HYDROMETALLURGICAL PROCESSING OF LATERITIC NICKEL

ORES

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# HYDROMETALLURGICAL PROCESSING OF LATERITIC NICKEL ORES

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# ABSTRACT

## HYDROMETALLURGICAL PROCESSING OF LATERITIC NICKEL ORES

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The objective of this thesis study is to recover nickel and cobalt at maximum efficiency from column leach liquor of lateritic nickel ores existing in Gördes region of Manisa by performing various hydrometallurgical methods under the optimum conditions. This column leach solution of nontronite type lateritic nickel ore was initially neutralized and purified from its basic impurities by a two stage iron removal process under the optimum conditions determined experimentally. Then, nickel and cobalt were precipitated in the form of mixed hydroxide precipitate from the purified leach solution by a two stage precipitation method called "MHP" and a manganese removal process was carried out also under the optimum conditions determined. By decreasing Mn concentration with this process to an acceptable level yielding at most 10% Mn in hydroxide precipitate, it was possible to produce a qualified MHP product suitable to the current marketing and standard conditions.

As a result of this thesis study, the experiments conducted showed that by recycle leaching with sulfuric acid about 81% of Ni and 63% of Co in the lateritic nickel ore (9.72 kg Ni / ton of ore and 0.28 kg Co / ton of ore) could be extracted as mixed hydroxide precipitate by MHP method. The MHP product contains 41.9% Ni, 1.0% Co, 2.3% Mn, 0.06% Al, 1.5% Mg, 0.02% Fe, 0.01% Cr, 0.25% Zn, 0.03% Cu and 4.73% S.

Keywords: Nickel, cobalt, nontronite, leach, MHP.

# ÖZ

## LATERİTİK NİKEL CEVHERLERİN HİDROMETALURJİK PROSES EDİLMESİ

Köse, Caner Hakkı

Yüksek Lisans, Metalurji ve Malzeme Mühendisliği Bölümü

Tez Yöneticisi: Prof. Dr. Yavuz A. Topkaya

Ağustos 2010, 178 sayfa

Bu tez çalışmasının amacı, Manisa'nın Gördes bölgesinde bulunan lateritik nikel cevherlerinin kolon liç çözeltisinden en uygun koşullarda çeşitli hidrometalurjik metotlar uygulayarak maksimum verimde nikel ve kobalt elde etmektir. Nontronit tipte lateritik nikel cevherinin bu kolon liç çözeltisi ilk başta nötrleştirilmiş ve iki aşamalı bir demir arıtma prosesi ile deneysel olarak belirlenen en uygun şartlarda ana kirletenlerinden arındırılmıştır. Daha sonra, yine belirlenen en uygun şartlarda nikel ve kobalt arıtılmış liç çözeltisinden karışık hidroksit çökelek şeklinde "MHP" denen iki aşamalı bir çöktürme metodu ile çöktürülmüş ve bir manganez arıtma prosesi gerçekleştirilmiştir. Bu prosesle Mn konsantrasyonu kabul edilebilir düzeye düşürüp hidroksit çökelekte en fazla %10 Mn sağlayarak, şu anki piyasaya ve standart koşullara uygun kaliteli bir MHP ürünü üretmek mümkün olmuştur.

Bu tez çalışmasının sonucu olarak, yürütülen deneyler sülfürik asitle olan yeniden kazanımlı liç ile lateritik nikel cevherindeki yaklaşık %81 Ni ve %63 Co'nun (9,72 kg Ni / ton cevher ve 0,28 kg Co / ton cevher) karışık hidroksit çökelek olarak MHP metodu ile elde edilebileceğini göstermiştir. MHP ürünü %41,9 Ni, %1,0 Co, %2,3 Mn, %0,06 Al, %1,5 Mg, %0,02 Fe, %0,01 Cr, %0,25 Zn, %0,03 Cu ve %4,73 S içerir.

Anahtar Kelimeler: Nikel, kobalt, nontronit, liç, MHP.

To My Family

# ACKNOWLEDGEMENTS

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# CHAPTER 1

## INTRODUCTION

Nickel has had a great importance throughout the history. Although Swedish scientist Cronstedt discovered nickel in 1751, the usages of nickel alloys had already been known for many years [1]. In the following century developments and a large variety of corrosion, heat resistant and magnetic alloys were discovered. Today, there is a large application of nickel in stainless and alloy steel production, chemical industry, electrical equipment and other fields which require a vast amount of nickel source.

Nickel-cobalt deposits are generally classified as sulfides, oxides, sulfosalts, and arsenides [2]. However, among them there are two principal types of nickel deposits that have taken more than 50 years experience to be processed for nickel and also cobalt contents: sulfide deposits and oxide or laterite deposits [3]. Nickel sulfide deposits mainly consist of pyrrhotite and pentlandite, with or without accompanying chalcopyrite, and closely associated with norite and peridotite whilst nickel laterite deposits occurring as weathering mantles that overlie peridotite; the nickel silicate variety, and serpentinite; the nickeliferous iron variety. The largest nickel sulfide deposits in the world are located in Scandinavia, the neighboring Kola Peninsula in Russia, Siberia and Canada in the Sudbury district, Ontario and in the Thompson district, Manitoba. Smaller deposits of this type are scattered

throughout Canada and the United States. On the other hand, most of the oxide nickel deposits, which are early major sources of nickel, are distributed in New Caledonia, Australia, Cuba, Brazil, Colombia, Greece, Philippines and Indonesia [4]. These nickel occurrences are explained in detail in the subsequent sections.

In the western part of Turkey there are low-grade lateritic nickel ores. They are generally found as limonitic laterites and, to a lesser extent, as nontronitic laterites. Extraction of nickel from these low-grade lateritic ores or those containing less than 2.0 wt% Ni has great importance by reason of the shortage of high-grade nickel sources [5] in the Earth. In addition to nickel, there is also cobalt, a valuable metal, which is present in lateritic layers of nickel ores.

Methods of recovering nickel together with cobalt from lateritic nickel ores are categorized as pyrometallurgical and hydrometallurgical methods. In pyrometallurgical methods ore is passed through certain processes at high temperatures; drying, calcination, roasting or reduction, smelting and converting whereas hydrometallurgical methods consist of atmospheric leaching (AL) and high pressure acid leaching (HPAL). There is also a process combining pyrometallurgical and hydrometallurgical methods which is called "Caron process".

After leaching process by hydrometallurgical methods a downstream processing of nickel laterite is required for nickel to be selectively recovered from the solution with cobalt and produced as intermediate products while certain elements such as iron and aluminum to be discarded. The main downstream nickel recovery processes from leach liquors are generally defined as mixed hydroxide precipitation (MHP), mixed sulfide precipitation (MSP), molecular recognition technology (MRT), ion exchange (IX) and resin-in-pulp method (RIP), and direct solvent extraction (DSX). Among

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them, MHP and MSP are commercially proven techniques. Although MSP has a greater history for winning nickel, today MHP has been taking an ascending interest for the extraction of nickel and cobalt from nickeliferous laterites because it has several advantages such as good production ability to achieve a readily saleable product and it requires moderate cost equipments as well as successful selective precipitation techniques used in purification and precipitation stages together to obtain nickel and cobalt as a concentrate of good economical quality.

The aim of this study was to recover nickel and cobalt as much as possible from the leach liquor of nontronite type lateritic ore which was sampled from Gördes in Manisa region of Turkey, while discarding impurities as much as possible under the optimum conditions by using effective hydrometallurgical methods. Iron purification, nickel and cobalt precipitation and manganese removal experiments were carried out by using the column leach solution, also called pregnant leach solution (PLS) that resulted from the sulfuric acid [$H_2SO_4$] column leaching of the Gördes nontronite ore. After completing the manganese removal experiments, magnesium removal process was also investigated but not studied due to excessive slaked lime consumption in the experiments which would yield an uneconomic process. Limestone [$CaCO_3$], magnesium oxide [$MgO$] and calcium hydroxide [$Ca(OH)_2$] were used as reactants in these experiments which were conducted at atmospheric pressure, varying pH, precipitation temperature and precipitation duration to find out the optimum conditions.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Nickel and Its Properties

Nickel is one of the main elements in the Earth's crust and for about a century it has been used commonly in the industries for the production of various alloys, metal plating and stainless steels. Boldt stated that nickel does not occur abundantly in the Earth's crust by the virtue of the fact that it ranks 24th element among the 90-odd elements in the order of abundance in the Earth's crust which contains about 0.008% nickel [4]. However, Alcock pointed out that in the overall surface to core composition of the Earth after iron, oxygen, magnesium, silicon and sulfur comprising more than 90% of the whole Earth, nickel is the 6th most abundant element by weight among the other elements that together found not only in the Earth's crust but in the whole Earth [6]. It composes probably as much as 3% whereas calcium, aluminum and cobalt are the following elements that may exist in amounts about 0.2 to 0.6%. The reason for the different nickel concentrations is that the interior sections of our globe are considerable richer in nickel than is the crust and below a depth of about 2900 kilometers the Earth's core consists of natural iron-nickel alloys as in metallic meteorites containing from about 5% to over 50% nickel [4].

Nickel is a white silvery metal with a lustrous appearance. It has a chemical symbol Ni with the atomic number of 28 and the atomic weight of 58.69

g/mol atom. Nickel is a face centered cubic element which confers perfect ductility. It is a very stable metal with a relatively high density and melting point of 8.908 g/cm$^3$ and 1453$^o$C, respectively. Its strength is considerable and its Mohs hardness is about 4.0. Nickel is also malleable; it can be easily shaped into very thin plates. It is a transition element in d block, 4$^{th}$ period and 10$^{th}$ group. The most common oxidation state of nickel is 2+ with various Ni compounds. It can easily form an adherent oxide film. It is one of the main ferromagnetic elements at room temperature. In the presence of a magnetic field nickel changes in length as it contracts. However, it occurs below its Curie point, 353$^o$C at which the change from ferromagnetism to paramagnetism takes place. It has also good conductivity of electricity and heat.

Nickel is highly corrosion resistant against air, atmospheric or sea water and non-oxidizing acids due to slowness of the oxidation reaction at these conditions at normal temperatures and pressures. For that reason, it has been used for centuries in coins, magnets, plating metals such as iron, brass and other corrosion sensitive metals, or certain alloys and chemical apparatus. It is readily deposited by electroplating. Nickel can form alloys both as solute and solvent and it is also one of the main constituents of super alloys and aerospace alloys. It increases strength, hardness, toughness and heat and corrosion resistance when it is alloyed with other elements based on the purity, temperature and the mechanical properties of the alloyed metal. Nickel indicates catalytic behavior in several important reactions including hydrogenation of vegetable oils, the formation of hydrocarbons and the production of fertilizers.

The most important ore minerals of nickel are limonite, nontronite, garnierite and pentlandite. Nickel is found in various forms when it substitutes for some specific elements in the certain complexes. For example, in olivine, which is a silicate of magnesium and iron, atoms of nickel may substitute for magnesium

or iron without distorting the lattice structure of the crystals and in goethite, which is an iron ore, nickel atoms usually substitute for iron atoms in the lattice structure by interstitial diffusion. Chemically, nickel is similar to iron and cobalt, as well as copper. Nickel is able to form several compounds such as sulfate, chloride, oxide and hydroxide and to react directly with carbon monoxide to produce a binary carbonyl complex that is volatile at room temperature.

## 2.2 Uses and Consumption of Nickel

Nickel is a very important element which has brought respected convenience to our lives for many years. Nickel-containing materials have made spectacular contributions to many aspects of modern technology for more than two centuries. Modern bathrooms typically have nickel plated handles and hinges, water faucets and shower heads. Razor blades comprise a small amount of nickel in electric shavers. Furthermore, kitchens are filled with nickel containing products. Pots, pans, stoves, electric stoves, their heating units, refrigerators, sinks are all made of alloys that contain some amount of nickel. By nickel and its alloys many applications become possible in buildings, infrastructure, communications, energy supply, engineering, automotive industry, transportation, chemical production, water treatment, environmental protection and so on. The uses of nickel for various sectors are illustrated in Figure 2.1. Nickel has long been used in many industrial and commercial products including mostly stainless steel, coins, rechargeable batteries, magnets, special alloys, jewelry and surgical wire, electrical guitar strings and so forth. The typical first and end uses of nickel for various applications are illustrated in Figure 2.2 and Figure 2.3. All these areas depend on nickel's unique combination of properties such as high ductility and strength, good thermal and electric conductivity and catalytic properties.
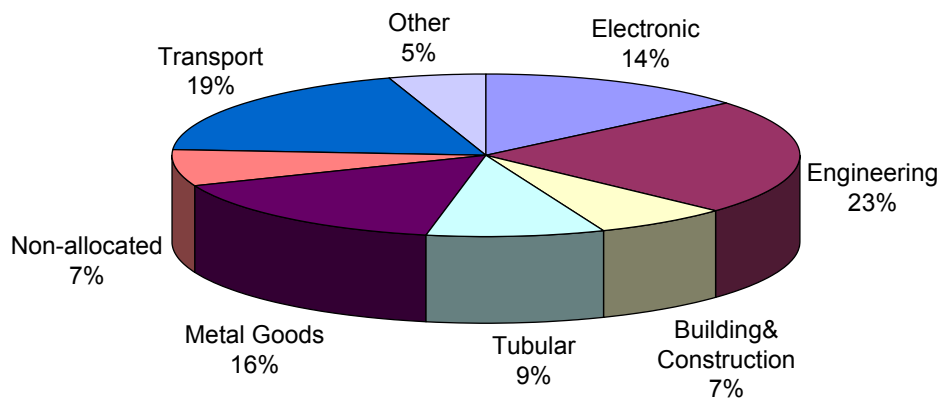
**Figure 2.1** Nickel use 2006 by sector (Pariser, 2007) [7].
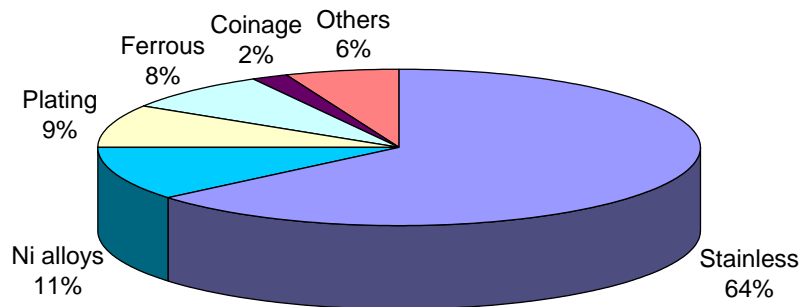
**Figure 2.2** First use of primary nickel in 2006 (Eramet Ni Research, INSG) [8].
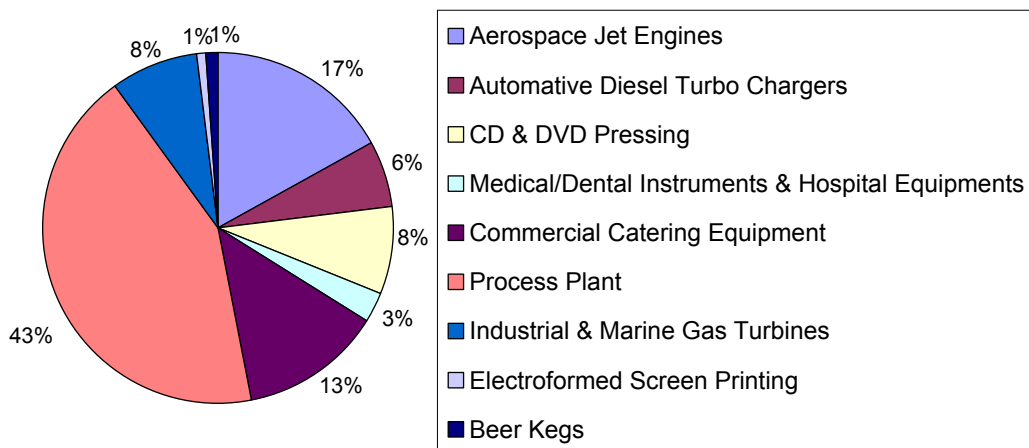
**Figure 2.3** Nickel *end use 2003 by (The Weinberg Group LLC, Inco) [9].

*End use critically depends on nickel, generally consists of nickel containing alloy that significantly transforms either the production process or the end product

Nickel's ability of resistance to corrosion is one of its major properties beneficiated in most of industries. Certain marine applications, oil, gas, power and chemical industries use duplex stainless steel which contains about 7% nickel because of severe environments endured. Copper-nickel alloys enhancing resistance to corrosion are especially used in marine environments. Cladding is an economical way of making a substance to resist to corrosion by using these high Ni alloys. Nickel is cladded on pipes, valves and similar parts provides long lasting use of equipments and protection. Furthermore, nickel and its alloys resist heat. Its unique structure and good alloying ability permit nickel to form a wide range of heat and creep resistant alloys that are necessary materials in the steel, chemical, energy, transport and aerospace industries. For a long time 80%Ni+20%Cr alloys have been produced as heating components [10].

Nickel plays an important role in power supply and electronic equipments. Up to date, nickel plates and nickel hydroxide have been used for several years in Ni-Cd rechargeable batteries. Nickel alloys are able to absorb large amounts of hydrogen which makes higher performance rechargeable nickel hydride batteries used in cordless power tools, portable computers and mobile electronic equipments. On the other hand, functions of electronic devices and electromagnetic circuits in computers and communication equipments rely mainly on the magnetic properties of nickel and its alloys. Coins, tokens, special symbols or emblems are easily identified in vending machines due to the electromagnetic response of the nickel alloys.

Recent developments have triggered the world markets to explore new nickel supplies because of its increasing use and contribution to stainless and alloy steel industries in which almost 80 percent of all nickel is used in the production. The market review of nickel between 1999 and 2009 is illustrated in Figure 2.4. Especially in 2007 nickel became a significant expensive source which hit almost 55000 US$/ton.
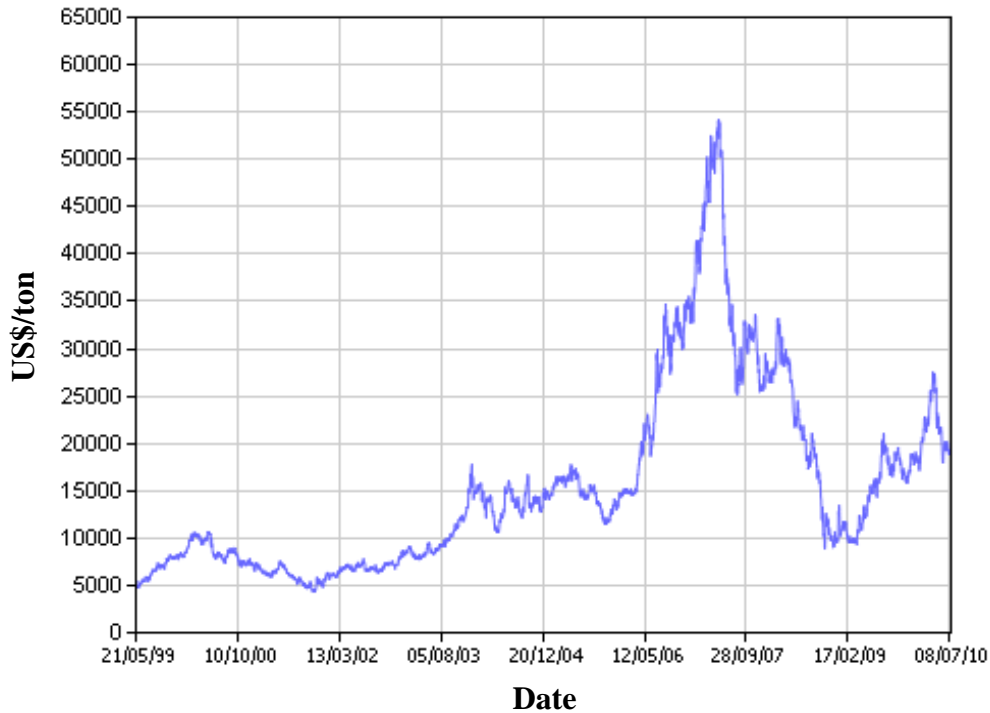
**Figure 2.4** Nickel prices between 1999 and 2010 [11].

Given its many essential uses and applications the decreasing nickel supply will not meet the required world nickel consumption in future. There is a gradual increase in global nickel usage more than production. Figure 2.5 shows primary nickel production and usage from 1990 to 2006 based on the International Nickel Study Group (INSG) statistics. It can be predicted that the world nickel production and the consumption will not be much different than each other, but there will always be a balance determined by the current economy at that year. In 1995 and 1999 there was a lack of nickel production whereas in 1992 nickel production was highly sufficient to meet all the nickel demands of the industries. According to the INSG study illustrated in Figure 2.6, the world primary nickel usage in 2008 was 1.39 million metric tons but in 2009 the global economic crisis broken out which resulted in reduced demand and nickel prices and the production of primary nickel dropped. Although the economy directly affects the nickel usage, in future there will be various new projects to contribute nickel stocks in order to satisfy increasing demands of world nickel.

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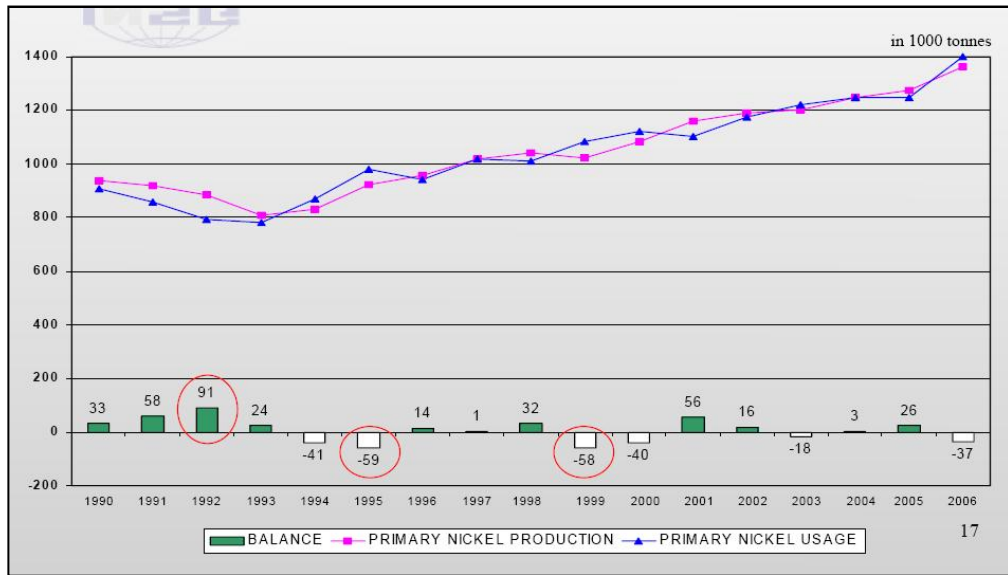
**Figure 2.5** World primary nickel balance 1990-2006 (INSG) [8].
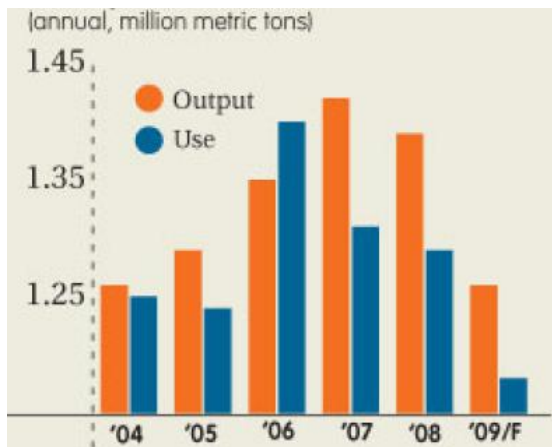


**Figure 2.6** World primary nickel production & consumption 2004-2009 (INSG) [12].

## 2.3 Origin of Nickel

Nickel occurs essentially as two types of ore deposits. The first are the lateritic ores in which the nickel is in oxide or silicate form. It is concentrated by rock weathering related to the condition of the erosion surface of the Earth.

The principal lateritic ores are nickeliferous limonite: $(Fe,Ni)O(OH).nH_2O$ and garnierite: $(Ni,Mg)_6Si_4O_{10}(OH)_8$. The second are the sulfide ores where nickel is associated with sulfur in various forms of nickel bearing minerals. They occur in the rocks at depths of many thousand meters below the existing surface of the Earth. In the sulfide ore deposits, nickel is found mainly as the mineral pentlandite: $(Ni,Fe)_9S_8$. The two ore types become different from each other in physical, mineralogical and chemical treatments of the deposit to extract nickel from them. There are other types of ore deposits of nickel such as arsenide, antimonide and arsenate but it is not economical to recover nickel from these ores.

Most of the nickel occurrence as it is stated before is concentrated in the Earth's core while the remaining nickel is scattered around the Earth's crust in various amounts. There is a relationship between nickel content and certain elements through the Earth's core. The higher the nickel contents the more iron-magnesium and the less silicon-aluminum the rocks contain. Table 2.1 shows that the average nickel content climbs up as the iron content increases and silica content of the igneous rocks decreases relatively [4].

**Table 2.1** Average nickel content as wt% for some rock types [4].

| Rock | Nickel | Iron Oxides Plus Magnesia | Silica Plus Magnesia |
|---|---|---|---|
| Peridotite | 0.20 | 43.3 | 45.9 |
| Gabbro | 0.016 | 16.6 | 66.1 |
| Diorite | 0.004 | 11.7 | 73.4 |
| Granite | 0.0002 | 4.4 | 78.7 |

## 2.4 Nickel and Associated Minerals

The Earth's crust is composed of many different types of minerals forming rocks. A large number of nickel bearing minerals are identified but relatively few are economically feasible to be extracted industrially. In these minerals nickel amounts always change because of substitution of one element for another but this change does not affect the ideal formula of the composition. Nickel substitutes essentially for iron (Fe) and magnesium (Mg) without distorting the lattice structure of rock forming structure depending on the type of mineralization. In certain minerals such as olivine, hypersthene, hornblende and biotite nickel is replaced with magnesium. A good chemical reason for the substitution of nickel for iron and magnesium is directly related to the similar diameters of the divalent ions of all three elements [4]. Table 2.2 shows the chief nickel bearing minerals found in nickel deposits with their chemical composition, nickel percentage and color [1, 4].

Pentlandite is the most common primary nickel sulfide mineral containing 25%-41% Ni [6]. It is very similar to pyrrhotite, iron sulfide, and almost invariably found in nature together with a large amount of pyrrhotite. Pyrrhotite, about 60% Fe and 40% S, is the most abundant sulfide mineral but it does not necessarily involve nickel since nickel may not be present in its composition. It has a formula written as $Fe_{n-1}S_n$. From place to place the values of n change and the composition varies from FeS to any $Fe_{n-1}S_n$. It generally carries some nickel in its crystal lattice by diffusion or substitution of nickel atoms and replacing some iron atoms making pyrrhotites nickeliferous in the diffusion site of the crystal [4]. The amount can be as high as 1.5% Ni [6]. Furthermore, it is mostly magnetic which makes ores susceptible to the magnetic ore prospecting and processing techniques.

Garnierite is the most common and abundant nickel carrier in laterite deposits in the world. In fact, it is classified as Ni-Mg hydrosilicates which generally

occur as a series of mixture that are commonly composed of two or more of the following minerals: serpentine, talc, sepiolite, smectite, chlorite, deweylite and saponite [4, 13]. Among these minerals nickel bearing clay minerals are serpentine [$(Mg,Fe,Ni)_3Si_2O_5(OH)_4$], smectite [$Na_{0.3}Al_2(Si_{3.7}Al_{0.3})O_{10}.(OH)_2$] and sepiolite [$(Mg,Ni)_4Si_6O_{15}(OH)_2.6H_2O$]. Garnierite also includes colloidal mixtures of silica and nickel hydroxide.

**Table 2.2** Nickel bearing minerals [1, 4].

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

Nickeliferous limonite is poorly crystalline to non-crystalline nickel bearing ferric oxide in laterite deposits produced from ultrabasic rocks [4]. Limonite name is also given as a zone which consists of an upper hematite rich section and a lower goethite rich section; both are rich in Fe, Al and Cr. Although limonite is an iron ore, its formula is written as (Fe,Ni)O.OH by the virtue of the fact that it usually contains valuable nickel amount. The nickel containing mineral in limonite is goethite and/or hematite, which are fine in particle size. Goethite [FeO.OH] is the primary constituent of nickel bearing limonite. Swampy noted that nickel generally exist in goethite in three modes based on the Schwertmann's X-Ray diffraction identification [14]. In first, it is associated with amorphous or poorly crystalline goethite, in second it is weakly adsorbed to the crystalline goethite surface and in third it becomes a substituent in the goethite structure. However, according to Trolard it is not the second case [15]. In nature goethite is associated with hematite, quartz and chromite. In nickeliferous limonite the nickel oxide is essentially in solid solution with the iron oxide and the amount of water changes with respect to its geophysical condition. Typical chemical composition of limonite involves 1.0-1.8% Ni, 0.05-0.3% Co, 35-50% Fe and 0.2-3.5% Mg.

Nontronite $[(Ca,Na,K)_{0.5}(Fe^{3+},Ni,Mg,Al)_4(Si,Al)_8O_{20}(OH)_4.nH_2O]$ is a greenish yellow ferric-iron nickel silicate hydroxide hydrate. It is a ferric iron containing member of the smectite group of clay minerals. Its name is also given to the intermediate zone between limonite and saprolite. Nontronite mineral zones are very common in tropical climates with prolonged dry seasons such as in Ivory Coast, the Western Australia, Cuba, Brazilian Shield, Greece and Turkey. Nickel content in the nontronite can be up to 4% whilst for the other smectite minerals, it is normally no more than 1.5%. Nontronite is usually found over serpentine rich saprolites and in practice it is difficult to distinguish nontronite from the saprolite but the latter contains more magnesium and coarse siliceous phases. Typical chemical composition of saprolite involves 1.2-3.5% Ni, 0.02-0.07% Co, 7-20% Fe and 10-20% Mg.

## 2.5 Nickel Ores

Nickel ores are essentially classified as sulfides and oxides according to their composition, abundance and extraction methods for nickel to be recovered economically.

### 2.5.1 Sulfide Nickel Ores

Although today sulfide nickel ores are not as an important source of nickel as oxide ores, approximately three-quarters of the world's supply are still obtained from sulfide ores. A sulfide nickel ore is a mixture of sulfide minerals with various worthless rock minerals associated. They contain 1-2% Ni usually with some Cu, Co and Fe sulfides, precious metals and also with undesirable minor constituents such as As, Te, Se, etc. In the sulfide ores, nickel is mainly found in pentlandite which accounts for nearly 90% of the nickel extracted from sulfide ores. It is associated with large amounts of pyrrhotite, commonly with some amount of chalcopyrite, $CuFeS_2$ and significant amounts of cobalt and precious metals such as gold and silver. So, they are suitable for upgrading by mineral dressing techniques to concentrates containing typically about 6-20% Cu-Ni.

### 2.5.2 Oxide (Lateritic) Nickel Ores

Oxide ores are the major sources of nickel. They are called "laterites" since almost all nickel oxides are contained in laterites. Laterite means 'brick' translated from the Latin and imparts hardening and highly resistant to weathering accompanied by significant addition of oxides [16]. About 72% world land based nickel resources exist in laterites [17]. Production of nickel from laterites has a great importance today. Easily mined sulfide deposits are not as much as in the past and the growing environmental concerns of processing these ores make laterite an increasingly important source of the

world's nickel and cobalt. Furthermore, increasing developments and improving technologies have been achieved in the methods of nickel extraction from laterites. Laterites are the future resource of world nickel and it is expected to raise over 50%, more than sulfide production, by 2012 [17].

Laterites contain about 1-3% Ni typically accompanied by some cobalt. They have nearly 30 to 45% $H_2O$ as moisture and are chemically bound in hydroxides. Unlike sulfides they have no fuel value. Sometimes, an upgrading by screening and magnetic separation can be necessary for laterites which usually contain boulders that may have no nickel value and typically surrounded by very fine, loosely adhering nickeliferous material [18]. These boulders may contain relatively high calcium oxide content, 18%, which has to be removed as much as possible to prepare a suitable sulfuric acid heap or agitation leaching feed which is further explained in Section 2.2.

Lateritic deposition is favored by warm conditions with abundant rainfall and occurs when rocks are exposed to the atmosphere at the Earth's surface for a long time, may be several centuries. It commences on peridotite which gradually decomposes magnesium, iron, nickel, cobalt and other constituents into solution with the help of the continued chemical and mechanical action of air, water, heat and cold. The nickel content present in the rock is accumulated into solution in the ground water and at greater depth concentrated in a zone to such a degree that the resulting deposits can be mined as a laterite nickel ore or be assessed as an abnormally high nickel belt of the deposit. The degree of concentration to result in a nickel ore is pleasing and satisfactory. The weathering process generally starts with peridotite containing 0.25% Ni and continues in lateritic soils then finishes in deeper zones of ultramafic rocks containing as much as 1.5% nickel ore, a promising grade for mining and metallurgical treatment [4].

In the first part of the weathering, a chemical reaction between ground water rich in carbon dioxide and the constituents of the igneous rock in some regions occurs. Olivine in these regions of the rock is consumed by carbon dioxide in water and decomposes magnesium and silica, most of nickel and cobalt into solution. During this naturally occurring process, these elements are leached and carried downward as iron is neutralized by reaction within soil and precipitates as iron oxide near the Earth's surface, then the residue left rich in iron with other minor constituents such as aluminum, chromium, manganese, also some nickel and cobalt. Through the core of the Earth, nickel and cobalt tend to precipitate as hydrous silicate in a zone or in cracks and fractures of the rock as the pH of the solution rises. These places in which nickel is higher in the precipitate than in the solution are important to prospect for a nickel ore. Then, magnesium becomes rich in the remaining solution when it flows deeper and accumulates in the bottom of the zone of weathering. This typical process can be followed from Figure 2.7. Lateritic formation causes various specific elements to accumulate and grade in different layers with respect to the physical and the chemical condition of the solution as it forms near the Earth's surface and becomes barren with very little amounts of elements at the end of weathering zone. As it is illustrated in Figure 2.7 these graded layers consist of an iron rich (hematitic) cap, a nickeliferous limonite layer and altered-unaltered peridotite layers. The nickel concentrations typically occur in one or more layers or in cracks within the profile and most strongly found close to the bottom of the zone of weathering. Complete separation of nickel, cobalt, iron or other elements into distinct zones are never realized.

Each classified type of minerals is variable based on the profile of the respected location. Figure 2.8 illustrates typical nickel laterite profiles published in the literature. The thicknesses of individual layers are highly variable and are influenced by faults extending upwards in the weathering

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profile. It is also distinctive that some profiles contain more nontronite and others more limonite.

| IDEALIZED LATERITE | APPROXIMATE ANALYSIS – % | | | | | EXTRACTIVE PROCEDURE |
|---|---|---|---|---|---|---|
| | NI | Co | Fe | $Cr_2O_3$ | MgO | |
| Hematitic Cap | < 0.8 | < 0.1 | > 50 | > 1 | < 0.5 | Overburden to Stockpile |
| Nickeliferous Limonite | 0.8 to 1.5 | 0.1 to 0.2 | 40 to 50 | 2 to 5 | 0.5 to 5 | Hydrometallurgy |
| Altered Peridotite | 1.5 to 1.8 | 0.02 to | 25 to 40 | 1 to | 5 to 15 | Hydrometallurgy or Pyrometallurgy |
| | 1.8 to 3 | 0.1 | 10 to 25 | 2 | 15 to 35 | Pyrometallurgy |
| Unaltered Peridotite | 0.25 | 0.01 to 0.02 | 5 | 0.2 to 1 | 35 to 45 | Left in Situ |

**Figure 2.7** Idealized section of a nickeliferous laterite formation [19].
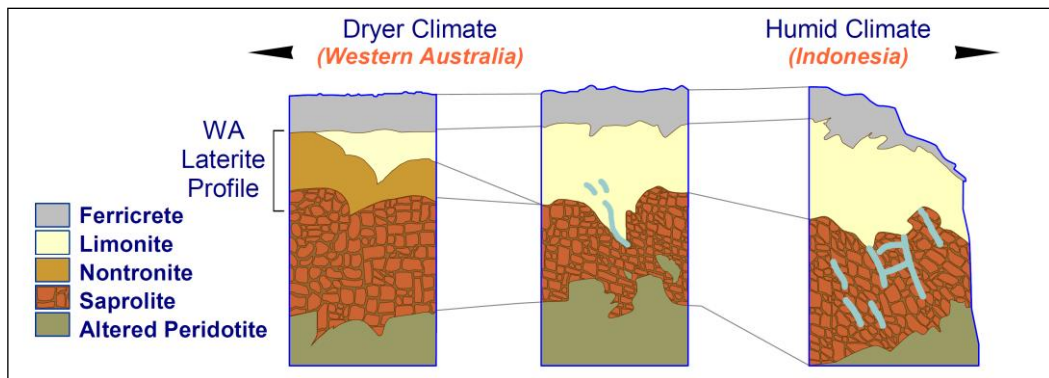


**Figure 2.8** Nickeliferous laterite profiles [17].

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## 2.6 Nickel Reserves

Increased growth in stainless steel sector and other industrial applications require vast nickel resources to meet the demand of economic development. This forces nickel to be extracted from deposits of nickel-bearing minerals found various land and ocean bases and deeper parts in the Earth's crust which were commercially unprofitable to be treated before, known as possible or probable ore bodies. Figure 2.9 illustrates typical locations of world nickel resources.

A large number of nickel bearing minerals have been identified but relatively few are abundant enough to be industrially profitable. Of these, commercially the most important nickel ores are sulfides and oxides (laterites). In addition, there are extensive resources of nickel associated with manganese and cobalt bearing sea nodules in large areas of ocean floors. Figure 2.9 shows the major areas of deep sea nodule accumulations.
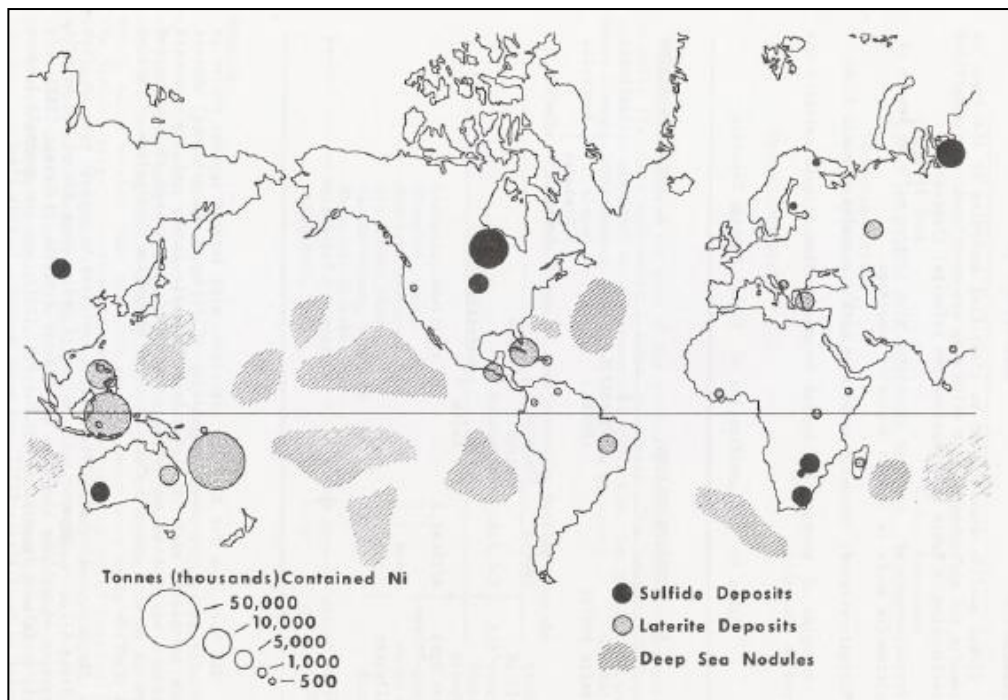
**Figure 2.9** World distributions of nickel resources [6].

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World reserves of nickel deposits containing an average grade of 0.97% are approximately 23 billion tons [20]. About 72% of total known nickel reserves, 12.6 billion tons, are oxide (lateritic) type of an average grade of 1.28% and about 28% of the world nickel reserves, 10.4 billion tons, are sulfide type of an average grade of 0.58%. The total contents of nickel metal in the world reserves are approximately 220 million tons; about 160 million tons belong to the lateritic type and about 60 million tons to the sulfide type. World reserves of nickel deposits are given in Table 2.3 [21].

**Table 2.3** World nickel reserves as contained nickel [21].

| Country | Proven Reserve (tons) | Possible Reserve (tons) |
|---|---|---|
| United States | - | 150,000 |
| Australia | 24,000,000 | 27,000,000 |
| Botswana | 490,000 | 920,000 |
| Brazil | 4,500,000 | 8,300,000 |
| Canada | 4,900,000 | 15,000,000 |
| China | 1,100,000 | 7,600,000 |
| Colombia | 830,000 | 1,100,000 |
| Cuba | 5,600,000 | 23,000,000 |
| Dominic Republic | 720,000 | 1,000,000 |
| Greece | 490,000 | 900,000 |
| Indonesia | 3,200,000 | 13,000,000 |
| New Caledonia | 7,100,000 | 15,000,000 |
| Philippines | 940,000 | 5,200,000 |
| Russia | 6,600,000 | 9,200,000 |
| South Africa | 3,700,000 | 12,000,000 |
| Venezuela | 560,000 | 630,000 |
| Zimbabwe | 15,000 | 260,000 |
| Other Countries | 2,100,000 | 5,900,000 |

In the case of both nickel sulfide and nickel laterite, six countries; Australia, New Caledonia, Russia, Cuba, Canada and Brazil account for 84% of the known world reserves. But, the world's largest nickel deposit is present at

Goro in New Caledonia owned by Vale-Inco with a production capacity of 54000 t Ni/year as nickel oxide [17]. Furthermore, the global resources of nickel in manganese nodules are estimated between 2 and 14 billion tons of contained nickel [6].

In Turkey the mineralization of both sulfide and lateritic type is found. The known principal nickel laterite reserves are in Eskişehir-Mihalıççık-Yunusemre, Manisa-Turgutlu-Çaldağ, Manisa-Gördes and Uşak-Banaz and sulfide reserves in Bitlis-Pancarlı, Bursa-Orhaneli-Yapköy and Sivas-Divriği-Gümüş [22]. Of these, Eskişehir-Mihalıççık-Yunusemre, Manisa-Gördes and Manisa-Çaldağ nickel laterite reserves have enough economic nickel value for the extraction and processing the ore unless the nickel prices climb up the limit by which the cut-off grade of the ore is determined. Turkey nickel reserves are given in Table 2.4 [22, 23].

**Table 2.4** Turkey nickel reserves, tons of ore [22, 23].

| Region | Proven Reserve | Probable Reserve | Possible Reserve |
|---|---|---|---|
| **Manisa - Çaldağ** | 33,000,000 | - | - |
| **Manisa - Gördes** | 32,000,000 | - | - |
| **Eskişehir-Yunusemre, Mihalıççık** | - | 86,625,000 | - |
| **Uşak-Banaz** | - | 11,601,500 | - |
| **Bursa - Yapköy** | - | 82,000 | 81,000 |
| **Bitlis - Pancarlı** | - | - | 15,500 |

World nickel mine production shows a typical trend. It increased gradually throughout the years parallel to the developments and innovations in the nickel extraction methods. World mine production for various countries from 2002 to 2006 is shown in Table 2.5 [24]. It reached 1,580 Mt in 2006 whereas it was 1,350 Mt in 2002. Since 1950, stainless steel production in the Western World has been growing at an average rate of 6.0% per year. It requires new

projects to be worked and new mines to be opened to extract more nickel in order to meet this growing steel industry production. Russia plays a significant role in global nickel production.

**Table 2.5** World nickel mine production, by country [24].

| Country | Capacity (tons of nickel produced) | | | | |
|---|---|---|---|---|---|
| | **2002** | **2003** | **2004** | **2005** | **2006** |
| **Australia** | 188,000 | 191,000 | 187,000 | 189,000 | 185,000 |
| **Botswana** | 28,600 | 38,230 | 35,163 | 39,305 | 38,000 |
| **Brazil** | 45,456 | 44,928 | 51,886 | 74,198 | 82,492 |
| **Burma** | 10 | 10 | 10 | 10 | 10 |
| **Canada** | 189,297 | 163,244 | 186,694 | 199,932 | 233,461 |
| **China** | 53,700 | 61,000 | 75,600 | 72,700 | 82,100 |
| **Colombia** | 58,196 | 70,844 | 75,032 | 89,031 | 94,105 |
| **Cuba** | 71,342 | 74,018 | 71,945 | 73,753 | 75,000 |
| **Dominic Republic** | 38,859 | 45,253 | 46,000 | 53,124 | 46,526 |
| **Finland** | 3,120 | 3,640 | 3,700 | 3,386 | 2,985 |
| **Greece** | 22,670 | 21,410 | 21,700 | 23,210 | 21,670 |
| **Indonesia** | 143,000 | 144,000 | 136,000 | 135,000 | 140,000 |
| **Kazakhstan** | -- | -- | -- | 193 | 200 |
| **Macedonia** | 5,149 | 5,555 | 5,300 | 8,100 | 10,900 |
| **Morocco** | 109 | 126 | 130 | 199 | 80 |
| **New Caledonia** | 99,841 | 112,013 | 119,199 | 111,939 | 102,986 |
| **Norway** | 2,052 | 169 | 181 | 342 | 362 |
| **Philippines** | 24,148 | 19,537 | 16,973 | 22,555 | 50,637 |
| **Russia** | 310,000 | 300,000 | 315,000 | 315,000 | 320,000 |
| **South Africa** | 38,546 | 40,842 | 39,851 | 42,392 | 41,599 |
| **Spain** | -- | -- | -- | 5,398 | 6,400 |
| **Turkey** | -- | 640 | 40 | 400 | 1350 |
| **Ukraine** | 2,000 | 2,000 | 2,000 | 6,000 | 12,000 |
| **Venezuela** | 18,600 | 20,700 | 20,468 | 20,000 | 20,000 |
| **Zimbabwe** | 8,092 | 9,517 | 9,776 | 8,556 | 8,825 |
| **World Wide Total** | 1,350,000 | 1,370,000 | 1,420,000 | 1,500,000 | 1,580,000 |

**2.7 Nickel Extraction Methods from Lateritic Nickel Ores**

The processing of lateritic nickel ore is quite difficult and they are not suited to most of the standard mineral extraction methods since the nickel content is finely disseminated in the ore bodies preventing physical concentration of nickel values by normal methods such as dressing. Hence, this renders the processing of laterites expensive and numerous means have been sought for many decades to reduce the costs of processing laterites. However, well established mineral processing techniques such as magnetic separation and flotation can be used for sulfide ores. It is possible to obtain a high percentage of the valuable minerals in a relatively small quantity of material and to discard the bulk of the waste with only a small loss of values. Today, either wet or dry screening is used to reject the oversize of lateritic ores, less weathered fragments containing nickel in small amount such as boulders of relatively high calcium oxide content. Although no standard methods exist for physically concentrating nickel in laterites, some efficient means can make it possible to collect a considerable amount of valuable nickel content of oxide ores. Up to now, the establishment of beneficiation techniques for laterite ores has long been needed. There are increasing amounts of practiced flow sheets to treat laterite nickel ores which are basically classified as pyrometallurgical and hydrometallurgical processes. Most of pyrometallurgical processes use traditional methods involving drying, calcining or/and reduction, roasting and electric furnace smelting whereas hydrometallurgical processes practice atmospheric pressure leach (AL), high pressure acid leach (HPAL) and Caron process as explained in detail in the following sections.

It is important to process a low grade nickel containing material rather than rich concentrate. Typical grades of laterite deposits are shown in Table 2.6 [25]. Most nickel mine output is the lower grade disseminated lateritic nickel ore that could not impart an economical value in the past. But, now low grade deposits can be treated economically and efficiently on account of the

availability of nickel extraction methods. Today, both pyrometallurgical and hydrometallurgical processes are applied commercially to the recovery of nickel and cobalt from lateritic nickel ores.

