HYDROMETALLURGICAL EXTRACTION OF NICKEL AND COBALT FROM ÇALDAĞ LATERITIC ORE

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ABSTRACT

HYDROMETALLURGICAL EXTRACTION OF NICKEL AND COBALT FROM ÇALDAĞ LATERITIC ORE

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In this study, an attempt has been made to hydrometallurgical extraction of cobalt and nickel by atmospheric pressure sulphuric acid leaching and a pug-roast-leach process using two stage roasting for lateritic ore. The ore used in the study was obtained from Çaldağ Lateritic Ore, Manisa, Turkey. The metal contents of the ore are 2.1 % Ni, 0.12 % Co, 32.45 % Fe, 1.01 % Mn, 2.58 % Cr, 0.78 % Mg and 1.01 % Al. The reserve of lateritic ore deposit is approximately 40 million tonnes.

In the study, first sulphuric acid leaching was applied at atmospheric pressure for leaching the Çaldağ lateritic ore. The effect of various parameters, such as leaching time, leaching temperature, particle size, pulp density and acid strength on Ni and Co extractions were determined. By leaching at 80^oC for 40 wt % H_2SO_4 addition of ore, 1/3 pulp density, Ni and Co extractions were found 44.49 % and 53.03 % respectively, yielded a pregnant solution containing 3.11 g/L Ni and 0.12 g/L Co. But the result of atmospheric pressure sulphuric acid leaching was considered insufficient from the recovery point of view.

In the pug-roast-leach process, which is consisted of a two stage roasting followed by water leaching, decomposition temperature differences of sulphates of cobalt, nickel and iron are exploited. In this process, amount of acid, sulphatization and decomposition temperature, sulphatization and decomposition time, leaching temperature and time, solid/liquid ratio, and the effect of water addition during pugging were optimized. Under the optimized conditions (sulphuric acid: 25 wt % of ore; moisture: 20 wt % of ore; sulphatization temperature: 450^{o}C; sulphatization time: 30 minutes; decomposition temperature: 700^{o}C; decomposition time: 60 minutes; leaching temperature: 70^{o}C; leaching time: 30 minutes and solid-liquid ratio: 1/4 by weight), Co and Ni extractions were found 91.4 and 84.4 percent, respectively. A pregnant solution containing 3.084 g/L Ni and 0.185 g/L Co was obtained. These results were considered sufficient for the leaching of lateritic nickel ores.

Keywords: Lateritic Ores; Roasting; Sulphuric Acid Leaching; Cobalt; and Nickel

ÖZ

ÇALDAĞ LATERİTİK CEVHERLERİNDEN HİDROMETALURJİK OLARAK NİKEL VE KOBALT KAZANIMI

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Bu çalışmada, lateritik cevher yatağından alınan numunelerde nikel ve kobalt elde etmek için atmosferik koşullarda sülfürik asit liçi ve iki aşamalı sülfatlama sonrası liç işlemlerine dayanan hidrometalurjik bir işlem uygulanmıştır. Bu çalışmada kullanılan cevher Manisa ili Çaldağ lateritik yatağından temin edilmiştir. Bu cevherin metal içeriği; % 2.1 Ni, % 0.12 Co, % 32.45 Fe, % 1.01 Mn, % 2.58 Cr, % 0.78 Mg ve % 1.01 Al olarak tespit edilmiştir. Çaldağ lateritik yatağı rezervi ise 40 milyon ton olarak belirlenmiştir.

Çalışmada önce atmosferik koşullarda sülfürik asit liçi uygulanmıştır. Burada liç süresi, liç sıcaklığı, tane boyu, pülp yoğunluğu ve asit miktarı gibi değişik parametrelerin Ni ve Co kazanımındaki etkisi belirlenmiştir. 80^{o}C liç sıcaklığında, cevher ağırlığının % 40 oranında sülfürik asit ilavesi ve 1/3 pülp yoğunluğu ile yapılan deney sonucu % 44.49 Ni ve % 53.03 Co kazanılmıştır; çözeltide 3.11 g/L Ni ve 0.12 g/L Co derişimi elde edilmiştir. Fakat sülfürik asit ile yapılan deneylerde elde edilen bu sonuçlar verim açısından yetersiz bulunmuştur.

İki aşamalı sülfatlayıcı kavurma ve su ile liç aşamalarından oluşan asitle muamele etme (pug)-kavurma-liç yönteminde kobalt, nikel ve demir gibi metaller, sülfatlarının bozulma sıcaklıklarından yararlanılarak kazanılmaktadır. Bu yöntemde şu parametreler optimize edilmiştir: Asit miktarı, sülfatlama sıcaklığı, sülfatlama süresi, bozundurma sıcaklığı, bozundurma süresi, liç sıcaklığı, liç süresi, pülp yoğunluğu ve sülfatlama öncesi cevherin nemlendirilmesi. Optimum koşullarda (sülfürik asit: %25, nem oranı: % 20, sülfatlama sıcaklığı: 450^{o}C, sülfatlama süresi: 30 dakika, bozundurma sıcaklığı: 700^{o}C, bozundurma süresi: 60 dakika, liç sıcaklığı: 70^{o}C, liç süresi: 30 dakika ve pülp yoğunluğu: %25) yapılan deneyde % 91.40 Co ve % 84.40 Ni kazanılmış, elde edilen çözeltide 3.084 g/L Ni ve 0.185 g/L Co derişimi elde edilmiştir. Elde edilen bu sonuçlar çözeltinin daha ileri rafinasyonu için yeterli bulunmuştur.

Anahtar Kelimeler: Lateritik cevherler; Kavurma; Sülfürik Asit Liçi; Kobalt ve Nikel

To My Wife Cemile

and

My Daughter Zeynep Beril

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INTRODUCTION

Lateritic ores occur at surface that allows economical open cast mining methods to extract ores. Laterites essentially may be classified as either limonite or serpentinite ore types (Hawkins, 1998; Piret, 1998). Each of these oxidic type ores require slightly different processing techniques to remove the contained impurities such as iron, magnesium, manganese, aluminium, and others (Krause, 1998). Extraction of nickel and cobalt from laterites is possible by using different processes. One of them is high pressure sulphuric acid leaching (PAL), which is widely used and depend on Moa Bay process (Carlson and Simons, 1960). PAL process can be used for low magnesium ores (Robisov et al., 2000; Robisov and Papagelakis, 2000a; Robisov and Papagelakis, 2000b). The restriction of this method is the high acid consumption. Many modified versions of this process are available and applied in different lateritic ores.

Nickel and cobalt can be extracted from laterites by roasting using varying properties of nickel, cobalt and iron sulphates (Zubryckj, Evans and Mackiw, 1965; Canterford, 1978; Singh, 1975). Selectivity of nickel and cobalt over iron depend on the decomposition temperature of these metal sulphates (Gilchrist, 1980). Recorded starting decomposition temperature of nickel, cobalt and iron sulphates under a current of air are given respectively 702^{o}C, 720^{o}C and 167^{o}C but, temperature of active decomposition are given as 764^{o}C, 770^{o}C and 480^{o}C (Stephens, 1953). Extraction of nickel from lateritic ores is possible by using sulphatization in two stages (Kar et al., 2000; Swamy et al., 2003).

The sulphatization of oxides such as NiO, CoO and Fe_xO_y take place in the presence of either SO_2 or SO_3 or both, depending on the temperature of roasting. The gases are formed in situ due to the thermal decomposition of some less stable sulphates such as ferric sulphate, aluminium sulphate, etc., which are produced during mixing of H_2SO_4 with ore at the initial stage of reaction. Thermodynamic calculations show that there is considerable difference in the free energy of reaction (ΔG^o) value for various metal sulphates formed with SO_2 or SO_3 at 700^{o}C. At this temperature, iron and aluminium sulphates decompose rapidly, whereas nickel sulphate and cobalt sulphate remain undisturbed (Swamy et al., 2003).

Atmospheric pressure sulphuric acid leaching of laterites has received relatively minor attention. Effect of laterite mineralogy, leaching temperature, acid strength and preheating temperature on Ni, Fe and Mg dissolution, using Australian laterites was investigated and over 90% Ni recovery could be achieved with an 100 kg/tonne of ore acid consumption (Canterford, 1978; 1979). In the present study various parameters were investigated by using atmospheric pressure sulphuric acid leaching and at the optimized conditions 44.49 % Ni and 53.03 % Co extraction obtained.

1.1 Objectives of the Thesis

The aim of this study is to perform a hydrometallurgical extraction experiments for selective extraction of cobalt and nickel from iron. For the extraction of cobalt and nickel two different methods were applied. The first one is atmospheric pressure sulphuric acid leaching and the second is a pug-roast-leach process using two stages roasting for lateritic ore. The ore used in the study was obtained from Çaldağ Lateritic Ore, Manisa, Turkey. The metal content of ore is 2.1 % Ni, 0.12 % Co, 32.45 % Fe, 1.01 % Mn, 2.58 % Cr, 0.78 % Mg and 1.01 % Al. The reserve of Çaldağ lateritic ore deposit is approximately 40 million tonnes.

The ore used in the study was obtained from Çaldağ lateritic ore deposit which has approximately 40 million tonnes of ore reserve. The Çaldağ lateritic iron, nickel-cobalt deposit is located about 15 km north of the town of Turgutlu, within the province of Manisa, Western Turkey. Some of the studies about Çaldağ dealt with the lateritic iron formations (Brennich, 1960; Sözen, 1966; Önder, 1974; Ünlü, 1976), whereas some other research works have been concentrated on the presence of nickel-cobalt in these deposits (Yıldız, 1977; Hirano and Boyalı, 1980). The process in which the lateritization of the serpentinite occuring at the bottom is thought to be responsible for the formation of iron-nickel-cobalt ore by all authors.

CHAPTER II

BACKGROUND

2.1 Nickel

2.1.1 History

The name nickel is derived from the German nickel, meaning Satan or Old Nick's, and from kupfernickel for Old Nick's copper, the mineral niccolite. Nickel had been in use centuries before its actual discovery and isolation. As far back as 3500 BC Syrian bronzes contained a small amount of the element. Nickel was first used as an alloy, mainly in coinage; copper-nickel coins were used in Bactria 2230 years ago. The ancient Chinese produced white copper (paktong), essentially the same as the modern alloy nickel-silver, by smelting ores containing copper, nickel and zinc. In 235 BC, coins in China were minted from nickel. However there was no real documentation of the element until thousand years later.

In the 17th century, German miners discovered a red coloured ore they believed to contain copper. They discovered upon analysis that there was no copper but that a useless, smelly material was actually present. Thinking the ore was evil they dubbed it “Kupfernickel” or Old Nick's Copper, which meant false or bad copper. Nickel was first isolated in 1751 when the Swedish chemist Baron Axel Frederic Cronstedt prepared an impure sample of the metal from an ore containing niccolite. He isolated nickel from an ore closely resembling kupfernickel. Hence, he named this new element after the traditional mineral. It was first prepared in relatively pure form by H.T. Richter in 1804.

At the time of its discovery nickel was thought to be useless but as its valuable properties came to light the demand for the metal increased dramatically. The usefulness of nickel as a material in alloys was eventually discovered as the strength, corrosion resistance and hardness it adds to other metals came to be appreciated. Nickel has been used in electroplating since 1843, and in steel alloys since about 1889. It was first used as a base for alloys with the introduction of Monel nickel-copper alloy in about 1905. In metric tons of nickel content terms, world nickel mine production for different countries are given in Table 1 (Kuck, 2005).

Table 1 World nickel mine production, by country.

Country	**Capacity[1, 2] (Metric tons of nickel content)**				
	2000	**2001**	**2002**	**2003**	**2004**
Australia	166500	205000	207800	210000	178100
Botswana	38420	26714	28600	32740	32980
Brazil	45317	45456[r]	44928[r]	45160[r]	45200[e]
Burma	403	40	30	30	30
Canada	190793	194058	189297	163244[r]	186546
China[e]	50300	51500	53700	61000[r]	64000
Colombia	58927	52962	58196	70844	75032
Cuba	68064	72585	71342	74018	72421
Dominican Republic	39943	39120	38859	45400[e]	47000[e]
Finland	3347	2,200	2500	2700	2800
Greece	19535	20830	22670	21410	21700
Indonesia	98200	102000			
Kazakhstan	3200[r]	--	--	--	--
Macedonia	--	2970[e]	5,149	5,555	5,500
Morocco	84	151	109	126	126[e]
New Caledonia	126041[r]	117734[r]	99841[r]	112013[r]	118279[p]
Norway	2538	2529	2052[r]	169[r]	181
Philippines	17388	27359	26532	19537[r]	16973[p]
Russia	315000	320000[r]	305000[r]	310000[r]	315000
South Africa	36616	36443	38546	40842	39850
Turkey	--	--	--	640	--
Ukraine	--	1500	2000	2000	2000
Venezuela	2540	13600	18600	20700	20468
Zimbabwe	8160	10120	8092	9517	9520
Grand total	1290000	1340000[r]	1350000	1390000[r]	1390000

[e] Estimated.; [p] Preliminary.;[r] Revised.; [--] Zero.

[1] World totals and estimated data are rounded to no more than three significant digits; may not add to totals shown.

[2] Insofar as possible, this table represents recoverable mine production of nickel. Where actual mine output is not available, data related to a more highly processed form have been used to provide an indication of the magnitude of mine output and this is noted parenthetically. North Korea may have an active nickel mine, but information is inadequate to make reliable estimates of output. Table includes data available through July 22, 2005.

Nickel gained commercial prominence in the late 1800s, when substantial reserves were found in New Caledonia in 1865 and at Sudbury in 1883, and the world's naval powers adopted nickel-bearing armour. Until about 1920, nickel markets depended upon military requirements, but following World War I, research into other potential uses substantially increased its applications in industry. Today, stainless steel, another nickel containing alloy, is one of the most valuable materials of the 20th century.

2.1.2 Properties

Nickel is the earth's 24th most abundant element and the 7th most abundant transition metal. It is a silver white crystalline metal that occurs in meteors or combined with other elements in ores. Nickel is one of the transition elements in Group VIIIB of the periodic table and has chemical similarities to iron and cobalt. Nickel is a hard silver white metal, which occurs as cubic crystals. It is malleable, ductile and has superior strength and corrosion resistance. The metal is a fair conductor of heat and electricity and exhibits magnetic properties below 345°C. Six isotopes of nickel are known.

In its metallic form nickel is chemically unreactive. It is insoluble in cold and hot water and ammonia and is unaffected by concentrated nitric acid and alkalis. It is however soluble in dilute nitric acid and sparingly soluble in dilute hydrochloric and sulphuric acids. The main properties of nickel are summarized in Table 2 (El-Dahshan, 1996).

2.1.3 Major Ores and Minerals of Nickel

Nickel ranks about 24th in natural abundance among elements in crustal rock, but it is concentrated in ultramafic igneous rocks (0.1-0.3% Ni) compared with silicic igneous rocks (<0.006% Ni). The most important ore minerals are sulphide types, pentlandite and pyrrhotite, and the oxide type, garnierite. Other nickel minerals include niccolite, millerite, breithauptite, choanthite, gersdorffite and ullmannite. Nickel may also be present in goethite (limonite) $(Ni,Fe)O(OH).nH_2O$.

Table 2 The main properties of nickel.

Property	**Value**
Symbol	Ni
Atomic number	28
Atomic weight (mass)	58.69 x 10^{-3} kg/m^3
Atomic radius	1.25 x 10^{-10}m
Valencies	2^+
Ionisation potential, Ni^{2+}	25.8 ev
Ni^+	7.61 ev
Isotopes: Ni^{56}	half-life 6 days
Ni^{57}	half-life 36 days
Ni^{59}	half-life 10^5 days
Ni^{63}	half-life 85 days
Ni^{65}	half-life 2.6 h
Ni^{66}	half-life 56 h
Colour – reflected light	white silvery
Crystallographic structure	
(α) Ni	Cph, a = 2.49, c = 2.49 x 10^{-10}m
(β) Ni	FCC, a = 2.49 x 10^{-10}m
Minimum interatomic distance	1.25 x 10^{-10}m
Density	8.9 x 10^{-3} kg/m^3
Melting point	1455°C
Boiling point	2730°C
Specific heat	0.112 cal/g/°C
Coefficient of thermal expansion (20-100°C)	13.3 x 10^{-6}
Thermal conductivity	0.14 cal/cm. S.°C.
Electrical resistivity, 20°C	6.9 X 10^{-3} ohm cm
Standard potential, Ni^{2+}	-0.3v
Hardness (Moh's scale)	3.5
Modulus of elasticity:	
In tension	2.039 x 10^5 MPa
In torsion	7.73 x 10^4 MPa
Heat of fusion	73.8 cal/g

Nickel occurs as a metal in meteorites and often serves as one of the criteria for distinguishing a meteorite from other rocks. Iron meteorites, or siderites, may contain 5-20% Ni. It has been compiled a very extensive list of nickel minerals. They can be classified into five groups by type:

i. Nickel Arsenites
ii. Nickel Sulfides
iii. Nickelt Sulfarsenites
iv. Oxidised Nickel Minerals
v. Antimonites

A list of common nickel minerals are given in Table 3 (Boldt, 1967).

The deposits of nickel can be classified under the following headings:

2.1.3.1 Magmatic deposits

Magmatic deposits of copper-nickel sulphide ores of liquation origin containing cobalt are known in Russia, Finland, Sweden, Canada, The United States, South African Republic, and Australia. They all are related to differentiated basic-ultrabasic massifs enriched in magnesium. These stratified intrusives in shields are composed of peridotites, pyroxenites, gabbro, norites and gabro-diorites of hypabysal facies, and gabro-dolerites, dolerites of subvolcanic facies in the platform sedimentary cover. More basic varieties compose the lower parts of the massifs (their basement), less basic varieties make up the upper horizons.

Ore bodies are located inside, on the periphery at the bottom part and outside, close the parent intrusives. Among them one finds: (1) hanging bodies of disseminated ores; (2) sheet and lenticular bottom-close bodies of massive “schlieren” and streaky-disseminated ores that sometimes extend in underlaying rocks; (3) lenses and irregular bodies of contact breccia ores; (4) vein-like and vein bodies of massive ores. The dimensions of the ore bodies vary from a few hundred metres to 1000-1500 metres long strikewise, and from a few hundred metres to 800-1000 metres along the dip, the thickness ranging from 1-2 to 40-50 metres. Occasionally, the thickness may be as high as 100 metres. The ores may be syngenetic which occur as disseminated, rarely as massive, and brecciated. Usually

Table 3 Nickel minerals.

Mineral Type	**Mineral Name**	**Ideal Formula**	**Nickel Content %**
Sulphides	**Pentlandite**	$(Ni,Fe)_9S_8$	34.22
	Millerite	NiS	64.67
	Heazlewoodite	Ni_3S_2	73.30
	Linnaeite series	$(Fe,Co,Ni)_3S_4$	Variable
	Polydymite	Ni_3S_4	57.86
	Violarite	Ni_2FeS_4	38.94
	Siegenite	$(Co,Ni)_3S_4$	28.89
Arsenides	**Niccolite**	$NiAs$	43.92
	Maucherite	$Ni_{11}As_8$	51.85
	Rammelsbergite	$NiAs_2$	28.15
	Gersdorffite	$NiAsS$	35.42
Arsenate	**Annabergite**	$Ni_3As_2O_8.8H_2O$	29.40
Antimonide	**Breithauptite**	$NiSb$	32.53
Silicate & Oxide	**Garnierite**	$(Ni,Mg)_6Si_4O_{10}(OH)_8$	Up to 47 %
	Nickeliferous limonite	$(Fe,Ni)O(OH).nH_2O$	Low but variable

the ores are complex and, besides nickel and cupper, contain Pt, Pd, Rh, Ru, Co, Se. and Te. The ore have rather regular mineral composition. The main ore-forming minerals are: pyrrhotite, chalcopyrite, pentlandite; subordinate minerals being magnetite, pyrite, cubanite, bornite, polydymite, niccolite, millerite, violarite, sperrylite and cooperite. The non-metal minerals are represented by olivine, basic plagioclase and pyroxene. Besides, there are also garnets, epidote, serpentine, actinolite, talc, chlorite and carbonates.

