

EXTRACTION OF NICKEL FROM LATERITIC ORES

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## ABSTRACT

### EXTRACTION OF NICKEL FROM LATERITIC ORES

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The aim of this study was to extract nickel and cobalt from the lateritic nickel ores of Gördes region by hydrometallurgical methods under the optimum conditions.

Limonitic and nontronitic types of Gördes lateritic nickel ores were used during experiments. Agitative and column leaching experiments at atmospheric pressure were conducted with various parameters; these were duration, temperature and initial sulfuric acid concentration of leach solution. It was shown that in agitative leaching, under the optimum conditions that were determined as 24 hours of leaching at 95°C with initial sulfuric acid concentration of 192.1 g/L for nontronite and 240.1 g/L for limonite, nickel and cobalt extractions were 96.0% and 63.4% for nontronite; 93.1% and 75.0% for limonite, respectively. Overall acid consumptions of ores were calculated as 669 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for nontronitic type nickel ore and 714 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for limonitic type nickel ore.

Column leaching experiments also showed that nickel and cobalt could be extracted from both ore types by heap leaching. Nontronite type of laterite was found to be more suitable for column leaching by sulfuric acid. In column leaching, the calculated nickel and cobalt extractions were 83.9% and 55.2% for nontronite after 122 days of leaching with 100 g/L sulfuric acid concentration. Acid consumption of nontronite was found to be 462 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore.

Keywords: Atmospheric Leaching, Laterite, Column Leaching, Agitative Leaching, Nickel, Cobalt.

## ÖZ

### LATERİTİK TİP NİKEL CEVHERLERİNDEN NİKEL KAZANIMI

Büyükakıncı, Ergin

Yüksek Lisans, Metalurji ve Malzeme Mühendisliği Bölümü

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Ocak 2008, 109 sayfa

Bu çalışmanın amacı, Gördes yöresinden temin edilmiş olan lateritik tipteki nikel cevherinden hidrometalurjik yöntemler kullanılarak optimum koşullarda nikel ve kobalt elde etmektir.

Gördes yöresinden temin edilen limonitik ve nontronitik tipte nikel cevherleri ile karıştırmalı ve kolon liçi deneyleri atmosferik basınç altında çeşitli değişkenler çalışılarak yürütülmüştür; bu değişkenler liç süresi, liç sıcaklığı ve liç çözeltisinin içindeki başlangıç sülfürik asit miktarıdır. Deneyler sonucunda her iki cevher için de optimum koşullar liç süresi için 24 saat, liç sıcaklığı için de 95°C olarak belirlenmiştir. Liç başlangıç asit konsantrasyonları ise nontronitik tip cevher için 192,1 gr/lt, limonitik tip cevher için 240,1 gr/lt olarak saptanmıştır. Belirlenen koşullarda nikel ve kobalt verimleri nontronitik tip cevher için sırasıyla %96,0 ve %63,4; limonitik tip cevher için ise sırasıyla %93,1 ve %75,0 olarak bulunmuştur. Optimum liç koşullarında yürütülen deneyler sonucunda belirlenen

sülfürik asit tüketimi deęerleri, nontronitik tip cevheri için 669 kg H<sub>2</sub>SO<sub>4</sub>/ton kuru cevher, limonitik tip cevheri için ise 714 kg H<sub>2</sub>SO<sub>4</sub>/ton kuru cevherdir. Yapılan kolon liçi deneyleri sonucunda nikel ve kobaltın yığın liçi yöntemiyle de liç çözeltilisine alınabileceęi belirlenmiştir. Nontronitik tip nikel cevherinin sülfürik asit ile kolon liçine daha yatkın olduęu görölmüştür. 100 gr/L sülfürik asit konsantrasyonu kullanılarak 122 günlük liç sonucunda elde edilen nikel ve kobalt liç verimleri sırasıyla %83,9 ve %55,2 olarak belirlenmiştir. Deney sırasında tüketilen sülfürik asit miktarı 462 kg H<sub>2</sub>SO<sub>4</sub>/ton kuru cevherdir.

Anahtar Kelimeler: Atmosferik Liç, Laterit, Kolon Liçi, Karıştırmalı Liç, Nikel, Kobalt.

*To my mother, Çiçek Büyükağınca*



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## TABLE OF CONTENTS

ABSTRACT.....	iv
ÖZ.....	vi
DEDICATION.....	viii
ACKNOWLEDGEMENTS.....	ix
TABLE OF CONTENTS .....	x
LIST OF TABLES .....	xii
LIST OF FIGURES .....	xiv
CHAPTER	
1 INTRODUCTION.....	1
2 LITERATURE REVIEW .....	3
2.1 Nickel and Its Properties .....	3
2.2 Nickel Reserves.....	4
2.3 Minerals and Origin of Nickel.....	9
2.4 Nickel Recovery Methods .....	12
2.4.1 Pyrometallurgical Treatment of Laterites.....	13
2.4.2 Hydrometallurgical Treatment of Laterites.....	15
2.4.2.1 Caron Process.....	16
2.4.2.2 High Pressure Acid Leaching .....	17
2.4.2.3 Atmospheric Pressure Acid Leaching .....	19
2.5 Thermodynamic and Kinetic Aspects of Atmospheric Leaching .....	34
3 EXPERIMENTAL MATERIALS AND METHODS.....	41
3.1 Materials .....	41

3.1.1 Lateritic Ores .....	41
3.1.1.1 Physical Characterization.....	42
3.1.1.2 Chemical Characterization.....	44
3.1.1.3 Mineralogical Characterization .....	48
3.2 Methods .....	52
3.2.1 Materials Sampling .....	52
3.2.2 Agitative Leaching Experiments.....	52
3.2.3 Column Leaching Experiments.....	54
3.3 Chemical Analysis.....	57
4 RESULTS AND DISCUSSION .....	58
4.1 Agitative Leaching .....	58
4.1.1 Effect of Time and Acid Concentration.....	58
4.1.2 Effect of Temperature .....	72
4.1.3 Effect of Particle Size.....	75
4.1.4 Multi-Step Agitative Leaching.....	78
4.2 Column Leaching .....	81
4.2.1 Effect of Acid Concentration .....	89
4.2.2 Effect of Flow Rate .....	92
5 CONCLUSION .....	96
REFERENCES .....	100
APPENDICES	
A. EXAMPLE OF RECOVERY CALCULATION .....	105
B. EXAMPLE OF THEORETICAL ACID CONSUMPTION CALCULATION .....	107

## LIST OF TABLES

### TABLES

Table 2.1	World nickel reserves [5].....	5
Table 2.2	Nickel ore reserves of Turkey, tons [6].....	5
Table 2.3	World nickel mine production, by country [8] .....	8
Table 2.4	Nickel bearing minerals [10].....	10
Table 2.5	Typical MHP product composition .....	30
Table 2.6	Typical MSP product composition .....	32
Table 3.1	Moisture contents of the representative ores .....	42
Table 3.2	Bulk densities of the as-received representative ores .....	42
Table 3.3	Densities of the representative ores.....	43
Table 3.4	Wet screen analysis results of Nontronite .....	43
Table 3.5	Wet screen analysis results of Limonite.....	44
Table 3.6	Chemical analyses of representative ores as wt % .....	45
Table 3.7	Normalized Ni, Fe, Co, As and Cr Distributions of Nontronite	46
Table 3.8	Normalized Ni, Fe, Co, As and Cr Distributions of Limonite ...	47
Table 4.1	Agitative leach recoveries of Nontronite .....	59
Table 4.2	Agitative leach recoveries of Limonite.....	60
Table 4.3	The optimum sulfuric acid concentration–time combinations..	68
Table 4.4	Analysis of Nontronite leach residue and calculated pregnant leach solution analysis at the optimum combination .....	70
Table 4.5	Analysis of Limonite leach residue and calculated pregnant leach solution analysis at the optimum combination .....	70

Table 4.6	Effect of temperature on agitative leach recoveries of Nontronite .....	73
Table 4.7	Effect of temperature on agitative leach recoveries of Limonite	74
Table 4.8	Effect of particle size on agitative leach recoveries of Nontronite .....	75
Table 4.9	Effect of particle size on agitative leach recoveries Limonite ....	76
Table 4.10	Screen analysis results of Nontronite (100% -0.589 mm).....	77
Table 4.11	Screen analysis results of leach residue of Nontronite .....	77
Table 4.12	Metal recoveries obtained in multi-step agitative leaching, without filtration of leach residue of Limonite.....	79
Table 4.13	Metal recoveries obtained in multi-step agitative leaching with filtration of leach residue of Limonite.....	80
Table 4.14	Metal recoveries obtained from pregnant leach solutions of Nontronite via AAS analysis .....	85
Table 4.15	Metal recoveries obtained from leach residues of Nontronite via ICP and XRF analyses .....	85
Table 4.16	Analyses of original ore sample and leach residues and calculated pregnant leach solutions analyses of experiments carried out with Nontronite.....	87
Table A.1	Experimental data obtained from agitative leaching of Nontronite .....	105

## LIST OF FIGURES

### FIGURES

Figure 2.1	Nickel consumption by use .....	6
Figure 2.2	Nickel supply vs. consumption [7] .....	7
Figure 2.3	Nickel prices between 1998 and 2007 [9] .....	9
Figure 2.4	Typical laterite type ore body formation [12] .....	12
Figure 2.5	Treatment of laterites .....	13
Figure 2.6	Pyrometallurgical treatments of laterites.....	14
Figure 2.7	Caron Process.....	17
Figure 2.8	Pressure acid leaching flow-sheet.....	18
Figure 2.9	Idealized kinetics of nickel dissolution from limonitic/saprolitic blends [39] .....	36
Figure 2.10	Pourbaix diagram of nickel–water system [41].....	37
Figure 2.11	Pourbaix diagram of iron–water system [41].....	38
Figure 2.12	Pourbaix diagram of cobalt–water system [41].....	39
Figure 3.1	DTA/TGA diagram of Nontronite .....	49
Figure 3.2	DTA/TGA diagram of Limonite.....	49
Figure 3.3	XRD pattern of Nontronite .....	51
Figure 3.4	XRD pattern of Limonite .....	51
Figure 3.5	Agitative leaching system .....	53
Figure 3.6	Column leaching system .....	55
Figure 4.1	Nickel recoveries at 2N sulfuric acid concentration with respect to time in agitative leaching .....	60

Figure 4.2	Nickel recoveries at 4N sulfuric acid concentration with respect to time in agitative leaching .....	61
Figure 4.3	Nickel recoveries at 5N sulfuric acid concentration with respect to time in agitative leaching .....	61
Figure 4.4	Iron recoveries at 2N sulfuric acid concentration with respect to time in agitative leaching.....	62
Figure 4.5	Iron recoveries at 4N sulfuric acid concentration with respect to time in agitative leaching.....	62
Figure 4.6	Iron recoveries at 5N sulfuric acid concentration with respect to time in agitative leaching.....	63
Figure 4.7	Cobalt recoveries at 2N sulfuric acid concentration with respect to time in agitative leaching .....	63
Figure 4.8	Cobalt recoveries at 4N sulfuric acid concentration with respect to time in agitative leaching .....	64
Figure 4.9	Cobalt recoveries at 5N sulfuric acid concentration with respect to time in agitative leaching .....	64
Figure 4.10	Arsenic recoveries at 2N sulfuric acid concentration with respect to time in agitative leaching .....	65
Figure 4.11	Arsenic recoveries at 4N sulfuric acid concentration with respect to time in agitative leaching .....	65
Figure 4.12	Arsenic recoveries at 5N sulfuric acid concentration with respect to time in agitative leaching .....	66
Figure 4.13	Chromium recoveries at 2N sulfuric acid concentration with respect to time in agitative leaching .....	66
Figure 4.14	Chromium recoveries at 4N sulfuric acid concentration with respect to time in agitative leaching .....	67

Figure 4.15 Chromium recoveries at 5N sulfuric acid concentration with respect to time in agitative leaching .....	67
Figure 4.16 XRD Patterns of Nontronite before agitative leaching (a) and after agitative leaching (b).....	71
Figure 4.17 XRD Patterns of Limonite before agitative leaching (a) and after agitative leaching (b).....	72
Figure 4.18 Effect of temperature on agitative leach recoveries of Nontronite .....	73
Figure 4.19 Effect of temperature on agitative leach recoveries of Limonite.....	74
Figure 4.20 Particle size distributions of ore sample and leach residue of Nontronite .....	78
Figure 4.21 Initial column leach recoveries of Nontronite.....	81
Figure 4.22 Initial column leach recoveries of Limonite .....	82
Figure 4.23 Nickel recoveries of Nontronite in column leaching .....	83
Figure 4.24 Iron recoveries of Nontronite in column leaching.....	84
Figure 4.25 Cobalt recoveries of Nontronite in column leaching .....	84
Figure 4.26 XRD Patterns of Nontronite before column leaching (a), after Experiment 1 (b) and after Experiment 2 (c) .....	89
Figure 4.27 Nickel recoveries of Nontronite at different acid concentrations in column leaching .....	90
Figure 4.28 Iron recoveries of Nontronite at different acid concentrations in column leaching .....	91
Figure 4.29 Cobalt recoveries of Nontronite at different acid concentrations in column leaching .....	91
Figure 4.30 Nickel recoveries of Nontronite at different flow rates in column leaching.....	93



Figure 4.31 Iron recoveries of Nontronite at different flow rates in column leaching.....	94
Figure 4.32 Cobalt recoveries of Nontronite at different flow rates in column leaching.....	94

## CHAPTER 1

### INTRODUCTION

Today, nickel is widely used in different areas of applications like alloying element in steelmaking, chemical and aerospace applications, magnets and rechargeable batteries.

To date, conventional nickel production from sulfide type nickel ores based on pyrometallurgical routes has been followed to supply nickel products for the metal market. However, due to dwindling nickel production from sulfide ores, extraction of nickel from oxide ores (laterites) is becoming more popular. In addition to that, about 80% of known nickel reserves and even greater portion of cobalt reserves of the world are found in lateritic type nickel deposits [1]. Consequently, this makes laterites more important in the future of nickel production process.

Methods to extract nickel from lateritic ores fall into two categories; pyrometallurgical methods and hydrometallurgical methods. A majority of pyrometallurgical processes (ferronickel and matte smelting) use conventional flow-sheet involving drying, calcination/reduction and electric furnace smelting. The two principal hydrometallurgical processes generally

practiced are Caron process and high pressure acid leaching (HPAL) process.

Atmospheric pressure acid leaching is a new technique that employs heap or agitative leaching of the laterites with dilute sulfuric acid, purification of the leach liquor produced by chemical precipitation at atmospheric pressure and recovery of nickel and cobalt from the purified leach liquor either by chemical precipitation or by solvent extraction and electrowinning.

The objective of this study was to extract nickel and cobalt from lateritic ores obtained from Gördes (Manisa) region of Turkey. Agitative and column leaching experiments were conducted by using dilute sulfuric acid solutions at atmospheric pressure to determine the optimum conditions.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Nickel and Its Properties

Nickel is a transition element, silvery white in color that exhibits a combination of ferrous and nonferrous metal properties [2]. Among others, nickel is the 7<sup>th</sup> most abundant transition element found in the Earth's crust.

Nickel is symbolized with Ni in the periodic table with its atomic number of 28 and atomic weight of 58.69 kg/kg-atom. Nickel has a density of 8.908 g/cm<sup>3</sup> and a relatively high melting point of 1453°C. Nickel forms a face-centered cubic crystal structure and it is ferromagnetic below its Curie point of 357°C. Nickel also shows good conductivity of heat and electricity.

Nickel is resistant to corrosion against air, seawater, alkalis and non-oxidizing acids. In contrast, nickel is attacked by aqueous ammonia solutions. It dissolves in dilute mineral acids and is insoluble in concentrated nitric acid. Among its -1, 0, +2, +3 and +4 oxidation states, +2 oxidation state is the most important oxidation state of Nickel. Nickel is stable in aqueous solutions in its +2 oxidation state.

The physical properties of nickel depend on its purity, physical state and its pretreatment [3]. Metallic nickel is a hard, lustrous, silvery white metal. On the other hand, major importance of nickel lies in its addition to other metals in alloying. Nickel increases strength, toughness and corrosion resistance of metal upon alloying. The most familiar are nickeliferous alloys used in stainless steel and copper nickel alloys used in coinage metal.

## **2.2 Nickel Reserves**

Estimated nickel concentration in the Earth's crust is 0.008% and ranks 24<sup>th</sup> in abundance of elements [4]. World reserves of nickel deposits which contain an average of 1% or greater nickel are given in Table 2.1 [5]. Although nickel is more abundant than many metals, there are few ore bodies which are commercially profitable. Nickel ores that are commercially important can be classified into two groups; sulfide and oxide (laterite) nickel deposits. About 80% of known reserves are lateritic type nickel deposits whereas 20% are sulfide type nickel deposits. In addition to known reserves, extensive resources of nickel are located in manganese and cobalt bearing nodules in ocean floors.

In Turkey, both sulfide and laterite type nickel ores are present. Laterite types of ores are mainly located in Çaldağ and Gördes regions of Manisa whereas sulfide type ores are located in Bursa and Bitlis [6]. Although new nickel deposits have been discovered in Mihalıççık (Eskişehir), Banaz (Uşak) and Divriği (Sivas), due to incomplete reserve studies, adequate information could not be obtained about the reserves of deposits. Nickel ore reserves of Turkey are given in Table 2.2.

**Table 2.1** World nickel reserves [5].

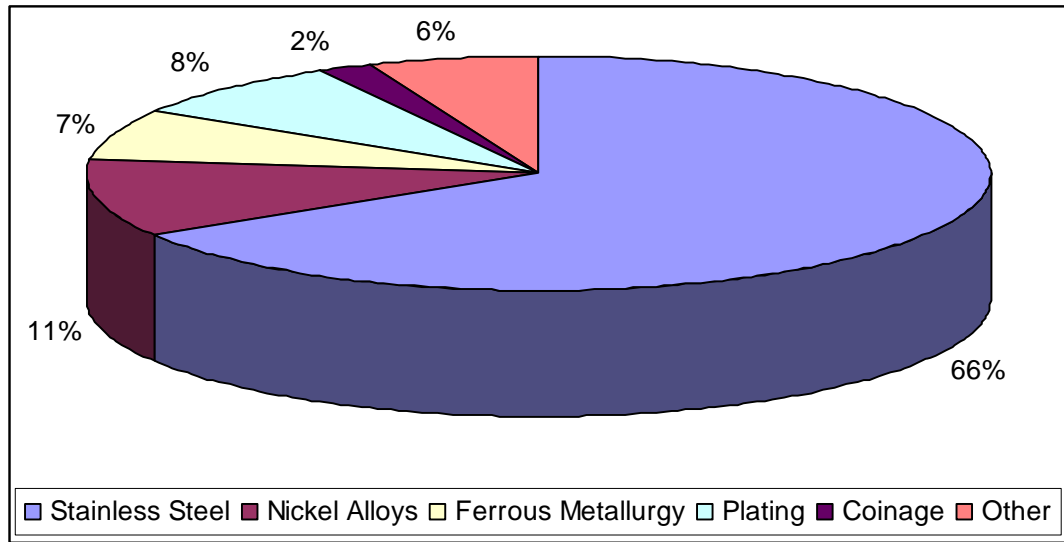
<b>Country</b>	<b>Proven Reserve (tons)</b>	<b>Possible Reserve (tons)</b>
<b>Australia</b>	24,000,000	27,000,000
<b>Botswana</b>	490,000	920,000
<b>Brazil</b>	4,500,000	8,300,000
<b>Canada</b>	4,900,000	15,000,000
<b>China</b>	1,100,000	7,600,000
<b>Colombia</b>	830,000	1,100,000
<b>Cuba</b>	5,600,000	23,000,000
<b>Dominic Republic</b>	720,000	1,000,000
<b>Greece</b>	490,000	900,000
<b>Indonesia</b>	3,200,000	13,000,000
<b>New Caledonia</b>	4,400,000	12,000,000
<b>Philippines</b>	940,000	5,200,000
<b>Russia</b>	6,600,000	9,200,000
<b>South Africa</b>	3,700,000	12,000,000
<b>Venezuela</b>	560,000	630,000
<b>Zimbabwe</b>	15,000	260,000
<b>Other Countries</b>	2,100,000	5,900,000

**Table 2.2** Nickel ore reserves of Turkey, tons [6].

<b>Region</b>	<b>Probable Reserve</b>	<b>Possible Reserve</b>
<b>Manisa - Çaldağ</b>	37,900,000	-
<b>Manisa - Gördes</b>	68,500,000	-
<b>Bursa - Yapköy</b>	82,000	81,000
<b>Bitlis - Pancarlı</b>	-	15,500

Steelmaking industry is the primary consumer of nickel. More than 60% of the world nickel production is used in stainless steelmaking to increase corrosion resistance and strength of stainless steels. Nickel alloy production takes second place in usage of nickel. Nickel alloys are used in wide range

of applications due to their high temperature resistance and fracture toughness. Ferrous metallurgy, coinage and plating are other major application areas of nickel. Graphical representation of nickel usage by use is given in Figure 2.1.

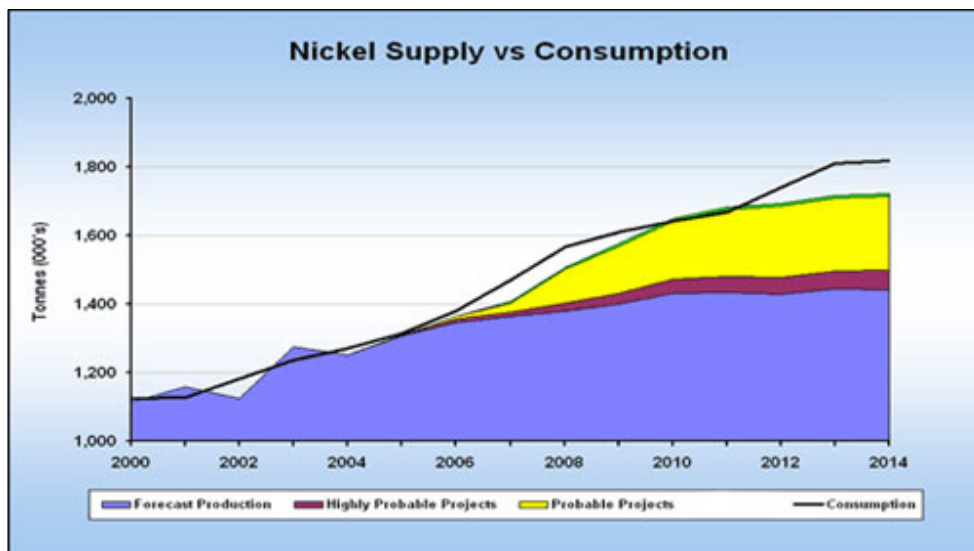


**Figure 2.1** Nickel consumption by use.

Past and future trends of nickel in metal market are well summarized in Figure 2.2 [7]. According to the diagram, the world nickel production increases annually and will increase further in the next decade. This prediction is supported by the statistical data obtained from the annual world nickel production between 2001 and 2005 which is given in Table 2.3 [8]. Again from the diagram, it can be stated that when a gap occurs between supply and demand, nickel prices increase.

Current increment in nickel prices which is given in Figure 2.3 is due to insufficient annual production to meet the growing global nickel demand, mostly driven by stainless steel industry [9].

However, current high nickel prices make treatment of low grade nickel ores profitable. This is going to pioneer probable projects to take place and contribute to annual nickel production. As foreseen in supply vs. consumption diagram, even all probable projects take place, the gap between supply and consumption is going to be present in the future and nickel prices are going to stay at high levels.



**Figure 2.2** Nickel supply vs. consumption [7].



**Table 2.3** World nickel mine production, by country [8].

Country	Capacit (tons of nickel produced)				
	2001	2002	2003	2004	2005
<b>Australia</b>	205,000	207,800	210,000	178,100	189,000
<b>Botswana</b>	26,714	28,600	32,740	32,980	28,000
<b>Brazil</b>	45,456	44,928	45,160	45,200	52,000
<b>Burma</b>	10	10	10	10	10
<b>Canada</b>	194,058	189,297	163,244	186,694	198,369
<b>China</b>	51,500	53,700	61,000	75,600	77,000
<b>Colombia</b>	52,962	58,196	70,844	75,032	89,031
<b>Cuba</b>	72,585	71,355	67,306	71,933	72,000
<b>Dominic Republic</b>	39,120	38,859	45,253	46,000	46,000
<b>Finland</b>	2,600	3,120	3,640	3,700	3,400
<b>Greece</b>	20,830	22,670	21,410	21,700	23,210
<b>Indonesia</b>	102,000	123,000	143,000	133,000	160,000
<b>Kazakhstan</b>	--	--	--	--	193
<b>Macedonia</b>	2,970	5,149	5,555	5,300	8,100
<b>Morocco</b>	151	109	126	130	130
<b>New Caledonia</b>	117,734	99,841	112,013	118,279	111,900
<b>Norway</b>	2,529	2,052	169	181	150
<b>Philippines</b>	27,359	26,532	19,537	16,973	26,636
<b>Russia</b>	320,000	310,000	300,000	315,000	315,000
<b>South Africa</b>	36,443	38,546	40,842	39,853	42,497
<b>Turkey</b>	--	--	640	40	1,000
<b>Ukraine</b>	1,500	2,000	2,000	2,000	2,000
<b>Venezuela</b>	13,600	18,600	20,700	20,468	20,000
<b>Zimbabwe</b>	10,120	8,092	9,517	9,520	9,500
<b>World Wide Total</b>	1,350,000	1,350,000	1,370,000	1,400,000	1,480,000



**Figure 2.3** Nickel prices between 1998 and 2007 [9].

### 2.3 Minerals and Origin of Nickel

Nickel does not occur as an individual element. Instead, minerals contain nickel as a substitution of another element in their atomic structure which is mainly iron (Fe) and magnesium (Mg), depending on the mineral type. The most important nickel bearing minerals and their formulas are given in Table 2.4 [10]. From these minerals listed, only pentlandite, garnierite (also known as saprolite) and limonite are economically profitable.

Nickel sulfide deposits are generally associated with rock bodies rich in iron and magnesium. These types of rock bodies are called ultramafic rocks and can be found in both volcanic and plutonic settings [2, 10]. Many of the

sulfide deposits occur at great depth. As given at the table above, in magmatic sulfide deposits the principal ore mineral bearing nickel is pentlandite.

**Table 2.4** Nickel bearing minerals [10].

Type of Mineral	Mineral	Ideal Formula	Nickel Content (%)
<b>Sulfides</b>	Pentlandite	$(\text{Ni,Fe})_9\text{S}_8$	34.22
	Millerite	$\text{NiS}$	64.67
	Heazlewoodite	$\text{Ni}_3\text{S}_2$	73.30
	Polydymite	$\text{Ni}_3\text{S}_4$	57.86
	Siegenite	$(\text{Co,Ni})_3\text{S}_4$	28.89
	Violarite	$\text{Ni}_2\text{FeS}_4$	38.94
<b>Arsenides</b>	Niccolite	$\text{NiAs}$	43.92
	Rammelsbergite	$\text{NiAs}_2$	28.15
	Gersdorffite	$\text{NiAsS}$	35.42
<b>Antimonides</b>	Breithauptite	$\text{NiSb}$	32.53
<b>Silicates &amp; Oxides</b>	Garnierite	$(\text{Ni,Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_8$	$\leq 47$
	Nickeliferrous Limonite	$(\text{Fe,Ni})\text{O}(\text{OH}) \cdot n\text{H}_2\text{O}$	low

Oxide (laterite) type ore bodies were formed during laterization, which is a tropical weathering process of ultramafic rocks that is favored by warm climate and abundant rainfall [11]. Peridotite is the rock that is attacked by carbon dioxide rich ground water. Peridotite is mainly composed of olivine, a silicate of iron and magnesium that contains small amounts of nickel.