**Table 2.6** Elemental compositions (%) of some nickeliferous laterites with their extraction methods used in nickel producing industries [25].

| Place | Cawse | Moa Bay | Murrin Murrin | Bulong | New Caledonia |
|---|---|---|---|---|---|
| **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[1] | 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$_2$O** | Up to 10 | >20 | About 30 | Up to 35 | |

[1] Contains significant free silica

## 2.7.1 Pyrometallurgical Processes

Pyrometallurgy processes refer to a class of high temperature industrial processes by which nickel and cobalt are extracted from raw materials and refined to market specifications. Pyrometallurgical techniques usually care for utilizing nickel ores containing high magnesium content and relatively low iron content predominantly saprolitic type ores. High temperature requiring processes typically involve drying, calcination/reduction, roasting and smelting or electric furnace smelting. Pyrometallurgy generally produces a ferronickel metal (Fe-Ni) or nickel sulfide matte, which are further refined to recover pure metal. New developments in pyrometallurgy of nickel use new physicochemical studies. They are classified as below [26]:

- The top blown rotary converter process for conversion of nickel matte to metallic nickel
- The vacuum desulfurization process for removal of residual copper, cobalt, and iron from crude nickel mattes by selective chlorination
- The process for production of pure nickel, iron, and cobalt by formation of volatile carbonyls under high pressure (70 atm) and their separation by distillation and decomposition of carbonyls to metal
- The process for upgrading of nickel laterites and deep sea manganese nodules by solid state reduction or by segregation process.

The disadvantages of these processes include the requirement for higher grade ores, some metal losses to discarded slags, substantial energy for the process, sulfur ($SO_2$) disposition problems and poor cobalt recoveries which in turn leads to high production cost per ton of nickel produced. Pyrometallurgical processes are energy intensive because all of the water content of the ore has to be removed, all of the material has to be calcined and then melted in the process to form an appropriate slag at approximately $1600^{o}C$ [17]. Great amount of mass follows a high temperature flow sheet to the end of the process. Therefore, both hydrocarbon fuels; coal, oil, or naphtha and electric power are required. In addition, in order to form a more easily heated liquid slag which needs lower energy input compared to that for limonite ores at high temperatures, ore must contain predominantly saprolite or lower iron and higher magnesium content. In smelter, ores are smelted to produce either ferronickel or matte. It depends on the $SiO_2/MgO$ ratio or the basicity of the slag in the furnace. The slag composition in the range 1.8 to 2.2 $SiO_2/MgO$ ratio is amenable for production of mattes while high melting slags of $SiO_2/MgO$ ratio either <2 or >2.5 are better suited to produce ferronickel [17]. Slag melting point, viscosity and electrical conductivity are important parameters and controlled by iron, magnesia and silica contents in the smelter.

With respect to sulfide and oxide type, nickel ores are passed through various pyrometallurgical processes. Figure 2.10 shows typical pyrometallurgical processes for laterites and sulfide type nickel ores.
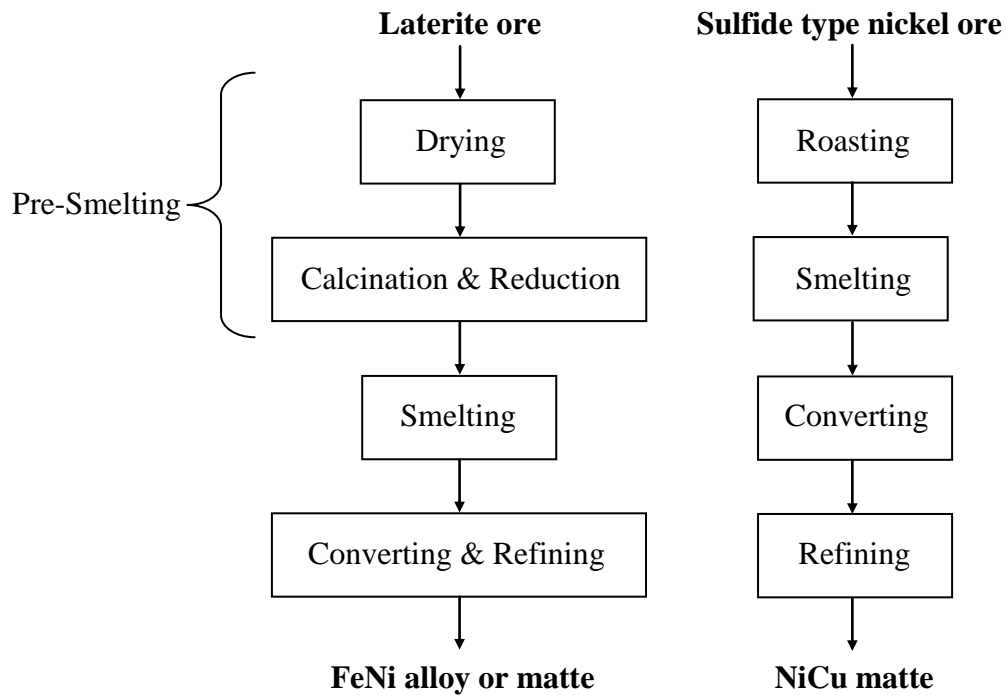


**Figure 2.10** Laterite and sulfide type nickel ores in nickel pyrometallurgy.

The pyrometallurgical processes of nickel sulfides are similar to that of copper sulfides. Iron and sulfur are eliminated by selective oxidation and fluxing. The primary product is a Ni-Cu matte with low Fe (0.5-3%) and certain S content (10-22%). A liquid nickel matte usually includes $Ni_3S_2$-FeS-$Cu_2S$, $Ni_3S_2$-$Cu_2S$ and $Ni_3S_2$-Ni [26]. Sulfur elimination from the concentrate before or during the smelting stage is important to control matte grade. It can be eliminated either by roasting or flash smelting. Capturing and fixing $SO_2$ gas is an environmental problem for the process. For this reason, sulfur input is minimized by eliminating as much of iron sulfides as possible before the pyrometallurgical stages. On the other hand, nickel oxides are upgraded by screening, passed through drying, calcination and reduction stages and sent to a smelter, become metal or matte product and slag is removed. In the kiln operation followed by electric furnace smelting generally

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a Fe-Ni alloy of about 35-40% Ni is produced [27]. Separation of nickel from refractory oxides is easier since there is a sufficient free energy difference formed between nickel oxide and gangue components during the process. But iron oxide is reduced while the reduction of nickel oxide. It means some iron always exists in matte [28]. For the design of the cost effective processes good separation of the ferronickel or matte from the gangue by smelting of all of the low graded ore and coping with great metallurgical and equipment obstacles, high water contents and high liquidus temperatures of slag and metal phases are significant. Sridhar and Bell found that the impurity elements could be discarded more selectively from mattes of low sulfur content (28-32% S) than from mattes of higher sulfur content (40-44% S) [29]. Depending on the suitability of the ore, availability and associated cost of consumables such as electric power and gaseous fuels, pyrometallurgical treatment of sulfide and/or laterite sources of nickel can provide an alternative to hydrometallurgical treatment. Ferronickel production is 19% of the annual new nickel output [27]. For profitable and favorable pyrometallurgical operation nickel content requires to be greater than about 2%, Fe/Ni ratio and moisture content to be low. Extensive energy requirement, off-gas treatment via acid plants for $SO_2$ fixation and impurity removal may affect the process followed. For completeness, other extraction processes may be practiced.

## 2.7.2 Hydrometallurgical Processes

Hydrometallurgical routes may become more appropriate and economical for the selected conditions when cost of energy rises and typical pyrometallurgical methods become economically marginal and unattractive to extract nickel from lateritic ores containing 0.95-1% nickel. Because treatment of oxide ores containing as high as 50% total water content and large amounts of high melting components requires substantial amounts of energy. Furthermore, direct application of the above pyrometallurgical methods to existing nickeliferous laterites can result in an undesirable process

because of the difficulty of melting the slag produced, poor metal-slag phase condition and $SO_2$ disposition problems. Combination or sequential treatments of laterites involving hydrometallurgical and pyrometallurgical routes can work out to extract nickel and cobalt from low grade nickel oxide ores in a more economical and efficient way. Caron process is a good example. It covers a variety of pyrometallurgical and leaching steps.

Hydrometallurgical processes propose direct solution of the nickel and cobalt values by sulfuric, hydrochloric or nitric acid leaching or organic/inorganic acid leaching. On the basis of the composition of a given laterite deposit, chemical and mineralogical distributions of oxides in the laterites, improved hydrometallurgical techniques increase selectivity of the methods over pyrometallurgical routes as the worldwide production of nickel derived from pyrometallurgical routes has been declining. Table 2.6 shows process types with respect to elemental composition of the resource. Depending on magnesia content and Ni/Fe ratio a hydro or pyrometallurgical extraction process is chosen [25]. Ni/Fe ratio of laterite deposits exposed to hydrometallurgical process is not as high as pyrometallurgical ones. Therefore, these advantages lead hydrometallurgical processes to become more applicable in mineral industry. Hydrometallurgical treatment of nickel laterites is mainly divided into 2 groups: Atmospheric leaching (AL) including heap leaching and agitation leaching and high pressure acid leaching (HPAL). It also includes Caron process but it is not a complete hydrometallurgical process to be counted in the group.

In recent years, heap leaching with diluted sulfuric acid at ambient temperature has been studied and developed by many groups to achieve the selectivity of nickel extraction over iron. Agatzini-Leonardou et al. has succeeded a complete hydrometallurgical process by heap leaching Greek laterites with diluted $H_2SO_4$ and subsequent purification and recovery steps as the laterites were limonitic and smectitic and contained significant amounts of

low reactivity hematite together with goethite [30]. When nickel laterites are predominantly of the limonitic type, low in magnesia and relatively high in iron, pressure acid leaching (HPAL) looks attractive by the virtue of the fact that it offers a recovery of 90% or more of both nickel and cobalt.

### 2.7.2.1 Caron Process

In Caron process nickel ore is dried, milled, calcined and selectively reduced at about 700-750$^o$C in a roaster to convert nickel and cobalt to their metallic form. In these appropriate conditions nickel and cobalt are favorably reduced to their metallic state whereas a small fraction of nickel bearing goethite is reduced leading to an alloy of Fe-Ni-Co and a largely unreduced gangue fraction. Next, the resulting product is selectively leached at low temperature, about 25-45$^o$C, atmospheric pressure and pH 10 with an ammonia-ammonium carbonate (ammoniacal) solution to dissolve nickel and cobalt as ammine complexes; Ni(II) and Co(II) ammines. Finally, ammonia is removed; nickel carbonate is precipitated to be calcined to produce nickel oxide [25]. In addition, cobalt is removed before nickel carbonate precipitation to produce pure nickel. It is separated from nickel either by solvent extraction or sulfide precipitation. In solvent extraction method the nickel ammine complex is extracted and cobalt remains in the raffinate by an organic reagent. Then, nickel is stripped with a higher concentrated ammonia solution from extraction solution. About 75-85% Ni and 45-55% Co are usually extracted depending on feed content [31]. Caron Process was first commercially tried for the extraction of nickel and cobalt in ammoniacal solution in 1942 at Nicaro, Cuba during the Second World War. It has several advantages. It is useful for treating high limonitic ores or ores containing more limonitic content. Ni/Co selectivity and a recyclable leaching reagent make process preferable. However, it is not suitable for ores containing high amount of saprolite since nickel and cobalt are stuck in a silicate matrix and are difficult to reduce at operated temperature [17]. Furthermore, calcination and reduction

steps need high energy and following hydrometallurgical steps require effective reagents. The recovery of nickel and especially cobalt is still lower than full scale pyrometallurgical and HPAL processes. Although Caron process has been limited because of these significant drawbacks, a lot of study has been carried out to eliminate these disadvantages. A typical flow sheet of Caron process is illustrated in Figure 2.11.

Laterite Ore

↓

Drying

↓

Milling

↓

Calcination & Reduction

↓

Ammoniacal Leaching

↓

Purification & Recovery

↓

Ni & Co
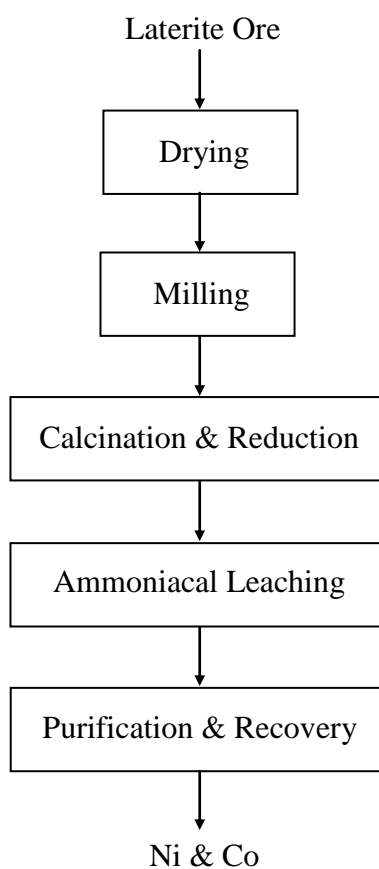
**Figure 2.11** Caron Process.

## 2.7.2.2 High Pressure Acid Leaching (HPAL)

A number of up-to-date hydrometallurgical processes have been being improved for extraction of nickel and cobalt from nickeliferous laterite ores. One of the most common and commercially used methods is high pressure

acid leaching (HPAL). It was first employed at Mao Bay in Cuba in 1959 and the following plants were constructed at Cawse, Bulong, Murrin Murrin and Ravensthrope in Western Australia and at Coral Bay in Philippines. Today, there are various HPAL projects which are developed now and planned to be operated in future: Goro (New Caledonia), Ambatovy (Madagascar), Vermelho (Brazil), Weda Bay (Indonesia), Ramu (Papua New Guinea), Gladstone (Australia), Syerston (Australia), Young (Australia), Mount Margaret (Australia), Nonoc (Philippines), Mindoro (Philippines), Fenix (Guatemala), Kalgoorlie (Australia) [32]. A typical HPAL process flow sheet is shown in Figure 2.12.
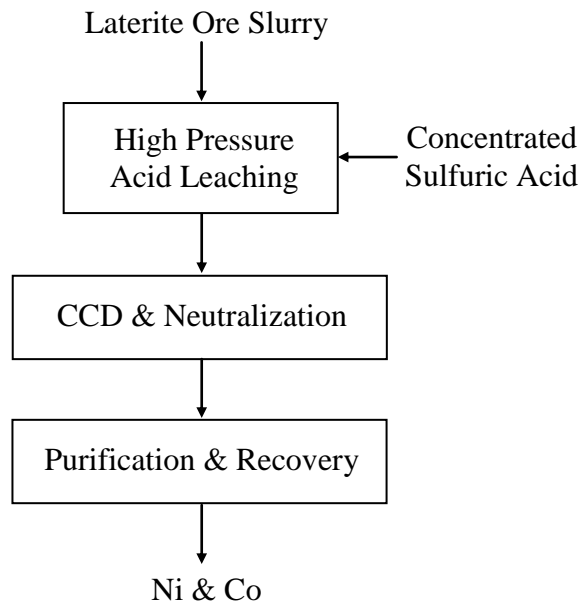


**Figure 2.12** HPAL process flow sheet.

Many of HPAL processes follow the dissolution of the metal values with sulfuric acid at high temperature (245-270$^o$C) and pressure (525-785 psig) in a titanium-clad autoclave followed by solid-liquid separation, neutralization of the excess acid and purification of PLS or direct solvent extraction up to recovery of dissolved nickel and cobalt at ambient conditions. Ore is slurried and thickened prior to feeding to autoclaves. Thickening involves generally about 40-45% solids depending on the hydrophilic nature of the ore present

and the rheology of laterite ore slurries. At 250$^o$C and 570 psi or 39 atm pressure in the autoclave the nickeliferous minerals in the ore are almost completely solubilized together with iron and aluminum. In literature, it has been studied that HPAL is most amenable for ores containing 40 wt% iron or greater. Below 40 wt% iron, lateritic ores start to consume higher amount of acid and therefore they lose their preference for direct HPAL. The dissolved iron is quickly precipitated as hematite or jarosite phase after passing goethite metastable phase depending on the leaching conditions and aluminum hydrolyses and precipitates as alunite phase at the high temperature and pressure of the autoclave. General reactions in HPAL are illustrated in Reactions 2.1 to 2.8 [33]:

$$(Fe,Ni)O.OH_{(s)} + (Mg,Ni)_2Si_2O_5(OH)_{4(s)} + H_2SO_{4(l)} \longrightarrow FeO.OH_{(s)} + NiSO_{4(aq)} + MgSO_{4(aq)} + SiO_{2(s)} + H_2O_{(l)} \tag{2.1}$$

$$NiO_{(s)} + 2H^+_{(aq)} \longrightarrow Ni^{2+}_{(aq)} + H_2O_{(l)} \tag{2.2}$$

$$CoO_{(s)} + 2H^+_{(aq)} \longrightarrow Co^{2+}_{(aq)} + H_2O_{(l)} \tag{2.3}$$

$$FeO.OH_{(s)} + 3H^+_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + 2H_2O_{(l)} \tag{2.4}$$

$$2Fe^{3+}_{(aq)} + 3H_2O_{(l)} \longrightarrow Fe_2O_{3(s)} + 6H^+_{(aq)} \tag{2.5}$$

$$6AlOOH_{(s)} + 9H_2SO_{4(s)} \longrightarrow 3Al_2(SO_4)_{3(aq)} + 12H_2O_{(l)} \tag{2.6}$$

$$Al_2(SO_4)_{3(aq)} + 14H_2O_{(l)} \longrightarrow 2(H_3O)Al_3(SO_4)_2(OH)_{6(s)} + 5H_2SO_{4(l)} \tag{2.7}$$

$$Al^{3+}_{(aq)} + SO_4^{2-}_{(aq)} + H_2O_{(l)} \longrightarrow AlOHSO_{4(s)} + H^+_{(aq)} \tag{2.8}$$
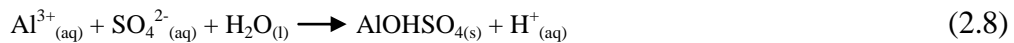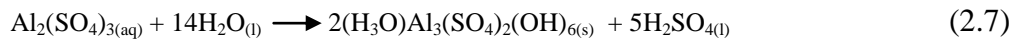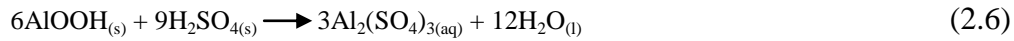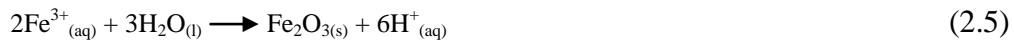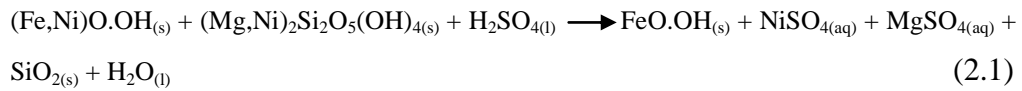
Hematite phase of iron causes scale formation inside the autoclave due to its large insolubility in acidic solutions at this temperature. Liu pointed out that

the solubility of the laterite minerals in sulfuric acid decreases in the following order: lizardite, goethite, maghemite, magnetite or hematite and chromite [34]. The insolubility of hematite also lowers the nickel recovery since nickel remains undissolved in the crystal structure of the hematite inside the autoclave. However, iron hydrolysis as whatever phase it precipitates regenerates acid and decreases the overall acid consumption of the HPAL method. Typical acid consumption of HPAL process is from about 250 to 350 kg $H_2SO_4$ per ton of dry lateritic ore. The residual free acid is typically in the range of 30-40 g/L. Then, the leach slurry is taken from the autoclave and the residual solids are separated from the leach liquor by counter current decantation (CCD). Next, the leach liquor is neutralized to discard ferric iron, aluminum and chromium (III) and the soluble nickel and cobalt are selectively recovered by subsequent processes. The nickel and cobalt present in the PLS are either precipitated as the sulfides by $H_2S$, carbonates or hydroxides by MgO or extracted directly by solvent extraction techniques. There is always a loss of nickel and cobalt value with the precipitation of solids on the leach products. However, this is usually less than 1% of the grade of the leached ore for both metals in continuous processes.

Nickel laterite ores with high MgO and Al content are not suitable for the direct use in the HPAL process since they increase the acid consumption of the HPAL process rendering an uneconomic extraction method. This is mainly resulted from increasing reagent cost needed to maintain an extra acid to overcome the negative effect of bisulfate ion ($HSO_4^-$) formation at high temperature. However, in high iron containing nickel laterites such as limonite it is not the case since high acid consumers, Al and Mg, are not present to cause a significant extra acid requirement during the HPAL. As in the literature there have been most of studies which followed an ore separation procedure depending on their magnesium and iron content. By separating laterite ore a low magnesium ore fraction and using in the HPAL process and neutralizing leach solution by the remaining high magnesium ore

fraction, the HPAL process becomes less acid consuming and higher nickel-cobalt extraction recovery is possible which makes the leaching more economical. The process of treating separated laterite ores instead of direct leaching is known as enhanced pressure acid leaching (EPAL). This was first accomplished by Queneau and Chou and patented in 1976 [35]. They combined the HPAL steps in which PLS from the HPAL process of low magnesium containing laterite, limonite, was neutralized by mixing at high temperature and pressure with PLS from the HPAL process of remaining high magnesium containing laterite, saprolite. However, this process has the drawback that it needs comparatively high pressure and temperature for the neutralization step. Similarly, Lowenhaupt has patented an EPAL method in which mixing of a low pressure leach of high magnesium ore with a HPAL of low magnesium ore occurred [36]. In the method iron and aluminum were precipitated as hematite and alunite after neutralization at greater than 1 atm and high temperature to achieve adequate nickel extraction and proper settling and filtration form.

A high extraction of nickel and cobalt is obtained by HPAL. Nickel is extracted at least about 90% and as high as 95% or more and cobalt is as much as 95% or more with about 5% to 10% iron extraction. It becomes more profitable and economical by the treatment of limonite ores in the HPAL. However, HPAL requires the use of titanium-lined or acid brick and lead-lined (Moa Bay Project) autoclaves, flash tanks, associated equipment and sophisticated materials of construction which imparts high investment and capital cost and the need of regular maintenance to withstand the corrosion, erosion and the abrasive effects of concentrated acid at high temperature and pressure, which also contributes the cost of the process. In HPAL scale formation is another problem to be considered by plant organizers. It can necessitate regular descaling or seed recycle during plant operation [37]. On the other hand, HPAL eliminates drying and calcination steps and yields to lower energy requirement and higher metal recovery within 1 or 2 hours in the

operated autoclave compared to Caron process. As it is stated, the most important drawback of the HPAL process is that it is restricted to treating largely limonite type ores since leaching saprolite or clay type ores raises sulfuric acid consumption which is the highest cost component in the HPAL process. In addition, increasing acid consumption means increasing lime consumption during the subsequent neutralization step. Up to 4% Mg has usually been accepted the limit for economically treatable ore in the HPAL [17]. Furthermore, the economical process also requires lower Al content due to Al contamination in subsequent recovery steps; MHP or ammonia re-leach steps. This is achieved by an addition of saline water containing sufficient sodium content. At Cawse, the use of saline bore water resulted in low aluminum extraction in PAL [37]. In a different manner, high acid consuming ore, saprolite, without passing the HPAL process or any leaching step is directly used in place of all or part of the limestone to neutralize residual leach acid in the discharge of an autoclave. Chou et al. in 1978 enhanced the neutralization capacity of high acid consuming ore by roasting below about 820$^{o}$C [38]. He pointed out better utilization of sulfuric acid and decrease in the consumption of limestone after the HPAL of limonite.

HPAL process has been continuing to be the most suitable direct nickel and cobalt extraction process from laterites after the grinders and crushers of run of mine since 1959. Excellent nickel and cobalt extractions were achieved rapidly from different type of Ambatovy deposits typically about 97% for both nickel and cobalt operating the autoclave at 36 hours of run time [39]. Recoveries up to 90% or more with leach times of between 1 and 2 days makes HPAL more favorable among the others for the treatment of nickel laterites up to date.

## 2.7.2.3 Atmospheric Pressure Acid Leaching

Atmospheric pressure acid leaching (AL) is principally grouped into in-situ leaching, heap or dump leaching and agitation leaching or vat leaching while atmospheric pressure leaching of laterites is carried out in one of the two distinct processes which are heap (or column) leaching and agitation leaching at atmospheric pressure and temperature up to $105^{\circ}$C either by organic or inorganic acids.

Heap leaching with diluted sulfuric acid is the process that simply includes piling raw ore into heaps varying in height (4-5m), passing a leaching solution from the top of the heap to the bottom while it percolates down and collecting effluent liquor, PLS, in a pond beneath the heap as necessary acid and water are added into the pond. Typical flow diagram of atmospheric heap leach of laterites from Çaldağ is shown in Figure 2.13. The collected PLS from Pond 3 is transported to a processing plant where the metal values are separated from the PLS and nickel and cobalt recovered. Heap leaching needs extensive leaching times over several months, perhaps years at ambient temperatures and compared to the HPAL and EPAL processes the poor selectivity of nickel over iron and magnesium becomes a problem for heap leaching processes. However, nickel recoveries of up to 85% were achieved in between 40 and 80 days with less than 50% iron in leach liquor by Agatzini-Leonardou et al. [30, 41].

Agitation leaching is performed either at atmospheric pressure or under pressure that the ore finely ground is leached by sulfuric acid in tanks where the solids are dispersed into the leaching solution by gas injection or mechanical agitation with a magnetic agitator. A flow diagram of agitation leaching is shown in Figure 2.14. A solid concentration of about 25-30% in both the limonite and saprolite slurries is most preferred [43]. In comparison with the other methods, agitation leaching time is lower due to the higher

specific surface area of the ore and the turbulence in the tank, which provides higher diffusion between reagent and ore. In addition, the leach reaction temperature is more effectively used in agitation leaching and it is usually carried out at the highest possible temperature up to $105^{o}C$ to accomplish rapid leaching and iron precipitation kinetics.
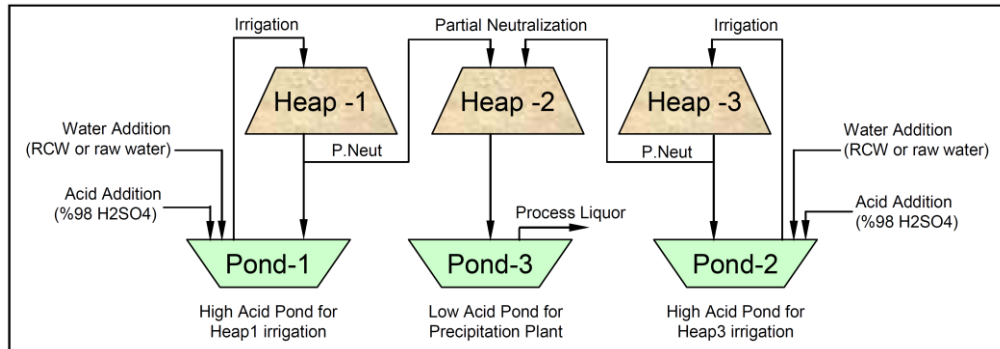


**Figure 2.13** Flow diagram of atmospheric heap leach of laterites with 98% sulfuric acid from Çaldağ [40].
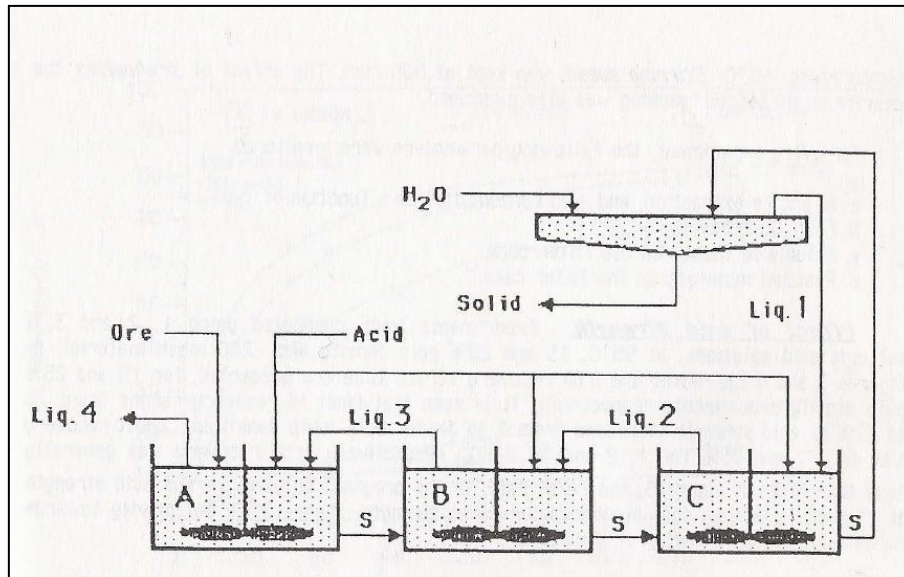


**Figure 2.14** Flow diagram of atmospheric agitation leach of laterites [42].

There are numerous laboratory works and pilot researches about nickel and cobalt extraction methods by agitation leaching of nickeliferous laterites with sulfuric acid at atmospheric conditions [44]. In 2008 an AL foundation was set in Ravensthorpe (Australia) belonging to BHP corporation for the saprolite

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ore containing higher than 6% magnesium while HPAL was built for the limonite ore having less than 6% magnesium [45]. Atmospheric leaching at lower temperature does not need expensive HPAL autoclaves as well as it is able to extract significant nickel and cobalt in AL. Generally, cobalt extraction is significantly less than that of nickel. It can result in 93 and 91% nickel and cobalt recoveries, respectively as in Taylor and Cairns test work for the Bulong project operated at 90-95$^o$C and 3 hours [46]. According to Curlook's agitation leach tests with highly serpentinized samples, at 80-100$^o$C, at pulp densities of 15-33% and acid addition of 800-1000 kg/t dry ore, more than 90% extractions of nickel were obtained within one hour [44]. However, AL is not selective over iron and almost all the iron is leached together with other metals from the solids, which yields a high acid consumption and it requires a significant initial acid addition such as 1000 kg/t ore by the virtue of the fact that the iron sulfates do not hydrolyze at low temperature. This can be seen in the heap leaching of the Çaldağ deposit from which 79.4% of Ni, 82.7% of Co, 30.0% of Fe, 78.9% of Mn and 37.1% of Al in solution were extracted [40]. In addition, at lower temperatures compared to HPAL, a longer time is required to achieve similar extractions as well as the more acid to ore ratio requirement. However, multi stage counter current leaching of serpentinitic laterites can reduce the acid consumption down to about 500-600 kg/t ore without affecting nickel and cobalt recoveries. Meanwhile, the significant concentrations of soluble iron, manganese, chromium, aluminum and arsenic which are likely to be found in PLS after AL results in further difficulties in the subsequent purification and recovery steps. They must be rejected selectively from PLS prior to the recovery steps or nickel and cobalt must be selectively extracted from PLS. These processes are explained in detail in the following sections.

In AL, iron is generally precipitated as goethite or another low sulfate containing form of iron oxide or iron hydroxide while it is hematite in HPAL. However, it converts to jarosite in the presence of sodium, alkaline metal and

ammonium ion content. General reactions in AL when goethite is formed are illustrated in Reactions 2.1, 2.2 and 2.3 while jarosite is precipitated in Reaction 2.9 [43].

$$Na^+_{(aq)} + (Fe,Ni)O.OH_{(s)} + (Mg,Ni)_2Si_2O_5(OH)_{4(s)} + H_2SO_{4(l)} \longrightarrow NaFe_3(SO_4)_2(OH)_{6(s)} +$$
$$NiSO_{4(aq)} + MgSO_{4(aq)} + SiO_{2(s)} + H_2O_{(l)} \tag{2.9}$$
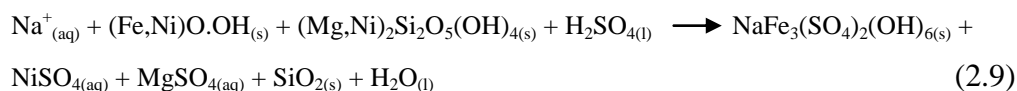
Jarosite is an unstable product and presence of jarosite in tailings potentially causes an environmental problem. Metals which are precipitated with the jarosite residues can dissolve into the soil and water attributed to the acid regeneration of the reverse Reaction 2.9 although it occurs in a slow process. Jarosite residue in waste stream is not environmentally acceptable. Nonetheless, jarosite residues offer substantial values as fertilizer and assist solid/liquid separation of the AL process. Arroyo et al. reported that crystallinity of ammonium jarosite makes hydroxides, which are produced at AL, easier to filter and settle thus resulting in less equipment for effective separation while obtaining maximum metal recovery [47]. On the other hand, forming jarosite rather than goethite decreases acid utilization because jarosite formation leads to the loss of 0.5 mol $H_2SO_4$ per mole of iron compared to the removal of iron in the goethite form. The removals of iron as jarosite and goethite are illustrated in Reactions 2.10 to 2.11, respectively [48]. 1 mol acid is produced per mole of iron precipitated in the jarosite formation whereas 1.5 mol acid is produced in the goethite formation.

$$0.5Na_2(SO_4)_{(aq)} + 1.5Fe_2(SO_4)_{3(aq)} + 6H_2O_{(l)} \longrightarrow NaFe_3(SO_4)_2(OH)_{6(s)} + 3H_2SO_{4(l)} \tag{2.10}$$

$$0.5Fe_2(SO_4)_{3(aq)} + 2H_2O_{(l)} \longrightarrow FeO(OH)_{(s)} + 1.5H_2SO_{4(l)} \tag{2.11}$$
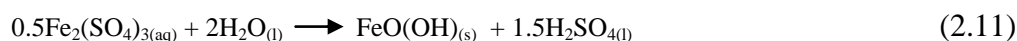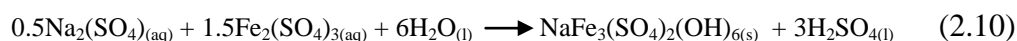
As in the case of the HPAL process, saprolitic fraction of the ore can be separated from the ore and leached at atmospheric condition in a different place in order to improve the recovery of nickel and cobalt and to minimize

the acid consumption. Then, limonite fraction of the ore is used in sulfuric acid pressure leaching which yields substantial extraction of the valuable metals as it is explained in the previous section.

Sometimes, lateritic ores that have a substantial clay component need to be pre-concentrated, pelletized or agglomerated prior to leaching on account of poor percolation rate during the heap or column leaching process. Heap permeability is critical. However, ore preparation and solid-liquid separation are cost intensive areas of agitation leaching process and they become more important for nickel bearing goethites. Duyvesteyn et al. reported that the permeability of lateritic ore is largely controlled by the type of mineral occurrence, mineral morphology and particle size [49]. In his previous patent with Liu, it is pointed out that clay type saprolite indicated poor permeability during filtration and he solved this problem by ore pre-treatment including ore selection, size reduction and pelletization of the ore. In addition, Canterford [50, 51] and Griffin et al. [52] reported that nickel is more readily extracted from clay-like silicate ores such as smectite, nontronite or saprolite than limonitic ores such as goethite ores. Figure 2.15 shows Canterford's analysis on the nickel extraction as a function of sample iron content after 3M HCl leaching [50]. Similar case was observed for sulfuric acid leaching but less extraction recovery obtained. The lower iron content range leads to higher amounts of nickel extracted. The reason of low extraction with high iron content is related to the crystal structure and the acidity. The nickel in the goethite cannot be sufficiently extracted as the acidity during the leach step is not strong enough to break down the goethite structure.

Canterford also reported that particle size of the ore subjected to AL is crucial to improve the extraction of nickel and cobalt depending on the content of the ore. The amount of nickel and iron extracted can climb up by reducing the particle size of the goethite sample whereas it marginally increases the amount of nickel extracted from the silica and serpentine samples. Unless

conditions are sufficiently corrosive to give rise to decomposition to silica, the structure of the clay does not change noticeably to affect the extraction; on the contrary, grinding can be detrimental to downstream processing due to improper settling conditions. Fine size usually enhances the leaching kinetics and increases the liberation of nickel containing minerals to the solution. However, nickel can be stuck or re-adsorbed by re-precipitated amorphous silica while leaching minerals containing significant amounts of silica. O'Neill pointed out that coarser silicate ore brought about slightly lower nickel extraction while the settling properties of the residue was better than that from finely ground ore [53].
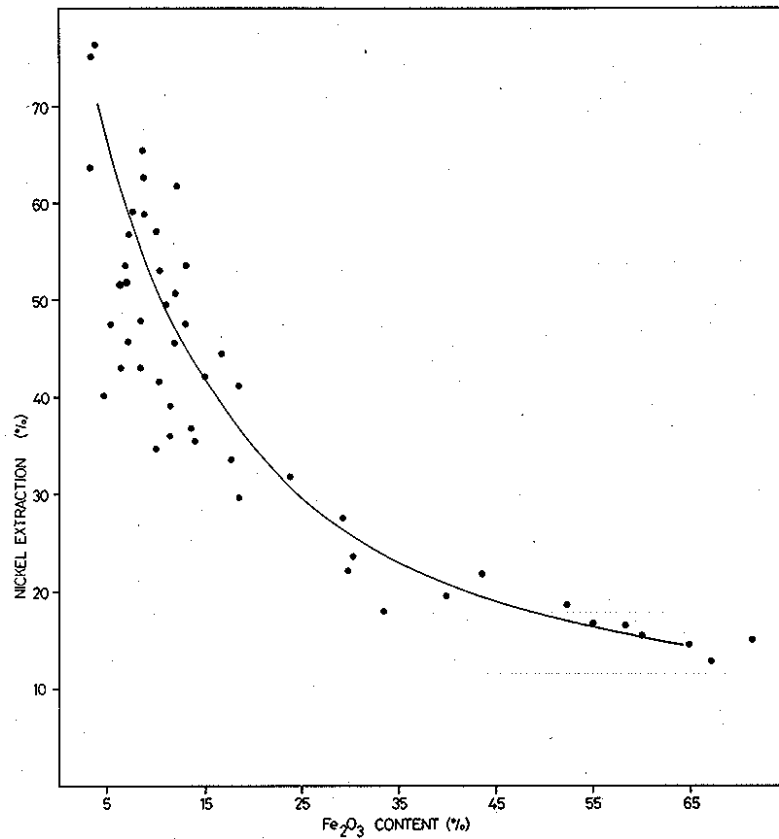


**Figure 2.15** Nickel extractions (%) as a function of sample iron content by 3M HCl leaching [50].

Atmospheric leaching of lateritic nickel ores generally takes advantage of reductants to improve Co recovery, thus to increase overall benefit of the process. Addition of sodium metabisulphite ($Na_2S_2O_5$) into process water with

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sulfuric acid used for leaching steps has a significant effect on cobalt recovery. Purkiss has found out that the addition of 5 g/L sodium metabisulphite into 75 g/L leach solution led to fast leaching of cobalt [54]. Cobalt is usually associated with limonite layer and predominantly found together with manganese minerals: Mn(III) and Mn(IV) containing oxides and hydroxides generally called asbolane and manganese nodules. In order to dissolve Co into solution, it is required to reduce $MnO_2$ to a soluble divalent salt in acidic medium by passing $SO_2$ or $NO_2$ into the feed slurry of laterite containing manganese minerals. By controlling the redox potential to preferably between 700 and 900 mV cobalt recovery is improved as well as ferrous ion formation minimized and chromate formation eliminated [37, 43]. It has been found by Canterford that the solubilisation of Mn and Co is parallel to each other (Mn is a bit more) but both are extracted at a greater rate than Ni [55]. In addition to improving cobalt recovery, decreasing redox potential also accelerates AL of lateritic ores. Senanayake and Das have reported that when the redox potential was decreased from an Eh value of 840 to 560 mV by adding $SO_2$ through PLS at 90$^o$C the nickel and iron extracted from the limonite ore after 6h were increased from about 40% to 85% [56].

Roasting of laterites in air or gas mixtures of $H_2$, CO and $CO_2$ can be beneficial to AL of lateritic nickel ores. McDonald and Whittington have reported various studies about roasting of laterites prior to AL [45]. Kontopoulos [57], Sukla and Das [58, 59] noted that for saprolitic ores roasting in air to convert goethite to hematite improves the reactivity and neutralization capacity of serpentine minerals as it is discussed in the previous section. Yorio et al. [60] also reported selectivity for nickel and cobalt over iron during column leaching could be possible by ore roasting. However, according to Canterford [51] and Panagiotopoulus et al. [61] it can promote a detrimental effect on nickel recovery and it is only beneficial if the temperature, ore/reductant molar ratio and reducing potential are carefully controlled. One of the main problems of roasting or pre-reduction steps

concerning the subsequent steps is a significant amount of the leached iron exists in the ferrous state in which iron does not precipitate in lower pH as in the ferric state and results in an iron separation problem before the metal recovery in downstream processes.

AL with organic acid or mineral acid including micro organism metabolites needs further attention and there are not many studies about them. Citric acid has been proved by many studies to be the most effective organic acid for nickel extraction from serpentinitic ores or Greek limonite ores in which iron oxides are less than other nickel containing minerals [62]. McDonald and Whittington have summarized several important studies on organic acid leaching [62]. Bosecker [63, 64] reported that limonitic ores are not leached notably by organic acids while Valix et al. [65] founded that citric acid is less effective in dissolving goethite. In addition, Chander classified a number of mineral acids with respect to their extraction strengths, increasing in the following order: percholoric, nitric, sulfuric, hydrochloric and oxalic [66].

Biological leaching also occurs at AL conditions and can be beneficiated with the help of fungus or bacterium triggering spontaneous leaching reactions. It has been observed by Bosecker [63] and Valix et al. [67] that at the same acid concentration biological leaching appears to be more effective than chemical leaching because the fungus or bacterium do not only attack the ore but also participate in the leaching process.

## 2.8 Nickel Extraction Methods for Nickel Laterite Leach Liquors

Nickel extraction methods from PLS of nickel laterites are growing worldwide interest and compatible nickel extraction flow sheets and increasing downstream processing techniques for nickel laterite heap leach liquors or HPAL liquors make possible to achieve high recovery of nickel with cobalt and the quality of desired intermediate product at an acceptable

cost. No matter how acid leaching is applied to a nickel laterite from which PLS collected has to be processed by downstream operations such as excess acid neutralization, iron precipitation, nickel-cobalt separation or precipitations and final product recovery in order to succeed in a saleable intermediate product or nickel-cobalt cathodes.

Until today, many groups have assessed the amenability of their ores to heap leaching or HPAL and adapted various downstream nickel recovery processes based on the ore conditions; location, type, tenor, mineralogy, etc. Various factors such as high nickel and cobalt prices, increasing demand for nickel metal and low sulfur and $H_2SO_4$ prices have encouraged the development of new projects for processing nickel laterites. Most of substantial refinement of process methods has been done for the development of nickel recovery from HPAL discharged liquors but not as many for heap leach liquors. Direct solvent extraction (DSX) has been adopted for nickel-cobalt separation by some of the existing and the majority of the proposed sulfuric acid laterite projects [68]. At the Bulong and the Goro circuits, clarified PLS has been used in the DSX process. In downstream processes existence of soluble iron, manganese, aluminum, chromium and magnesium in PLS always cause a number of challenges and obstacles which have been tried up to now to be diminished and overcome by the various studies. Mixed hydroxide precipitation (MHP) and mixed sulfide precipitation (MSP) are compatible recovery techniques which face these difficulties to provide appropriate nickel-cobalt precipitation. MSP is the older nickel recovery method which has already been used commercially at Moa Bay while pilot plant tests using MHP started at Hazen Research in Colorado in April 1996 [37]. In MHP nickel and cobalt are recovered from the PLS through the addition of calcined magnesia after the purification stage or stages whereas in MSP nickel and cobalt are precipitated as mixed sulfide precipitates by reaction with hydrogen sulfide gas after partial neutralization stages or pre-reduction steps. Rather than using these recovery methods, various laterite projects propose the use of

ion exchange method (IX) to separate nickel and cobalt with the help of resin-in-solution (RIS) and resin-in-pulp technologies (RIP). Although there is an increasing amount of patent applications about RIS and RIP, these technologies are not commercially applied as primary means of nickel-cobalt extraction but used in a number of other industries. The reason is that it becomes risky to use IX as a primary extraction process for nickel laterite leach liquors because IX processes are unprecedented commercial applications and no fundamental reasons why these technologies can be used in nickel laterite flow sheets as a major step [68].

Heap leach liquors from AL, used as feed of downstream processes, are solids-free solution at ambient temperature containing typically 2-4 g/L Ni, 30-50 g/L $H_2SO_4$, 15-30 g/L Fe and 2-5 g/L Al while HPAL produces a hot slurry composed of 20-25% solids and a PLS containing typically 4-6 g/L Ni, 40-60 g/L $H_2SO_4$, <8 g/L Fe and <3 g/L Al [69]. Although MHP is one of the major downstream processes for obtaining nickel and cobalt from HPAL liquor of nickel laterite ores, there is no certain rule to obtain particularly favored intermediate products over others from PLS of nickel laterites by downstream recovery methods. Mixed hydroxides, mixed sulfides and mixed carbonates of nickel and cobalt can be produced before metallic production. Sulfides are suitable for smelting and hydrometallurgical refining while minimizing co-precipitation of certain impurities such as iron, aluminum and manganese. Hydroxides and carbonates are mostly suitable for hydrometallurgical refining including either ammoniacal or acid leaching to resolubilize the nickel and cobalt [71]. At the final step, these products are passed through such operations as electrolysis or reduction with hydrogen for the recovery of nickel and cobalt in metallic form.

The choice of one method over another depends on several factors such as PLS composition, impurity contents, process economics, environmental factors and etc. Most important and commercially proven downstream

precipitation and recovery techniques to produce intermediate products are MSP and MHP technologies. They both offer a conventional nickel laterite downstream process to obtain the highest product grade with minimal impurities. Environmental, safety and infrastructure aspects determine the choice between them in the production of a hydroxide or a sulfide product. These technologies are explained in detail in the following sections.

## 2.8.1 Direct Solvent Extraction (DSX)

DSX was first commercially operated at the Bulong circuits to recover nickel from dilute leach liquor containing less than 4 g/L Ni using solvent extraction process without the need of nickel precipitation. Donegan has defined improved metallurgical performance of the Bulong DSX process at the time of plant closure [72]. Initially it was unable to achieve design availability, recovery and product quality at an appreciable cost by the SX process. After subsequent development in optimization and successful modification in the process, SX became applicable for a while (between 1999 and 2003) at Bulong circuits. However, it was then failed to reach the projected production levels and Bulong operations were stopped owing to the considerable financial burden and operational problems in the Bulong industrial operation. Bulong DSX circuit is shown in Figure 2.16.
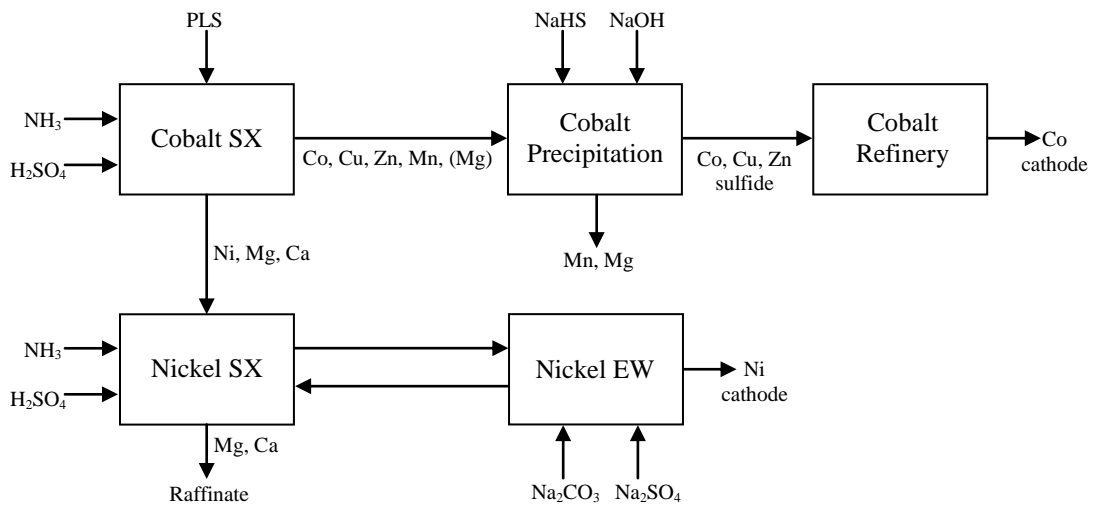


**Figure 2.16** Bulong DSX circuit [72].

The Bulong leach plant was composed of ore preparation, HPAL of PLS with sulfuric acid, neutralization step, CCD and again solution neutralization step to obtain a mildly acidic sulfate based PLS containing low levels of Fe, Al and Cr. Firstly, PLS after the HPAL process and the neutralization step was fed to cobalt solvent extraction (CoSX). Then, an organic substance containing Cyanex 272 (C272) separated Co, Zn, Fe, Cu and Mn from Ni. Next, the Co in the loaded strip liquor (LSL) was separated from Mn and Mg by sulfide precipitation while Ni, Fe(III), Zn and Cu were co-precipitated. Afterwards, the filtered sulfide product was sent to the processing in the cobalt refinery to obtain Co cathode whereas the barren solution containing Mn and Mg was discarded to the tailings. On the other hand, CoSX raffinate was transferred to the nickel solvent extraction (NiSX) circuit where an organic substance containing Versatic 10 (V10) separated Ni from Ca and Mg. Finally, the Ni loaded organic strip passed through an electrowinning step to accumulate Ni cathode.