2.1.3.2 Plutonogenic hydrothermal deposits

Plutonogenetic hydrothermal deposits of cobalt are known in Russia, Central Asia, Germany, Czeck Republic, Norway, Morocco, Canada, the USA, and Australia. They are related to granitoid intrusions. The enclosing rocks are represented by sedimentary and metamorphic formations, skarns or serpentinites. Ore bodies have the form of complex (Co-Ni, Co-Ni-Ag,Co-Ni-Bi-Ag-U, and Co-N-Cu-Pb-Zn). Pre-ore altera-tions of the rocks consisted of tourmalinization, biotitization, sometimes skarnification or sericitization. The alterations surrounding ore bodies consisted of silicification, epidotization, chloritization and carbonatization. Formation of minerals occurred in several stages, three of them being principal: (1) arsenopyrite-cobaltite-quartzite; (2) smaltite-chloantite; and (3) sulphide-carbonate.

Among plutonogenic hydrothermal deposits of cobalt one can be distinguish the following ore formations: (1) smaltite-chloantite-nickeline-argentine; (2) arsenopyrite-glaucodot-cobaltite; (3) five metals formation C0-Ni-Bi-Ag-U.

2.1.3.3 Deposits of weathering

Deposits of silicate nickel ores in weathering crusts are known in New Caledonia, Indonesia, Cuba, Brazil, USA, Australia, USSR, Greece, and Albania. The nickel-bearing laterite weathering crusts which developed over massifs of serpentinized ultrabasic rocks of variable age were formed in the Kimmerian and, especially, Alpine epochs. In the course of chemical weathering of ultrabasic rocks, particularly under conditions of a tropical climate, decomposition of olivine and serpentine which contained nickel in isomorphous with magnesium form was developed. Nickel was freed and transported, often together with cobalt, from the upper horizons of weathering crust to the lower ones. Here, since the alkalinity of infiltrating solution increased, precipitation of secondary nickel-containing minerals, such as garnierite, nontronite, revdinskite, and asbolane, occurred.

Among the weathering crusts one can distinguish two types, i.e. kerolith-nontronite-ochreous (full profile) and kerolith-ochreous (incomplete profile). Full profile consists of the following zones (downwards): (1) ochreous-siliceous formations; (2) nontronitized serpentinites; (3) leached serpentinites. The thickness of each zone varies from a few metres to 30-50m. In incomplete profile the nontronite zone is not present.

In terms of structural and morphological features three of weathering crusts could be identified: (1) areal (Kempirsai, and Sakharinsk in Urals, and the deposits in Cuba); (2) linear, or fracture-related, that are often found in combination with the first type (deposits in New Caledonia); (3) contact-karstic related to the tectonic contact of serpentinites and limestones (Ufalei).

2.1.4 Uses of Nickel

The primary use of nickel is in the preparation of alloys such as stainless steel, which accounts for approximately 65% of all nickel used in manufacture. The greatest application of stainless steel is in the manufacturing of kitchen sinks but it has numerous other uses as well.

Other nickel alloys also have important applications. An alloy of nickel and copper for example is a component of the tubing used in the desalination of sea water. Nickel steel is used in the manufacture of armour plates and burglar proof vaults. Nickel alloys are especially valued for their strength, resistance to corrosion and in the case of stainless steel for example, aesthetic value.

Electroplating is another major use of the metal. Nickel plating is used in protective coating of other metals. In wire form, nickel is used in pins, staples, jewellery and surgical wire. Finely divided nickel catalyses the hydrogenation of vegetable oils. Nickel is also used in the colouring of glass to which it gives a green hue.

Other applications of nickel include:

- Coinage
- Transportation and construction
- Petroleum industry
- Machinery and household appliances
- Chemical industry.

Nickel compounds also have useful applications. Ceramics, paints and dyes, electroplating and preparation of other nickel compounds are all applications of these compounds. Nickel oxide for example is used in porcelain painting and in electrodes for fuel cells. Nickel acetate is used as a mordant in the textiles industry. Nickel carbonate finds use in ceramic colours and glazes.

More than 65 percent of the nickel produced is used in alloys with iron and steel, about 15 percent is used in corrosion-resistant alloys with copper and in heat resistant alloys with chromium, 5 percent is used in alloy castings, and only the remaining 15 percent is used in unalloyed forms, either in electroplating (10%) or for various minor applications such as batteries, catalysts, magnets and ceramics.

Nickel steels contain 0.5-7 percent Ni in the "low-nickel steels" and 7-35 percent in "high-nickel steels", nickel-irons from 0.5-15% Ni, nickel brasses and bronzes 0.5-7 percent Ni, copper-nickel alloys from 2.5-5 percent Ni, Monel metal 67 percent Ni, and special alloys up to 80 percent Ni.

Nickel is used in alloys to impart toughness, strength, lightness, and resistance to heat and/or corrosion. Nickel steels and alloys are used for moving and wearing parts of various machines, tools, shafts, bolts, axles, and gears, in automobiles, airplanes, and ships, and in railway, power, agricultural, crushing, mining, milling and pressing equipment. Nickel silver, also called German silver, (typically 55-65% Cu, 18% Ni and the rest Zn), is used as the base for tableware, jewellery, and other articles to be silver plated. Nickel alloys are used extensively in coinage (25% Ni and 75% Cu).

Nickel metal is used to form protective coatings on other metals, particularly iron and steel, that are susceptible to corrosion. Finely divided nickel absorbs 17 times its own volume of hydrogen and is used as a catalyst in many processes, including the hydrogenation of unsaturated organic compounds such as vegetable oils and fats. Nickel is also used in the manufacture of Alnico magnets, and it is added to glass to give a green colour.

Nickel sulphate is used for electroplating and in the preparation of catalysts, ground-coat enamels, and mordants (fixatives) for dying and textile printing. Nickel oxide and nickel peroxide are prepared for use in fuel cells and storage batteries, respectively. Nickel ferrites are utilised as magnetic cores for various type of electrical equipment such as antennas and transformers.

Both plant and animal tissues contain small amounts of nickel. Normal human diet contains about 0.3 to 0.5 milligrams of nickel per day. If taken beyond a certain tolerance level, not yet determined with precision, nickel produces toxic effects through inhibition of certain enzyme systems.

2.2 Cobalt

2.2.1 History

Cobalt is not one of the major industrial metals, either in terms of the tonnage consumed or its value; however, it ranks high in respect of its strategic importance. Cobalt was first used as a pigment about 2000 B.C., when naturally occurring cobalt compounds were used to colour glass. This remained its sole use until 1742, when it was isolated as a metal by the Swedish scientist, G. Brandt. About 40 years later, in 1780, T. Bergman established cobalt as an element (William, 1985). Isolation of cobalt metal was first carried out in 1735, although compounds derived from mineral ores containing cobalt had been used for many centuries as colouring agents for glass and ceramics. Blue glazed pottery found in Egyptian tombs has been found to contain cobalt, and many of the bright colours used by the ancient Greeks and Romans contained compounds of this metal.

The use of cobalt as a metal began in 1907, when Elwood Haynes received a patent on a series of cobalt-chromium alloys, named Stellites, which forerunners of today’s superalloys.

In Japan, reports were published in 1920 on the magnetic properties of steels with high cobalt content. With this research as a foundation, it was discovered in 1930, that adding cobalt to certain alloys of iron, aluminium, and nickel enhanced their outstanding permanent-magnet properties.

Subsequently, a series of permanent-magnet alloys containing aluminium, nickel, and cobalt (Alnico) were developed. The first alloy in the Alnico series was announced by General Electric Co. in 1936. The cobalt content of this alloy was found to improve both its magnetic properties and its response to heat treatment. Basic research in the 1950's included investigations of the binary, ternary, and quarternary alloys of cobalt (William, 1985).

The word is generally accepted as derived from the Greek via medieval German. Records of the name only go back to 1335 when it was applied to gnomes living in the mines in the Schneeberg Mountains in Germany. However, cobalt colouring of ceramics has been known for well over 2,000 years in Persia and Egypt so it must have had an unknown earlier name.

Cobalt occurred in the Schneeberg with silver and nickel and it was silver that was of interest then. When problems arose, they were blamed on the "Kobolds" - later it was found to be the cobalt ore that caused the problems - hence the name transference. Problems from nickel were blamed on a higher cause - and Nick to Nickel is a short step. Colourings from oxides and silicates were the main use up to the 20th Century and even in 1916, total output was only 554 tonnes with 400 of it as oxides.

Cobalt has been used to colour pottery and glass from at least 2600 BC and cobalt-containing glazes have been found in Egyptian tombs of that period. Chinese pottery from Tang (600-900 AD) and Ming dynasties (1350-1650 AD) also contained blue colours made from cobalt-containing minerals. The Co-Cr alloys, and superalloys in general, which caused the great leap in cobalt use are of course still in use as are the Alnico series of magnets invented in the 1930's.

Cobalt sources have changed over its history, from Norway, Sweden, Hungary and Germany to a dependence on the African Copper Belt in the 1970's and 1980's. In the last decade, sources have diversified with increasing amounts coming from nickel ores in Australia. The present situation is changing again. In metric tons of cobalt content terms, world cobalt mine production for different countries are given in Table 4 (Shedd, 2004).

These figures are of necessity for guidance only. The likelihood is that the trend towards Australia, Cuba and the Pacific will increase as new nickel production becomes viable. One cannot however now ignore Canada with the possibility of growth through Voisey's Bay. As usual, in most cases, cobalt is a by-product. The balance is swinging towards nickel as the main product, but although refined production in Africa had declined in recent years, the amount of cobalt produced as a by-product of Africa copper ores/slags is still substantial. The current split is 50% nickel, 45% copper and 5% primary cobalt.

Table 4 World cobalt mine production, by country.

Country	**Capacity[1, 2] (Metric tons of cobalt content)**				
	2000	**2001**	**2002**	**2003**	**2004[e]**
Australia[e]	5600	6300[r]	6700	6900	6700
Botswana	308	325	269	294[r]	2236
Brazil[e]	900	1100	1200	1300	1400
Canada	5298	5326	5148	4327[r]	5197
China[e]	90	150	1,000	700[r]	800
Congo (Kinshasa)[e]	11000	15000	14500	12000	16000
Cuba	2852[r]	3417[r]	3384[r]	3465[r]	3580
Kazakhstan[e]	300	300	300	300	300
Morocco	967[r]	1242	1453[r]	1391[r]	1600
New Caledonia[e]	1,200	1400	1400	1400	1400
Norway[e]	100	100	100	--	--
Russia[e]	4000	4600	4600	4800	4700
South Africa[e]	580	560[r]	520[r]	400	460
Zambia[e]	4600	8000	10000	11300	10000
Zimbabwe	79	95	87	79[r]	596
Total[e]	37900[r]	47900[r]	50700[r]	48700[r]	52400

[e] Estimated.; [r] Revised.; -- Zero.

[1] World totals and estimated data are rounded to no more than three significant digits; may not add to totals shown.

[2] Table includes data available through June 18, 2005. Figures represent recoverable cobalt content of ores, concentrates, or intermediate products from copper, nickel, platinum, or zinc operations. Morocco was the only country where cobalt was mined as a primary product.

2.2.2 Properties

Cobalt is a silvery metal having a close packed hexagonal crystal structure. Cobalt is a transition metal, appearing between iron and nickel. It is a group VIII metal.

Atomic Number = 27
Atomic Mass = 58.93 (59) 27 Protons, 32 Neutrons

The structure accounts for the variable valency of cobalt with Co^{2+} being the obvious one with the two 4s electrons removed. Cobalt ions Co^{3+} occur by electron addition and Co^{+1} occurs in a few complex salts. The properties quoted in Table 5 (El-Dahshan, 1996), have been selected as representative of the highest purity metal available, since the physical and mechanical properties of metallic cobalt are particularly susceptible to the variation in impurities. Co^{60}, by virtue of its reasonable half-life and its emission of γ rays of energies 1.17 and 1 .33 Mev, is the most widely used source of radioactivity for such purposes as radiography, radiotherapy, food sterilization, etc.

2.2.3 Major Ores and Minerals of Cobalt

Cobalt is produced mainly as a by-product of the mining and processing of the ores of other metals, particularly those of copper, nickel, and silver, but also those of gold, lead, and zinc. It has been compiled a very extensive list of cobalt minerals. They can be classified into four groups by type:

i. Cobalt Arsenites
ii. Cobalt Sulphides
iii. Cobalt Sulfarsenites
iv. Oxidised Cobalt Minerals

A list of common cobalt minerals are given in Table 6.

The deposits of cobalt can be classified under the following headings:

Table 5 Properties of Cobalt.

Property	**Value**
Symbol **Atomic number**	Co 27
Atomic weight (mass)	58.93 x 10^{-3} kg/m^3
Atomic radius	1.25,1.26
Valencies	2^+, 3^+
Isotopes: Co^{55}	half-life 18.2 h
Co^{56}	half-life 80 days
Co^{57}	half-life 270 days
Co^{58}	half-life 72 days
Co^{60}	half-life 5.3 years
Colour – reflected light	white silvery
Crystallographic structure	
(ε) Co, below 400°C	Cph, a = 0.250,°c = 0.407 x 10^{-10}m
(α) Co, above 400°C	FCC, a = 0.356 x 10^{-10}m
Minimum interatomic distance	2.51 x 10^{-10}m
Density	8.9 x 10^{-3} kg/m^3
Melting point	1480°C
Boiling point	2900°C
Curie temperature	1121°C
Coefficient of thermal expansion (20-100°C)	12.08 x 10^{-6}
Thermal conductivity	0.165 cal/cm.S.°C.
Electrical resistivity, 20°C	9.7 X 10^{-3} ohm cm
Standard potential, Co^{2+}	-0.277v
Co^{3+}	1.8v
Hardness (Moh's scale)	5.5
Modulus of elasticity:	
In tension	1.74 x 10^5 MPa
In torsion	6.48 x 10^4 MPa
Heat of fusion	58.38 cal/g

Table 6 Common Cobalt minerals.

Mineral Name	Ideal Formula	Cobalt Content, %
Cattierite	CoS_2 (pure)	47.8
Linnaeite	Co_3S_4 (pure)	58.0
Siegenite	$(Co.Ni)_3S_4$	20.4-26.0
Carrollite	$(Co_2Cu\ )S_4$	35.2-36.0
Cobaltite	$(Co.Fe)AsS$	26.0-32.4
Safflorite	$(Co.Fe)As_2$	13.0-18.6
Smaltite	$(Ca.\ Ni)As_2$	Ca. 21
Glaucodot	$(Co.Fe)AsS$	12.0-31.6
Skutterudite	$(Co.Fe)As_3$	10.9-20.9
Heterogenite	$CoO(OH)$ (pure)	64.1
Asbolite	$(Co,Ni)_{1-y}(Mn^{4+}O_2)_{2-x}(OH)_{2-2y+2x}\bullet n\ H_2O$	0.5-5.0
Erythrite	$(CoNi)_3(As0_4)_2 .8\ H_20$	18.7-26.3
Gersdorffite	$(Ni,Co)AsS$	(low)
Pyrrhotite	$(Fe,Ni,Co)_{x-1}S_x$	up to 1.00
Pentlandite	$(Fe,Ni.Co)_9S_8$	up to 1.50
Pyrite	$(Fe,Ni,Co)S_2$	up to 13.00
Sphalerite	$Zn(Co)S$	up to 0.30
Arsenopyrite	$Fe(Co)AsS$	up to 0.38
Manganese oxide minerals	-	0.10-1.0

2.2.3.1 Magmatic deposits

Magmatic deposits of copper-nickel sulphide ores of liquation origin containing cobalt are known in Russia, Finland, Sweden, Canada, The United States, South African Republic, and Australia. They all are related to differentiated basic-ultrabasic massifs enriched in magnesium. They are described in the section (2.1.3.1).

2.2.3.2 Skarn deposits

Skarn iron ore deposits containing cobalt bearing pyrite are presented by lime skarns and magnesian skarns. Skarn magnetite deposits are related to plagiogranites which are the early stage of geosynclinal development.

Skarn deposits can be classified according to geological environment into lime-skarn, magnesium skarn and magnesian-lime-skarn, scapolite-albite and scapolite-albite-skarn, magnetite and hematite hydrosilicate which could be considered as formations of skarn iron ore deposits.

2.2.3.3 Plutonogenetic Hydrothermal Deposits

Plutonogenetic hydrothermal deposits of cobalt are known in USSR, Central Asia, Germany, Czeck Republic, Norway, Morocco, Canada, the USA, and Australia. They are related to granitoid intrusions. They are described in section (2.1.3.2).

2.2.3.4 Stratiform deposits

Commercial concentrations of cobalt are found stratiform deposits of cupriferous sandstones in Zambia and Zaire. These include bedded ores of copper which occur in terrigenous sequences and do not show any relation to magmatic rocks. They are represented by large deposits of cupriferous sandstones and cupriferous shales. The stratiform deposits are formed at the final stages of the geosynclinal regime and under platform conditions. They are confined to the depressions filled with rhythmically interbedded sandstones, shales and dolomites of lagoon-delta and near-shore facies. These rocks, characterized by a relatively high content of organic carbon (over 2%), compose the initial transgressive or final regressive parts of the section.

These ores occurs concordant sheets, lenticular and ribbon bodies usually gently dipping. Their width varies from tens of centimetres to first tens metres; they extend for many kilometres along the dip. Typical are multi-stage bodies showing gradual transitions to weakly mineralized rocks. Locally, there occur cross-cutting ore veins and crush zones. The main ore minerals are chalcocite, bornite, chalcopyrite, pyrite; subordinate minerals include copper grey ores and covallite, in some places galena, sphalerite, etc.; the gangue minerals are represented by quartz, calcite and barite. Pb, Zn, Ag and trace elements, occasionally cobalt and uranium are by products. The enclosing rocks are weakly altered (carbonatized, silisified).

2.2.3.5 Deposits of weathering

Nickel bearing weathering crusts contain cobalt ores that are represented by asbolane. These deposits of silicate nickel ores in weathering crusts are known in New Caledonia, Indonesia, Cuba, Brazil, USA, Australia, USSR, Greece, and Albania. They are described in section (2.1.3.3).

2.2.4 Uses of Cobalt

Cobalt has developed from an obscure colouring additive, first used several thousand years ago, into a strategically important metal, the use of which is essential in the production of many defence-related items. Because of its diverse physical properties, it has many diverse end uses. In most of its applications, cobalt imparts essential qualities such as heat resistance, high strength, wear resistance, and superior magnetic properties. Major uses include jet engine parts, cutting tools, electrical devices, permanent magnets, catalysts, and pigments and dryers for paints and allied products. Main uses of cobalt are given in Table 7.

Cobalt now has a wide range of practical applications, but almost all of these involve its use as an alloying constituent or as a chemical compound. The inclusion of cobalt in the various alloys confers specific advantages:

- It holds more permanent magnetism than any other commercial material.
- Its alloys can he rolled, drawn and heat-treated.
- It improves both physical and mechanical properties of the base metal.

Table 7 Main Uses of Cobalt.

Metallurgical	Superalloys Wear Resistant Coatings High Speed Steels Prosthetics Low Expansion Alloys Steels Corrosion Resistant Alloys Spring Alloys
Magnetic Alloys	Alnico’s Rare Earths Soft Magnetic Materials
Chemicals	Catalysts Adhesives - Cobalt Soaps Specialist Chemicals: Driers, Pigments, Colours Electroplating Agriculture and Medicine Electro-Magnetic Recording
Cemented Carbides **Bonded Diamonds**	
Electronics	Recording Material Matched Expansion Alloys Leads
Ceramics & Enamels and china	Colours in glass Enamels Pottery

- It improves castability when it is used as an alloying element.
- It gives high resistance to severe wear.
- It retains its mechanical properties at high temperature (up to 900 ^{o}C); at 1000 ^{o}C it sheds only a few points of its hardness. This property is known as “red hardness.”