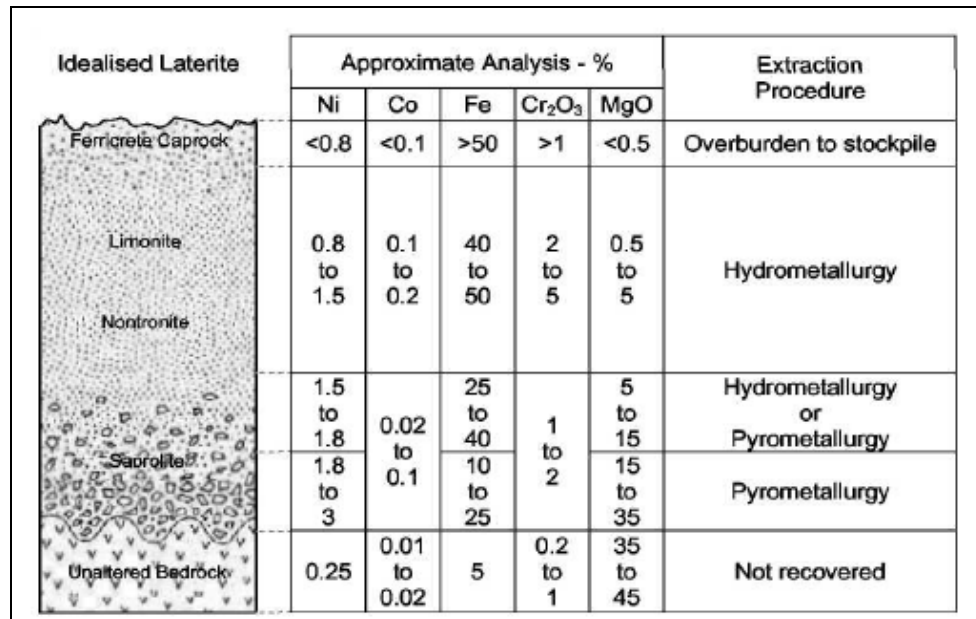
During laterization, olivine decomposes and iron, magnesium and nickel dissolve into solution. Due to oxidizing conditions, iron precipitates as goethite and hematite. On the other hand nickel and magnesium close to

surface are washed and re-deposited at deeper zones by precipitating as hydrous silicates as the acidity of water decreases due to reactions that occur in soil. This long term process that can take up to million years, results in a layer formation rich in nickel. Therefore, in lateritic ore bodies nickel concentration tends to increase towards to the bottom of the zone.

In limonitic parts, nickel is found in goethite  $[(\text{Fe},\text{Ni})\text{O}.\text{OH}]$  whereas in saprolitic parts, nickel bearing clay minerals are serpentine  $[(\text{Mg},\text{Fe},\text{Ni})_3\text{Si}_2\text{O}_5(\text{OH})_4]$  and smectite  $[\text{Na}_{0.3}\text{Al}_2(\text{Si}_{3.7}\text{Al}_{0.3})\text{O}_{10}.\text{(OH)}_2]$ . Although lateritic ore bodies differ from each other due to non-uniform laterization process throughout the world, a typical lateritic ore body formation with its approximate chemical analysis and possible treatment procedure is given in Figure 2.4 [12].

Upper part of laterite section consists of an iron cap which is mainly goethite [5]. This section is followed by a limonitic zone that is rich in iron content. Distinct boundary formations do not exist throughout the ore body between one zone and another, transition zones occur instead of this as laterization is a time consuming process.

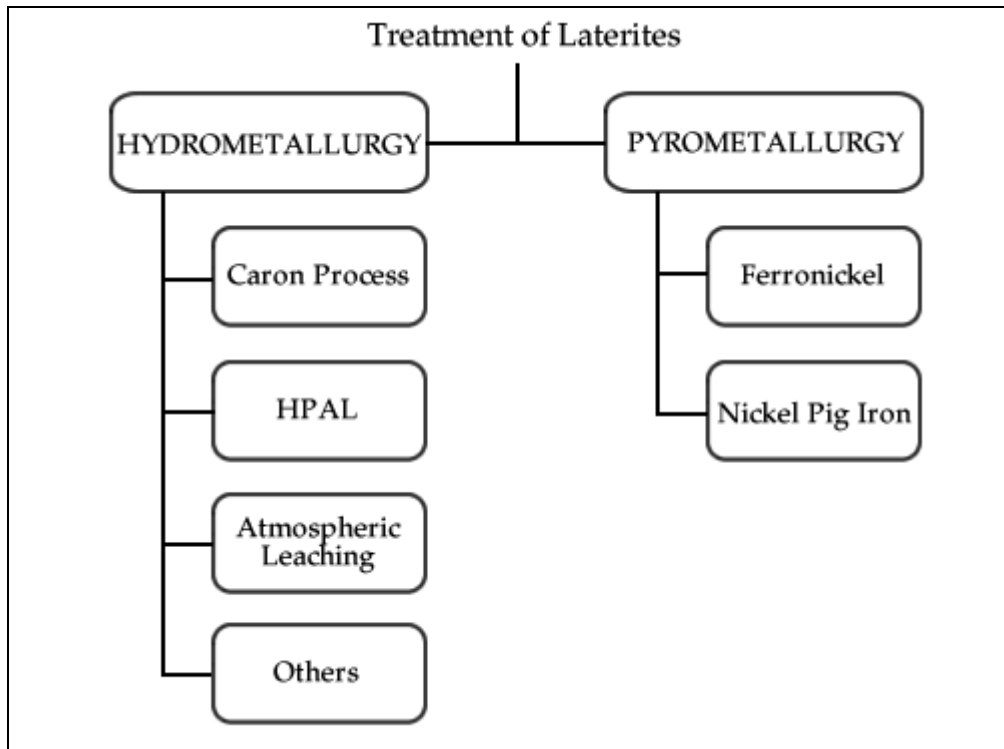
Nontronite  $[(\text{Fe}^{4++})(\text{Si}_{7.33}\text{Al}_{0.67})\text{O}_{20}.\text{(OH)}_4]$  or Fe-smectite is the name given for the transition zone between limonite and saprolite. Moving down to saprolitic region, nickel and magnesium contents of the ore increase whereas iron content decreases due to the effect of laterization process.



**Figure 2.4** Typical laterite type ore body formation [12].

## 2.4 Nickel Recovery Methods

Extractive metallurgy of nickel is dependent on the type of ore body. Although recovery of nickel from sulfide ores is based on only pyrometallurgical methods, flow-sheets of nickel extraction from laterites are based on both pyrometallurgical and hydrometallurgical methods which are schematically given in Figure 2.5.



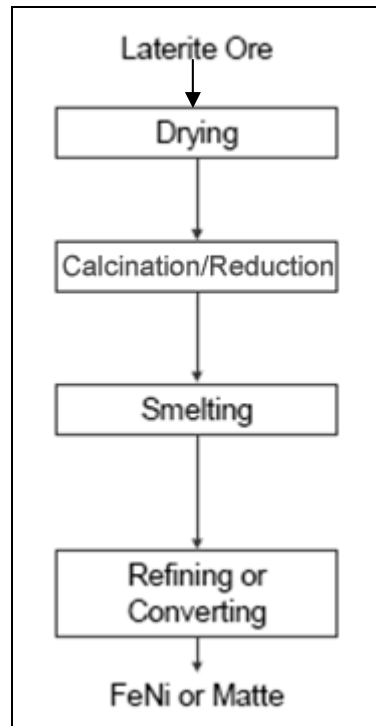
**Figure 2.5** Treatment of laterites.

### 2.4.1 Pyrometallurgical Treatment of Laterites

A majority of pyrometallurgical processes (ferronickel and matte smelting) use conventional flow-sheet involving drying, calcination/reduction and smelting as given in Figure 2.6.

Lateritic ores contain high moisture content (up to 45%) additional to chemically bounded water in hydroxide form [3]. Drying is carried out to reduce moisture content of the ore to eliminate problems in the following steps. Calcination/reduction process taking place around 800–900°C results in dehydration and pre-reduction of oxides to metals. Smelting step achieves selective reduction of nickel and high grade nickel product is

obtained; iron-nickel alloy called ferronickel or in case of sulfur addition, high grade nickel matte.



**Figure 2.6** Pyrometallurgical treatments of laterites.

Limonitic ores are not suitable for this process due to their high iron content. Considerable amounts of heat must be supplied to laterites due to their high moisture content. As pyrometallurgical processes are energy intensive, production costs per ton of nickel produced are high.

Nickel pig iron production is a newer way of treating lateritic ores via pyrometallurgical methods. Although it was first developed 50 years ago, it was not put into commercial scale production until the Chinese government has forced to shut down small scale blast furnaces that were producing pig

iron. All those small scale producers changed their production flow-sheet to nickel pig iron production with zero initial cost.

Nickel pig iron is a pig iron containing 3–5% nickel. It contains much less nickel than conventional ferronickel (25–40%) and has higher concentrations of sulfur and phosphorous. The ore, containing low grade nickel, is processed in small blast furnaces similar to pig iron production. Process consists of sintering and smelting in blast furnace. The resulting nickel pig iron is currently being used to produce 200 series stainless steels.

#### **2.4.2 Hydrometallurgical Treatment of Laterites**

Hydrometallurgical or combination of pyrometallurgical and hydrometallurgical treatments of laterite ores rely on the homogeneous chemical and mineralogical distributions within the laterites. As described in previous sections, in laterites nickel is mainly present in goethite, serpentine, smectite and in manganese oxides together with cobalt (asbolane). Since cobalt is associated with nickel, processes to extract nickel are also applicable to extract cobalt. Therefore, hydrometallurgical treatments are based on extracting nickel and cobalt from iron, magnesium and manganese oxides, based on leaching procedures.

Various hydrometallurgical routes have been studied for laterite treatment. On commercial level, only two of them have been commercialized to recover nickel and cobalt; namely Caron process and pressure acid leaching with sulfuric acid. However, in pilot plant level, commercial application of atmospheric heap leaching with sulfuric acid is being tried out in Çaldağ

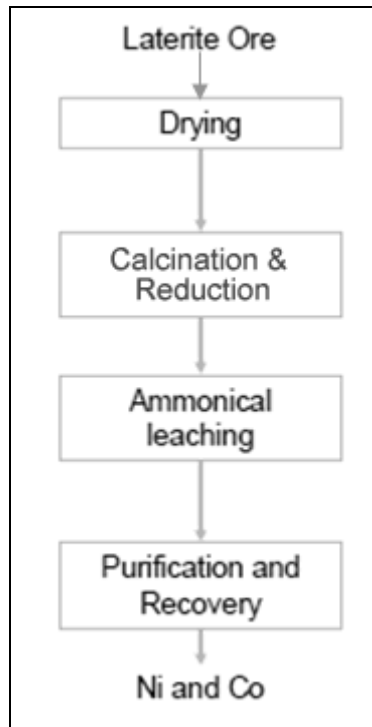


(Turkey), Murrin Murrin (Western Australia) etc. Also in Kazakhstan, a new nickel plant (Shevchenko Project by Oriel Resources) is under construction based on agitative tank leaching.

#### **2.4.2.1 Caron Process**

Caron process was patented by M.H. Caron in 1924 for the treatment of laterites via reduction roasting followed by ammoniacal ammonium carbonate  $[\text{NH}_3\text{-(NH}_4)_2\text{CO}_3]$  leaching. Caron process is currently being used in Nicaro (Cuba), Punta-Gorda (Cuba) and Yabulu (Australia).

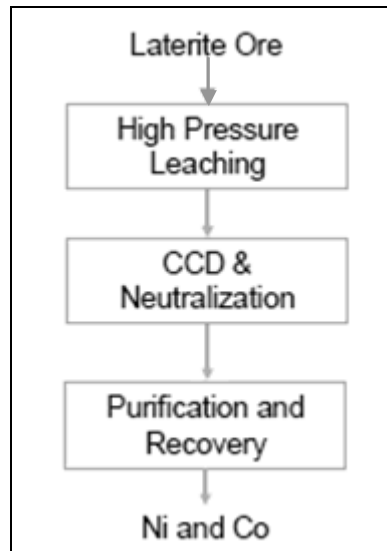
The Caron process could be used for limonitic ores or a mixture of limonite and saprolite. Initially, drying step takes place to reduce moisture content of the ore. Following the drying step, ore is reduced in roaster by fuel oil in a deficiency of air at around  $700^\circ\text{C}$ . In the last step of Caron process, metals are extracted by leaching in an ammoniacal solution which was followed with purification and heating of pregnant leach solution to recover nickel as  $3\text{Ni(OH)}_2\cdot 2\text{NiCO}_3$  precipitate. Since 1988, pregnant leach solution is being treated by solvent extraction to separate nickel and cobalt. An organic reagent is used to extract nickel selectively from the pregnant solution. Then nickel is recovered from solvent by stripping with concentrated ammoniacal ammonium carbonate solution. Disadvantage of Caron process is its high energy intensive steps. In economical aspect, high energy consumption brings additional production cost. Therefore, Caron process has a limited application today because of its higher cost per ton of nickel produced, when compared to high pressure acid leaching process. Flow-sheet of Caron process is given in Figure 2.7.



**Figure 2.7** Caron Process.

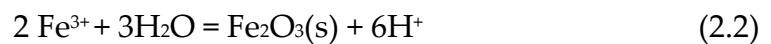
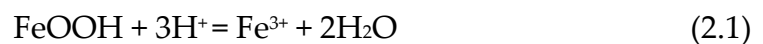
#### **2.4.2.2 High Pressure Acid Leaching**

Pressure acid leaching (high pressure acid leaching) was introduced to eliminate high energy consuming steps of Caron process by direct leaching of the ore. On commercial level, it is being used in Moa Bay (Cuba), Coral Bay (Philippines), Murrin Murrin (Australia) and Cawse (Australia). Generalized flow-sheet of pressure acid leaching process is given in Figure 2.8. Direct leaching avoids drying and reduction steps and therefore results in energy savings throughout the treatment.



**Figure 2.8** High pressure acid leaching flow-sheet.

Pressure acid leaching of laterites involves extraction of nickel and cobalt by leaching ground ore with sulfuric acid solution at high temperature and pressure at which goethite dissolution takes place by Reaction 2.1. Then, it is followed by immediate iron precipitation as hematite described by Reaction 2.2.



This precipitation behavior enables very low iron/nickel (Fe/Ni) ratio in the leach liquor in which nickel dissolution takes place by Reaction 2.3 and does not precipitate during process.



Following leaching, counter current decantation (CCD), neutralization and precipitation steps takes place and nickel is recovered together with cobalt.

Also in literature, it was reported that nickel and magnesium can be precipitated as mixed sulfate salts if acidity at reaction temperature is below 0.1 mol/L. Application of this process is limited by the high acid consuming minerals within the ore although overall acid consumption is low (300-450 kg H<sub>2</sub>SO<sub>4</sub>/ton of dry lateritic ore) due to regeneration of sulfuric acid during iron precipitation. Especially high magnesium oxide levels increase the acid consumption and therefore increase operation costs of the process.

Main disadvantage of high pressure acid leaching is the cost of titanium autoclaves used in process and the erosion of high pressure flash valves. Titanium is preferred in autoclave manufacturing due to its reliable corrosion resistance at sulfuric acid leaching environment. But due to their large dimensions (3-5 meters in diameter and 15-30 meters in length) titanium autoclaves bring high initial investment and maintenance costs throughout their process life cycle. With its disadvantages, in the absence of a competitive process, pressure acid leaching is still the most popular route for the treatment of low grade laterites to produce nickel.

#### **2.4.2.3 Atmospheric Pressure Acid Leaching**

Leaching of laterites at atmospheric pressure has been proposed to replace the pressure acid leaching process. Proposed leaching process includes direct leaching of laterites with inorganic and organic acids by either agitative or heap leaching.

Heap leaching of metallic ores is a widely used process especially in copper industry. In heap leaching, crushed ore is heaped and then fed by acid solution from the top. As the acid solution permeates through the heap, metals within the ore dissolve and get into the leach solution. Collected pregnant leach solution is then treated chemically for metal precipitation and recovery.

In agitative leaching, crushed and ground ore is leached in leaching tanks. Agitative leaching is capable of taking advantage of temperature effect during leaching. Temperature can be controlled by heating the tank for more rapidly metal dissolution in acid solution due to faster kinetics and therefore shorter process duration. After leaching, pregnant leach solution is taken to metal recovery as in heap leaching.

Agitative acid leaching with various types of acids were studied for hydrometallurgical treatment of laterites. Chander [13] stated that at the same concentration, the amount of nickel recovery increases in the order of perchloric, nitric, sulfuric, hydrochloric, hydrofluoric and oxalic acid after carrying out experiments with Indian limonitic laterites. It was also stated that nickel dissolution was strongly related to amount of iron dissolution that resulted in contaminated pregnant leach solution and high acid consumption.

Atmospheric chloride leach is one of the developing methods for laterite treatment. Nickel and cobalt can be recovered in this method by using a mixed chloride lixiviant without significant iron and magnesium dissolution in the pregnant solution. It is followed by standard precipitation

methods to obtain nickel and cobalt hydroxide product from pregnant leach solution [14].

Biohydrometallurgy or bacterial metal extraction concept was introduced to use microorganisms in extraction of nickel and cobalt from laterites [15]. In this method, bio-assisted heap leaching process takes place via using several microorganisms that produce acids during their metabolic cycle. Heap is leached with acids produced by microorganisms. Leaching can take place by either directly placing microorganisms within the heap or indirectly production of acids with microorganisms followed by spraying over the heap.

Until recently, atmospheric pressure leaching of laterites using sulfuric acid has been receiving less attention compared to pressure acid leaching. First study about the process was conducted by Apostolidis et al. [16]. Reduction roasting was carried out prior to leaching due to high magnesium content of the lateritic ore. It was reported that reduction with  $H_2$  at 500–900°C followed by sulfuric acid leaching at 70°C at atmospheric pressure results in 80% nickel recovery and only 8% magnesium recovery in pregnant leach solution where without reduction equal amounts of nickel and magnesium recoveries have been obtained.

Furthermore, Canterford [17] reported that nickel could be recovered 90% with an acid consumption of 1000 kg/ton ore from Australian laterites. In his study, it was stated that the conditions required to achieve about 90% nickel recovery were dependent on the types of nickel bearing minerals present in the ore, leaching temperature and sulfuric acid concentration.

Sukla et al. [18] studied nickel and cobalt recovery from roasted copper converter slag via leaching at atmospheric pressure with ammonium sulfate and sulfuric acid. It was reported that under the optimum conditions, nickel and cobalt recoveries were found to be 81% and 85% with ammonium sulfate and 90% and 99% with sulfuric acid, respectively. Also, it was reported that roasting process using sulfuric acid has resulted in lowering the iron content down to about 3% in the sulfate product without much affecting the recovery of other metal values.

Panagiotopoulos et al. [19] studied the agitative leaching behavior of Greek laterites. It was stated that the recovery values were highly dependent on leaching temperature and acid concentration where pulp density and grain size had smaller effect. It was reported that 75–80% of nickel and cobalt could be recovered by using 3N sulfuric acid concentration, pulp density of 15% and leaching for 4 hours at 95°C by agitative leaching. Iron and magnesium recoveries were said to be 55% and 80%, respectively. Overall acid consumption was stated as 1600 kg/ton ore. It was stated that counter-current leaching set-up with two or more stages could be used to reduce the acid consumption down to 650 kg/ton ore.

The same author also studied leaching behavior of laterites from other regions of Greece with the three stage counter-current set-up that was proposed [20]. Single batch leaching tank was used to demonstrate agitative leaching behavior with several steps of leaching at 95°C and constant sulfuric acid concentration. Pulp densities of 25 and 30 wt% solid were studied at 1.5 hours leaching duration per stage. Similar recovery values were reported with previous study whereas acid consumption was reported

as 850 kg/ton ore. Also a simple column leaching experiment was carried out to demonstrate heap leaching but although Fe/Ni ratio in the pregnant leach solution obtained was 5.25/1, nickel recovery was very low to be considered as a feasible treatment.

Agitative leaching behavior of laterites from Çaldağ region of Turkey was studied by Arslan et al. [21] as the preliminary study about the heap leaching process which is currently under development on pilot plant scale. It was found that nickel recoveries increased with respect to time and leaching temperature. Nickel and cobalt recoveries were reported as 90.2% and 96.8%, respectively, after 8 hours of agitative leaching with 200 g/L sulfuric acid concentration at 80°C.

Agitative leaching was also studied by Curlook with the highly serpentinized saprolite fractions of laterites from New Caledonia [22]. It was reported that 85% nickel and high amount of cobalt recoveries were achieved by sulfuric acid leaching at temperatures between 80–100°C in an hour. Overall acid consumption of the leaching process was reported as 80–100% of the ore used by weight. It was also stated that the sulfuric acid leaching is economically applicable at places where a cheap sulfuric acid source is available.

High acid consumption of atmospheric leaching was the driving force of new studies focusing on new processes to lower the acid used during leaching. Liu et al. [23] developed a multi-step leaching process for ore deposits consisting of both limonite and saprolite fractions. In this process limonite is leached first with dissolving goethite which is the nickel bearing



mineral. Then, saprolite is introduced together with goethite-containing seed to the system resulting in precipitation of dissolved iron in the form of goethite and released acid is used in leaching of saprolite. It was reported at the end of agitative leaching tests, 91–100% nickel and 83–90% cobalt extractions were achieved in 10–12 hours of leaching at 95–105°C. Reported acid/ore ratios were 0.59 to 0.74 with a saprolite/limonite ratio of 0.61/1.25. This proposed treatment method was patented by the author [24].

Combinations of various leaching techniques about multi-step leaching processes involving both atmospheric pressure and high pressure leaching were studied and patented. A patent granted in USA gives detailed information about combination leaching process of laterites in which limonitic fraction of ore body is leached in autoclaves followed by addition of saprolite and secondary leaching at atmospheric pressure [25]. In this process iron is precipitated as jarosite. This process has been tested in pilot plant level and commercialized in Ravensthorpe nickel plant located in Australia [26].

A reverse process is also discovered and patented [27]. In this process limonite is leached at atmospheric pressure and then following to saprolite addition to pulp, pressure acid leaching takes place.

Another combination of agitative leaching at atmospheric pressure together with pressure acid leaching was studied and patented [28]. In this process low and medium magnesium bearing ore fractions are leached in autoclaves whereas high magnesium bearing ores are leached at atmospheric pressure.

Then, both leach residues are re-leached at atmospheric pressure and pregnant leach solution is taken to precipitation.

In the literature of sulfuric acid leaching at atmospheric pressure, together with agitative leaching, studies on heap leaching were also conducted. A well developed approach to treat lateritic ores by heap leaching was developed and patented by Agatzini et al. [29] after carrying out studies on laboratory scale. This method employs heap leaching of the ore with dilute sulfuric acid at ambient temperature, purification of the leach liquor produced by chemical precipitation at atmospheric pressure, and recovery of nickel and cobalt from the purified leach liquor either by chemical precipitation or by solvent extraction and electrowinning.

Agatzini et al. [30] reported their work by simulating heap leaching behavior of lateritic ores supplied from Litharakia (Greece) with column leaching experiments. It was reported that acrylic columns with 100 mm internal diameter and heights between 1 m and 2.5 m and 8 to 22 kg of ore samples were used during experiments. Ore was agglomerated prior to leaching to prevent permeability problems and sulfuric acid solution was circulated with a peristaltic pump. The pH of solution was kept constant during leach cycle by titration. It was reported that nickel and cobalt recoveries were 85% and 70%, respectively, after 40 days together with iron dissolution around 20%. It was also stated that dissolving metals resulted in contamination of cations of nickel in pregnant leach solution which was unavoidable. Obtained recovery values showed that heap leaching favored selective leaching of laterites compared to other atmospheric leaching techniques due to lower Fe/Ni ratio in pregnant leach solution which was

given as 15/1 in the ore and 5/1 in pregnant leach solution. It was concluded that for ores with nickel bearing minerals other than goethite, fast kinetics of dissolution could be obtained due to faster dissolution of magnesium.

Agatzini et al. [31] published another study about leaching behaviors of poor nickel laterites supplied from Kastoria (Greece) using both agitative and heap leaching techniques. Column leaching was carried out in columns which were 10 cm in diameter with various heights. Flow rate of leach solution was stated as 4 L/day with a sulfuric acid concentration of 2N–3N. At the end of 10 days of column leaching, nickel and cobalt recoveries were reported as 60% and 45%, respectively for serpentinitic laterites; 50% and 30% for limonitic laterites. Overall acid consumption was given as 40 kg sulfuric acid for serpentine and 27 kg for limonite per kg of nickel extracted. Fe/Ni ratio was stated as 37/1 in the limonitic ore which was reduced to 5/1 in pregnant leach solution. In the case of serpentinitic laterite, Fe/Ni ratio was reduced to 1-1.4/1 from 6.2-6.8/1.

In agitative leaching tests of serpentinitic laterite, with an acid consumption of 55 kg sulfuric acid per kg nickel, nickel and cobalt recoveries were achieved as 74% and 51%, respectively in 2 hours. Negative effect of high calcite content on both permeability of columns and overall acid consumption was reported together with the high acid consumption problem due to presence of magnesium in serpentine phase of laterites.

Initial results of heap leach pilot plant located in Çaldağ indicated 79.4%, 82.7%, 30.0%, 78.9% and 37.1% recoveries for nickel, cobalt, iron, manganese and aluminum, respectively after 548 days of leaching with 528 kg

H<sub>2</sub>SO<sub>4</sub>/ton dry ore of acid consumption [32]. Heap was constructed with 3251 dry tons of -30 mm agglomerated limonite. It was reported that the leaching period consisted of three leaching phases namely, neutralization, primary and secondary stage in which primary phase was faster due to extraction of easily accessible nickel. Following to primary phase, it was reported that leaching rates became stable.

Studies about the atmospheric leaching of laterites show variations in results of recoveries of nickel and cobalt as well as dissolved amount of iron in pregnant leach solution. This can be explained by the variations in lateritic formation occurrence throughout the world. However, all studies carried out have common results as high acid consumption and high residual acid concentration together with the high dissolved iron content of pregnant leach solution. Liberating nickel from nickel containing minerals is the key point of atmospheric leaching process and also it is the leading issue affecting the parameters like recoveries, Fe/Ni ratio and acid consumption as stated above.

Due to nature of leaching process, most of the metals within the ore are dissolved in leach solution and should be taken to precipitation for selective recovery of wanted species. As iron is precipitated during pressure acid leaching, iron removal is not an important issue in HPAL. On the other hand, iron removal is the primary concern in purification of leach liquors obtained with atmospheric leaching.

Heap leach liquors differ from high pressure acid leaching liquors with their low process temperature, low nickel and high iron content. Also leach

liquor of heap leaching process is solid free unlike the pressure acid leach liquor in which 20–25% solid by weight is present.