In addition to Bulong's DSX process, there were other DSX routes studied with various extractants such as Cyanex 272, versatic acid, hydroxyl oximes and di-2-ethylhexylphosphoric acid (D2EHPA) proposed by many groups. In one of them, Heckley and Ibana in May 2003 pointed out a novel separation technique which was electrostatic pseudo liquid membrane (ESPLIM) [73]. This method combines the advantage of SX, liquid membrane and electrostatic dispersion. Extraction and stripping occurred simultaneously in ESPLIM while at the end of the process the separation of nickel and cobalt was attempted.

In solvent extraction the aim is to separate pure $NiSO_4$ and also $CoSO_4$ from impurities, typically Zn, Fe, Cu, etc. and make a further use of both nickel and cobalt sulfate concentrates produced. The separation of $NiSO_4$ with minimum co-extraction of contaminants was achieved by Ritcey and Ashbrook in 1966 just using D2EHPA [74]. In order to extract nickel and cobalt more

selectively over other elements from the PLS best extractants must be found and extractive features of the element must fit the SX condition; in other words there must be more affinity for extraction and collection of nickel and cobalt over others in the organic phase. Otherwise, DSX involves a number of risks due to insufficient separation of nickel and cobalt from impurities. Today most reagents used in DSX and SX circuits are usually Cyanex series: Cyanex 272, 301, 302 and similar type organic phases.

## 2.8.2 Ion Exchange (IX) and Resin-In-Pulp (RIP)

Ion exchange or resin-in-pulp method is a new option among the others for treatment of solutions after the leaching of nickel laterites. This method was initially used for the recovery of uranium and gold, evolved from carbon-in-pulp (CIP) process in which activated carbon is replaced with ion exchange resin and followed by resin-in-pulp process [75]. In RIP, the PLS from AL or HPAL stages is contacted with ion exchange resin which selectively loads the nickel and cobalt from the pulp. According to Mendes and Berni [75], RIP is composed of three different stages: adsorption, elution and regeneration. Nickel and cobalt are selectively loaded in the adsorption stage.

RIP can be preferred instead of such conventional techniques as solvent extraction and precipitation methods because of efficient recovery, selective extraction of low concentrations of nickel and cobalt over an excess of impurities, high mechanical strength, its operational simplicity, low losses resulted from contamination by organic matter and etc. The use of IX based systems for selective nickel extraction, especially from ferrous iron and aluminum is an alternative option for nickel and cobalt recovery from the leach pulp. Inversely, ferric iron, Fe(III), and Cu(II) can be removed and loaded over nickel and cobalt from the leach pulp by an ion exchange resin.

Nowadays, a large number of ion exchange resins are available commercially and are widely used in hydrometallurgy while cation exchange resin and weakly acidic resins have been proposed and used for adsorption of nickel and cobalt from hydrometallurgical process solutions. Furthermore, there are various chelating resins found out which selectively adsorb nickel and cobalt, such as bispicolylamine, aminophosphonic acid and amidoxime [76].

### 2.8.3 Molecular Recognition Technology (MRT)

Molecular recognition technology (MRT) applies "host guest" chemistry which is a highly selective, non ion exchange system [77]. It utilizes metal complexing compounds which are chemically bonded to solids such as silica gel or polymer substrates called as SuperLig®. In MRT, the feed solution is transferred to the column(s) and the desired ion is removed selectively from the PLS. Willis noted an MRT SuperLig® product which selectively accumulates nickel and cobalt at an acid concentration of approximately pH 1 [69]. The nickel accumulated is then eluted by using a 5M sulfuric acid solution rendering an acidic nickel sulfate solution which is then crystallized and recovered by centrifuging and producing a high purity product. Cobalt can also be recovered in a similar manner as a cobalt sulfide, cobalt carbonate or cobalt hydroxide.

The MRT process has various advantages. It has high selectivity, high binding factors, and rapid reaction kinetics leading to a very efficient separation. SuperLig® products can hold ions even when they are in extremely low concentrations in the presence of very high levels of competing ions and even in highly acidic and basic solutions [77]. However, laboratory and/or pilot test work and a preliminary study are required for the economics of the process in which low nickel and cobalt concentrations exist.

**2.8.4 Mixed Sulfide Precipitation (MSP)**

A range of downstream processing options have been developed for nickel and cobalt recovery from heap and HPAL leach PLS. One of the most commercially practiced options is mixed sulfide precipitation (MSP) which has 50 years experience up to date. The precipitation of nickel and cobalt as mixed sulfides with hydrogen sulfide gas has been successfully started in the Mao Bay Plant in Cuba and soars to the Murrin-Murrin plant in Western Australia and the Coral Bay Nickel plant in Philippines using a similar MSP route. Moreover, today there are several MSP projects which have been developed and planned to be worked in future. These are Syerston in Australia, Weda Bay in Indonesia, Ambatovy in Madagascar, Gladstone in Australia, Nonoc and Mindoro in Philippines.

Willis has discussed a suitable MSP route and summarized the general MSP process flow sheet [69]. Figure 2.17 shows a general MSP circuit. It was pointed out that MSP is highly selective for nickel and cobalt over iron, aluminum, chromium and manganese although copper and zinc are reported as minor impurities that can be tolerated in the mixed sulfide product. The MSP process can be used for all laterite ores but it is especially well suited to limonitic ores containing low nickel and high iron or aluminum content. In addition, it is a better alternative to the MHP process for nickel laterite ores containing a nickel to manganese ratio of less than 3:1. Hence, there is no need to remove ferrous iron, aluminum, manganese and chromium before the nickel and cobalt precipitation as in the MHP process. In the MSP process, a lower nickel tenor renders less redissolving of the nickel-cobalt values of the sulfide precipitates in the sulfuric acid. It means lower grade of the deposit resulting in less loss of soluble values in the sulfide precipitation process.

MSP process is conducted either in an autoclave operated at up to 1034 kPa and 121$^{\circ}$C for about 10 to 30 minutes retention time or in a multi reactor at

about 200 to 400 kPa and 80 to 95$^{\text{o}}$C for 60 to 90 minutes retention time. It is possible to produce higher than 99% recovery in one pass [70].
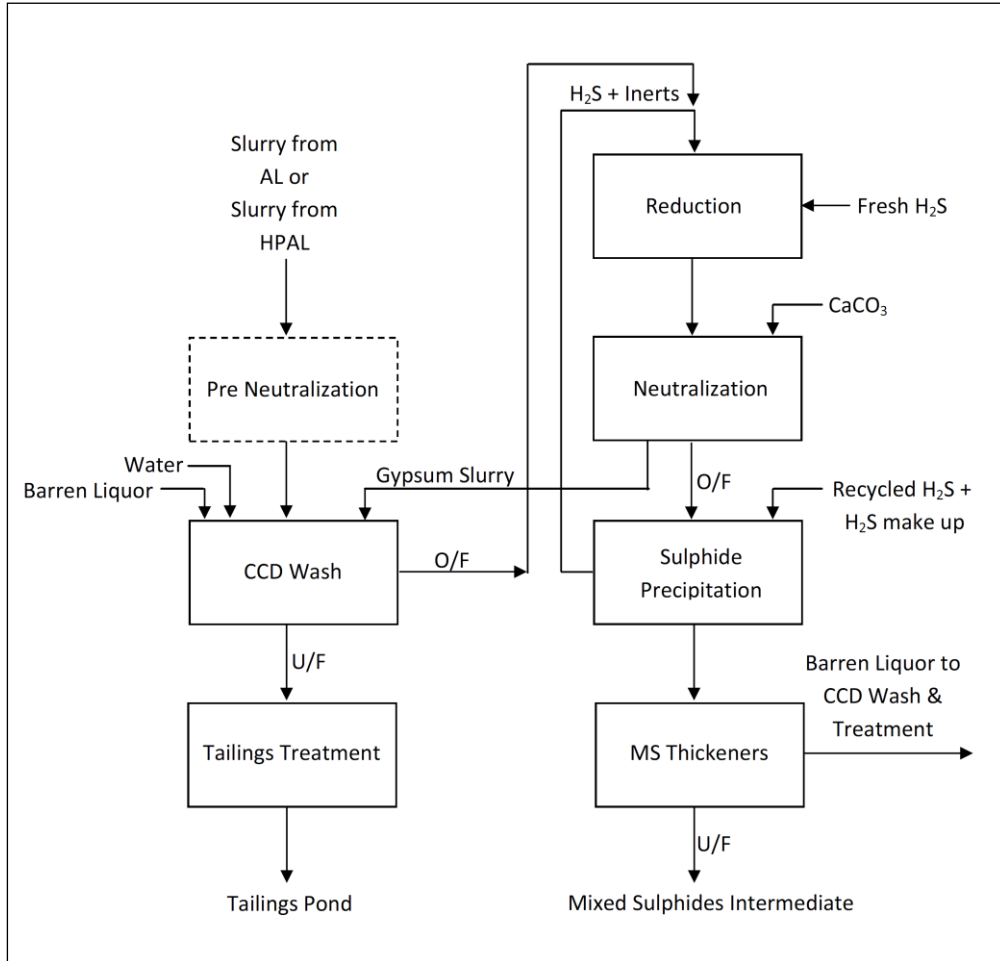


**Figure 2.17** Mixed sulfide precipitation (MSP) process general circuit [78].

Before the MSP reaction, the slurry from AL or HPAL is sent to the thickeners for solid-liquid separation. The PLS from CCD wash circuit is sent to a reduction stage if it is desired to remove copper from the mixed sulfide product. Copper is selectively precipitated with hydrogen sulfide gas as copper sulfide by carefully controlling redox conditions (at about 380 mV) while ferric iron and hexavalent chromium, $Fe^{3+}$ and $Cr^{6+}$, are reduced to ferrous iron and trivalent chromium, $Fe^{2+}$ and $Cr^{3+}$ [69]. The chemistry of the MSP process is better understood by the sulfide precipitation selectivity graph which is illustrated in Figure 2.18.

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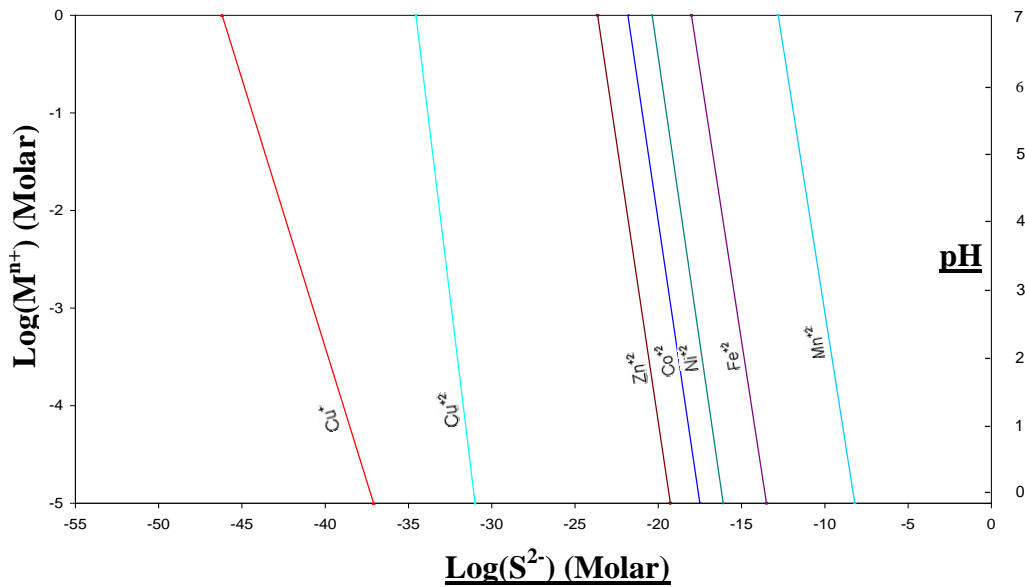
**Figure 2.18** Sulfide precipitation selectivity graph [70].

Figure 2.18 shows the precipitation order of ions according to pH and $S^{2-}$ ion concentration of the PLS to be precipitated. The line of $Fe^{2+}$ ion comes after the lines of $Ni^{2+}$ and $Co^{2+}$ means that ferrous iron does not precipitate until the substantial precipitation of nickel and cobalt. This is unwanted condition in heap leach PLS since the Fe/Ni ratio is high in the PLS and iron will highly remain in solution up to the following process steps without being precipitated. It will both impure the MSP product and the recycle water for heap leaching. This is also the case for the HPAL leach PLS. Therefore, an extra iron removal or neutralization step is required for decreasing the iron content. In the reduction step $H_2S$ is sent from the sulfide precipitation reactor's vapor space and fresh supply [78]. After the reduction step, discharge liquor flows to the neutralization step where free acid is neutralized with limestone. The purpose of neutralization is to adjust the feed liquor pH to achieve the optimum conditions for nickel and cobalt precipitation prior to sulfide precipitation. It is recommended by Willis to neutralize the PLS by limestone to pH 2.5-3.0 and 70-90°C [69]. At pH 2.5-3.0 most of the iron (ferric) is precipitated which will result in less capital and operating costs for hydrogen sulfide production because the ferric to ferrous iron reduction

during sulfide precipitation significantly consume more hydrogen sulfide than other reactions. On the other hand, an operating temperature between $70^{\circ}C$ and $90^{\circ}C$ rather than ambient temperature favors fast reaction kinetics and nullifies viscosity problems. In the acid neutralization reaction gypsum is precipitated, Fe(III) decreased to a residual concentration of less than 200 mg/L and chromium removed to very low levels but aluminum is around 2000 mg/L. At these precipitation conditions, Ni and Co are co-precipitated in minor amounts typically less than 0.5%. The discharge gypsum slurry is then thickened and soluble nickel and cobalt are recovered if present by CCD washing. The washed solids are disposed of as tails in the tailing pond.

After the neutralization reaction, fine recycled freshly precipitated sulfide is added as seed to the overflow neutral solution then heated with steam and directed to the sulfide precipitation step in autoclaves or MSP reactors. Seed addition in the form of fine particles is necessary on account of avoiding significant scaling of the process equipment such as agitator blades resulted from insufficient seed surface area. Recycled $H_2S$ and additional amount from the $H_2S$ plant are pumped to the respected autoclave or the reactor and metal precipitation occurs on the surface of existing particles. Nickel and cobalt can substantially be precipitated with $H_2S$ gas from a neutral solution at pH > 2.5 and a pre-defined $H_2S$ overpressure in the autoclave or the reactor vessel. Under these conditions nickel become less than 30 mg/L in the residual solution [69]. Willis underlined that with the addition of hydrogen sulfide ferric iron, aluminum, chromium, manganese and magnesium are precipitated while any Cr(VI), Mn(IV) and Fe(III) present are reduced to Cr(III), Mn(II) and Fe(II), respectively. In addition, magnesia slurry or caustic soda can be added to control the final pH of the solution in case sulfuric acid produced as a product causes slow reaction kinetics and the solubility of MSP products increases. In this step a higher nickel grade renders undesired loss of values with $H_2SO_4$ produced in the residual solution as it is previously mentioned.

After the MSP product slurry is discharged and the vent gas cooled by steam flashing, the dilute slurry of mixed sulfides is directed to the thickeners where flocculants are added to decrease the losses which can be arisen from the fines discarded with the overflow [78]. The thickener overflow can be rejected or cleaned from impurities by precipitation of the heavy metals mostly Fe(II) and the other polluting elements at a pH greater than that in the MSP step. Firstly, Fe(II) is oxidized to Fe(III) by air injection and removed from the barren solution at pH 2.0-2.5 and secondly, the same procedure is followed for manganese except that manganese is precipitated at pH 8.5-9.0 as manganese hydroxide  The overflow slurry is then passed through a wash filtration and used in the CCD wash circuit at pH 1.5-2.0 as a supply for make-up water. The requirement of this final neutralization circuit is important to prevent ferrous iron accumulation in the circuit due to the foregoing reduction step or to satisfy the environmental regulations if the barren solution is discarded. In this manner, most of the Mn and Mg remaining in the barren solution after Ni-Co precipitation are removed. At the same time, the discharged slurry from the thickener underflow is dried and bagged and shipped to the corresponding refineries as in Moa and Coral Bay. Typical MSP product composition is shown in Table 2.7 [69].

**Table 2.7** Typical MSP product composition [69].

| Component | Unit | Value |
|-----------|------|-------|
| Nickel | wt% (dry) | 55-61 |
| Cobalt | wt% (dry) | 3-6 |
| Zinc | wt% (dry) | 2-6 |
| Copper | wt% (dry) | 1-5 |
| Manganese | wt% (dry) | < 0.1 |
| Magnesium | wt% (dry) | < 0.1 |
| Iron | wt% (dry) | < 0.8 |
| Aluminum | wt% (dry) | < 0.1 |
| Sulfur | wt% (dry) | 34-36 |
| Moisture | wt% | 10-15 |

## 2.8.5 Mixed Hydroxide Precipitation (MHP)

Mixed hydroxide precipitation (MHP) is a well-established and inexpensive method to recover nickel and cobalt as an intermediate product from the solution containing soluble heavy metal ions. The intermediate product is further processed before sale as a nickel compound or pure metal. A mixed hydroxide precipitate can be precipitated from the PLS of nickeliferous laterite by various downstream processing options to selectively recover nickel and cobalt. Iron purification, nickel-cobalt precipitation and manganese or magnesium removal operations make up these options for MHP to be an applicable nickel-cobalt extraction process for nickeliferous laterites. These techniques will be explained in great detail in the following pages. Although the MHP processes in Cawse and Ravensthorpe were stopped due to the economical reasons, today there is a wide range of developed MHP projects which will be set to work in the near future. These are META Gördes in Turkey, again Ravensthorpe in WA (First Quantum Minerals Ltd. is the new owner of the project), Vermelho in Brazil, Ramu in Papua New Guinea and Young, Mount Margaret and Kalgoorlie in WA.

Generally, an alkaline reagent is used to increase the solution pH to lower the solubility of the metallic constituent and so giving rise to precipitation. Caustic soda [NaOH], soda ash [$Na_2CO_3$], hydrated or slaked lime [$Ca(OH)_2$], magnesium hydroxide [$Mg(OH)_2$] and magnesia [MgO] are commonly used in MHP as precipitating agents. Magnesia is more frequently used to precipitate nickel and cobalt. It is cheaper than caustic soda and soda ash and does not give as much contaminated product as slaked lime. The mixed hydroxide precipitate typically contains 15 to 25% Ni with 0.1 to 1% Co but less than 40% Ni on dry basis [37, 69]. Main problem in MHP is that hydroxide precipitate is commonly contaminated with Mn, Al, Ca and unreacted MgO. In addition, in MHP process MgO consumption is an important parameter for economics of the process. MHP is not very selective

for Ni and Co over Mn and preferably performed in two stages to control the Mn flow in the circuit and also to obtain purer product. The electrochemical mechanism of the MHP can be best followed by MHP selectivity graph which is shown in Figure 2.19. As it is shown in the mentioned figure, $Mn^{2+}$ and $Mg^{2+}$ precipitate after $Ni^{2+}$ and $Co^{2+}$ when pH increases. This results in manganese and magnesium contamination in MHP product. The $Fe^{2+}$ and $Zn^{2+}$ precipitation lines also show that there will be zinc and iron deportment to the MHP product if they are present in PLS. The precipitation order is from left to right and it starts with $Fe^{3+}$ precipitation as pH increases.
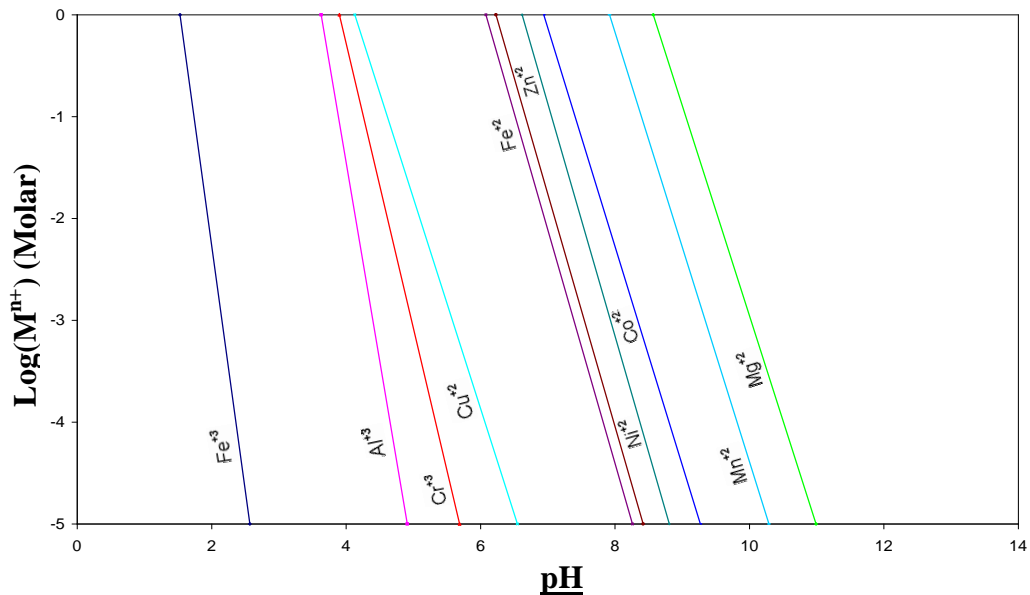


**Figure 2.19** Mixed hydroxide precipitation selectivity graph [70].

Main issue of MHP is to add sufficient caustic calcined magnesia to precipitate as much as nickel and cobalt while precipitating as low as manganese and limiting magnesium contamination after iron removal process. Hence, the nickel hydroxide intermediate product recovery process consists of successful removal of iron, nickel and cobalt, and manganese and magnesium. A typical MHP route proposed by Willis is shown in Figure 2.20.

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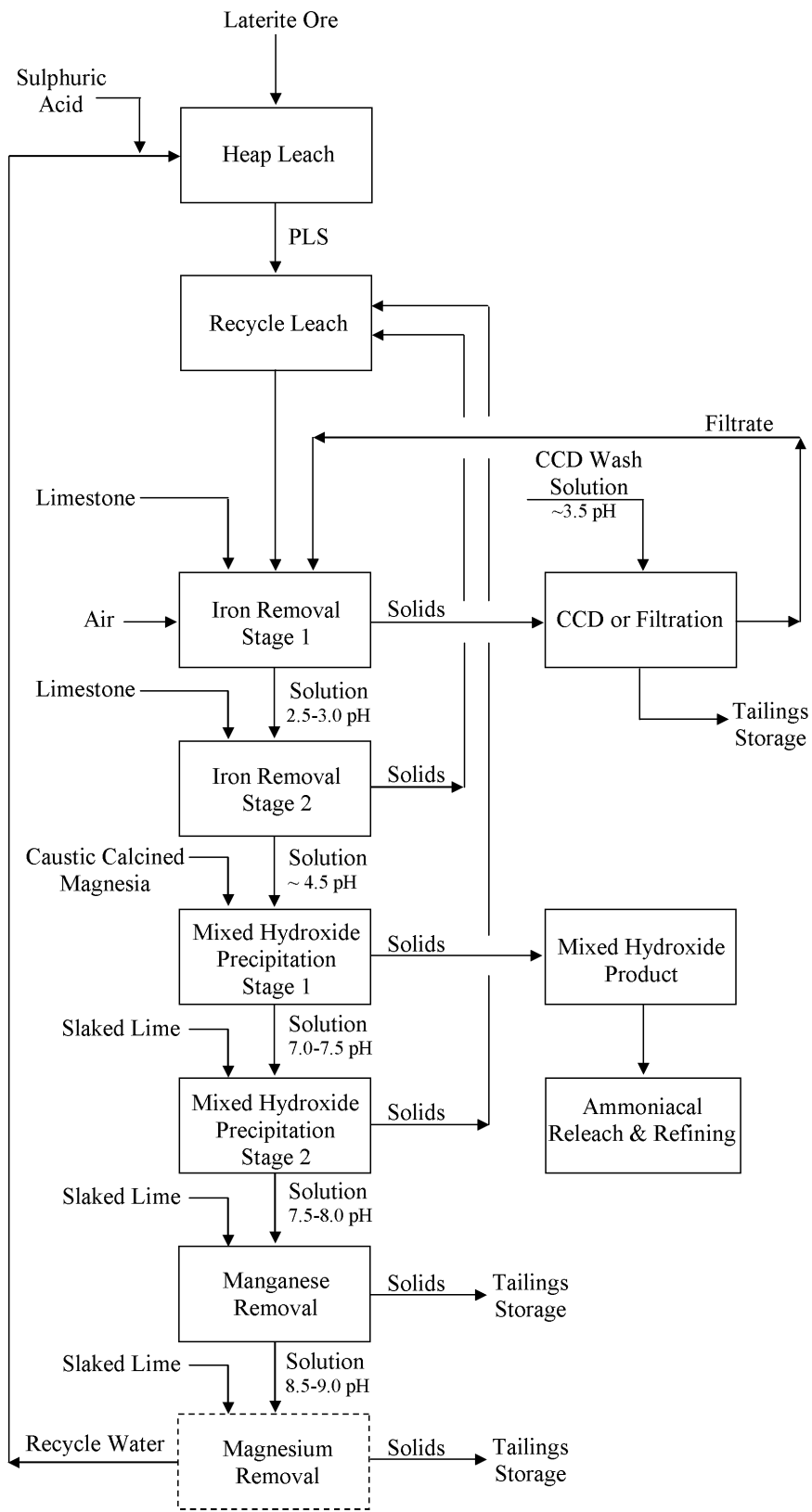
**Figure 2.20** Mixed hydroxide precipitation circuit after the heap leach [69].

Mixed hydroxide precipitation of PLS from the heap leach step is composed of recycle leach, two-stage iron removal, two-stage nickel-cobalt precipitation and manganese removal or following magnesium removal if required. It is a bit different from the MHP for the HPAL process because two-stage iron removal is not required for the PLS from the HPAL process which includes less iron to be precipitated.

The MHP process for the PLS from the heap leach was selected to be explained in detail rather than that from the HPAL on account of the fact that a stock of the PLS from the column leach of Gördes nontronite was used in the thesis study. Most of Fe, Al, Cr, As, Cu and Zn of PLS from the heap leach are removed before Ni-Co precipitation. However, according to Willis's MHP selectivity graph, Figure 2.19, $Mn^{2+}$ cannot be removed before Ni-Co precipitation and some Mn contamination of the MHP product must be allowed in order to obtain desired Ni and Co grade of the MHP product since Ni-Co precipitation is not possible practically without some Mn precipitation.

A recycle leach and iron removal stages are required to prepare the desired quality of feed solution prior to precipitate mixed nickel-cobalt hydroxide product. As in the case of Cawse plant, the contamination of the MHP product by Fe, Al and Si can be prevented by following successful purification operations. Otherwise, the presence of Al and Si causes low nickel recovery in subsequent ammonia leaching step. The aim of recycle leach is to benefit from the residual acid in the heap leach PLS to re-dissolve any Ni and Co which are co-precipitated as hydroxides in both second stage iron removal and second stage mixed hydroxide nickel-cobalt precipitation. The recycle leach is usually carried out at higher temperatures than ambient temperature, especially $>50^{o}C$, and at sufficient sulfuric acid concentration, especially $>20$ g/L, in order to achieve both fast and increased Ni and Co recoveries up to 95-100% [69]. During recycle leaching of Ni and Co, substantial quantities of any Fe, Al, Mn and other hydroxides can also re-dissolve but it will not be a

problem unless exceeding the critical value and it is generally not the case since all the significant quantities are precipitated in first iron removal and first Ni-Co precipitation stage as well as most of Mn and Mg are rejected from the circuit at the end of the process.

The iron content of nickeliferous laterites generally ranges from about 10% to over 50% and 20-50% of this contained iron is dissolved by AL or heap leaching [69, 79]. As it is given in the nickel extraction methods, pregnant leach solutions from AL and HPAL typically include 15-30 g/L and <8 g/L Fe, respectively. At pH 2.5-3.0 almost all iron content in heap leach liquor tends to precipitate except for ferrous iron. Therefore, first of all, there must be a purification stage or stages in MHP circuit for heap leach liquor prior to precipitate nickel-cobalt product at pH 7.0-7.5 to reject most of the iron soluble in PLS of nickeliferous laterites. However, as it is explained previously, HPAL liquors do not include as much iron content as AL (heap) liquors because iron is hydrolyzed and precipitated as hematite, $Fe_2O_3$, leaving a lower residual iron soluble in PLS during pressure leaching. In literature, it was reported that iron can be removed either by solvent extraction or precipitation techniques in hydrometallurgy. There are numerous papers which have published up to date explaining iron extraction techniques by several organic solvents and di-2-ethylhexylphosphoric acid (D2EHPA) whilst they are used in limited applications in industry [79, 80]. D2EHPA was chosen by Agatzini et al. because of having certain advantages over other organic solvents such as chemical stability, low solubility in water and good loading and stripping characteristics [79]. On the other hand, iron elimination from the leach solution by precipitation techniques consists of jarosite, magnetite, hematite and goethite methods [80-83]. The Eh-pH Pourbaix diagram of iron-water systems which is given in Figure 2.21 best describes the iron precipitation mechanism in leach liquors. At ambient conditions, iron is stable and soluble as either $Fe^{3+}$ or $Fe^{2+}$ ions up to certain pH values, 1.617 and 6.64, respectively [82].

The jarosite precipitation method, which is most widely used in zinc hydrometallurgy, enables higher recoveries of metals [83]. Maraboutis and Kontopoulos noted that a residual Fe concentration could be achieved as low as 0.3 to 0.5 g/L with relatively small Ni-Co losses when precipitating Na-jarosite at constant pH 1.5 which was controlled by $CaCO_3$ additions [85]. But, Dutrizac et al. verified that co-precipitation of metals climbs up when pH of the solution and concentration of impurities increase whereas it reduces with Fe concentration in the jarosite product [80]. Jarosite precipitation method is not suitable for $Fe^{2+}$ removal and an oxidation step at pH 1.617 for $Fe^{3+}$ hydrolysis is needed. Jarosite precipitate can also be added as seed material to improve crystal growth.
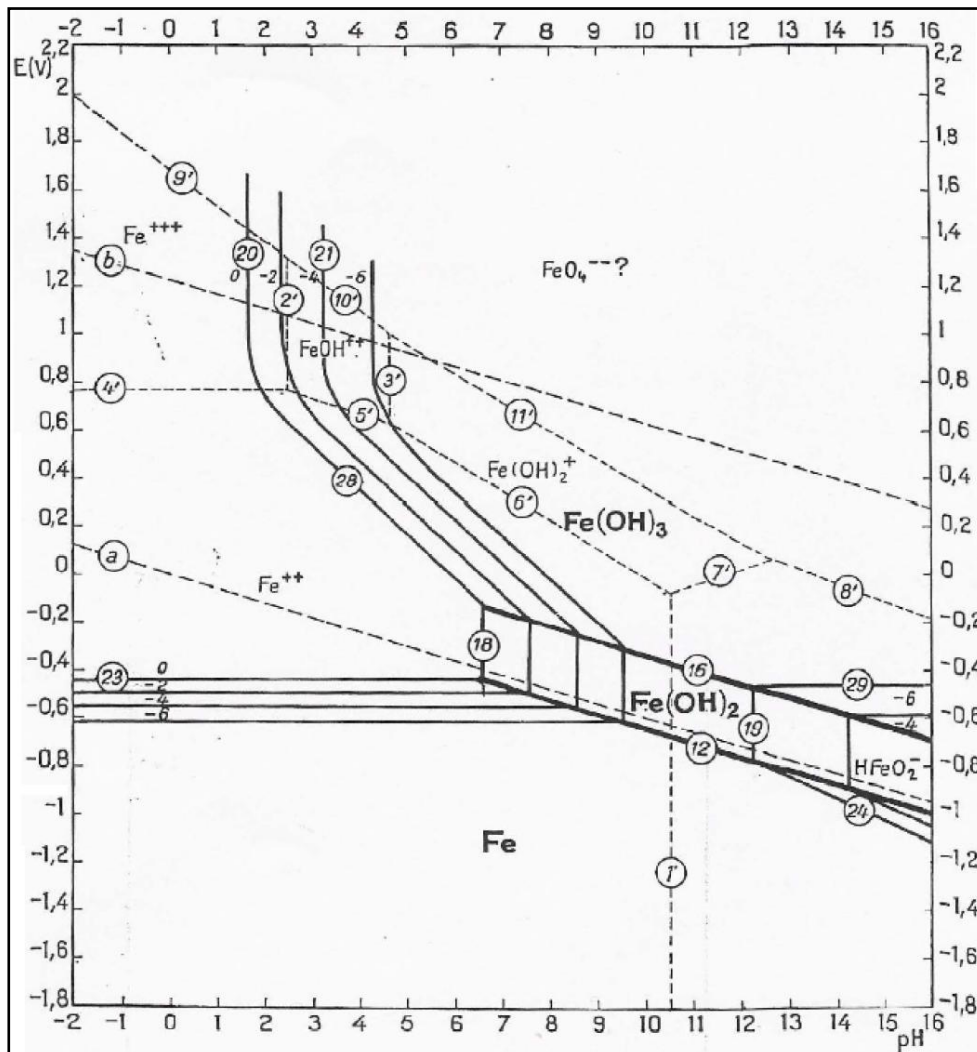


**Figure 2.21** Pourbaix diagram for $Fe-H_2O$ system at $25^oC$ [84].

Other than jarosite precipitation method, magnetite precipitation method is a new commercial application while hematite precipitation method is a more recent innovation in the zinc industry [83]. Among them, goethite precipitation method is better for heap leach liquors of low grade nickeliferous laterites since very low residual iron remains in solution as less than 0.05 g/L, thickening and filtration properties of the goethite precipitate are superior, high concentration of iron in the precipitate obtained and stability of the precipitate is good without need of special equipment [79]. Zhang and Mei reported that at 90-95°C, pH 3-3.5, 3-4 hours reaction time and addition of seed crystals, iron (ferric) ions can be removed from sulfate solutions in readily filterable form by the goethite method [82]. The product of the process is commonly FeOOH, the $\alpha$-form of goethite [86].

The discharge slurry from the recycle leach is sent to iron removal stages in Figure 2.20. The aim in iron removal is both to neutralize excess acid in the heap leach PLS and to reject basic impurities such as iron and aluminum from the solution by $CaCO_3$ addition before nickel-cobalt precipitation. As it can be seen in Figure 2.19, at pH 2.5 to 3.0 almost all ferric iron, Fe(III), can be removed from PLS to a residual concentration of less than 200 mg/L [69] as well as chromium and aluminum removed to low concentrations. Also, co-precipitation of nickel and cobalt in this pH range is insignificant, typically less than 0.5% of the precipitate as Willis noted. Similarly, Sarma et al. reported that complete removal of iron and about 95% removal of silica can be succeeded at about pH 3.5 by conducting the precipitation at 80-90°C for one hour [87]. Gypsum, $CaSO_4.2H_2O$, is a precipitated product of the acid neutralization reaction between sulfuric acid and limestone. Particularly, limestone is used to give better dewatering properties to the precipitate than slaked lime as well as it is a cheaper reagent [88].

Temperature and especially pH are the most important variables controlling the iron precipitation mechanism which determines the degree of iron

removal, nickel-cobalt losses, crystallinity of the precipitate and sedimentation and filtration properties. An operating temperature between 70 and 95$^{\circ}$C or the boiling temperature of the slurry is preferred to yield fast reaction kinetics and to decrease the slurry viscosity, then better filtration properties in the sequential filtration step. However, operations at ambient temperature render poor reaction kinetics. Primary neutralization temperatures at Ravensthorpe were kept at 95$^{\circ}$C to enhance iron precipitation as jarosite and to improve aluminum rejection [37]. It is important to note that aluminum should be as low as possible, especially less than 50 mg/L by adjusting a pH between 4.4 and 4.8 in order to satisfy the nickel-cobalt dissolution in the following ammonia leaching step [69]. The reason for this is known that aluminum presence in mixed hydroxide precipitate causes a gelatinous and amorphous structure which hinders some of nickel and cobalt leaching and makes them unrecoverable inside the unbroken bonds of the aluminum hydroxide. In addition, co-precipitation of nickel and cobalt is significant at this pH range compared to the first iron removal stage, typically 4-10% [69]. The increase of co-precipitation of nickel and cobalt with pH is shown in Figure 2.22.
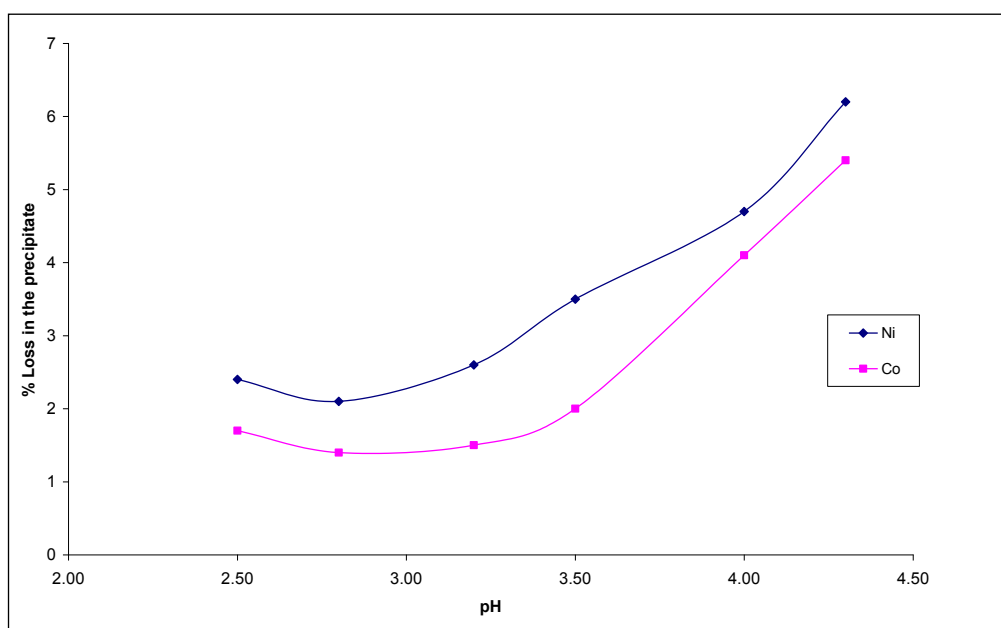


**Figure 2.22** Percent of nickel and cobalt losses with pH in the precipitate [89].

Agatzini et al. reported that at pH 3.5, 99.9% of iron, 98.9% of aluminum and 99.1% of chromium were precipitated while only 3.5% nickel and 2.0% cobalt co-precipitated based on the analyses of the precipitates [30]. Meanwhile, rate of pH change is an important factor for the quality of the product. Agatzini et al. has also emphasized that during the precipitation process by adding 20% CaO pulp, the pH increase rate was fixed to a low value within a practical period of time up to 12 hours in order to prevent supersaturation of iron, aluminum and chromium and the production of an amorphous precipitate which causes deterioration in the filtration and settling characteristics [30, 89].

Direct precipitation of iron and aluminum at a certain pH and temperature in a single stage yields significant loss of values with impurities as well as increased capacities of purification plant rendering an uneconomic process. Thus, for a complete removal of iron, aluminum and other impurities and minimum nickel and cobalt losses, iron removal process of MHP occurs in two stages as in Figure 2.20. By carrying out two-stage iron purification process for the leach liquors, with the limestone addition, most of the iron content of PLS removed and the decreased load of the PLS is subjected to the subsequent precipitation process for decreasing mainly its aluminum and chromium and also the remaining iron contents to very small values while co-precipitated nickel and cobalt hydroxide re-dissolve in the recycle leach. At the same time, manganese dioxide, $MnO_2$, or oxygen, $O_2$, can be added as a catalyst to convert ferrous iron to ferric iron if there is significant concentrate of ferrous iron in the PLS. Ferric iron is then precipitated with various base additions according to the following reactions [90]:

$$Fe_2(SO_4)_3 + 6CaO + 3H_2SO_4 \longrightarrow 2Fe(OH)_3 + 6CaSO_4 \tag{2.12}$$

$$Fe_2(SO_4)_3 + 6CaCO_3 + 3H_2SO_4 \longrightarrow 2Fe(OH)_3 + 6CaSO_4 + 6CO_2 \tag{2.13}$$

$$Fe_2(SO_4)_3 + 6Na_2CO_3 + 3H_2SO_4 \longrightarrow 2Fe(OH)_3 + 6Na_2SO_4 + 6CO_2 \tag{2.14}$$

$$Fe_2(SO_4)_3 + 6NaOH \longrightarrow 3Na_2SO_4 + 2Fe(OH)_3 \tag{2.15}$$
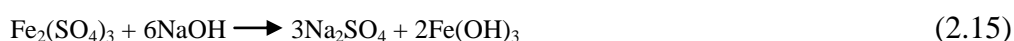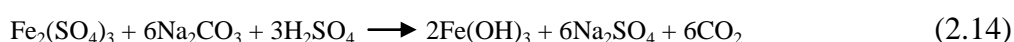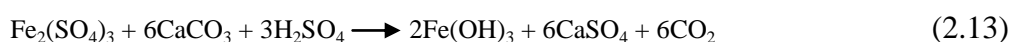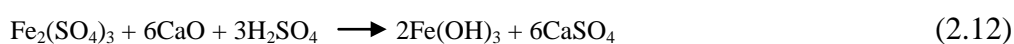
Aluminum and chromium can effectively be rejected from leach liquors at higher than 95% during the iron removal process. Agatzini and Oustadakis have reported that aluminum and chromium were precipitated as 99% and 97%, respectively at 95$^{\circ}$C and 1 atm as easily filterable basic sulfate salts of the jarosite-alunite type, with minor amount of nickel and cobalt co-precipitated by gradually increasing the pH of the PLS to an equilibrium pH value of 3.5 [89]. The remaining Al and Cr concentrations achieved after the precipitation were lower than 200 ppm and 50 ppm, respectively while the residual iron concentration was 30 ppm [30, 89]. The target pH primarily depends on the desired residual aluminum concentration in solution.

After the iron removal stages the PLS is forwarded to mixed hydroxide nickel-cobalt precipitation stages as seen in Figure 2.20. The reason for performing two-stage nickel-cobalt precipitation is due to controlling the extent of manganese contamination in the mixed hydroxide product. Nickel to manganese ratio in the feed stream is very important for the MHP process to be applicable in industry because MHP is not selective for high manganese containing ores. In the first stage of MHP the solution is usually fixed to pH 7.0-7.5 at 50-80$^{\circ}$C for two or three hours by the addition of freshly prepared magnesia to achieve the maximum practical nickel and cobalt precipitation possible as well as limiting the manganese content of the precipitated solids to less than 5% and minimizing magnesium contamination [37, 69]. Willis noted that at this pH range almost 90-95% of the nickel, cobalt, copper and zinc are precipitated together with 15-35% manganese and nearly all the remaining iron, aluminum and chromium in the PLS. This is also apparent in Figure 2.19. An operating temperature of higher than 50 or 60$^{\circ}$C is preferred for higher reaction kinetics while low temperature treatment yields slow kinetics. Some magnesium can also be present in the form of unreacted magnesium oxide in the MHP product depending on reactivity of magnesia used for pH adjustment. When magnesia forms brucite, $Mg(OH)_2$, in the precipitation reaction, it acts as seed material for nickel precipitation. In Hazen Research

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pilot plant built in Colorado in 1996, the mixed hydroxide precipitates obtained were of poor quality attributed to mainly magnesium contamination. It was found that caustic calcined magnesia is at its most reactive condition when it is used dry and mixing with water for longer than a few minute changes its reactivity and results in product contamination [37]. Magnesia should not have any contact with air and used as dry or slurried with water within a few minutes and consumed freshly. Furthermore, insufficient magnesia leads to excess nickel passing to second stage precipitation, increased slaked lime consumption, and losses attributed to additional recycles [37]. However, instead of magnesia, caustic soda (sodium hydroxide), hydrated lime (calcium hydroxide) or soda ash (sodium carbonate) can be used as precipitating agent. Although they eliminate the unreacted magnesium content of the MHP product and some provide more quantitative recovery of nickel and cobalt, caustic soda is expensive, lime results in gypsum contamination and the selectivity for nickel over manganese is diminished by the use of soda ash. The discharge slurry from the first stage of MHP (MHP1) is sent to a thickener and purified from soluble impurities by wash filtration and solid MHP1 products become ready for ammoniacal re-leach and refining while the overflow solution is directed to the second stage of MHP (MHP2). In MHP2, the solution is typically fixed to pH 7.5-8.0 at 50-80$^o$C for one or two hours by addition of sufficient slaked lime to precipitate all residual nickel and cobalt whereas 20-30% of the remaining manganese is co-precipitated in the PLS coming from the first stage [69]. Willis pointed out that at this pH range the precipitates generally contain 10-20% manganese but final nickel and cobalt concentrations can be successfully decreased to less than 5 ppm. The nickel and cobalt hydroxides in the precipitated solids after the second MHP stage are re-dissolved together with manganese hydroxide by the reaction with acidic PLS coming from the heap leach. The reason why the second mixed hydroxide precipitate is not saleable as an intermediate product is that marketing options restricts the manganese content to less than 10%. Some Ni and Co values should be sacrificed in order to produce saleable

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MHP product which contains less than limiting Mn content. Thus, the optimum pH depends on the desired residual Ni and Co concentrations in the remaining solution and the limited Mn content in the precipitate. Sist and Demopoulos realized in the experiments that the concentration of Ni in the aqueous phase (solubility) decreased with increasing pH and temperature which control precipitation mechanism as in the iron removal process. It was noted that increasing pH by one unit decreased the Ni concentration by a half an order of magnitude while increasing temperature from $60^{o}C$ to $70^{o}C$ reduced Ni concentration by 50% [91].