The chief outlet of cobalt metal is as an alloying element and about 75 percent of that produced is used in this form, for the production of:

- Magnetic material.
- High creep-resisting alloys.
- Cobalt-base tool material for jet propulsion and gas turbine engines.
- Cemented carbide-cutting tools.
- Radioactive material, Co^{60} isotopes.
- Cobalt is also used in its non-metallic state as the black oxide (Co_30_4) and grey oxide (CoO). These are used in the ceramic industry as a glaze stain. Certain metallic organic compounds are used in paints as a drier.
- alloyed with iron, nickel and other metals to make Alnico, an alloy of unusual magnetic strength with many important uses (jet engines and gas turbine engines).
- used in magnet steels and stainless steels.
- used in alloys used in jet turbines and gas turbine generators.
- used in electroplating because of its appearance, hardness, and resistance to oxidation.
- salts are used for the production of brilliant and permanent blue colours in porcelain, glass, pottery, tiles, and enamels.
- cobalt-60, an artificial isotope, is an important γ ray source, and is extensively used as a tracer and a radiotherapeutic agent. Single compact sources of Co^{60} are readily available.
- compounds are used as paint pigments.

2.3 Laterites

It is noteworthy that lateritic ores account for over two-thirds of the worldwide reserves for important nonferrous metals such as nickel and cobalt. It is not possible to quantify the amount of nickel contained in deep-sea nodules with any accuracy at present. The nickel-magnesium-silicate is associated with mixtures ranging from Serpentine, which is a hydrated magnesium silicate, to the clay-like Saponite and Deweylite minerals. Nickeliferous limonite is comprised of nickel bearing ferric oxides in deposits formed from ultrabasic rocks. The mineral ‘‘Limonite’’ usually contains Goethite and varies in water content. Lateritic ore deposits are found in tropical regions and/or areas that were sub-tropical in past geologic epochs. The deposits apparently originated on levelled land forms of low elevation-peneplains. The dominant theory is that the Upper Mantle is basically a magnesium silicate, i.e., ‘‘Peridotite’’ which hosts various elements such as Ni, Cu, Co, Fe, Mn, Si, Au, Ag, and others. Lateritic ore deposits were not discovered in Northern regions with the exception of northern Oregon which was laterized and contained nickeliferous magnesium silicates. This source provided feedstock for Hanna’s ferronickel production facility which was last operated by a subsidiary of Cominco and now shut down indefinitely. Northern areas, such as in the Canadian Shield, were strongly glaciated thereby removing unconsolidated surface deposits (Moskalyk and Alfantazi, 2002).

Laterites formed mostly in the sub-tropical and tropical regions of the world between about 25^o north and 25^o south latitudes. Those that are located in temperate regions are fossil laterites that formed when those regions were tropical millions of years ago.

2.3.1 Definition

Laterite is a surface formation in tropical areas which is enriched in iron and aluminium and develops by intensive and long lasting weathering of the underlying parent rock. Nearly all kinds of rocks can be deeply decomposed by the action of high rainfall and elevated temperatures. The percolating rain water causes dissolution of primary rock minerals and decrease of easily soluble elements as sodium, potassium, calcium, magnesium and silicon. This gives rise to a residual concentration of more insoluble elements predominantly iron and aluminium.

Laterites consist mainly of the minerals kaolinite, goethite, hematite and gibbsite which form in the course of weathering. Moreover, many laterites contain quartz as relatively stable relic mineral from the parent rock. The iron oxides goethite and hematite cause the red-brown colour of laterites.

Laterization is a chemical weathering process whereby atmospheric, groundwater and biologic processes interact through exposed rock surfaces and fractures in the bedrock to decompose the primary rock minerals and form more stable mineral phases in the weathering zone. There are significant variations between different laterite profiles and within each laterite profile. Local and seasonal climatic conditions have the most significant effect on the weathering profile as seen in the following figure that illustrates the main types of profile from the dry to seasonally wet to humid wet tropical conditions. The formation of each laterite deposit is influenced by the parent bedrock, the degree of serpentinization, the local bedrock structures, topography and climate.

Nickel laterite forms over ultramafic rocks in a tropical to semi-tropical climate associated with heavy rainfall. Weathering begins on joints and fractures and initially forms large blocks or boulders with subordinate soil. As the weathering progresses, the more mobile elements, silica and magnesium, are leached and deposited at the base of the laterite profile or are flushed from the system.

Iron and alumina are less soluble and are enriched in the upper portion forming the uppermost hematite-rich iron cap or pisolitic layer followed below by the hydrated hematite, the limonite layer rich in goethite, which collapses under its own weight as the weathering removes large quantities of the mobile elements. As weathering progresses the original fabric or texture of the rock is destroyed. Nickel, cobalt and manganese are enriched in the limonite layer, especially near the interface of the limonite and saprolite (hydrated silicates) layers which is the contact of the active zone of current weathering.

With further weathering the peridotite boulders form saprolized crusts as the weathering process proceeds from the surface of the boulder to the core. During this process the relic boulders are reduced in size and the clay component, typical of the saprolite layer, becomes dominant. In the saprolite clay-boulder mix the structure of the parent rock is preserved. The saprolite profile consists of a complex mixture of fine-grained Ni-Mg hydrosilicates and altered boulders which may be enriched in nickel or may be barren.

Silicate nickel content in the original host rock is about 0.3% or less, contained within the mineral olivine. The nickel is residually concentrated but can be liberated during the leaching process, migrating downward, carried by the groundwater, in the laterite profile.

The cobalt remains with the iron hydroxides but may migrate with depth to become concentrated within the limonite, particularly at the transition zone between the saprolite and the limonite layers. Almost invariably cobalt is associated with manganese in asbolane.

2.3.2 Laterite Formations

The history of a nickel deposit has a significant impact both on the formation of a commercially viable resource and the processing route chosen to utilise the resource. An understanding of the history of a deposit is important in assessing possible processing routes to utilising the resource.

Lateritic ore reserves show significant changes in structure compared to the parent rock as a result of natural weathering. At shallow crustal depths the ultramafic base rock, commonly peridotite or dunite rocks composed mainly of olivine $(Mg,Fe)_2SiO_4$, will convert in varying amounts to serpentine, $Mg_3(Si_2O_5)(OH)_4$. The weathering of the resulting serpentinized rock results in a volume reduction as magnesia, silica and other soluble components are removed. The deposit becomes enriched in weathering products such as goethite, and limonite and nontronite clays. The goethite and clays contain enriched amounts of relatively insoluble iron, aluminium, nickel, cobalt and chromium. The leaching process results in a horizontally defined deposit with the main zones being unaltered bedrock, saprolite, clays (limonite and nontronite) and caprock can be seen in Figure 1 (Roorda and Hermans, 1981). The degree of zone development and the transition characteristics are dependent on the local conditions.

The characteristics of the saprolite zone are dependent on the amount of serpentine in the bedrock. Relatively low serpentine levels result in a saprolite zone with substantial remnant bedrock. As the serpentine content increases so does the leachability of the bedrock. Nickel does not occur in distinct minerals but substitutes in the serpentine lattice as magnesium is leached. In locations with arid environments or poor drainage silica enrichment may also occur. Serpentine may be replaced by nontronite clays or silica boxwork. The silica may have associated garnierite (a brilliant green clay, $(Ni,Mg)_3Si_4O_{10}(OH)_2$) or nontronite. Without associated clays the silica will be nickel barren. Magnesite ($MgCO_3$) veinlets and accretions may also occur in the saprolite zone.

The clay zone may be minimal in well-drained locations but will be dominated by nontronite clays in locations with arid environments or poor drainage. Nontronite clays, $Fe(Al,Si)_8O_{20}(OH)_4$, can undergo substantial cation exchange and most of the nickel in this zone is associated with them. This zone will have high moisture content due to the hygroscopic nature of nontronite clays and may also contain goethite inclusions. Manganese oxides may persist in this zone and if so will contain significant adsorbed cobalt and some nickel.

The limonite zone, characteristic of humid, well-drained regions, is dominated by goethite, FeO.OH. There is some substitution of nickel for iron in the newly formed mineral. Limonite is an amorphous form of hydrous ferric oxides. Chromite and manganese oxides may also be found. Laterites formed under arid conditions often contain substantial inclusions of the limonitic clay, kaolin, $Al_4(Si_4O_{10})(OH)_8$, in this zone.

The caprock or ferricrete zone is usually dominated by hematite, Fe_2O_3, with some chromite present. In humid climates the breakdown of this surface layer may have commenced. Many arid zone laterite deposits have an alluvial layer covering the caprock (Lanagan, 2002).

2.3.3 Metal Distribution in Laterite Deposits

In humid, well-drained environments the nickel distribution is concentrated in the upper section of the saprolite zone with a bulk concentration approaching 3 percent. The nickel content steadily decreases towards the caprock. Cobalt values are generally low throughout the profile. Iron content is relatively low in the saprolite zone reaching a maximum of about 25 percent with a sharp transition to the limonite zone. Silica and magnesia show inverse behaviour compared to iron, increasing in concentration closer to the bedrock.

Laterites that develop in areas of poor drainage or an arid climate have a significantly different metal distribution. In these areas nickel is often concentrated in the nontronite clays along with cobalt and manganese. Significant nickel and cobalt concentrations may also be incorporated in the limonite zone. Silica content also peaks in the clay zone. Iron content increases steadily from the base of the profile reaching a maximum at about 35 percent in the caprock. Magnesia content decreases from about 35 percent at the base of the saprolite zone to a minimum of about 2 percent near the top of the clay zone. This value is maintained through the remainder of the profile. If kaolin is present, usually in the limonite zone, then the alumina content will follow the same profile. The chromium content is 2-3 times greater in the upper levels of the profile than in the saprolite zone.

A summary of the metal distribution in each layer is shown in Figure 1 (Roorda and Hermans, 1981).

Elevated nickel and cobalt values will often be found adsorbed on manganese oxides in the nontronite zone and local concentrations of 5 percent are common in these areas. Up to 50 percent of limonitic nickel may be present in manganese oxides (Golightly, 1981). Moisture content is dependent on the composition of the profile, especially the clays in the deposit. Alumina-rich clays tend to be hydrophilic with moisture levels up to 35 percent. Iron-rich limonitic clays are more hydrophobic. The proportions and locations of these phases will determine the overall nature of the deposit.

Lateritic ore deposits are generally found quite close to the surface and do not extend to great depths however they may cover a large area. The pre-mining deposits at Moa Bay, Cuba extended over approximately 41 km (Chalkley and Toirac, 1997). In general the total depth rarely exceeds 100 metres and 20-60 metres is quite common. The caprock may exist to around 5 metres from the surface of the deposit, discounting any alluvial layer. The limonite (ferralite) layer may range in depth from almost non-existent up to 30 metres. A similar depth range exists for the nontronite zone. The saprolite zone, although up to 30 metres deep, usually contains nickel at commercial grades only in the upper 5-15 metres.

Typical bulk compositions of various laterite type nickel deposits and their dominant source of metal values are shown in Table 8. The operations detailed have all produced commercial nickel product.

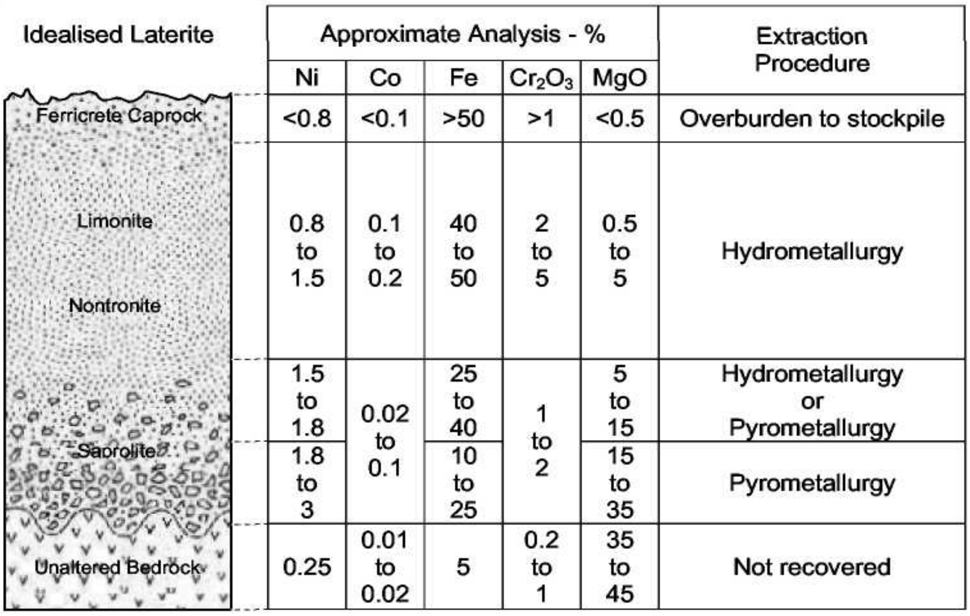
2.3.4 Processing of Nickel Laterites

The composition of a given laterite deposit will be dependent on the type of parent rock, the climate in which the deposit was formed and the weathering history. This gives rise to an almost infinite number of deposit specific relationships between components and consequent processing options and constraints. There are several processing routes available for nickel laterites and these can be classified as shown in Figure 1 (Roorda and Hermans, 1981).

Table 8 Elemental composition (%) of some laterite deposits in operation.

	Cawse[1]	**Moa Bay**[2]	**Murrin Murrin**[2]	**Bulong**[1]	**New Caledonia**[2]
Source	**Limonite**	**Limonite**	**Nontronite**	**Nontronite**	**Saprolite**
Process	**Hydro-metallurgy**	**Hydro-Metallurgy**	**Hydro-metallurgy**	**Hydro-metallurgy**	**Pyro-metallurgy**
Ni	1.0	1.3	1.2	1.1	2.5
Co	0.07	0.12	0.08	0.08	0.04
Fe	18	48	22	21	12
SiO_2	42	9.0	42	43	47
Mg	1.6	0.55	3.7	4.6	15
Al	1.7	4.8	2.7	2.8	1.3
Mn	0.17	0.8	0.4	0.36	0.6
Cr	0.92	2.0	1.0	0.6	1.4
H_2O	Up to 10	>20	About 30	Up to 35	

[1] (Kyle, 1996).
[2] (Motteram, Ryan and Weizenbach, 1997).



Approximate Analysis - %					Extraction Procedure
Ni	Co	Fe	Cr_2O_3	MgO	
<0.8	<0.1	>50	>1	<0.5	Overburden to stockpile
0.8 to 1.5	0.1 to 0.2	40 to 50	2 to 5	0.5 to 5	Hydrometallurgy
1.5 to 1.8	0.02 to 0.1	25 to 40	1 to 2	5 to 15	Hydrometallurgy or Pyrometallurgy
1.8 to 3		10 to 25		15 to 35	Pyrometallurgy
0.25	0.01 to 0.02	5	0.2 to 1	35 to 45	Not recovered

Figure 1 An idealised laterite profile showing the general processing routes available with variation in composition.

On the basis of magnesia content and nickel to iron ratio a choice is made between a hydro- or pyrometallurgical extraction process. The degree of inherent homogeneity within a deposit will also have an impact on process choice with hydrometallurgical routes generally requiring a more homogeneous feed (Roorda and Hermans, 1981).

The processing of nickel laterites via pyrometallurgical routes (Roorda and Hermans, 1981; Reid, 1996) is favoured by a low iron to nickel ratio and low moisture content. These requirements limit this processing route to predominantly saprolitic type ores. Nickel content needs to be greater than about 2% for profitable operation. Pyrometallurgical treatment of lateritic ores involves drying, reduction and smelting stages. This produces a ferronickel with 20 to 50 percent nickel content. Nickel sulphide matte can also be produced but the sulphur required must be purchased and introduced at some point in the process. This allows recovery of some cobalt as a by-product.

Pyrometallurgical treatment, although seen as a relatively robust process for its ability to treat heterogeneous silicates, must have a controlled feed in order to maintain suitable slag chemistry. In particular, the iron, magnesia and silica content must be regulated to control the slag melting point, viscosity and electrical conductivity. Pyrometallurgical treatment cannot be utilised for laterites containing less than 2 percent nickel and more than 25 percent iron. This restriction excludes pyrometallurgical processing as an option for a significant portion of known laterite reserves (Lanagan, 2002).

In order to treat the reserves of material not amenable to pyrometallurgical processing, projects have turned to hydrometallurgical processing options. Nickel not found in the saprolitic region of a lateritic ore deposit will usually be associated with limonite or nontronite clays. Limitations imposed by the chemistry of this environment have restricted the number of commercial processing routes to two general options:

- Caron Process, and
- Sulphuric Acid Pressure Leach.

2.3.4.1 Caron Process

Although developed in the 1920s the Caron process was not commercialised until 1944 (Reid, 1996). In this process the ore is dried and milled, then roasted in a reducing atmosphere to convert nickel and cobalt to their metallic form. The resulting product is selectively leached with an ammonia-ammonium carbonate solution at low temperature and atmospheric pressure. Removal of ammonia causes precipitation of nickel carbonate that can be calcined to produce nickel oxide.

Production of pure nickel requires removal of cobalt which, if integrated with the process as described, will occur before nickel carbonate precipitation. Separation of nickel and cobalt in order to achieve the production of pure nickel can be achieved using solvent extraction. The use of solvent extraction also allows the recovery of cobalt. A simplified flowsheet of this modified Caron process, as operated by Queensland Nickel Industries (QNI) Limited nickel and cobalt refinery in Yabulu, Queensland, Australia, is shown in Figure 2 (Fittock, 1997).

The solvent extraction process uses a modified Lix 84 reagent in ammoniacal solution. This reagent was later designated Lix 87QN (Bhaskara, Sarma and Nathsama, 1996). The nickel ammine complex is extracted and cobalt(III) remains in

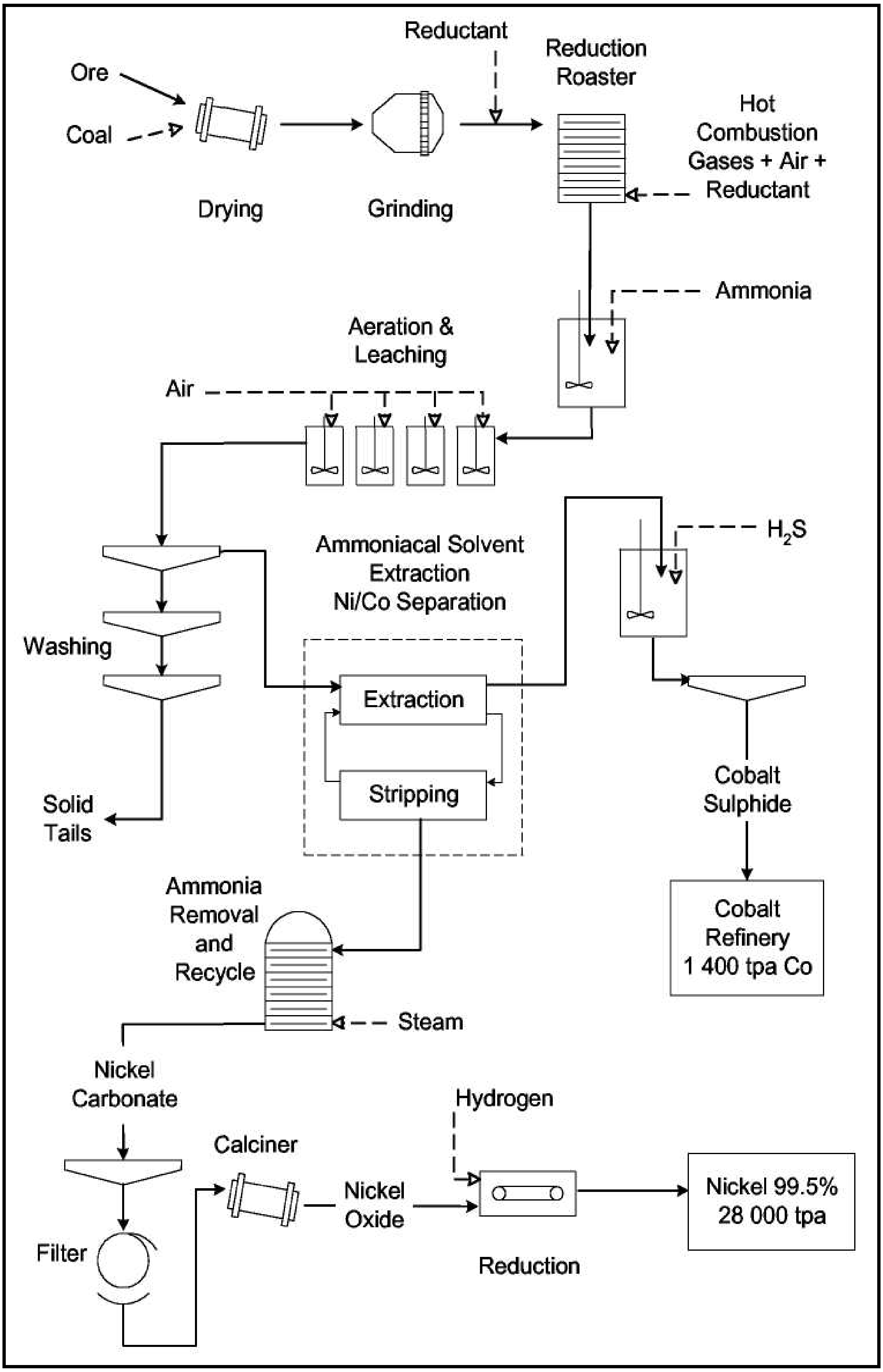


Figure 2 Simplified QNI Refinery flowsheet.

the raffinate. The nickel is stripped with an ammonia solution that has a higher ammonia concentration than the extraction solution (Price and Reid, 1993). Although recoveries in the solvent extraction circuit are good, overall metal recovery for the process is only approximately 84% for nickel and 45% for cobalt (Reid, 1996) depending on the feed material.

