberated into the solution [62, 63] ;

$$Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+} \tag{4.3}$$

The same constant test parameters were used as given in Table 4.19 as in the case of ferrous ion addition and the corresponding experimental findings of cuprous ion addition are given in Figure 4.12.
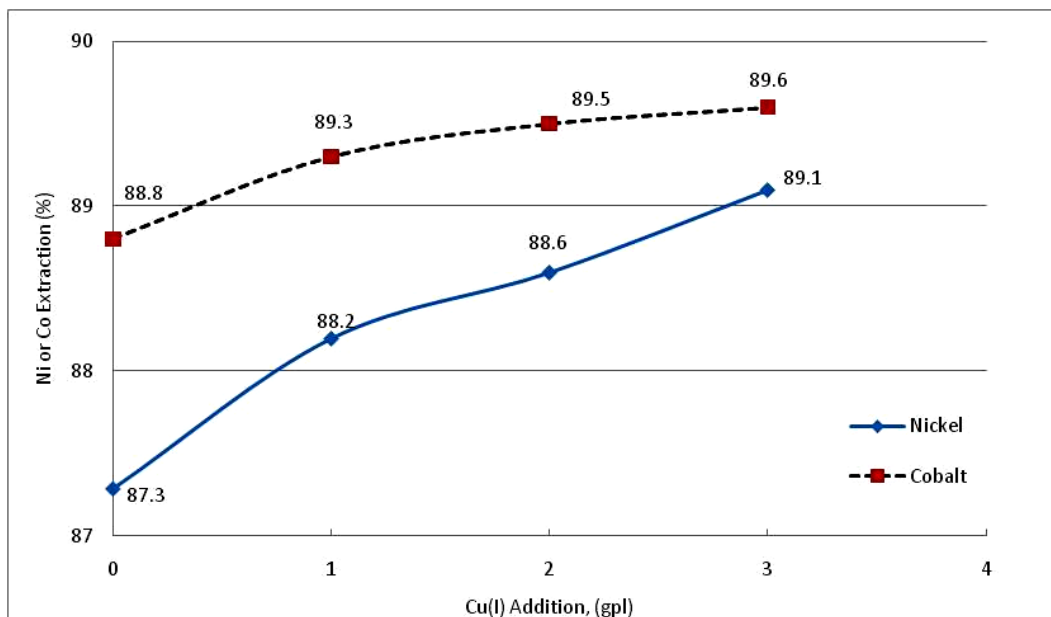
Figure 4.12 Effect of cuprous ion addition upon degree of nickel and cobalt extractions

According to the experimental findings, the positive catalytic effect of cuprous ions in extracting the nickel present in the crystal lattice of hematite mineral was observed similar to the previous studies performed by other researchers. In the case of cobalt, the previous work has reported that the extraction of cobalt could be enhanced when the potential of the solution was adjusted to a more reducing character [40]. This statement was verified by the addition of reducing ferrous ions into the leach solution. Similarly, upon the addition of cuprous ions in increasing amounts, the reduction potential of solution was lowered from 489 mV to 449, 440, and 410 mV, respectively. However, the expected enhancement in the extraction behavior of cobalt was not as good as the one obtained by ferrous ion addition. According to Figure 4.12, only a slight increase in the extraction of cobalt was observed when compared with nickel. Other than nickel and cobalt, there was not a remarkable change in the extraction behaviors of other elements. Therefore, the details of them are not given. In conclusion, similar to the effect of reducing ferrous ions in the leach solution, decreases in the reduction potential of the solution served effective in enhancing the extraction behaviors of nickel and cobalt to a limited extent. However, the findings were not as good as in the case of iron sulphate addition.