Seed addition for both stages of MHP enhances product quality and settling and filtration characteristics of precipitates by producing well-grown crystalline particles. Precipitates formed by homogenous nucleation typically causes small particles, low slurry pulp density, slow settling rates and high impurity uptake. If seed is introduced, a substrate for the precipitation is provided; heterogeneous nucleation occurs and improves the precipitate properties [91]. In addition to produce more filterable high quality precipitates, seed addition is expected to accelerate precipitation reaction, to produce coarser precipitates and to suppress undesirable side reactions [92]. It has been reported in the literature that the nickel hydroxide in the MHP product can exist in one of the two phases, both crystallizing in a layered hexagonal structure: $\alpha$ and $\beta$ phases. The $\alpha$-nickel hydroxide can be represented by the general formula $Ni(OH)_{2-x}A^{n-}_{x/n} \cdot yH_2O$ where x is 0.2-0.4 and A is chloride, nitrate, sulfate or carbonate, and y is 0.6-1 while the $\beta$–nickel hydroxide is thermodynamically more stable and forming like a mineral brucite structure without any hydrogen bonding between layers [93]. A similar $\alpha$ and $\beta$ modifications of cobalt hydroxide, $Co(OH)_2$, was also studied by Rajamathi et al. [93]. A typical X-Ray diffraction graph of mixed hydroxide precipitate produced by precipitating the purified PLS using MgO pulp as a neutralizing agent is shown in Figure 2.23. The mineralogical phases are theophrastite $[Ni(OH)_2]$, brucite $[Mg(OH)_2]$, a hydrated form of nickel

hydroxide and small quantities of silica ($SiO_2$) while phases of cobalt and manganese were not detected due to their low content in the mixed hydroxide precipitate.
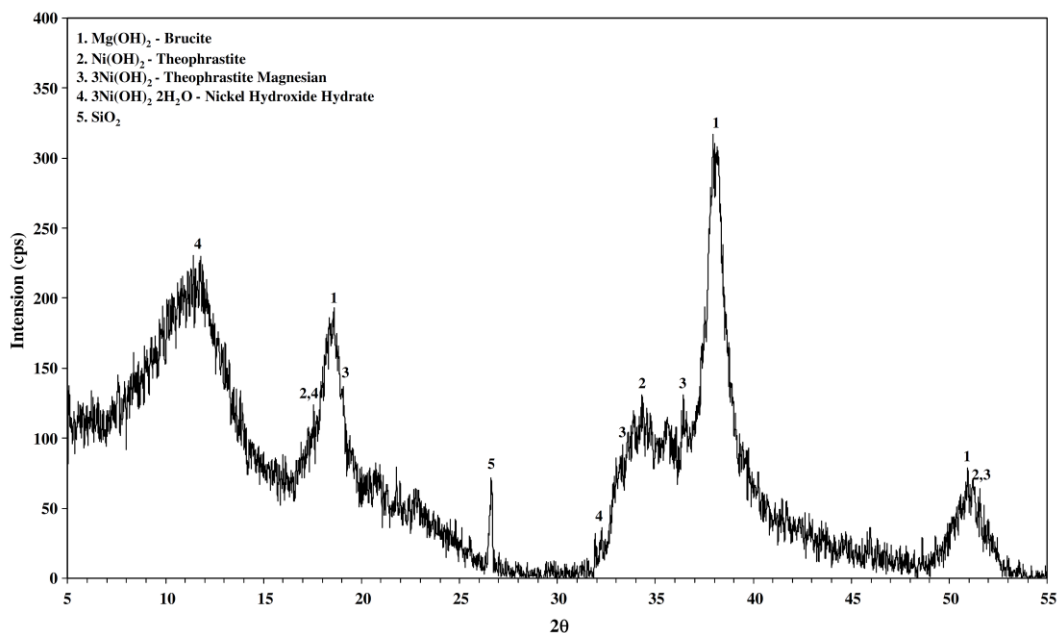


**Figure 2.23** An XRD graph of the produced solid MHP product using MgO as neutralizing agent [92].

The typical MHP product composition is shown in Table 2.8 [69]. In addition to know the chemical structure of the solid MHP product, aqueous electrochemistry of Ni-Ni$(OH)_2$ and Co-Co$(OH)_2$ is important to determine species which are stable during the precipitation reaction depending on pH and oxidation-reduction potential of the solution liquor. Figure 2.24 and Figure 2.25 show the Pourbaix diagrams for Ni-$H_2O$ and Co-$H_2O$ systems at 25$^o$C, correspondingly. Between water lines, $Ni^{2+}$ and $Co^{2+}$ are stable up to the pH values that projection of line 7 in Figure 2.24 and line 8 in Figure 2.25 intersect the pH axis between 6 and 7. At these points nickel and cobalt become hydroxides, Ni$(OH)_2$ and Co$(OH)_2$, as long as pH does not exceed about 12 and 13, respectively. In heap leach and iron purification stages at pH <6 and at 200 to 600 mV ORP (Oxidation-Reduction Potential), nickel and cobalt are soluble in PLS or solution liquors as divalent forms and are not

precipitated unless pH becomes the pH for the commencement of the hydrolysis reaction.

**Table 2.8** Typical MHP product composition [69].

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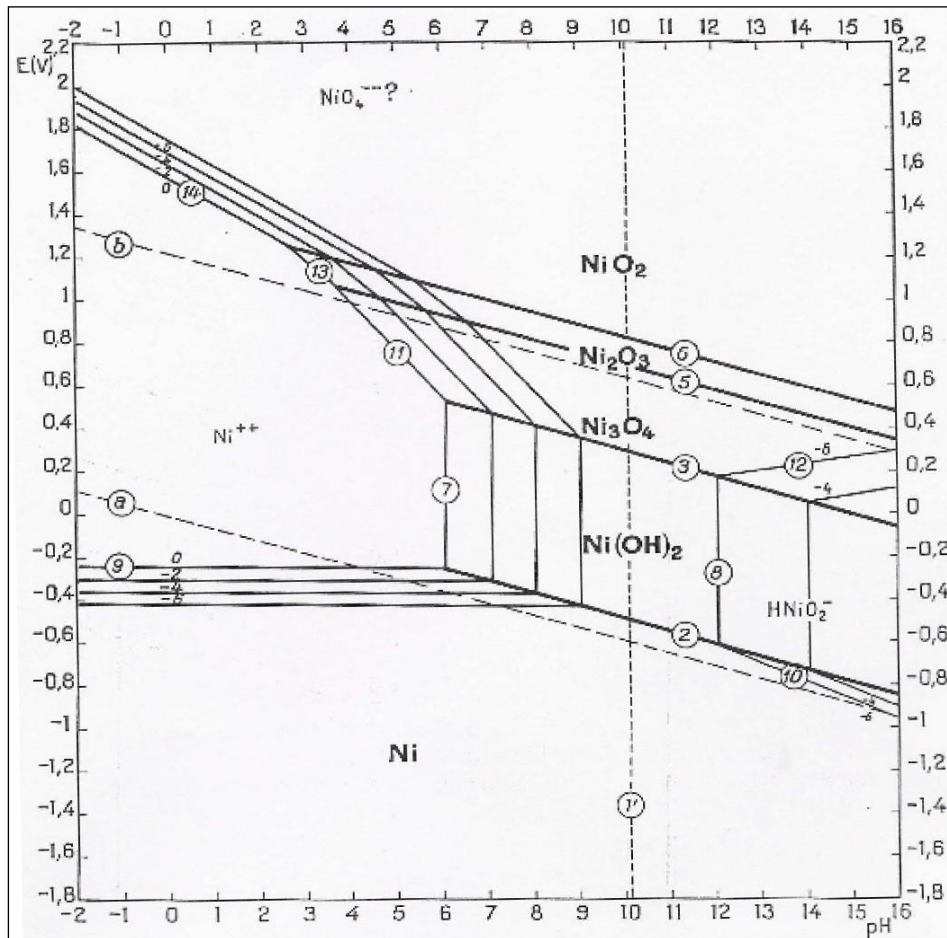


**Figure 2.24** Pourbaix diagram for Ni-$H_2O$ system at 25$^\circ$C [84].
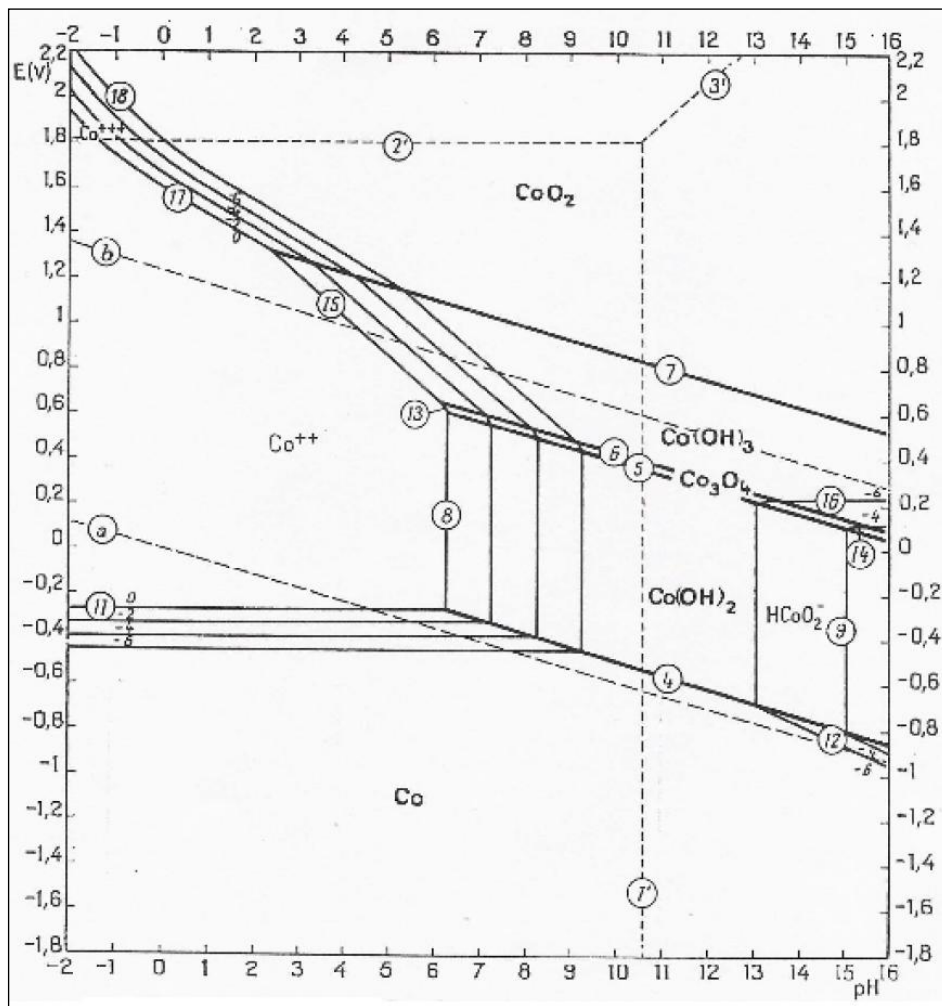
**Figure 2.25** Pourbaix diagram for Co-H$_2$O system at 25$^o$C [84].

Thickener overflow solution after the second MHP stage in Figure 2.20 is transferred to manganese removal. The aim in manganese removal is to reject as much manganese as possible from the discharge liquors. As it is underlined before, Willis noted that MHP process is not suitable for ores with high manganese content, especially for ores having manganese to nickel ratio greater than 1:3 and best applied to ores of higher nickel content and low iron and aluminum content attributed to high nickel-cobalt losses with co-precipitation [69]. Therefore, MHP is well suited to saprolitic ores and limited to certain limonites. The reason why requiring low manganese content for MHP process hides in high recovery percentages of manganese with nickel and cobalt. This is apparent in Figure 2.26.

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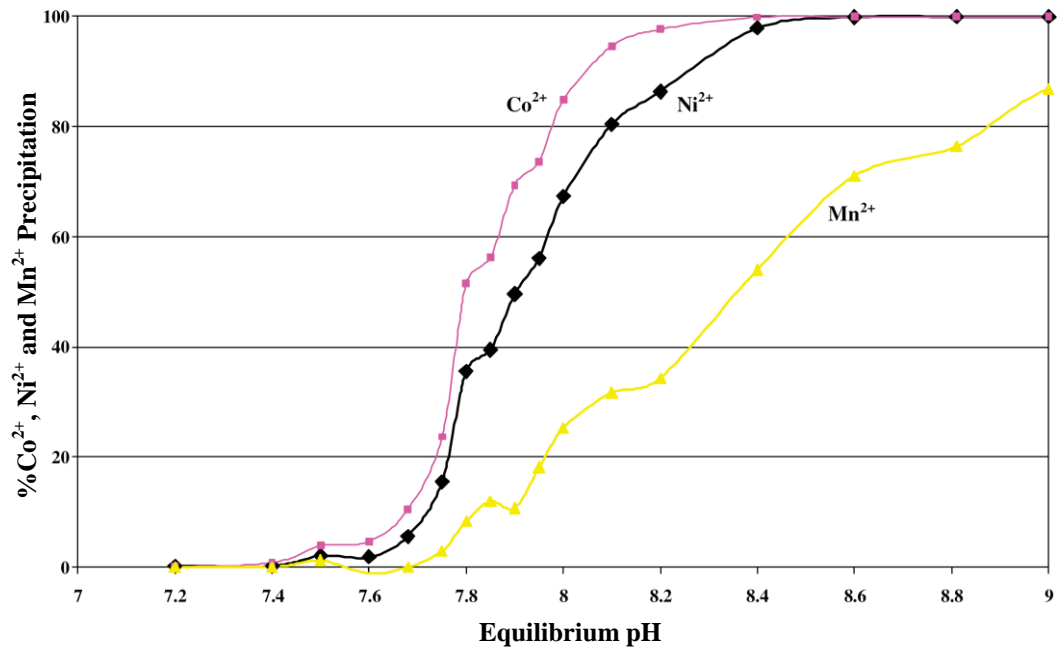
**Figure 2.26** Nickel, cobalt and manganese precipitation using MgO slurry as neutralizing agent [92].

Oustadakis et al. used a synthetic solution without containing any impurities such as iron, aluminum and chromium except for manganese to show the precipitation of nickel and cobalt with respect to manganese co-precipitation as a function of pH by addition of 20% MgO slurry. The precipitation of nickel and cobalt was achieved as 99.9% and 99%, respectively while manganese precipitation reached 80% by gradually raising and keeping the pH of the leach liquor at a value of 9.0 at ambient temperature and pressure [92]. The precipitate produced contained 25% Ni, 1.5% Co and 3% Mn, in spite of the high manganese recovery in the precipitation because manganese to nickel ratio in feed stream was less than 1:6 and manganese concentration was 800 ppm which sufficiently met the requirement of MHP.

In contrast with Willis, Zhang et al. reported a study of two-stage manganese removal from nickel laterite leach liquor in mixed hydroxide precipitation circuit prior to nickel-cobalt precipitation [94]. It is claimed in the study that a feasible way can be possible before MHP to partially discard soluble

manganese by oxidative precipitation at two neutralization steps with minimal loss of nickel and cobalt. At the primary neutralization stage, pH 3 and $60^oC$-$80^oC$ were tried but about 15% of the manganese in the leach liquor from HPAL slurry was reported to be precipitated at $60^oC$ with 3.8% $SO_2$ in air and leading to an insignificant co-precipitation of nickel and cobalt whereas the higher temperature treatment ($80^oC$) causes the slow mass transfer of oxygen in air through the viscous slurry which hinders the manganese precipitation. At the secondary stage, precipitation was conducted at pH 4.0 and $60^oC$ with the same sulfur dioxide concentrate but 56% of manganese was precipitated with higher nickel and cobalt co-precipitations, 10% and 25%, respectively. Next, the precipitate was sent to a recycle leaching stage to re-dissolve nickel and cobalt using 30 g/L $H_2SO_4$ at $95^oC$. It was found out in the previous study of Zhang et al, that the rate of oxidation of Mn(II) is slow at pH less than 3 and rises rapidly at pH higher than 4 [95]. Meanwhile, the introduction of sulfur dioxide to the leach slurry, which is a reducing agent, gives rise to chromate reduction and ferrous iron formation. However, the latter is not desired in MHP. Thus, any ferrous iron is needed to be oxidized to ferric state and precipitated prior to manganese oxidation.

Without operating pre-manganese purification stage as Zhang et al. suggested, manganese usually accumulates in the circuit when the depleted solution is recycled within the process or used as make-up water to heap leaching which will adversely affect product quality. Typically, more than 50% of the manganese remains in solution after two-stage nickel-cobalt precipitation [69]. Furthermore, environmental regulations can necessitate removal of aqueous manganese. Therefore, the overflow solution of the second MHP stage is generally purified from most of its manganese content, generally less than 100 ppm manganese left in solution by adjusting the solution pH to 8.5-9.0 operating at $50$-$60^oC$ for a time between half an hour and 2 hours and precipitating manganese hydroxide [69]. Oxidation by air injection can be

required for the formation of manganese dioxide in order to achieve a residual concentration of about 10 ppm.

Thickener overflow solution after the manganese precipitation in Figure 2.20 can be passed through magnesium removal process if there will be magnesium accumulation in the MHP circuit. However, it is not a selective process after pH 8.5 because consumption of reagent (slaked lime) is excessive attributed to buffer effect. Magnesium can be present in solution because of leaching magnesium from nickeliferous laterites and using magnesia as a neutralizing agent in nickel-cobalt precipitation stage. In the PLS resulting from heap leaching of hematitic/limonitic ores, magnesium concentration is in the range of 6 g/L while for serpentinic ores it is in the range of 50 g/L [41]. High soluble levels of magnesium can affect heap leach performance such as double salt precipitation in the heap so that concentration levels must be under control below certain levels [96]. The chemical precipitation of magnesium, by calcium hydroxide, $Ca(OH)_2$, from a leach solution resulting from heap leaching of nickeliferous laterites with sulfuric acid was studied by Karidakis et al. [97]. It was found that a minimum value of pH 8.5 is required to precipitate higher than 97% magnesium from the leach solution. Magnesium removal was achieved by using calcium hydroxide in solid form and producing a precipitate comprising a mixture of magnesium hydroxide [$Mg(OH)_2$] and gypsum [$CaSO_4.2H_2O$]. Karidakis et al. also reported that temperature and stoichiometric quantity of $Ca(OH)_2$ are significant variables in magnesium removal process. However, temperature was effective on magnesium precipitation only when calcium hydroxide used in stoichiometric quantity. The resulting final solution is a barren solution containing only magnesium and calcium after iron removal, nickel-cobalt precipitation and manganese removal processes. By removing magnesium as a mixed hydroxide precipitate, the barren solution which contains 1-10 ppm Mg can be recycled to the heap leaching stage and saved as process water in

the circuit and it also becomes possible to save the cost of waste disposal by selling magnesium hydroxide precipitate with a market value.

As a conclusion, MHP process has been taking increasing attentions on practical recovery of nickel and cobalt from leach solution of nickeliferous laterites since it was invented. Ravensthorpe Nickel Operation will be expected again to produce nickel intermediate product by MHP process after HPAL and AL of nickel laterites [45] while META Gördes Project will start to produce mixed hydroxide precipitate from Gördes within a few years [23]. A typical MHP processing route was also followed for the present thesis work [98] after the extraction of nickel from lateritic ores at atmospheric pressure with column and agitation leaching as reported [99, 100]. Commercialization of MHP process will gain importance in future due to its bringing obvious advantages into reality in extractive metallurgy of nickel.

# CHAPTER 3

# EXPERIMENTAL MATERIALS AND METHODS

## 3.1 Materials

A nontronite type lateritic ore was sampled from Gördes region in Manisa, located in the western part of Turkey, and used for this thesis study. Experiments were conducted by using stocks of pregnant leach solution, PLS, resulting from column leaching of the nontronite ore. Column leaching of the nontronite ore was done by a previous thesis study using dilute sulfuric acid solutions at atmospheric conditions [99]. The sulfuric acid solutions were then accumulated and stocked in order to use in iron removal, nickel-cobalt precipitation, manganese and magnesium removal processes. Sodium hydroxide and di–potassium oxalate monohydrate were used as a neutralizing agent and a catalyst, respectively, for acid titration experiments to estimate free acid content of the PLS. Limestone [$CaCO_3$], magnesia [$MgO$] and slaked lime [$Ca(OH)_2$] were used as neutralizing and precipitating agents for iron removal, nickel-cobalt precipitation and manganese and magnesium removal experiments, correspondingly.

### 3.1.1 Nontronite Ore

Nontronite ore sample was supplied from Gördes region in Manisa with the help of META Nikel Kobalt A.Ş. The sample was representative for the entire ore body located in Gördes region which has an estimated total ore reserve of 32 million tons, 1/3 of this reserve is nontronite. The nontronite sample was crushed and screened to -2 cm and weighed 410 kg. Physical, chemical and mineralogical characterizations of the nontronite sample used in this study are presented in the following sections.

### 3.1.1.1 Physical Characterization

Physical characterization of the representative nontronite ore is given in Table 3.1. Nontronite ore was homogenized and sampled through coning and quartering method. During coning and quartering divided ore samples were stocked except for the one that was used in the present study. The nontronite ore was dried at $105^{o}C$ in a drying oven until a constant sample weight was attained. Then, the moisture content of the nontronite sample was determined by weight loss resulting from the evaporation of physically bonded water. Next, bulk density of original ore and solid density of the dried nontronite ore sample were determined. To determine the solid density, the dried nontronite ore sample was ground to 100% -0.038 mm (-38 μm) and sent to METU Central Laboratory for the measurement. The solid density of the nontronite sample was found out by helium pycnometer at $26.7^{o}C$.

**Table 3.1** Physical analysis of the representative nontronite ore [99].

| Representative Ore Sample | Nontronite |
|---|---|
| % Water (physical) | 40.10 |
| Bulk Density (g/cm$^3$) | 0.93 |
| Solid Density (g/cm$^3$) | 2.64 |

In addition, wet screen analysis of the dried representative nontronite sample was carried out to determine particle size distributions of the nontronite. Wet screen analysis was done by using an eight-sieve nest system that was vibrated continuously until the water which was poured to the top came clear from the bottom. After screening, all oversize and undersize particles in each sieve were dried at 105°C and weighed. Screen analysis result of the nontronite sample is shown in Table 3.2.

**Table 3.2** Wet screen analysis results of nontronite [99].

| Size(mm) | Weight (%) | $\sum$ wt % oversize | $\sum$ wt % undersize |
|---|---|---|---|
| +3.327 | 9.21 | 9.21 | 90.79 |
| +2.362 | 2.09 | 11.30 | 88.70 |
| +1.168 | 2.13 | 13.43 | 86.57 |
| +0.589 | 3.87 | 17.30 | 82.70 |
| +0.295 | 4.98 | 22.28 | 77.72 |
| +0.147 | 9.24 | 31.52 | 68.48 |
| +0.074 | 12.70 | 44.22 | 55.78 |
| +0.038 | 15.44 | 59.66 | 40.34 |
| -0.038 | 40.34 | - | - |
| $\sum$ | 100 | - | - |

**3.1.1.2 Chemical Characterization**

The complete chemical analyses of the representative nontronite sample were performed by using Inductively Coupled Plasma (ICP) and X-Ray Fluorescence (XRF) methods. Particle size of dried sample used for the chemical characterization was 100% -0.038 mm. Results of complete chemical analyses of the representative nontronite ore are shown in Table 3.3.

**Table 3.3** Chemical analyses of representative nontronite ore as wt% [99].

| Component (%) | Nontronite |
|:---:|:---:|
| Fe | 15.95 |
| Ni | 1.20 |
| Co | 0.044 |
| $Cr_2O_3$ | 0.99 |
| MnO | 0.34 |
| As | 0.020 |
| $Al_2O_3$ | 4.17 |
| $SiO_2$ | 44.9 |
| MgO | 6.91 |
| CaO | 2.15 |
| $K_2O$ | <0.122 |
| $TiO_2$ | 0.08 |
| CuO | 0.009 |
| ZnO | 0.025 |
| PbO | <0.010 |
| $P_2O_5$ | 0.050 |
| S | <0.01 |
| Loss of Ignition | 8.81 |

### 3.1.1.3 Mineralogical Characterization

Thermo Gravimetric (TGA) and Differential Thermo Gravimetric (DTA) analyses were carried out for mineralogical characterization of the representative nontronite sample and the samples of the precipitates obtained from MHP1, MHP2 and manganese removal processes. Analyses of the nontronite sample ground to 100% -0.038 mm were conducted between $35^{o}$C and $1000^{o}$C while maintaining a linear heating rate of $10^{o}$C/min in air. In addition, analyses of the finely ground MHP1, MHP2 and manganese precipitate samples were carried out by a Simultaneous Setaram TGA and DTA equipment. Linear heating rate of $5^{o}$C/min was maintained between $25^{o}$C and $700^{o}$C in air for the MHP samples and between $25^{o}$C and $1000^{o}$C in $N_2$ gas for the manganese precipitate sample.

Plotted DTA/TGA diagram of the nontronite sample is shown in Figure 3.1. In Figure 3.1, it is seen that around $100^{\circ}$C there was a weight loss and an endothermic peak because of the evaporation of physically present water. On heating up to $269^{\circ}$C, an endothermic reaction occurred together with a weight loss attributed to the transformation of goethite into hematite shown in reaction 3.1. On the other hand, the exothermic peak at $819^{\circ}$C was because of the transformation of serpentine to forsterite [$2MgO.SiO_2$].

$$2FeO.OH \longrightarrow Fe_2O_3 + H_2O \tag{3.1}$$

X-Ray Diffraction (XRD) analysis was conducted on the representative nontronite sample and the precipitates produced by the iron removal, the Ni-Co precipitation and the manganese removal experiments with Rigaku Multiflex Powder X-Ray diffractometer using Cu-$K_{\alpha}$ radiation. XRD pattern of the representative nontronite sample is shown in Figure 3.2. It is apparent that smectite, serpentine, goethite, hematite and quartz were present in nontronite.
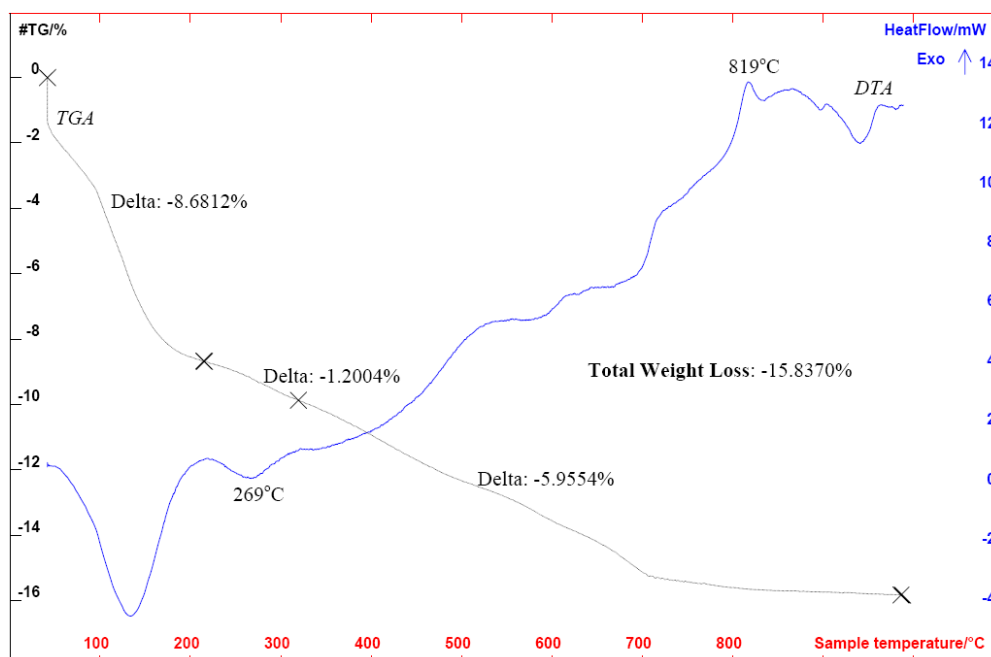


**Figure 3.1** DTA/TGA diagram of nontronite [99].
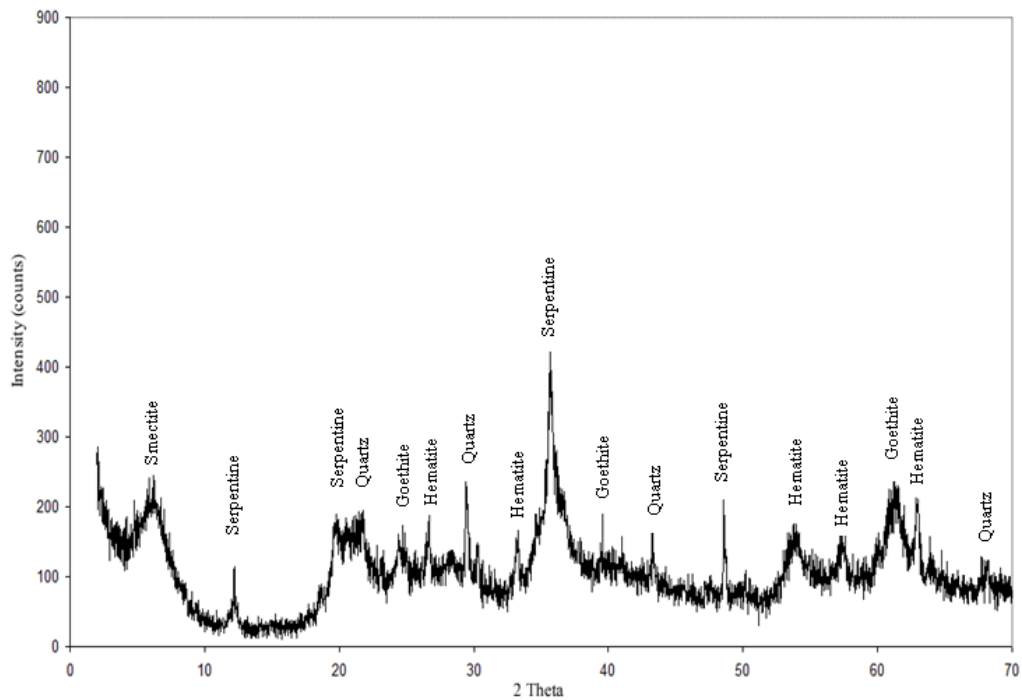
**Figure 3.2** XRD pattern of nontronite.

## 3.2 Methods

### 3.2.1 Materials Sampling

Material sampling was carried out for the nontronite ore by using coning and quartering method. In this method, aim was to homogenize the nontronite ore and to obtain a representative sample of the nontronite ore, which would be used in the subsequent experiments, by a special ore sampling technique. It was carried out by firstly heaping the ore as a uniform cone shape then smoothing the top part of the cone by putting a shovel on the top and turning the shovel three or four rounds on the circumference of the cone base while spreading the top part near the edges and making a circular form with uniform thickness, i.e. truncated cone. After a uniform circular shape of the heaped ore obtained, it was divided into four equal quarters and two opposite quarters were taken and packed into bags. The remaining quarters were collected and blended with the shovel then heaped into a uniform cone again. This procedure was repeated until a desired sample weight was obtained.

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### 3.2.2 Column Leaching Experiments

Column leaching experiments were performed in order to observe heap leaching behavior of the representative nontronite ore taken from the Gördes region [99]. Schematic drawing of the column leaching experimental set-up is shown in Figure 3.3.
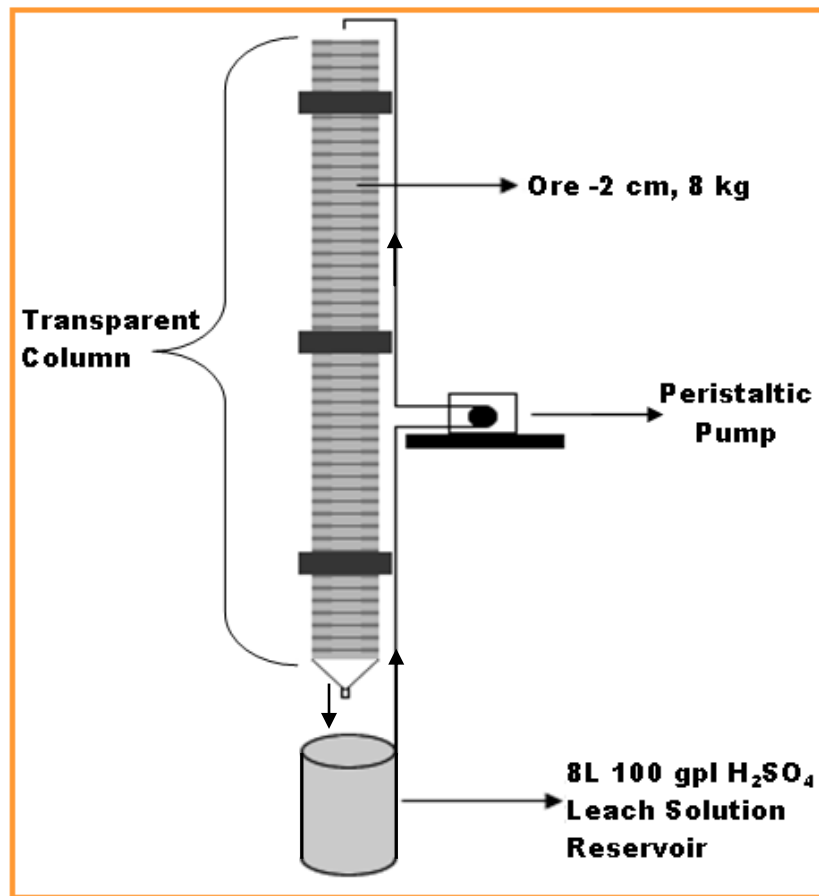


**Figure 3.3** Typical column leaching system.

The entire set-up for the leaching experiments was comprised of a number of columns, each of which had a 100 mm internal diameter and 1.25 m height mounted on a wall. A peristaltic pump was used for each column to render a cycle of solution flow. A specific amount of sulfuric acid of 95-98% w/w technical grade was added into a certain amount of deionized water then this sulfuric acid solution was introduced to the top of the column with the help of

the pump. While the sulfuric acid solution percolated through the ore in the column, the metal containing solution, PLS, collected in the reservoir which was placed under the column.

At the beginning of the column leaching, solution analyses were carried out once a week until the change in the acidity of the PLS became gradual, then they were analyzed once a month. In titration procedure, free acid presented in the PLS sample was determined by oxalate method in which di–potassium oxalate monohydrate [$K_2C_2O_4.H_2O$] was used to prevent interfering elements such as Fe from consuming hydroxide ions during titration. In the first step of titration, 20 cc of potassium oxalate solution with a concentration of 280 g/L was diluted by 5 cc of deionized water, then the pH of solution was waited to be stabilized between pH 7.00 and 8.00 during magnetic stirring. After the fixed pH of the solution was noted, 5 cc of PLS sample was added to the solution while the pH decreased to a certain value between 2.00 and 4.00. In the second step of titration, the solution was titrated with 0.2M sodium hydroxide [NaOH] solution in order for the decreased pH of the solution to return back to the noted initial pH value. Prior to each titration, pH electrode was calibrated using pH 7.00 buffer and oxidation-reduction potentials (ORP) of PLS samples were determined by Pt–Ag/AgCl (saturated with KCl) electrode. These ORP values could then be converted into the Standard Hydrogen Electrode (SHE) potential by adding 198 mV. At the end of the leaching period, the leach residue was unloaded from the column and washed for several times in a bowl with addition of new fresh water, which was continued for 7 days. Then, the leach residue was dried at 105°C for at least 2 days in a drying oven. Finally, the dried leach residue was ground to a fine size and sent to ICP and XRF analyses to find out the extraction values of metals from the leach residue.

In the column leaching of nontronite ore, preliminary leaching behavior of the representative nontronite ore was determined by conducting an experiment at

1/1 kg/L for solid/liquid ratio (1 kg of as-received nontronite ore per 1 L of leaching solution in the reservoir), 100 g/L for sulfuric acid concentration and 330 mL/hour (1000 L/day/m$^2$) for solution flow rate. At these constant conditions, 3 similar column leaching experiments of the nontronite ore were conducted for about 3 months with 85.5% Ni extraction [99]. Then, about 22 L PLS was collected by mixture of the pregnant leach solutions of these experiments. This PLS was stocked in a sealed plastic container.

### 3.2.3 Downstream Nickel and Cobalt Recovery Experiments

This thesis study started with using the stock of the PLS, obtained as it is stated above, in downstream nickel and cobalt recovery (MHP) experiments including neutralization and iron removal, nickel-cobalt precipitation and manganese and magnesium removal stages. This typical MHP process carried out in the study is shown briefly in Figure 3.4. It is important to note that recycle leach was not studied and Mg removal was only investigated after Mn precipitation and it was found to be effective by the addition of Ca(OH)$_2$ slurry up to the pH value of 10.00, but it was not found an economic process due to the consumption of excessive amount of slaked lime. At the end of the MHP process, the solution purified from heavy metals became the solution which could be re-used as process water in the plant, especially in thickeners.

Typical experimental set-up used in the experiments is shown in Figure 3.5. All the downstream purification and nickel and cobalt recovery experiments were carried out in 250 and/or 500 mL glass balloons with 4 necks. A condenser, a contact thermometer and a pH electrode were placed in the three available necks, while the reagents in the slurry form and seeds of precipitated solids were added through the feed neck.

Nontronite Ore

Column Leach

Sulphuric Acid and Water →

→ Leach Residue

Solution

Recycle Leach

Solution → PLS Stock

Leach Residue

<span style="color:red">From this line the thesis study started</span>

Precipitation Conditions Studied

Limestone —

Precipitates ←

First Iron Removal

→ pH, Temperature, Duration

Limestone —

Solution
pH 2.50 at 90°C

Precipitates ←

Second Iron Removal

→ pH, Temperature, Duration

Caustic Calcined Magnesia —

Solution
pH 4.25 at 70°C

Precipitates ←

First Mixed Hydroxide Precipitation

→ pH, Temperature, Duration

Slaked Lime —

Solution
pH 7.00 at 50°C

Precipitates ←

Second Mixed Hydroxide Precipitation

→ pH, Temperature, Duration

Slaked Lime —

Solution
pH 7.50 at 50°C

Precipitates ←

Manganese Removal

→ pH, Temperature, Duration

Solution
pH 8.50 at 50°C

- - - - - - - - - The dashed line indicates the process which was not studied but proposed for the future work.

**Figure 3.4** MHP process carried out in the thesis study.
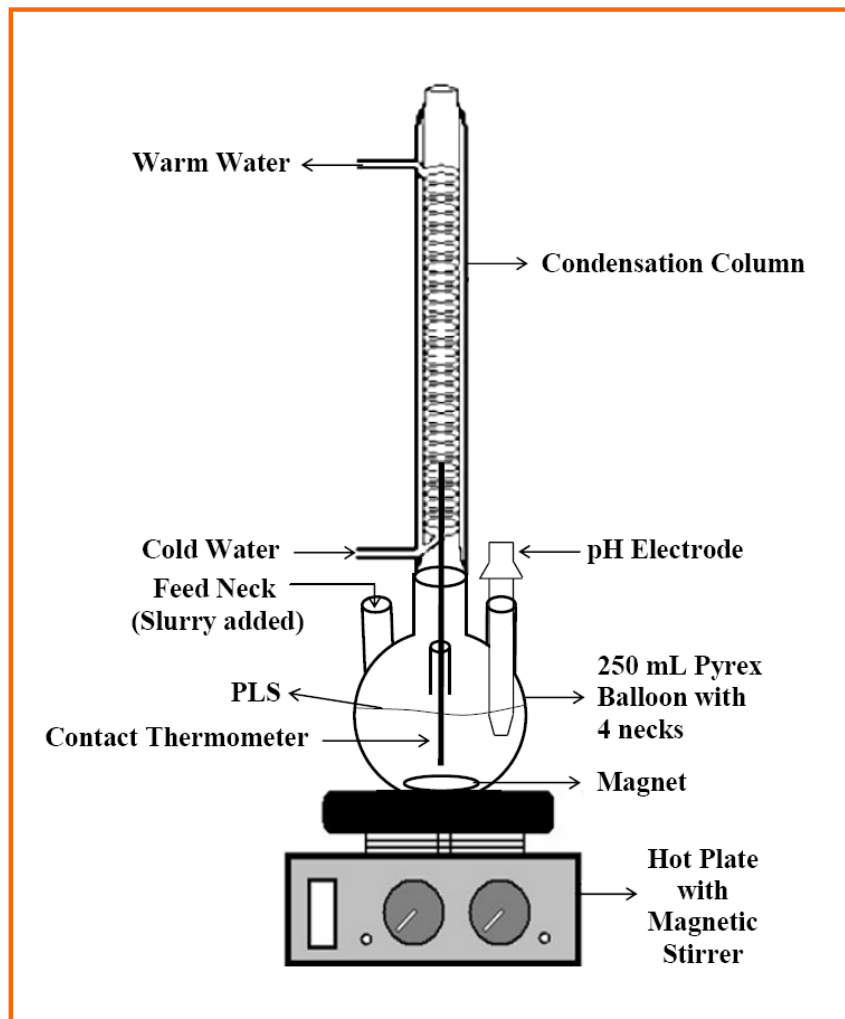
**Figure 3.5** Downstream (neutralization, purification, MHP1, MHP2, manganese and magnesium removal) experimental set-up.

After the precipitation experiments, each PLS was filtered through circle ashless filter paper (Wathman No 42/110mm) which was placed onto a Buchner funnel with a 1000 mL Pyrex flask. An acid resistant vacuum pump connected to the Pyrex flask was used for filtering process. Then, the precipitated solid was washed on the filter paper with enough deionized water and dried at 105°C for at least a day in a drying oven, while the filtrate was stocked in a bottle. At the end of each experiment, the filtrate obtained was sent for AAS analyses and the precipitate was analyzed at XRF or AAS units. Precipitation recovery calculations were carried out using precipitate weights

and solution volumes as well as AAS and XRF analyses data of the experiments.

### 3.2.3.1 First Iron Removal Experiments

Iron removal from the PLS by NaOH and $CaCO_3$ additions were studied. The experiments with NaOH yielded satisfying results but $CaCO_3$ was chosen since limestone is cheaper and more readily available. Therefore, a slurry of 25% w/w $CaCO_3$ was prepared by using 25 g pure $CaCO_3$ powder (~14 µm) (Merck 2066) which was mixed with 100 mL deionized water by a magnetic stirrer in a beaker at room conditions. 100 mL PLS samples taken from the PLS stock were used in each experiment. With the help of 5 mL pipette, the prepared homogeneous slurry of $CaCO_3$ was added into 100 mL PLS which was agitated with a magnetic stirrer in a 250 mL glass balloon. It was also necessary to add the slurry of $CaCO_3$ in a very slow manner drop by drop into the PLS, which took about 45-50 minutes while the pH gradually changed and was carefully controlled to prevent supersaturation of iron, aluminum and chromium in solution and the production of an amorphous precipitate which could deteriorate the filtration and settling characteristics. The first parameter to study was the variation of pH at fixed temperature ($90^oC$) and precipitation duration (2 hours). After the pH was decided to be the optimum, it was fixed for the subsequent experiments in which temperature and duration were studied and the same procedure was followed for precipitation temperature and duration optimization in turn. All the experiments were started after heating the solution and adding the required amount of the slurry of $CaCO_3$ into the heated solution. Furthermore, to keep pH at desired value during the experiments, a required amount of $CaCO_3$ slurry was also added. When the experiments were ended, each PLS was filtered through the above mentioned filter paper and the precipitated solid was washed and dried at 105°C for at least a day in a drying oven. Finally, the filtrates were sent to AAS analyses whereas the precipitates were sent to XRF analyses.

### 3.2.3.2 Second Iron Removal Experiments

The same procedure was followed as in the first iron removal experiments. For the second iron removal experiments, a new stock of PLS which was prepared by conducting the first iron removal process again at the optimum conditions was to be produced. For this purpose, 40 experiments were carried out using 100 mL PLS samples taken from the PLS stock and adding 48 mL $CaCO_3$ slurry (25% w/w) into solution in each experiment to maintain pH 2.50 at $90^{o}C$ of precipitation temperature and 2 hours of precipitation duration. These optimum conditions were previously decided after studying various conditions (pH, temperature and duration) in the first iron removal experiments. As a result of these experiments, Ni, Co and Fe analyses of the neutralized and partially purified pregnant leach solutions and produced precipitates were conducted for controlling purposes and each neutralized PLS was collected in a container for the second iron removal and the following MHP experiments. Totally, a new stock of 2.75 L neutralized PLS was collected. Metal concentration values in this new stock of PLS were determined by AAS analyses. Furthermore, the free acidity, density and ORP values of the produced stock of the PLS were measured.

Second iron removal experiments were conducted by using 50 mL of PLS samples taken from the stock of the neutralized PLS and applying the same procedure as in the first iron removal experiments at higher pH values by adding $CaCO_3$ slurry (12.5% w/w) into solution with a pipette drop by drop in a slow manner (in 45 minute). In the first set of experiments, different pH values of the PLS were studied at different precipitation temperatures ($25^{o}C$, $70^{o}C$, $90^{o}C$) and fixed precipitation duration (1 hour). Then, pH value of the PLS was set to 4.25 by adding the required amount of $CaCO_3$ slurry into solution and experiments at various temperatures were studied at 1 hour of precipitation duration. In the final set of experiments, precipitation duration was studied at fixed pH (4.25) and precipitation temperature ($70^{o}C$).

### 3.2.3.3 First Mixed Hydroxide Precipitation (MHP1) Experiments

For the first mixed hydroxide precipitation (MHP1) experiments, a new stock of PLS which was prepared by conducting the second iron removal process again on the remaining stock of the neutralized PLS at the optimum conditions had to be produced. For this purpose, 7 experiments were carried out using 250 mL PLS samples from the stock and adding 27.25 mL $CaCO_3$ slurry (12.5% w/w) into solution to maintain pH 4.25 at 70$^o$C of precipitation temperature and 1 hour of precipitation duration. These optimum conditions were previously decided after studying various conditions (pH, temperature and duration) in the second iron removal experiments. As a result of the experiments, Ni, Co, Fe, Cr, Al, Mn and Mg analyses of the purified pregnant leach solutions and precipitates were conducted for controlling purposes and each purified PLS was collected in a container for the first mixed hydroxide precipitation experiments. Totally, a new stock of 1.75 L purified PLS was collected. Metal concentration values in this stock of PLS were determined by AAS analyses. Furthermore, the free acidity, density and ORP values of the new stock of PLS were measured.

The MHP1 experiments were conducted by using 50 mL of PLS samples taken from the new stock of purified PLS in which the first and second iron removal processes had been completed. Procedure in MHP1 experiments was similar to the first and second iron removal experiments except that the precipitating reagent was very fine powder of magnesia (98-100.5% MgO) in Merck 5862 quality. The magnesia which was kept away from $CO_2$ and moisture of air in a sealed container was used freshly in slurry form by mixing it with deionized water using a magnetic stirrer in a beaker at room temperature just before each experiment. In order to prepare the slurry, 0.50 g MgO was added into 50 mL deionized water (1% w/w slurry) contained in a beaker. The prepared slurry was slowly added drop by drop in 30-40 minutes with the help of a 5 mL pipette. First set of experiments were conducted at

fixed precipitation temperature ($50^{o}$C) and precipitation duration (1 hour) to determine the amount of MgO which would be added to precipitate nickel and cobalt in the solution as much as possible, while keeping the manganese precipitation below a certain value. To find the optimum pH condition for the MHP1, the volume of MgO slurry added was controlled after a stoichiometric calculation in order to precipitate desired Ni and Co, instead of conducting experiments directly following pH change due to the difficulties experienced in controlling the pH during the precipitation. Therefore, MgO slurry volume was carefully changed between 7.0 mL and 12 mL in the first set of experiments. In the second set of experiments, different precipitation temperatures were studied at fixed 10 mL MgO slurry volume and the optimum condition for the temperature was determined. In the final set of experiments, precipitation duration was studied at the fixed MgO slurry addition (10 mL) and precipitation temperature ($50^{o}$C).

### 3.2.3.4 Second Mixed Hydroxide Precipitation (MHP2) Experiments

For the second mixed hydroxide precipitation (MHP2) experiments, a new stock of solution which was prepared by conducting MHP1 again on the remaining stock of the purified PLS at the optimum conditions had to be produced. For this purpose, 5 experiments were carried out using 250 mL solution samples taken from the stock of the purified PLS in which the first and second iron removal process had been completed by adding 40 mL MgO slurry (1% w/w) into solution to maintain pH 7.00 at $50^{o}$C of precipitation temperature and 1 hour of precipitation duration. These optimum conditions were previously decided after studying various conditions (pH, temperature and duration) in MHP1 experiments. As a result of the experiments, Ni, Co, Fe, Cr, Al, Mn and Mg analyses of the residual leach solutions and precipitates were conducted for controlling purposes and each residual solution was collected in a container for the second mixed hydroxide precipitation experiments. Totally, a stock of 1.25 L residual solution was

collected. Metal concentration values in this new residual solution stock were also determined by AAS analyses. Furthermore, the free acidity, density and ORP values of the new solution stock were measured.