2.3.4.2 Pressure Acid Leach (PAL)

The first and, for more than 35 years the only, commercial pressure acid leach (PAL) operation was constructed at Moa Bay, Cuba, in 1959 (Simons, 1988). The PAL process involves leaching the slurried ore with sulphuric acid at elevated temperatures and pressures causing almost total dissolution of the feed material. The use of PAL achieves much higher nickel and cobalt dissolution with only half to one third of the energy requirements of the Caron process (Reid, 1996). However acid consumption is a major cost component, downstream processing is more complex and effluent disposal can pose difficulties.

Once the nickel and cobalt are in solution a wide variety of processing options are available. These include a range of intermediate precipitation products which may be redissolved and various applications of solvent extraction technology. A range of processing routes have been shown to be technically and commercially viable and those recently implemented are discussed below.

2.3.4.2.1 Pressure Acid Leach Operations in Australia

The recent commissioning of three significant nickel-cobalt operations in Western Australia has resulted in increased interest in the commercial application of PAL technology to lateritic ores. The use of PAL at the front of the processing circuit is common to all three of the new operations. Of interest is the choice of different processing routes following leaching. These are divided into two groups: direct and indirect separation. Direct separation involves the application of solvent extraction to separate nickel and cobalt directly from the pregnant liquor stream (pls). Indirect separation uses an intermediate precipitation and re-leach step to remove impurities before solvent extraction to separate nickel and cobalt. The differences in process selection arise due to differences in the ore mineralogy and behaviour, production philosophy, perceived technical risk and financial considerations. The chosen process routes are discussed below.

2.3.4.2.1.1 The Murrin Murrin Process

The largest of the new operations with an identified resource of 116 million tonnes of ore grading 1.10% nickel and 0.08% cobalt, Murrin Murrin also has the most conservative process flowsheet as identified by technical, start-up and financial risk analysis. The process route is shown in Figure 3 (Motteram, Ryan and Weizenbach, 1997). The ore is leached with sulphuric acid, produced on site by a sulphur burning acid plant, at 255°C and 4300 kPa for 90 minutes. The leached slurry is fed to a counter-current decantation (CCD) circuit for washing and pH adjustment to 2.4-2.6 with locally available calcrete (calcium carbonate). Adjustment to a higher pH (3.5-4.0) in order to remove iron, aluminium and chromium was attempted but caused unacceptable loss of nickel and cobalt through coprecipitation and/or adsorption (Motteram et al., 1996).

The solution at pH 2.4-2.6 then undergoes sulphide precipitation at 90°C and 105 kPa hydrogen sulphide, also produced on site. Sulphide precipitation rejects a large proportion of the impurities such as aluminium, magnesium and manganese found in the liquor. The relatively mild sulphide precipitation conditions, compared to Moa Bay at 121°C and 1034 kPa (Chalkley and Toirac, 1997) are made possible by using seed recycle and solutions containing high levels of magnesium. A clean water wash is used to remove chlorides from the mixed sulphide precipitate, which is then ready for treatment in the independent on-site refinery.

The mixed sulphide precipitate is slurried in water and leached under oxygen pressure of 400 kPa (total pressure 1100 kPa) at 165°C giving near total dissolution of the precipitate. Iron is removed via pH adjustment with ammonia. Copper and most zinc are removed by atmospheric sulphide precipitation.

The remaining zinc is removed by solvent extraction with Cyanex® 272. After adjusting the pH, Cyanex 272 is used in a second extraction circuit to remove cobalt. Cobalt is stripped and further refined before hydrogen reduction and briquetting to produce 99.8% cobalt briquettes. The raffinate from cobalt solvent extraction is

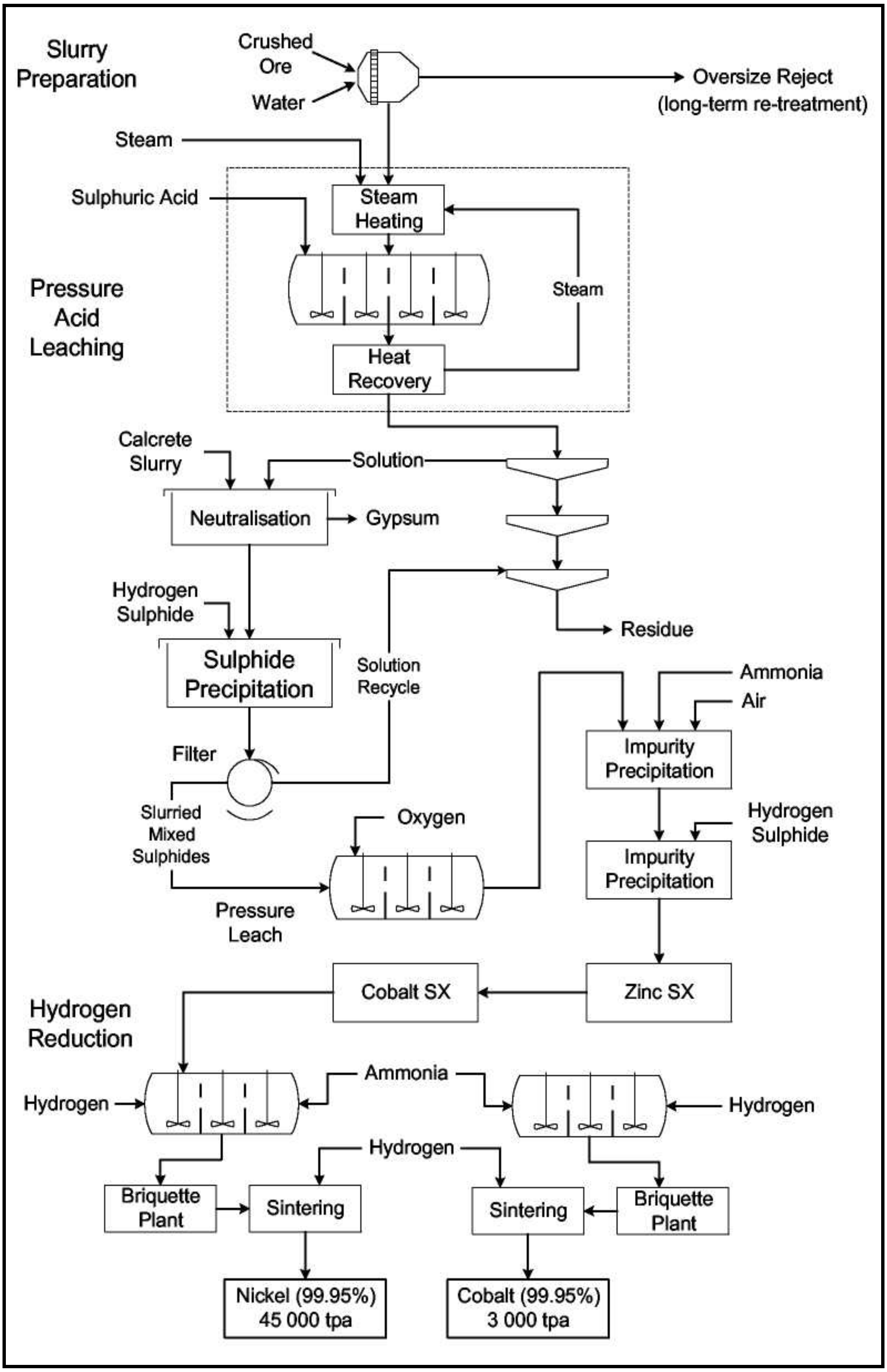


Figure 3 Flowsheet of the Murrin Murrin process.

treated by conventional hydrogen reduction, briquetting and sintering to produce 99,95% nickel briquettes. Design output is approximately 45 000 tpa nickel and 3 000 tpa cobalt (Lanagan, 2002).

2.3.4.2.1.2 The Cawse Process

The Cawse Nickel Project is utilising a resource of 52.8 million tonnes of ore grading 1.0% nickel and 0.07% cobalt (Hellsten and Lewis, 1996). The process flowsheet is shown in Figure 4 (Kyle and Furfaro, 1997).

The Cawse resource is the only example of the three Western Australian laterites discussed here which is amenable to physical upgrading of the ore feed before PAL. Removed of the coarse silica fraction (+212 μm) increases the nickel and cobalt feed grade by 30-50% while retaining 70-80% of the metal value (Hellsten and Lewis, 1996; Kyle and Furfaro, 1997). After removal of the coarse silica fraction, The thickened slurry is led to the leach autoclave where conditions are 250^{o}C, 3800 kPa and a residence time of 75-105 minutes.

The leach liquor is adjusted to pH 3.5 with limestone slurry. Air addition is used to aid oxidation of iron(II) to iron(III), which is subsequently precipitated. The resulting slurry is washed and separated through a CCD circuit before a second stage of iron removal by adjustment to pH 6.0. The second stage solids are recycled back to first stage pH adjustment to recover co-precipitated nickel and cobalt. The nickel and cobalt are then removed from the neutralised liquor by hydroxide precipitation. Hydroxide precipitation recovers most of the nickel and cobalt as well as many other metals such as copper, zinc and manganese which are in solution.

The processing of a mixed hydroxide precipitate is then carried out in a similar way to the previously proven operation at QNI Limited. That is, the mixed hydroxide precipitate is selectively re-leached with an ammonia-ammonium carbonate solution producing a solution containing nickel, cobalt, copper and zinc with some manganese, magnesium and iron.

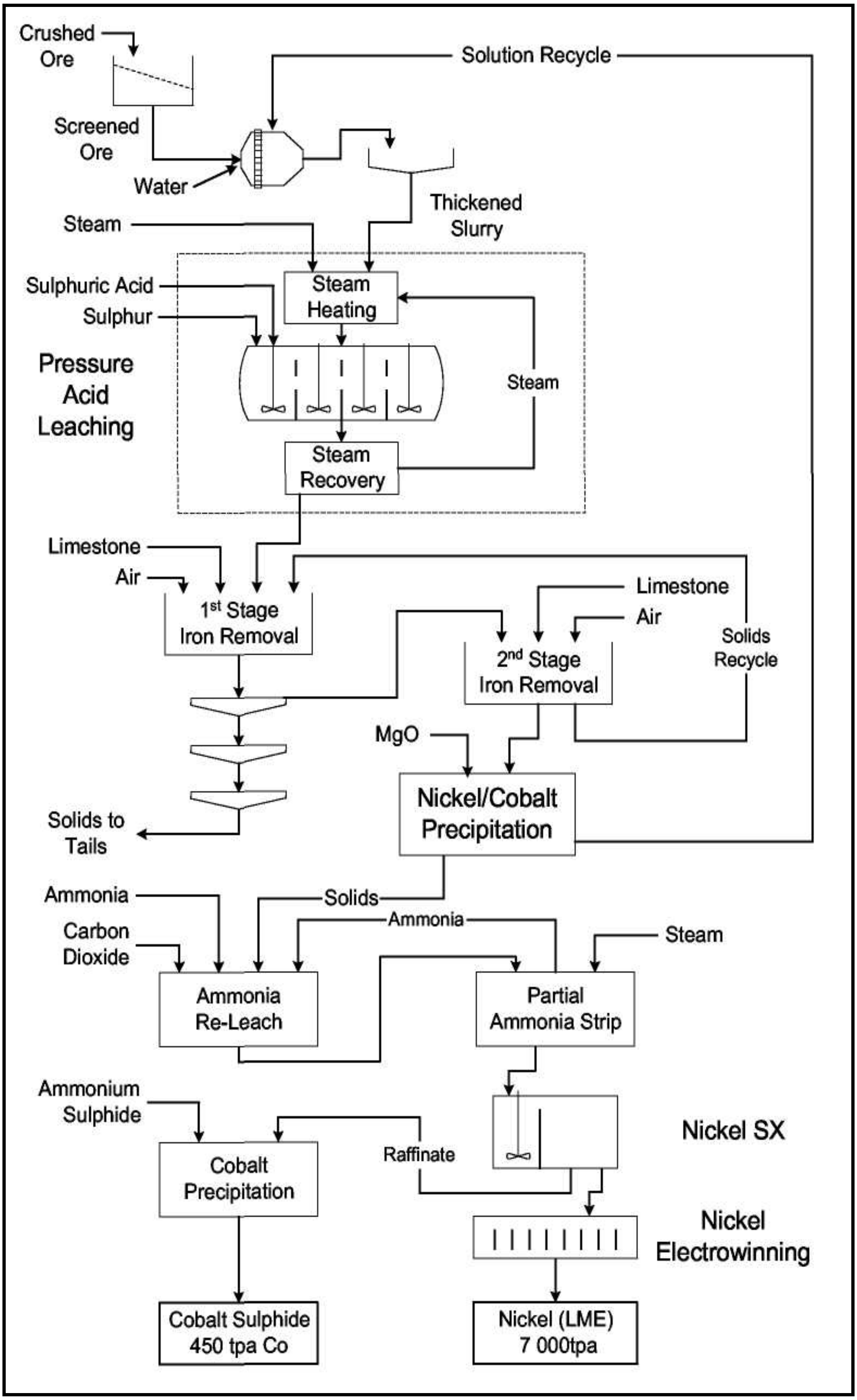


Figure 4 Flowsheet of the Cawse process.

Cobalt(II) oxidation to cobalt(III) occurs readily under the conditions present in the re-leach liquor. The change in oxidation state of cobalt prevents its co-extraction in the nickel solvent extraction circuit.

Partial ammonia stripping results in re-precipitation of weak amine complexes such as those formed by zinc and manganese impurities. Nickel solvent extraction is carried out with LIX® 841 in kerosene. This process is selective for nickel under these conditions. The organic phase is scrubbed to remove ammonia and then stripped using sulphuric acid.

Nickel is recovered from the strip liquor by electrowinning to produce nickel cathode. Cobalt is precipitated from the raffinate as a sulphide. It was originally planned to incorporate production of cobalt metal. Initial design output was 8500 tpa nickel and 2000 tpa cobalt by means of selective mining of high-grade zones. The life-of-project design output was 7000 tpa nickel and 450 tpa cobalt (Hellsten and Lewis, 1996).

2.3.4.2.1.3 The Bulong Process

Bulong Nickel Operations are operating from a proven and probable resource of 41 million tonnes at 1.14% nickel and 0.09% cobalt (Burger, 1996). The given flowsheet is the only example of nickel production from a laterite source using direct solvent extraction i.e. without intermediate precipitation and re-leach steps. Flowsheet of the Bulong process is given in Figure 5 (Kopejtka, 2000).

The thickened ore is leached at 250°C and 4000 kPa with a residence time in the autoclave of 75 minutes. A seven stage CCD circuit clarifies the pregnant liquor prior to partial neutralisation. Suspended solids are removed and the liquor pumped to a storage pond ready for treatment in the separate solvent extraction and electrowinning section of the plant.

The clarified pregnant leach liquor is fed directly to the cobalt solvent extraction circuit. The extractant is Cyanex® 272 in Shellsol® 2046 as the diluent. Tributyl phosphate was used as a third phase inhibitor during testwork (Soldenhoff et al., 1998) but was not incorporated into the operating plant. At pH 5.5, the cobalt circuit

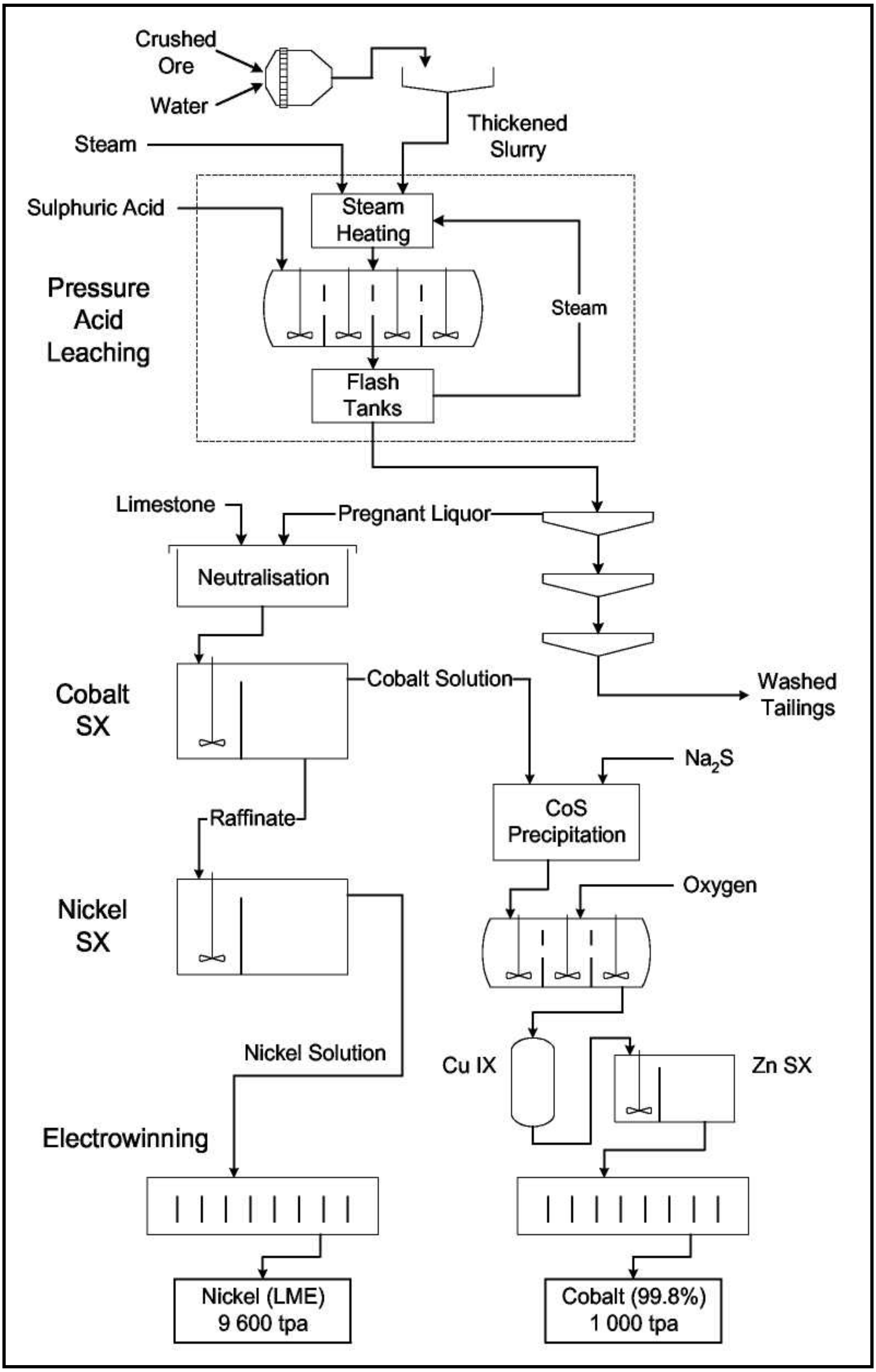


Figure 5 Flowsheet of the Bulong process.

removes cobalt and scavenges impurities such as copper, zinc, manganese and any remaining iron and aluminium from the liquor. After stripping, cobalt is precipitated as sulphide. The cobalt sulphide undergoes a pressure oxygen re-leach, the copper is removed by ion exchange and the zinc is removed by solvent extraction before electrowinning the resulting solution to produce cobalt metal.