4.2.10 Effect of S Addition upon Nickel and Cobalt Extractions

Experimental evidences up to this stage have shown that there is a close relationship between the electrochemical nature of the leaching solution and the terminal nickel and cobalt extractions. To test this argument once more, the same constant test parameters were used as given in Table 4.19, and the addition of sulphur to change the reduction potential of the leach solution was planned in order to facilitate the electron transfer in the solution. For this purpose, 1, 2 and 3 kilograms of sulphur per ton of dry limonitic ore was mixed and added into the leach solution initially and the change in reduction potential of the solution was measured. For no-sulphur added experiment the reduction potential was 489 mV. However; upon the addition of sulphur, the reduction potentials were measured as 373, 349, and 334 mV, respectively as a result of increasing sulphur content. According to the measured values, sulphur seemed to be very effective in controlling the reduction potential of the leach solution. The extraction results of nickel and cobalt are presented in Figure 4.13.
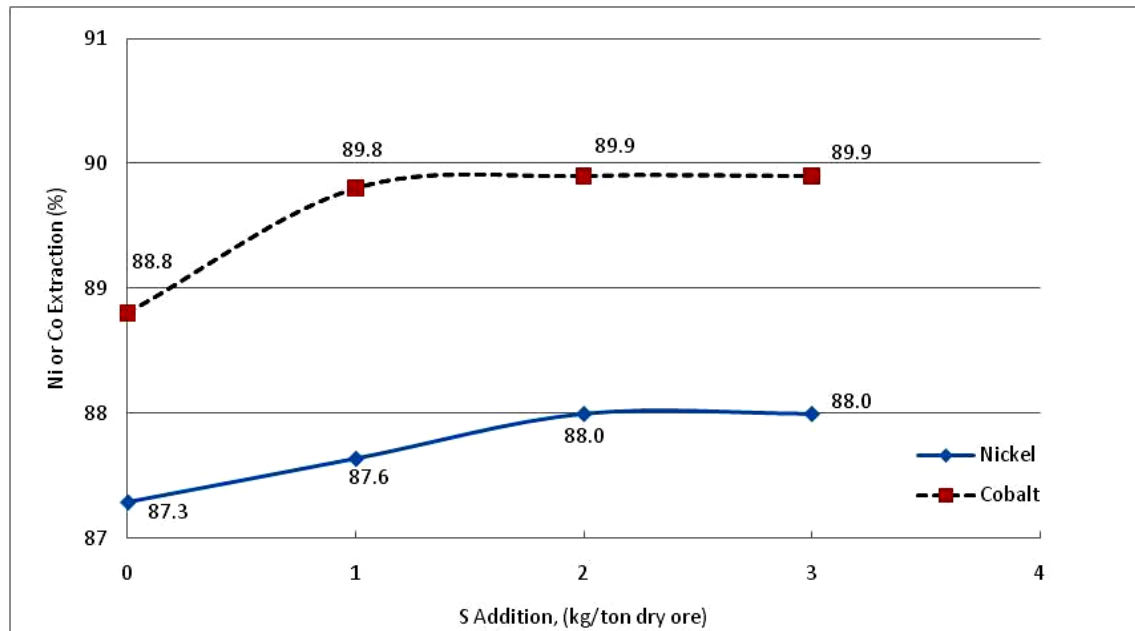

Figure 4.13 Effect of sulphur addition upon degree of nickel and cobalt extractions

According to the experimental findings, almost the same extraction behaviors of nickel and cobalt were observed as in the case of cuprous ion addition. Specifically, slight increases in the extractions of nickel and cobalt were seen as a result of more reducing solution character. Therefore, the same comment given in the case of cuprous ion addition may also be given in the case of sulphur addition for nickel and cobalt.

When other elements besides nickel and cobalt are considered, only a remarkable increase in the extraction of iron from 1.9% to 4.4, 6.0, and 8.8%, respectively, worth mentioning with increasing sulphur addition. Similar to iron a slight increase in the extraction of arsenic from 2.7% to 3.4, 3.9 and 4.1%, respectively, was realized. Finally, the extraction of magnesium has decreased from 82.8 to 69.6% linearly with the increasing sulphur addition, and there was not a considerable change in the extraction behavior of other elements in the final leach solution.

In conclusion; the addition of sulphur in order to get a more reducing leach solution seemed to affect the final nickel and cobalt extractions. However, the obtained results both from cuprous ion and sulphur additions were not as effective as in the case of ferrous ion addition. Therefore, it can be concluded that controlling the reducing character of the leach solution is effective in enhancing the final nickel and cobalt extractions, but it is not the reducing behavior of the solution itself but also the type of reagent used during the control of solution potential is important as experienced in the case of iron sulphate addition.

CHAPTER 5

CONCLUSION

During this thesis study, the main aim was to obtain the maximum nickel and cobalt extractions with the minimum acid consumption and impurity concentrations in the pregnant leach liquor. So throughout the experimental investigations, various process parameters were studied in order to find the most cost effective way of reaching this goal.