MHP2 experiments were conducted by using 50 mL of solution samples taken from the new stock of solution in which the first and second iron removal and also MHP1 had been completed. Procedure in MHP2 experiments was similar to MHP1 experiments except that the precipitating reagent was very fine powder of slaked lime $[Ca(OH)_2>96\%, CaCO_3\leq3\%]$ of Merck 2027 quality. The slaked lime which was kept away from air in a sealed container was used freshly in slurry form by mixing 0.50 g $Ca(OH)_2$ with 50 mL deionized water with a magnetic stirrer in a beaker at room temperature before each experiment. The slaked lime slurry (1% w/w) prepared in the beaker was slowly added drop by drop in 30-40 minutes with the help of a 5 mL pipette. First set of experiments were started at fixed precipitation temperature ($60^{o}C$) and precipitation duration (1 hour) to determine the amount of $Ca(OH)_2$ which would be needed to precipitate expected amount of elements. Second set of experiments were done at fixed pH (7.50) and precipitation temperature ($50^{o}C$) and continued at another fixed pH (7.75) and precipitation temperature ($60^{o}C$). In the final set of experiments, precipitation duration was studied at fixed pH (7.50) and precipitation temperature ($60^{o}C$).

### 3.2.3.5 Manganese Removal (MnR) Experiments

For the manganese removal experiments, a new stock of solution was prepared by conducting MHP2 on the remaining stock of the residual solution of MHP1 at the optimum conditions. For this purpose, 2 experiments were carried out using 400 mL solution samples taken from the remaining stock of the solution in which the first and second iron removal and MHP1 had been completed by adding 57.4 mL slaked lime slurry (1% w/w) into solution to maintain pH 7.50 at $50^{o}C$ of precipitation temperature and 3 hours of

precipitation duration. These optimum conditions were previously decided after studying various conditions (pH, temperature and duration) in MHP2 experiments. As a result of the experiments, Ni, Co, Mn and Mg analyses of the residual solutions and precipitates were conducted for controlling purposes and each residual solution was collected in a container for the manganese removal experiments. Totally, a new stock of 800 mL residual solution was obtained. Metal concentration values in this solution stock were determined by AAS analyses. Furthermore, the free acidity, density and ORP values of the new solution stock were measured.

Manganese removal experiments were conducted by using 50 mL of solution samples taken from the new stock of solution in which the first and second iron removal and MHP1 and MHP2 processes had been completed. Procedure in the manganese removal experiments was similar to MHP2 experiments such that the precipitating reagent was slaked lime, the same used in the MHP2 process. Likewise, slaked lime was used freshly in slurry form by mixing it with deionized water using a magnetic stirrer in a beaker at room temperature before each experiment. 10 g $Ca(OH)_2$ was added into 50 mL deionized water for the preparation of the slurry in the beaker. The prepared slurry (20% w/w) was slowly added again drop by drop in 30-40 minutes with the help of a 5 mL pipette. First set of experiments were started at fixed precipitation temperature ($50^oC$) and precipitation duration (1 hour) to determine the amount of $Ca(OH)_2$ which would be added to precipitate expected amount of elements. Second set of experiments were carried out at fixed pH (8.50) and precipitation duration (1 hour). In the final set of experiments, precipitation duration was studied at fixed pH (8.50) and precipitation temperature ($50^oC$).

### 3.2.3.6 Magnesium Removal Experiments

A limited number of experiments were also done in order to precipitate Mg from the remaining solution. For this purpose a solution purified of Fe, As, Cr, Al and gone through MHP1 and MHP2 as well as Mn purification process at the optimum conditions determined was used. The precipitating reagent was again $Ca(OH)_2$. The experimental results indicated that the consumption of reagent was excessive due to buffering effect. So, it was decided not to report the magnesium precipitation results within the content of this study.

### 3.3 Chemical Analysis

The chemical analyses of PLS were conducted by using AAS method while dried and ground fine solid precipitates were generally analyzed using XRF and AAS methods. The chemical analysis of the PLS stock used throughout this study is shown in Table 3.4. In addition, analyses of the precipitates produced at the optimum conditions by the first-second iron removal, MHP1-MHP2 and manganese removal experiments were carried out by AAS and wet chemical analyses methods.

**Table 3.4** Chemical analysis of PLS stock by AAS.

| Components of PLS | Concentration (ppm) |
|---|---|
| Ni | 4800 |
| Co | 114 |
| Fe | 38600 |
| $Fe^{2+}$ | 0.34 |
| Mg | 16750 |
| Al | 3950 |
| Ca | 104 |
| Mn | 620 |
| Cr | 1060 |
| As | 46 |
| Zn | 31.5 |
| Cu | 3.8 |
| $H_2SO_4$ | 14600 |

# CHAPTER 4


# RESULTS AND DISCUSSIONS



Typical MHP process carried out in this study is shown briefly in Figure 3.4. The MHP process was repeated twice by doing more than 200 experiments and studying various parameters to find the optimum conditions in each stage to recover nickel and cobalt in a saleable form of hydroxide from the PLS which was previously produced by the column leaching of the nontronite ore. The MHP process followed during the thesis study was composed of two-stage neutralization and iron purification, a two-stage nickel-cobalt precipitation and a manganese removal processes. Although any recycle leach was not studied, it was put into the MHP circuit and assumed that at least 95% nickel-cobalt extraction recoveries were achieved. Each stage started after the results of the experiments in the previous stage were gathered and the new stock of PLS was produced at the optimum conditions determined as it was explained in Chapter 3. The promising results obtained from the MHP process showed that hydrometallurgical processing of lateritic nickel ores was feasible and MHP, a new integrated nickel recovery method from the leach solution at atmospheric condition, resulted in great advantages for the recovery of nickel and cobalt from the low grade laterite ores both efficiently and economically. In the study, it was observed that the results of the MHP process conducted were very similar to those found in the literature.

The AAS analysis of 22 L of PLS stock is shown in Table 3.4. In this solution stock, 14.6 g/L residual free acid was present. The ORP (or SHE) value and the density of the PLS stock were 675 mV (or 873 mV) and 1.24 $g/cm^3$, respectively. To compare, as it is stated in Chapter 1, Willis reported that PLS produced from heap leaching at ambient temperature contains typically 2000-4000 ppm Ni, 30000-50000 ppm $H_2SO_4$, 15000-30000 ppm Fe and 2000-5000 ppm Al [69] while Agatzini et al. noted that a typical composition of the PLS from heap leaching of Greek low-grade nickeliferous laterites with sulfuric acid is made up of 5000 ppm Ni, 300 ppm Co, 23000 ppm Fe, 6000 ppm Al, 1000 ppm Cr, 1000 ppm Mn and 8000 ppm Mg [30]. Most of these concentration values reported are very close to the values given in Table 3.4 except that sulfuric acid concentration is more than twice in Willis's report due to higher acid consumers (Al and Mg) in the ore composition. Furthermore, the concentration of Fe and Mg are less and Al is higher in some degree in Agatzini's paper attributed to the typical Greek laterite in which iron and magnesium oxides are less and aluminum oxides greater than that were found in the nontronite ore used in the study. The results of the first and the second iron removal, MHP1-MHP2 and the manganese removal experiments are given in detail and interpreted in the following parts.

## 4.1 First Iron Removal

In the first iron removal experiments, the optimum conditions were investigated to remove as much iron and other impurities as possible together with $H_2SO_4$ from the PLS using 25% w/w $CaCO_3$ slurry as both neutralizing and precipitating agent provided that very small amounts of nickel and cobalt were lost to the precipitate (<0.5%). The main aim was to neutralize acid and precipitate iron as much as possible, because Fe was the impurity of the highest quantity in the PLS and it could be precipitated at lower pH, without losing notable nickel and cobalt to the precipitate. Also, aluminum and chromium were partially precipitated.

### 4.1.1 Effect of pH

In the first set of experiments, effect of pH was studied with 25% w/w $CaCO_3$ slurry aiming to determine the optimum pH value at which maximum iron together with aluminum and chromium precipitation would occur with the minimum nickel and cobalt losses. At the fixed conditions (90$^o$C of precipitation temperature and 2-hour precipitation duration) pre-determined from the literature [30, 69, 70, 79, 89], precipitation recoveries with respect to various pH values were recorded and pH 2.50 was found to be the most effective pH and was decided to be the optimum. An example of precipitation recovery calculation by using the results of AAS analysis of the PLS and XRF analysis of the precipitate is given in Appendix A. The results of the precipitation recovery calculations are shown in Table 4.1.

**Table 4.1** Precipitation recoveries with respect to pH of PLS at 90$^o$C of precipitation temperature and 2-hour precipitation duration.

| pH | Fe (%) | Ni (%) | Co (%) | Mn (%) | Cr (%) | Al (%) | Cu (%) | Zn (%) |
|------|--------|--------|--------|--------|--------|--------|--------|--------|
| 2.00 | 81.0 | 0.3 | 0.4 | 7.2 | 17.5 | 17.9 | 0.0 | 0.0 |
| 2.25 | 91.0 | 0.4 | 0.4 | 9.2 | 71.6 | 39.2 | 0.0 | 0.0 |
| 2.50 | 99.0 | 0.4 | 0.4 | 10.3 | 73.7 | 55.8 | 7.0 | 0.0 |
| 2.75 | 99.2 | 1.8 | 1.6 | 13.2 | 83.7 | 79.1 | 24.1 | 0.0 |
| 3.00 | 99.4 | 3.9 | 6.2 | 13.5 | 83.9 | 87.6 | 54.3 | 0.0 |
| 3.25 | 99.9 | 4.4 | 6.9 | 14.6 | 97.5 | 89.4 | 86.9 | 13.9 |
| 3.50 | 100.0 | 15.7 | 16.1 | 19.3 | 99.6 | 92.6 | 92.8 | 24.2 |
| 3.75 | 100.0 | 17.7 | 22.5 | 24.1 | 99.9 | 98.9 | 93.7 | 32.0 |

In order to prevent significant Ni and Co losses and to remove iron from the PLS at an efficient degree, pH had to be kept below 2.75 and controlled favorably at about 2.50. Iron could be removed from the PLS to a residual concentration of less than 300 ppm at pH 2.50, while Willis noted that it could be possible to remove Fe to less than 200 ppm at pH 2.50-3.00 [69] which was also be achieved in the first iron removal experiments. In addition, as it is apparent in Table 4.1, more than 50% of aluminum and 70% of chromium were removed at pH 2.50 so that most of the impurities of the PLS were significantly decreased by the first addition of $CaCO_3$ in slurry form which resulted in a cleaner solution from which better nickel recovery conditions in

subsequent ammonia leaching step after MHP would be possible. The graphical presentations of the precipitation recoveries of Ni, Co, Mn, Fe, Al and Cr with respect to pH at $90^{\circ}C$ of precipitation temperature and 2-hour precipitation duration are given in Figures 4.1 and 4.2.
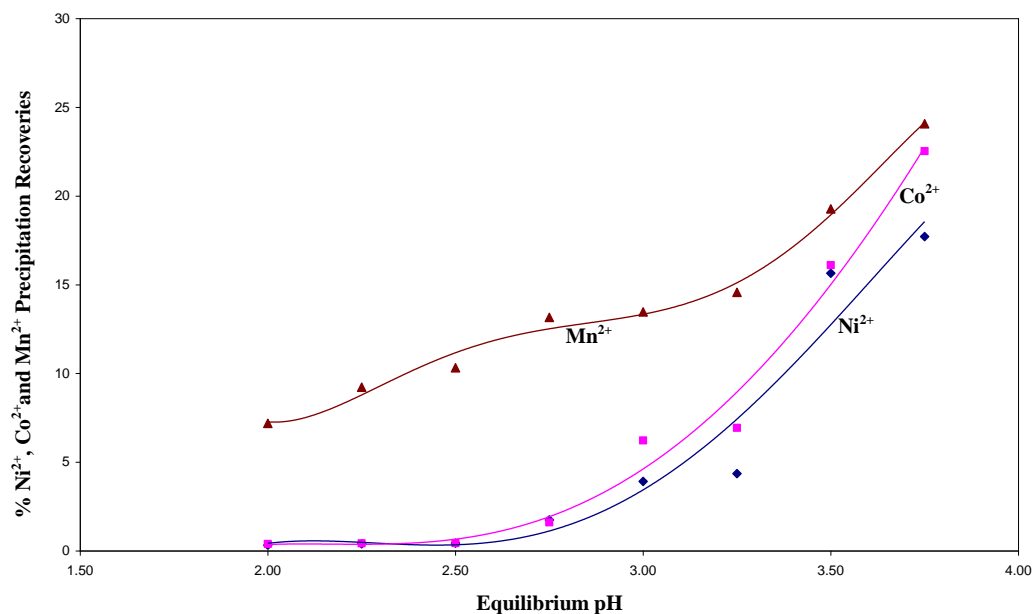


**Figure 4.1** Precipitation recoveries (%) of nickel, cobalt and manganese with respect to pH at $90^{\circ}C$ of precipitation temperature and 2-hour precipitation duration.
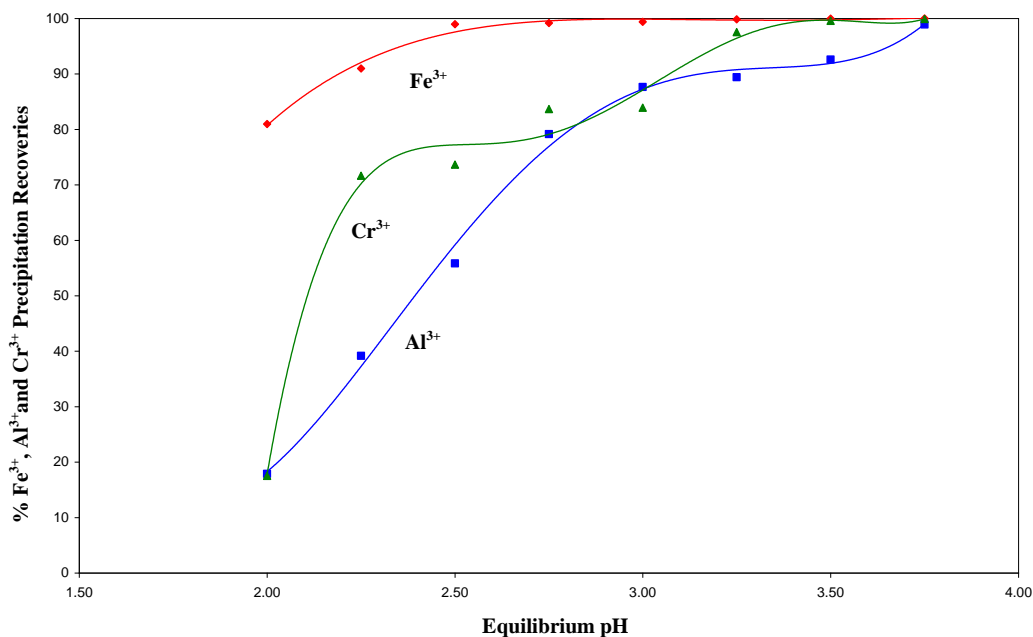


**Figure 4.2** Precipitation recoveries (%) of iron, aluminum and chromium with respect to pH at $90^{\circ}C$ of precipitation temperature and 2-hour precipitation duration.

At pH 2.50 the precipitation recoveries of nickel and cobalt were below 1% and that of iron was about 99% which satisfied the desired conditions. After pH 2.50, there was a gradual increase in the loss of nickel and cobalt while more than 3% of Ni and 6% of Co in solution lost between pH 3.00 and 3.25 and there was a sharp increase beyond pH 3.25. Almost all of iron, most of which was in ferric state in the PLS was precipitated up to pH 2.50 by the addition of $CaCO_3$ slurry. Agatzini and Oustadakis reported that at pH 2.50, 90.2% of iron, 60.9% of Al and 65.1% of Cr were precipitated with only 2.4% Ni and 1.70% Co losses by the addition of MgO slurry with water (100gpl) and seed of jarosite precipitate into a feed leach liquor solution at 95$^{o}$C [89]. More or less the values obtained at pH 2.50 are close to the percentages in the Agatzini and Oustadakis's paper with less nickel and cobalt precipitation values determined. At pH 3.50, 100% of Fe, 92.6% of Al, and 99.6% of Cr were precipitated which were similar to the values reported by Agatzini et al. [30]. But, both Ni-Co losses more than 5% were not desirable and should not be allowed to be lost in the precipitate. Thus, pH 2.50 was decided to be the optimum pH for the first iron precipitation.

## 4.1.2 Effect of Precipitation Temperature

In the second set of experiments, the precipitation temperatures between 25$^{o}$C and 90$^{o}$C were studied at pH 2.50 and 2-hour precipitation duration using 25% w/w $CaCO_3$ slurry to determine the optimum precipitation temperature and to check the pre-determined temperature in the first set whether it was the optimum precipitation temperature. Results of the second set of experiments are given in Table 4.2. It was observed that there was a distinct increase in the precipitation of all the metals depending on the rising precipitation temperature.

**Table 4.2** Precipitation recoveries with respect to precipitation temperature at pH 2.50 and 2-hour precipitation duration.

| T$^o$C | Fe (%) | Ni (%) | Co (%) | Mn (%) | Cr (%) | Al (%) | Cu (%) |
|---|---|---|---|---|---|---|---|
| **25** | 5.8 | 0.0 | 0.1 | 7.5 | 63.3 | 0.0 | 0.0 |
| **50** | 21.3 | 0.1 | 0.2 | 8.1 | 67.7 | 36.5 | 0.0 |
| **75** | 77.5 | 0.1 | 0.3 | 9.4 | 68.5 | 45.4 | 0.0 |
| **90** | 99.0 | 0.4 | 0.4 | 10.3 | 73.7 | 55.8 | 7.0 |

In the graphical forms, the presentations of the precipitation recoveries of Ni, Co, Mn, Fe, Al and Cr with respect to precipitation temperature are given in Figures 4.3 and 4.4. So, 90$^o$C of precipitation temperature was decided to be the optimum precipitation temperature to achieve maximum iron precipitation with insignificant Ni and Co losses as well as yielding fast reaction kinetics and decreasing slurry viscosity for better filtration properties of precipitate. It was also checked that the experiments in the first set of experiments had been carried out at the optimum precipitation temperature. On the other hand, as it is stated in Chapter 2, operations at ambient temperature cause poor reaction kinetics leading to time consuming reactions for desired recoveries. Thus, precipitation temperatures between 70 and 95$^o$C, or at the boiling temperature of the PLS were preferred to study more to obtain the required conditions above.
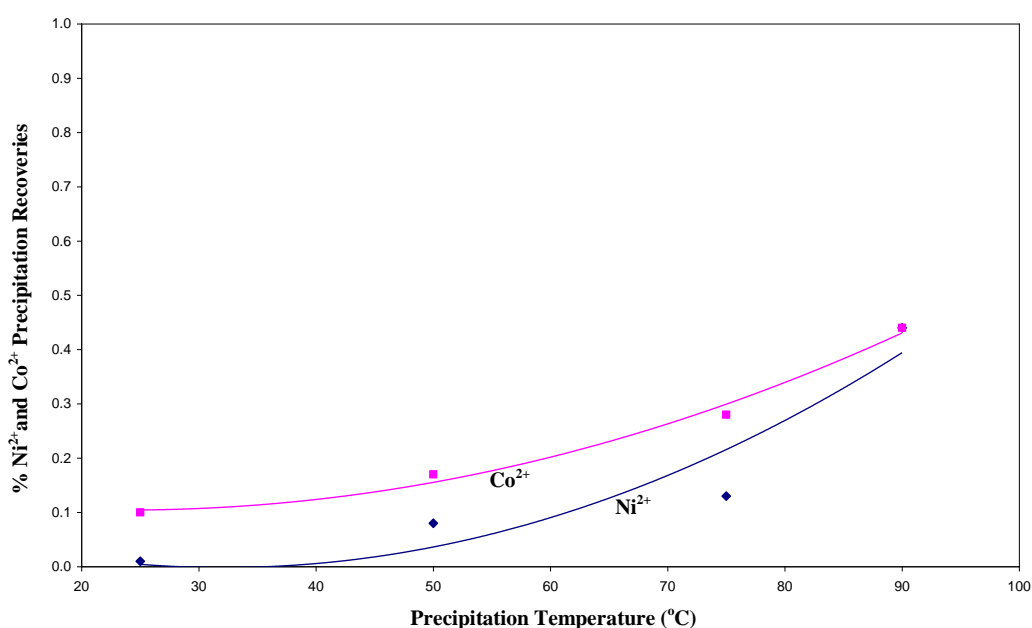


**Figure 4.3** Precipitation recoveries (%) of nickel and cobalt with respect to precipitation temperature at pH 2.50 and 2-hour precipitation duration.

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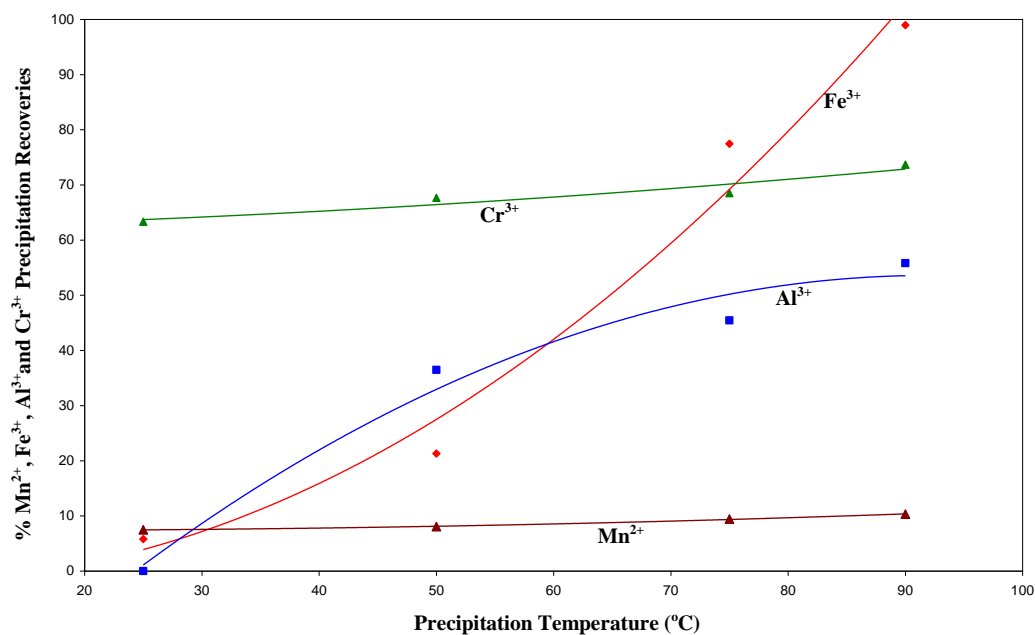
**Figure 4.4** Precipitation recoveries (%) of manganese, iron, aluminum and chromium with respect to precipitation temperature at pH 2.50 and 2-hour precipitation duration.

## 4.1.3 Effect of Precipitation Duration

In the third set of experiments, the precipitation durations between 0.5 and 4 hours were studied at pH 2.50 and $90^{\circ}C$ of precipitation temperature using 25% w/w $CaCO_3$ slurry aiming to determine the optimum precipitation duration at which maximum iron together with aluminum and chromium precipitation would occur provided that nickel and cobalt losses were minimized. As it is stated in Chapter 2, precipitation duration is generally between 90 and 180 minutes combined residence time [69]. Therefore, 2 hours had been chosen as the precipitation duration in the first set of experiments and now it was also tested whether it was the optimum for the specified condition; pH 2.50 and $90^{\circ}C$ of precipitation temperature. Precipitation recoveries with respect to precipitation duration resulted from the experiments at pH 2.50 and $90^{\circ}C$ of precipitation temperature are shown in Table 4.3. In the graphical form, the precipitation recoveries of Ni, Co, Mn, Fe, Al and Cr with respect to precipitation duration are shown in Figures 4.5 and 4.6.

**Table 4.3** Precipitation recoveries with respect to precipitation duration at pH 2.50 and 90$^o$C of precipitation temperature.

| Duration (hour) | Fe (%) | Ni (%) | Co (%) | Mn (%) | Cr (%) | Al (%) | Cu (%) |
|---|---|---|---|---|---|---|---|
| 0.5 | 87.0 | 0.2 | 0.4 | 7.9 | 66.9 | 22.9 | 0.0 |
| 1.0 | 93.7 | 0.2 | 0.4 | 8.1 | 67.5 | 23.3 | 1.4 |
| 1.5 | 98.3 | 0.3 | 0.4 | 8.2 | 68.3 | 53.5 | 1.7 |
| 2.0 | 99.0 | 0.4 | 0.4 | 10.3 | 73.7 | 55.8 | 7.0 |
| 4.0 | 99.6 | 11.2 | 4.4 | 11.3 | 89.1 | 89.3 | 13.6 |

In order to attain the desired iron, aluminum and chromium precipitations and sufficient reaction time for metal precipitations and bassanite crystallization, the precipitation duration had to be long enough. However, it was also needed to yield minimum nickel and cobalt losses to the precipitate. Therefore, 2 hours of precipitation duration was chosen as the optimum since about 99% of iron and less than 0.5% of nickel and cobalt could be precipitated as well as approximately 74% of chromium and 56% of aluminum precipitated at the first stage of iron removal. In addition, CaCO$_3$ slurry addition rate was kept low within precipitation duration to prevent supersaturation of Fe, Al and Cr.
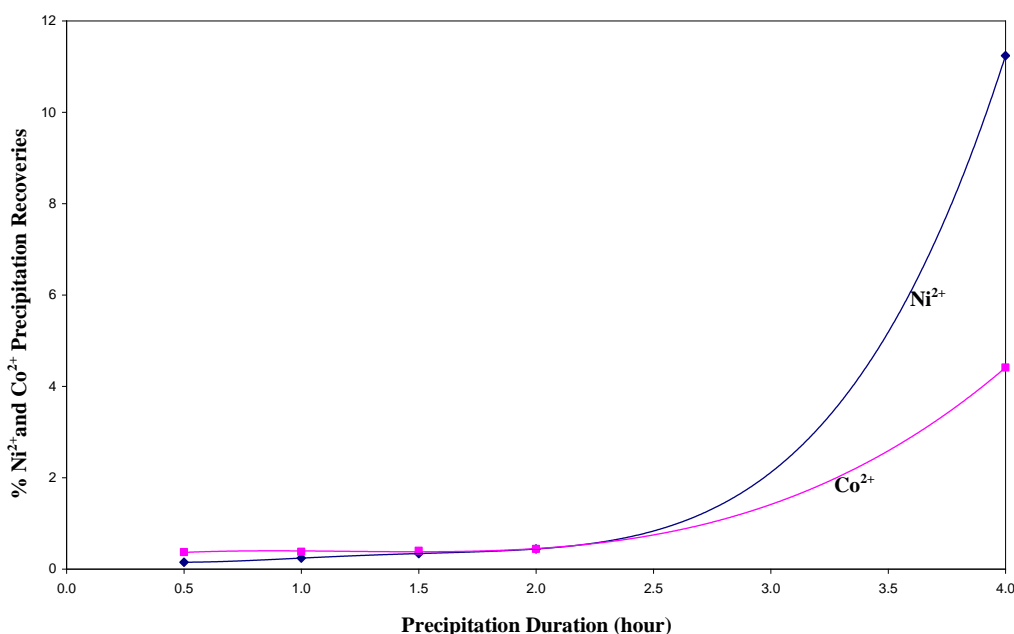


**Figure 4.5** Precipitation recoveries (%) of nickel and cobalt with respect to precipitation duration at pH 2.50 and 90$^o$C of precipitation temperature.
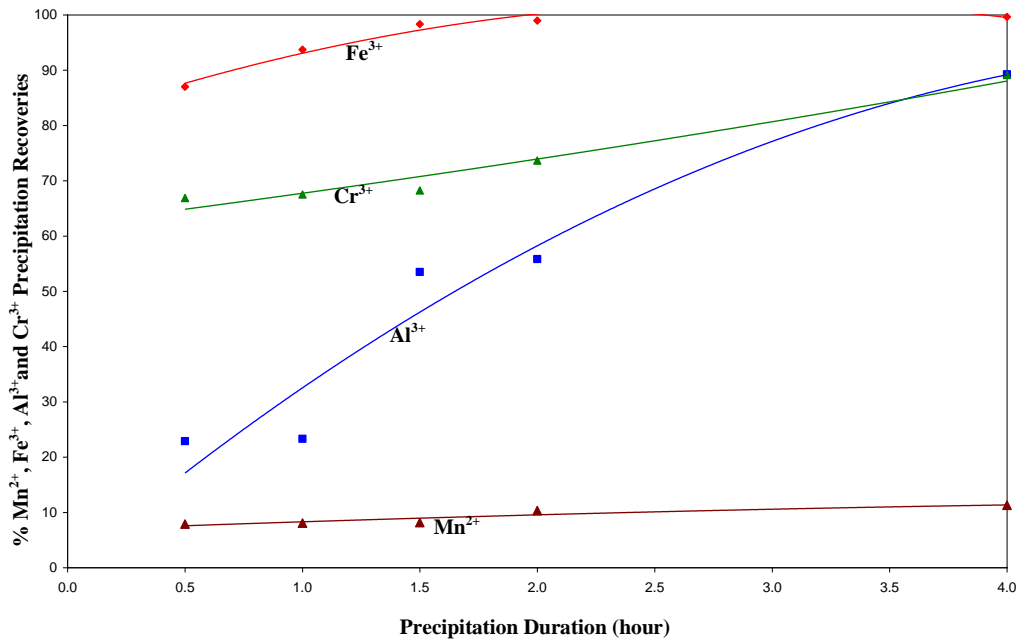
**Figure 4.6** Precipitation recoveries (%) of manganese, iron, aluminum and chromium with respect to precipitation duration at pH 2.50 and 90$^o$C of precipitation temperature.

At the end of the third set of experiments, the optimum conditions for the first iron removal step were finally determined as pH 2.50, 90$^o$C of precipitation temperature and 2 hours of precipitation duration. At these conditions, the amount of CaCO$_3$ slurry consumed was 48 cc (12 g CaCO$_3$ / 100 cc PLS) (120 kg CaCO$_3$ / m$^3$ PLS) and the weight of the precipitate after the first iron removal was 24.5 g for 100 cc PLS. Free acidity of PLS was reduced from 14.6 g/L to 1.4 g/L according to Reaction 4.1 by consuming 5 cc 25% w/w CaCO$_3$ slurry (1.25 g CaCO$_3$ / 100 cc PLS) (12.5 kg CaCO$_3$ / m$^3$ PLS) (0.95 kg CaCO$_3$ / kg H$_2$SO$_4$).

$$CaCO_{3(s)} + H_2SO_4 \longrightarrow CaSO_4 + CO_{2(g)} + H_2O \tag{4.1}$$
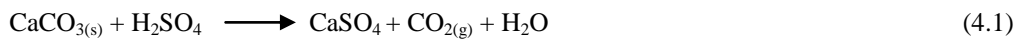
After the first iron removal step, about 91% of arsenic, 7% of copper, 10% of manganese and 3% of magnesium were also precipitated together with great amount of iron, while the amount of calcium in solution was determined to be increased because of the addition of CaCO$_3$ as slurry. The precipitate analysis

is given in Table 4.5. The increase of calcium in both the precipitate and the PLS are apparent in Tables 4.4 and 4.5.

**Table 4.4** Composition analysis of the precipitate produced from the PLS by the first iron removal process at the optimum conditions.

| Components of the precipitate | Value (%w/w dry) |
|:---:|:---:|
| Ni | 0.009 |
| Co | 0.0002 |
| Fe | 15.6 |
| Ca | 16.8 |
| Mn | 0.026 |
| Al | 0.9 |
| Cr | 0.3 |

High percentages of Fe and Ca were present in the precipitate. Some Al and Cr also precipitated at the optimum conditions, with only very low Ni and Co losses. It is important to note that Fe, Al, Cr impurities in the PLS had been decided to be removed during the two-stage iron removal process in order to lose minimum amount of nickel and cobalt so that the percentages obtained were less than the one-stage processes reported in the literature [30, 89]. The precipitates obtained from the experiments settled down quickly and were easily filtered. They showed similar characteristics; filterability, color and brittleness. However, it was observed by trial experiments that filterability, crystallinity and color could change when the rate of $CaCO_3$ addition was increased attributed to the supersaturation of iron, aluminum and chromium rendering to amorphous precipitates which were difficult to filter out as well as less time for atoms to be in crystalline state. The X-Ray diffraction data of the precipitate produced from the PLS at the optimum conditions using 25% w/w $CaCO_3$ slurry is shown in Figure 4.7.

1. CaSO₄.0.5H₂O-Bassanite
2. CaSO₄.2H₂O-Gypsum
3. Fe₂O₃-Hematite
4. α-FeOOH-Goethite
5. CaCO₃-Calcite
6. Ca₃Al₂(OH)₁₂-Katoite
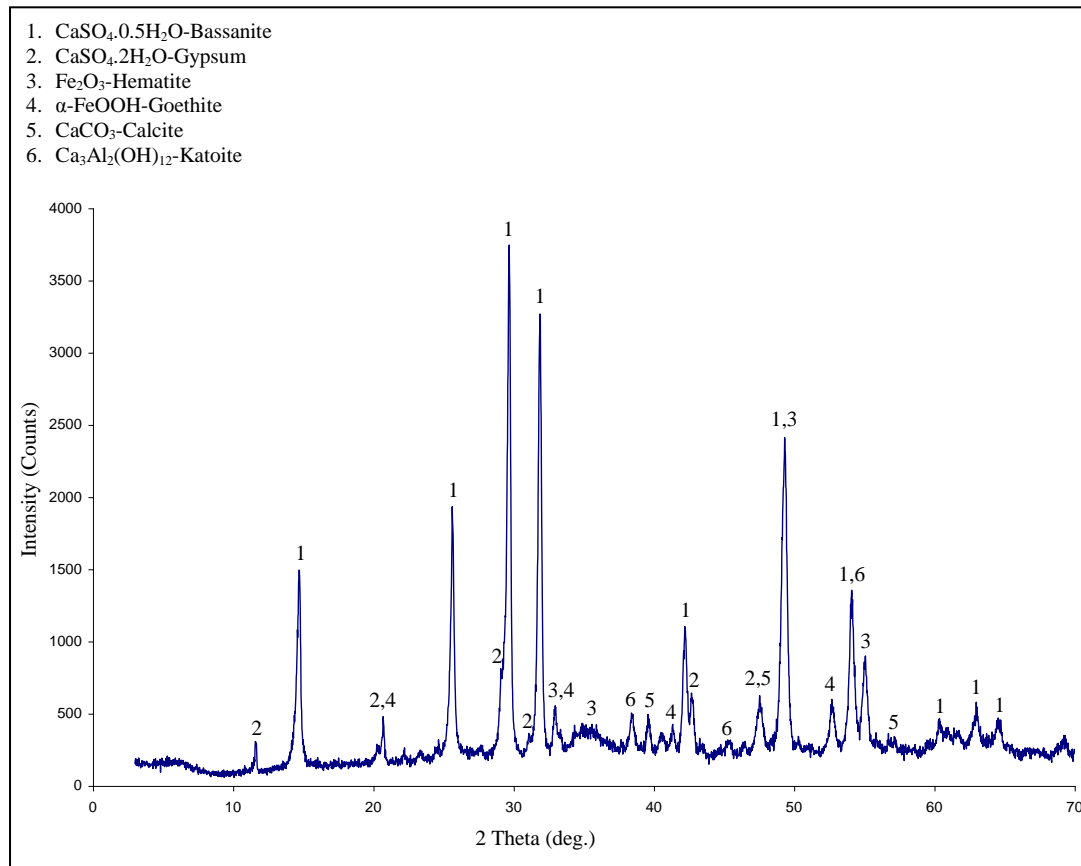
**Figure 4.7** XRD pattern of the precipitate produced from the PLS by the first iron removal process at pH 2.50, 90°C of precipitation temperature and 2 hours of precipitation duration with addition of $CaCO_3$ slurry.

The main mineralogical phase was bassanite [$CaSO_4.0.5H_2O$] and other phases were gypsum [$CaSO_4.2H_2O$], hematite [$Fe_2O_3$] and goethite [α-FeOOH] together with some calcite [$CaCO_3$] and katoite [$Ca_3Al_2(OH)_{12}$]. Iron, mostly in ferric state, precipitated as goethite and hematite from the PLS since ferric iron precipitates from the solution resulted from the $CaCO_3$ slurry addition as in Reactions 4.2 and 4.3. Mostly bassanite was formed and for higher moles of $H_2O$, gypsum was precipitated.

$$3CaCO_{3(s)} + Fe_2(SO_4)_3 + 2.5H_2O \longrightarrow 3CaSO_4.0.5H_2O_{(s)} + 2FeOOH_{(s)} + 3CO_{2(g)} \qquad (4.2)$$

$$3CaCO_{3(s)} + Fe_2(SO_4)_3 + 1.5H_2O \longrightarrow 3CaSO_4.0.5H_2O_{(s)} + Fe_2O_{3(s)} + 3CO_{2(g)} \qquad (4.3)$$

The main peaks, which correspond to [CaSO$_4$.0.5H$_2$O], were sharper and with greater intensity, compared with other peaks which displayed lower intensity and higher peak width. The differences between phases caused by the differences in the degree of crystallinity of the products and some phases such as bassanite rendered a better-crystallized compound. Furthermore, there were no nickel, cobalt, manganese and chromium containing phases detected which was attributed to their low content in the precipitate as seen in Table 4.4. At the end of the first iron removal process, a new PLS stock which would be used in the second iron removal process was produced by carrying out the first iron removal at the optimum conditions. The AAS analysis of the new stock of 2.75 L neutralized PLS is illustrated in Table 4.5. In the PLS stock, 1.4 g/L free acid was present. The ORP (or SHE) value and the density of the PLS stock were 475 mV (or 673 mV) and 1.08 g/cm$^3$, respectively.

**Table 4.5** Chemical analysis by AAS of the new PLS stock produced by the first iron removal process at the optimum conditions.

| Components of PLS | Concentration (ppm) |
|:---:|:---:|
| Ni | 3450 |
| Co | 82 |
| Fe | 290 |
| Fe$^{2+}$ | 0.08 |
| Mg | 11750 |
| Al | 1260 |
| Ca | 162 |
| Mn | 401 |
| Cr | 202 |
| As | 3 |
| Zn | 22.7 |
| Cu | 2.6 |
| H$_2$SO$_4$ | 1400 |

**4.2 Second Iron Removal**

In the second iron removal experiments, the optimum conditions were studied to remove the remaining aluminum (Al$^{3+}$), chromium (Cr$^{3+}$) and iron (Fe$^{3+}$)

completely from the new PLS with some but minimum amount of nickel and cobalt losses to the precipitate which would be regained during the recycle leach. The aim of the second iron removal experiments was to precipitate all the remaining impurities, except $Mn^{2+}$ and $Mg^{2+}$, in the PLS by adding $CaCO_3$ slurry into the neutralized and partially purified PLS without much caring for nickel and cobalt losses to the precipitate unless they were excess. Because after the second iron removal, all the expected decreased impurity levels in the PLS had to be achieved.

### 4.2.1 Effect of pH

In the first set of experiments, pH variations were studied in the range of 3.50-5.25 aiming to determine the optimum pH value at which the maximum aluminum, chromium and iron precipitation would occur with the minimum nickel and cobalt losses with addition of the required amount of $CaCO_3$ slurry (12.5% w/w). At the fixed conditions (90, 70 and 25$^o$C of precipitation temperature and 1 hour of precipitation duration) pre-determined from the literature [30, 69, 70, 79, 89], precipitation recoveries with respect to various pH values were recorded. The results are shown in Tables 4.6, 4.7 and 4.8. From these precipitation recoveries, it is apparent that to achieve the maximum aluminum, chromium and iron precipitation together with the minimum nickel and cobalt losses, pH 4.25 was found to be the best and decided to be the optimum at 70$^o$C of precipitation temperature. At 90$^o$C of precipitation temperature, aluminum, chromium and iron precipitation recoveries were all around 99-100% except that at pH 3.50, precipitation recoveries of aluminum and chromium were both 88%, whereas nickel and cobalt losses were higher than 10%. However, when the precipitation temperature was reduced to 70$^o$C, the losses decreased whereas there was a small reduction in the recoveries of aluminum, chromium and iron. In order to purify the solution from the aluminum, chromium and iron impurities, pH had to be minimum 4.25 at 70$^o$C of precipitation temperature. Otherwise, the PLS

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would not be purified completely and there would always be some aluminum, chromium and iron concentrations higher than 5-10 ppm in the PLS after the purification stage. As it also is apparent in Figure 2.19, aluminum and chromium precipitations started at around pH 4.00. Thus, at pH 4.25, 70$^o$C of precipitation temperature was chosen as the optimum in order to obtain at least 99% Fe, Al and Cr precipitations with minimum nickel (17%) and cobalt (25%) losses.

**Table 4.6** Precipitation recoveries with respect to pH of PLS at 90$^o$C of precipitation temperature and 1 hour of precipitation duration.

| pH | Fe (%) | Ni (%) | Co (%) | Mn (%) | Cr (%) | Al (%) | Cu (%) | Zn (%) |
|---|---|---|---|---|---|---|---|---|
| **3.50** | 98.6 | 10.5 | 15.9 | 9.9 | 87.7 | 87.9 | 74.8 | 21.0 |
| **4.00** | 99.6 | 15.5 | 26.1 | 22.0 | 99.5 | 98.7 | 98.7 | 55.0 |
| **4.25** | 99.8 | 25.6 | 48.8 | 24.7 | 99.6 | 99.7 | 99.9 | 71.2 |
| **4.50** | 99.9 | 44.7 | 53.6 | 26.8 | 99.8 | 99.9 | 99.9 | 73.7 |
| **4.75** | 99.9 | 60.1 | 66.6 | 27.4 | 99.9 | 99.9 | 99.9 | 74.0 |
| **5.00** | 99.9 | 73.5 | 77.5 | 33.1 | 99.9 | 99.9 | 99.9 | 75.0 |
| **5.25** | 100.0 | 84.0 | 87.6 | 36.8 | 99.9 | 99.9 | 99.9 | 78.2 |

**Table 4.7** Precipitation recoveries with respect to pH of PLS at 70$^o$C of precipitation temperature and 1 hour of precipitation duration.

| pH | Fe (%) | Ni (%) | Co (%) | Mn (%) | Cr (%) | Al (%) | Cu (%) | Zn (%) |
|---|---|---|---|---|---|---|---|---|
| **3.25** | 94.7 | 6.5 | 12.9 | 3.6 | 84.7 | 84.5 | 18.0 | 12.2 |
| **3.50** | 95.6 | 7.5 | 13.2 | 5.7 | 97.4 | 94.6 | 18.9 | 19.8 |
| **4.25** | 99.5 | 17.2 | 24.9 | 13.0 | 99.6 | 99.7 | 33.2 | 31.1 |
| **4.50** | 99.8 | 24.1 | 25.7 | 21.9 | 99.8 | 99.9 | 86.6 | 43.9 |
| **4.75** | 99.9 | 53.3 | 54.1 | 23.2 | 99.9 | 99.9 | 99.9 | 72.7 |

**Table 4.8** Precipitation recoveries with respect to pH of PLS at 25$^o$C of precipitation temperature and 1 hour of precipitation duration.

| pH | Fe (%) | Ni (%) | Co (%) | Mn (%) | Cr (%) | Al (%) | Cu (%) | Zn (%) |
|---|---|---|---|---|---|---|---|---|
| **4.25** | 69.4 | 0.7 | 8.8 | 4.8 | 82.4 | 82.4 | 19.6 | 7.1 |
| **4.75** | 82.7 | 26.8 | 23.1 | 21.5 | 99.9 | 99.6 | 63.6 | 38.9 |
| **5.25** | 95.8 | 28.6 | 28.1 | 22.0 | 99.9 | 99.7 | 99.9 | 70.9 |

On the other hand, the experiments carried out at room temperature showed that the precipitation recoveries were low for the impurities but less for nickel and cobalt losses at the same pH conditions. At pH 4.25 and 25$^o$C of

precipitation temperature, iron precipitation recovery was 69% with less than 1% of nickel and 9% of cobalt losses, while at the same pH and 70°C of precipitation temperature, it was about 100% with 17% of nickel and 25% of cobalt losses. The reason of the less precipitation recoveries at 25°C of precipitation temperature lies in poor reaction kinetics and increased slurry viscosity. Willis pointed out this condition that operation at ambient temperature is possible but the kinetics is slow [69]. More reaction time was required for the experiments at ambient temperature. Figures 4.8-4.13 display the graphical presentations of the precipitation recoveries of Ni, Co, Mn, Fe, Al and Cr with respect to pH at different temperatures.
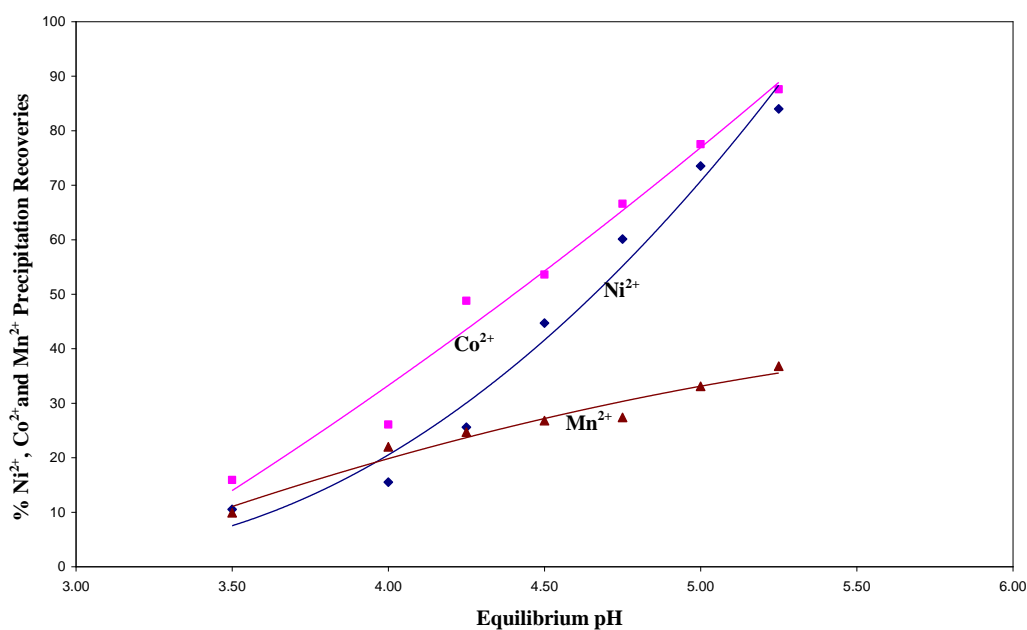


**Figure 4.8** Precipitation recoveries (%) of nickel, cobalt and manganese with respect to pH at 90°C of precipitation temperature.

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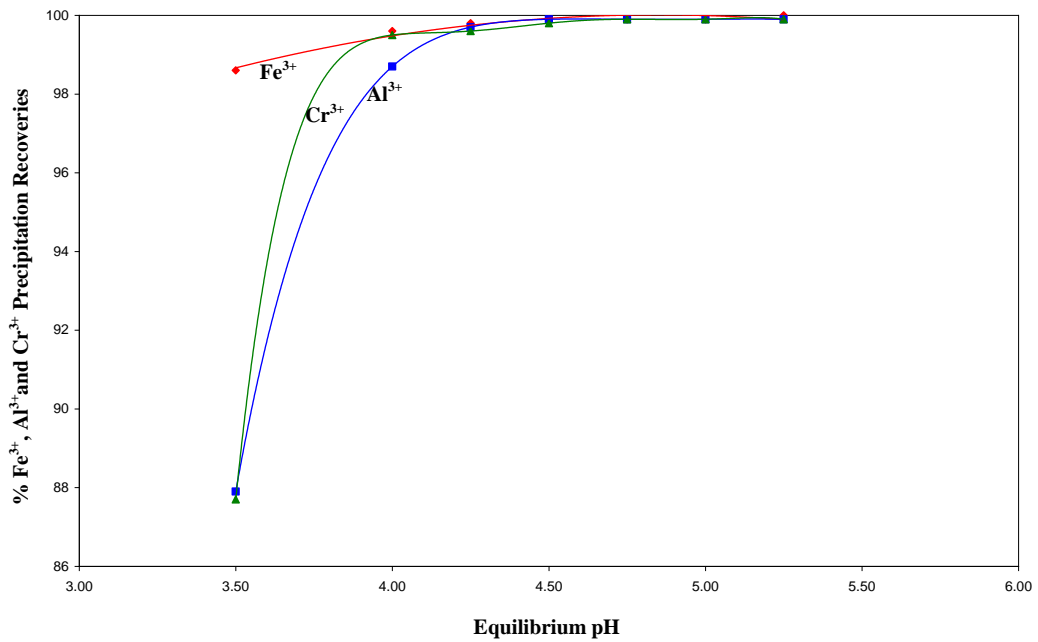
**Figure 4.9** Precipitation recoveries (%) of iron, aluminum and chromium with respect to pH at $90^{\circ}C$ of precipitation temperature.