Removal of iron from pregnant leach solutions was studied widely in literature and well summarized by Mei [33]. In the mentioned study, three different removal methods together with kinetics were reported. Iron precipitates as goethite, hematite and jarosite. Hematite precipitation does not take place under atmospheric leaching conditions. Jarosite precipitation is possible with the addition of a precipitating agent which is selected from the group consisting of alkali metals, ammonium ions and mixtures. The amount of precipitating agent is at least the stoichiometric amount needed to precipitate all the iron. Reaction of jarosite precipitation is given in Reaction 2.4.



In Reaction 2.4, M corresponds to Na, Li, K, or NH<sub>4</sub>. However in industry, Na or NH<sub>4</sub> is preferred due to economical reasons.

Flow-sheets about nickel recovery from heap leach liquors were studied and summarized by Willis [34]. It was stated that the main recovery procedures to be followed based on the intermediate nickel product are mixed hydroxide precipitation (MHP) and mixed sulfide precipitation (MSP).

MHP process enables iron, aluminum and chromium removal prior to nickel and cobalt precipitation but consequently some nickel loss during removal of other elements is unavoidable. Also manganese removal does

not take place during process which makes this route not suitable for ores with high manganese content. Manganese removal should be carried out additionally after precipitation if needed. Therefore, MHP process, as itself, is applicable to ores with low manganese content (nickel/manganese should be less than 3/1), especially saprolitic type laterites.

In MHP, the first stage of iron removal takes place by neutralizing residual sulfuric acid with limestone addition and adjusting the pH to 2.5–3.0 at which gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is precipitated together with iron and chromium. Series of tanks, each heated up to 70–90°C, are used for iron removal and removal period takes around 2–3 hours in each tank. During iron removal air is introduced to the system to remove carbon dioxide formed and oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . Secondary iron removal takes place with continuous limestone addition and by adjusting the pH to 4.4–4.8. Although iron can be removed in single stage by adjusting the pH to 4.4–4.8, this increases nickel losses. Remaining iron together with chromium and most of aluminum are precipitated with small amounts of nickel and cobalt losses. Solution is then taken to next stage of precipitation whereas discharge is recycled to the system with pregnant leach solution.

Nickel-Cobalt hydroxide precipitation takes place in two stages to minimize manganese content of the end product. In first stage around pH 7.2–7.5, nickel, zinc, copper and cobalt are precipitated with magnesia or caustic soda (sodium carbonate) addition. Residual elements left from iron removal step are also precipitated. Precipitated mixed hydroxide is washed, dried and shipped to nickel refineries. Typical dried MHP product composition is

given in Table 2.5. It should be noted that the original MHP product contains 35–45% moisture.

In the second stage of mixed hydroxide precipitation, residual nickel and cobalt are recovered at a pH level of 7.5–8.0 together with some amounts of remaining manganese. Manganese removal, if required, is the last step of MHP process. Lime addition results in a pH level of 8.5–9.0 at which manganese is precipitated as manganese hydroxide. Throughout the MHP process, operating temperatures and times may vary depending on the ore type but generally temperatures around 60–90°C are preferred for faster kinetics.

**Table 2.5** Typical MHP product composition.

<b>Component</b>	<b>wt % (dry)</b>
Nickel	30–39
Cobalt	2–5
Zinc	1–4
Copper	1–4
Manganese	4–9
Magnesium	3–5
Iron	<0.5
Aluminum	<0.5
Sulfur	3–5

Mixed Sulfide Precipitation (MSP) is another approach for selective removal of nickel and cobalt from iron, aluminum, chromium and manganese. MSP is a preferred route for limonitic ores due to their high Fe/Ni ratio. Also, it is applicable to other type of ores which have Ni/Mn ratio more than 3/1.

In MSP, pregnant leach solution and hydrogen sulfide gas are mixed in a reactor for pre-reduction stage. Product slurry is then degassed and taken to partial neutralization. Pre-reduction enables selective precipitation of copper and transformation of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  however; this is undesirable as  $\text{Fe}^{2+}$  remain in solution through the other precipitation steps. On the other hand, hydrogen sulfide has serious negative effects on environment and people so it should be stored and processed carefully.

Partial neutralization following pre-reduction, is similar to one in MHP, at which gypsum is precipitated by limestone addition and adjusting the pH to 2.5–3.0 resulting in precipitation of most of iron, chromium and some of aluminum. The solution is taken to precipitation step where it is heated and blended with seed slurry. Introducing hydrogen sulfide to the system yields metal sulfide precipitation on the seed particles. Submarine autoclaves (Moa Bay) or vertical reactor vessels (AMAX process) can be used during precipitation. The discharge is washed and recovered as filter cake.

Iron removal is an optional stage which is related to pre-reduction stage. As stated above in pre-reduction  $\text{Fe}^{2+}$  transformation occurs and results in high  $\text{Fe}^{2+}$  content of solution. Iron is removed to avoid viscosity problems in leaching as the solution is recycled and taken to leaching after MSP. Typical dried MSP product composition is given in Table 2.6. It should be noted that the original MSP product contains 10–15% moisture.

To compare the two methods, although precipitating as MSP provides better selectivity than MHP, the process is more complex and the use of this toxic gas is extremely undesirable. In addition, a number of methods



employed in processing the intermediate product cannot tolerate sulfur as an impurity.

Moreover, the initial investment and process costs are relatively lower in MHP process as well as more energy input is required for MSP due to hydrogen sulfide gas production. As a result, nickel hydroxide precipitation may be the preferred alternative. Unfortunately, the precipitation of nickel hydroxide by alkali addition is not very selective. Therefore, conditions should be optimized well including temperature and pH of all steps to minimize nickel and cobalt losses especially during iron removal.

**Table 2.6** Typical MSP product composition.

Component	wt % (dry)
Nickel	55–61
Cobalt	3–6
Zinc	2–6
Copper	1–5
Manganese	<0.1
Magnesium	<0.1
Iron	<0.8
Aluminum	<0.1
Sulfur	34–36

Alternative routes to be followed in order to separate nickel and cobalt from iron in pregnant leach solutions are currently under development. A conceptual technique called Molecular Recognition Technology (MRT) uses a resin that loads selectively nickel and cobalt in acidic environment. Then, nickel and cobalt are eluted from that resin under strong acidic

environment yielding high quality end product. On the same basis, another approach is to selectively load iron on to resins from pregnant leach solutions. Due to inadequate laboratory and pilot plant work, economical aspects of using resins are unknown. Major problems of resin usage are loading the wanted metal selectively from solution and elution of loaded metal from resin at the end of process.

Resin in pulp (RIP) is another proposed technique to remove iron from agitative tank leaching pregnant solutions. Difference between MRT and RIP is that the RIP is applied before solid-liquid separation step at which resin selectively loads iron from pulp [34].

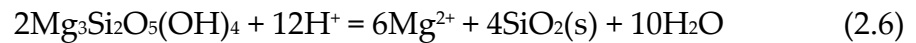
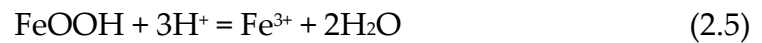
Solvent extraction (SX) which is used to separate metals based on their relative distributions in two different immiscible liquids, is another method for selective iron removal. This method was investigated in literature mainly by using di-2-ethylhexylphosphoric acid (D2EHPA) [35]. In this method, D2EHPA is loaded with  $Fe^{3+}$  ions without any reported nickel and cobalt co-extraction. However, efficient stripping and recovery of iron from loaded organic phase are still under development.

SX method was tried in commercial level in Bulong nickel refinery between April 1999 and October 2003 [36]. In the flow-sheet, two step SX was proposed; first cobalt was extracted from pressure acid leach solution via Cyanex 272, following nickel solvent extraction was via Versatic 10. However, commercialized operation was not able to achieve design goals and product quality; therefore it was shut down.

Major problem of nickel and cobalt SX is the co-extraction of impurities. Extractants used for SX have generally higher affinities for other metals present in leach solution than nickel and/or cobalt. Moreover, in some cases, metal loading process is irreversible.

## 2.5 Thermodynamic and Kinetic Aspects of Atmospheric Leaching

As stated above, in atmospheric leaching, the key point is extraction of nickel from nickel containing minerals. Consequently, depending on the nickel bearing mineral's behavior in acidic environment, dissolution rates change. Dissolution reactions for limonitic and saprolitic laterites in sulfuric acid media are given in Reactions 2.5 and 2.6, respectively.



Cobalt leaching from asbolane by mild reduction with sulfur dioxide is reported in literature by Reaction given in 2.7. It was found out that by maintaining the potential of the leach slurry at about 900 mV versus the standard hydrogen electrode (SHE) with sulfur dioxide gas, reduction of ferric iron is substantially avoided and cobalt dissolution is enhanced [37].



Also in literature, it is stated that to increase the recovery values of cobalt, sulfur can be introduced to the system as sodium metabisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ )

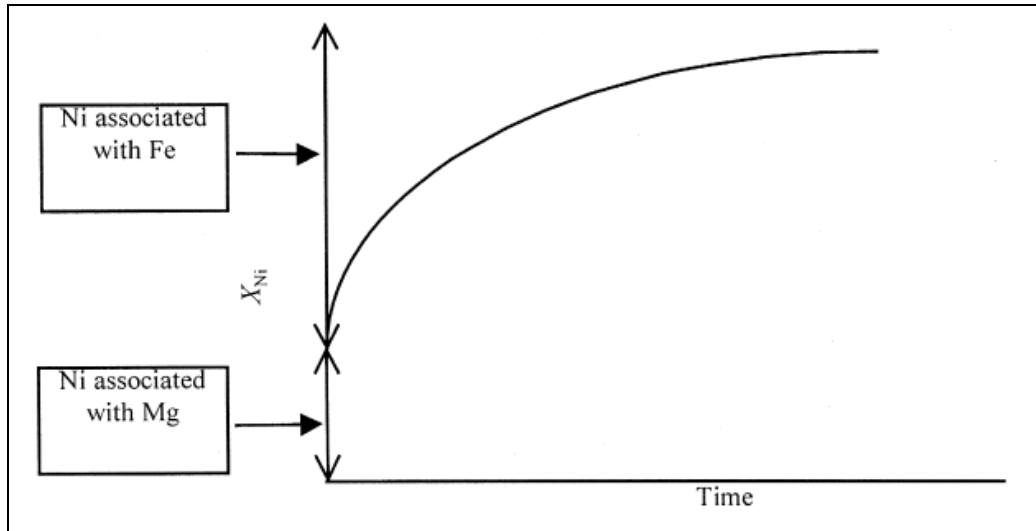
or elemental sulfur instead of sulfur dioxide gas [38]. Sodium metabisulphite addition to sulfuric acid results in increased recoveries of both nickel and cobalt, with the most marked improvement being found with respect to cobalt recovery. Proposed amount of addition is 5 g/L for sulfuric acid solution and should be kept constant during leaching process.

The cobalt recoveries in most leach tests will remain limited due to the high oxidation reduction potentials (ORP) in the pulps. It is known from past experience that the ORP needs to be below 800 mV to achieve high cobalt recovery. This is due to the association between cobalt and manganese minerals. The manganese will not leach readily in the +4 state as in  $\text{MnO}_2$ , so a reductant needs to be added to alter the Mn to the +2 form. For this purpose usually sodium metabisulphite is used as the reductant.

Dissolution kinetics of laterites was studied by Rubisov et al. [39] to derive a kinetic model of nickel dissolution in laterites. By determining the acidity at temperature, more reliable data could be used for kinetic equations. Although experiments were carried out in pressure acid leaching conditions, it is applicable to other leaching processes except iron precipitation.

Due to natural occurrence of saprolites, as stated above, nickel is found as a substituting element of magnesium. In this study, it was reported that magnesium dissolution takes place very rapidly therefore, nickel associated with magnesium dissolves instantaneously in sulfuric acid media from limonitic/saprolitic blends. On the other hand, the dissolution of nickel which is associated with iron is a time-dependent process. Idealized

dissolution kinetics of nickel obtained in that study is schematically given in Figure 2.9 [39].



**Figure 2.9** Idealized kinetics of nickel dissolution from limonitic/saprolitic blends [39].

Potential–pH diagrams are used to demonstrate equilibrium relationships between species in aqueous solutions [40]. The Eh–pH diagrams of nickel–water, iron–water and cobalt–water systems are given in Figure 2.10, Figure 2.11 and Figure 2.12, respectively [41].

As can be seen from the Pourbaix diagram of nickel, nickel is stable and soluble as  $Ni^{2+}$  and  $HNiO_2^-$  ions in aqueous solutions. However, the dominant soluble species is determined by the potential and pH of solution. In atmospheric leaching, due to presence of acidic media nickel is stable as  $Ni^{2+}$  in leach solutions.

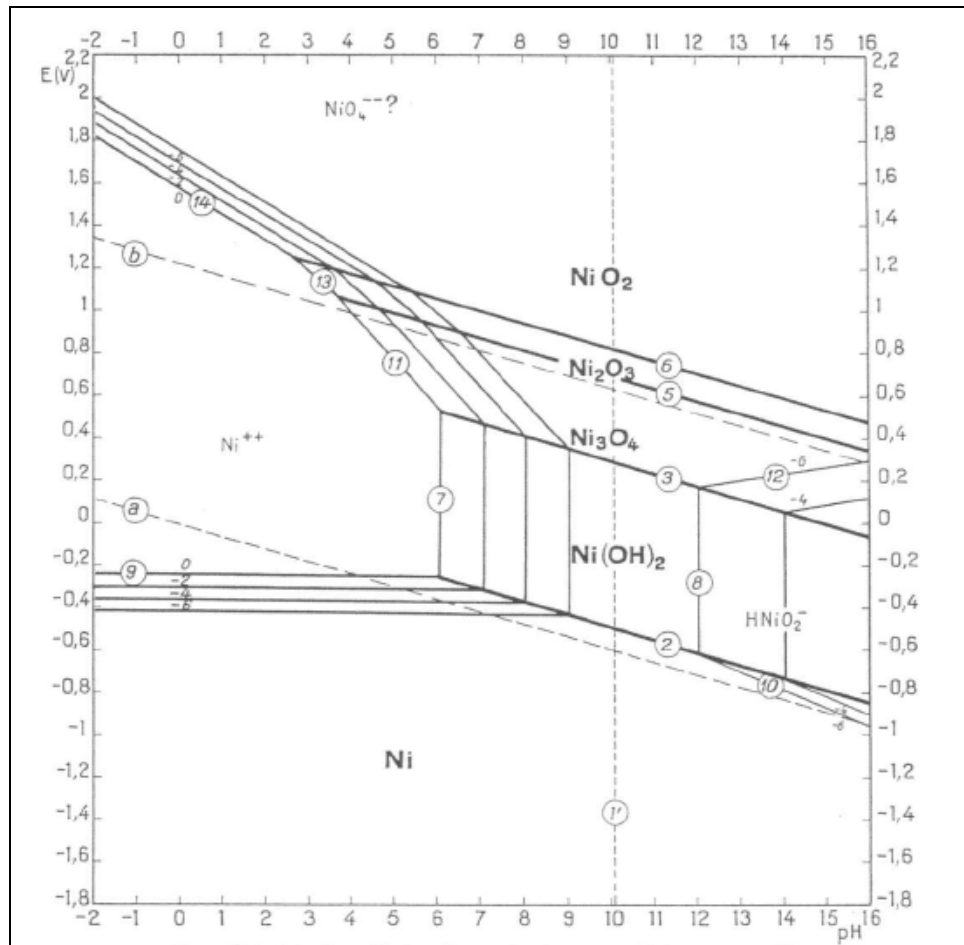
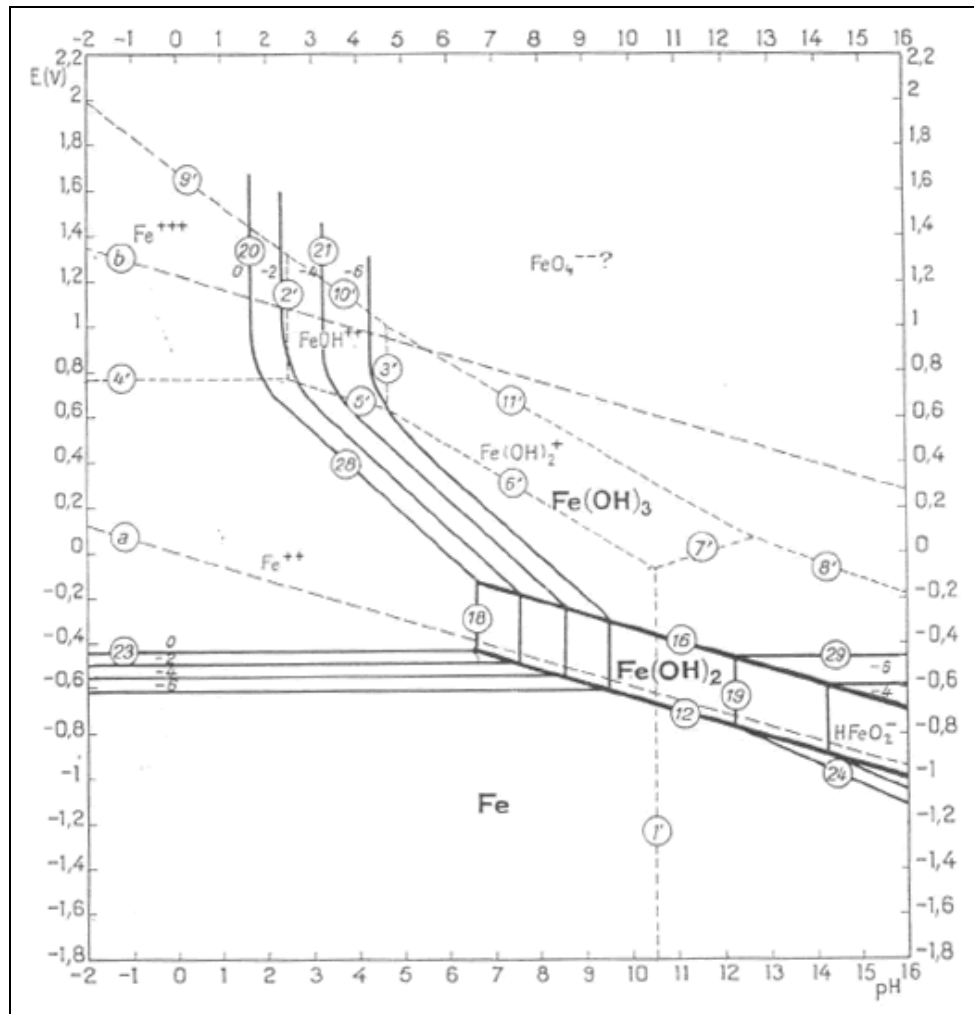
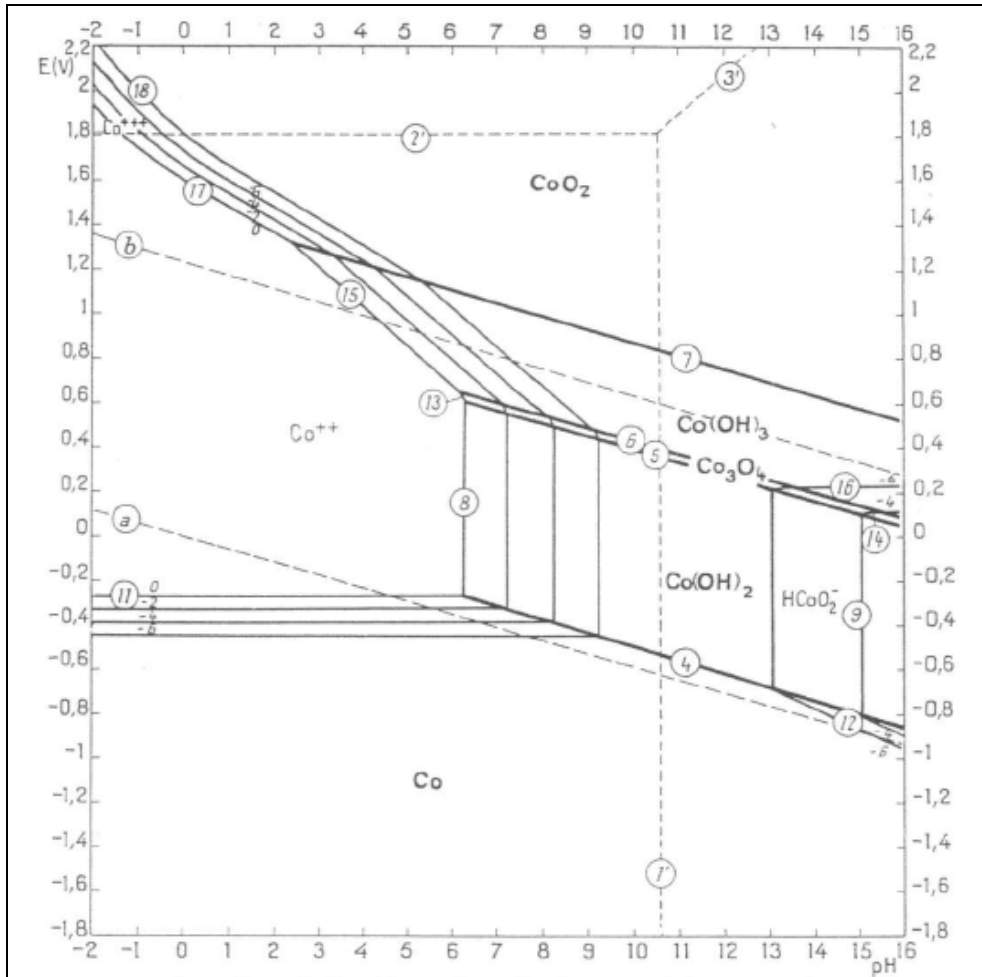


Figure 2.10 Pourbaix diagram of nickel–water system [41].



**Figure 2.11** Pourbaix diagram of iron–water system [41].

The Pourbaix diagram of iron indicates that iron is stable and soluble as either  $Fe^{2+}$  or  $Fe^{3+}$  ions at low pH values. The dominant factor for which ion will be present in solution depends on the potential of the solution since used acid concentrations in literature results in pH values less than 2.0. Moreover, as stated above,  $Fe^{2+}/Fe^{3+}$  ratio is important for atmospheric leaching process.  $Fe^{2+}$  ions remain in solution during precipitation due to pH values of precipitation process and should be oxidized to  $Fe^{3+}$  prior to precipitation.



**Figure 2.12** Pourbaix diagram of cobalt–water system [41].

As can be seen from the Pourbaix diagram given in Figure 2.12, cobalt behaves similar to nickel in aqueous solutions. Cobalt is stable and soluble as  $\text{Co}^{2+}$  and  $\text{HCoO}_2^-$  ions in aqueous solutions. Potential and pH of system are the dominating factors of which species will be present in solution. In atmospheric leaching, due to low pH cobalt is stable as  $\text{Co}^{2+}$  in leach solutions.



The kinetics of atmospheric leaching of laterites has been also investigated by various workers [42, 43 and 44]. In these studies, the previously established shrinking core models expressed by Equations 2.8 and 2.9 were used.

$$1 - (1 - a)^{1/3} = k_1 t \quad (2.8)$$

$$1 - 2/3a - (1 - a)^{2/3} = k_2 t \quad (2.9)$$

Where  $a$  is the dissolved iron fraction at time  $t$  and  $k_1$  and  $k_2$  are the rate constants. Equation 2.8 assumes that the chemical reaction taking place on the mineral surface is the step that controls leaching rate. On the other hand, Equation 2.9 assumes that diffusion is the rate controlling step. It was reported that the iron dissolution behavior of laterites gives straight lines according to Equation 2.9. From the plotted diagram, the activation energy was calculated and reported within the range of 44.2–48.6 kJ/mol.

Arslan et al. carried out some kinetic experiments with Çaldağ laterites and in that study the activation energy was reported as 47.34 kJ/mol [45]. This value was within the previously reported range.

## CHAPTER 3

### EXPERIMENTAL MATERIALS AND METHODS

#### 3.1 Materials

During this study, lateritic ores from Gördes region, Manisa were used. Experiments were carried out by using dilute sulfuric acid solutions as acidic media. Also sodium hydroxide and di-potassium oxalate monohydrate were used for the free acid determination during experiments.

##### 3.1.1 Lateritic Ores

Two types of lateritic ore were supplied from Gördes, namely nontronitic (Nontronite) and limonitic (Limonite) type lateritic ores. Supplied ores that were crushed and screened to -2 cm, were representative samples of the whole ore body in Gördes region which has an estimated ore reserve of 68.5 million tons. Supplied Limonite was 200 kg and Nontronite was 410 kg. The characterization steps of lateritic ores used in this study are given in the following sections.

### 3.1.1.1 Physical Characterization

In physical characterization, initially moisture contents of the representative ores were determined. Representative samples were obtained from ores via ore sampling method called coning and quartering. Each representative sample was dried at 105°C until a constant sample weight was achieved. Then, the moisture content of each sample was calculated via weight loss due to evaporation of physically bonded water. Moisture contents of the representative ore samples are given in Table 3.1. Bulk densities of the as-received representative ores are given in Table 3.2.

**Table 3.1** Moisture contents of the representative ores.

<b>Representative Ore</b>	<b>Moisture (%)</b>
Nontronite	40.10
Limonite	23.47

**Table 3.2** Bulk densities of the as-received representative ores.

<b>Representative Ore</b>	<b>Bulk Density (g/cm<sup>3</sup>)</b>
Nontronite	0.93
Limonite	1.04

Representative samples taken from the lateritic ores that were dried and ground to 100% -0.038 mm (-38 microns), were taken to METU Central Laboratory for density determination. Densities determined by helium pycnometer at 26.7°C are given in Table 3.3.

**Table 3.3** Densities of the representative ores.

<b>Representative Ore</b>	<b>Density (g/cm<sup>3</sup>)</b>
Nontronite	2.64
Limonite	3.26

In the last step of physical characterization, wet screen analyses were conducted with the dried representative samples in order to determine particle size distributions of ores. Wet screen analyses were done with an eight-sieve system that was vibrated continuously until the water came clear from the bottom. After screening, oversize particles for each sieve as well as -0.038 mm particles were dried at 105°C and weighed. Screen analyses results are given in Table 3.4 for Nontronite and in Table 3.5 for Limonite.

**Table 3.4** Wet screen analysis results of Nontronite.

<b>Size (mm)</b>	<b>weight (%)</b>	<b>Σ wt % retained</b>	<b>Σ wt % undersize</b>
+3.327	9.21	9.21	90.79
+2.362	2.09	11.30	88.70
+1.168	2.13	13.43	86.57
+0.589	3.87	17.30	82.70
+0.295	4.98	22.28	77.72
+0.147	9.24	31.52	68.48
+0.074	12.70	44.22	55.78
+0.038	15.44	59.66	40.34
-0.038	40.34	-	-
Σ	100.00	-	-

**Table 3.5** Wet screen analysis results of Limonite.

<b>Size (mm)</b>	<b>weight (%)</b>	<b>Σ wt % retained</b>	<b>Σ wt % undersize</b>
+3.327	5.50	5.50	94.50
+2.362	7.83	13.33	86.67
+1.168	5.55	18.88	81.12
+0.589	6.47	25.35	74.65
+0.295	5.38	30.73	69.27
+0.147	6.40	37.13	62.87
+0.074	6.39	43.52	56.48
+0.038	7.81	51.32	48.68
-0.038	48.68	-	-
Σ	100.00	-	-

### **3.1.1.2 Chemical Characterization**

In chemical characterization, the complete chemical analyses of the representative samples taken from ores were determined via Inductively Coupled Plasma (ICP) and X-ray Fluorescence (XRF) methods. Particle sizes of both dried samples used for chemical characterization were 100% -0.038 mm. Results of complete chemical analyses are given in Table 3.6. Analyses of metals and their normalized distributions in each screen size fraction are given in Table 3.7 for Nontronite and in Table 3.8 for Limonite, respectively. As it can be seen from Tables 3.7 and 3.8, about 40–49% of each sample was below 0.038 mm and the concentration of nickel was higher in the finer fractions. The physical concentration of samples by just screening was found to be not very effective.