In the course of this study, the importance of understanding the mineralogical characteristics of the lateritic nickel ores as well as the reaction mechanism and chemistry of the process became very clear. In fact, the response of various minerals present in lateritic nickel ores in an acidic environment is strongly dependent upon the state of the valuable metals within the crystal lattice of the relevant minerals. For example, due to the presence of most of the nickel within the crystal lattice of goethite and smectite minerals in the nontronitic sample, about 98% of the nickel present in this lateritic sample was extracted easily within just one hour of leaching duration at 255 °C with 425 kilograms of sulphuric acid addition per ton of dry nontronitic ore. However; for the limonitic laterite sample, the presence of some of the nickel within the hematite mineral led to serious difficulties during leaching and extraction values remained mostly within the range of 86-88% with nearly the similar process parameters.

This was also verified by prior heat treatment of the limonitic sample at 350 °C. Upon transforming all of the goethite to hematite within the limonitic sample, the nickel extraction values dramatically decreased from 86-88% to 75-76% which

indicated that there is a strong correlation with the type of the mineral that valuable metal is present in and the ease of extraction. Therefore, most of the remaining study was concentrated on the limonitic sample and various strategies were devised in order to increase the lower nickel and cobalt extraction values with respect to the nontronitic sample. The results obtained from the experimental study are listed below:

1-) The leaching experiments conducted between the temperature ranges of 245-270 °C have shown that the increase in the pressure leaching temperature was very effective in increasing the desired nickel and cobalt extractions. However, there was a limit of this increase in the process temperature due to the concerns related to the process economics and technical considerations at high pressures. Generally speaking, in this study the leaching temperature was chosen as 255 °C due to design limitations at very high pressures and acceptable extraction rates were aimed to be obtained. However, the exact temperature should be decided according to the current prices of energy, capital and operating costs of the plant and the nickel-cobalt metal prices.

2-) The leaching duration experiments have indicated that prolonged leaching durations had a positive effect upon the desired nickel and cobalt extractions. Therefore; it was concluded that depending on the compensation of the production expenses due to longer leaching, the limonitic ore might be leached for longer durations than one hour for extra nickel and cobalt credits.

3-) The amount of most appropriate sulphuric acid addition was tested and it was noticed that 300 kilograms of sulphuric acid addition per ton of dry limonitic ore would be a proper selection for the desired nickel and cobalt extractions with the minimum consumption of costly consumables, limited impurity concentrations and minimum residual acid in the pregnant leach solution.

4-) Investigation of the particle size upon metal extractions has shown that extra particle surface area per unit weight provided by size reduction has enhanced the leaching behavior of the limonitic sample. Especially; the size reductions beyond 100% -425 μ gave very satisfactory results for nickel and cobalt extractions.

5-) Upon studying the effect of temperature, leaching duration, acid to ore ratio and particle size of the limonitic sample, the difficulty faced during the extractions of nickel and cobalt has led to the conclusion that the presence of primary hematite might be the possible cause of these low extraction results.

6-) In order to solve the problem caused by the presence of primary hematite mineral in the limonitic ore, the addition of small amounts of HCl together with H_2SO_4 was found to be effective in reaching this goal. However, the extremely corrosive behavior of this complex acid mixture complicated the process by attacking the leaching equipment.

7-) After HCl addition, the effect of Na_2SO_4 addition was investigated but the results were not satisfactory possibly due to the loss of nickel and cobalt in the newly formed natroalunite and natrojarosite precipitate as a result of extra sodium ions supplied to the solution. Also, possibly due to the formation of colloidal silica after Na_2SO_4 addition, the solid-liquid separation process has become more complicated which contributed to the observed nickel and cobalt losses.

8-) Finally, the reduction potential of leach solution was controlled according to the information given in literature in such a way that the presence of reducing species facilitated bond breakage of the iron oxide lattice and aided oxide dissolution via electron transfer in the leach solution. So, further tests were devised in order to reduce the reduction potential of the solution by adding suitable additives, thus increasing the extraction of valuable metals from goethite and hematite matrix. For this purpose, the effect of ferrous ions (Fe^{2+}), cuprous ions (Cu^+), and finally sulphur additions were investigated, respectively and these three additives were found to be

very effective in controlling the potential of the leach solution. Among them the addition of ferrous ions was found to be the most effective way of enhancing the desired nickel and cobalt extractions. The other additives were also found to be effective but the results were not as satisfactory as in the case of ferrous ion addition.