**Figure 4.10** Precipitation recoveries (%) of nickel, cobalt and manganese with respect to pH at $70^{\circ}C$ of precipitation temperature.
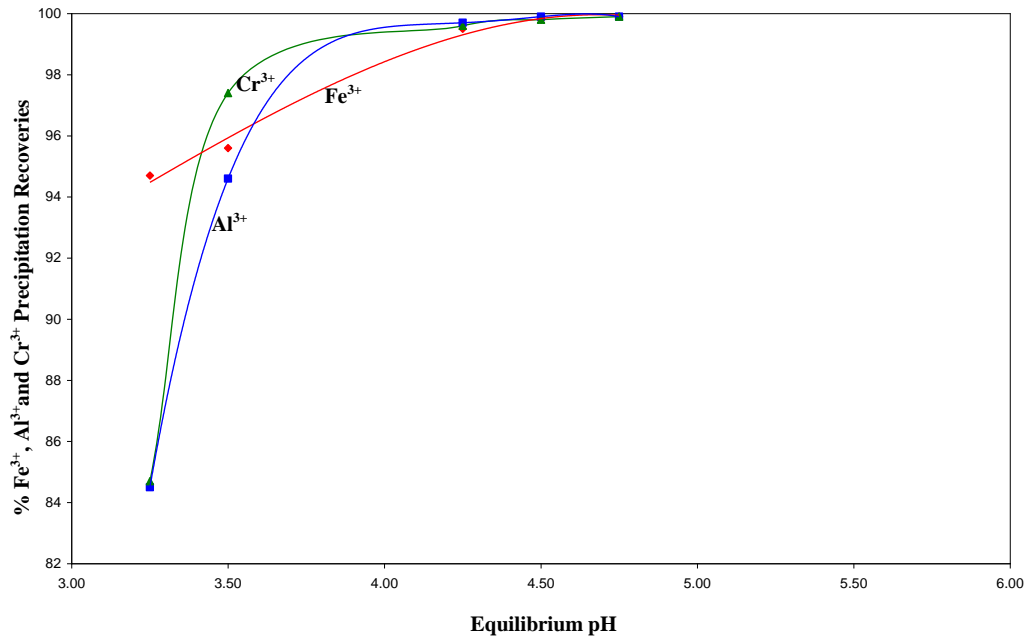
**Figure 4.11** Precipitation recoveries (%) of iron, aluminum and chromium with respect to pH at $70^{\circ}C$ of precipitation temperature.



**Figure 4.12** Precipitation recoveries (%) of nickel, cobalt and manganese with respect to pH at $25^{\circ}C$ of precipitation temperature.
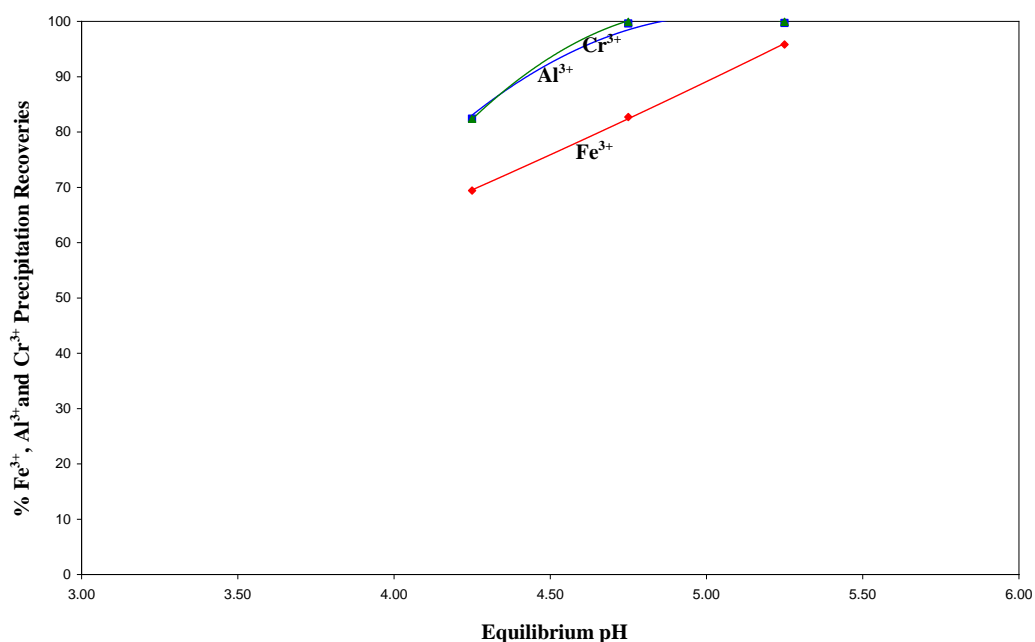
**Figure 4.13** Precipitation recoveries (%) of iron, aluminum and chromium with respect to pH at $25^{o}$C of precipitation temperature.

As seen in Figures 4.8 through 4.13, at pH 4.25 and $70^{o}$C of precipitation temperature, 99.5% of iron, 99.7% of aluminum and 99.6% of chromium precipitation recoveries were exactly fulfilled the required conditions of the second iron removal process with 17.2% of nickel and 24.9% of cobalt lost compared to other recovery values at different pH and temperatures. However, when complete purification of iron, aluminum and chromium impurities in PLS was tried to be achieved, it was observed that there was much loss of nickel and cobalt in the precipitate. Agatzini and Oustadakis reported that at pH 3.50, 96.4% of iron, 97.1% of aluminum and 93.3% of chromium precipitated with only 3.5% of nickel and 2.0% of cobalt losses [89]. In the study of Agatzini and Oustadakis, the lower values of nickel and cobalt losses than the values obtained from the present experiments are believed to be due to applying one-stage iron removal process at a lower pH and the use of MgO slurry as neutralizing agent in the mentioned study. However, these nickel and cobalt losses would be recovered during the recycle leach from the precipitate which was produced in small quantities.

The second iron removal step at above pH 4.25 was not thought to be feasible because co-precipitation is significant. As it is stated in Chapter 2, Willis noted that co-precipitation of nickel and cobalt (4-9% Ni-Co in solution precipitated) is considerable at pH range between 4.4 and 4.8 compared to the first iron removal stage [69, 70]. The increase of co-precipitation of nickel and cobalt with pH is also shown in Figure 2.22. The losses are less than the obtained values due to the experiments being conducted in a continuous process in the Willis's study. Willis also reported that the aluminum should be less than 50 mg/L after the second iron removal step in order to satisfy the desired nickel-cobalt dissolution from MHP in the following ammonia leaching step. This was achieved by reducing the aluminum concentration to 3.6 mg/L with addition of the required amount of $CaCO_3$ slurry (13.6 g/L) into the PLS up to pH 4.25 at the second iron removal process.

### 4.2.2 Effect of Precipitation Temperature

In the second set of experiments, the precipitation temperatures between $25^oC$ and $90^oC$ were studied at pH 4.25 by fixing the addition of 12.5% w/w $CaCO_3$ slurry for 1 hour of precipitation duration to specify the optimum precipitation temperature at which the maximum residual aluminum, chromium and iron precipitation would occur with the minimum nickel and cobalt losses. Results of the experiments are given in Table 4.9.

**Table 4.9** Precipitation recoveries with respect to precipitation temperature at pH 4.25 and 1 hour of precipitation duration.

| $T^oC$ | Fe (%) | Ni (%) | Co (%) | Mn (%) | Cr (%) | Al (%) | Cu (%) | Zn (%) |
|---|---|---|---|---|---|---|---|---|
| 25 | 69.4 | 0.7 | 8.8 | 4.8 | 82.4 | 82.4 | 19.6 | 7.1 |
| 50 | 97.3 | 3.7 | 19.7 | 5.5 | 89.5 | 88.1 | 29.4 | 15.7 |
| 70 | 99.5 | 17.2 | 24.9 | 13.0 | 99.6 | 99.7 | 33.2 | 31.1 |
| 90 | 99.8 | 25.6 | 48.8 | 24.7 | 99.6 | 99.7 | 99.9 | 71.2 |

As seen in Table 4.9, similar to Table 4.2, there was a distinct increase in the precipitation recoveries with the increasing precipitation temperature at pH 4.25 and 1 hour of precipitation duration. Above $50^oC$ of precipitation

temperature, iron precipitation and above 70°C of precipitation temperature, aluminum and chromium precipitations became greater than 97% where as more than 4% nickel and 20% cobalt losses for the former and more than 17% nickel and 25% cobalt losses for the latter were obtained.

The graphical presentations of the precipitation recoveries of Ni, Co, Mn, Fe, Al and Cr with respect to precipitation temperature are given in Figure 4.14 and 4.15.



**Figure 4.14** Precipitation recoveries (%) of nickel and cobalt with respect to precipitation temperature at pH 4.25 and 1 hour of precipitation duration.

At 50°C of precipitation temperature, although the loss of nickel and cobalt was decreased desirably the required levels of iron, aluminum and chromium removal were not achieved and more than 5-10 ppm iron, aluminum and chromium were left in the purified PLS. Therefore, 70°C of precipitation temperature was decided to be the optimum precipitation temperature to achieve at least the desired iron, aluminum and chromium precipitation with some but minimum nickel and cobalt losses as well as better reaction kinetics, less viscous slurry and better filtration properties of the precipitate. On the

other hand, as it is apparent in Figure 4.15, purification of impurities at 90$^{o}$C of precipitation temperature resulted in the highest precipitation recoveries, faster reaction kinetics and excellent filtration properties of the precipitate. However, it was not selected to be the optimum because of nickel and cobalt losses being higher than 25% and 48%, respectively.
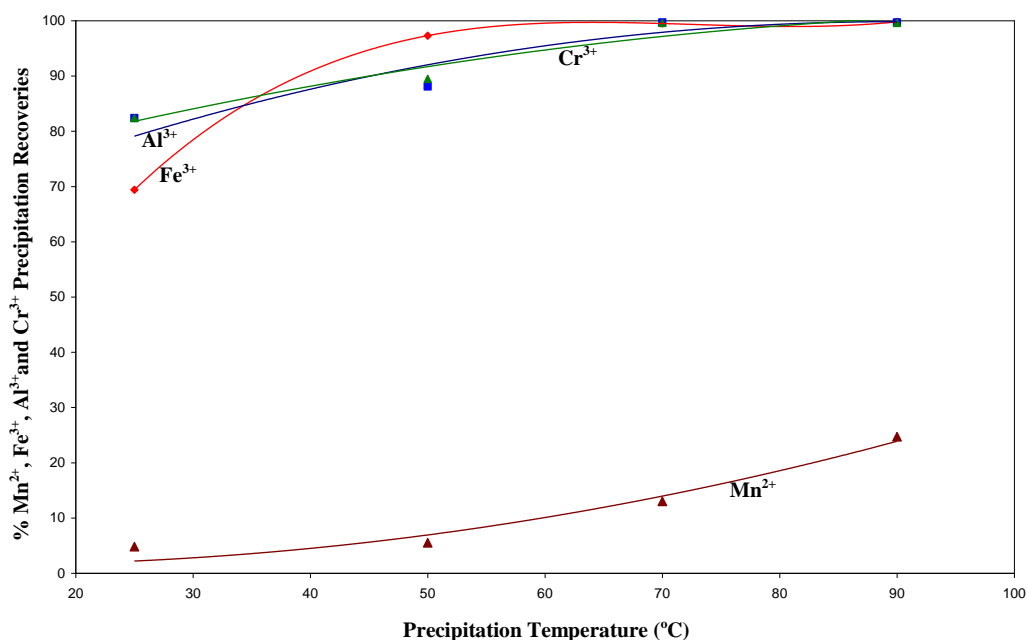


**Figure 4.15** Precipitation recoveries (%) of manganese, iron, aluminum and chromium with respect to precipitation temperature at pH 4.25 and 1 hour of precipitation duration.

### 4.2.3 Effect of Precipitation Duration

In the third set of experiments, the precipitation durations between 0.5 and 1.5 hours were studied at pH 4.25 and 70$^{o}$C of precipitation temperature using 12.5% w/w CaCO$_3$ slurry aiming to determine the optimum precipitation duration at which maximum residual aluminum, chromium and iron precipitation would occur with minimum nickel and cobalt losses. Precipitation recoveries with respect to precipitation duration obtained from the experiments at pH 4.25 and 70$^{o}$C of precipitation temperature are shown in Table 4.10.

**Table 4.10** Precipitation recoveries with respect to precipitation duration at pH 4.25 and 70$^o$C of precipitation temperature.

| Duration (hour) | Fe (%) | Ni (%) | Co (%) | Mn (%) | Cr (%) | Al (%) | Cu (%) | Zn (%) |
|---|---|---|---|---|---|---|---|---|
| **0.5** | 95.6 | 5.9 | 1.5 | 11.2 | 99.1 | 99.1 | 30.1 | 29.5 |
| **1.0** | 99.5 | 17.2 | 24.9 | 13.0 | 99.6 | 99.7 | 33.2 | 31.1 |
| **1.5** | 99.7 | 18.9 | 26.6 | 20.9 | 99.9 | 99.9 | 34.5 | 34.5 |

Iron, aluminum and chromium precipitation recoveries were higher than 95% whereas around 30% of copper and zinc and more than 10% of manganese were precipitated from the PLS with more than 5% of nickel and 1% of cobalt were lost in the precipitate. Although precipitation duration is generally between 90 and 180 minutes as it is stated in Willis' report [69], 60 minutes of precipitation duration was selected as the optimum since more losses of nickel and cobalt were observed in more than 1 hour of precipitation duration, while the iron precipitation recovery was stable at 99-100% for both 1.0 and 1.5 hours of precipitation durations. On the other hand, the precipitation durations of less than 1 hour resulted in iron precipitation recoveries of less than 99%, which was not desired in the last stage of the iron removal since at least 99% of iron precipitation (<5 ppm in PLS) had to be achieved from the PLS for a clean solution which would be used in the MHP process. Figures 4.16 and 4.17 illustrate the graphical presentations of the precipitation recoveries of nickel, cobalt, manganese, iron, aluminum and chromium with respect to precipitation duration. As can be seen from the figures, there was not a significant change in the precipitation recoveries according to precipitation duration except those of nickel and cobalt which increased more with the increasing precipitation duration.

At the end of the third set of experiments, the optimum conditions were finally chosen as pH 4.25, 70$^o$C of precipitation temperature and 1 hour of precipitation duration for the second iron removal stage. At these conditions, the amount of CaCO$_3$ slurry consumed was 5.45 cc (0.681 g CaCO$_3$ / 50 cc PLS) (13.6 kg CaCO$_3$ / m$^3$ PLS) and the weight of the precipitate after the second iron removal was, 1.4 g / 50 cc , 11% of the precipitate weight produced from 50 cc PLS by the first iron removal. It is important to note that

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in contrast to the first iron removal, the loss of nickel and cobalt in the precipitate produced by the second iron removal had to be recovered from the precipitate by performing recycle leaching.
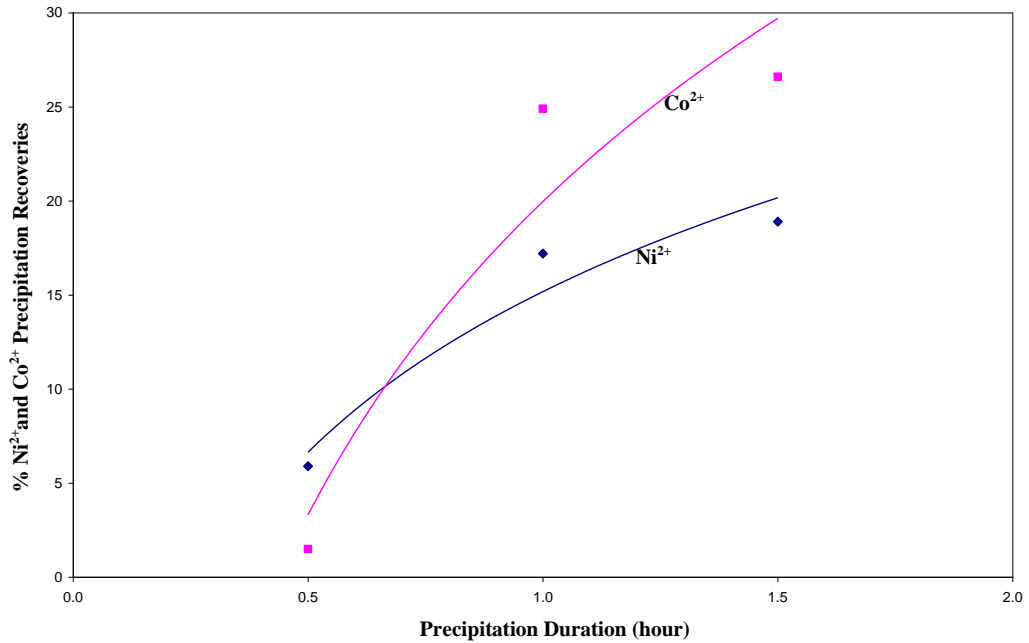


**Figure 4.16** Precipitation recoveries (%) of nickel and cobalt with respect to precipitation duration at pH 4.25 and 70°C of precipitation temperature.



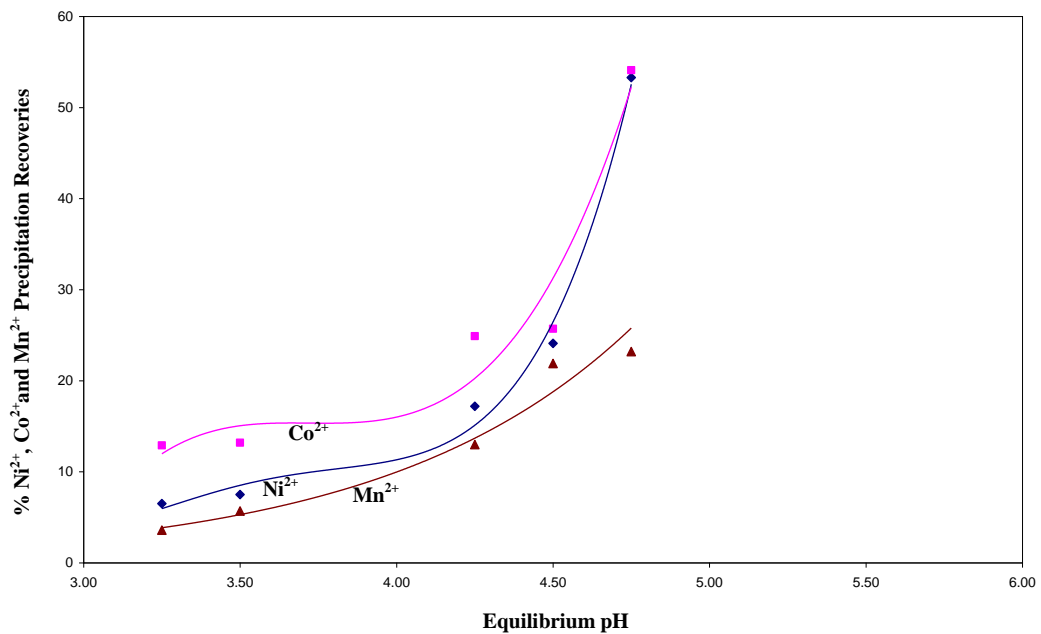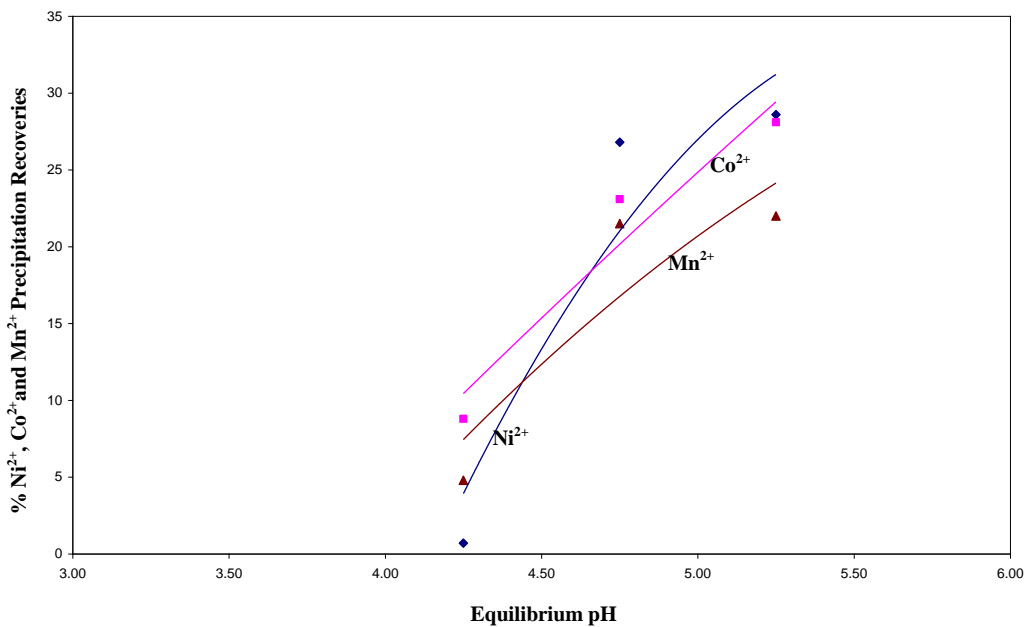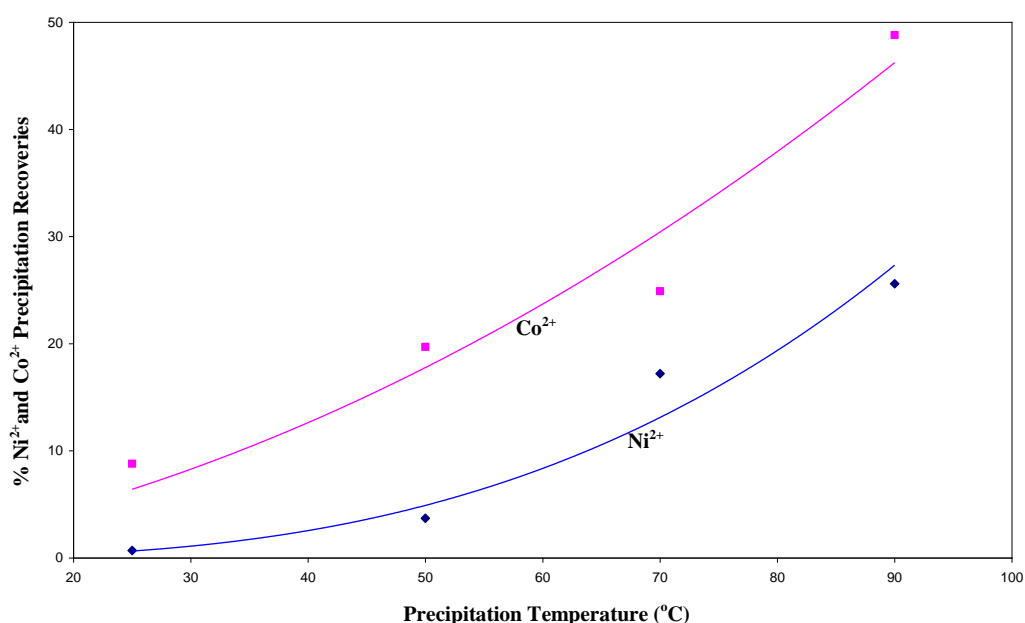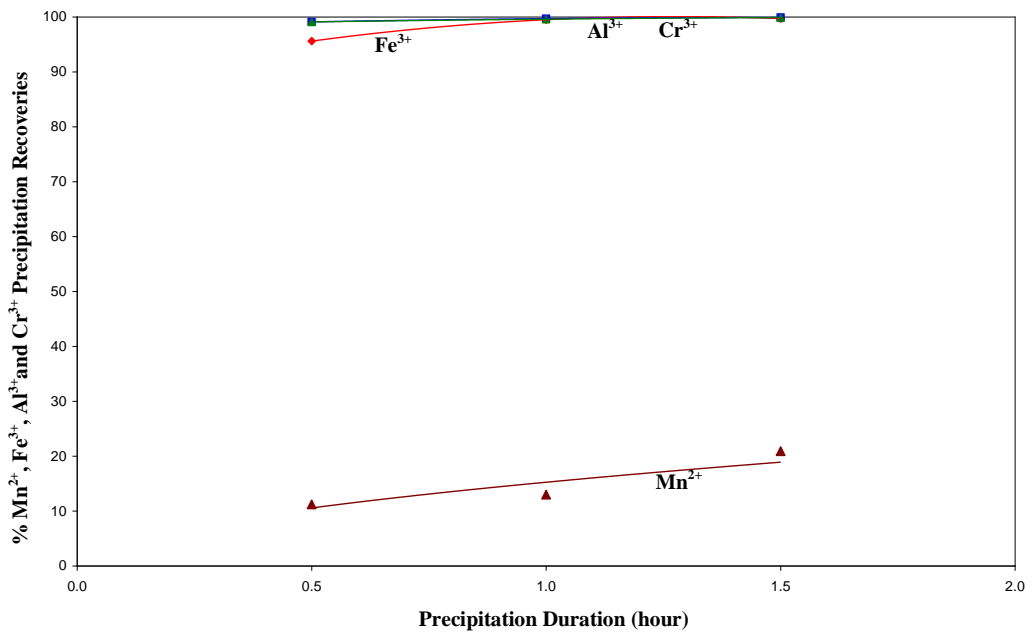**Figure 4.17** Precipitation recoveries (%) of manganese, iron, aluminum and chromium with respect to precipitation duration at pH 4.25 and 70°C of precipitation temperature.

Free acidity of PLS was reduced from 1.4 g/L to 0.2 g/L by consuming 0.50 cc 12.5% w/w $CaCO_3$ slurry (0.063 g $CaCO_3$ / 50 cc PLS) (1.25 kg $CaCO_3$ / $m^3$ PLS) (1.04 kg $CaCO_3$ / kg $H_2SO_4$). After the second iron removal process, 33.2% of copper, 31.1% of zinc, 13% of manganese and 38.9% of magnesium in PLS were precipitated while calcium in solution was increased, as in the first stage, to 870 ppm because of the addition of $CaCO_3$ slurry. The precipitate analysis is given in Table 4.11. The increase of calcium content in both the precipitate and the PLS is apparent in Tables 4.11 and 4.12. Relatively, high percentages of Ca and Al were present in the precipitate as well as some Ni and Fe precipitated at the optimum conditions selected, with low Cr, Co and Mn percentages. It is important to note that all important impurities like Fe, Cr and Al, except for Mn and Mg in the PLS had been rejected to the precipitate and each mentioned impurity was decreased to less than 5 ppm in the PLS.

**Table 4.11** Composition analysis of the precipitate produced from the PLS by the second iron removal process at the optimum conditions.

| Components of the precipitate | Value (%w/w dry) |
|---|---|
| Ni | 2.12 |
| Co | 0.073 |
| Fe | 1.03 |
| Ca | 12.8 |
| Mn | 0.19 |
| Al | 4.5 |
| Cr | 0.72 |

In the second iron removal process, it was initially planned to study the oxidation of ferrous iron ($Fe^{2+}$) in the PLS to ferric iron ($Fe^{3+}$) by introducing air into solution. Since the analysis of the ferrous iron in the PLS after the column leaching showed that it was present in very small amounts in the PLS as seen in Table 3.4, it was not considered necessary to use air throughout the iron removal process.

The precipitates resulted from the experiments settled down quickly and were easily filtered. They showed similar characteristics of filterability, color and brittleness. It was observed that the color of the precipitate was lighter than the precipitate produced in the first iron removal process. Furthermore, the rate of $CaCO_3$ slurry addition during the experiments was controlled to prevent supersaturation of iron, aluminum and chromium leading to amorphous precipitates which would be difficult to filter out.

The X-Ray diffraction data of the precipitate produced from the PLS at the optimum conditions using 12.5% w/w $CaCO_3$ pulp as precipitating agent is shown in Figure 4.18.



1. $CaSO_4.0.5H_2O$-Bassanite
2. $CaSO_4.2H_2O$-Gypsum
3. $Fe_2O_3$-Hematite
4. $\alpha$-FeOOH-Goethite
5. $CaCO_3$-Calcite
6. $Ca_3Al_2(OH)_{12}$-Katoite
7. $Al(OH)_3$-Bayerite
8. $Ni(OH)_2$-Theophrastite
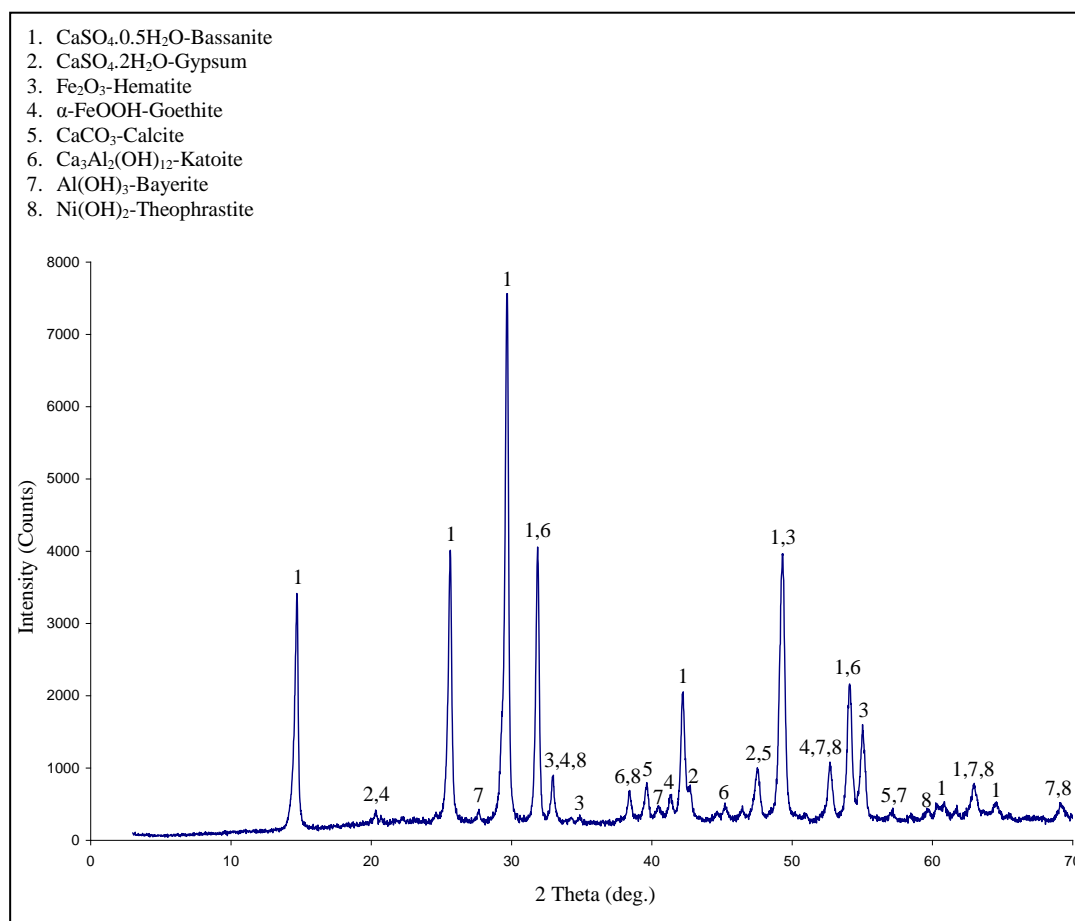
**Figure 4.18** XRD pattern of the precipitate produced from the PLS by the second iron removal process at pH 4.25, 70°C of precipitation temperature and 1 hour of precipitation duration with addition of $CaCO_3$ slurry.

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The main mineralogical phase was still bassanite [$CaSO_4.0.5H_2O$] and other phases were gypsum [$CaSO_4.2H_2O$], hematite [$Fe_2O_3$] and goethite [$\alpha$-FeOOH] together with some calcite [$CaCO_3$] and katoite [$Ca_3Al_2(OH)_{12}$]. Bassanite was a better-crystallized phase than others. The difference from the first iron removal process is that there were also Al and Ni containing products present as bayerite [$Al(OH)_3$] and theophrastite [$Ni(OH)_2$], respectively. The main peaks, which correspond to [$CaSO_4.0.5H_2O$], were again sharper and with greater intensity, compared with other peaks displaying lower intensity and higher peak width such as the peaks of hematite and goethite. Also, there were no Co, Mn and Cr containing phases detected because of their low content in the precipitate as seen in Table 4.11.

At the end of the second iron removal process, a new PLS stock which would be used in the MHP process was produced by carrying out the second iron removal process at the optimum conditions. The AAS analysis of the new 1.75 L PLS stock is illustrated in Table 4.12. In the PLS stock, 0.2 g/L free acid was present. The ORP (or SHE) value and the density of the PLS stock were 257 mV (or 455 mV) and 1.05 g/cm$^3$, respectively. Prior to MHP experiments, the Ni/Mn ratio was calculated as 8.17.

**Table 4.12** Chemical analysis by AAS of the new PLS stock produced by the second iron removal process at the optimum conditions.

| Components of PLS | Concentration (ppm) |
|---|---|
| Ni | 2713 |
| Co | 58.5 |
| Fe | 1.38 |
| Fe$^{2+}$ | 0 |
| Mg | 6815 |
| Al | 3.6 |
| Ca | 870 |
| Mn | 332 |
| Cr | 0.77 |
| As | 0 |
| Zn | 14.9 |
| Cu | 1.62 |
| H$_2$SO$_4$ | 200 |

There was very little iron and aluminum left in the PLS. This would give an important advantage to the following steps otherwise the presence of iron and aluminum in the precipitate could suppress re-leaching of nickel and cobalt from the precipitates produced at the MHP processes [101]. In the iron removal, seed recycle was also studied and the performance of the process was little enhanced with the seed additions of 5%, 10% and 15% w/w of the precipitate produced at the optimum condition.

## 4.3 First Mixed Hydroxide Precipitation (MHP1)

In the MHP experiments, the optimum conditions were studied in order to precipitate as much nickel and cobalt as possible with minimum amount of manganese in a mixed saleable hydroxide form from the PLS after the second iron removal stage. Most especially, the objective of the MHP experiments was to find a proper way to precipitate almost all nickel and cobalt from the PLS and to leave less than 10 ppm [69] nickel in solution providing that small amount of manganese was present in the precipitate being not higher than 10%. However, it was a trade off process. Therefore, it was decided to perform MHP process in two stages in order to control the extent of manganese contamination in the mixed hydroxide product. The reason for aiming minimum manganese precipitation, which is described earlier in Chapter 2, is that nickel to manganese ratio in feed stream and resulted manganese in mixed hydroxide product are crucial for MHP process to be applicable in industry because MHP precipitate is further treated to separately recover nickel and cobalt at a satisfactory purity. Hence, MHP is not selective for high manganese containing ores. The nontronite ore treated in this study had a low manganese content of 0.34 wt%. Likewise, Willis noted that MHP is best applied to ores with low manganese content in which nickel/manganese ratio is greater than 3:1 [69]. For this reason, this ratio had been taken into consideration before MHP1 experiments started and it was 3.53:1 in the ore and 8.17:1 in the PLS. In MHP1 experiments, the most

important parameter to control was manganese precipitation recovery which had to be kept as low as possible since there would be no way for manganese to be discarded from MHP1 precipitate to satisfy 10%. At the same time, nickel and cobalt precipitation had to be above at least 90% for the feasible process. In addition, it was also desired an MHP1 product in which there would be no magnesium contamination due to unreacted magnesium oxide.

### 4.3.1 Effect of pH

In the first set of experiments, pH was typically adjusted to in the range of pH 7.00-7.50 with 1% w/w freshly slurried reactive magnesia (in milk form). The objective was to determine the optimum pH value at which maximum practical Ni and Co precipitation would occur providing that Mn contamination could not exceed 10% in the precipitate. At the fixed conditions ($50^{o}$C of precipitation temperature and 1 hour of precipitation duration) pre-determined from the literature [69, 70, 92, 101], precipitation recoveries with respect to various pH values recorded when 5.0-15.0 cc MgO slurry was added and pH 7.00 was found to be the most effective pH and was decided to be the optimum. The results are shown in Table 4.13.

**Table 4.13** Precipitation recoveries with respect to pH of the PLS and the volume of the MgO slurry added at $50^{o}$C of precipitation temperature and 1 hour of precipitation duration.

| MgO slurry Addition (cc) | pH | Ni (%) | Co (%) | Mn (%) | Cr (%) |
|---|---|---|---|---|---|
| **5.0** | 6.63 | 47.3 | 40.7 | 14.2 | 34.3 |
| **6.0** | 6.74 | 56.8 | 46.9 | 15.5 | 74.0 |
| **7.0** | 6.84 | 71.2 | 92.4 | 17.3 | 77.1 |
| **8.0** | 6.88 | 78.9 | 96.1 | 25.1 | 77.3 |
| **9.0** | 6.94 | 84.2 | 97.2 | 32.2 | 83.6 |
| **10.0** | 7.00 | 89.6 | 97.4 | 40.4 | 86.0 |
| **11.0** | 7.05 | 94.7 | 98.9 | 61.4 | 87.9 |
| **12.0** | 7.10 | 95.7 | 99.3 | 67.3 | 96.3 |
| **13.0** | 7.44 | 98.6 | 99.4 | 98.0 | 98.7 |
| **15.0** | 7.52 | 99.6 | 99.9 | 98.8 | 100.0 |

The graphical demonstration of the precipitation recoveries of Ni, Co and Mn with respect to pH at 50°C of precipitation temperature and 1 hour of precipitation duration is given in Figure 4.19.
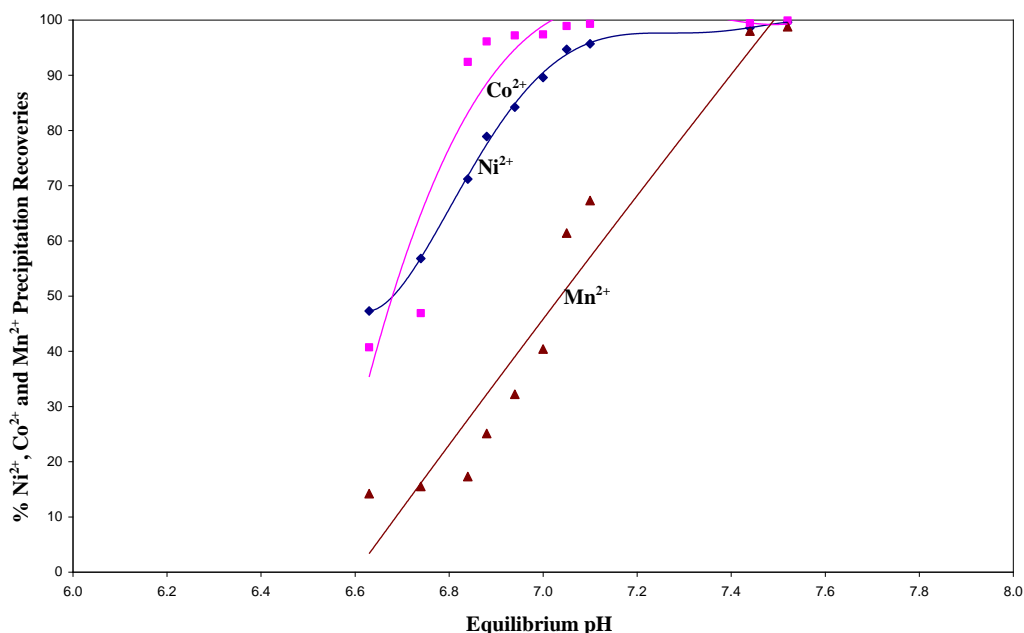


**Figure 4.19** Precipitation recoveries (%) of nickel, cobalt and manganese with respect to pH at 50°C of precipitation temperature and 1 hour of precipitation duration.

With increasing pH of the PLS, the amount of nickel and cobalt precipitated as hydroxide were increased. However, with this increase in pH, it was observed that manganese and chromium precipitations also increased and contaminated the MHP1 product. Chromium contamination was not important due to very low chromium concentration (0.77 ppm) in the PLS. But, the manganese contamination was very important. Therefore, in order to prevent unfavorable manganese precipitation partially and to achieve at least about 90% nickel and cobalt precipitation, the amount of 1% w/w MgO slurry which would be added was decided to be 10 cc (0.10 g MgO / 50 cc PLS) (2 kg MgO / m$^3$ PLS) leading to pH 7.00.

In the other sets of the experiments of MHP1, the fixed 10 cc MgO slurry volume would be used to maintain manganese precipitation low and attain the

desired nickel-cobalt precipitation recoveries. The graphical demonstration of the precipitation recoveries of Ni, Co, and Mn with respect to stoichiometric amount of magnesium oxide is given in Figure 4.20. It is important to note that the selected 10 cc caustic calcined magnesium oxide slurry volume was 94% of the theoretical amount of magnesium oxide being determined by stoichiometric reactions to completely precipitate nickel, cobalt and manganese from the PLS while the stoichiometric reactions are Reactions 4.4, 4.5 and 4.6, respectively. The MgO slurry theoretically needed for the complete precipitation was 9.20 cc for nickel, 0.20 cc for cobalt and 1.21 cc for manganese according to these reactions, if the efficiency of the magnesium oxide was assumed to be 100%.
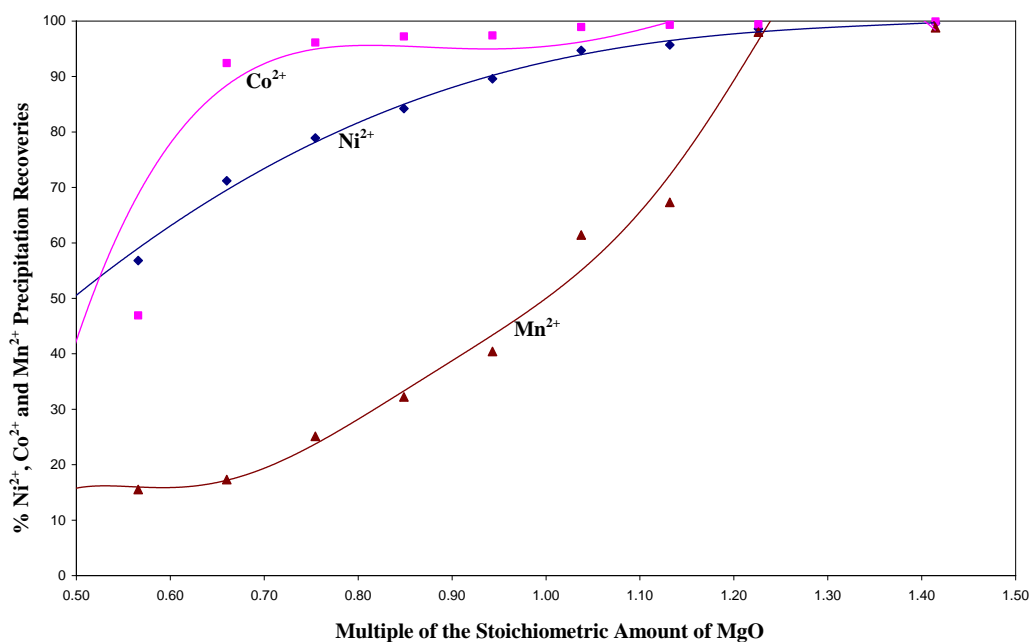


**Figure 4.20** Precipitation recoveries (%) of nickel, cobalt and manganese at 50$^{o}$C of precipitation temperature with respect to stoichiometric amount of MgO completely precipitating nickel, cobalt and manganese from the PLS.

Furthermore, as pH of the PLS was increased, precipitation with the caustic calcined magnesia was expected to give rise to the dissolution of magnesium to form soluble magnesium oxide as in Reactions 4.4, 4.5 and 4.6 to result in a desired nickel-cobalt product containing no magnesium. However, as it is

pointed out in the literature [101], all the products contained some levels of magnesium. White reported that the efficiency of the magnesium oxide is around 70-90%. Thus, in order for the complete precipitation of nickel, cobalt and manganese from the PLS, the addition amount of magnesium oxide was required to be around 11.8-15.2 cc. But, 10 cc was selected due to the undesired manganese precipitation at these volumes.

$$NiSO_4 + MgO + H_2O \longrightarrow MgSO_4(s) + Ni(OH)_2(s) \qquad (4.4)$$

$$CoSO_4 + MgO + H_2O \longrightarrow MgSO_4(s) + Co(OH)_2(s) \qquad (4.5)$$

$$MnSO_4 + MgO + H_2O \longrightarrow MgSO_4(s) + Mn(OH)_2(s) \qquad (4.6)$$
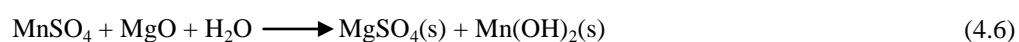
It was observed and exampled by White that adding freshly slurried caustic magnesium oxide to the solution could precipitate a high amount of nickel and cobalt with a minor amount of manganese in solution [101]. However, if the amount of MgO slurry is not correctly adjusted and overdosed the selectivity decreases. Therefore, the MgO slurry volume was controlled during the experiments instead of directly following pH change to prevent overdosing of magnesium oxide. Otherwise, it would result in significantly less selectivity of nickel and cobalt precipitation over manganese precipitation as well as magnesium contamination. As White pointed out, it can be preferable to think of the reaction as a solid-solution exchange between magnesium as magnesium oxide and nickel together with cobalt and manganese rather than supposing the precipitation as being a pH adjustment similar to nickel exchange with copper in sulfide matte leaching [37]. In one of the examples White noted that when the MgO slurry was added until the pH of the PLS became within the range of 5.6 to 8.8 [101], this yielded 88.4% of nickel, 83.7% of cobalt and 57.8% of manganese precipitation recoveries. The process mentioned was not selective for nickel and cobalt precipitation over manganese. On the other hand, as seen in Figure 4.20, the manganese precipitation recoveries, obtained from MHP1 experiments, were much lower compared to the values that White recorded because it was believed to be the one-stage MHP used in the White's study in which addition of the MgO slurry

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was overdosed leading to pH 7.52. In contrast to overdosing magnesia, insufficient magnesia can also result in a problem where excess nickel passes to second stage MHP, slaked lime consumption is raised and losses attributed to additional recycles will result. Furthermore, White reported that the substantial proportion of nickel and cobalt in solution precipitated is composed of most preferably about 90% of the nickel and cobalt in solution, respectively, while the minor proportion of manganese is composed of from about 5% to about 15% of the manganese in solution. Although the preferable nickel and cobalt precipitation recoveries in the MHP1 experiments were achieved as seen in Table 4.13 and Figure 4.19, the manganese precipitation recoveries were higher than the preferred ones except for the first two experiments leading to less than 60% of nickel and cobalt precipitation recoveries. The reason was believed to be the discontinuous MHP circuit followed in the laboratory scale. However, the precipitate produced at pH 7.00 comprised still less than 10% manganese as seen in Table 4.16.

## 4.3.2 Effect of Precipitation Temperature

The precipitation temperatures between $50^{o}C$ and $70^{o}C$ were studied at pH 7.00 and 1 hour of precipitation duration using 1% w/w freshly slurried reactive magnesia as precipitating agent aiming to determine the optimum precipitation temperature at which maximum practical Ni and Co precipitation would occur providing that Mn contamination was minimum and could not exceed 10% in the precipitate. Results of the experiments are given in Table 4.14 and in the graphical form Figure 4.21 shows the precipitation recoveries of Ni, Co and Mn with respect to precipitation temperature at pH 7.00 and 1 hour of precipitation duration.