**Table 3.6** Chemical analyses of representative ores as wt%.

<b>Component (%)</b>	<b>Nontronite</b>	<b>Limonite</b>
Fe	15.95	28.70
Ni	1.20	1.28
Co	0.044	0.083
Cr <sub>2</sub> O <sub>3</sub>	0.99	1.99
MnO	0.34	0.59
As	0.020	0.680
Al <sub>2</sub> O <sub>3</sub>	4.17	5.83
SiO <sub>2</sub>	44.9	28.8
MgO	6.91	2.26
CaO	2.15	1.27
K <sub>2</sub> O	<0.122	0.120
TiO <sub>2</sub>	0.08	0.13
CuO	0.009	0.039
ZnO	0.025	0.037
PbO	<0.010	<0.011
P <sub>2</sub> O <sub>5</sub>	0.050	<0.020
S	<0.01	0.43
Loss on Ignition	8.81	8.45

**Table 3.7** Normalized Ni, Fe, Co, As and Cr Distributions of Nontronite.

Size (mm)	Weight (%)	Ni		Fe		Co		As		Cr	
		Grade (%)	Dist. (%)	Grade (%)	Dist. (%)	Grade (%)	Dist. (%)	Grade (%)	Dist. (%)	Grade (%)	Dist. (%)
+3.327	9.21	0.49	3.68	6.51	3.59	0.000	0.00	0.015	7.24	0.502	6.00
+2.362	2.09	0.75	1.29	9.42	1.18	0.000	0.00	0.019	2.13	0.593	1.61
+1.168	2.13	0.99	1.73	11.87	1.51	0.000	0.00	0.026	2.91	0.723	2.00
+0.589	3.87	1.04	3.31	13.75	3.19	0.031	2.33	0.030	6.20	1.050	5.27
+0.295	4.98	1.25	5.12	16.41	4.89	0.048	4.59	0.020	5.36	0.867	5.60
+0.147	9.24	1.28	9.70	17.56	9.73	0.064	11.50	0.016	8.07	1.204	14.44
+0.074	12.70	1.30	13.57	19.57	14.90	0.067	16.57	0.015	10.35	1.190	19.61
+0.038	15.44	1.36	17.23	20.07	18.57	0.082	24.48	0.016	13.04	0.889	17.81
-0.038	40.34	1.34	44.35	17.55	42.43	0.052	40.48	0.021	44.63	0.529	27.67
Σ	100	1.20	100	15.95	100	0.044	100	0.020	100	0.762	100

**Table 3.8** Normalized Ni, Fe, Co, As and Cr Distributions of Limonite.

Size (mm)	Weight (%)	Ni		Fe		Co		As		Cr	
		Grade (%)	Dist. (%)	Grade (%)	Dist. (%)	Grade (%)	Dist. (%)	Grade (%)	Dist. (%)	Grade (%)	Dist. (%)
+3.327	5.50	0.74	3.18	38.34	7.35	0.073	4.87	0.561	4.54	1.152	4.66
+2.362	7.83	1.01	6.16	28.46	7.77	0.083	7.82	0.645	7.43	0.702	4.04
+1.168	5.55	1.06	4.59	30.62	5.92	0.082	5.47	0.712	5.80	0.803	3.27
+0.589	6.47	1.09	5.50	32.10	7.23	0.081	6.29	0.779	7.41	1.016	4.83
+0.295	5.38	1.25	5.26	30.93	5.79	0.086	5.57	0.772	6.11	1.442	5.70
+0.147	6.40	1.27	6.34	29.03	6.47	0.091	7.03	0.696	6.55	3.250	15.30
+0.074	6.39	1.42	7.07	27.83	6.19	0.096	7.41	0.646	6.06	2.968	13.94
+0.038	7.81	1.38	8.38	27.07	7.37	0.082	7.69	0.590	6.77	1.569	9.01
-0.038	48.68	1.41	53.50	27.07	45.90	0.082	47.96	0.689	49.33	1.096	39.24
Σ	100	1.28	100	28.70	100	0.083	100	0.680	100	1.360	100



### 3.1.1.3 Mineralogical Characterization

In mineralogical characterization, Thermo Gravimetric (TGA) and Differential Thermo Gravimetric (DTA) analyses were conducted on the representative samples.

Analyses were carried out in METU Central Laboratory, between 35°C – 1000°C temperature range with a linear heating rate of 10°C/min in air by using samples ground to 100% -0.038 mm.

Plotted DTA/TGA diagram of Nontronite given in Figure 3.1, indicates a weight loss and an endothermic peak around 100°C which is due to the evaporation of water. Upon heating to 269°C, an endothermic reaction takes place and weight loss occurs due to the transformation of goethite into hematite according to Reaction 3.1. The exothermic peak at 819°C is due to the transformation of serpentine to forsterite (2MgO.SiO<sub>2</sub>).



DTA/TGA diagram of Limonite given in Figure 3.2 indicates a weight loss around 100°C accompanied with an endothermic peak which is due to the evaporation of water. Upon heating to 270°C, an endothermic reaction takes place and weight loss occurs due to the transformation of goethite into hematite as before.

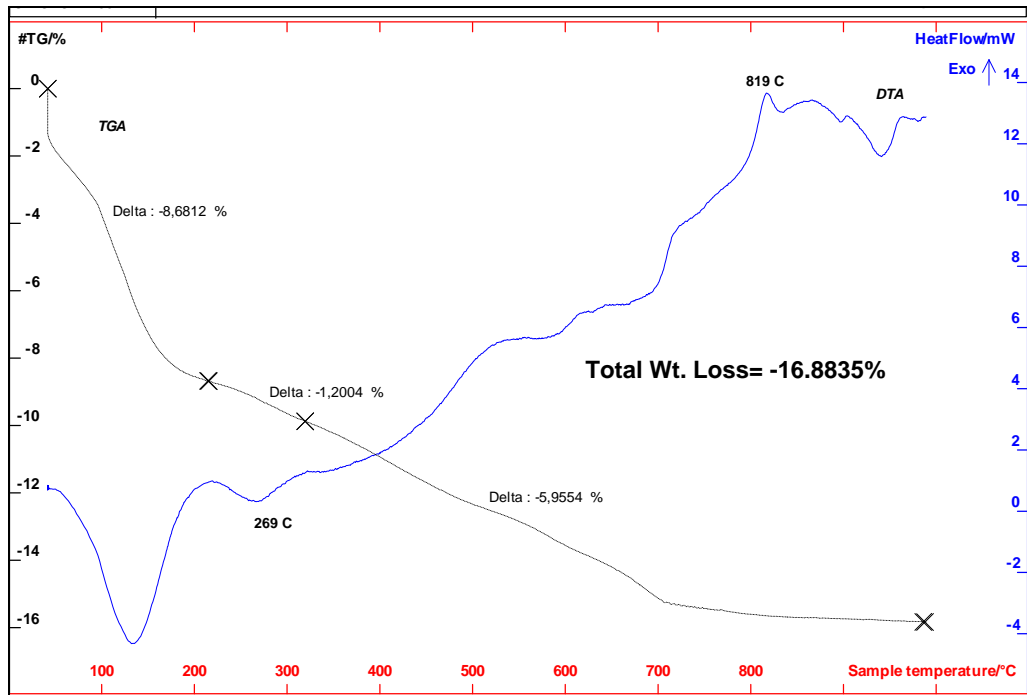


Figure 3.1 DTA/TGA diagram of Nontronite.

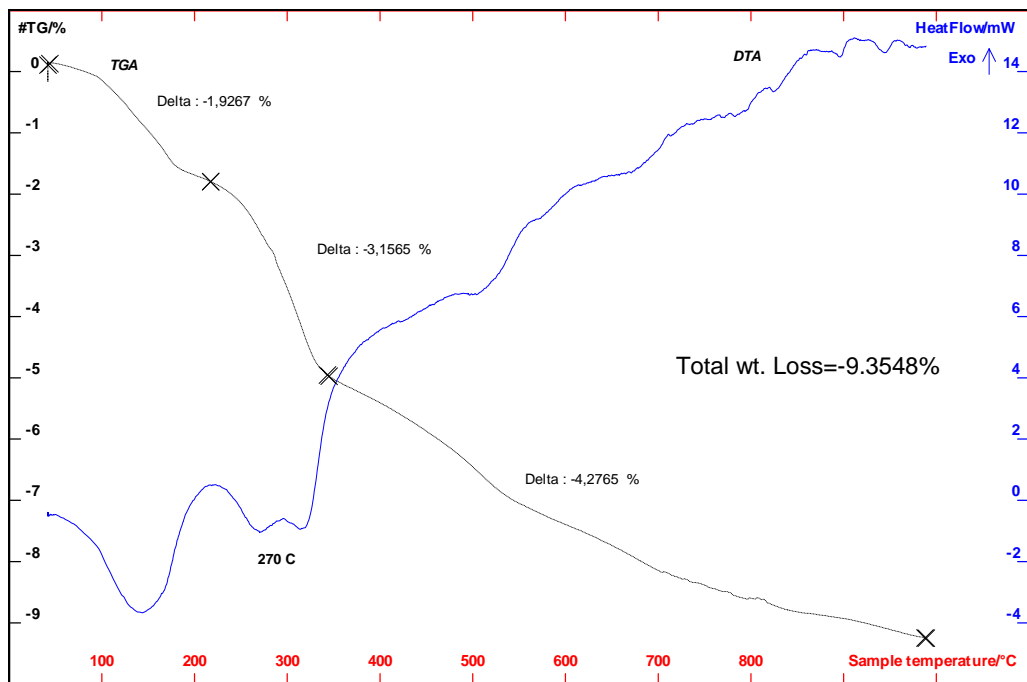


Figure 3.2 DTA/TGA diagram of Limonite.

X-Ray Diffraction (XRD) analysis was performed on both of the representative samples with Rigaku Multiflex Powder X-Ray diffractometer with Cu-K $\alpha$  radiation.

XRD diagram given in Figure 3.3 indicates that smectite, serpentine, goethite, quartz and calcite were present in Nontronite. Plotted XRD diagram of Limonite given in Figure 3.4 indicates that Limonite sample consisted of mainly goethite, hematite, quartz and calcite and to a lesser extent serpentine and smectite.

In the last step of mineralogical characterization, Scanning Electron Microscopy (SEM) analyses were carried out with the representative samples by JEOL JSM-6400 Electron Microscope.

In SEM analyses of both samples, it was seen that nickel was present in laterites as replacements or substitutions in the atomic structure of goethite, serpentine, smectite and asbolane. Cobalt was in the atomic structure of asbolane mineral. It was also found that arsenic was present in the atomic structure of goethite. Therefore, the presence of high goethite amount results in a high arsenic percentage in the chemical composition of limonitic laterite ore.

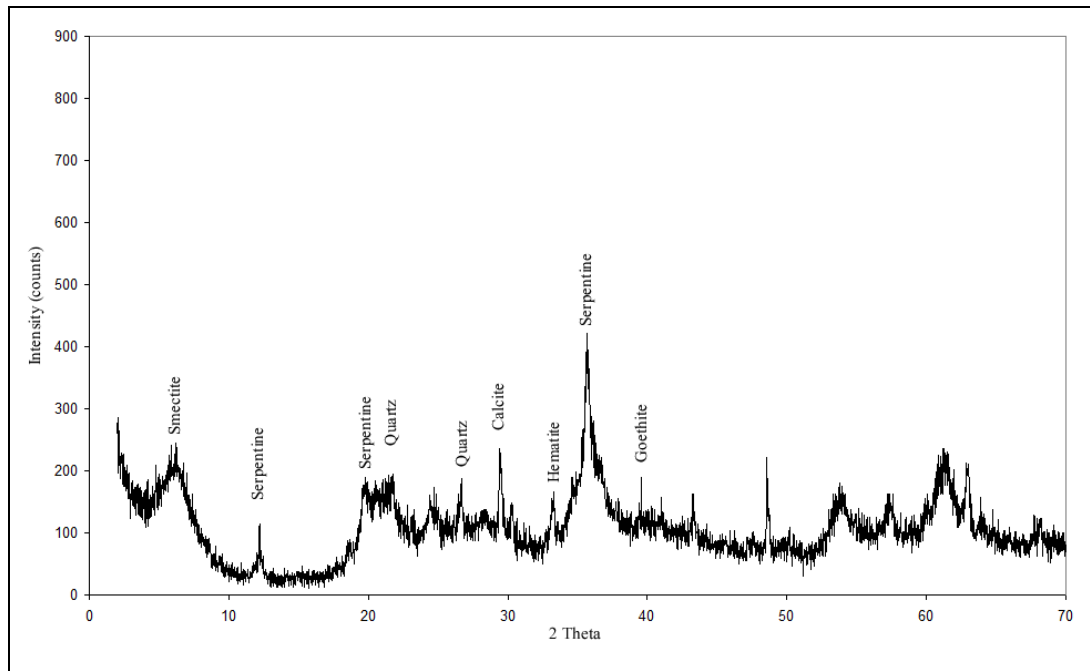


Figure 3.3 XRD pattern of Nontronite.

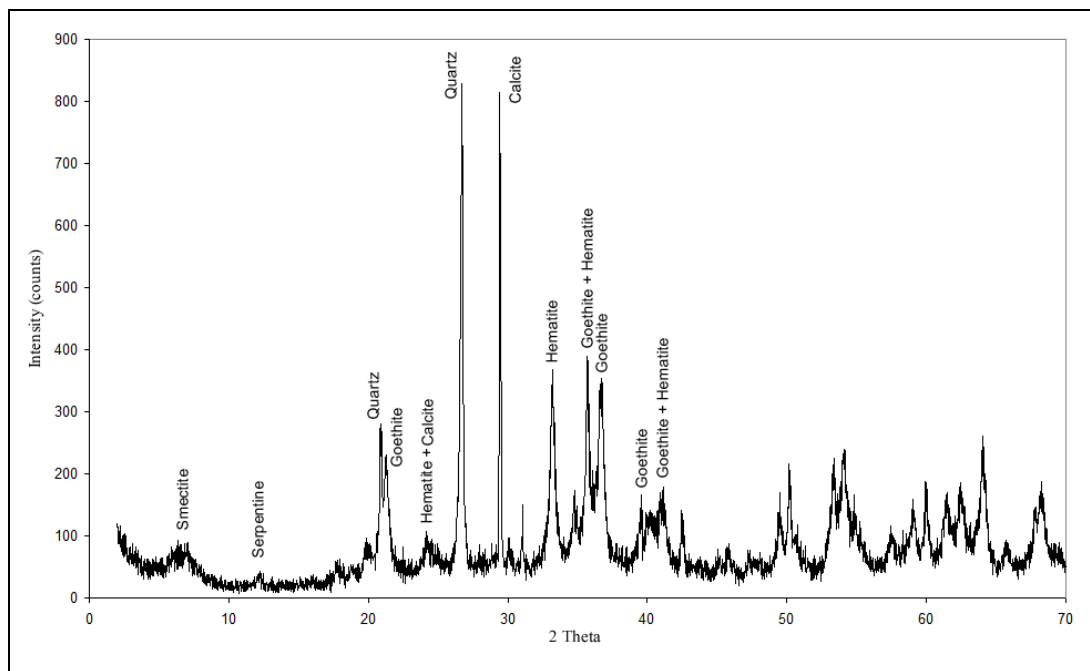


Figure 3.4 XRD pattern of Limonite.

## **3.2 Methods**

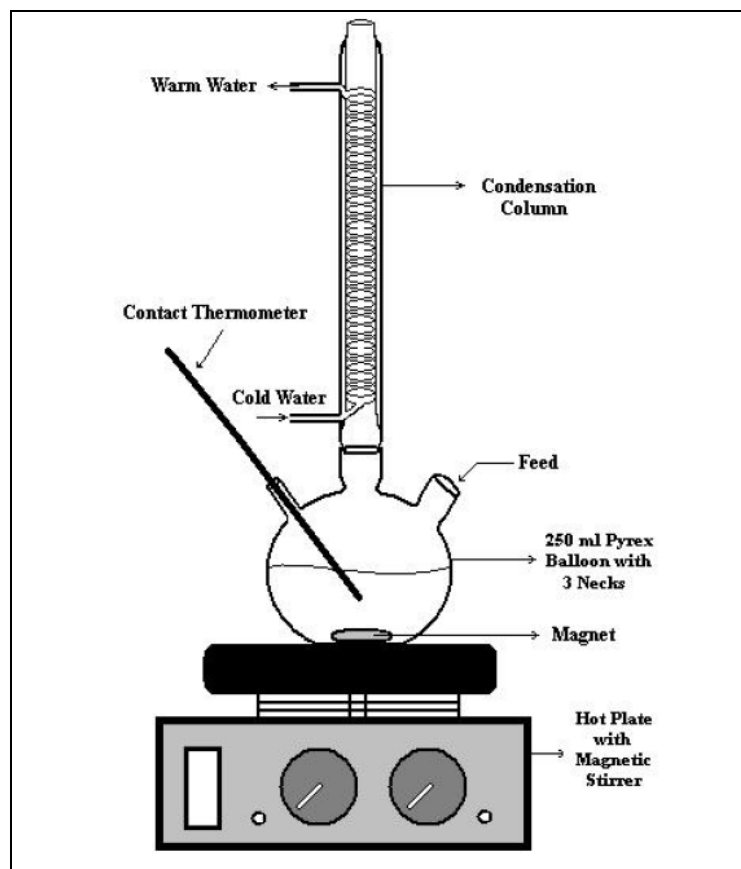
### **3.2.1 Materials Sampling**

In this study, coning and quartering method was used for sampling the lateritic ores. In this method, each ore was first heaped into a uniform cone shape then the cone formed was layered into circular form with uniform thickness by shoveling the top part and spreading near the edges, i.e., it was truncated. After a uniform layer has been obtained, it was divided into four equal quarters; two opposite quarters were taken as sample. This procedure was repeated until a desired sample size was achieved.

### **3.2.2 Agitative Leaching Experiments**

Agitative leaching experiments were carried out with the experimental set-up shown in Figure 3.5. Leaching set-up consisted of a magnetically stirrer hot plate with temperature controller, a 250 ml glass balloon and a condenser. Condenser was used to avoid evaporation losses of leach solution during leaching. Prepared leach solution of known volume at the desired sulfuric acid concentration was placed into the glass balloon and temperature of leach solution was kept constant with the help of hot plate and contact thermometer. Once the desired temperature was reached, ore sample of known weight was added from the feed opening and stirred at a constant speed by a magnet to obtain sufficient mixing at the desired temperature and time period. At the end of leaching, the leached ore was filtered and washed with distilled water using a Büchner funnel. Occasionally, pregnant and wash water solutions were analyzed by Atomic

Adsorption Spectrophotometer (AAS) to check recovery values of metals at the end of leaching. Perkin Elmer 2380 Atomic Adsorption Spectrophotometer was used during analyses. Leach residue was dried at 105°C, weighed and also analyzed by X-Met 820 XRF analyzer of META. Based on residue analysis, the recoveries were calculated. During the experiments, Merck quality sulfuric acid (95–98%, by weight) was used.



**Figure 3.5** Agitative leaching system.

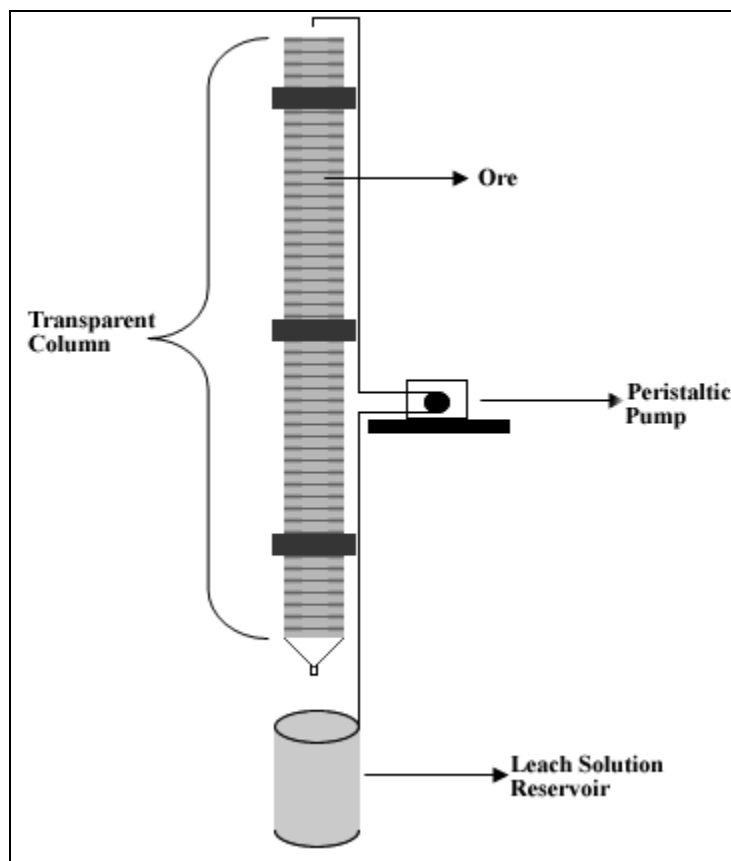
In agitative leaching experiments, initially, the recoveries of metals at different acid concentrations (2N, 4N and 5N) with respect to time (1 hr, 3 hr, 5 hr and 24 hr) were investigated. During these experiments temperature

and particle size were kept constant as 95°C and 100% -0.074 mm, respectively. By evaluating the results of experiments, the optimum sulfuric acid concentration–time combinations were chosen for Limonite and Nontronite. The optimum conditions were chosen in order to maximize nickel and cobalt recovery values and minimize iron recovery values. Effect of temperature (95°C, 75°C, 50°C and 25°C) and particle size (each 100% - 1.168, -0.589, -0.295, -0.147 and -0.074 mm) on recovery values of metals were investigated by using those optimum conditions for each representative ore. In all of the experiments 15 g of the dried representative sample and 75 cc of sulfuric acid solution were used.

### **3.2.3 Column Leaching Experiments**

Column leaching experiments were carried out to demonstrate heap leaching behavior of the representative ores. Schematic drawing of column leaching experimental set-up is given in Figure 3.6.

Whole set-up consisted of a number of columns where each column was with 100 mm internal diameter and 1.25 m height, mounted on a wall. For each column, a peristaltic pump was used to generate a cycle of solution flow. Sulfuric acid solution was applied to the ore from the top and pregnant solution was collected from the bottom of column into the reservoir. At the bottom of each column, plastic veil was used to prevent the ore from plugging the outlet.



**Figure 3.6** Column leaching system.

During leaching period, samples from each reservoir were taken in regular basis to adjust the acidity (pH level) of the solution by titration. In titration, free acid in leach solution was determined by the oxalate method. In this method, di-potassium oxalate monohydrate ( $K_2C_2O_4 \cdot H_2O$ ) was used to mask interfering elements such as Fe that might have consumed hydroxide ions during titration. In the first step of titration, 20 cc of potassium oxalate solution with a concentration of 280 g/L was diluted by 5 cc of distilled water and the initial pH of solution was noted. Then, 5 cc of pregnant solution sample was added to the solution and in the presence of continuous magnetic stirring; solution was titrated back to initial pH level by 0.2M sodium hydroxide (NaOH) solution. Before each titration, pH



probe was calibrated using pH 4.00 and 7.01 buffers. Prior to titration, oxidation reduction potentials (ORP) of solution samples were determined by Pt–Ag/AgCl (saturated with KCl) electrode. Then, they were converted into the Standard Hydrogen Electrode (SHE) potential by adding 198 mV.

Samples taken from the reservoir were analyzed by AAS to get leach recovery values of nickel, iron and cobalt at regular periods. While calculating recovery values, dissolved metals in leach solution present within the column, apart from those present in leach solution in the reservoir, were added to recovery values obtained from AAS results. This assumption was made on the basis of volume of leach solution present within the column during the leaching period. At the beginning of leaching period, ore in the column kept some volume of leach solution until an equilibrium level was obtained. Once equilibrium was obtained, volume difference in the reservoir between the initial and equilibrium levels was considered as the volume of leach solution present in the column throughout the leaching period.

At the end of leaching period, leach residue in the column was washed for four times. Each washing cycle continued for 7 days and at the end of each cycle new fresh water was circulated. Analyses of pregnant leach solution and washing solutions were obtained and recoveries were calculated for the pregnant solution and the wash, later these values were added together to check final recovery values of metals. Also at the end of column leaching period, each washed leach residue was dried at 105°C, weighed and analyzed via ICP and XRF to get recovery values of metals on the basis of leach residues.

In column leaching, preliminary leaching behavior of the representative ores were investigated by carrying out experiments under the initial conditions. The initial starting conditions were set as 1/1 kg/L for solid/liquid ratio (given as 1 kg of as-received lateritic ore per liter of leaching solution in the reservoir), 100 g/L for sulfuric acid concentration and 1000 L/day/m<sup>2</sup> for solution flow rate.

In the second stage of experiments, column leach recovery values were investigated at different sulfuric acid concentrations (50 g/L, 100 g/L and 150 g/L) and flow rates (250 L/day/m<sup>2</sup>, 500 L/day/m<sup>2</sup>, 750 L/day/m<sup>2</sup> and 1000 L/day/m<sup>2</sup>).

### **3.3 Chemical Analysis**

During this study, the chemical analyses of pregnant solutions and wash waters were done by Chemical Laboratory in Metallurgical and Materials Engineering Department by using AAS. Analyses carried out on dry representative ores and leach residues were done in Meta Nikel Kobalt A.Ş. and AlsChemex (Canada) by using XRF and ICP methods, respectively.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Agitative Leaching

Prior to column leaching tests, the representative ore samples were subjected to agitative leaching experiments to determine the leaching behaviors of samples in short time intervals. Agitative leaching experiments enabled studying leaching behaviors of the representative ore samples in different time periods, acid concentrations, temperatures and particle size distributions. The results of agitative leaching experiments are presented in the following sections.

##### 4.1.1 Effect of Time and Acid Concentration

In order to study the recovery values at different time periods, agitative leaching experiments were carried out for 1, 3, 5 and 24 hours with 2N (96 g/L), 4N (192.1 g/L) and 5N (240.1 g/L) sulfuric acid concentrations which corresponded to 480, 960 and 1200 kg sulfuric acid/dry ton of lateritic ore, respectively.

During the experiments, weight of dried ore sample (15 g), particle size of the representative ore sample (100% -0.074 mm), solid/liquid ratio (1/5 g/cc) and temperature (95°C) were kept constant.