The raffinate from cobalt solvent extraction, containing predominantly nickel, magnesium and calcium, is sent to the nickel solvent extraction circuit where Versatic® 10 is used to preferentially extract the nickel. After scrubbing and stripping, nickel metal is recovered by electrowinning. Design output is 9600 tpa nickel and 1000 tpa cobalt (Lanagan, 2002).

2.4 Roasting

Roasting represents a significant milestone in the journey of raw materials (ores) to metals as a finished product. Specifically, roasting covers operations between ore dressing or concentration on the one hand, and actual metal recovery and finishing on the other. Traditional roasting involves a chemical reaction with the furnace atmosphere at a temperature below the fusion point of the charge or product. Reactions in the molten state to produce metal, matte, or slag are distinguished as smelting.

In considering the thermodynamics of roasting of metal oxides at low temperatures, it should be noted that sulphur trioxide is formed in the gas phase according to the reaction:

$$SO_2 + 1/2O_2 \longrightarrow SO_3 \qquad (2.1)$$

Oxide-sulphate equilibrium can be considered in the form:

$$MeO + SO_3 \longrightarrow MeSO_4 \qquad (2.2)$$

By adding the two equations (2.1) and (2.2), we get:

$$MeO + SO_2 + 1/2O_2 \longrightarrow MeSO_4 \qquad (2.3)$$

Outokumpu Oy has a method of cobalt and nickel extraction process. The idea of the sulphatizing roasting is expressed as to convert the non-ferrous metals into water soluble sulphates while leaving the iron as an insoluble oxide.

Reactions of the following type take place:

$$MeS + 1\frac{1}{2}O_2 \longrightarrow MeO + SO_2 \qquad (2.4)$$

$$SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3 \qquad (2.5)$$

$$MeO + SO_3 \longrightarrow MeSO_4 \qquad (2.6)$$

Me represents Co, Ni, Cu, Zn.

This operation is accomplished in two fluidized bed roasters. The rectangular roaster is divided into four compartments.

The calcine, which represents the main part of the feed, is fed to the first compartment and flows through the roaster. The order to maintain the accurate sulphatizing temperature of about 680^{o}C and the proper gas composition, some concentrate is added to each compartment.

The sulphatized material is discharged from the last compartment and cooled to about 100^{o}C. After magnetic separation the magnetic part is fed back to the roaster and the non-magnetic part is quenched in cobalt sulphate solution (Outokumpu News, 1969).

2.5.1 Roasting with Sulphuric Acid

To convert water insoluble metal oxides to water soluble metal sulphates by roasting, sulphuric acid could be used as a source of sulphur. During the formation of sulphates the following reactions take place:

$$MeO + H_2SO_4 \longrightarrow MeO + SO_3 + H_2O \qquad (2.7)$$

$$MeO + SO_3 + H_2O \longrightarrow MeSO_4 + H_2O \qquad (2.8)$$

By adding the two equations (2.7) and (2.8), we get:

$$MeO + H_2SO_4 \longrightarrow MeSO_4 + H_2O \qquad (2.9)$$

The temperature of the above equations could be distinguished so that you could eliminate the formation of some metal sulphates. Therefore, selective leaching could be achieved.

A pilot plant operation has confirmed the validity of the process for the recovery of nickel and cobalt from the ores of laterite deposits by using the above method (Zubryckyj et al., 1965).

2.5 Çaldağ Lateritic Ore Deposit

The Çaldağ deposit was discovered and investigated by the MTA (General Directorate of Mineral Research and Exploration) in the late 1970's and early 1980's. MTA comprehensively explored the area, including geological mapping, excavating trenches and shafts, drilling approximately 100 holes and assaying at least 7,000 drill hole samples for Ni and Co, and subsets of those samples for Fe, SiO_2, Mg, Al, Ca, Mn and Cr.

The Çaldağ lateritic nickel deposit is located 15km north of the town of Turgutlu, approximately 70km east of İzmir, within the province of Manisa, western Turkey. Turgutlu is currently one of Manisa's largest towns with a population of approximately 70000. The nickel mineralization mainly occurs at altitudes above 600m, this area generally has a steep and undulated topography.

2.5.1 Geology

The rocks in the Çaldağ area are Palaeozoic, Mesozoic and Tertiary aged (Oğuz, 1967). Palaeozoic rocks are represented by phyllite, sandstone and crystallized limestone. The grey coloured crystallized limestones occurring at the bottom are represented by the white dolomite strata at the top. The ophiolitic complex formed during Upper Cretaceous shows all the units described elsewhere. The Çaldağ iron-nickel-cobalt deposit was developed on the serpentinite. The serpentinite, as a source rock (protore) of lateralisation, is surrounded by the re-crystallized Palaeozoic limestone on the east and south. The ophiolitic complex, including the serpentinite, extends towards the west and north-west (Oğuz, 1967). The Tertiary rocks consisting of green argillaceous strata and limestones formed in inland water conditions are partly eroded and rest on the serpentinite as isolated masses (Ozansoy, 1960; Hirano and Boyalı, 1980). These rocks are unconformable with the serpentinite and the laterite zones. Eocene age has been given to the upper limestones by Hirano and Boyalı (1980).

The area is affected by at least two tectonic phases after the emplacement of the Cretaceous ophiolitic complex. The first phase has occurred at the beginning or before the Eocene for a short time after the lateralisation, while the second one took place after the Eocene. These features can clearly be seen around the deposit. The plasticity of the serpentinite played an important role during the tectonic deformation which caused the parting of the laterite zones. The erosion proceeded to the unweathered serpentinite in places. The remaining laterite and serpentinite were covered by the Eocene sedimentary rocks. The tectonic activities developed after the Eocene caused dividing of the Eocene sedimentary rocks together with the serpentinite and laterite and gave these rocks dips ranging between 40-50 degrees. Later the fossil laterite zones eroded in places again but this time the erosion was restricted because of the Tertiary cover.

Detailed geological work from drilling data and local-scale mapping by the MTA has identified the broad geological framework seen at Çaldağ, which occurs as an isolated mountain sequence consisting of various geological formations surrounded by a plain of younger sediments . The stratigraphic column is given in Figure 6.

2.5.2 Mineralization

Genetic Consideration from the considerable amount of geological work undertaken on the deposit, a genetic model has been developed from which a number of significant economic considerations can be drawn. These are:

i. Transported laterite may be significant in the Çaldağ deposit.

ii. The laterite sequence at Çaldağ has been subject to mild burial metamorphism by the superimposed Pliocene sediments.

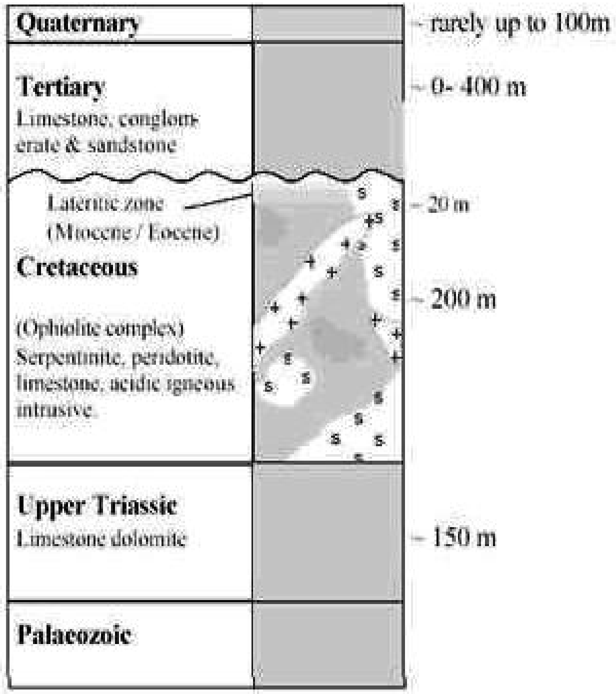


Figure 6 Stratigraphic sequence for the Çaldağ Deposit.

It is considered that the laterite profile has undergone epigenetic processes during subsidence, burial below fresh water sediments and after emergence in Tertiary and Quaternary times. These processes involved pervasive deposition of carbonates and silica in the upper part of the laterite.

A clear understanding of the resultant geochemistry is essential. Particular attention should be given to identification of the spatial distribution of both the silicate and carbonate rich zones within the laterite profile, both of which may affect the leach characteristics of the ore. Metal distribution of laterite zone and enrichment of different metals are represented in Figure 7 (Çağatay et al., 1983).

The limits of mineralization are imposed by the extent of the laterite, which has been fully mapped by MTA. It is bounded by Triassic limestone in the east along a thrust fault and serpentinite in the northeast, north and west. The extent of laterite remains open in the south and southeast. The footwall is generally weathered serpentinite, except in the southeast where it is Triassic limestone.

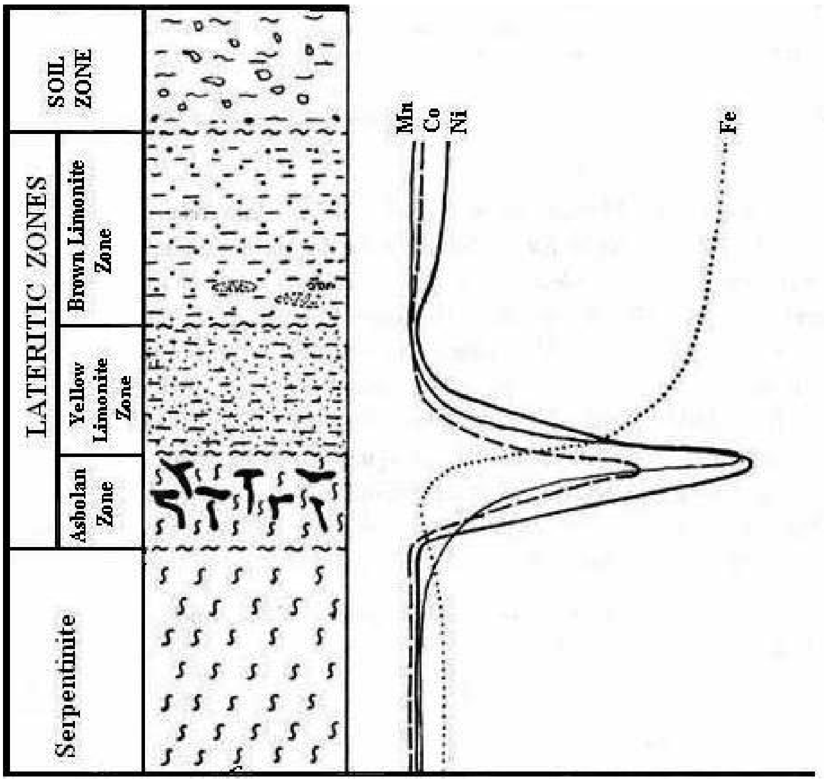


Figure 7 Co, Ni, Fe and Mn distribution of Çaldağ Deposit.

CHAPTER III

EXPERIMENTAL MATERIALS AND METHODS

3.1 Materials

The ore used in the study was obtained from Çaldağ Lateritic Ore, Manisa, Turkey. The reserve of Çaldağ lateritic ore deposit is approximately 40 million tonnes. The ore was characterized using XRD and DTA/TG. The samples were crushed, groud and dried, and 50 grams of dried ore was used for all tests carried out. The chemical composition of the lateritic ore used in the experiments is given in Table 9.

Table 9 Elemental composition of Çaldağ lateritic ore sized to -75 µm.

Composition	Metal %
Ni	2.10
Co	0.12
Fe	32.45
Al	3.90
Mg	0.78
Mn	1.01
Cr	2.58
Ca	1.18
Si	13.70

3.1.1 XRD Analyses

X-Ray Diffraction Spectrometry (XRD) was applied in this study to analyse the mineral composition of lateritic ore sample. The peaks of diffraction were recorded and plotted against a horizontal scale in degrees of 2θ, which is the angle of the detector rotation in order to catch the diffracted X-Ray. The identified minerals were quartz and goethite as major minerals, smectite (which includes pyrophyllite, talc, vermiculite, sauconite, saponite, nontronite and montmorillonite), serpentinite and some clay minerals as minor minerals. The XRD results of the lateritic ore samples are presented in Figure 8.

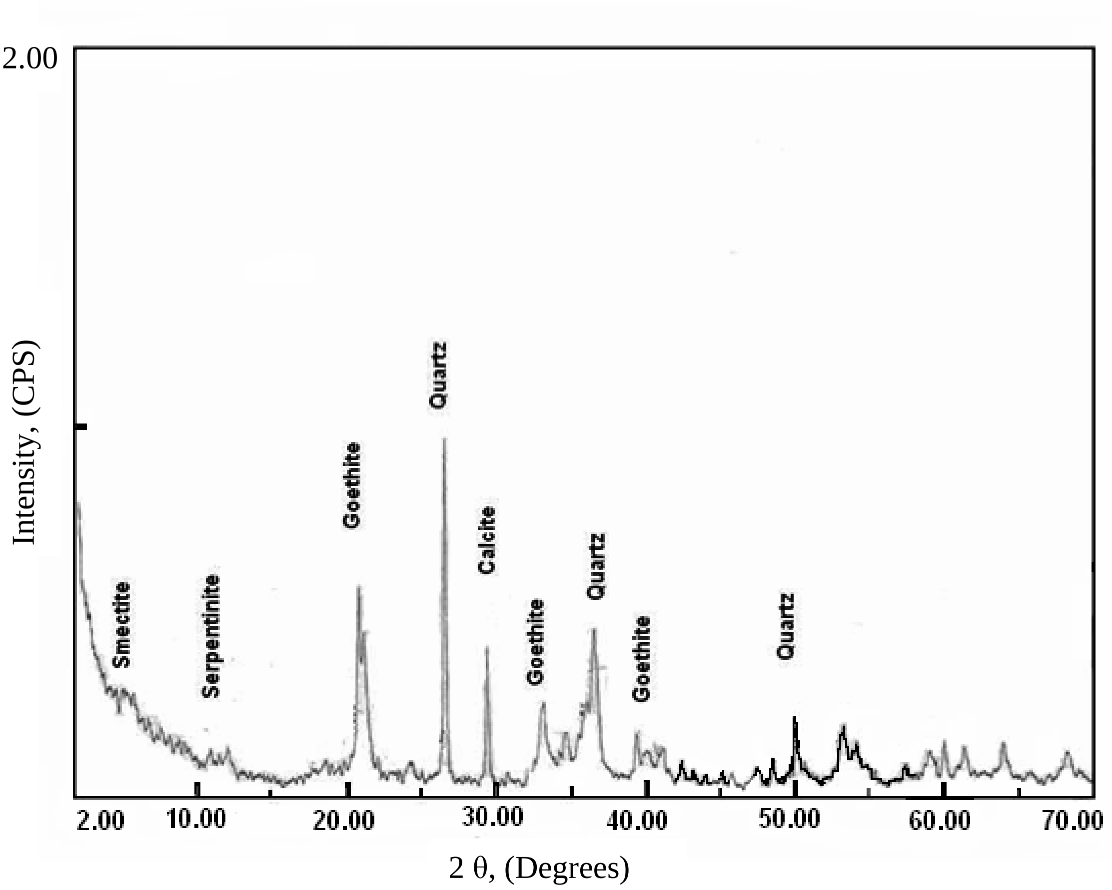


Figure 8 XRD graph of lateritic ore sample.

3.1.2 DTA-TG Analyses

Thermogravimetric and differential thermal analyses were carried out to see thermal behaviours of the ore (Figure 9). 100 mg of ore samples were analysed with a linear heating rate of 20°C/min in air (using Rigaku Thermal Analyzer Ver2.22E2).

The free moisture removal is initiated at 40°C and continues up to 180°C and this free water is completely removed and then some further water, probably strongly absorbed moisture, is removed at a relatively slow and constant rate until about 250°C. Above this temperature, goethite begins to be converted into hematite according to the following reaction:

$$2FeO.(OH) = Fe_2O_3 + H_2O \qquad (3.1)$$

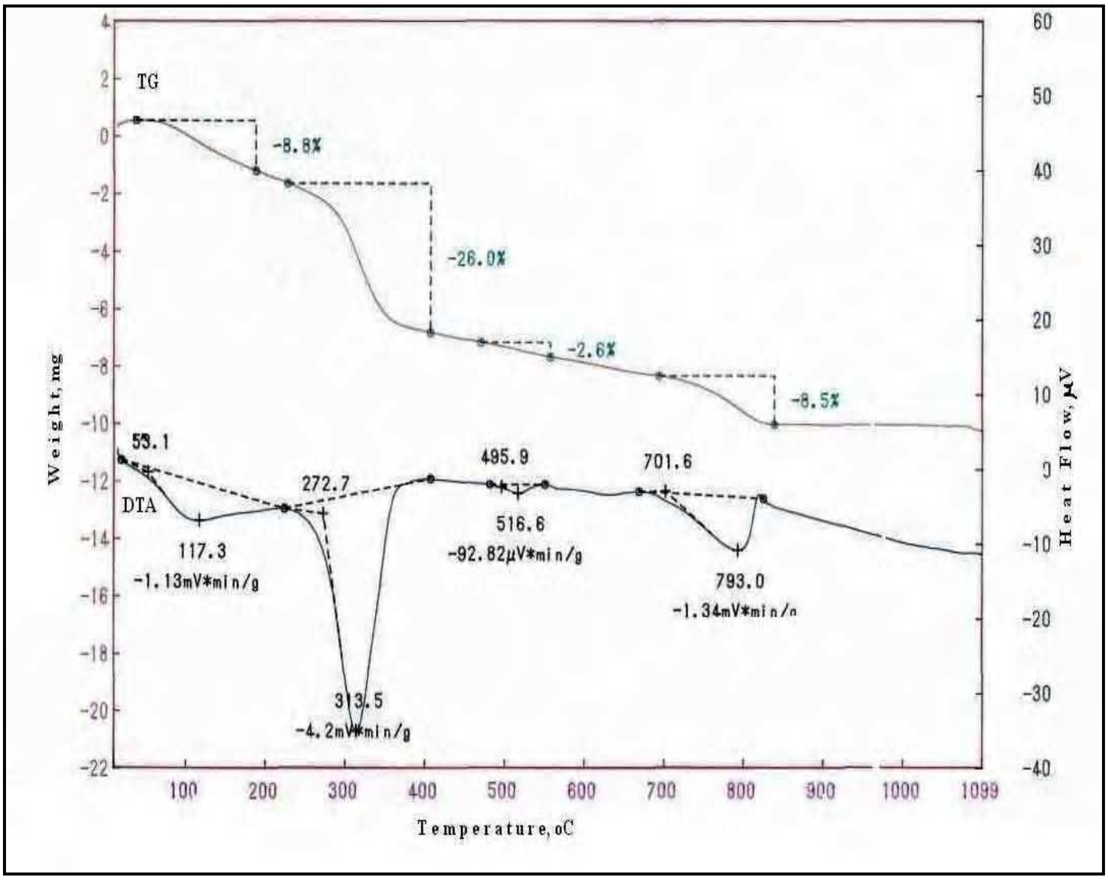


Figure 9 DTA-TG graph of the laterite sample.

And the rate of dehydration increased to a maximum of 4.2 mV*min/g at a temperature 313.5°C. The strong endothermic peak in region of 272.7°C – 400°C is caused by the dehydration of goethite. Generally, the endothermic peak representing goethite-hematite transformation is sharp at 385°C for highly crystalline goethite (Schwertmann et al., 1982), but for fine grained and poorly crystalline goethite, the dissociation temperature is always lower. DTA data indicate that the goethite decomposition temperature is 313.5°C.

3.1.4 Particle Size of Ore

The ore was ground by using a ball mill and wet screen analyses was performed. The size distribution of the samples used in the experiments is given in Table 10. And finally to see the grinding properties of the crushed ore sample, a grindability test was carried out and the result of this is given in Table 11 and Figure 10.

Table 10 Wet screen sieve test analysis after grinding.