**Table 4.14** Precipitation recoveries with respect to precipitation temperature at pH 7.00 and 1 hour of precipitation duration.

| $T^{o}C$ | Ni (%) | Co (%) | Mn (%) |
|---|---|---|---|
| 50 | 89.6 | 97.4 | 40.4 |
| 60 | 91.2 | 98.2 | 52.0 |
| 70 | 97.7 | 98.3 | 80.8 |
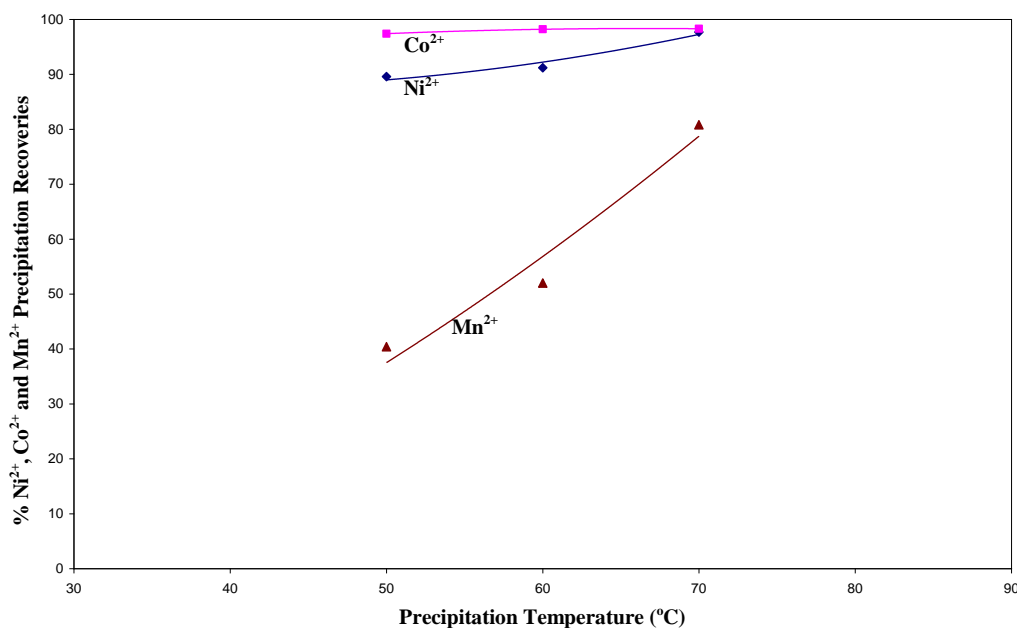
**Figure 4.21** Precipitation recoveries (%) of nickel, cobalt and manganese with respect to precipitation temperature at pH 7.00 and 1 hour of precipitation duration.

All the precipitation recoveries were increasing with the increase in precipitation temperature. Because of the high manganese precipitation recoveries obtained, the precipitation temperature was decided to be kept as low as possible and $50^{o}$C was selected as the optimum. Agatzini et al. studied nickel-cobalt precipitation using MgO pulp at ambient temperature [92]. However, filterability of precipitate was negatively affected and the kinetics became slow leading to a reaction time more than a day at the ambient temperature precipitation. Willis also reported this condition in MHP1 as in the iron removal processes and recommended an operating temperature greater than $60^{o}$C for the fast reaction kinetics of the precipitation [69]. In addition, it was observed from the MHP1 experiments that at pH 7.00, increasing the temperature from $50^{o}$C to $60^{o}$C reduced the nickel concentration by 15% and from $60^{o}$C to $70^{o}$C by 74%. Meantime, the manganese precipitation recovery abruptly increased from 40% to 80% with the increasing precipitation temperature while there was a gradual increase in the nickel and cobalt precipitation recoveries. Therefore, $50^{o}$C of precipitation temperature would be the right choice for the minimum manganese

precipitation required at MHP1 as nickel and cobalt precipitation recoveries were in the range of 90-100%. White pointed out that the precipitation temperature is preferably from about 30$^{o}$C to about 90$^{o}$C, but a temperature of about 50$^{o}$C is especially suitable [101].

### 4.3.3 Effect of Precipitation Duration

In the third set of experiments, the precipitation durations between 0.5 and 1.5 hours were investigated at pH 7.00 and 50$^{o}$C of precipitation temperature using 1% w/w freshly slurried reactive magnesia as precipitating agent in order to determine the optimum precipitation duration at which the maximum practical nickel and cobalt precipitations would occur from the PLS with the minimum manganese contamination leading to not exceeding 10% Mn in the precipitate. The results of the experiments are shown in Table 4.15.

**Table 4.15** Precipitation recoveries with respect to precipitation duration at pH 7.00 and 50$^{o}$C of precipitation temperature.

| Duration (hour) | Ni (%) | Co (%) | Mn (%) |
|---|---|---|---|
| 0.5 | 85.4 | 97.0 | 35.4 |
| 1.0 | 89.6 | 97.4 | 40.4 |
| 1.5 | 91.6 | 97.5 | 45.1 |

In the literature, reaction durations between 1 and 9 hours are recommended to achieve a substantial precipitation of the nickel and cobalt in solution with precipitation of a minor proportion of the manganese in solution [101]. Precipitation duration is preferably from 1 to 6 hours and most preferably from 3 to 5 hours to allow enough time for reaction of magnesium oxide to proceed substantially. In this study, 1 hour of precipitation duration was decided to be the optimum in order to achieve at least about 90% nickel and cobalt precipitation recoveries while manganese precipitation was kept at less than 10% Mn in the precipitate in spite of about 40% Mn in solution being precipitated. Willis pointed out that in the first stage of Ni-Co precipitation 15-35% Mn in solution precipitated, yielding <5% Mn in product [70]. On the

other hand, the reason to maintain at least 90% nickel and cobalt precipitation recoveries was attributed to producing a saleable hydroxide product without losing much nickel and cobalt. As it is stated in Chapter 2, some nickel and cobalt values should be sacrificed in order to produce saleable MHP product which contains less than limiting manganese content. Mg contamination was also considered and not allowed to be higher than 2%. In the graphical form, the presentation of the precipitation recoveries of Ni, Co and Mn with respect to precipitation duration is given in Figure 4.22.
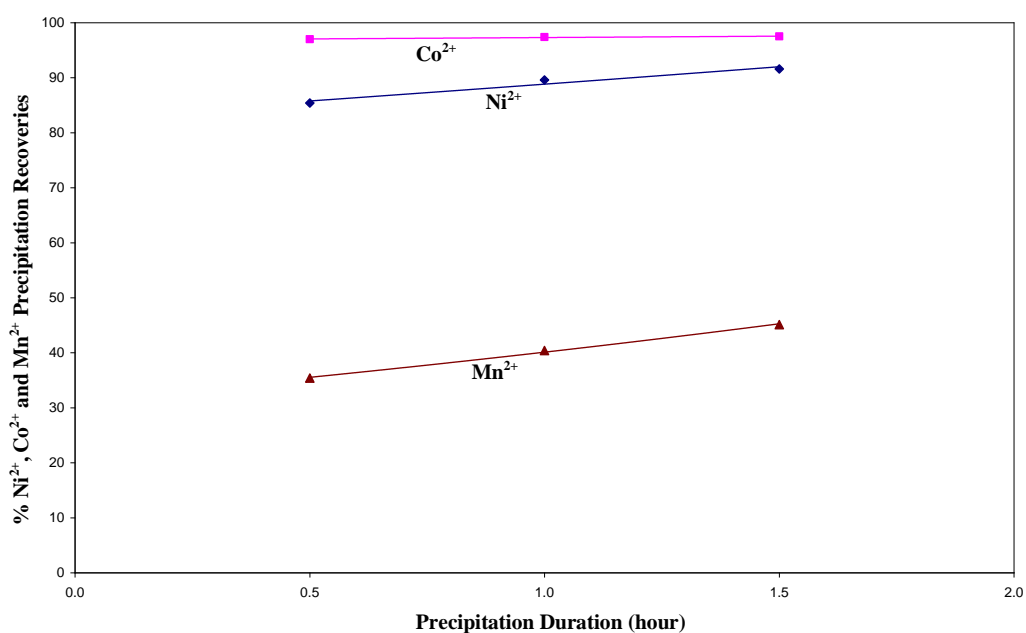


**Figure 4.22** Precipitation recoveries (%) of nickel, cobalt and manganese with respect to precipitation duration at pH 7.00 and 50$^{\circ}$C of precipitation temperature.

The decrease in the precipitation duration resulted in both nickel and cobalt precipitation recoveries to be slightly decreased but leading to nickel precipitation recovery of less than 90% which was out of the purpose of MHP1. It has been reported that if the residence time is less than 1 hour, incomplete dissolution of magnesium oxide occurs and the solid precipitate recovered is contaminated with magnesium oxide [101]. Therefore, 0.5 hour of precipitation duration was not decided to be the optimum while 1.5 hours of precipitation duration resulted in higher manganese precipitation recovery

which would decrease the selectivity of the MHP process over manganese and the precipitate would contain higher levels of precipitated impurities.

At the end of the third set of experiments, the optimum conditions were finally chosen as pH 7.00, 50$^{o}$C of precipitation temperature and 1 hour of precipitation duration for the first mixed hydroxide precipitation. At these conditions, the weight of the precipitate produced by MHP1 was 0.29 g. Free acidity of PLS was reduced from 0.2 g/L to 0 g/L according to Reaction 4.7 by consuming 0.41 cc 1% w/w MgO slurry (0.004 g MgO / 50 cc PLS) (0.08 kg MgO / m$^{3}$ PLS).

$$H_2SO_4 + MgO \longrightarrow MgSO_4 + H_2O \hspace{2cm} (4.7)$$

After MHP1, about 90% of nickel, 97% of cobalt, 40% of manganese, 86% of chromium, 99% of zinc and about 100% of copper in solution were precipitated at the optimum conditions. The precipitate analysis is given in Table 4.16. The increased nickel and cobalt contents in the precipitate and the decrease of these elements in the PLS resulting from the MHP1 process are apparent in Tables 4.16 and 4.18, respectively.

**Table 4.16** Composition analysis of the mixed hydroxide precipitate produced from the PLS by MHP1 at the optimum conditions.

| Components of the precipitate | Value (%w/w dry) |
|---|---|
| Ni | 41.91 |
| Co | 1.0 |
| Fe | 0.024 |
| Ca | 1.44 |
| Mn | 2.31 |
| Mg | 1.50 |
| Al | 0.06 |
| Cr | 0.011 |
| Zn | 0.25 |
| Cu | 0.03 |
| S | 4.73 |

High percentages of nickel and cobalt in the precipitate were achieved at the optimum conditions as well as some manganese and magnesium precipitation, with only very low iron, aluminum and chromium contaminations. In addition, there was some sulfate precipitation together with metal hydroxides. It is important to note that the ratio, by weight, of (Ni+Co)/Mn was 18.58 in the precipitate and 8.35 in the PLS prior to the MHP1 process. The ratio in the precipitate was 2.2 times larger than that in the PLS prior to precipitation. However, White reported that it is especially preferred that the ratio in the precipitate should be at least five times larger than the ratio in the PLS before the precipitation [101]. Although the ratio in the precipitate resulting from MHP1 tests was less than the preferred one, the manganese percentage was 2.31% in the precipitate which was less than 10% satisfying the marketing condition as Willis reported [69]. To compare, the typical mixed hydroxide precipitate analyses obtained from MHP process carried out at Ravensthorpe reported by White is similar to the results obtained in this study [37]. Final the product had a nickel content of 42% on dry basis. The extraction and precipitation recoveries from the crude nontronite ore to the saleable Ni-Co hydroxide product are shown in Table 4.17.

**Table 4.17** Extraction and precipitation recoveries from the run of mine nontronite ore (-2 cm) up to the saleable Ni-Co hydroxide product after the column leach, the first and the second iron removal and the MHP1.

| | Ni (%) | Co (%) |
|---|---|---|
| **Column Leach** (Ore → PLS) | 85.5 | 65.0 |
| **First Iron Removal** (PLS → Filtrate) | 99.6 | 99.6 |
| **Second Iron Removal** (PLS → Filtrate) | 82.8 | 75.1 |
| **MHP1** (PLS → Saleable Product) | 89.6 | 97.4 |

The highest amounts of nickel and cobalt losses were observed in the second iron removal process. However, these nickel-cobalt losses would be re-extracted from the precipitate by recycle leaching and recovered in the mixed

hydroxide precipitate as MHP1 product. As it is stated in Chapter 2, Willis reported that by dissolving the solids produced in the second iron removal and MHP2 by the required amount of sulfuric acid solutions (greater than 20 g/L) at an operating temperature of higher than $50^{\circ}C$ and 1-2 hours of precipitation duration, 95-100% nickel and cobalt recoveries from the precipitates can be attained [69]. Therefore, by maintaining at least 95% of Ni-Co extraction recoveries from the precipitates produced in the second iron removal by recycle leaching with sulfuric acid, about 75% of Ni and 62% of Co could totally be extracted from the nontronite ore by MHP1 (9 kg Ni / ton of ore and 0.27 kg Co / ton of ore). An example of total extraction recovery calculation is given in Appendix B. Total extraction recoveries of nickel and cobalt with respect to number of recycle leach of the precipitates are shown in Figure 4.23. After the third recycle leaching, total extraction recoveries would become constant. Total extraction recoveries would be further increased by recycle leaching of the precipitates produced by MHP2 which will be reported in the following part.
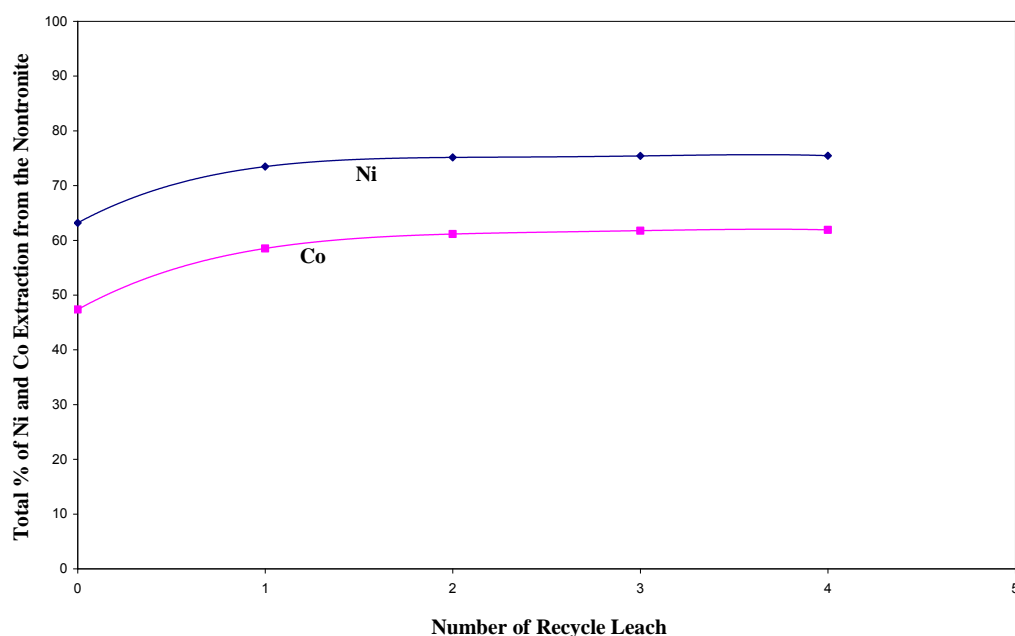


**Figure 4.23** Total extraction recoveries (%) of Ni and Co from the crude laterite ore to the hydroxide precipitate produced by the MHP1with respect to number of recycle leach of the precipitates produced by the second iron removal.

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The precipitates from the MHP1 experiments showed favorable settling and filtration properties. It was observed that the color of the PLS after the addition of the magnesium oxide slurry changed from green to slightly brown. If the slurry was too green there would be insufficient nickel precipitation giving rise to metal losses and if the slurry was too brown there would be too much manganese precipitation leading to product contamination [37]. The X-Ray diffraction data of the mixed hydroxide precipitate produced from the PLS at the optimum conditions using 1% w/w fresh MgO slurry as precipitating agent is shown in Figure 4.24.



1. $Ni(OH)_2$-Theophrastite
2. $3Ni(OH)_2$-Theophrastite Magnesian
3. $3Ni(OH)_2.2H_2O$-Nickel Hydroxide Hydrate
4. $Mg(OH)_2$-Brucite
5. $SiO_2$-Silica
6. $MnO(OH)$-Groutite
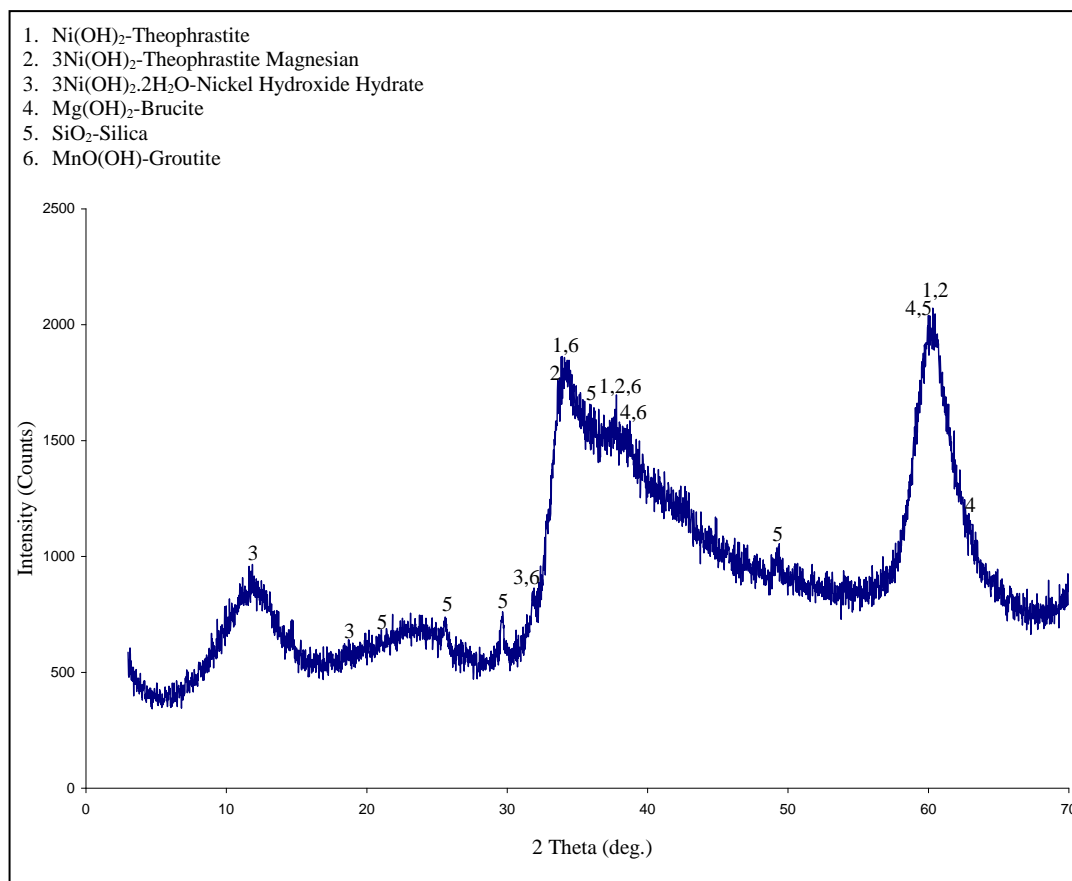
**Figure 4.24** XRD pattern of the mixed hydroxide precipitate produced from the purified PLS by MHP1 at pH 7.00, $50^{o}C$ of precipitation temperature and 1 hour of precipitation duration with addition of fresh MgO slurry.

The main mineralogical phases were theophrastite [$Ni(OH)_2$], theophrastite magnesian [$3Ni(OH)_2$] and nickel hydroxide hydrate [$3Ni(OH)_2.2H_2O$]. Other

phases were brucite [Mg(OH)$_2$], groutite [MnOOH] and silica [SiO$_2$]. The main peaks, matching with [Ni(OH)$_2$] and [3Ni(OH)$_2$], were sharper and with greater intensity compared with other peaks which indicated lower intensity and greater peak width. Mineralogical phases of other components were not detected due to their low content in the mixed hydroxide precipitate. As seen in Figure 4.24, the crystallinity of the phases were not well developed and not as good as of the products from the iron removal processes since the addition rate of the precipitating agent, i.e. fresh magnesium oxide slurry, was higher in order to maintain good magnesia reactivity with the components of the PLS leading to less time for the ordering of the atoms and the molecules in the mixed precipitate. TGA and DTA analysis of the produced mixed hydroxide precipitate is shown in Figure 4.25.
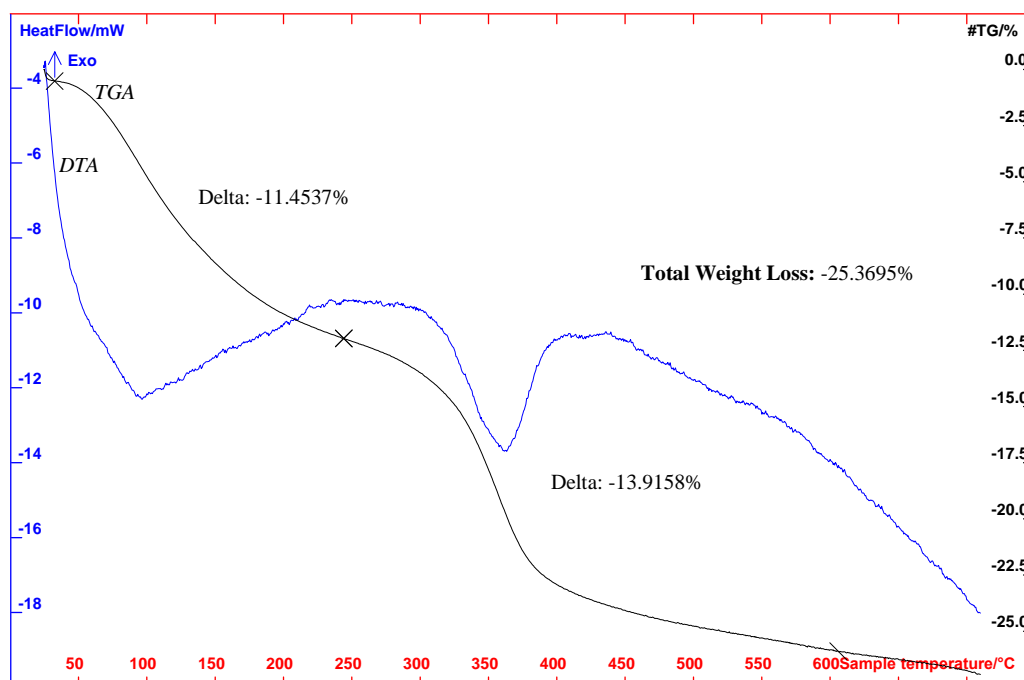


**Figure 4.25** TGA and DTA diagram of the mixed hydroxide precipitate produced from the purified PLS by MHP1 at pH 7.00, 50$^o$C of precipitation temperature and 1 hour of precipitation duration with addition of fresh MgO slurry.

The weight loss (11.4%) up to 100$^o$C was most probably due to the removal of physically bonded water whereas the weight loss (13.9%) up to 400$^o$C and

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the heat absorbance at $360^{o}C$ were most likely to be due to the dehydroxylation reaction of hydroxides and the water taken away from $[Ni(OH)_2]$, $[3Ni(OH)_2]$ and $[3Ni(OH)_2.2H_2O]$ and $[Mg(OH)_2]$ according to Reactions 4.8, 4.9, 4.10 and 4.11, respectively [92].

$$Ni(OH)_2 \longrightarrow NiO + H_2O \qquad\qquad (4.8)$$

$$3Ni(OH)_2 \longrightarrow 3NiO + 3H_2O \qquad\qquad (4.9)$$

$$3Ni(OH)_2.2H_2O \longrightarrow 3Ni(OH)_2 + 2H_2O \qquad\qquad (4.10)$$

$$Mg(OH)_2 \longrightarrow MgO + H_2O \qquad\qquad (4.11)$$
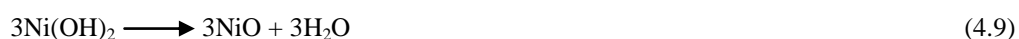
At the end of MHP1 study, a new PLS stock which would be used in MHP2 was produced by carrying out MHP1 at the optimum conditions. The AAS analysis of the new 1.25 L PLS stock is illustrated in Table 4.18

**Table 4.18** Chemical analysis by AAS of the new PLS stock produced by MHP1 at the optimum conditions.

| Components of PLS | Concentration (ppm) |
|---|---|
| Ni | 260 |
| Co | 1.4 |
| Fe | 0 |
| Mg | 7046 |
| Al | 0 |
| Ca | 725 |
| Mn | 182 |
| Cr | 0.10 |
| Zn | 0.15 |
| Cu | 0 |
| $H_2SO_4$ | 0 |

In the PLS stock there was no free acid present and before MHP2, Ni/Mn ratio was 1.43. The ORP (or SHE) value and the density of the PLS stock were 220 mV (or 418 mV) and 1.04 $g/cm^3$, respectively. In addition, the very small amounts of iron, aluminum, chromium and copper remaining in the PLS

after the second iron removal was almost completely removed from the PLS during MHP1. Now, the PLS was a residual leach liquor solution containing small amounts of some ions of elements as expressed in Table 4.18.

## 4.4 Second Mixed Hydroxide Precipitation (MHP2)

In the MHP2, which is called scavenging nickel precipitation, the optimum conditions were studied in order to precipitate residual nickel completely from the residual solution with some but the minimum amount of manganese in a mixed hydroxide form which would be re-dissolved in the recycle leach for recovery of nickel and cobalt. Since the residual solution contained significant amounts of nickel, MHP2 was found to be necessary to gain the nickel loss from the liquor. Therefore, a non-selective precipitation of nickel was decided to be carried out using hydrated lime slurry as the precipitating agent. Magnesium oxide slurry was not selected since it was not targeted to produce saleable hydroxide product as in MHP1. In addition, there is no study reported in the literature in which magnesium oxide slurry is used in MHP2. The purpose of the MHP2 experiments was to find an appropriate way to precipitate almost all the remaining nickel together with cobalt from the residual leach liquor leaving less than 10 ppm nickel in the solution by adding 1% w/w $Ca(OH)_2$ slurry into the residual solution without considering manganese limitation unless it was much more than expected (>10% in the precipitate). In contrast to MHP1, in MHP2 the most important parameter was the nickel precipitation recovery which had to be maintained as high as possible because there was no other further step for the nickel to be recovered from the leach liquor. Simultaneously, manganese precipitation recovery had to be low by the virtue of the fact that manganese would be re-leached from the precipitate together with nickel and cobalt during the recycle leach leading to an increased load of manganese in the MHP circuit.

## 4.4.1 Effect of pH

In the first set of experiments, pH was typically kept in the range of pH 7.50-8.50 with 1% w/w of freshly slurried slaked (hydrated) lime aiming to determine the optimum pH value at which maximum practical nickel precipitation would be achieved providing that manganese contamination could not be so much giving rise to an undesired increase in manganese concentration in the MHP circuit.

At the fixed conditions ($60^{o}$C of precipitation temperature and 1 hour of precipitation duration) pre-determined from the literature [69, 70, 92, 101], precipitation recoveries with respect to various pH values were recorded as the volume of the slaked lime slurry was changed. The results are shown in Table 4.19 and Figure 4.26 displays the graphical presentation of the precipitation recoveries of Ni, Co and Mn with respect to pH at $60^{o}$C of precipitation temperature and 1 hour of precipitation duration.

**Table 4.19** Precipitation recoveries with respect to pH of the leach liquor at $60^{o}$C of precipitation temperature and 1 hour of precipitation duration.

| pH | Ni (%) | Co (%) | Mn (%) |
|---|---|---|---|
| 7.50 | 91.6 | 92.7 | 29.0 |
| 7.75 | 99.9 | 100.0 | 90.9 |
| 8.00 | 99.9 | 100.0 | 99.4 |
| 8.50 | 99.9 | 100.0 | 100.0 |

Optimum pH depends on the desired residual nickel and cobalt concentrations in the remaining solution and the desired manganese content in the precipitate. After pH 7.75, nickel and cobalt precipitation recoveries became almost 100% but more than 90% of manganese precipitated yielding to an undesired manganese concentration in the precipitate. The manganese increase with pH especially between pH 7.50 and 8.00 is also seen in Figure 4.26. Thus, the optimum pH was decided to be less than pH 8.00. Although at pH 7.50, the manganese precipitation recovery was desirable while nickel

precipitation recovery was about 92%, this percentage could be increased up to 97-100% without so much manganese precipitation by conducting MHP2 at a different precipitation temperature and duration combination which will be explained in the following parts.
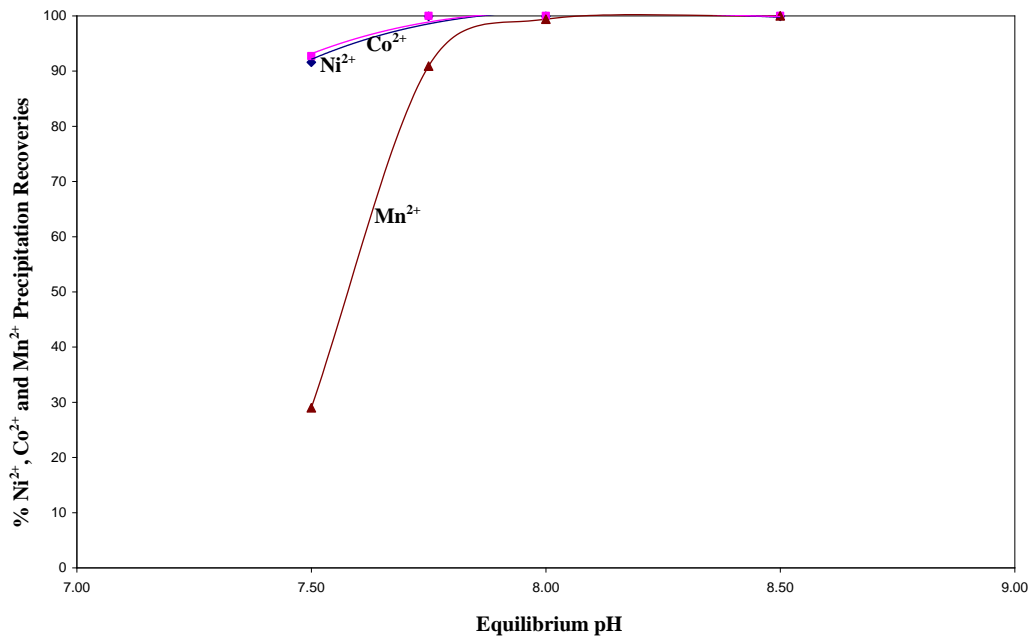


**Figure 4.26** Precipitation recoveries (%) of nickel, cobalt and manganese with respect to pH at 60°C of precipitation temperature and 1 hour of precipitation duration.

As it is stated in Chapter 2, Sist and Demopoulos reported that the solubility of nickel in the aqueous phase decreased with increasing pH [91], so effecting the precipitation mechanism as in the iron removal process which can be also be concluded from Figure 4.26.

## 4.4.2 Effect of pH, Precipitation Temperature and Duration Combinations

In the second set of experiments, different pH, precipitation temperature and duration combinations were investigated. Firstly at pH 7.50 and 50°C of precipitation temperature, and secondly at pH 7.75 and 60°C of precipitation

temperature, various precipitation durations were studied using 1% w/w freshly slurried reactive slaked lime as precipitating agent aiming to determine the optimum pH, precipitation temperature and duration at the same time in order to achieve maximum residual nickel precipitation which would occur while manganese contamination was minimum and could not exceed so much in the precipitate. Results of the experiments are given in Table 4.20. In graphical forms, demonstrations of the precipitation recoveries of Ni, Co, and Mn at pH 7.50 and 50$^o$C of precipitation temperature and at pH 7.75 and 60$^o$C of precipitation temperature according to precipitation duration are given in Figures 4.27 and 4.28, respectively.

**Table 4.20** Precipitation recoveries at pH 7.50 and 50$^o$C of precipitation temperature and at pH 7.75 and 60$^o$C of precipitation temperature with respect to precipitation duration.

| T$^o$C | Duration (hour) | pH | Ni (%) | Co (%) | Mn (%) |
|---|---|---|---|---|---|
| 50 | 0.5 | 7.50 | 56.4 | 62.9 | 10.4 |
| 50 | 1 | 7.50 | 60.8 | 66.7 | 11.1 |
| 50 | 3 | 7.50 | 97.4 | 100.0 | 62.5 |
| 60 | 0.5 | 7.75 | 97.2 | 97.6 | 86.0 |
| 60 | 1 | 7.75 | 99.9 | 100.0 | 90.9 |
| 60 | 3 | 7.75 | 99.9 | 100.0 | 100.0 |

Sist and Demopoulos [91] reported that the solubility of nickel in the aqueous phase is also decreased with increasing temperature which is seen in Figure 4.29 and Table 4.21 when compared with Figure 4.27 and Table 4.20, respectively. It was observed from the MHP2 experiments that at pH 7.50, increasing the temperature from 50$^o$C to 60$^o$C decreased the nickel concentration by more than 75% and increasing precipitation duration from 1 to 2 hours by more than 90%.
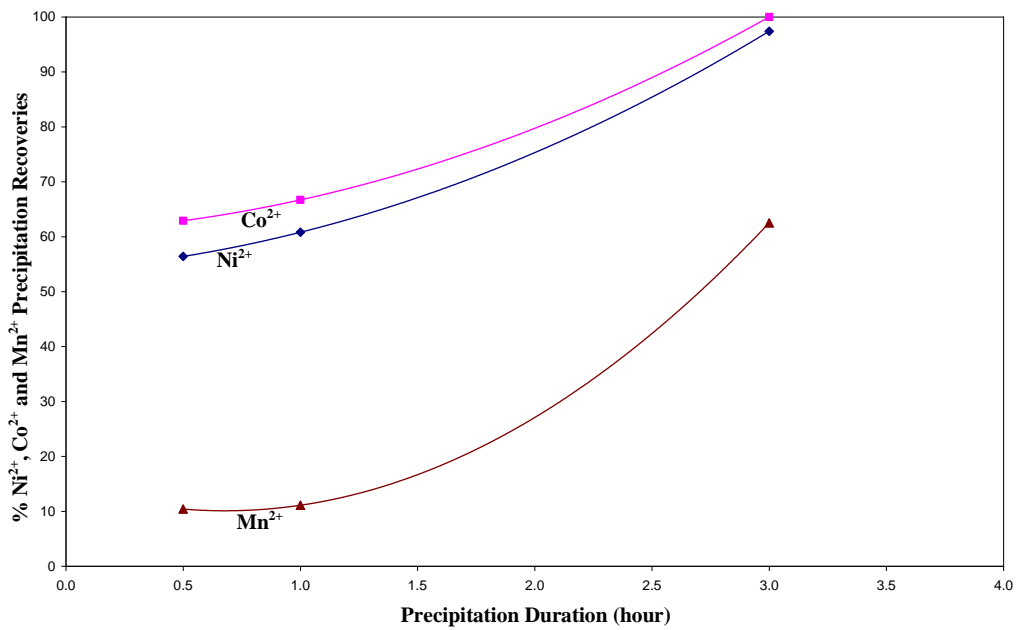
**Figure 4.27** Precipitation recoveries (%) of nickel, cobalt and manganese at pH 7.50 and 50$^{\circ}$C of precipitation temperature with respect to precipitation duration.
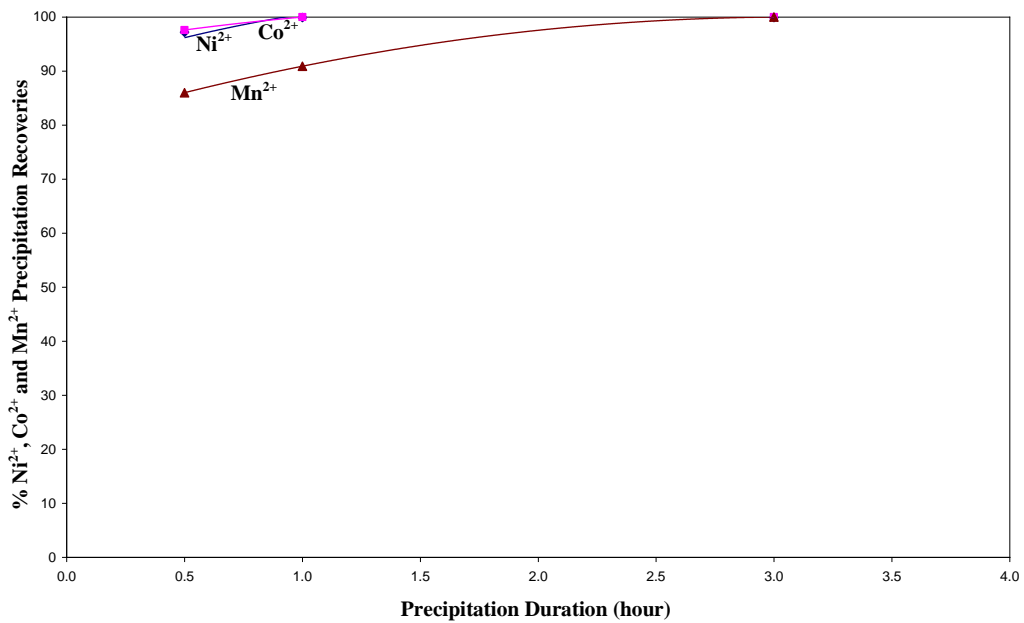


**Figure 4.28** Precipitation recoveries (%) of nickel, cobalt and manganese at pH 7.75 and 60$^{\circ}$C of precipitation temperature with respect to precipitation duration.

In the final set of experiments, the precipitation duration was studied at a fixed pH (7.50) and precipitation temperature ($60^oC$) before deciding the optimum conditions. The results of the experiments are shown in Table 4.21 and Figure 4.29 illustrates the graphical presentation of the precipitation recoveries of Ni, Co and Mn with respect to precipitation duration.

**Table 4.21** Precipitation recoveries at pH 7.50 and $60^oC$ of precipitation temperature with respect to precipitation duration.

| Duration (hour) | Ni (%) | Co (%) | Mn (%) |
|---|---|---|---|
| 1.0 | 91.6 | 92.7 | 29.0 |
| 1.5 | 99.7 | 95.2 | 78.9 |
| 2.0 | 99.9 | 100.0 | 89.9 |
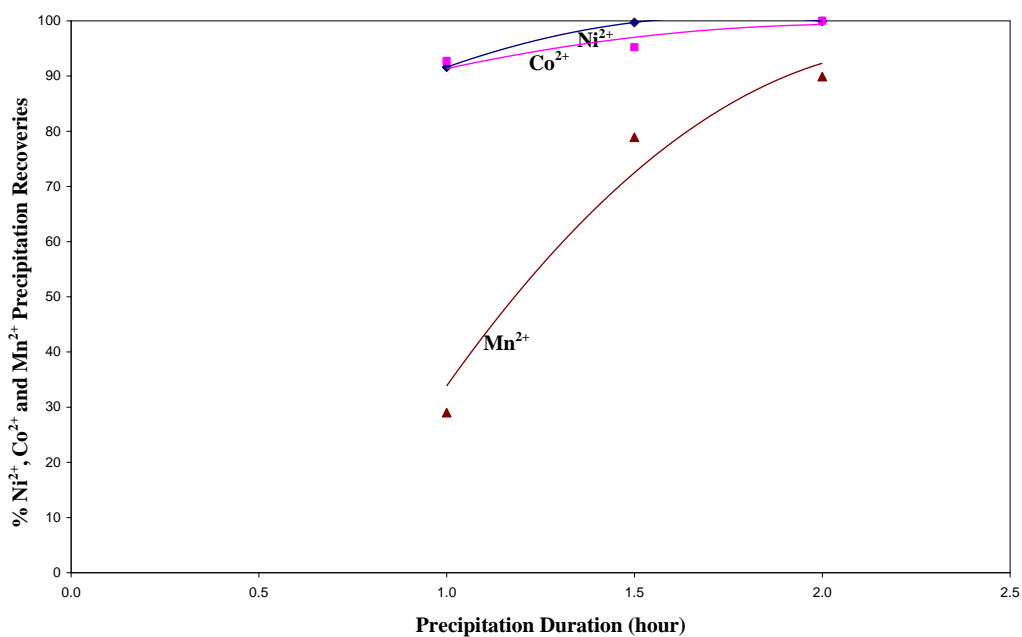


**Figure 4.29** Precipitation recoveries (%) of nickel, cobalt and manganese at pH 7.50 and $60^oC$ of precipitation temperature with respect to precipitation duration.

$Mn^{2+}$ concentration in the residual solution was abruptly decreased after 1 hour of precipitation duration while $Ni^{2+}$ and $Co^{2+}$ precipitation recoveries from the residual solution gradually increased between 90% and 100%. But, at least 95% nickel precipitation recovery was required in MHP2 stage to

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decrease nickel loss to a minimum. Thus, 1.5 hours of precipitation duration was selected to achieve the desired minimum Ni concentration (10 ppm) in the residual solution at pH 7.50 and 60$^{o}$C of precipitation temperature while taking about 79% Mn in solution into the precipitate.

At the end of the MHP2 experiments, in order to achieve less than 10 ppm Ni in the residual solution while minimum amount of manganese precipitated without much contaminating the MHP2 product and undesired manganese accumulation in the MHP circuit, the optimum conditions were determined to be at pH 7.50, 3 hours of precipitation duration and 50$^{o}$C of precipitation temperature or 1.5 hours of precipitation duration and 60$^{o}$C of precipitation temperature. From among the two conditions, 3 hours of precipitation duration and 50$^{o}$C of precipitation temperature were preferred attributed to leading to less manganese precipitation recovery as seen in Tables 4.20 and 4.21. At the chosen condition, the amount of Ca(OH)$_2$ slurry consumed was 2.7 cc (0.027 g Ca(OH)$_2$ / 50 cc residual solution) (0.54 kg Ca(OH)$_2$ / m$^3$ residual solution) and the weight of the precipitate produced was, 0.05 g / 50 cc, 17% of the precipitate weight by MHP1. It is important to note that in contrast to MHP1, the nickel in the precipitate produced in less amounts had to be recovered by recycle leaching providing that at least 95% Ni together with Co extraction recoveries from the precipitates would be attained.

After MHP2, about 97% of nickel, 100% of cobalt, 63% of manganese and less than 0.5% of magnesium in solution were precipitated at the optimum conditions chosen (pH 7.50, 50$^{o}$C of precipitation temperature, 3 hours of precipitation duration). The precipitate analysis is given in Table 4.22. Nickel content as well as manganese, calcium and sulfur was relatively high in the precipitate. But, the MHP2 product contained 11.4% Mn. According to Willis, second stage MHP product typically contains 10-20%Mn [70]. At MHP2, there was calcium sulfate precipitation as bassanite due to the reaction between calcium hydroxide and metal sulfates left in the residual solution

after MHP1 as in Reactions 4.12, 4.13, 4.14 and 4.15. The decrease of nickel, cobalt and manganese in the residual solution resulting from these reactions at MHP2 is also apparent in Table 4.23.

**Table 4.22** Composition analysis of the hydroxide precipitate produced from the residual solution of the MHP1 by MHP2 at the optimum conditions.

| Components of the precipitate | Value (%w/w dry) |
|---|---|
| Ni | 25.32 |
| Co | 0.14 |
| Mn | 11.4 |
| Mg | 1.9 |
| Cr | 0.010 |
| Ca | 11.6 |
| Zn | 0.008 |
| S | 11.13 |

$$Ca(OH)_{2\,(s)} + Ni(SO)_{4\,(aq)} \longrightarrow CaSO_{4\,(s)} + Ni(OH)_{2\,(s)} \qquad (4.12)$$

$$Ca(OH)_{2\,(s)} + Co(SO)_{4\,(aq)} \longrightarrow CaSO_{4\,(s)} + Co(OH)_{2\,(s)} \qquad (4.13)$$

$$2Ca(OH)_{2\,(s)} + 2Mn(SO)_{4\,(aq)} + 1/2O_{2\,(g)} \longrightarrow 2CaSO_{4\,(s)} + 2MnOOH_{(s)} + H_2O_{(l)} \qquad (4.14)$$

$$Ca(OH)_{2\,(s)} + Mg(SO)_{4\,(aq)} \longrightarrow CaSO_{4\,(s)} + Mg(OH)_{2\,(s)} \qquad (4.15)$$
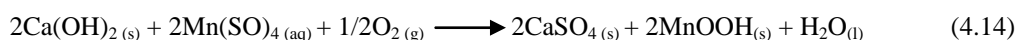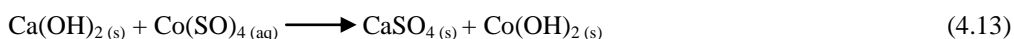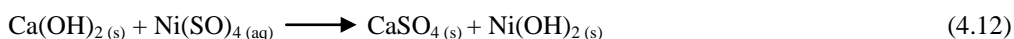
As seen in Reaction 4.14, manganese in the solution was oxidized by oxygen in air to form typical manganese oxides which are manganite and groutite and became $Mn^{3+}$ in the precipitate from $Mn^{2+}$ in the solution. The ratio of (Ni+Co)/Mn was 2.23 in the precipitate and 1.44 in the PLS prior to the MHP2 process. Although the mixed hydroxide product had a nickel content of about 25% on dry basis, MHP2 was not selective over manganese for the recovery of nickel. According to Zhang et al., MHP intermediates remain contaminated with manganese and must be further refined in the downstream process [95]. Furthermore, the precipitate was contaminated with calcium sulfate resulting in an economically valueless product according to marketing conditions. However, the mixed hydroxide products at the end of MHP2 would be sent to the recycle leach stream where the nickel and cobalt values were re-dissolved from the mixed precipitates by sulfuric acid leaching while

achieving at least 95% of leach extraction recovery for nickel. Therefore, most of the loss of nickel in the residual solution was recovered by MHP2 and the recycle leaching while some calcium and manganese would go into solution. Total extraction recoveries of nickel and cobalt with respect to number of recycle leach of the precipitates produced by both the second iron removal and MHP2 are shown in Figure 4.30. An example of total extraction recovery calculation including recycle leach of precipitates produced by second iron removal and MHP2 is given in Appendix B.
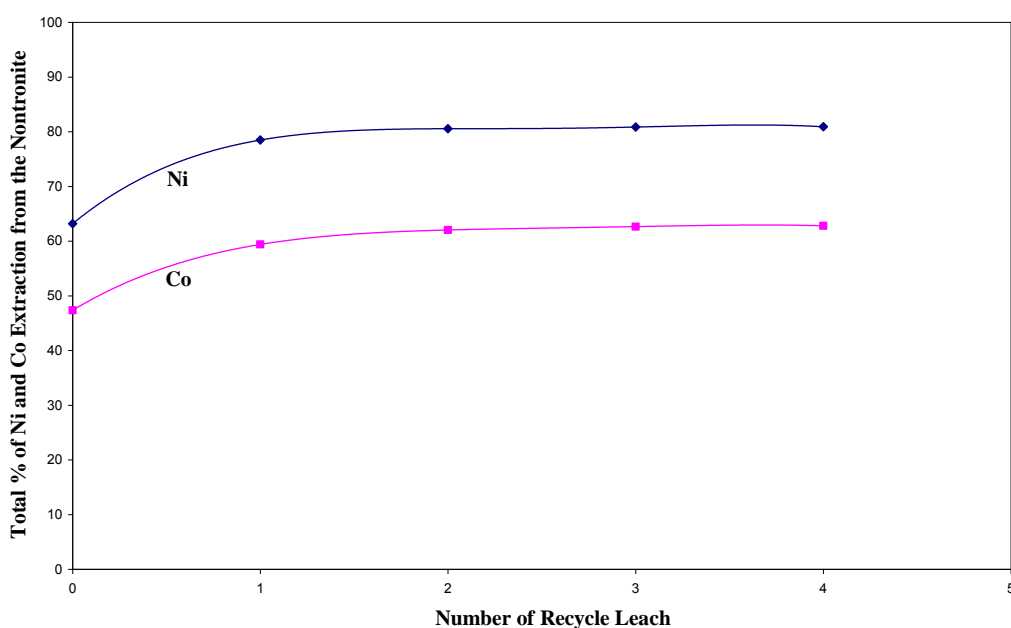


**Figure 4.30** Total extraction recoveries (%) of Ni and Co from the crude laterite ore to the hydroxide precipitate produced by the MHP1 with respect to number of recycle leach of the precipitates produced by the second iron removal and MHP2.