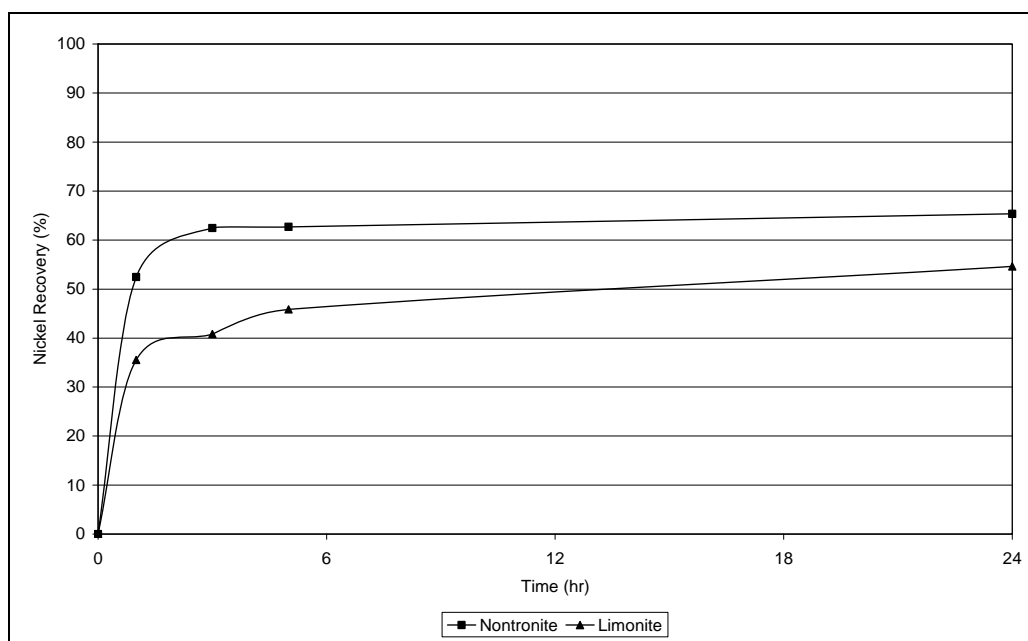
A series of experiments were conducted with each sulfuric acid concentration at different time intervals stated above for both representative ore samples. Nickel, iron, cobalt, arsenic and chromium recovery values obtained via XRF analysis of leach residues from the experiments carried out with Nontronite and Limonite in different durations and sulfuric acid concentrations are given in Tables 4.1 and 4.2, respectively. An example of leach recovery calculation from XRF analysis of a leach residue is given in Appendix A. Graphical presentations of leach recovery values obtained from the experimental data are given in Figures 4.1–4.15.

**Table 4.1** Agitative leach recoveries of Nontronite.

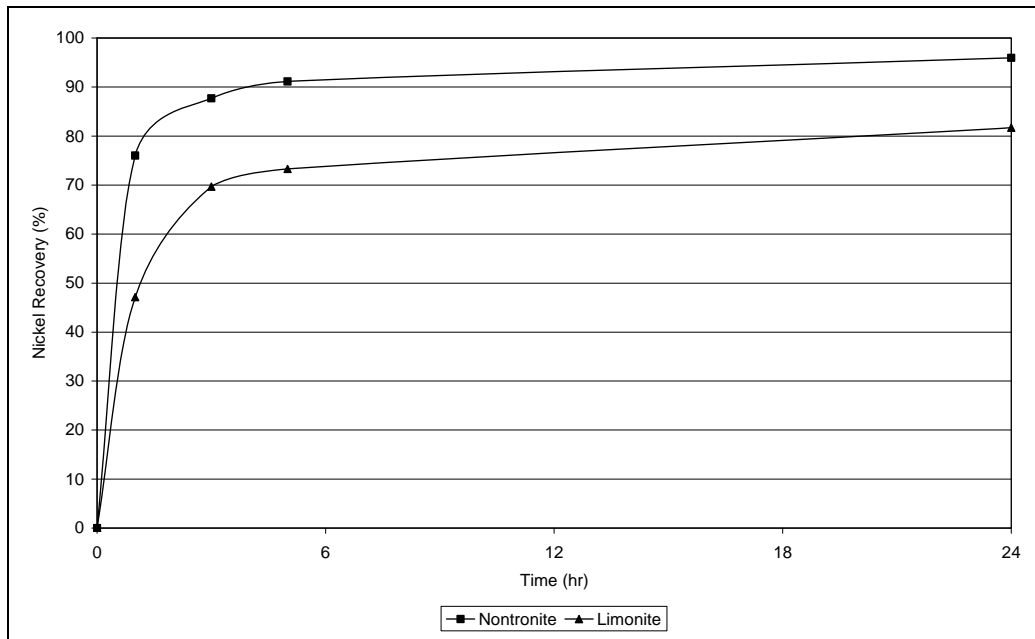
<b>Sulfuric Acid Concentration</b>	<b>Time (hr)</b>	<b>Ni (%)</b>	<b>Fe (%)</b>	<b>Co (%)</b>	<b>As (%)</b>	<b>Cr (%)</b>
<b>2N</b>	<b>1</b>	52.5	22.5	19.5	18.7	22.3
	<b>3</b>	62.5	31.9	25.4	21.6	30.6
	<b>5</b>	62.7	31.1	31.5	25.5	33.1
	<b>24</b>	65.4	29.4	30.0	21.7	37.3
<b>4N</b>	<b>1</b>	76.0	52.9	30.8	48.7	33.2
	<b>3</b>	87.7	61.7	45.3	52.7	37.6
	<b>5</b>	91.1	73.3	58.6	55.8	46.7
	<b>24</b>	96.0	81.8	63.4	57.6	46.7
<b>5N</b>	<b>1</b>	87.5	68.1	35.1	52.2	39.6
	<b>3</b>	94.4	78.2	50.3	58.5	45.5
	<b>5</b>	96.1	83.0	58.8	59.8	47.3
	<b>24</b>	98.6	88.2	65.1	63.1	50.8

**Table 4.2** Agitative leach recoveries of Limonite.

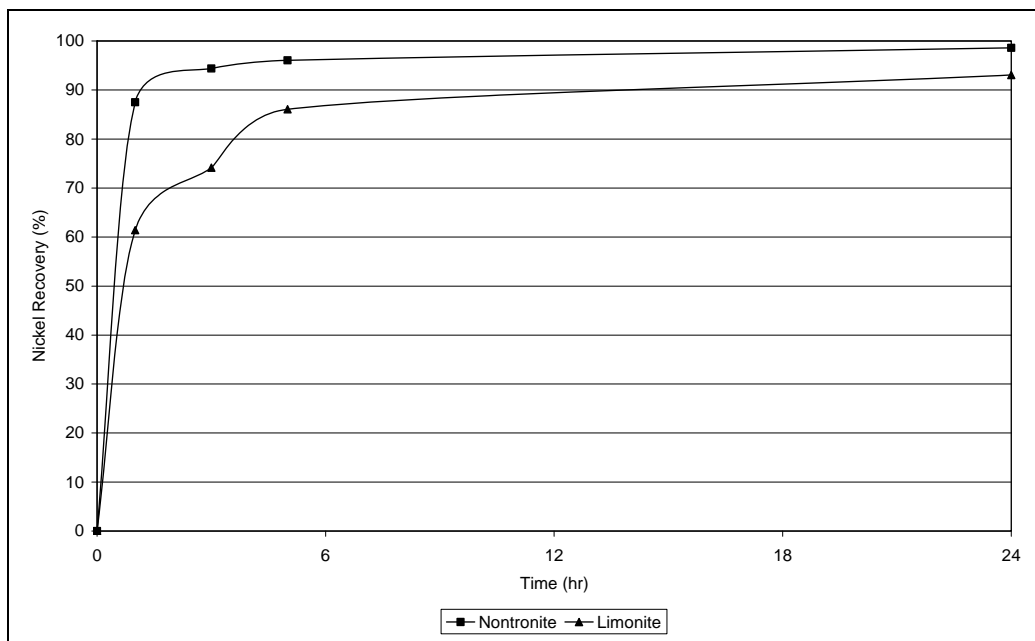
Sulfuric Acid Concentration	Time (hr)	Ni (%)	Fe (%)	Co (%)	As (%)	Cr (%)
2N	1	35.6	13.3	26.7	9.7	7.6
	3	40.8	16.6	28.1	10.3	8.5
	5	45.9	18.2	32.2	14.0	12.9
	24	54.6	25.8	41.2	12.6	20.4
4N	1	47.1	31.1	41.5	29.6	19.5
	3	69.7	45.1	56.3	42.6	19.6
	5	73.3	49.1	58.1	50.2	24.9
	24	81.7	57.6	62.8	59.0	24.5
5N	1	61.4	42.4	53.3	43.7	20.7
	3	74.2	61.8	58.9	53.4	21.1
	5	86.1	70.9	67.2	61.7	25.0
	24	93.1	81.4	75.0	60.1	39.8



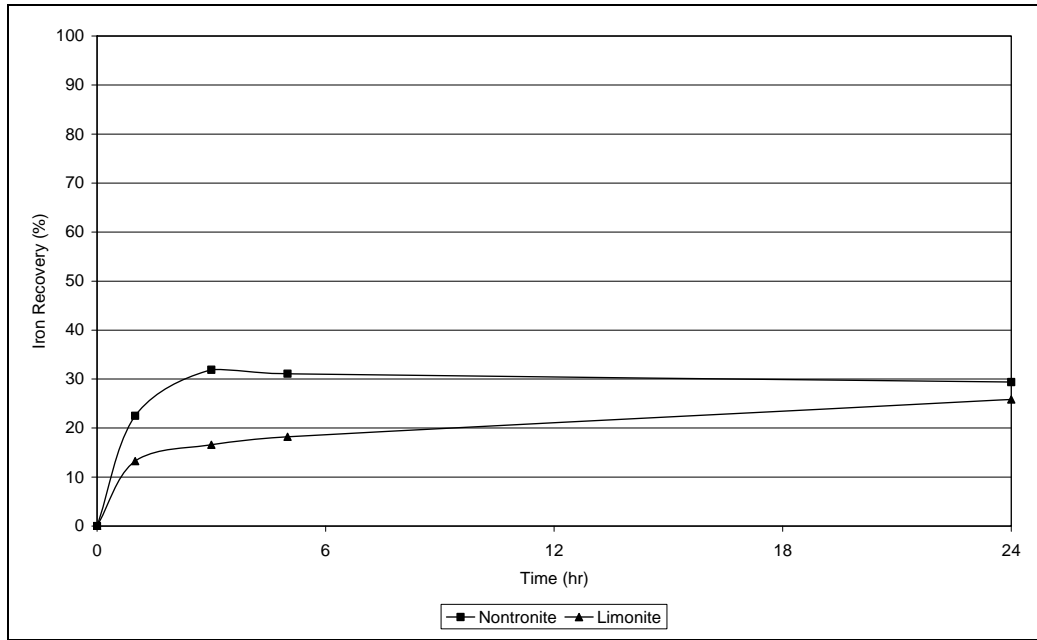
**Figure 4.1** Nickel recoveries at 2N sulfuric acid concentration with respect to time in agitative leaching.



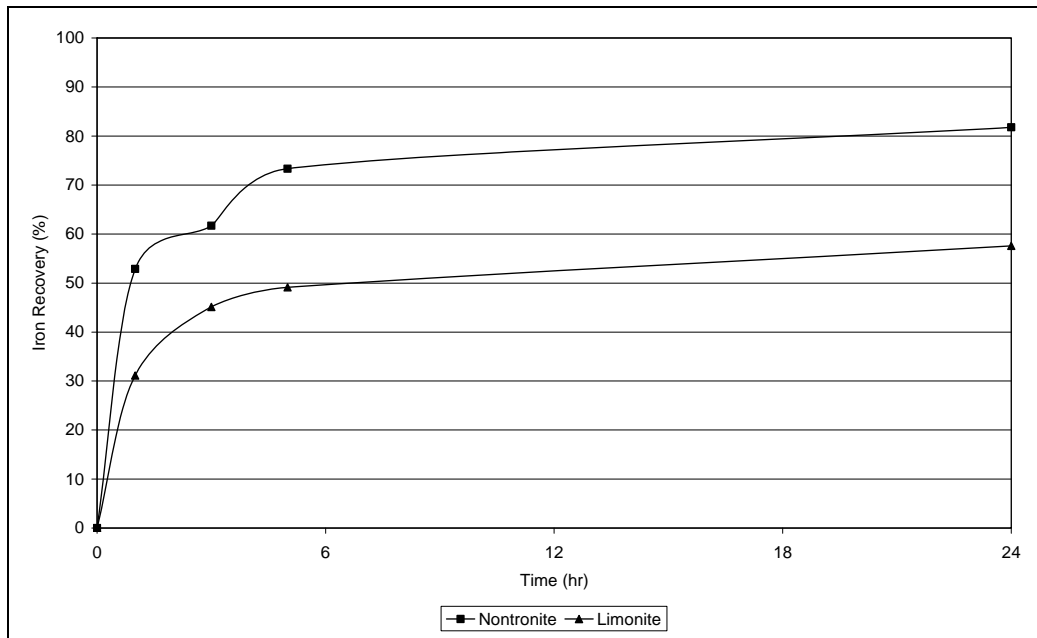
**Figure 4.2** Nickel recoveries at 4N sulfuric acid concentration with respect to time in agitative leaching.



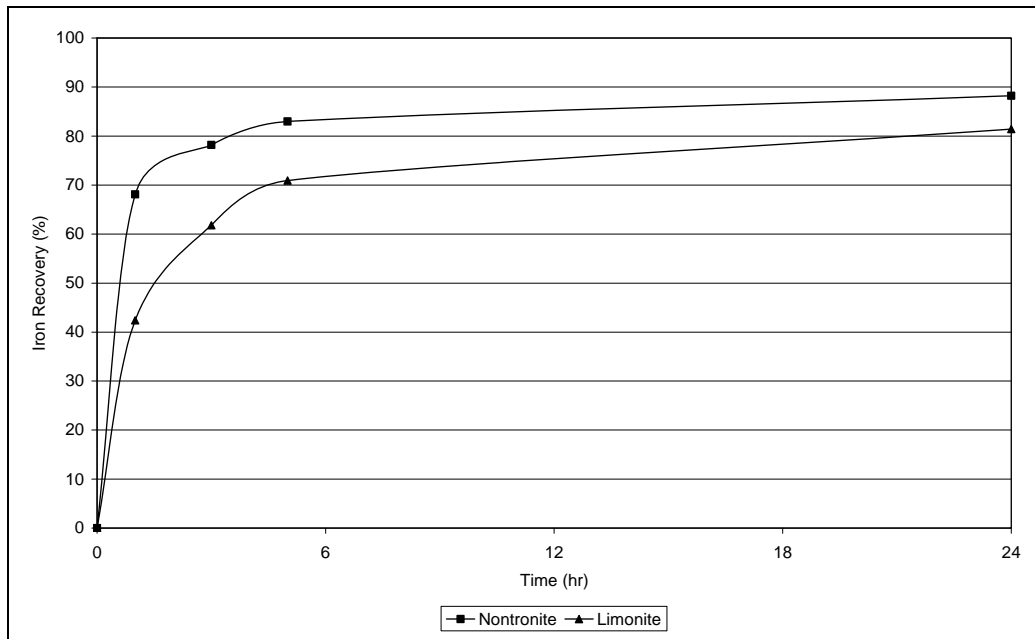
**Figure 4.3** Nickel recoveries at 5N sulfuric acid concentration with respect to time in agitative leaching.



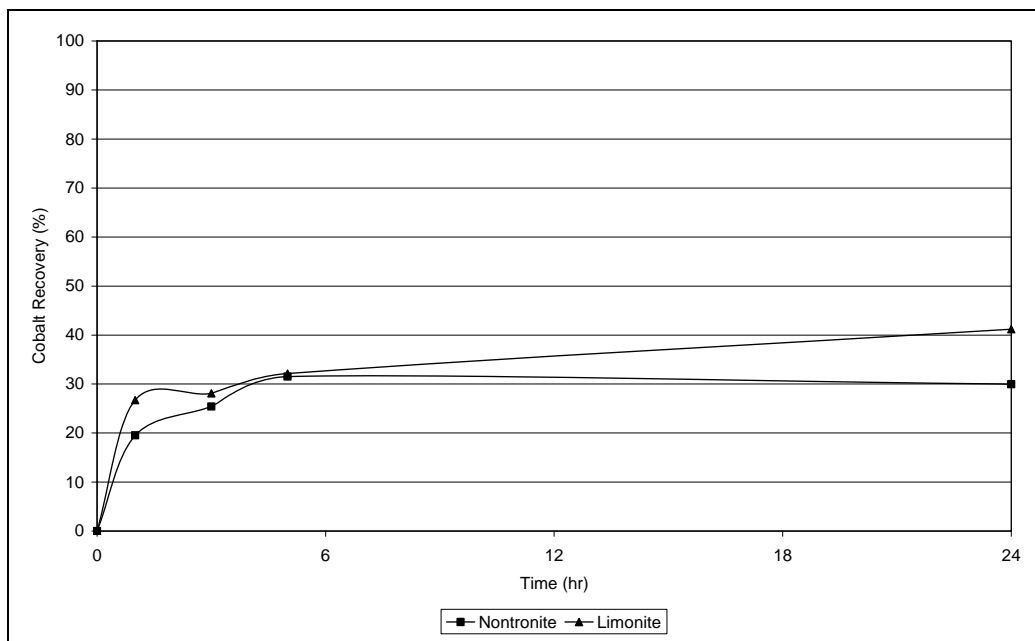
**Figure 4.4** Iron recoveries at 2N sulfuric acid concentration with respect to time in agitative leaching.



**Figure 4.5** Iron recoveries at 4N sulfuric acid concentration with respect to time in agitative leaching.

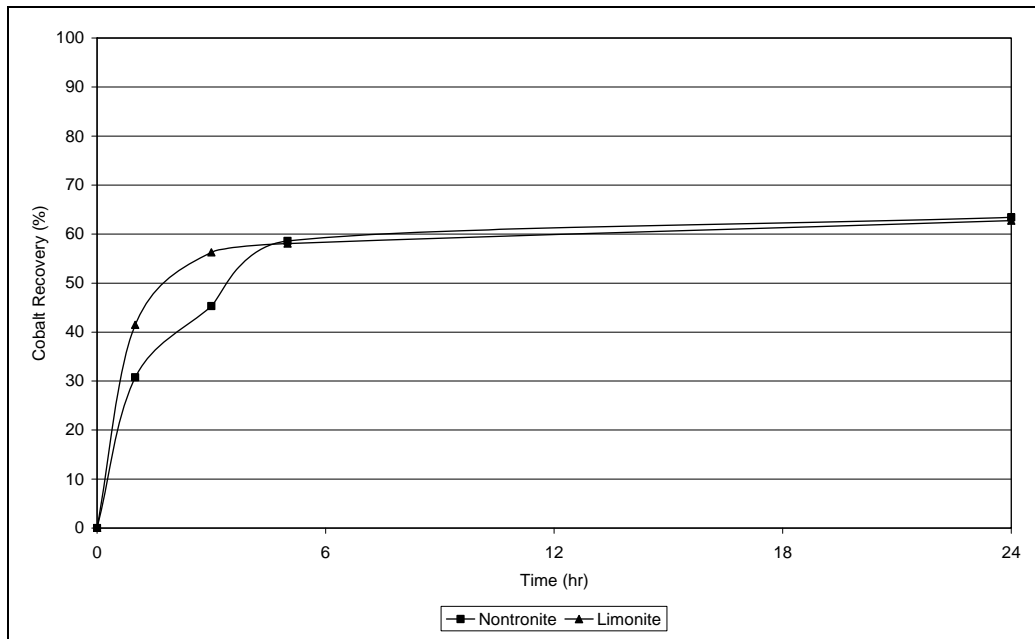


**Figure 4.6** Iron recoveries at 5N sulfuric acid concentration with respect to time in agitative leaching.

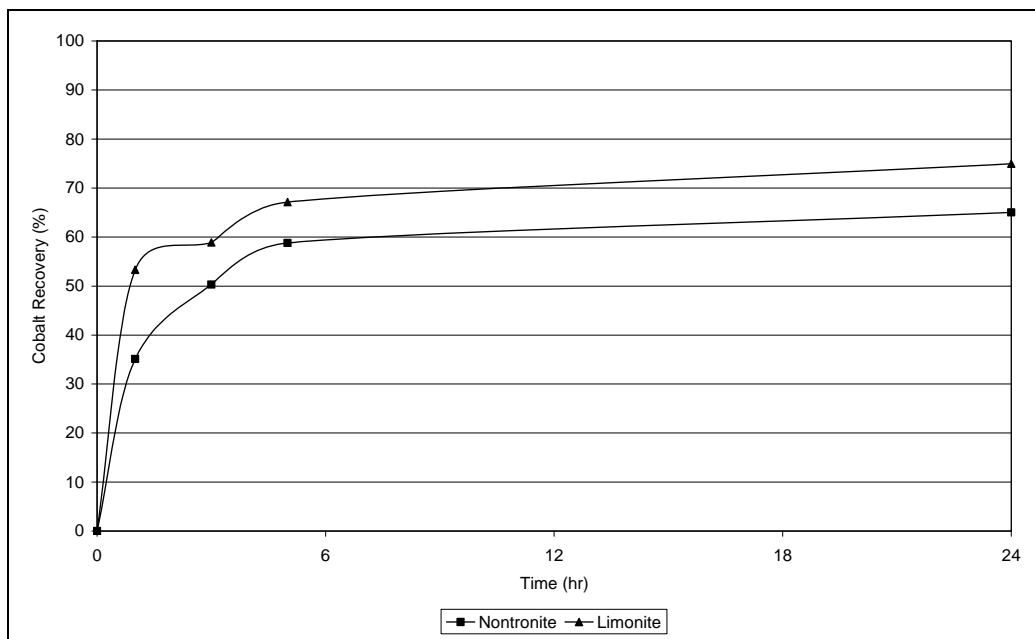


**Figure 4.7** Cobalt recoveries at 2N sulfuric acid concentration with respect to time in agitative leaching.

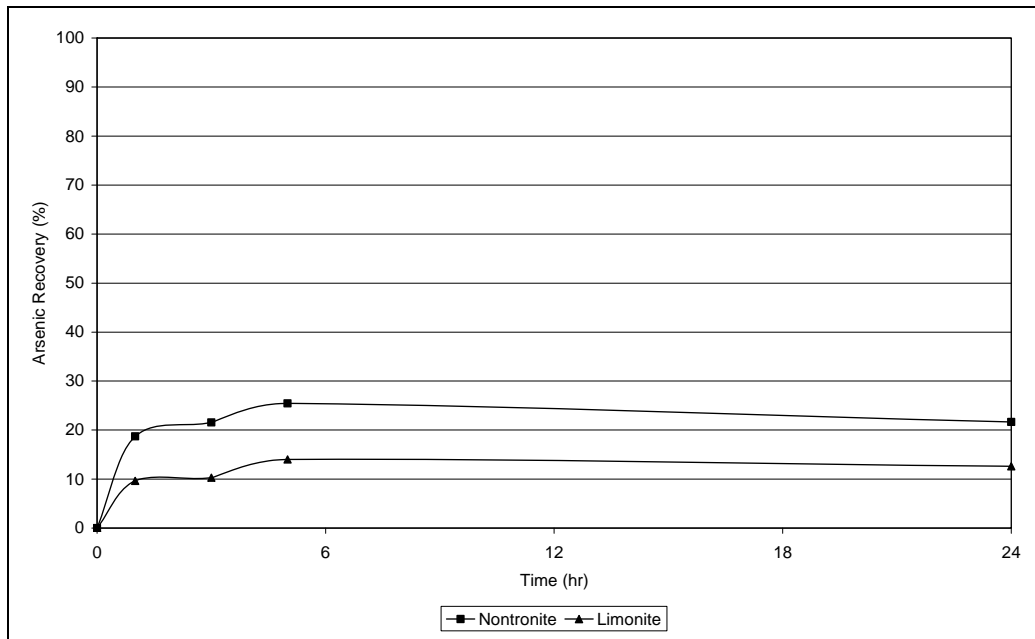




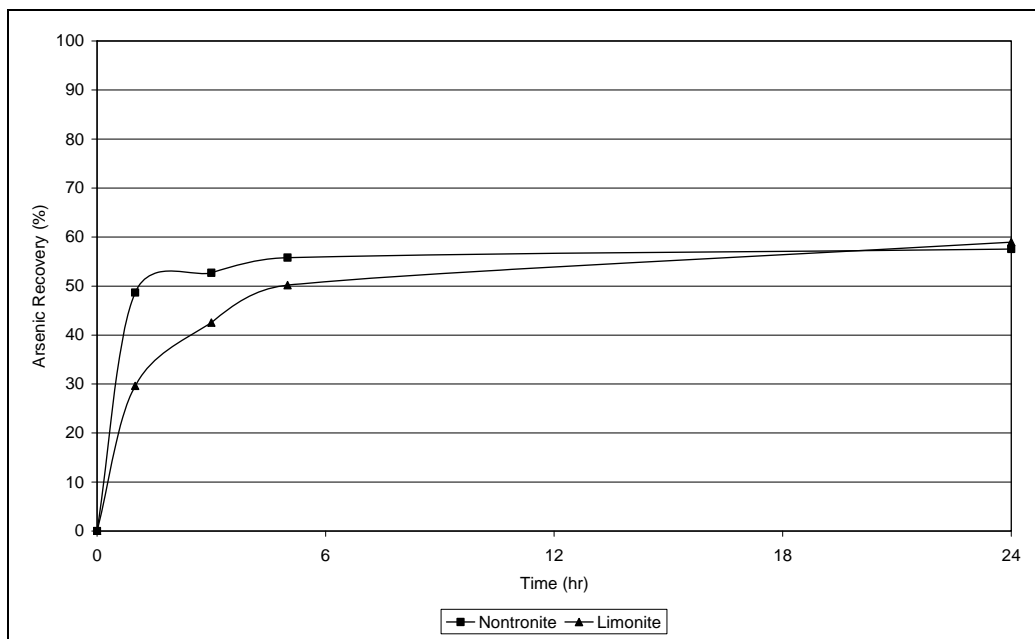
**Figure 4.8** Cobalt recoveries at 4N sulfuric acid concentration with respect to time in agitative leaching.



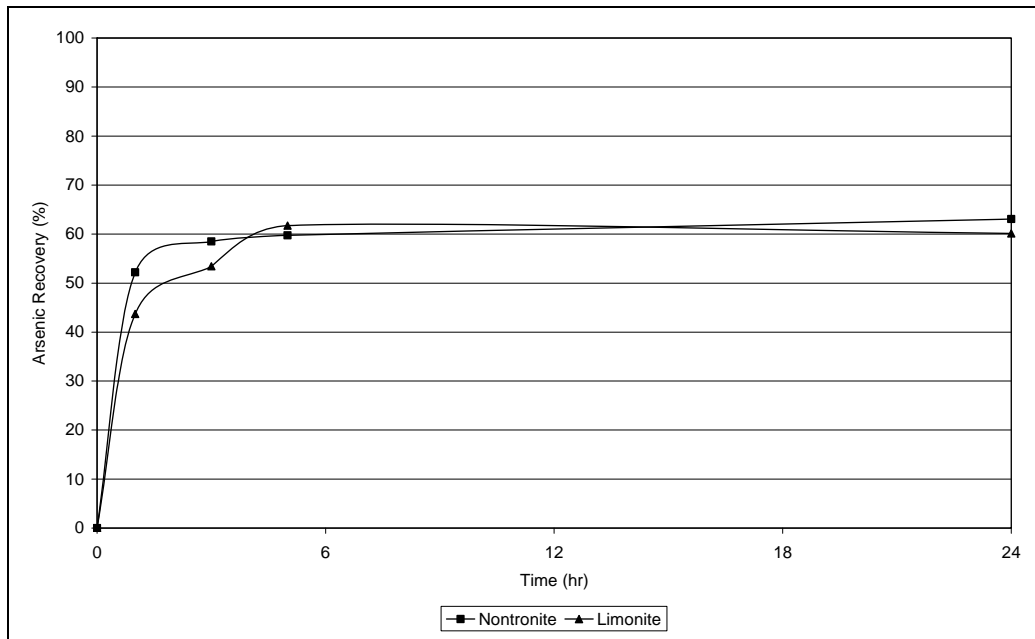
**Figure 4.9** Cobalt recoveries at 5N sulfuric acid concentration with respect to time in agitative leaching.