In order to obtain higher nickel and cobalt extractions, the testing procedure should continue and the following studies should be done in the future:

1. Organic acids such as oxalic, citric, acetic or their cocktails with sulphuric acid should be tried.
2. Detailed microprobe study on leach residues should be carried out in order to characterize the nickel losses in refractory minerals.
3. It's known that differences in mineral reactivity are due to mineral size, shape, degree of crystallinity and substitution of cations for iron in goethite and hematite structures. From these points of view, especially the hematite mineral present in limonitic ore should be examined in detail.
4. Effect of arsenic on solution chemistry and reaction kinetics of pressure leaching of lateritic ores should be investigated.
5. Neutralization and purification of pregnant leach solution as well as the recovery of Ni and Co should be studied.

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APPENDIX A

EXAMPLE OF THEORETICAL SULPHURIC ACID CONSUMPTION CALCULATION

Theoretical sulphuric acid consumption of metals present in the lateritic ore was performed by assuming as if all the metals were present in their 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.
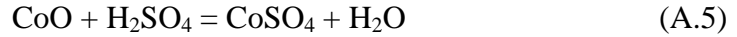
$$M_xO_y + y\ H_2SO_4 = M_x(SO_4)_y + y\ H_2O \tag{A.1}$$
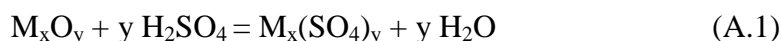
$$H_2SO_4 \text{ consumed (kg / ton of dry ore)} = \left[\frac{M_xO_y\ (\%)}{100} \times \frac{y \times MW_{H_2SO_4}}{MW_{MO}} \times 1000 \right] \tag{A.2}$$

Theoretical H_2SO_4 consumption of nickel oxide per ton of dry limonitic ore:
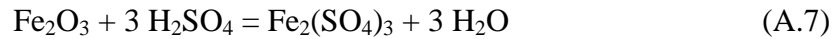
$$NiO + H_2SO_4 = NiSO_4 + H_2O \tag{A.3}$$
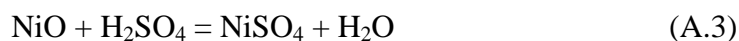
$$\left[\frac{1.63}{100} \times \frac{1 \times 98}{75} \times 1000 \right] = 21.3 \text{ kg } H_2SO_4 \tag{A.4}$$

Theoretical H₂SO₄ consumption of cobalt oxide per ton of dry limonitic ore:
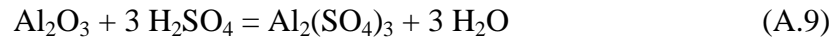
$$CoO + H_2SO_4 = CoSO_4 + H_2O \tag{A.5}$$

$$\left[\frac{0.11}{100} \times \frac{1 \times 98}{75} \times 1000\right] = 1.4 \text{ kg } H_2SO_4 \tag{A.6}$$

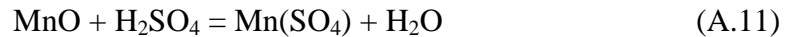**Theoretical H₂SO₄ consumption of iron oxide per ton of dry limonitic ore:**

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

$$\left[\frac{41.03}{100} \times \frac{3 \times 98}{160} \times 1000\right] = 753.9 \text{ kg } H_2SO_4 \tag{A.8}$$

Theoretical H₂SO₄ consumption of aluminum oxide per ton of dry limonitic ore:

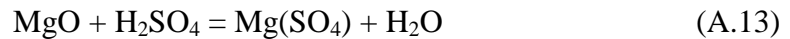$$Al_2O_3 + 3\ H_2SO_4 = Al_2(SO_4)_3 + 3\ H_2O \tag{A.9}$$

$$\left[\frac{5.83}{100} \times \frac{3 \times 98}{102} \times 1000\right] = 168.0 \text{ kg } H_2SO_4 \tag{A.10}$$

Theoretical H₂SO₄ consumption of manganese oxide per ton of dry limonitic ore:

$$MnO + H_2SO_4 = Mn(SO_4) + H_2O \tag{A.11}$$
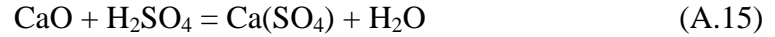
$$\left[\frac{0.59}{100} \times \frac{1 \times 98}{71} \times 1000\right] = 8.1 \text{ kg } H_2SO_4 \tag{A.12}$$

Theoretical H₂SO₄ consumption of magnesium oxide per ton of dry limonitic ore:

$$MgO + H_2SO_4 = Mg(SO_4) + H_2O \tag{A.13}$$

$$\left[\frac{2.26}{100} \times \frac{1 \times 98}{40} \times 1000\right] = 55.4 \text{ kg } H_2SO_4 \tag{A.14}$$