Sieve size range (µm)	**Sieve fractions**		**Nominal aperture size (µm)**	**Cumulative wt % retained**	**Cumulative wt % passing**
	weight (gr)	**weight (%)**			
+150	11.58	1.80	150	1.80	98.20
- 150 + 106	16.94	2.63	106	4.43	95.57
-106 + 75	42.93	6.67	75	11.10	88.90
-75 + 53	75.30	11.70	53	22.80	77.20
-53 + 45	16.57	2.57	45	25.37	74.63
-45 + 38	60.42	9.39	38	34.76	65.24
- 38	420.05	65.24			

Table 11 Grindability test for –75µm.

Time minute	**Cummulative wt % passing**
10	48.00
20	61.24
30	70.96
40	79.37
50	85.03
60	88.83

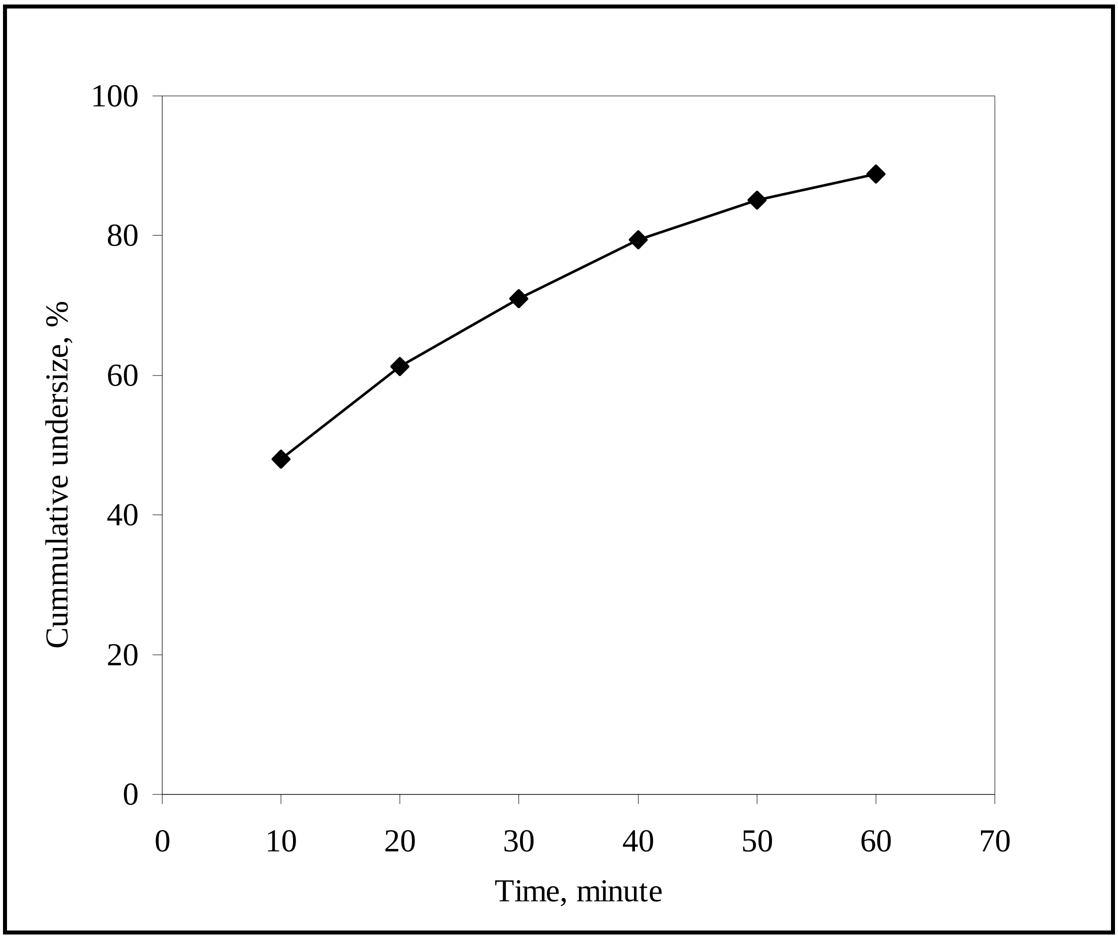


Figure 10 Grindability test for -75µm.

3.3 Method

The atmospheric pressure sulphuric acid leaching experiments was conducted with fifty grams of ore. In the study 100 mesh (150 µm), 150 mesh (106 µm), 200 mesh (75 µm) and 350 mesh (45 µm) feed material were tested to see the effect of particle size. And thereafter 80 % passing 200 mesh particle sized material was used for atmospheric pressure sulphuric acid leaching tests. All tests conducted in appropriate beakers and stirred with Fisher Scientific Stedy-Speed Adjustable Stirrer. Leach solution is filtered by a vacuum pump using a suitable filtering paper. During all the tests Merck sulphuric acid and distilled water were used.

In order to determine the leachability of Çaldağ lateritic ore with sulphuric acid under atmospheric pressure, the parameters such as the effect of particle size, pulp density, acid strength, leaching temperature and time were optimized.

All of the roasting experiments were carried out with fifty grams of ore (-200 mesh) and a predetermined amount of sulphuric acid which were mixed thoroughly in a silica crucible. The crucible was inserted in a preheated muffle furnace and material was kept in isothermal condition for the first stage at the predetermined temperature and period. After the first stage the lumpy mass was ground to a finer size (-100 mesh). The ground material was roasted at an elevated temperature for a desired time. The sulphated mass was cooled to room temperature and leached with hot water.

The optimised parameters of this process were amount of acid, temperature of sulphatization and decomposition, time for sulphatization and decomposition, leaching temperature and time, solid/liquid ratio, and finally the effect of water addition during pugging.

A mass balance was carried out for all experiments based on amount of cobalt, nickel and iron in the feed, the leach solution and the residue. Therefore, these values were used to calculate extraction rates.

The analyses of nickel, cobalt were performed by ICP-OES Perkin Elmer Optima 4300 DV and that of iron by volumetric method.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Atmospheric Pressure Sulphuric Acid Leaching

In order to determine the leachability of Çaldağ lateritic ore with sulphuric acid under atmospheric pressure, a series of tests were carried out. In these tests, the effect of particle size, pulp density, acid strength, leaching temperature and time were investigated. The results are presented in the following sections.

4.1.1 Effect of Particle Size

The particle size of the feed is very important for the recoveries and also energy consumption. It is common that the leaching recoveries are inversely related to particle size. The aim should be to reach an optimum recovery with the coarsest feed material.

In the study 100 mesh, 150 mesh, 200 mesh and 350 mesh feed material were tested to see the effect of particle size. During the experiments other parameters were kept constant at: Acid strength: 40 % by wt of ore; solid-liquid ratio; 1/2 by weight; leaching time: 3 hours; leaching temperature: 20^{o}C.

The results of the experiments are given in Table 12 and Figure 11. As can be seen from these results 200 mesh of particle size could be sufficient from the feed size point of view.

Table 12 Effect of particle size on the metal recovery.

Particle size	**Metal recovery, %**			
mesh	**Co**	**Ni**	**Mg**	**Mn**
100	7.00	5.05	8.94	1.77
150	8.00	5.16	9.53	2.09
200	17.98	7.28	14.17	2.82
350	17.85	7.29	12.62	2.71

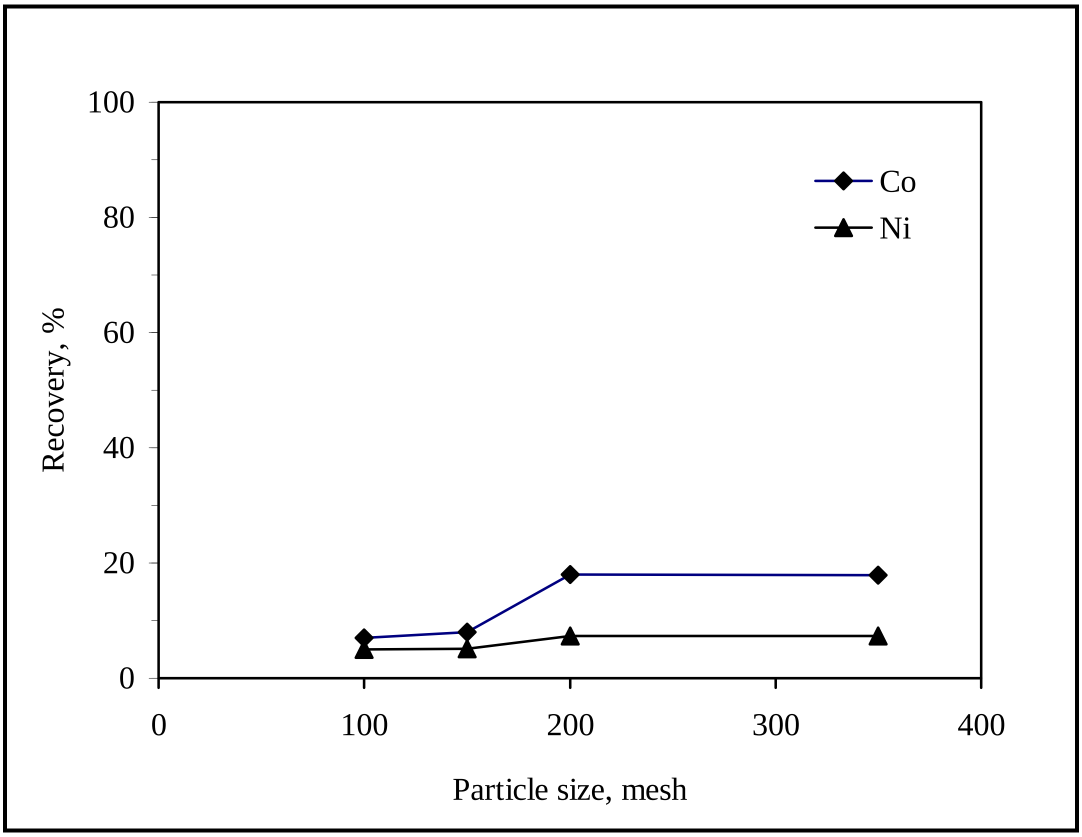


Figure 11 Effect of particle size on the metal recovery.

4.1.2 Effect of Pulp Density

In the study the effect of pulp density was also investigated. For this purpose five different solid-liquid ratios, namely 1/1, 1/2, 1/3, 1/4, and 1/5 by weight, were used for the experiments. During these experiments the following parameters were kept constant: Acid concentration: 2.25 Molar; particle size of feed: 200 mesh; leaching time: 3 hours; leaching temperature: 20°C.

The results of the experiments are given in Table 13 and Figure 12. As can be seen from these results, the recovery increased with decreasing pulp density up to 1/3 solid-liquid ratio by weight and remained constant thereafter, indicating that a solid-liquid ratio of 1/3 is sufficient for leaching.

Table 13 Effect of pulp density on the metal recovery.

Pulp density	**Metal recovery, %**			
Solid/Liquid	**Co**	**Ni**	**Mg**	**Mn**
1/1	8.03	4.20	7.07	5.86
1/2	8.02	3.81	7.04	5.44
1/3	15.54	5.37	8.92	7.82
1/4	15.21	4.86	8.91	6.71
1/5	15.99	6.29	10.61	7.42

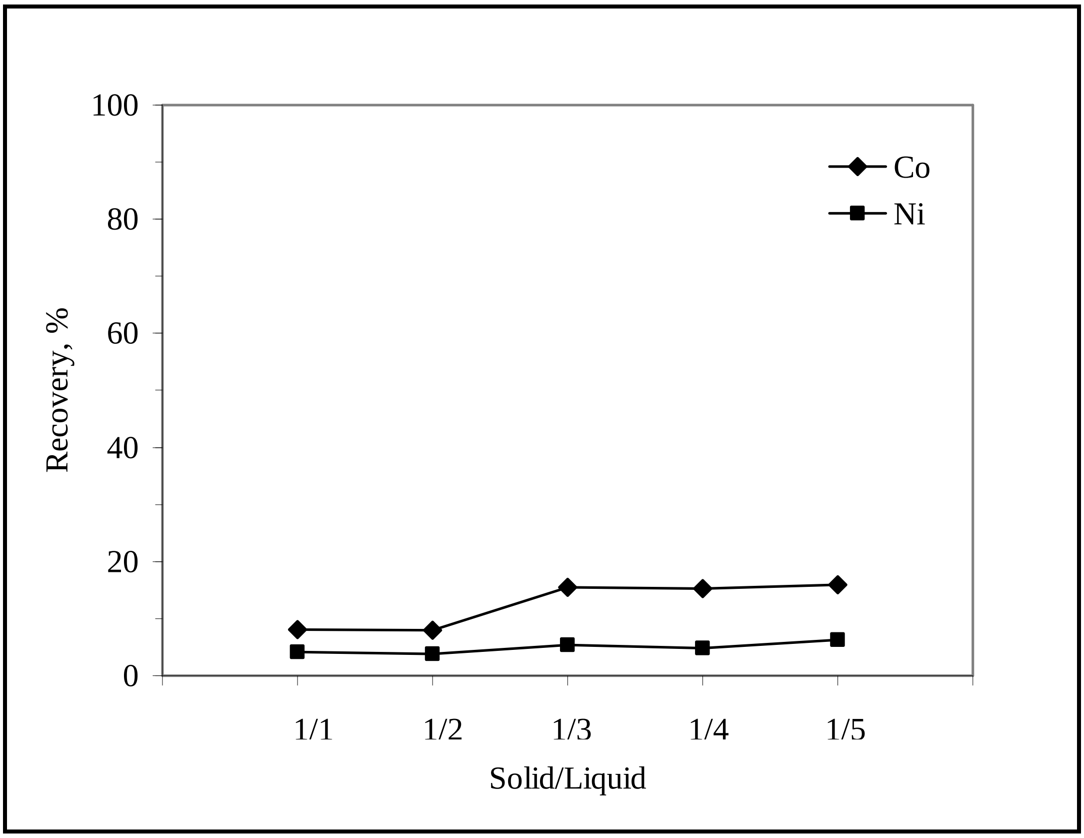


Figure 12 Effect of pulp density on the metal recovery.

4.1.3 Effect of Acid Strength

Acid strength of solution may be the most effective parameter during leaching. In the study, six different levels of sulphuric acid strength 30, 40, 50, 60, 70 and 80 wt % of ore were tested. During the tests the following parameters were kept constant: Solid-liquid ratio: 1/3 by w/v; leaching time: 3 hours; leaching temperature: 20°C; particle size of feed: 200 mesh.

The results of the experiments are given in Table 14 and Figure 13. From these results, it can be concluded that a minimum acid strength of 70 wt % of ore is required to obtain any substantial increase in the recovery.

Table 14 Effect of acid strength on the metal recovery.

Acid strength weight % of ore	**Metal recovery, %**			
	Co	**Ni**	**Mg**	**Mn**
30	9.99	4.32	8.01	5.55
40	10.77	4.47	7.85	5.73
50	9.83	4.26	7.53	5.49
60	9.96	4.76	8.35	5.58
70	23.87	6.94	9.66	14.34
80	24.07	7.07	11.82	14.20

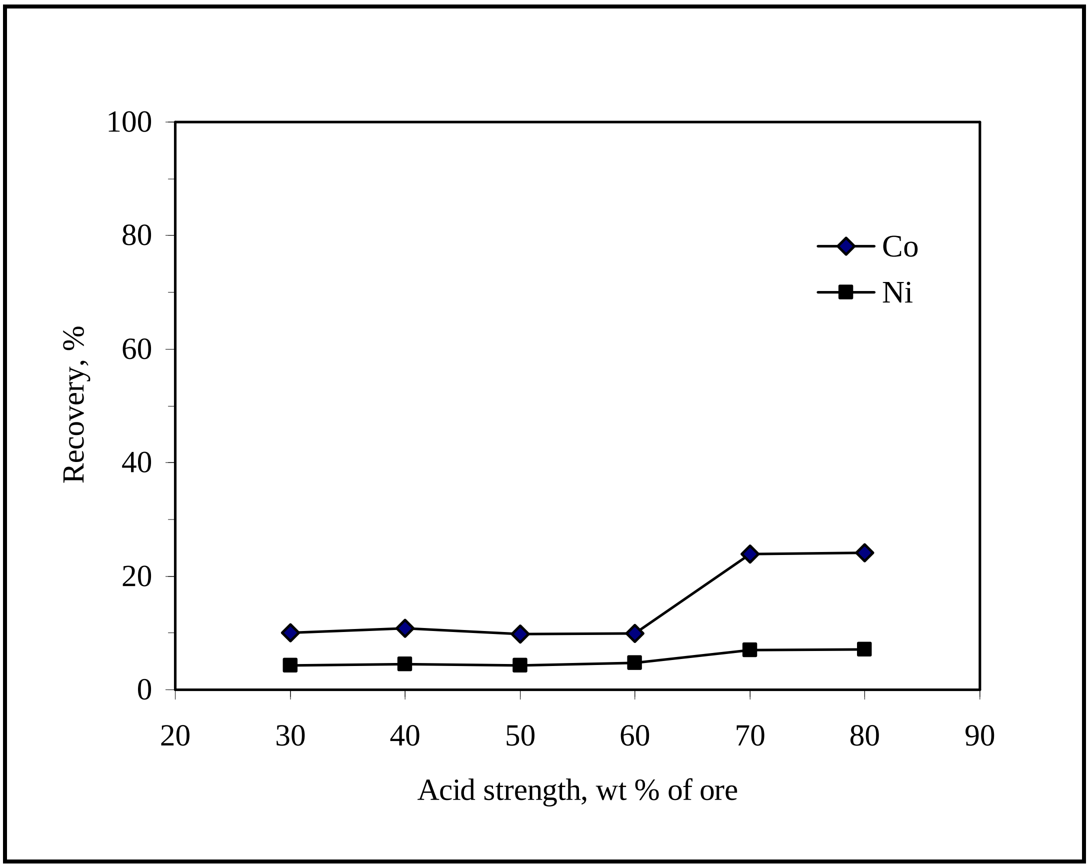


Figure 13 Effect of acid strength on the metal recovery.

4.1.4 Effect of Leaching Temperature

Leaching temperature during atmospheric pressure sulphuric acid leaching has an important effect on the metal recoveries. In this study effect of leaching temperature was also investigated. For this purpose 20, 40, 60, 80 and 95 ^{o}C leaching temperatures were tested.

During the tests, the following parameters were kept constant: Acid strength: 40 weight % of ore; solid-liquid ratio: 1/3 by weight; leaching time: 3 hours; particle size of feed: 200 mesh.

The results of the experiments are given in Table 15 and Figure 14. From these results it can be concluded that increase in the temperature increases the metal recoveries up to 60^{o}C for Co and 80^{o}C for Ni. No further improvements in the metal recoveries were observed after these temperatures. Thus, the optimum leaching temperature was assumed to be 80^{o}C.

Table 15 Effect of leaching temperature on the metal recovery.

Temperature	**Metal recovery, %**			
^{o}C	**Co**	**Ni**	**Mg**	**Mn**
20	16.54	5.37	8.92	7.82
40	28.78	15.91	3038	12.85
60	51.76	32.93	32.47	37.63
80	53.03	44.49	34.98	57.44
95	53.53	41.74	32.32	57.49

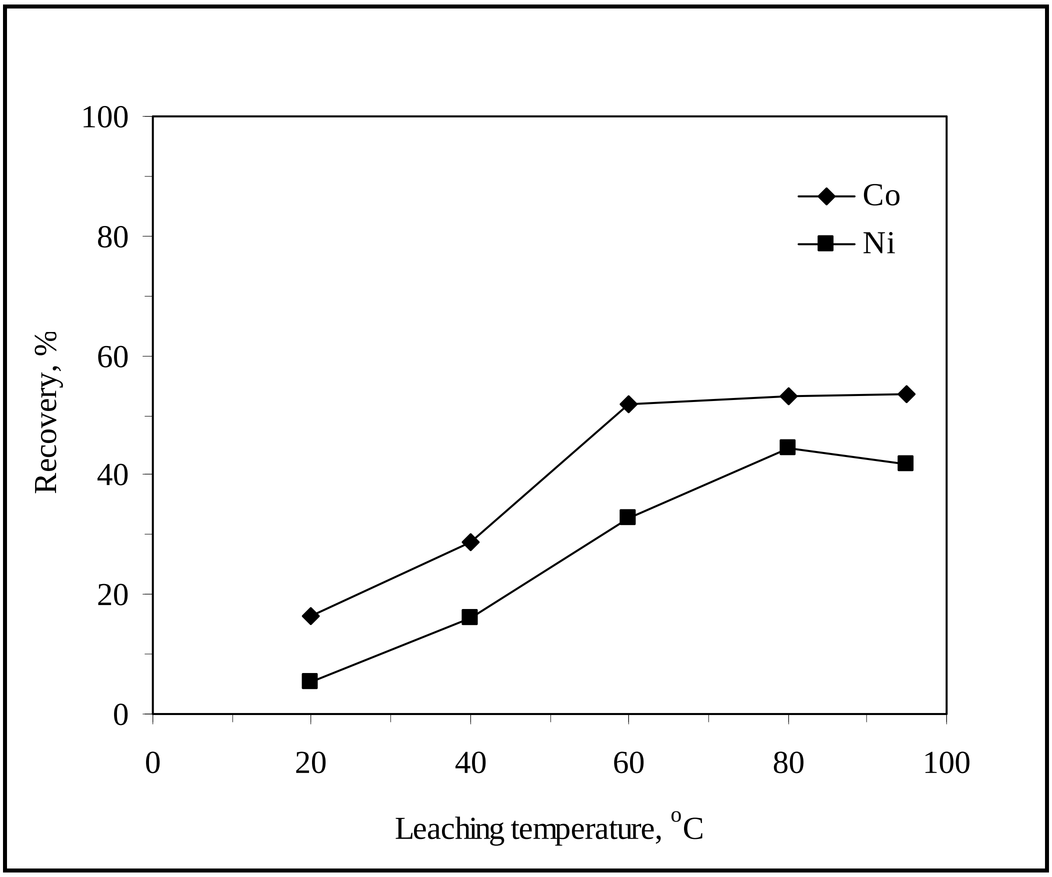


Figure 14 Effect of leaching temperature on the metal recovery.