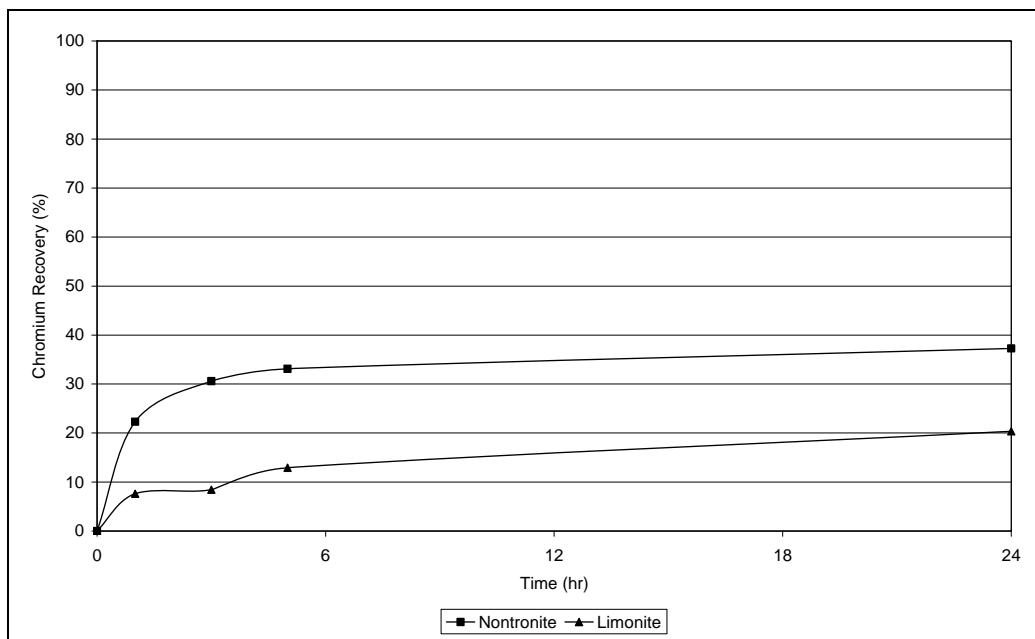
**Figure 4.10** Arsenic recoveries at 2N sulfuric acid concentration with respect to time in agitative leaching.



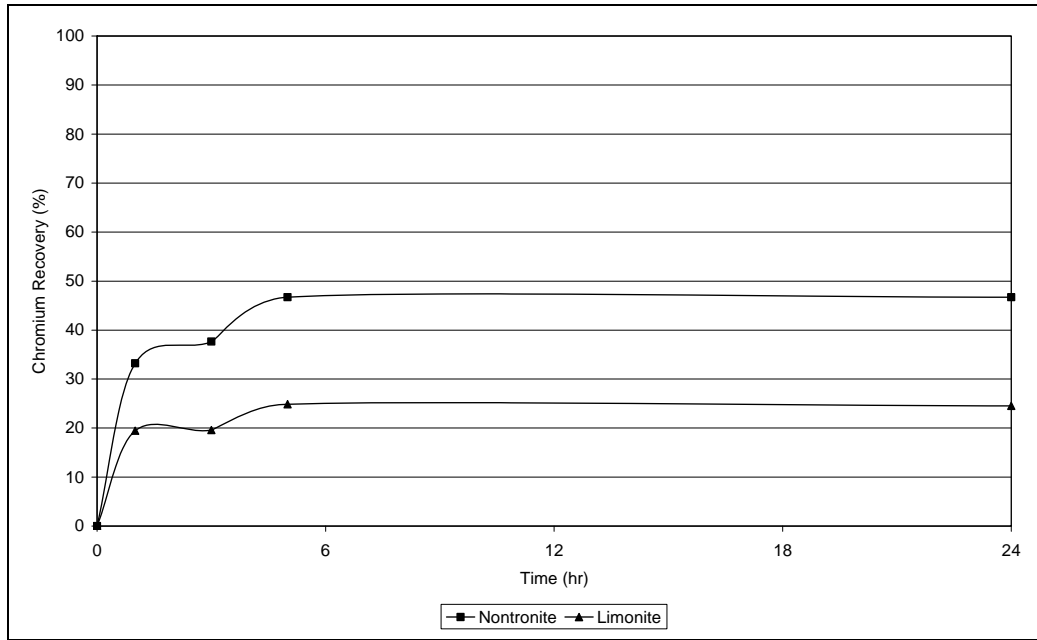
**Figure 4.11** Arsenic recoveries at 4N sulfuric acid concentration with respect to time in agitative leaching.



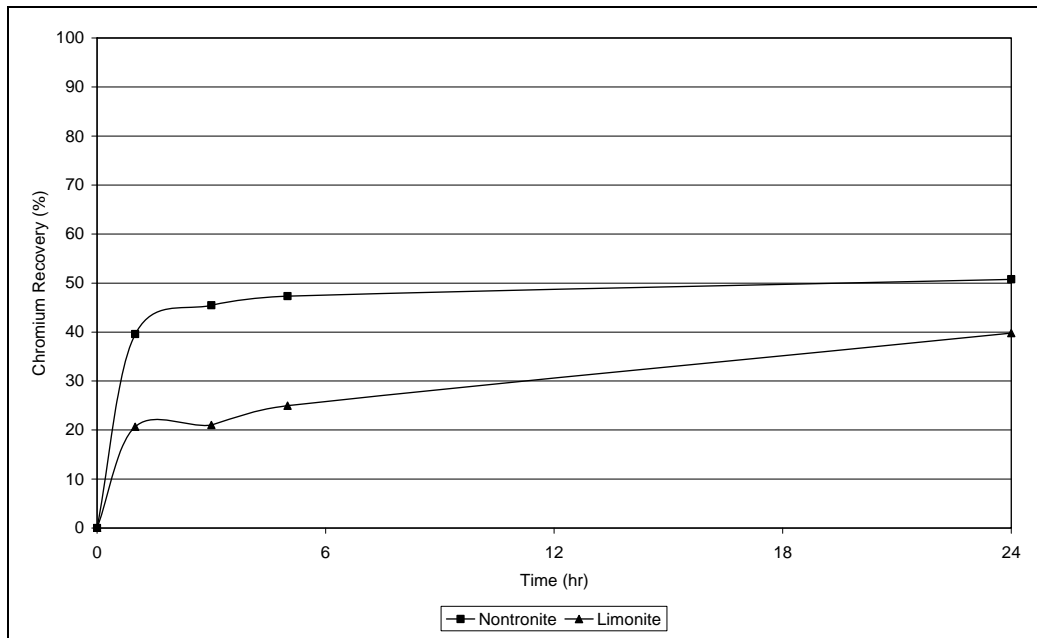
**Figure 4.12** Arsenic recoveries at 5N sulfuric acid concentration with respect to time in agitative leaching.



**Figure 4.13** Chromium recoveries at 2N sulfuric acid concentration with respect to time in agitative leaching.



**Figure 4.14** Chromium recoveries at 4N sulfuric acid concentration with respect to time in agitative leaching.



**Figure 4.15** Chromium recoveries at 5N sulfuric acid concentration with respect to time in agitative leaching.

From the results, it can be concluded that increasing leaching time resulted in an increase in leach recovery values in each sulfuric acid concentration studied. Although the highest leach recovery values were obtained in the experiments carried out for 24 hours, it can be seen that after a certain time period, recovery values showed a linear trend rather than a sharp continuous increase with respect to time.

Furthermore, keeping time constant and increasing the sulfuric acid concentration yielded an increase in recovery values of metals. This behavior was expected as higher sulfuric acid concentrations used in the experiments resulted in more rapid dissolution of metals from the ore and therefore their more rapid transfer to the pregnant leach solution.

In order to study the effects of other parameters on agitative leaching, the optimum sulfuric acid concentration–time combinations were needed to carry out further experiments. By evaluating the leach recovery data obtained from the first group of experiments, the optimum sulfuric acid concentration–time combinations were chosen for each representative ore sample and are given in Table 4.3.

**Table 4.3** The optimum sulfuric acid concentration–time combinations.

<b>Ore Sample</b>	<b>The Optimum Combination</b>
Nontronite	4N–24 Hours
Limonite	5N–24 Hours

For the optimum conditions given above, at the end of leaching process, free acid in pregnant leach solutions was determined by titration. As the acid concentration was known prior to leaching, the difference between the initial and final states was the amount of sulfuric acid consumed during leaching. Acid consumptions of ores were calculated as 669 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for Nontronite and 714 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for Limonite.

The acid consumptions were found to be less than the theoretical acid consumptions calculated based on 100% metal recoveries which were found as 785 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for Nontronite and 1068 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for Limonite. The difference can be explained by not achieving 100% metal recoveries during leaching. An example of theoretical sulfuric acid consumption calculation for Nontronite is given in Appendix B.

ORP values of pregnant leach solutions obtained at the optimum conditions were calculated as 776 mV for Nontronite and 787 mV for Limonite after measurement with Pt-Ag/AgCl electrodes. The measured values were slightly below 800 mV which is needed to achieve high cobalt recoveries. Analyses of leach residues and calculated pregnant leach solution analyses for the optimum combinations of Nontronite and Limonite are given in Tables 4.4 and 4.5, respectively.

**Table 4.4** Analysis of Nontronite leach residue and calculated pregnant leach solution analysis at the optimum combination.

Sample		Leach Residue				Pregnant Solution			
Weight: 15 g		Weight: 8.49 g				Volume: 75 cc			
Ni (g)	0.18	Ni (%)	0.09	Ni (g)	0.01	Ni (g)	0.17	Ni (g/L)	2.30
Fe (g)	2.39	Fe (%)	5.28	Fe (g)	0.45	Fe (g)	1.94	Fe (g/L)	25.92
As (g)	0.00	As (%)	0.03	As (g)	0.00	As (g)	0.00	As (g/L)	0.01
Co (g)	0.01	Co (%)	0.02	Co (g)	0.00	Co (g)	0.00	Co (g/L)	0.06
Cr (g)	0.10	Cr (%)	0.94	Cr (g)	0.08	Cr (g)	0.02	Cr (g/L)	0.29

**Table 4.5** Analysis of Limonite leach residue and calculated pregnant leach solution analysis at the optimum combination.

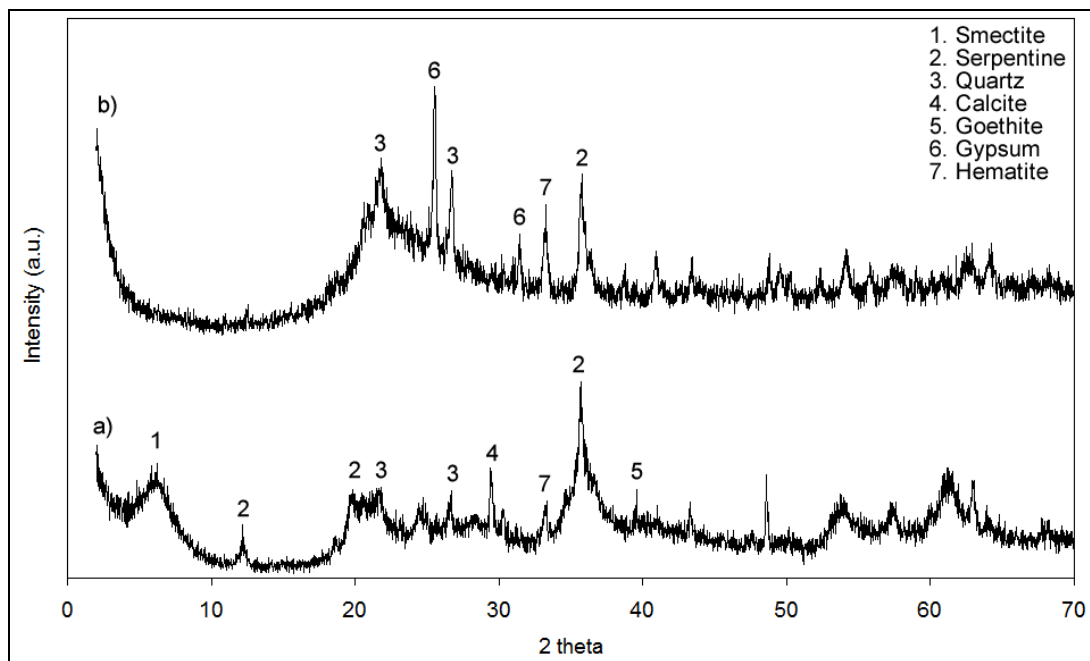
Sample		Leach Residue				Pregnant Solution			
Weight: 15 g		Weight: 7.27 g				Volume: 75 cc			
Ni (g)	0.19	Ni (%)	0.18	Ni (g)	0.01	Ni (g)	0.18	Ni (g/L)	2.38
Fe (g)	4.31	Fe (%)	12.30	Fe (g)	0.89	Fe (g)	3.41	Fe (g/L)	45.48
As (g)	0.10	As (%)	0.63	As (g)	0.05	As (g)	0.06	As (g/L)	0.75
Co (g)	0.01	Co (%)	0.05	Co (g)	0.00	Co (g)	0.01	Co (g/L)	0.12
Cr (g)	0.21	Cr (%)	2.53	Cr (g)	0.18	Cr (g)	0.02	Cr (g/L)	0.31

According to the results of the optimum combination of Nontronite, Fe/Ni ratio was calculated as 11.3 in the pregnant leach solution whereas it was 13.3 in the ore. In Limonite, Fe/Ni ratio was calculated as 19.1 in the pregnant leach solution and 22.7 in the ore prior to agitative leaching. Decrease in Fe/Ni ratio indicates that nickel was extracted selectively to some degree over iron during agitative leaching.

Leach residues obtained under the optimum combinations were taken to XRD analysis. XRD patterns of Nontronite (a) and its leach residue (b) are

given in Figure 4.16. It can be seen from the patterns that all smectite and calcite peaks together with some serpentine and goethite peaks disappeared after agitative leaching.

Quartz and hematite peaks were still present in both patterns and were more prominent in the leach residue as expected. In the pattern of leach residue, gypsum formation was observed which was also expected.

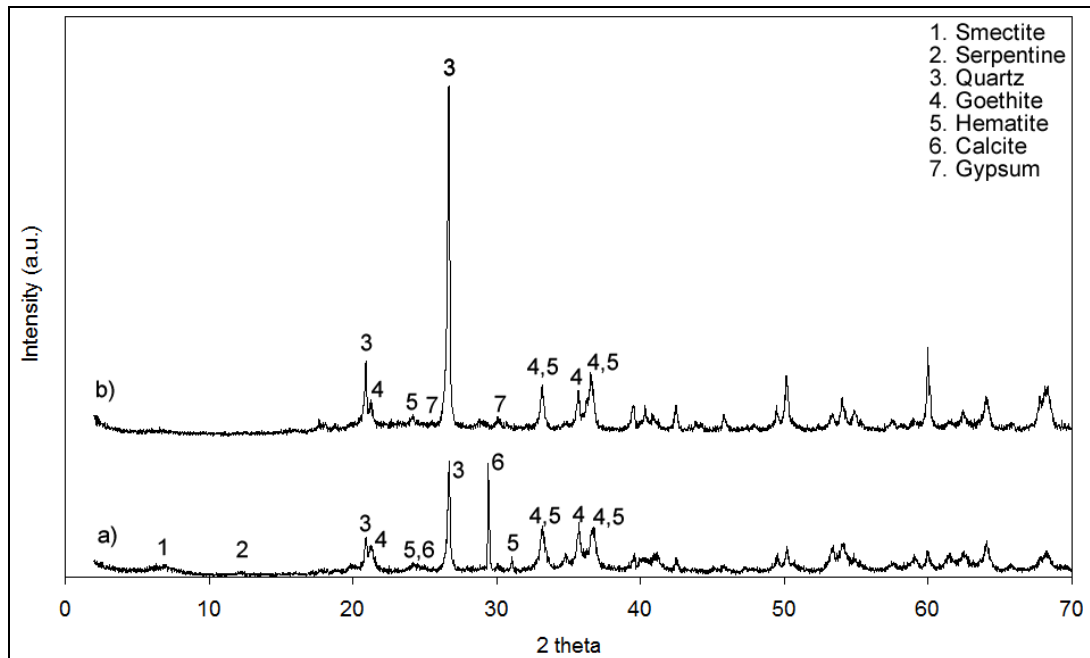


**Figure 4.16** XRD Patterns of Nontronite before agitative leaching (a) and after agitative leaching (b).

XRD patterns of Limonite (a) and its leach residue (b) are given in Figure 4.17. It can be seen from the patterns that all calcite and smectite peaks disappeared after agitative leaching. Quartz peaks were present in both XRD patterns but were more distinct in the leach residue as expected.



Gypsum formation was also observed in the XRD pattern of limonite leach residue.



**Figure 4.17** XRD Patterns of Limonite before agitative leaching (a) and after agitative leaching (b).

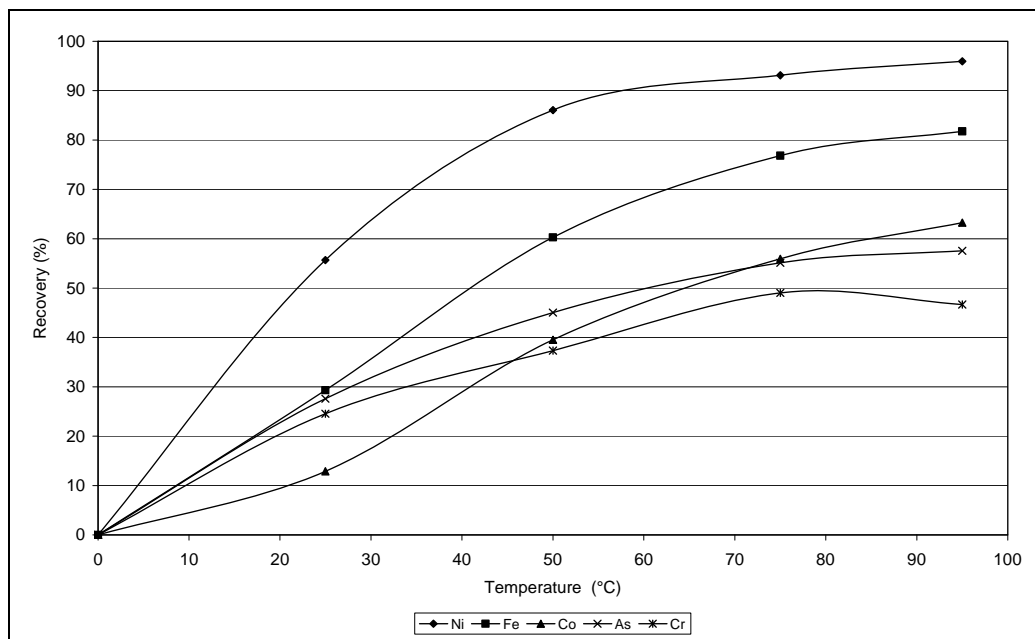
#### 4.1.2 Effect of Temperature

In order to study the leach recovery values of metals at different temperatures, agitative leaching experiments were carried out at 25°C, 50°C, 75°C and 95°C. During the experiments, the weight of representative dried ore sample (15 g), particle size of ore sample (100% -0.074 mm), solid/liquid ratio (1/5 g/cc) were kept constant. Series of experiments with each representative ore were conducted at the optimum sulfuric acid concentration–time combinations given above. Nickel, iron, cobalt, arsenic

and chromium recovery values obtained via XRF analyses of leach residues from the experiments carried out at different temperatures are given in Table 4.6 and Figure 4.18 for Nontronite and Table 4.7 and Figure 4.19 for Limonite, respectively.

**Table 4.6** Effect of temperature on agitative leach recoveries of Nontronite.

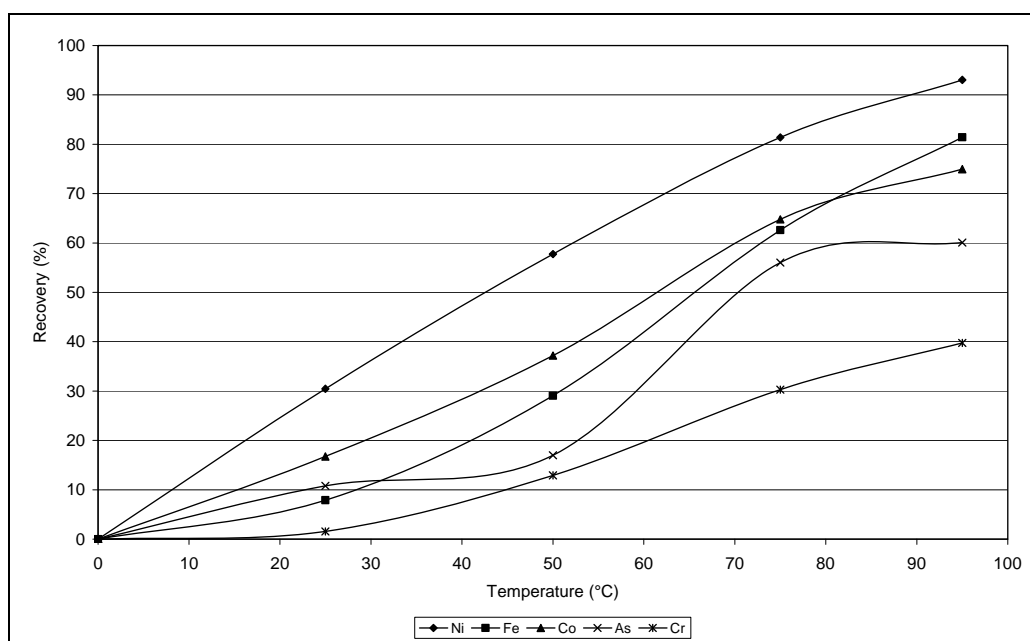
Temperature (°C)	Ni (%)	Fe (%)	Co (%)	As (%)	Cr (%)
95	96.0	81.8	63.4	57.6	46.7
75	93.1	76.8	55.9	55.1	49.0
50	86.1	60.3	39.6	45.1	37.3
25	55.7	29.3	12.9	27.6	24.5



**Figure 4.18** Effect of temperature on agitative leach recoveries of Nontronite.

**Table 4.7** Effect of temperature on agitative leach recoveries of Limonite.

Temperature (°C)	Ni (%)	Fe (%)	Co (%)	As (%)	Cr (%)
95	93.1	81.4	75.0	60.1	39.8
75	81.4	62.6	64.8	56.1	30.3
50	57.8	29.1	37.2	17.0	12.9
25	30.5	7.9	16.8	10.8	1.6



**Figure 4.19** Effect of temperature on agitative leach recoveries of Limonite.

According to the results, it was concluded that increasing temperature had a positive effect on leach recovery values of metals in both samples studied. Highest recoveries were obtained at experiments carried out at 95°C temperature. Therefore, 95°C was chosen as the optimum temperature for agitative leaching experiments.

#### 4.1.4 Effect of Particle Size

Particle size is another important factor in hydrometallurgical processes. In agitative leaching studies, a number of experiments were carried out to study the leach recovery values with different particle sizes. In these experiments, each ore sample was ground to 100% -0.074 mm, -0.147 mm, -0.295 mm, -0.589 mm and -1.168 mm. Experiments were carried out for both lateritic ore samples.

Experiments for each representative ore with different particle sizes were conducted at the optimum sulfuric acid concentration–time combinations as done in studying the effect of temperature. Also during the experiments, the weight of dried lateritic ore sample (15 g), solid/liquid ratio (1/5 g/cc) and the optimum temperature chosen above (95°C) were kept constant. Nickel, iron, cobalt, arsenic and chromium leach recovery values obtained by XRF analyses of leach residues of the experiments carried out with Nontronite and Limonite at different particle sizes are given in Tables 4.8 and 4.9, respectively.

**Table 4.8** Effect of particle size on agitative leach recoveries of Nontronite.

Particle Size (mm)	Ni (%)	Fe (%)	Co (%)	As (%)	Cr (%)
-0.074	96.0	81.8	63.4	57.6	46.7
-0.147	92.3	76.5	48.8	54.7	47.8
-0.295	92.9	76.0	40.3	50.6	42.5
-0.589	93.2	76.2	40.4	51.8	40.8
-1.168	95.0	78.5	27.5	53.5	42.6

**Table 4.9** Effect of particle size on agitative leach recoveries Limonite.

<b>Particle Size (mm)</b>	<b>Ni (%)</b>	<b>Fe (%)</b>	<b>Co (%)</b>	<b>As (%)</b>	<b>Cr (%)</b>
<b>-0.074</b>	93.1	81.4	75.0	60.1	39.8
<b>-0.147</b>	88.6	74.3	72.7	81.9	43.2
<b>-0.295</b>	88.3	74.5	70.8	81.7	41.1
<b>-0.589</b>	88.4	74.3	71.0	82.6	43.0
<b>-1.168</b>	88.5	73.7	71.5	84.1	45.0

The results obtained from the two different lateritic ores showed a similar behavior. In the studied particle size range, particle size did not have a considerable effect on leach recovery values of most metals. This was thought to be due to the decrease in particle size of ore samples in the acidic environment during agitative leaching experiments.

This behavior was confirmed by carrying out screen analysis on one of the leach residues. Leach residue of experiment carried out with Nontronite ground to 100% -0.589 mm was chosen for screen analysis. The results of screen analyses of ore ground to 100% -0.589 mm prior to leaching and after leaching are given in Tables 4.10 and 4.11, respectively.

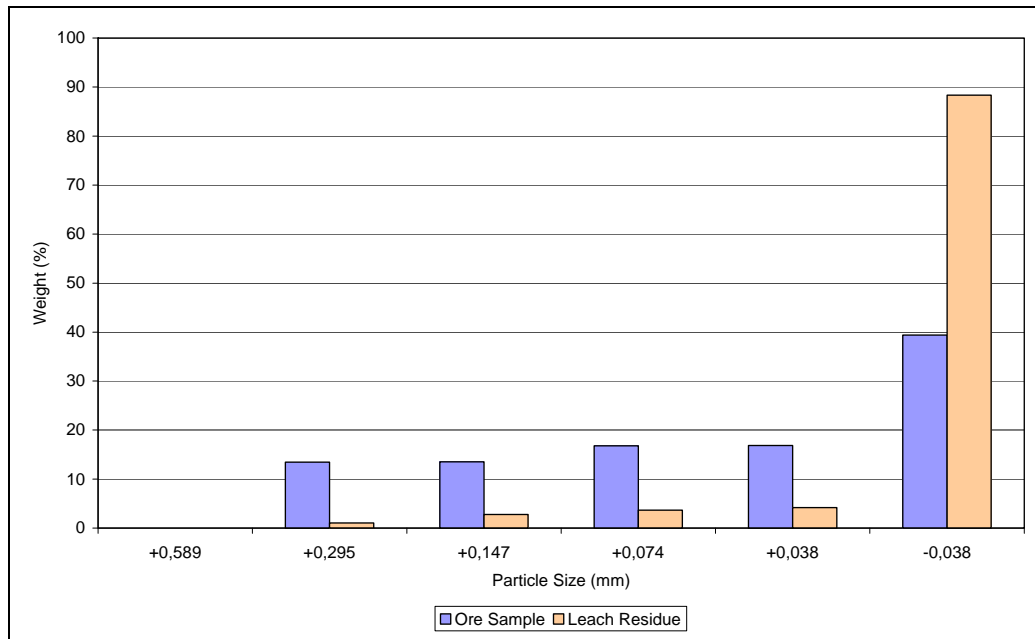
Particle size distributions obtained at the end of screen analyses are given in Figure 4.20. As it can be seen from Figure 4.20, the amount of -0.038 mm particles was 39.40% before acid leaching which increased to 88.37% after leaching.