Theoretical H₂SO₄ consumption of calcium oxide per ton of dry limonitic ore:

$$CaO + H_2SO_4 = Ca(SO_4) + H_2O \qquad \text{(A.15)}$$
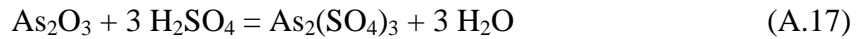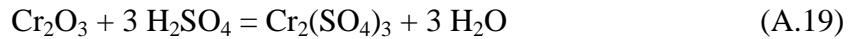
$$\left[\frac{1.27}{100} \times \frac{1 \times 98}{56} \times 1000\right] = 22.2 \text{ kg H}_2\text{SO}_4 \qquad \text{(A.16)}$$

Theoretical H₂SO₄ consumption of arsenic oxide per ton of dry limonitic ore:

$$As_2O_3 + 3 H_2SO_4 = As_2(SO_4)_3 + 3 H_2O \qquad \text{(A.17)}$$

$$\left[\frac{0.90}{100} \times \frac{3 \times 98}{198} \times 1000\right] = 13.4 \text{ kg H}_2\text{SO}_4 \qquad \text{(A.18)}$$

Theoretical H₂SO₄ consumption of chromium oxide per ton of dry limonitic ore:

$$Cr_2O_3 + 3 H_2SO_4 = Cr_2(SO_4)_3 + 3 H_2O \qquad \text{(A.19)}$$

$$\left[\frac{1.99}{100} \times \frac{3 \times 98}{152} \times 1000\right] = 38.5 \text{ kg H}_2\text{SO}_4 \qquad \text{(A.20)}$$

When 100% extraction of the metals present in the limonitic ore was assumed, it was found that 1082.2 kg of H_2SO_4 was required for ton of dry limonitic ore. Similarly, theoretical H_2SO_4 requirement of nontronitic ore was calculated to be 791.1 kg per ton of dry nontronitic ore. The actual H_2SO_4 requirements during pressure leach experiments were calculated according to the metal extraction values predicted by Sherritt Gordon and were found to be 300 and 425 kg, respectively for the limonitic and nontronitic nickel laterite ores of Gördes [37].

APPENDIX B

EXAMPLE OF METAL EXTRACTION CALCULATION

Metal extraction calculations of nickel and cobalt present in the lateritic ore were performed according to the AAS analysis results of the leach residue done by META Nikel ve Kobalt A.Ş. after pressure leaching. To be more specific; the extraction of nickel and cobalt was found according to Equation B.1 given below:

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

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 obtained at the optimum condition for limonitic ore given in Table B.1.

Table B.1 Experimental data of limonitic ore obtained at the optimum pressure acid leaching condition for nickel and cobalt

Limonite Ore and Corresponding Leach Residue Data	Nickel	Cobalt
Residue Weight (g)	139.87	139.87
Weight % Ni or Co in the Residue	0.17	0.008
Ore weight (g)	150	150
Weight % Ni or Co in the Ore	1.25	0.066

$$\text{\% Extraction of Ni} = \left[100 - \frac{139.87 * 0.17}{150 * 1.25} * 100 \right] = 87.3 \qquad \text{(B.2)}$$

$$\text{\% Extraction of Co} = \left[100 - \frac{139.87 * 0.008}{150 * 0.066} * 100 \right] = 88.8 \qquad \text{(B.3)}$$

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. To be more specific; the extraction calculation of the other metals was found according to Equation B.4 given below:

$$\text{\% Metal Extraction} = \left[\frac{\text{Preg Volume}(cc) * \text{ppm Metal}\left(\frac{\text{mg}}{\text{liter}}\right) * 10^{-6}}{\text{Ore Weight} * \text{\% Metal in the ore}} \right] * 100 \quad \text{(B.4)}$$

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

Table B.2 Experimental data of limonitic ore obtained at the optimum pressure acid leaching condition for iron and aluminum

Limonite Ore and Corresponding Pregnant Leach Solution Data	Iron	Aluminum
Preg. Volume (cc)	350.6	350.6
Fe or Al in the Preg. (ppm)	2296	2620
Ore weight (g)	150	150
Weight % Fe or % Al in the Ore	28.70	3.09

$$\text{\% Extraction of Fe} = \left[\frac{350.6 * 2296 * 10^{-6}}{150 * 28.70} *100\right] = 1.9 \tag{B.5}$$

$$\text{\% Extraction of Al} = \left[\frac{350.6 * 2620 * 10^{-6}}{150 * 3.09} *100\right] = 19.8 \tag{B.6}$$