4.1.5 Effect of Leaching Time

In order to see the effect of leaching time on the metal recoveries, leaching tests carried out for 90, 180, 270 and 360 minutes durations.

During these tests, the following parameters were kept constant: Acid strength: 40 wt % of ore; solid-liquid ratio: 1/3 by w/v; leaching temperature: 20°C and particle size of feed: 200 mesh.

The results of the experiments are given in Table 16 and Figure 15. From these results it can be concluded that increasing the leaching time has almost no effect on the metal recoveries. As the atmospheric pressure sulphuric acid leaching experiments for relatively short periods (carried out in this study) yielded rather low recoveries, it can be concluded that this method is not suitable for the extraction of nickel and cobalt from lateritic ore.

Table 16 Effect of leaching time on the metal recovery.

Leaching time minute	**Metal recovery, %**			
	Co	**Ni**	**Mg**	**Mn**
90	21.85	5.47	9.46	5.51
180	22.54	5.37	8.92	6.82
270	22.65	7.00	12.26	6.41
360	23.05	7.71	14.60	6.90

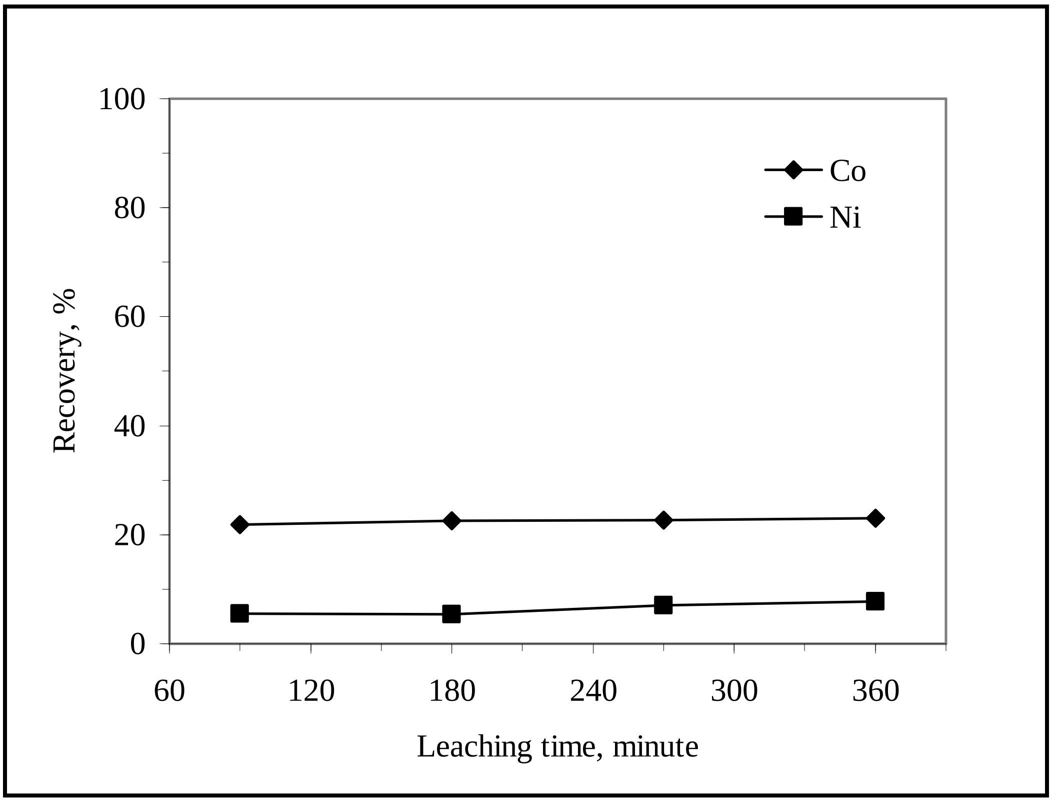


Figure 15 Effect of leaching time on the metal recovery.

4.2 Sulphatization Roasting

Another method of extraction of nickel and cobalt for lateritic ores at atmospheric pressure is the leaching with water after roasting the ore with sulphuric acid (Pug-roast-leach process). In this method, the aim is to selectively convert the metal oxides to water soluble sulphates. For lateritic ores, this can be done at two different temperatures in two stages. In the first stage, at 450°C both iron oxides and Co and Ni oxides are converted into sulphate salt of the respective metals. In the second stage, which takes places at a relatively higher temperatures around 700-800°C, while iron sulphates are decomposed into oxide and SO_3 gas, Co and Ni sulphates remain unaffected upon cooling, two main products are obtained.

1. Water soluble sulphates of Co and Ni.
2. Water insoluble oxides of iron.

The chemical reactions during two stages roasting can be summarized as follows:

The first stage roasting reactions (partially take place during pugging):

$$2[FeO(OH)]\,(s) + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3\,(s) + 4H_2O \qquad (4.1)$$

$$MeO\,(s) + H_2SO_4 \longrightarrow MeSO_4\,(s) + H_2O \qquad (4.2)$$

where Me stands for Co and Ni.

$$2[FeO(OH)]\,(s) \longrightarrow Fe_2O_3\,(s) + H_2O \qquad (4.3)$$

The second (decomposition of iron) stage reactions:

$$Fe_2(SO_4)_3\,(s) \longrightarrow Fe_2O_3\,(s) + SO_3\,(g) \qquad (4.4)$$

$$MeO\,(s) + SO_3\,(g) \longrightarrow MeSO_4\,(s) \qquad (4.5)$$

where Me stands Co and Ni, which were converted to water soluble sulphates. But iron was converted to hematite which allows selective leaching of cobalt and nickel over iron.

Thermogravimetric and differential thermal analyses of samples after the first and the second stages of roasting were carried out to see thermal behaviour of the roasted ore

(Figure 16 and Figure 17). 100 mg of ore samples were analysed with a linear heating rate of 20°C/min in air (using Rigaku Thermal Analyzer Ver2.22E2).

After the first stage of roasting at 450°C, it was seen in the TG-DTA graphs that most of the iron oxides were converted to iron sulphates as there appeared a noted decomposition between 670.3°C and 794.4°C, reaching to a large endothermic peak at 723°C. The second endothermic peak at 815.1°C is assumed to be the decomposition of nickel sulphates (Figure 16).

After the second stage of roasting at 700°C, most of the iron sulphates were converted to iron oxides. As a result, the peak at 723°C disappeared. Nickel sulphate continued to exist in the roast indicated by the endothermic peak at 811°C (Figure 17).

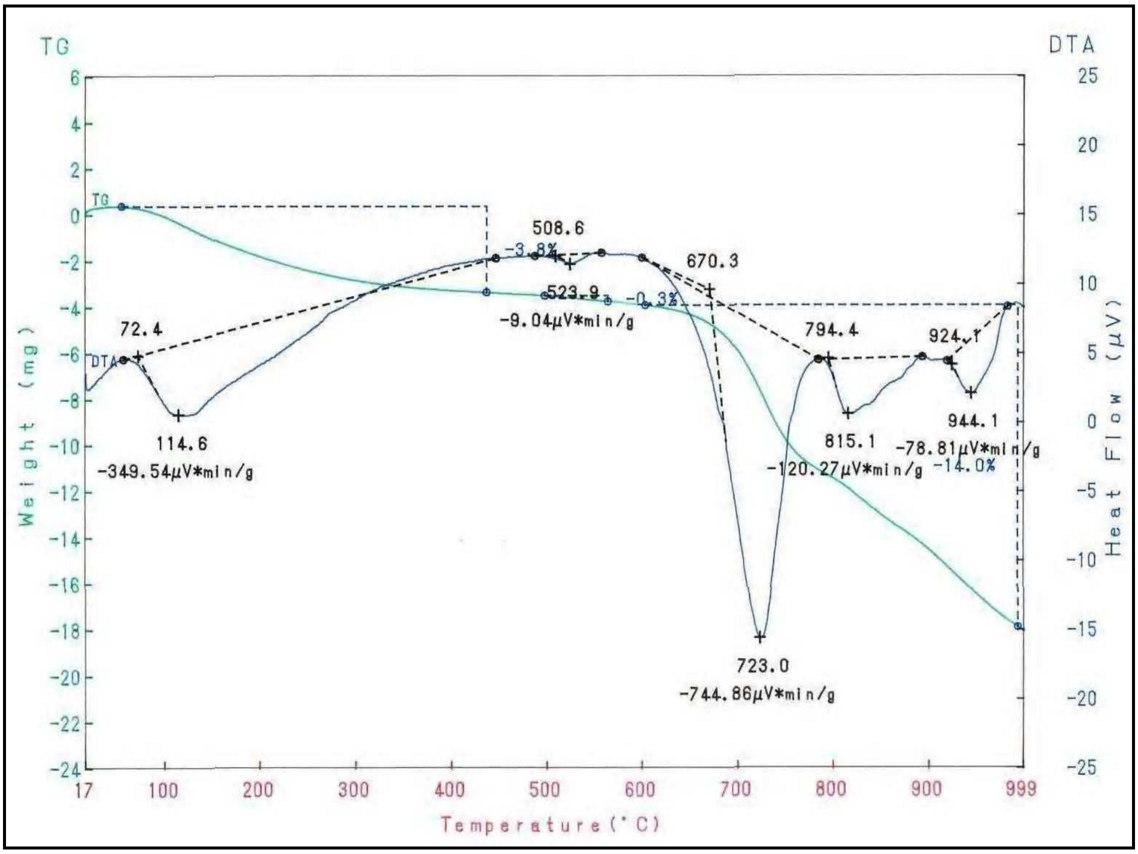


Figure 16 DTA-TG graph of the laterite sample after the roasting at 450°C.

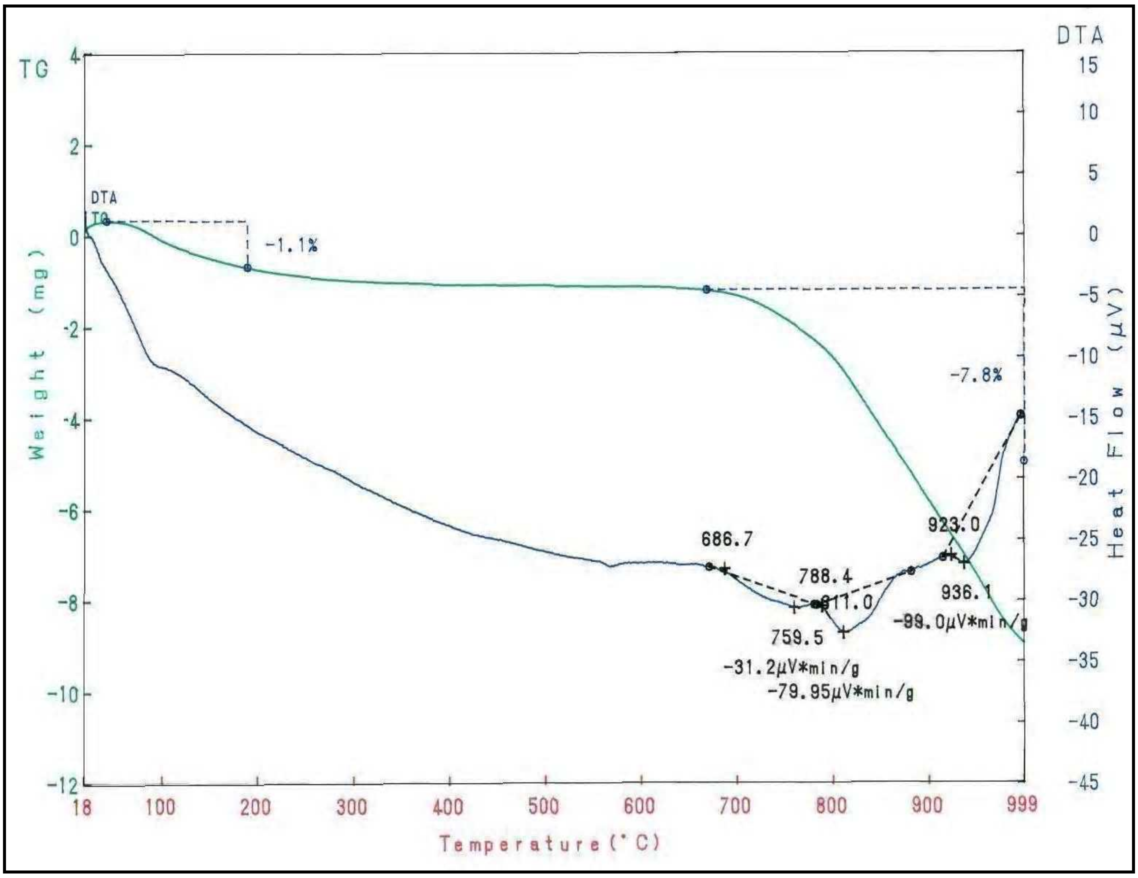


Figure 17 DTA-TG graph of the laterite sample after the roasting at 700°C.

4.2.1 Effect of Acid Strength

The effect of sulphuric acid concentration was investigated by varying the amount of acid from 15 to 55 by wt % of ore. During the tests carried out, the following parameters were kept constant: Sulphatization temperature: 450°C; sulphatization time: 30 minutes; decomposition temperature: 700°C; decomposition time: 15 minutes; leaching temperature: 70°C; leaching time: 30 minutes.

As it was observed in experiments that the strength of sulphuric acid was an important parameter. It was playing a significant role on the recoveries of cobalt, nickel and iron. Increasing the acid amount causes increase on the metal recoveries. But increase in iron recovery was not desired so the strength of sulphuric acid could not be increase after 30 wt % of ore as seen in Table 17 and Figure 16.

Table 17 Effect of amount of acid on the metal recovery.

Acid strength wt % of ore	Metal recovery, %		
	Co	**Ni**	**Fe**
15	76.58	63.06	4.32
25	79.34	69.47	6.23
30	83.89	73.23	7.71
35	86.23	79.32	12.46
45	87.29	82.17	20.42
55	88.43	88.50	30.55

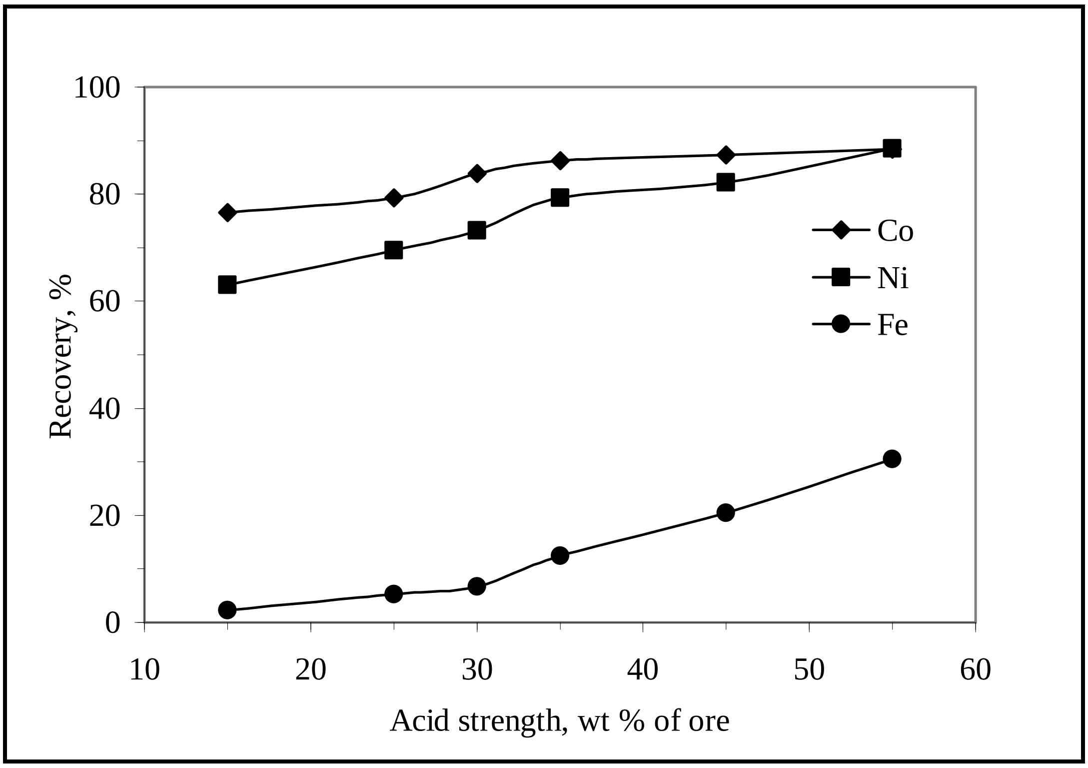


Figure 18 Effect of sulphuric acid strength on the metal recovery.

4.2.2 Effect of Sulphatization Temperature

The effect of sulphatization temperature was also studied. During the experiments the other parameters were maintained at the optimum values determined by the experiments conducted earlier. During the tests, the following parameters were kept constant: Acid strength: 35 wt % of ore; sulphatization time: 30 minutes; decomposition temperature: 700°C; decomposition time: 15 minutes; leaching temperature: 70°C; leaching time: 30 minutes.

As it was demonstrated in the experiments sulphatization temperature was more effective on the iron recovery than sulphatization time. Although sulphatization temperature must be below 500°C due to decrease in recoveries of cobalt and nickel, it is also well known that the rate of reaction increases with the temperature. This implies that the optimum sulphatization temperature can be 450°C before iron sulphates begin to decompose which can be seen in Table 18 and Figure 17.

Table 18 Effect of sulphatization temperature on the metal recovery.