**Table 4.10** Screen analysis results of Nontronite (100% -0.589 mm).

<b>Particle Size (mm)</b>	<b>Weight (%)</b>	<b>Σ wt % retained</b>	<b>Σ wt % undersize</b>
+0.589	0.00	0.00	100.00
+0.295	13.47	13.47	86.53
+0.147	13.53	27.00	73.00
+0.074	16.77	43.77	56.23
+0.038	16.83	60.60	39.40
-0.038	39.40	-	-
Σ	100.00	-	-

**Table 4.11** Screen analysis of leach residue of Nontronite.

<b>Particle Size (mm)</b>	<b>Weight (%)</b>	<b>Σ wt % retained</b>	<b>Σ wt % undersize</b>
+0.589	0.00	0.00	100.00
+0.295	1.04	1.04	98.96
+0.147	2.78	3.82	96.18
+0.074	3.65	7.47	92.53
+0.038	4.16	11.63	88.37
-0.038	88.37	-	-
Σ	100.00	-	-



**Figure 4.20** Particle size distributions of ore sample and leach residue of Nontronite.

This decrease in particle size may have been the reason for solid-liquid separation problems encountered by filtration. Another reason could be the formation of silica gel during acid leaching.

#### 4.1.5 Multi-Step Agitative Leaching

In agitative leaching experiments, although high metal recoveries were obtained with both ore types under the determined optimum conditions, high residual acid concentrations of pregnant leach solutions would be a disadvantage in neutralization in down-stream processes.

Residual sulfuric acid concentrations of pregnant leach solutions were calculated as 58.2 g/L for Nontronite and 97.2 g/L for Limonite at the end of

experiments carried out under the optimum conditions where the initial sulfuric acid concentrations of solutions were 192.1 g/L for Nontronite and 240.1 g/L for Limonite.

In order to reduce the residual sulfuric acid concentration of pregnant leach solutions, a series of experiments were carried out. In the experiments, Limonite sample was leached under the optimum conditions determined in earlier sections (15 g dry Limonite with 100% -0.074 mm particle size, 75 cc 5N sulfuric acid concentration, 24 hours of leaching period and leaching temperature of 95°C), and then Nontronite sample was introduced to the system and leached for another 24 hours with the residual acid present within the Limonite pregnant leach solution.

Amount of Nontronite addition (5 g, 10 g and 15 g) was studied as variable parameter. Experiments were carried out with and without filtration of leach residue after Limonite leaching. Overall nickel, iron and cobalt recoveries obtained at the end of experiments carried out without filtration of the leach residue of Limonite are given in Table 4.12. Recovery values were obtained via XRF analysis of the final leach residues.

**Table 4.12** Metal recoveries obtained in multi-step agitative leaching, without filtration of leach residue of Limonite.

<b>Nontronite Addition</b>	<b>Nickel Recovery (%)</b>	<b>Iron Recovery (%)</b>	<b>Cobalt Recovery (%)</b>
5 g	89.8	79.0	71.8
10 g	86.6	73.7	65.4
15 g	85.5	68.4	57.4



At the end of experiments, the final residual sulfuric acid concentrations of pregnant leach solutions were determined by titration and found to be 70.6 g/L, 40.0 g/L and 29.8 g/L for 5 g, 10 g and 15 g of Nontronite additions, respectively. As stated before, the initial sulfuric acid concentration was 240.1 g/L.

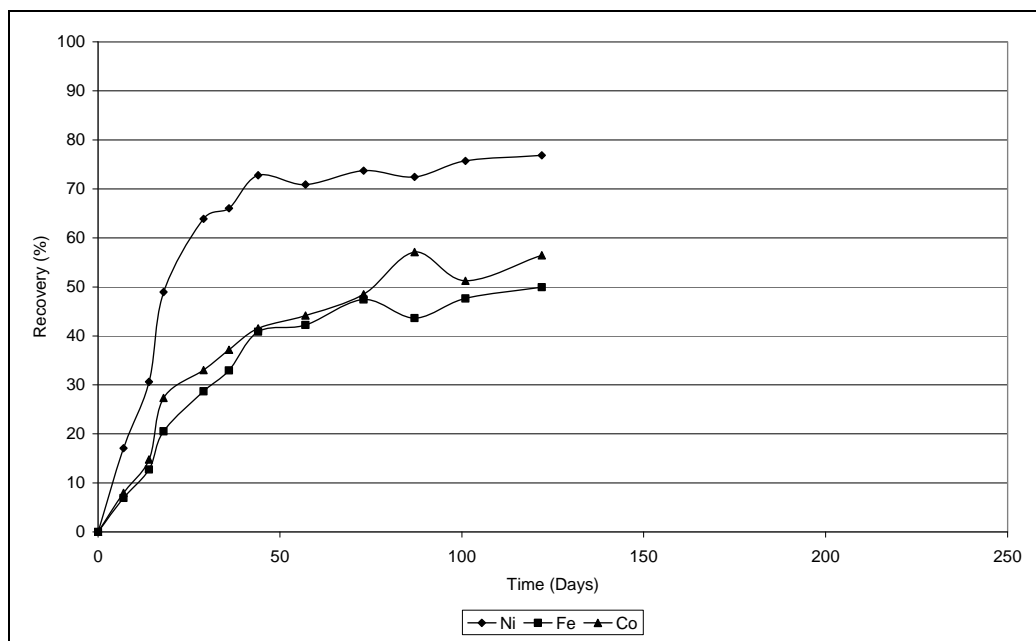
Nickel, iron and cobalt recoveries obtained at the end of experiments that were carried out with filtration of the leach residue of Limonite are given in Table 4.13. In Table 4.13 given below, “LL” represents the recovery values obtained from Limonite after leaching, and “NL” represents the recovery values obtained from Nontronite after leaching. Recovery values were determined via XRF analysis of leach residues. At the end of these experiments, the residual sulfuric acid concentrations of the pregnant leach solutions were determined as 77.8 g/L, 38.6 g/L and 27.1 g/L for 5 g, 10 g and 15 g of Nontronite additions, respectively. Multi-step leaching was found to be the key factor of atmospheric leaching by means of which reduction in the residual acid concentration of pregnant leach solution and a decrease in acid consumption was possible, although a decrease in leach recoveries was also observed as the amount of nontronite addition was increased.

**Table 4.13** Metal recoveries obtained in multi-step agitative leaching, with filtration of leach residue of Limonite.

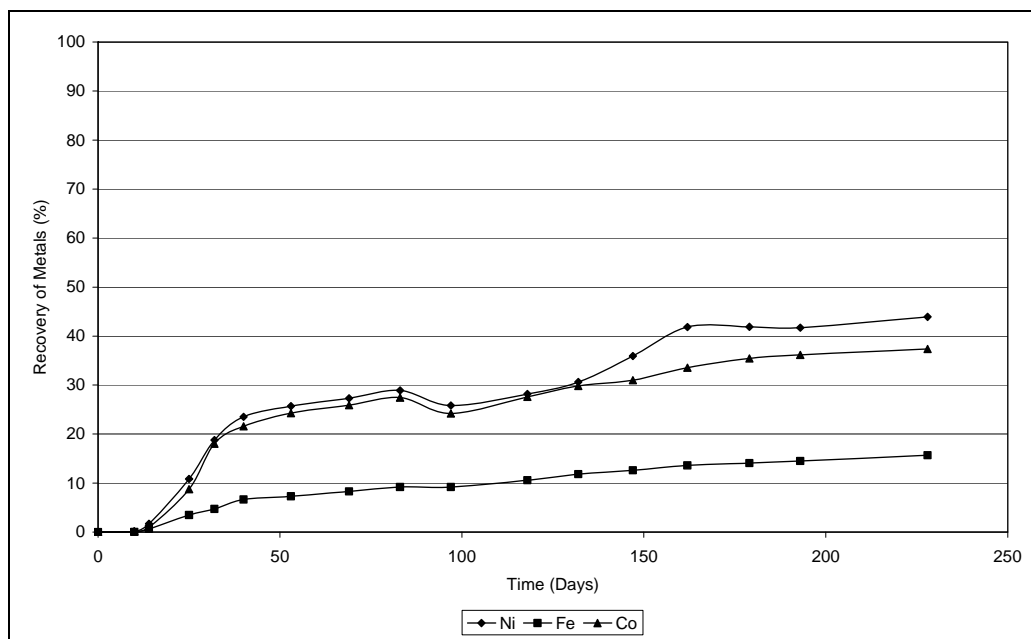
Nontronite Addition	Nickel Recovery (%)		Iron Recovery (%)		Cobalt Recovery (%)	
	LL	NL	LL	NL	LL	NL
5 g	93.3	87.6	81.5	64.2	71.5	39.4
10 g	91.6	77.4	83.6	45.0	74.8	28.3
15 g	92.5	74.8	82.5	29.9	73.1	14.3

## 4.2 Column Leaching

Column leaching experiments were conducted to demonstrate the heap leaching behavior of lateritic ore samples. Column leaching set-up as described in earlier sections was used for the experiments. Initial experiments with the representative ores were carried out by keeping solid/liquid ratio (1kg/1L), flow rate (1000 L/day/m<sup>2</sup>) and sulfuric acid concentration of solution (100 g/L) constant. In the experiments, 8 kg of as-received ore for Nontronite and 9 kg as-received ore for Limonite were used. Nickel, iron and cobalt leach recovery values obtained during the experiments via AAS analysis of pregnant leach solutions are given at Figure 4.21 for Nontronite and Figure 4.22 for Limonite, respectively.



**Figure 4.21** Initial column leach recoveries of Nontronite.



**Figure 4.22** Initial column leach recoveries of Limonite.

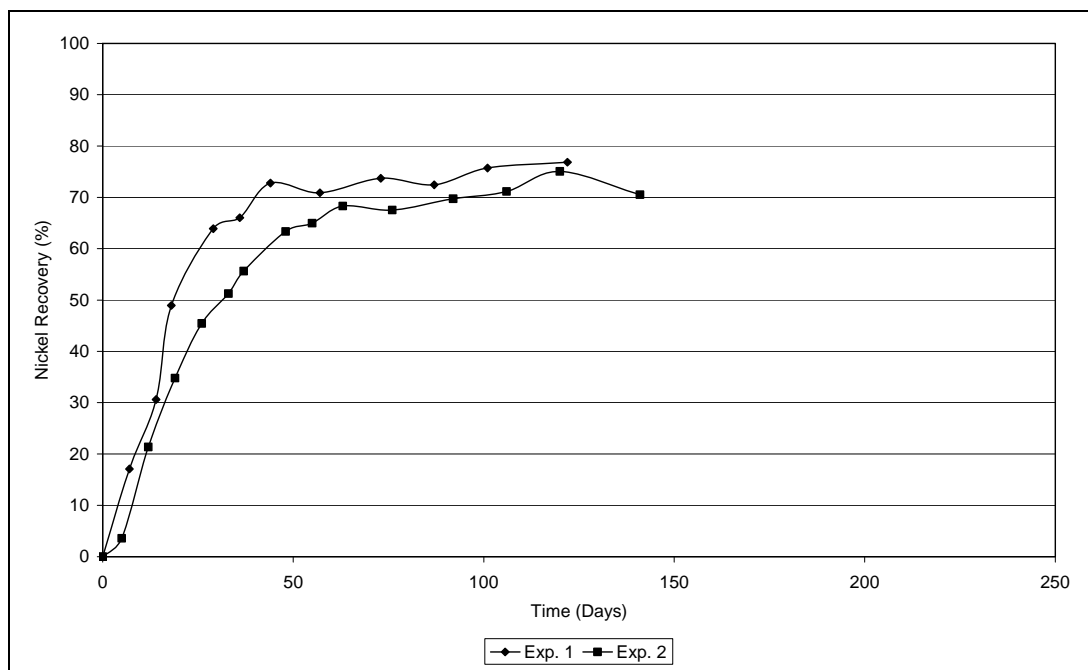
At the end of initial column leaching experiments, higher recovery values were obtained with Nontronite in a very short time interval whereas lower recovery values of metals were obtained with Limonite. Leach recovery values obtained by AAS analysis with Nontronite in 122 days were 76.9%, 49.9% and 56.4% for nickel, iron and cobalt, respectively. In the column leaching of Limonite, 43.9%, 15.7% and 37.4% recovery values were achieved in 228 days for nickel, iron and cobalt, respectively. Due to slow leaching process, the column leaching experiment of limonite was still in progress at the submission date of this thesis. Extrapolation of the recovery curve indicated that the complete nickel recovery could only be obtained in more than 500 days.

Acid consumption of ores based on total sulfuric acid addition during titrations were calculated as 462 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for Nontronite and

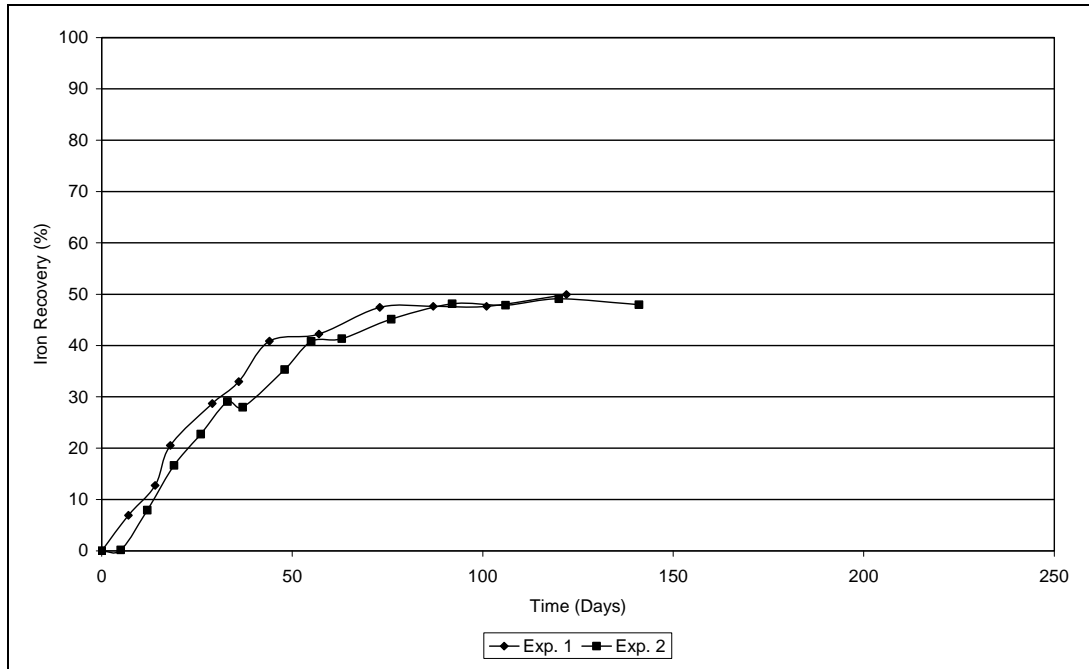
135 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for Limonite for the time period of 122 and 228 days, respectively.

In order to carry out experiments for studying the effects of different parameters on column leaching behavior, Nontronite was preferred due to slower leaching kinetics of Limonite.

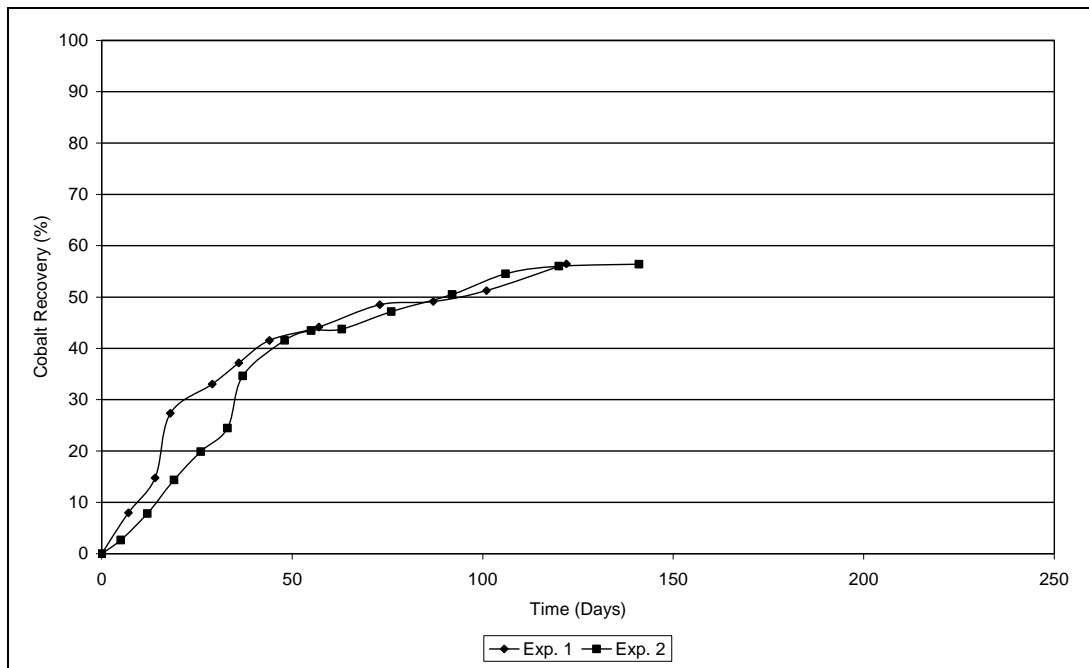
In order to check the quick leaching behavior of Nontronite, another experiment (Exp. 2) was conducted under the same conditions. Recovery values obtained throughout the experimental durations via AAS analyses for nickel, iron and cobalt are given in Figure 4.23, Figure 4.24 and Figure 4.25, respectively.



**Figure 4.23** Nickel recoveries of Nontronite in column leaching.



**Figure 4.24** Iron recoveries of Nontronite in column leaching.



**Figure 4.25** Cobalt recoveries of Nontronite in column leaching.

Results of Exp. 1 and Exp. 2 were in good agreement with each other and the recovery profiles with respect to time showed the reproducibility of metal recoveries of Nontronite in column leaching experiments.

At the end of experiments, the leach residues were taken to ICP and XRF analyses which were reported on dry basis. Recovery values obtained from the pregnant leach solutions via AAS analysis and those obtained from leach residues at the end of experiments are given in Tables 4.14 and 4.15, respectively.

**Table 4.14** Metal recoveries obtained from pregnant leach solutions of Nontronite via AAS analysis.

	<b>Metal Recoveries (from Pregnant Leach Solution)</b>		
	<b>Ni(%)</b>	<b>Co(%)</b>	<b>Fe(%)</b>
<b>Exp. 1</b>	70.5	53.4	47.9
<b>Exp. 2</b>	76.9	56.4	50.0

**Table 4.15** Metal recoveries obtained from leach residues of Nontronite via ICP and XRF analyses.

	<b>Metal Recoveries (from Leach Residue)</b>							
	<b>Ni(%)</b>	<b>Co(%)</b>	<b>Fe(%)</b>	<b>As(%)</b>	<b>Cr(%)</b>	<b>Mn(%)</b>	<b>Mg(%)</b>	<b>Al(%)</b>
<b>Exp. 1</b>	83.9	55.2	55.8	27.0	44.7	57.1	89.9	56.4
<b>Exp. 2</b>	82.4	40.2	52.2	24.9	33.4	53.6	89.5	49.4

Metal recovery results obtained from the pregnant leach solutions and leach residues differed from each other. This was due to mathematical assumptions that were made during the recovery calculations from

pregnant leach solutions. In calculations, the results of metal analyses in pregnant leach solution were multiplied by the total volume of solution within the system.

However, due to the moisture content of ore, saturation of ore within the column and continuous evaporation especially during summer time, the total amount of solution within the system changed all the time. Therefore, the initial assumptions made on the total volume differed and resulted in lower recovery values.

However, analyses carried out on solution gave an idea about the leaching behavior and recovery values throughout the experimental durations as the exact recovery values could only be obtained at the end of leaching process based on analyses of dried leach residues. On the other hand, leach recoveries calculated based on pregnant leach solution and wash water analyses confirmed the leach recovery values found from leach residues.

In order to obtain the correct data about pregnant leach solutions, back calculations were carried out. Based on analyses of original Nontronite ore sample and leach residues, calculated pregnant leach solution analyses were found and are summarized in Table 4.16.

**Table 4.16** Analyses of original ore sample and leach residues and calculated pregnant leach solution analyses of experiments carried out with Nontronite.

<b>Experiment 1</b>				<b>Experiment 2</b>			
Sample Dry Weight: 4792 g				Sample Dry Weight: 4792 g			
Ni (%)	1.20	Ni (g)	57.50	Ni (%)	1.20	Ni (g)	57.50
Co (%)	0.044	Co (g)	2.11	Co (%)	0.044	Co (g)	2.11
Fe (%)	15.95	Fe (g)	764.32	Fe (%)	15.95	Fe (g)	764.32
As (%)	0.020	As (g)	0.96	As (%)	0.020	As (g)	0.96
Cr (%)	0.677	Cr (g)	32.44	Cr (%)	0.675	Cr (g)	32.35
Mn (%)	0.267	Mn (g)	12.79	Mn (%)	0.267	Mn (g)	12.79
Mg (%)	1.148	Mg (g)	55.01	Mg (%)	1.148	Mg (g)	55.01
Al (%)	2.208	Al (g)	105.81	Al (%)	2.208	Al (g)	105.81
<b>Leach Residue</b>				<b>Leach Residue</b>			
Dry Weight: 3600 g				Dry Weight: 3500 g			
Ni (%)	0.28	Ni (g)	10.12	Ni (%)	0.26	Ni (g)	9.24
Co (%)	0.035	Co (g)	1.26	Co (%)	0.027	Co (g)	0.95
Fe (%)	10.15	Fe (g)	365.40	Fe (%)	9.65	Fe (g)	337.75
As (%)	0.020	As (g)	0.72	As (%)	0.020	As (g)	0.70
Cr (%)	0.600	Cr (g)	21.60	Cr (%)	0.513	Cr (g)	17.96
Mn (%)	0.163	Mn (g)	5.87	Mn (%)	0.155	Mn (g)	5.425
Mg (%)	0.582	Mg (g)	20.95	Mg (%)	0.576	Mg (g)	20.16
Al (%)	1.488	Al (g)	53.57	Al (%)	1.318	Al (g)	46.13
<b>Pregnant Leach Solution</b>				<b>Pregnant Leach Solution</b>			
Volume: 8000 cc				Volume: 8000 cc			
Ni (g)	47.39	Ni (g/L)	5.92	Ni (g)	48.26	Ni (g/L)	6.03
Co (g)	0.848	Co (g/L)	0.11	Co (g)	1.163	Co (g/L)	0.15
Fe (g)	398.92	Fe (g/L)	49.87	Fe (g)	426.57	Fe (g/L)	53.32
As (g)	0.238	As (g/L)	0.03	As (g)	0.258	As (g/L)	0.03
Cr (g)	10.746	Cr (g/L)	1.34	Cr (g)	14.487	Cr (g/L)	1.81
Mn (g)	6.93	Mn (g/L)	0.87	Mn (g)	7.37	Mn (g/L)	0.92
Mg (g)	34.06	Mg (g/L)	4.26	Mg (g)	34.85	Mg (g/L)	4.36
Al (g)	52.24	Al (g/L)	6.53	Al (g)	59.68	Al (g/L)	7.46

Based on the data given in Table 4.16, Fe/Ni and Al/Ni ratios in pregnant leach solutions were calculated as 8.8 and 1.2 for Exp. 1; 8.4 and 1.1 for Exp.

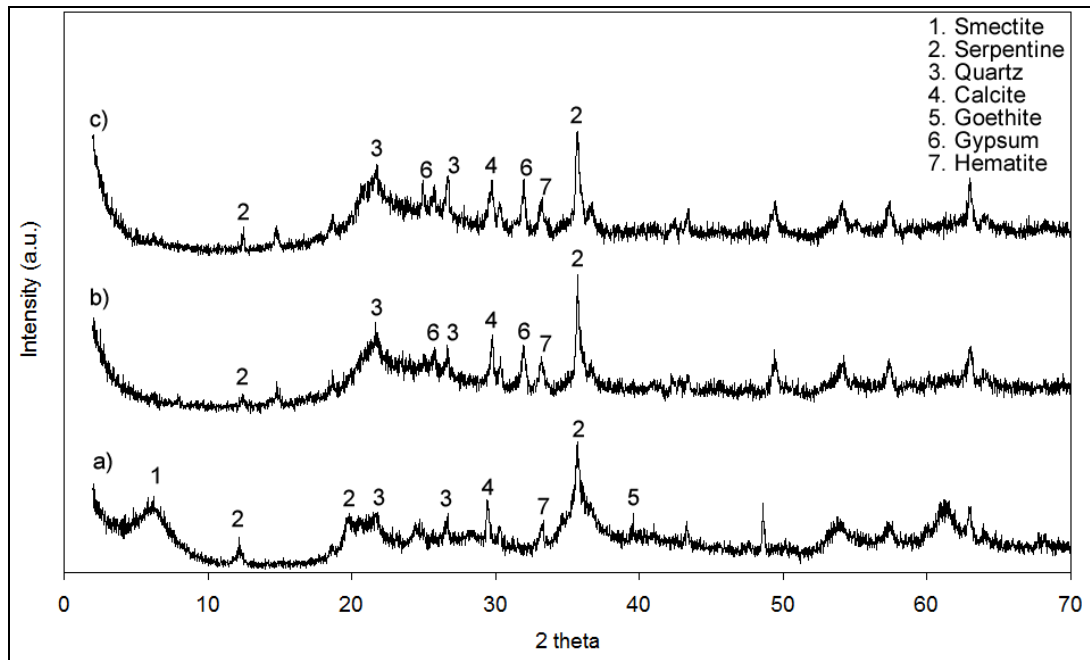


2, respectively. In the ore sample, prior to column leaching, Fe/Ni and Al/Ni ratios were 13.3 and 1.8, respectively. It can be concluded that nickel was extracted selectively to some degree over iron and aluminum during column leaching.

In the experiments that were carried out, the acid consumptions were calculated as 462 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for Exp. 1 and 514 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for Exp. 2.

ORP values of final pregnant leach solutions were measured as 883 mV for Exp. 1 and 890 mV for Exp. 2. It is known from past experience that the ORP value needs to be below 800 mV to achieve high cobalt recovery. Since the measured values were above 800 mV, the column leach recoveries of cobalt were relatively low. This could only be increased by the addition of sodium metabisulphite to sulfuric acid leaching solution.

Leach residues obtained from Experiment 1 and Experiment 2 were taken to XRD analyses. Plotted XRD patterns of Nontronite (a) Experiment 1 (b) and Experiment 2 (c) are given in Figure 4.26.