Sulphatization temperature	**Metal recovery, %**		
°C	**Co**	**Ni**	**Fe**
200	86.34	77.63	12.59
300	87.85	80.47	12.19
400	86.53	77.87	12.25
450	86.23	79.32	9.46
500	85.74	79.81	5.27
700	85.19	76.47	3.54

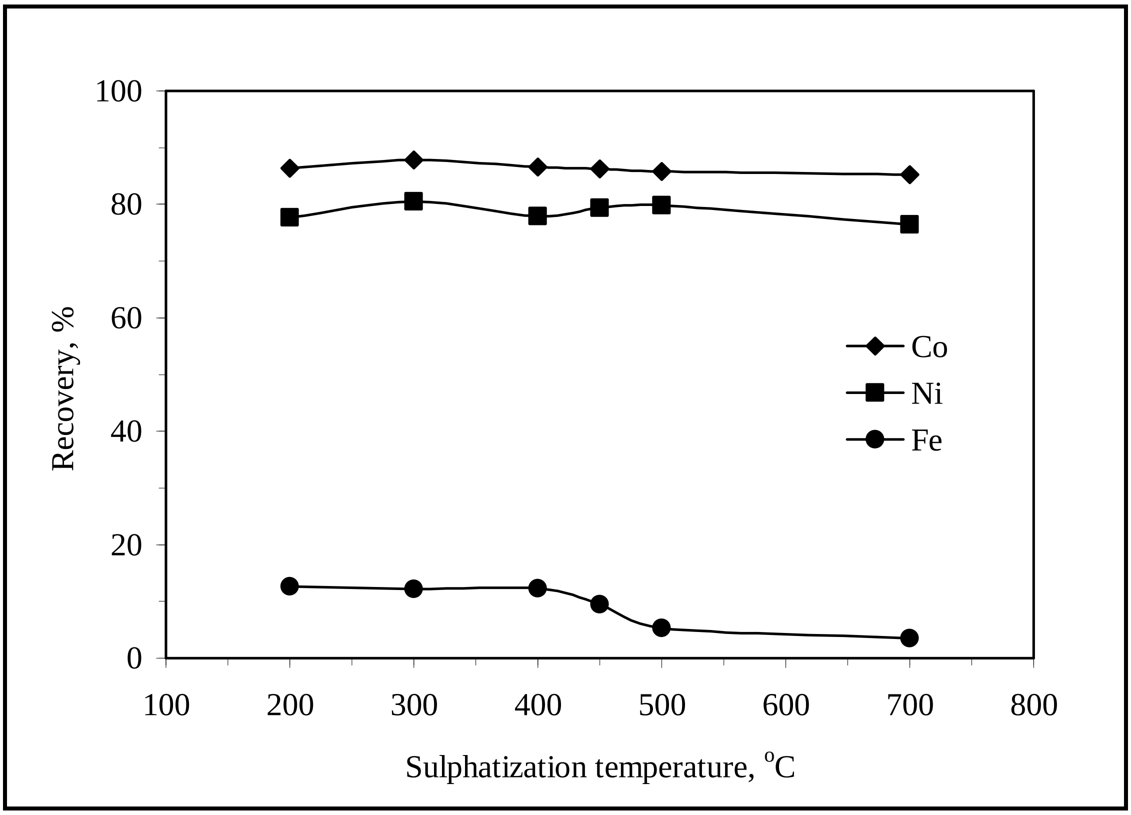


Figure 19 Effect of sulphatization temperature on the metal recovery.

4.2.3 Effect of Sulphatization Time

The effect of sulphatization time was also tested. During the experiments the other parameters were maintained at the optimum values determined by the experiments conducted earlier. During the tests the following parameters kept constant: Acid strength: 35 wt % of ore; sulphatization temperature: 450°C; decomposition temperature: 700°C; decomposition time: 15 minutes; leaching temperature: 70°C; leaching time: 30 minutes.

As it was demonstrated in the experiments sulphatization time did not have very much effect on the metal recoveries. 30 minutes was sufficient for an optimum sulphatization time as seen in Table 19 and Figure 18.

Table 19 Effect of sulphatization time on the metal recovery.

Sulphatization time	**Metal recovery, %**		
minute	**Co**	**Ni**	**Fe**
15	86.57	82.16	16.70
30	86.23	79.32	12.46
45	89.03	81.04	13.33
60	87.49	80.27	12.07
90	85.38	76.59	13.82
120	87.42	81.44	12.36

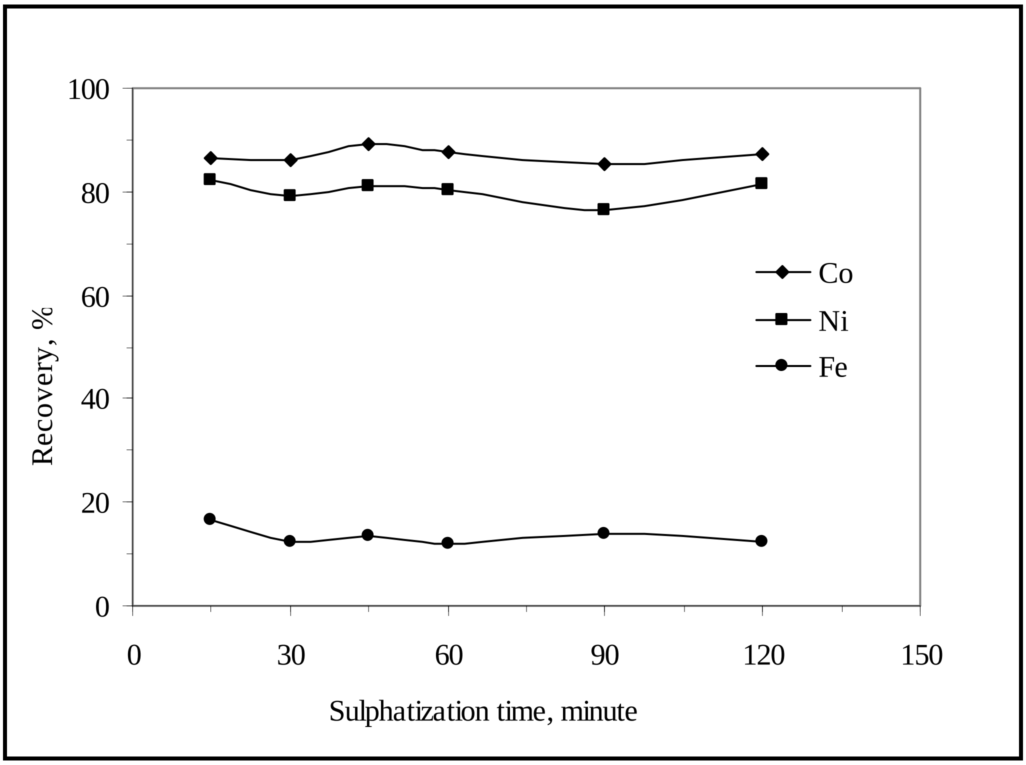


Figure 20 Effect of sulphatization time on the metal recovery.

4.2.4 Effect of Decomposition Time

The effect of decomposition time of sulphates on the leaching metal recoveries was investigated by varying the time from 15 to 75 minutes. During the tests the following parameters were kept constant: Acid strength: 30 wt % of ore; sulphatization temperature: 450^{o}C; sulphatization time; 30 minutes; decomposition temperature: 700^{o}C; leaching temperature: 70^{o}C; leaching time: 30 minutes. 45 minutes could be taken as the optimum by considering the cobalt and nickel recoveries which is shown in Table 20 and Figure 19. As it was observed that, increasing the decomposition time curved a decrease in the level of iron concentration. But at the same time increasing the decomposition time causes fluctuation in the recovery of nickel and cobalt.

Table 20 Effect of decomposition time on the metal recovery.

Decomposition time	**Metal recovery, %**		
minute	**Co**	**Ni**	**Fe**
15	83.89	73.23	6.71
30	85.33	75.01	3.97
45	89.00	79.35	1.32
60	87.17	74.38	1.10
75	87.97	74.54	0.65

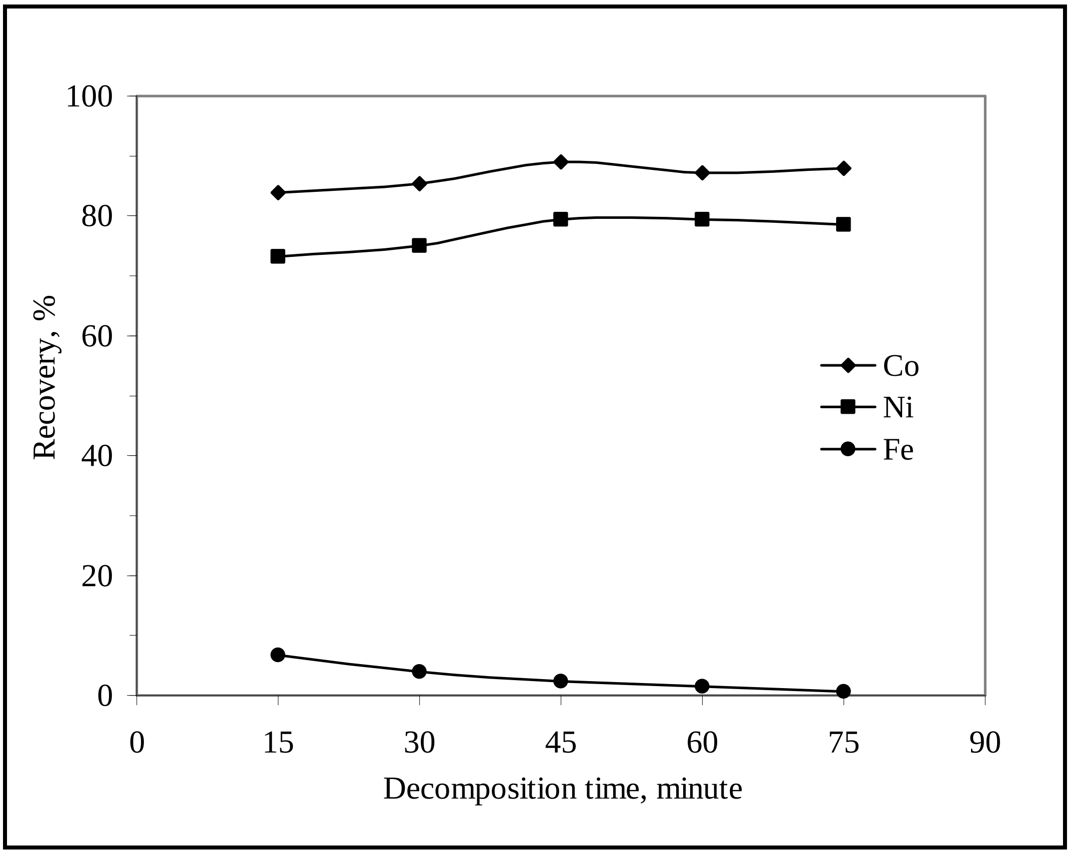


Figure 21 Effect of decomposition time on the metal recovery.

4.2.5 Effect of Decomposition Temperature

The effect of decomposition temperature of sulphates on the leaching metal recovery was investigated by varying the decomposition temperature between 550 to 850^{o}C. During the tests the following parameters were kept constant: Acid strength: 30 wt % of ore; sulphatization temperature: 450^{o}C; sulphatization time: 30 minutes; decomposition time:15 minutes; leaching temperature: 70^{o}C; leaching time: 30 minutes. As it was observed in the results of experiments the most effective parameter was temperature of decomposition, Table 21 and Figure 20. Increase in the temperature after 700^{o}C caused a substantial decrease in cobalt, nickel as well as iron recoveries. This implies that the temperature must not be greater than 700^{o}C.

Table 21 Effect of decomposition temperature on the metal recovery.

Decomposition temperature	**Metal recovery, %**		
^{o}C	**Co**	**Ni**	**Fe**
550	74.70	66.20	10.10
600	84.20	70.80	9.30
650	85.30	72.60	6.10
700	87.20	74.40	4.10
750	82.60	68.20	1.10
800	64.30	50.40	0.50
850	26.00	2.80	0.20

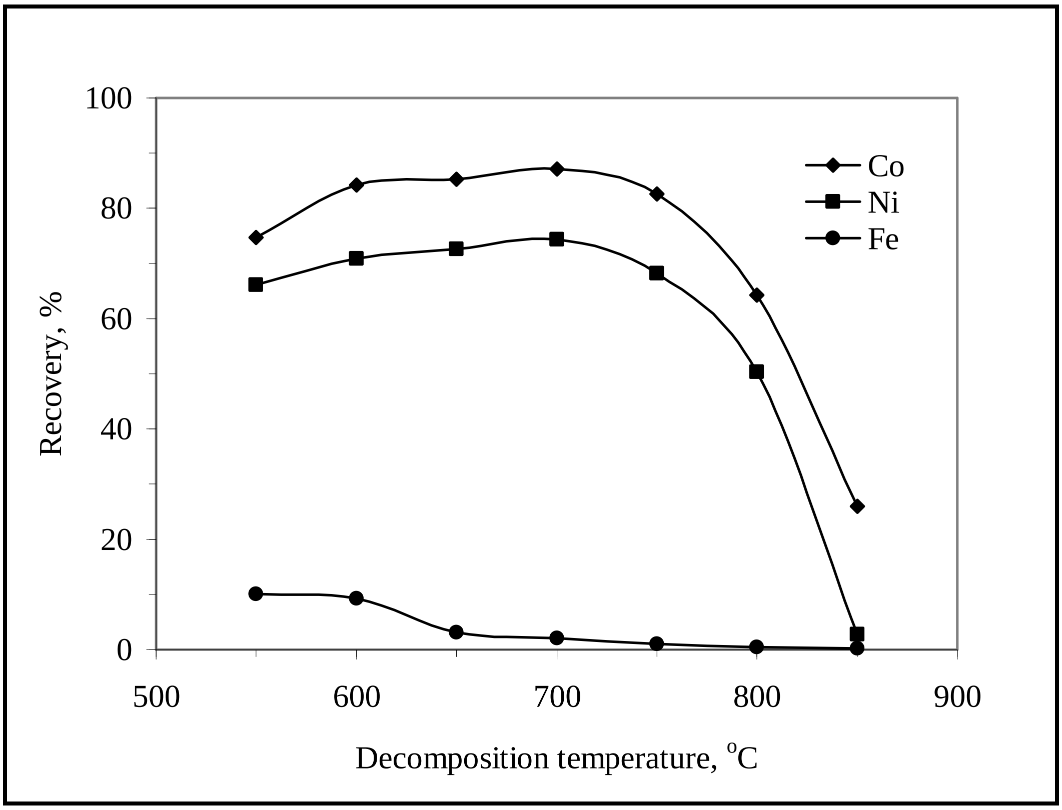


Figure 22 Effect of decomposition temperature on the metal recovery.

4.2.6 Effect of Leaching Time

The effect of leaching time was investigated by varying the time between 15 to 120 minutes. During the tests the following parameters were kept constant: Acid strength: 30 weight % of ore; sulphatization temperature: 450°C; sulphatization time: 60 minutes; decomposition temperature: 700°C; decomposition time: 15 minutes; leaching temperature: 70°C. Leaching recoveries of metals are given in Table 22 and Figure 21. The results indicated that the optimum leaching time was 30 minutes after which no further improvement in the recovery was observed.

Table 22 Effect of leaching time on the metal recovery.

Leaching time	**Metal recovery, %**		
minute	**Co**	**Ni**	**Fe**
15	80.55	74.15	2.05
30	86.65	79.05	2.62
45	86.36	79.08	2.10
60	86.36	79.68	3.36
90	87.01	79.77	3.25
120	85.94	80.38	3.24

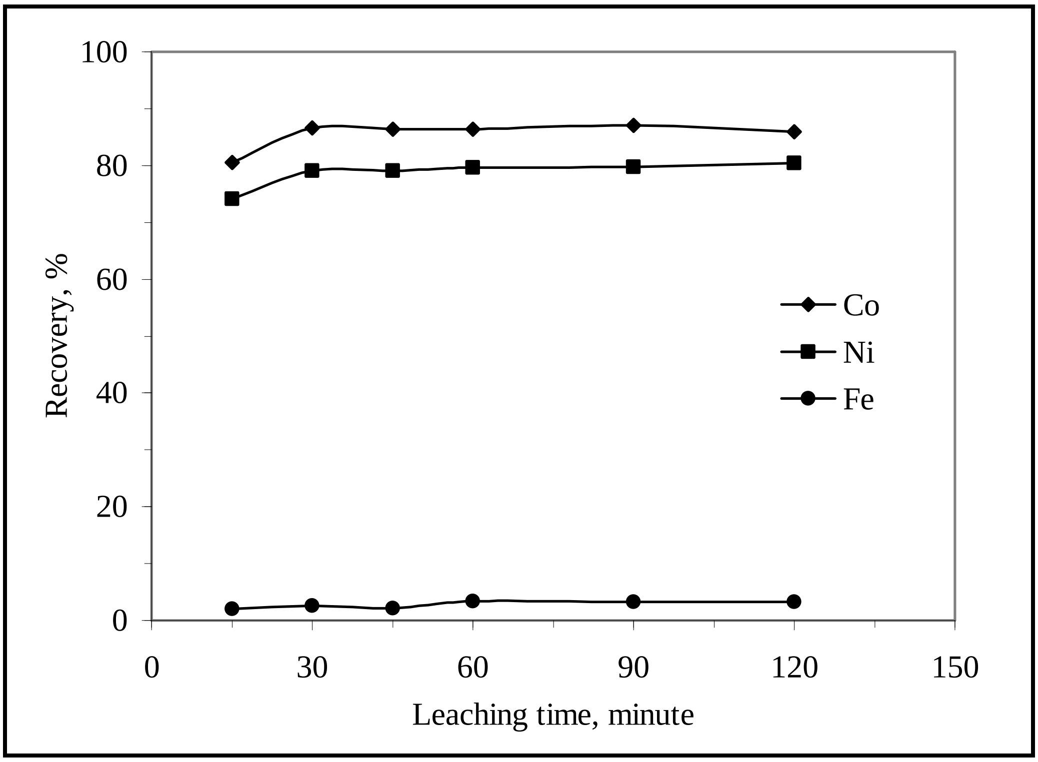


Figure 23 Effect of leaching time on the metal recovery.

4.2.7 Effect of Water Addition During Pugging

At the optimized conditions cobalt, nickel recoveries were suitable for the further treatment of solution. To increase the effect of sulphuric acid, water was added during pugging and as a result of water addition recovery of iron was decreased and recoveries of nickel and cobalt were increased (Kar and Swamy, 2000; Kar et al., 2000; Swamy et al., 2003).

For this purpose water (20 % dry weight of ore) was added. The other conditions during the experiments conducted were as follows: Sulphuric acid amount: 25 wt % of ore; moisture (water added): 20 wt % of ore; sulphatization temperature: 450°C; sulphatization time: 30 minutes; decomposition temperature: 700°C; decomposition time: 60 minutes; leaching temperature: 70°C; leaching time: 30 minutes were kept constant. The results showed that it is possible to increase recoveries of cobalt and nickel and decrease the iron by adding water during pugging as given in Table 23.

Table 23 Effect of water addition on the metal recovery.

	Metal recovery, %		
	Ni	**Co**	**Fe**
Metal in original sample	100	100	100
Recovery without moisture	78.80	87.50	3.20
Recovery with moisture	84.40	91.40	0.87

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

This study was designed to recover cobalt and nickel selectively against iron. For this reason two different methods were applied for the recovery of nickel and cobalt. The first one is the atmospheric pressure sulphuric acid leaching and the second one is a pug-roast-leach process with two stages roasting.

At atmospheric pressure for leaching the Çaldağ lateritic ore, the effect of various parameters, such as leaching time, leaching temperature, particle size, pulp density and acid strength on Ni and Co extraction were determined. By leaching at 80^{o}C for 40 wt % H_2SO_4 addition of ore, 1/3 pulp density, Ni and Co extractions were found 44.49 and 53.03 percent, respectively which yielded a pregnant solution containing 3.11 g/L Ni and 0.12 g/L Co.

The results of atmospheric pressure sulphuric acid leaching experiments were considered insufficient due to low cobalt and nickel recoveries and lack of selectivity of cobalt and nickel from iron.

In pug-roast-leach process, the determined parameters affecting the recovery of cobalt and nickel were investigated. Decomposition temperature and time of cobalt, nickel and iron; amount of sulphuric acid used for pugging were the most important parameters for this process. Other parameters such as leaching time, sulphatization temperature and time were minor effect on the process. It was also seen that addition of water increased the recovery of cobalt, nickel and decreased the recovery of iron.

In this process, amount of acid, sulphatization and decomposition temperature, sulphatization and decomposition time, leaching temperature and time, solid/liquid ratio, and the effect of water addition during pugging were optimized. Under the optimized conditions (sulphuric acid: 25 wt % of ore; moisture: 20 wt % of ore; sulphatization temperature: 450^{o}C; sulphatization time: 30 minutes; decomposition temperature: 700°C; decomposition time: 60 minutes; leaching temperature: 70°C; leaching time: 30 minutes and solid-liquid ratio: 1/4 by weight), Co and Ni extractions were found as 91.40 and 84.40 percent, respectively.

This study has shown that selective leaching of cobalt and nickel from iron was possible and a pregnant solution containing 3.084 g/L Ni and 0.185 g/L Co could be obtained.

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