**Figure 4.26** XRD Patterns of Nontronite before column leaching (a), after Experiment 1 (b) and after Experiment 2 (c).

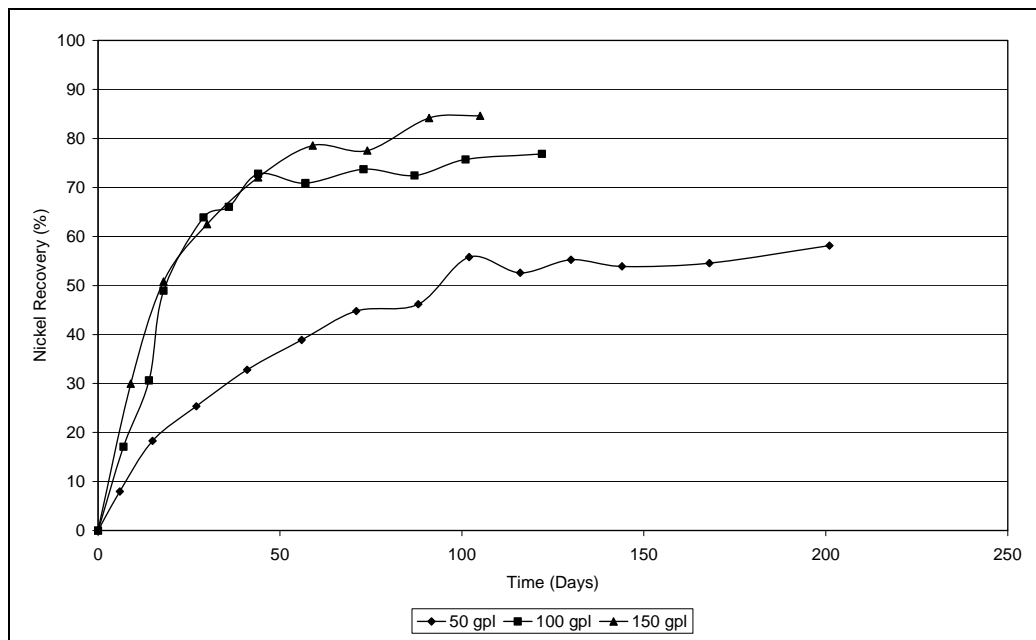
It can be seen from the XRD patterns that all smectite and goethite peaks together with some serpentine peaks disappeared after column leaching. Quartz and hematite peaks were still present in all patterns. In the pattern of leach residues, gypsum formations were observed as expected.

#### 4.2.1 Effect of Acid Concentration

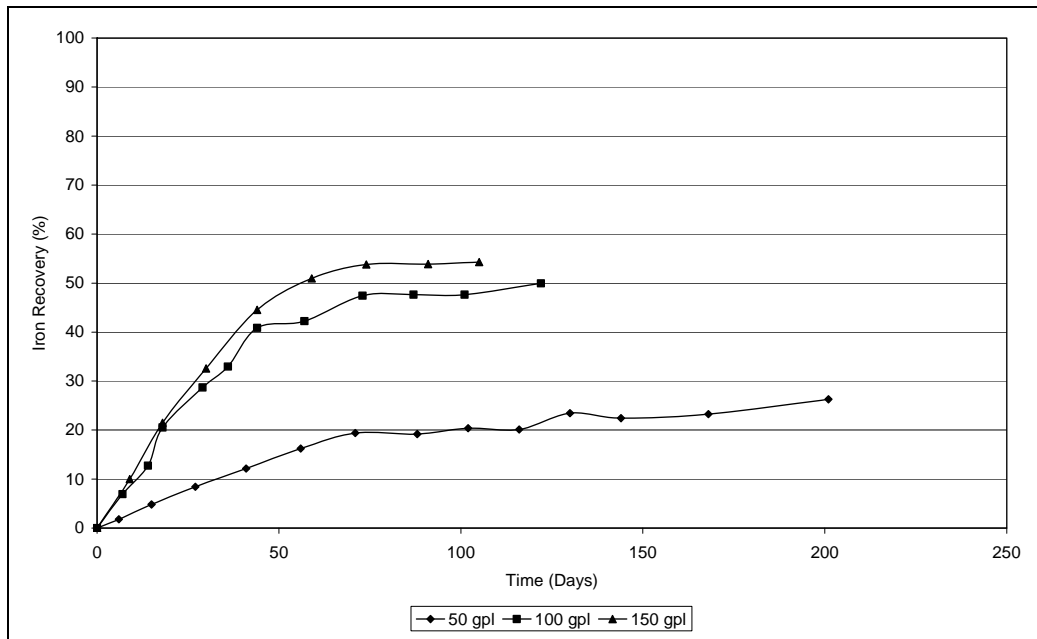
In order to study the effect of acid concentration on column leaching behavior and recovery values, experiments were also carried out with different sulfuric acid concentrations using Gördes Nontronitic laterite.

To carry out the experiments, three different sulfuric acid concentrations for leach solution were chosen namely 50 g/L, 100 g/L and 150 g/L. In all three

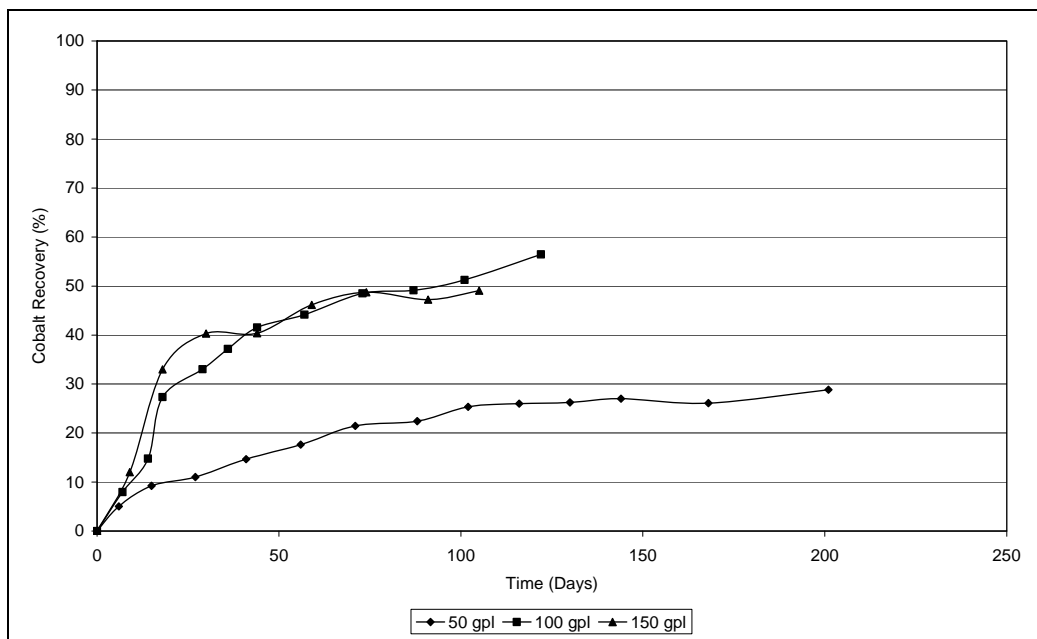
experiments, 8 kg as-received Nontronite ore was used. During the experiments, solid/liquid ratio (1kg/1L) and flow rate (1000 L/day/m<sup>2</sup>) were kept constant. Leach recovery values obtained during the experiments for nickel, iron and cobalt via AAS analysis are given in Figure 4.27, Figure 4.28 and Figure 4.29, respectively.



**Figure 4.27** Nickel recoveries of Nontronite at different acid concentrations in column leaching.



**Figure 4.28** Iron recoveries of Nontronite at different acid concentrations in column leaching.



**Figure 4.29** Cobalt recoveries of Nontronite at different acid concentrations in column leaching.

Results of experiments carried out with different sulfuric acid concentrations showed that increases in acid concentration resulted in higher nickel and cobalt recovery values. Therefore, higher acid concentration enabled faster leaching process. On the other hand, the amount of iron leached also increased with respect to sulfuric acid concentration of leach solution making the pregnant leach solution dirtier or contaminated and more problematic from the point of view of solution purification which is the following step after leaching and solid-liquid separation.

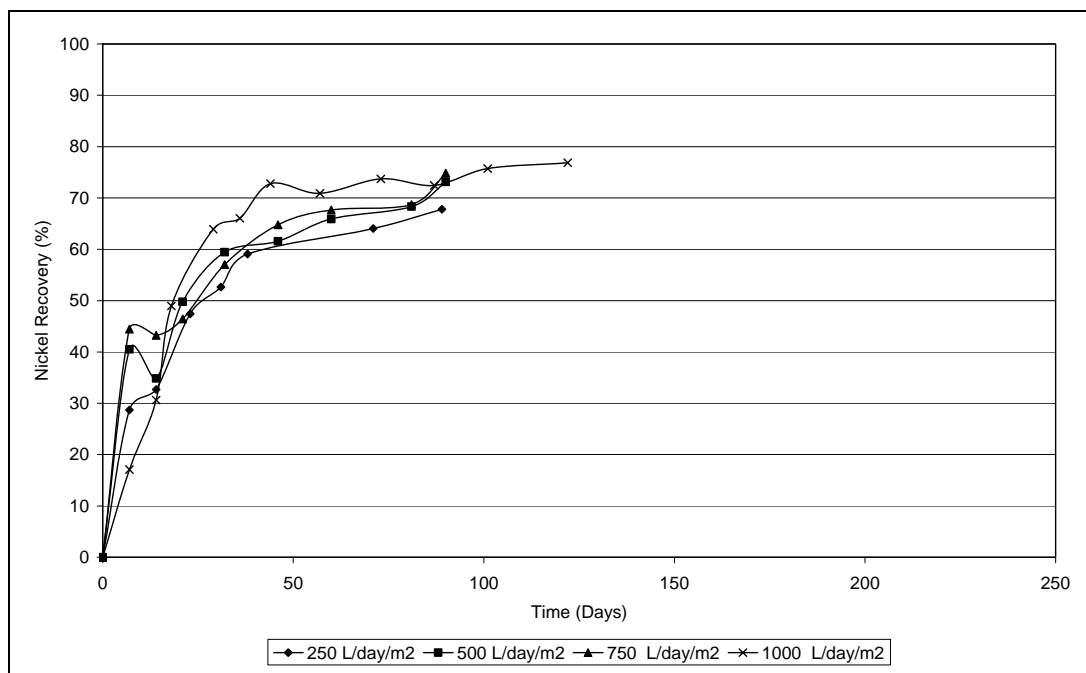
Acid consumptions were calculated as 351 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for the experiment carried out with 50 g/L sulfuric acid concentration, 462 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for the experiment carried out with 100 g/L sulfuric acid concentration and 497 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for the experiment carried out with 150 g/L sulfuric acid concentration. The reason of lower acid consumption of the experiment that was carried out with 50 g/L sulfuric acid concentration was due to lower iron dissolution as iron is the major acid consuming component in leaching. On the other hand, as the acid concentration was increased to 150 g/L, the acid consumption increased since the amount of iron that was leached also increased.

#### **4.2.2 Effect of Flow Rate**

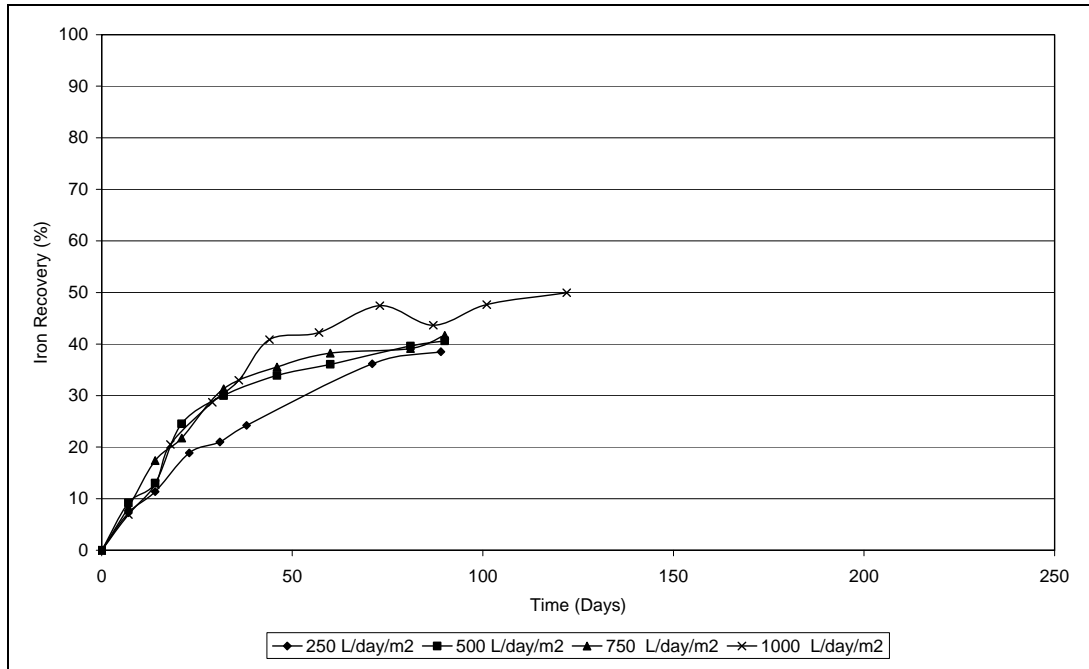
Flow rate expressed as the liters of solution fed to one square meter area of ore in one day (L/day/m<sup>2</sup>) is another important parameter in hydrometallurgy especially in heap leaching.

To carry out experiments and observe the effect of flow rate on leach recovery values of metals, four different flow rates (1000, 750, 500 and 250 L/day/m<sup>2</sup>) were chosen. During the experiments, sulfuric acid concentration of leach solution (100 g/L) and solid/liquid ratio (1kg/1L) were kept constant. Experiments were carried out with 8 kg as-received Nontronite ore.

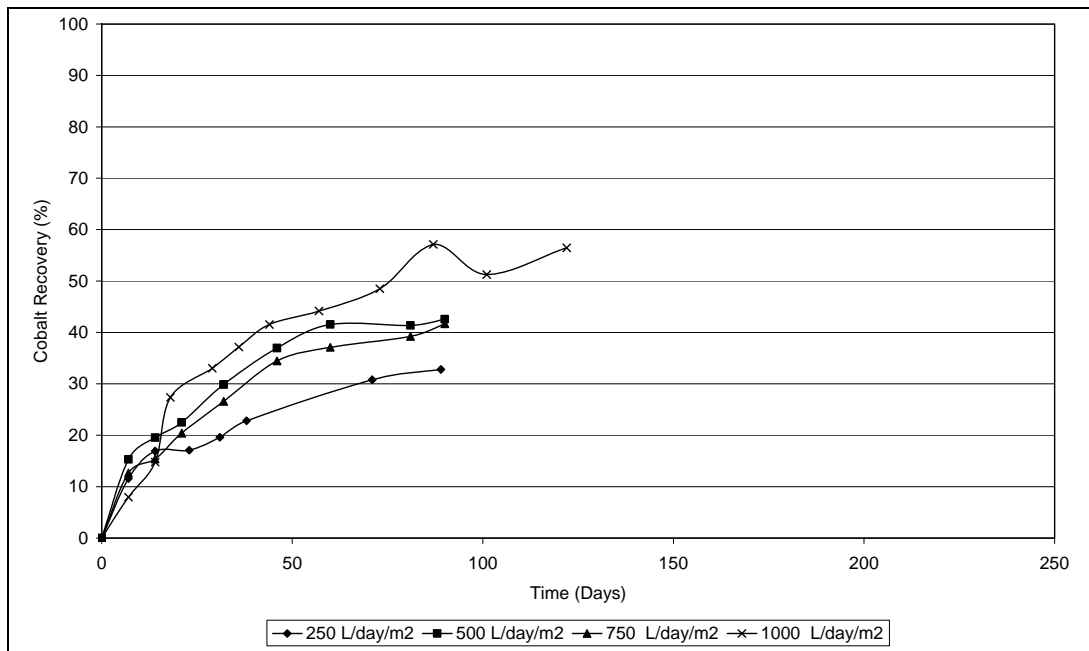
Recovery values obtained during the experiments for nickel, iron and cobalt via AAS analysis of pregnant leach solutions are given in Figure 4.30, Figure 4.31 and Figure 4.32, respectively.



**Figure 4.30** Nickel recoveries of Nontronite at different flow rates in column leaching.



**Figure 4.31** Iron recoveries of Nontronite at different flow rates in column leaching.



**Figure 4.32** Cobalt recoveries of Nontronite at different flow rates in column leaching.

Results obtained during the experiments showed that, in the studied flow rate range, increasing flow rate favored higher nickel and iron recoveries up to 20% in overall recovery of metals. Effect of flow rate can be seen more clearly in cobalt leach recoveries given in Figure 4.31 in which cobalt recovery doubles when the flow rate is changed from 250 to 1000 L/day/m<sup>2</sup>.

Overall acid consumptions of experiments were calculated as 380 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for the experiment carried out with 250 L/day/m<sup>2</sup> flow rate, 390 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for the experiment carried out with 500 L/day/m<sup>2</sup> flow rate, 402 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for the experiment carried out with 750 L/day/m<sup>2</sup> flow rate and 462 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for the experiment carried out with 1000 L/day/m<sup>2</sup> flow rate.



## CHAPTER 5

### CONCLUSION

During this study, lateritic ores from Gördes region Manisa, were used to investigate the optimum conditions for nickel and cobalt extraction using hydrometallurgical methods under atmospheric pressure.

Supplied ores which were representative samples of the whole ore body in Gördes region, were taken to characterization studies. It was shown that smectite, serpentine, goethite, quartz and calcite were present in Nontronite; goethite, hematite, quartz and calcite and to a lesser extent serpentine and smectite were present in Limonite. In SEM analyses of both samples, it was seen that nickel was present in laterites as replacements or substitutions in the atomic structure of goethite, serpentine, smectite and asbolane. Cobalt was in the structure of asbolane mineral.

Agitative leaching experiments were conducted with various parameters to determine the optimum conditions. It was found that increasing temperature, acid concentration and leaching time increased the metal recoveries in both ore samples. In the studied particle size range of 100% -1.168 mm and 100% -0.074 mm, it was shown that particle size did not have a considerable effect on most of the metal recoveries. This was due to

the decrease in particle size of ore samples in the acidic environment during agitative leaching. This behavior was confirmed by carrying out wet screen analysis on the leach residue.

In agitative leaching, the optimum conditions were determined as 24 hours leaching at 95°C with a solid to liquid ratio of 1/5 g/cc for both ore samples. Initial sulfuric acid concentrations of leach solutions were determined as 192.1 g/L for Nontronite and 240.1 g/L for Limonite. Under these optimum conditions, the nickel and cobalt recoveries were 96.0% and 63.4% for nontronite; 93.1% and 75.0% for limonite, respectively.

According to the results for the optimum combination of Nontronite, Fe/Ni ratio was calculated as 11.3 in the pregnant leach solution whereas it was 13.3 in the ore. In Limonite, Fe/Ni ratio was calculated as 19.1 in the pregnant leach solution and 22.7 in the ore prior to agitative leaching. Decreases in Fe/Ni ratio indicated that nickel was extracted selectively to some degree over iron during agitative leaching of each laterite sample.

Acid consumptions of ores were calculated as 669 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for Nontronite and 714 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore for Limonite. Multi-step leaching was found to be effective in reduction of acid consumption as well as the residual acid concentration of pregnant leach solution.

In column leaching with 100 g/L sulphuric acid solution with a flow rate of 1000 L/day/m<sup>2</sup>, it was shown that Nontronite could be leached in 122 days with metal recoveries of 83.9% and 55.2% for nickel and cobalt, respectively with 462 kg H<sub>2</sub>SO<sub>4</sub>/ton dry ore acid consumption. In the column leaching of

Limonite, 43.9% and 37.4% recovery values were achieved in 228 days for nickel and cobalt, respectively. It was concluded that Limonite was not suitable for column leaching due to slow leaching process.

In column leaching of Nontronite, Fe/Ni and Al/Ni ratios in pregnant leach solutions were calculated to be in the range of 8.4–8.8 and 1.1–1.2, respectively whereas prior to column leaching, Fe/Ni and Al/Ni ratios were 13.3 and 1.8, respectively. It was concluded that nickel was extracted selectively to some degree over iron and aluminum during column leaching.

Conducted column leaching experiments showed that increasing sulfuric acid concentration and flow rate had a positive effect on metal recoveries with respect to time. However, it was seen that, the amount of iron leached also increased with increasing sulfuric acid concentration of leach solution making the pregnant leach solution dirtier or contaminated and more problematic from the point of view of solution purification which is the following step after leaching and solid-liquid separation.

For the future work, following suggestions can be made:

1. The problems encountered in solid-liquid separation by filtration should be further investigated and a solution should be found for agitative leaching.
2. Precipitation of iron from pregnant leach solution without losing too much nickel and cobalt to the precipitate should be investigated. As an alternative solvent extraction of iron could be researched. Then, the precipitation of nickel and cobalt as hydroxide or sulfide or ion

exchange of nickel and cobalt prior to iron precipitation needs to be studied. Finally, purification of pregnant leach solution from manganese and magnesium should be investigated so as to recycle the process water to leaching operation.

3. Pilot plant testing and feasibility studies should be conducted.

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## APPENDIX A

### EXAMPLE OF RECOVERY CALCULATION

Leach recovery values were calculated by using the Equation A.1 given below;

$$\text{Recovery of Metal (\%)} = \left[ 100 - \frac{\text{Metal \% in residue} \times \text{Weight of residue}}{\text{Metal \% in ore} \times \text{Weight of ore}} \times 100 \right] \quad (\text{A.1})$$

Results of XRF analysis together with weights of dried ore sample and dried leach residue obtained from the experiment carried out with Nontronite (5N sulfuric acid concentration, leaching temperature of 95°C and 24 hours of leaching) are given Table A.1.

**Table A.1.** Experimental data obtained from agitative leaching of Nontronite

Ore						Leach Residue					
Wt. (g)	Ni (%)	Fe (%)	As (%)	Co (%)	Cr (%)	wt. (g)	Ni (%)	Fe (%)	As (%)	Co (%)	Cr (%)
15	1.289	16.40	0.036	0.037	0.995	7.67	0.035	3.78	0.026	0.0253	0.958

According to experimental data and Equation A.1, the recoveries of nickel, iron, cobalt, chromium and arsenic were calculated as;

$$\text{Recovery of Nickel (\%)} = \left[ 100 - \frac{0.035 \times 7.67}{1.289 \times 15} \times 100 \right] = 98.6 \quad (\text{A.2})$$

$$\text{Recovery of Iron (\%)} = \left[ 100 - \frac{3.78 \times 7.67}{16.40 \times 15} \times 100 \right] = 88.2 \quad (\text{A.3})$$

$$\text{Recovery of Cobalt (\%)} = \left[ 100 - \frac{0.0253 \times 7.67}{0.037 \times 15} \times 100 \right] = 65.1 \quad (\text{A.4})$$

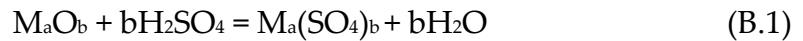
$$\text{Recovery of Arsenic (\%)} = \left[ 100 - \frac{0.026 \times 7.67}{0.036 \times 15} \times 100 \right] = 63.1 \quad (\text{A.5})$$

$$\text{Recovery of Chromium (\%)} = \left[ 100 - \frac{0.958 \times 7.67}{0.995 \times 15} \times 100 \right] = 50.8 \quad (\text{A.6})$$

## APPENDIX B

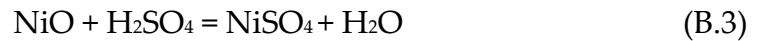
### EXAMPLE OF THEORETICAL ACID CONSUMPTION CALCULATION

The theoretical acid consumption of Nontronite was calculated based on 100% recoveries of metals. Sulfuric acid consumptions of metals per ton of dry ore were calculated according to Equation B.1 and Equation B.2, where M denotes various metals;



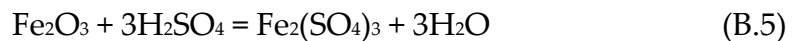
$$H_2SO_4 \text{ used (kg / ton ore)} = \left[ \frac{M_aO_b \text{ (\%)}}{100} \times \frac{b \times MW_{H_2SO_4}}{MW_{MO}} \times 1000 \right] \quad (B.2)$$

#### Sulfuric acid consumption of nickel per ton of ore



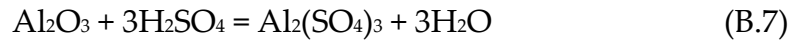
$$\left[ \frac{1.52}{100} \times \frac{1 \times 98}{75} \times 1000 \right] = 19.9 \text{ kg } H_2SO_4 \quad (B.4)$$

#### Sulfuric acid consumption of iron per ton of ore



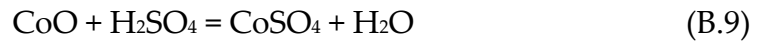
$$\left[ \frac{22.52}{100} \times \frac{3 \times 98}{160} \times 1000 \right] = 413.8 \text{ kg } H_2SO_4 \quad (B.6)$$

**Sulfuric acid consumption of aluminum per ton of ore**



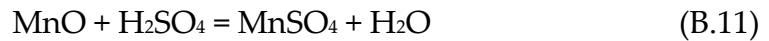
$$\left[ \frac{4.17}{100} \times \frac{3 \times 98}{102} \times 1000 \right] = 120.3 \text{ kg H}_2\text{SO}_4 \quad (\text{B.8})$$

**Sulfuric acid consumption of cobalt per ton of ore**



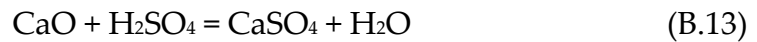
$$\left[ \frac{0.056}{100} \times \frac{1 \times 98}{75} \times 1000 \right] = 0.7 \text{ kg H}_2\text{SO}_4 \quad (\text{B.10})$$

**Sulfuric acid consumption of manganese per ton of ore**



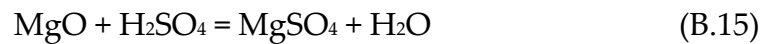
$$\left[ \frac{0.34}{100} \times \frac{1 \times 98}{71} \times 1000 \right] = 4.7 \text{ kg H}_2\text{SO}_4 \quad (\text{B.12})$$

**Sulfuric acid consumption of calcium per ton of ore**



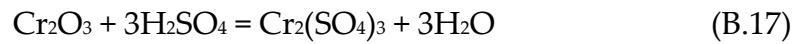
$$\left[ \frac{2.15}{100} \times \frac{1 \times 98}{56} \times 1000 \right] = 37.6 \text{ kg H}_2\text{SO}_4 \quad (\text{B.14})$$

**Sulfuric acid consumption of magnesium per ton of ore**



$$\left[ \frac{6.91}{100} \times \frac{1 \times 98}{40} \times 1000 \right] = 169.3 \text{ kg H}_2\text{SO}_4 \quad (\text{B.16})$$

### Sulfuric acid consumption of chromium per ton of ore



$$\left[ \frac{0.988}{100} \times \frac{3 \times 98}{152} \times 1000 \right] = 19.1 \text{ kg H}_2\text{SO}_4 \quad (\text{B.18})$$

Overall theoretical acid consumption of Nontronite was calculated as 785.4 kg for ton of dry ore. Similar calculation was also done for Limonite and the total theoretical acid consumption was found to be 1068.5 kg for ton of dry ore.