By maintaining recycle leaching with sulfuric acid at a desired efficiency, about 81% of Ni and 63% of Co could totally be extracted from the nontronite ore by MHP1 (9.72 kg Ni / ton of ore and 0.28 kg Co / ton of ore) after the fourth recycle leaching. These total extraction recoveries are higher and more close to the column leach extraction recoveries (86% Ni and 65% Co) if it is compared to the total extraction recoveries including no recycle leaching or recycle leaching of the precipitates produced by only the second iron removal as seen in Figures 4.23. About 63% of Ni and 47% of Co in the nontronite

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(7.56 kg Ni / ton of ore and 0.21 kg Co / ton of ore) were extracted by MHP without any recycle leaching.

The precipitates from the MHP2 experiments also showed favorable settling and filtration properties. It was observed that the color of the residual solution after the addition of the hydrated lime slurry changed from light green to dark green and light brown which was believed to be the indicator for the contamination of the mixed hydroxide product due to the insoluble calcium sulfate. The X-Ray diffraction data of the mixed hydroxide precipitate produced by MHP2 at the optimum conditions using 1% w/w fresh $Ca(OH)_2$ slurry as precipitating agent is shown in Figure 4.31.



1. $CaSO_4.0.5H_2O$-Bassanite
2. $Ni(OH)_2$-Theophrastite
3. $3Ni(OH)_2$-Theophrastite Magnesian
4. $NiSO_4.6H_2O$-Nickel Hexahydrite
5. $Ca_3Mn(SO_4)_2(OH)_6.3H_2O$-Despujolsite
6. $Ca(OH)_2$-Portlandite
7. $MnO(OH)$-Groutite
8. $\gamma$-$MnOOH$-Manganite
9. $MgSO_4.6H_2O$-Hexahydrite
10. $Mg(OH)_2$-Brucite
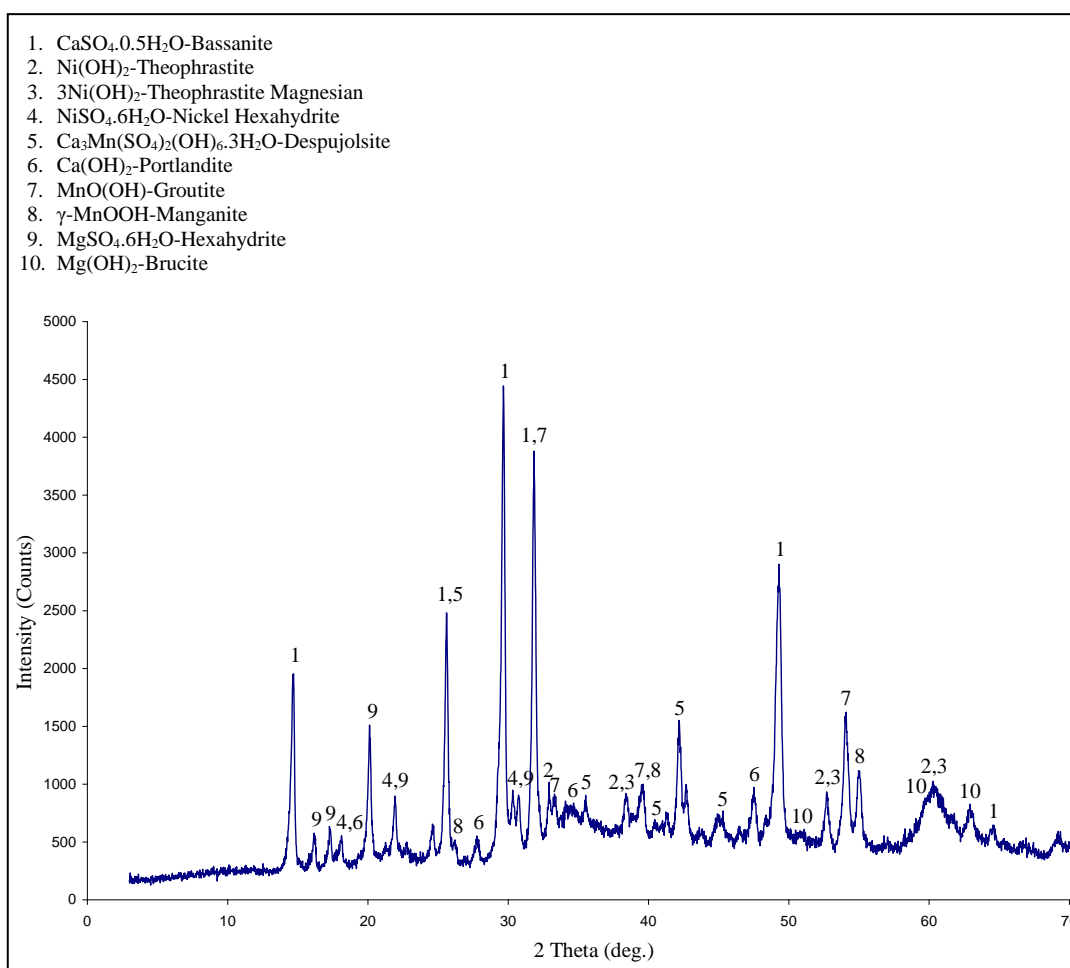
**Figure 4.31** XRD pattern of the mixed hydroxide precipitate produced from the residual solution by MHP2 at pH 7.50, $50^{\circ}C$ of precipitation temperature and 3 hours of precipitation duration with addition of fresh $Ca(OH)_2$ slurry.

The main mineralogical phase was bassanite as in the iron removal stages, which was formed in the mixed hydroxide product because precipitation with calcium hydroxide brings about the formation of an insoluble calcium sulfate precipitate resulting in contamination of the mixed hydroxide product [101]. Other phases were groutite [MnOOH], manganite [γ-MnOOH], despujolsite [$Ca_3Mn(SO_4)_2(OH)_6.3H_2O$], hexahydrite [$MgSO_4.6H_2O$], theophrastite, theophrastite magnesian, nickel hexahydrite, brucite and portlandite [$Ca(OH)_2$]. The main peaks belonging to bassanite and some peaks matching to groutite, manganite, despujolsite and hexahydrite were sharper and with greater intensity while other peaks belonging to the all phases except for bassanite showed lower intensity and greater peak width. XRD pattern of the MHP2 precipitate showed that some Ni, Mg and Mn precipitated in sulfate-hydrate form while the others were in hydroxide forms except for bassanite. Furthermore, as in MHP1, a mineralogical phase of cobalt was not detected due to its low content in the mixed hydroxide precipitate. TGA and DTA analysis of the produced mixed hydroxide precipitate is shown in Figure 4.32. The weight loss (9.0%) up to $120^oC$ was most probably due to the removal of physically bound water while the weight loss (8.3%) up to $400^oC$ and the heat absorbance at $310^oC$ and $395^oC$ were most likely to be due to the dehydroxylation reactions of hydroxides: groutite, manganite, theophrastite, theophrastite magnesian, portlandite and brucite and the water taken away from bassanite, hexahydrite, nickel hexahydrite and despujolsite.

At the end of MHP2, a new solution stock which would be used in the manganese precipitation process was produced by conducting MHP2 at the optimum conditions. The AAS analysis of the new 800 mL residual solution stock is illustrated in Table 4.23.

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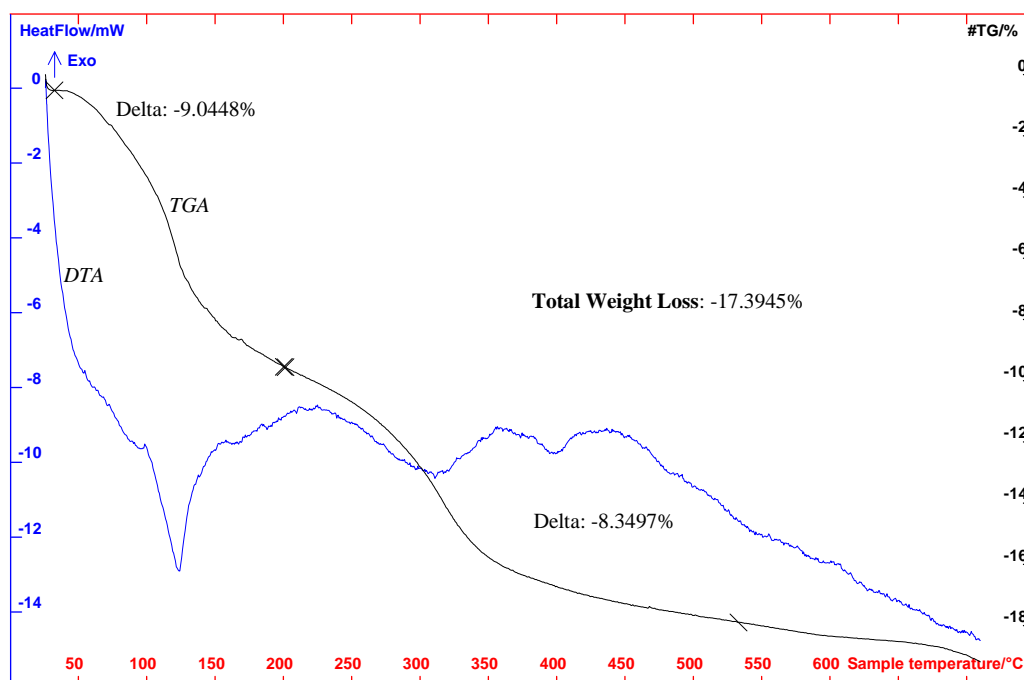
**Figure 4.32** TGA and DTA diagram of the mixed hydroxide precipitate produced from the residual leach solution by MHP2 at pH 7.50, 50°C of precipitation temperature and 3 hours of precipitation duration with addition of fresh Ca(OH)$_2$ slurry.

**Table 4.23** Chemical analysis by AAS of the new residual leach solution stock produced by MHP2 at the optimum conditions.

| Components of PLS | Concentration (ppm) |
|:---:|:---:|
| Ni | 6.5 |
| Co | 0 |
| Mg | 6731 |
| Ca | 726 |
| Mn | 65.4 |
| Cr | 0 |
| Zn | 0.07 |

In the solution stock, there were only magnesium, calcium and manganese left with some nickel and very small amount of zinc after MHP2. Therefore, the residual solution stock was now called barren solution. The ORP (or SHE) value and the density of the barren solution were 210 mV (or 408 mV) and 1.0 g/cm$^3$, respectively.

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## 4.5 Manganese Removal (MnR)

In the manganese removal experiments, the optimum conditions were studied to precipitate the remaining manganese completely from the barren solution with some magnesium using slaked lime slurry as precipitating agent in order to eliminate manganese from the MHP circuit and also discharge liquors to be able to use within the process as make-up water for heap (column) or recycle leaching. After the two-stage nickel-cobalt precipitation (MHP1-MHP2), 20% of the manganese remained in the solution. However, Willis reported that generally more than 50% of the manganese is left in the liquor after the two MHP stages [69]. Although the amount of the manganese precipitated after MHP1-MHP2 in this study was higher than that reported in the literature, it was not a problem because in MHP1, 55% of the manganese remained in the solution and it did not exceed 10% Mn in the precipitate which was saleable and suitable to the marketing conditions.

It was aimed in the manganese removal experiments that less than 5 ppm residual manganese would be achieved in the barren solution by adding fresh 20% w/w $Ca(OH)_2$ slurry into the solution. Therefore, the most important parameter in this last step of the MHP process was the manganese precipitation recovery which had to be kept as high as possible. Otherwise, manganese would accumulate in the circuit and adversely affecting the product quality.

## 4.5.1 Effect of pH

In the first set of experiments, pH was kept in the range of 8.00-9.00 with 20% w/w freshly slurried slaked lime to determine the optimum pH value at which maximum practical manganese precipitation would be attained. At the fixed conditions ($50^{o}C$ of precipitation temperature and 1 hour of precipitation duration) pre-determined from the literature [69, 70, 94, 95], precipitation

recoveries with respect to various pH values were recorded. When 0.4 cc Ca(OH)$_2$ slurry was added, pH 8.50 obtained was found to be the most effective pH and was decided to be the optimum. The results are shown in Table 4.24

**Table 4.24** Precipitation recoveries of manganese and nickel with respect to pH of the barren liquor at 50$^o$C of precipitation temperature and 1 hour of precipitation duration.

| pH | Mn (%) | Ni (%) |
|------|--------|--------|
| 8.00 | 63.1 | 98.5 |
| 8.50 | 99.8 | 100.0 |
| 9.00 | 100.0 | 100.0 |

Manganese precipitation increased with pH between pH 7.50 and 8.50, so at pH 8.50, 100% Mn precipitation was achieved yielding a desired manganese concentration less than 1 ppm in the solution. As it is stated in Chapter 2, a considerable manganese precipitation starts at pH 8.00 and continues between pH 8.00 and 10.00 whereas the molarity of manganese changes as it is apparent in Figure 2.19. It is important to note that the amount of the slaked lime slurry to maintain pH 9.00 at 50$^o$C for 1 hour of precipitation was 7.7 cc (1.54 g / 50 cc barren solution) while it was around 0.1-0.4 cc for the precipitation at pH 8.00 and 8.50, respectively. This showed that the amount of the precipitating agent to increase pH from 8.50 to 9.00 was about 24 times higher than the amount to attain pH 8.50 from 8.00. For this reason, pH 9.00 was not selected as the optimum for the manganese removal attributed to the excessive consumption in the amount of the precipitating agent in spite of 100% Mn precipitation satisfied. The reason for the high consumption was believed to be the buffering effect at this pH range.

According to Willis, the residual solution after the two MHP stages is typically adjusted to pH 8.50-9.00 at 50-60$^o$C of precipitation temperature and 0.5-2 hours of precipitation duration to achieve a residual manganese concentration of <100 ppm by precipitating manganese hydroxide [69, 70]. In addition, a residual concentration of about 10 ppm Mn can be achieved by air

injection by utilizing 10-20% oxygen. In this study during manganese removal experiments, air could also be injected for manganese oxidation. However, it was not found necessary because it was believed that the spiral movement of the magnetic stirrer during manganese precipitation experiments enabling required oxygen in the air to take part in the precipitation reaction (Reaction 4.14). Zhang et al. studied the effect of pH on the kinetics of $Mn^{2+}$ oxidation and reported that the oxidation of $Mn^{2+}$ with $O_2$ is slow but strongly pH dependent as the pH increases above 4.50 [95]. As a result of the manganese oxidation while pH of the solution was increased from 7.50, $Mn^{3+}$ was formed in groutite and manganite from $Mn^{2+}$ in the solution.

**4.5.2 Effect of Precipitation Temperature**

In the second set of experiments, the precipitation temperatures between $50^{o}C$ and $70^{o}C$ were studied at pH 8.50 and 1 hour of precipitation duration using 20% w/w freshly slurried slaked lime aiming to specify the optimum precipitation temperature at which maximum practical Mn precipitation would occur. Results of the experiments are shown in Table 4.25.

**Table 4.25** Precipitation recoveries of manganese and nickel from the barren solution with respect to precipitation temperature at pH 8.50 and 1 hour of precipitation duration.

| $T^{o}C$ | Mn (%) | Ni (%) |
|---|---|---|
| 50 | 99.8 | 100.0 |
| 60 | 100.0 | 100.0 |
| 70 | 100.0 | 100.0 |

There was a small increase in precipitation recovery of manganese with increases in the precipitation temperature while the residual nickel (6.5 ppm) was totally precipitated from the barren solution. Since a precipitation temperature at which 100% manganese precipitation recovery first attained from the solution was required when precipitation temperature was increased, $50^{o}C$ was selected as the optimum precipitation temperature for the manganese removal. Although higher temperatures could also be selected for

100% Mn precipitation recovery, they were out of selection due to unnecessary heating above 50$^{\circ}$C for the same manganese precipitation recovery needed. In addition, Zhang et al. reported that the oxidative precipitation of $Mn^{2+}$ with air occurs at the temperature range of 25-80$^{\circ}$C at pH 6.00 [95]. However, for oxidative manganese precipitation at pH <3.50, a precipitation temperature above 60$^{\circ}$C is not recommended since it leads to the slow mass transfer of oxygen in air through the viscous slurry at relatively high temperature [94]. On the other hand, an operating temperature less than 50$^{\circ}$C resulted in slower reaction kinetics of 100% manganese precipitation and negatively affected the filterability of precipitate.

### 4.5.3 Effect of Precipitation Duration

In the final set of experiments, the precipitation durations between 0.5 and 1.5 hours were studied at pH 8.50 and 50$^{\circ}$C of precipitation temperature using 20% w/w freshly slurried $Ca(OH)_2$ as precipitating agent in order to find out the optimum precipitation duration at which 100% manganese precipitation recovery would be achieved from the PLS at the desired conditions. The results of the experiments are shown in Table 4.26.

**Table 4.26** Precipitation recoveries of manganese and nickel from the barren solution with respect to precipitation duration at pH 8.50 and 50$^{\circ}$C of precipitation temperature.

| Duration (hour) | Mn (%) | Ni (%) |
|---|---|---|
| 0.5 | 97.0 | 100.0 |
| 1.0 | 99.8 | 100.0 |
| 1.5 | 100.0 | 100.0 |

As in the precipitation temperature, there was a small increase in precipitation recovery of manganese with increases in the precipitation duration, while the residual nickel and manganese were almost completely depleted from the barren solution during the waiting time to bring pH from 7.50 to 8.50 at 50$^{\circ}$C of temperature. The same option as in the previous set was also applied to

select the optimum precipitation duration. Therefore, 1 hour of precipitation duration was decided to be the optimum due to attaining 100% Mn at first.

At the end of the third set of experiments, the optimum conditions were finally chosen at pH 8.50, 50$^{o}$C of precipitation temperature and 1 hour of precipitation duration for the manganese removal. At these conditions, the weight of the precipitate produced by the manganese removal process was about 0.05 g and the amount of Ca(OH)$_2$ slurry consumed was 0.4 cc (0.080 g Ca(OH)$_2$ / 50 cc barren solution) (1.6 kg Ca(OH)$_2$ / m$^3$ barren solution). After the manganese removal, only calcium and magnesium were left in the barren solution. The precipitate analysis is given in Table 4.27. Manganese, calcium, magnesium and sulfur were the main constituents of the precipitate. As it is apparent in Table 4.27, there was a small amount of nickel loss in the manganese precipitate which would be insignificant in the economic view of the process.

**Table 4.27** Composition analysis of the manganese precipitate produced from the barren solution by the manganese removal process at the optimum conditions.

| Components of the precipitate | Value (%w/w dry) |
|---|---|
| Ni | 0.65 |
| Mn | 6.53 |
| Mg | 2.8 |
| Zn | 0.01 |
| Ca | 14.8 |
| S | 10.0 |

The precipitates from the manganese removal experiments showed favorable settling and filtration properties as in the previous precipitation processes. It was observed that the color of the barren solution after the addition of the calcium hydroxide slurry changed from transparent to white which was believed to be due to the unreacted calcium hydroxide solid suspended in the solution. The precipitate produced was also white in color.

The X-Ray diffraction data of the manganese hydroxide precipitate produced from the barren solution at the optimum conditions using 20% w/w fresh $Ca(OH)_2$ slurry is shown in Figure 4.33.



1. $CaSO_4.0.5H_2O$-Bassanite
2. $Ni(OH)_2$-Theophrastite
3. $\alpha$-MnOOH-Groutite
4. $\gamma$-MnOOH-Manganite
5. $Ca_3Mn(SO_4)_2(OH)_6.3H_2O$-Despujolsite
6. $Ca(OH)_2$-Portlandite
7. $Mg(OH)_2$-Brucite
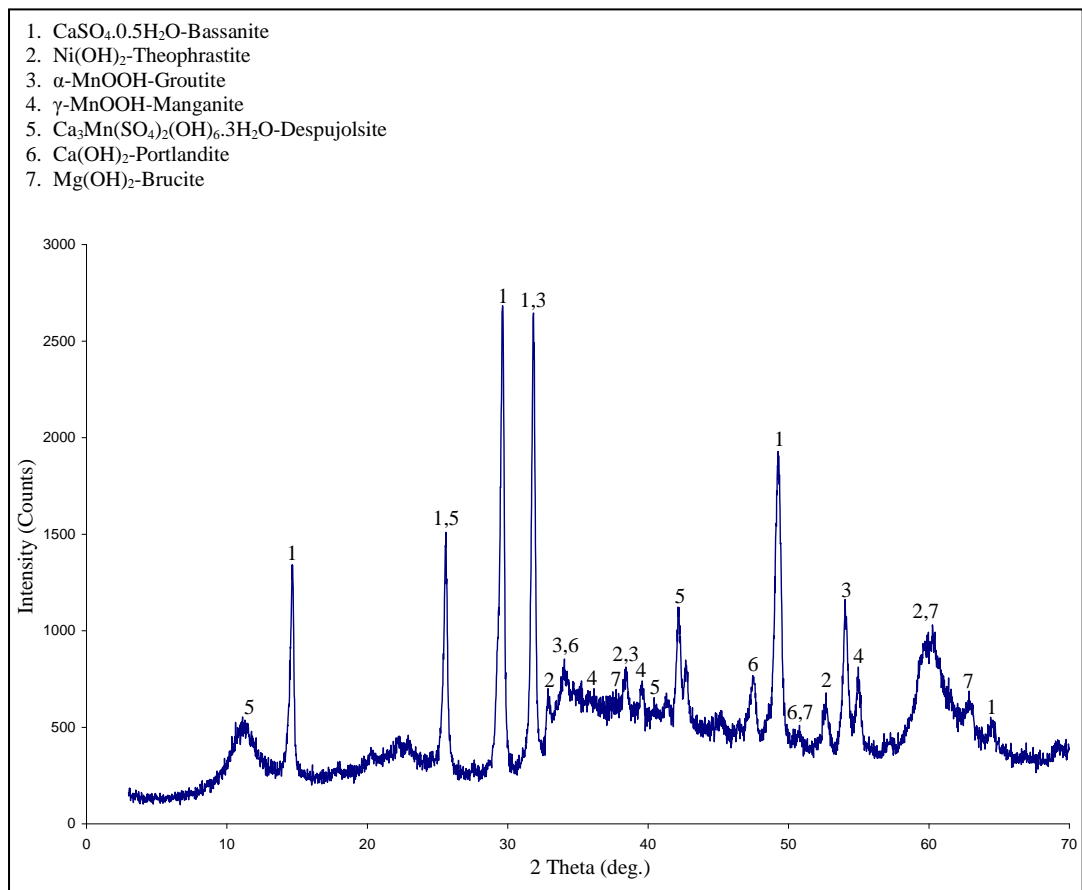
**Figure 4.33** XRD pattern of the manganese hydroxide precipitate produced from the barren solution by manganese removal at pH 8.50, $50^{\circ}C$ of precipitation temperature and 1 hour of precipitation duration with addition of $Ca(OH)_2$ slurry.

The main mineralogical phase was bassanite as in MHP2 and the iron removal stages by the virtue of the fact that the precipitation with calcium hydroxide gives rise to the formation of an insoluble calcium sulfate precipitate leading to the contamination of the hydroxide product. The formation of bassanite can also be predicted from high calcium and sulfur concentration in the precipitate shown in Table 4.27. Other phases were groutite, manganite, despujolsite,

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theophrastite, brucite and portlandite. The main peaks belonging to bassanite and some peaks matching to groutite, manganite, despujolsite and portlandite were sharper and with greater intensity while other peaks belonging to the all phases except for bassanite showed lower intensity and greater peak width. Nickel hydroxide was not easily detected in the manganese hydroxide product due to its low amount as in the MHP2 product. TGA and DTA analysis of the produced manganese hydroxide precipitate is shown in Figure 4.34.
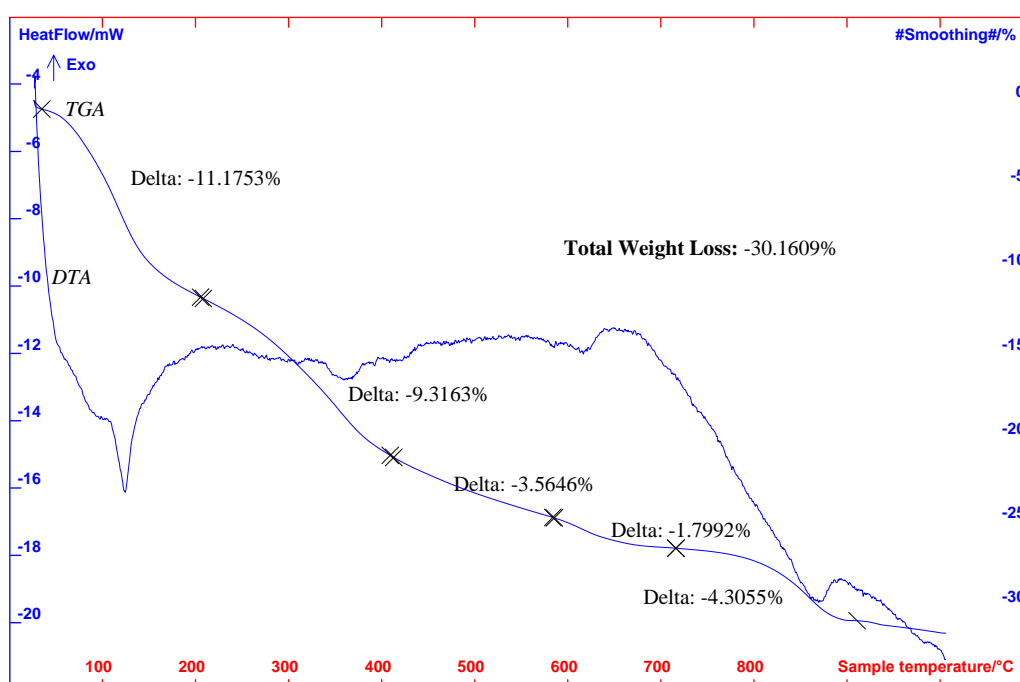


**Figure 4.34** TGA and DTA diagram of the manganese hydroxide precipitate produced from the barren solution by manganese removal at pH 8.50, 50$^{o}$C of precipitation temperature and 1 hour of precipitation duration with addition of fresh Ca(OH)$_2$ slurry.

The weight loss (11.2%) up to 120$^{o}$C was most probably attributed to the removal of physically held water while the weight loss (19.0%) from 120$^{o}$C up to 900$^{o}$C and the heat absorbance at 365$^{o}$C, 617$^{o}$C and 867$^{o}$C were most likely be attributed to the dehydroxylation reaction of hydroxides: [MnOOH], [$\gamma$-MnOOH], [Ni(OH)$_2$], [Ca(OH)$_2$] and [Mg(OH)$_2$] and the water taken away from [CaSO$_4$.0.5H$_2$O] and [Ca$_3$Mn(SO$_4$)$_2$(OH)$_6$.3H$_2$O]. Particularly, at 867$^{o}$C,

the endothermic peak was believed to be the dehydroxylation reaction of [MnOOH] and [γ-MnOOH] since a similar peak is present in the DTA-TGA of manganese (III) oxide which is shown in Figure 4.35.

MANGANESE (III) OXIDE
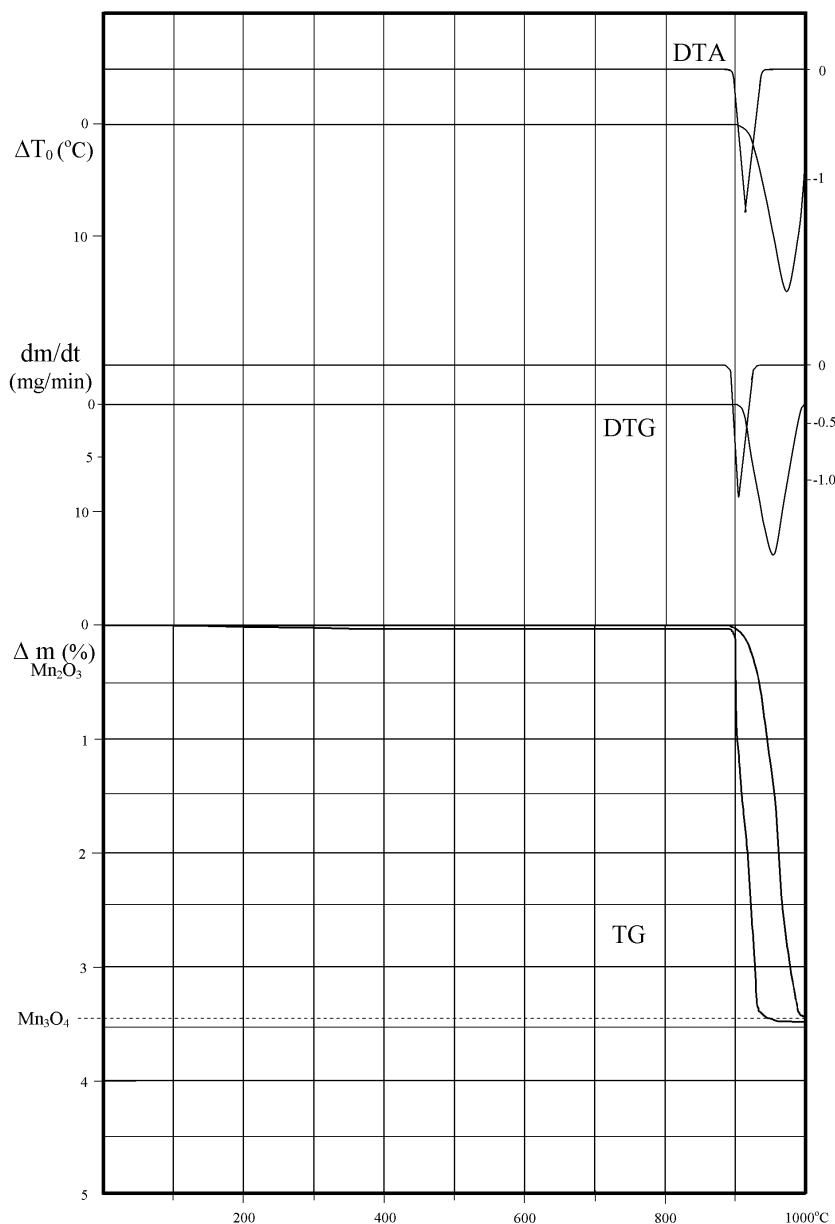


**Figure 4.35** DTA and TGA of manganese (III) oxide [102].

At the end of the manganese removal, the final barren solution which would be now used as make-up water for column or recycle leaching was produced. The AAS analysis of this solution is given in Table 4.28. The ORP (or SHE) value and the density of the solution after the manganese removal were 190 mV (or 388 mV) and 1.0 $g/cm^3$, respectively.

**Table 4.28** Chemical analysis by AAS of the solution which would be used as make-up water for column or recycle leaching produced from the barren solution by the manganese removal process operated at the optimum conditions.

| Components of PLS | Concentration (ppm) |
|---|---|
| Ni | 0 |
| Mg | 6703 |
| Ca | 727 |
| Mn | 0.13 |
| Zn | 0 |

There were only magnesium and calcium left in the barren solution which would be accumulated in the circuit by means of recirculating the solution through the recycle leach after the manganese removal. Magnesium can also be removed from the MHP circuit by precipitation with the addition of fresh $Ca(OH)_2$ slurry if required and as long as it is economical. However, if the equilibrium concentration of magnesium in the circuit does not adversely alter product quality, then magnesium removal can be excluded.

**CHAPTER 5**

**CONCLUSIONS**

Nickel and cobalt could be recovered efficiently in a saleable mixed hydroxide precipitate form from the PLS produced by column leaching of nontronite ore originating from Manisa-Gördes. A typical MHP process was followed in this study and promising results were obtained very similar to those presented in the literature. The age long experimental work has proven that iron extracted into solution by column leaching could successfully be rejected from PLS together with aluminum and chromium by a two-stage iron removal process. At each stage, a slurry of $CaCO_3$ could be used which is the most suitable and the cheapest precipitating and neutralizing agent for iron removal process. Nickel and cobalt losses in the precipitate produced by the second iron removal and MHP2 were required to be regained by means of the recycle leach.

After the neutralization of the PLS and the first iron removal stage by the addition of $CaCO_3$ slurry, a high proportion of ferric iron and arsenic could be substantially precipitated while aluminum and chromium partially precipitated from solution. In the second iron removal stage, the residual iron, aluminum and chromium were almost completely removed from the PLS with some but minimum amount of nickel and cobalt losses to the precipitate. Therefore, the impurities contaminating the PLS such as Fe, Cr, Al and As could be

diminished to less than 5-10 ppm each in solution. The experiments of the iron removal have shown that as a result of the neutralization of the PLS obtained from the column leaching of the nontronitic laterite ore and the purification of the PLS from Fe, As, Al and Cr at two stages by the addition of $CaCO_3$ slurry, the expected results existing in the literature could practically be achieved for a nontronitic type laterite ore.

The method of the two-stage precipitation of nickel and cobalt as mixed hydroxide products from the remaining solution cleaned from most of the impurities has appeared to be the most appropriate method for the extraction of nickel and cobalt from the leach liquor. For MHP1, the precipitation with fresh MgO slurry gave very effective results whereas for MHP2, fresh $Ca(OH)_2$ slurry used led to the desired conditions in which nickel and cobalt could efficiently be recovered with the minimum amount of manganese. The analyses of MHP1 and MHP2 experimental products showed that MHP1 was a saleable nickel-cobalt hydroxide with very good quality, while the mixed hydroxide precipitate resulting from MHP2 was of poor quality and was not qualified for the marketing conditions. Therefore, nickel and cobalt in the MHP2 precipitate was required to be recovered by re-leaching methods and recycled back to the MHP circuit to regain losses. By maintaining recycle leaching with sulfuric acid at a desired efficiency for the precipitates produced by the second iron removal and MHP2, high extraction recoveries of nickel and cobalt from the nontronite ore could be achievable by the MHP process carried out. About 81% of Ni and 63% of Co in the lateritic nickel ore (9.72 kg Ni / ton of ore and 0.28 kg Co / ton of ore) could be extracted as mixed hydroxide precipitate by MHP with recycle leaching. This hydroxide product contained about 42% Ni, 1% Co, 2% Mn and 2% Mg.

After the two-stage MHP, a manganese removal stage was required because the equilibrium concentration of manganese in the circuit would negatively affect the product quality. After the manganese removal, a magnesium

removal could also be followed to reject magnesium from MHP circuit if it was needed to decrease magnesium accumulation in the circuit. However, the experimental results indicated that the consumption of $Ca(OH)_2$ slurry was excessive due to the buffering effect which would yield an uneconomic process. At the end of the MHP process, the solution which was almost free of metals could be used as make-up water for heap or recycle leaching.

For the future work, following suggestions can be made:

1. The problems due to high $CO_2$ emission at $90^oC$ and high amount of solid waste in the form of precipitate produced at low pH (2.50) in the first iron removal, possible solutions should be considered and a remedy should be found for the disposals of gaseous and solid wastes of the first iron removal in accordance with the environmental regulations.

2. First iron removal at ambient conditions needs to be studied to attain the same or better precipitation recoveries with less amount of heat energy consumed providing that filtration and settling properties of the precipitate are not negatively affected.

3. A mechanical agitator can be used instead of a magnetic stirrer for more homogeneous mixing of solution with the slurry of $CaCO_3$ and a different type or shape of container can be found for the iron removal process to decrease the losses of precipitate to a minimum on the inside wall of the container.

4. Precipitation of iron, aluminum and chromium from the pregnant leach solution at the second iron removal stage with less nickel and cobalt losses to the precipitate needs to be studied by adding seeds of the precipitate into the solution.

5. Recycle leach of precipitates produced by second iron removal and MHP2 with sulfuric acid should be investigated experimentally and at least 95% nickel-cobalt extraction recoveries from the precipitates

should be aimed for achieving maximum recoveries of nickel and cobalt as mixed hydroxide product from the crude nontronite ore.

6. In MHP1, the same or greater precipitation recoveries of nickel and cobalt with less amount of manganese precipitating from the purified PLS by addition of fresh MgO slurry should be further investigated and volume of MgO slurry added into solution during MHP1 should be controlled instead of pH control as in the other processes to achieve desired precipitation recoveries. In addition, MgO slurry should be used freshly within 2 or 3 minutes.

7. In MHP2, a different precipitating agent ($CaO$, $CaCO_3$, etc.) and seed addition of MHP2 precipitate can be studied at different conditions such as pH, precipitation temperature and duration to achieve better nickel and cobalt recoveries and/or less amount of manganese precipitated.

8. Manganese removal before MHP can be investigated to reject manganese from the circuit prior to nickel-cobalt precipitation and to attain a desired purer mixed hydroxide product containing no or very small amount of manganese.

9. Purification of residual leach solution from magnesium in an economic manner should be investigated so as to use the residual solution as make-up water for heap or recycle leaching in the circuit without leading to any considerable magnesium accumulation.

10. Pilot plant testing and feasibility studies of MHP process developed in this thesis study should be carried out to see the applicability and workability of MHP executed.

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**APPENDIX A**

**EXAMPLE OF PRECIPITATION RECOVERY CALCULATION**

Precipitation recovery values were calculated by putting experimental data into Equation A.1 given below.

$$\text{Precipitation Recovery of Metal} = \frac{\text{Metal \% in precipitate x Weight (mg) of precipitate}}{\text{Metal (mg) in PLS x Volume (cc) of PLS x } 10^{-3}} \quad (A.1)$$

Results of AAS analysis of the PLS and XRF analysis of the precipitate produced from the PLS by the first iron removal at pH 2.50, $90^{\circ}$C of precipitation temperature and 2 hours of precipitation duration are indicated in Table A.1.

**Table A.1** Experimental data obtained from the AAS analysis of the PLS and XRF analysis of the precipitate produced by the first iron removal at the optimum conditions.

| PLS (mg/L) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Vol. (cc) | Ni | Co | Fe | Mn | Cr | Al | Cu |
| 100 | 4800 | 114 | 38600 | 620 | 1060 | 3950 | 3.8 |

| Precipitate | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wt. (mg) | Ni (%) | Co (%) | Fe (%) | Mn (%) | Cr (%) | Al (%) | Cu (%) |
| 24500 | 0.0086 | 0.0002 | 15.59 | 0.0261 | 0.3187 | 0.9 | $1.08 \times 10^{-4}$ |

According to the experimental data and Equation A.1, the precipitation recoveries from the PLS at the first iron removal done at the optimum conditions were calculated as follows:

$$\text{Recovery of Ni (\%)} = \frac{0.0086 \times 24500}{4800 \times 100 \times 10^{-3}} = 0.44 \tag{A.2}$$

$$\text{Recovery of Co (\%)} = \frac{0.0002 \times 24500}{114 \times 100 \times 10^{-3}} = 0.44 \tag{A.3}$$

$$\text{Recovery of Fe (\%)} = \frac{15.59 \times 24500}{38600 \times 100 \times 10^{-3}} = 98.96 \tag{A.4}$$

$$\text{Recovery of Mn (\%)} = \frac{0.0261 \times 24500}{620 \times 100 \times 10^{-3}} = 10.32 \tag{A.5}$$

$$\text{Recovery of Cr (\%)} = \frac{0.3187 \times 24500}{1060 \times 100 \times 10^{-3}} = 73.66 \tag{A.6}$$

$$\text{Recovery of Al (\%)} = \frac{0.9 \times 24500}{3950 \times 100 \times 10^{-3}} = 55.82 \tag{A.7}$$

$$\text{Recovery of Cu (\%)} = \frac{1.08 \times 10^{-4} \times 24500}{3.8 \times 100 \times 10^{-3}} = 6.96 \tag{A.8}$$

# APPENDIX B

## EXAMPLE OF TOTAL EXTRACTION RECOVERY CALCULATION

Total extraction recovery values of metals from the ore to the product were calculated by putting metal extraction recovery values found at each stage into Equation B.1 given below.

$$TE_M = CL \times M1 \times M2 \times P \times 100 \tag{B.1}$$

$TE_M = Total\,Extraction\,Recovery\,of\,Metal$
$CL : (\%)\,Column\,Leach\,Recovery\,of\,Metal$
$M1 : \%\,of\,Metal\,in\,PLS\,Left\,in\,PFe1\,Filtrate$
$M2 : \%\,of\,Metal\,in\,PLS\,Left\,in\,PFe2\,Filtrate$
$P : Precipitation\,Recovery\,of\,Metal\,(\%)\,in\,MHP1$

The extraction and precipitation recoveries from the crude nontronite ore to the saleable Ni-Co hydroxide product found by using the experimental data obtained from each hydrometallurgical process carried out at the optimum conditions are shown in Table B.1. By substituting the extraction and precipitation recovery values of nickel at each stage into Equation B.1, total extraction recovery of nickel was calculated as follows:

$$TE_{Ni} = \frac{85.5}{100} \times \frac{99.6}{100} \times \frac{82.8}{100} \times \frac{89.6}{100} \times 100 = 63.18 \tag{B.2}$$

**Table B.1** Extraction and precipitation recoveries from the run of mine nontronite ore (-2 cm) up to the saleable Ni-Co hydroxide product after the column leach, the first and the second iron removal, MHP1 and MHP2.

| | Ni (%) | Co (%) |
|---|---|---|
| **Column Leach** (Ore ⟶ PLS) | 85.5 | 65.0 |
| **First Iron Removal (PFe1)** (PLS ⟶ Filtrate) | 99.6 | 99.6 |
| **Second Iron Removal (PFe2)** (PLS ⟶ Filtrate) | 82.8 | 75.1 |
| **MHP1** (PLS ⟶ Saleable Product) | 89.6 | 97.4 |
| **MHP2** (Leach Solution ⟶ Precipitate) | 97.4 | 100.0 |

However, in Equation B.1 recycle leaching of the precipitates produced in second iron removal and MHP2 is not taken into consideration. Therefore, the exact recovery value should be more than 63.2%. In order to find the exact value of total extraction recovery of nickel, recycle leach recoveries of nickel from the precipitates produced by second iron removal and MHP2 should be accounted and added to the value found in Equation B.2. A schematic diagram is given in Figure B.1 to show the extraction and precipitation recoveries of nickel at each stage including recycle leach. As it is seen from Figure B.1, it is assumed that 95% of nickel in the precipitates produced by second iron removal and MHP2 is recovered by recycle leach.

Just after the first recycle leach of the precipitate produced by the second iron removal, the total extraction recovery of nickel was calculated without considering any recycle leach of nickel from MHP2 precipitate as follows:

$$TE_{Ni} = \left( \frac{85.5}{100} \times \frac{99.6}{100} \times \frac{82.8}{100} \times \frac{89.6}{100} \times 100 \right) + \left( \frac{85.5}{100} \times \frac{99.6}{100} \times \frac{100 - 82.8}{100} \times \frac{95}{100} \times \frac{99.6}{100} \times \frac{82.8}{100} \times \frac{89.6}{100} \times 100 \right)$$

$$TE_{Ni} = 73.46 \tag{B.3}$$

S: Solution
P: Precipitate
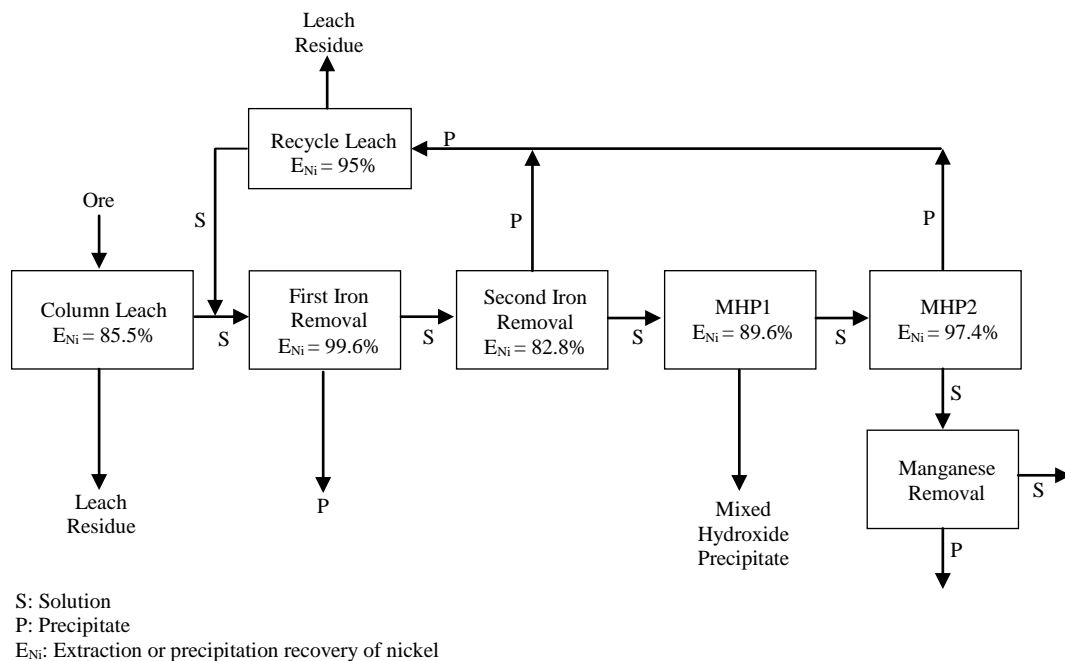$E_{Ni}$: Extraction or precipitation recovery of nickel

**Figure B.1** Schematic diagram of nickel extraction recovery.

Then, after succeeding second, third and fourth recycle leaching the precipitates, total extraction recovery would become approximately 75% of nickel in the ore (9 kg Ni / ton of ore). The total extraction recoveries of nickel with respect to number of recycle leach of the precipitates produced by second iron removal are tabulated and shown in Table B.2.

**Table B.2** Total extraction recoveries of nickel from the run of mine nontronite ore (-2 cm) up to the saleable Ni-Co hydroxide product with respect to number of recycle leach of the precipitates produced by only the second iron removal.

| $TE_{Ni}$ | Number of Recycle Leach |
|-----------|-------------------------|
| 63.18     | 0                       |
| 73.46     | 1                       |
| 75.13     | 2                       |
| 75.41     | 3                       |
| 75.45     | 4                       |

By following the same principle, after the first recycle leach of the precipitate produced by the second iron removal and MHP2, the total extraction recovery of nickel was calculated now considering all recycle leaching as follows:

$$\mathrm{TE_{Ni}} = \left( \frac{85.5}{100} \times \frac{99.6}{100} \times \frac{82.8}{100} \times \frac{89.6}{100} \times 100 \right) + \left( \frac{85.5}{100} \times \frac{99.6}{100} \times \frac{100\text{-}82.8}{100} \times \frac{95}{100} \times \frac{99.6}{100} \times \frac{82.8}{100} \times \frac{89.6}{100} \times 100 \right)$$

$$+ \left( \frac{85.5}{100} \times \frac{99.6}{100} \times \frac{82.8}{100} \times \frac{100-89.6}{100} \times \frac{97.4}{100} \times \frac{95}{100} \times \frac{99.6}{100} \times \frac{82.8}{100} \times \frac{89.6}{100} \times 100 \right)$$

$$\mathrm{TE_{Ni}} = 78.47 \tag{B.4}$$

By completing second, third and fourth recycle leaching the precipitates, total extraction recovery would become about 81% of nickel in the ore (9.72 kg Ni / ton of ore). The extraction recoveries of nickel with respect to number of recycle leach of the precipitates produced by the second iron removal and MHP2 are tabulated and shown in Table B.3.

**Table B.3** Total extraction recoveries of nickel from the run of mine nontronite ore (-2 cm) up to the saleable Ni-Co hydroxide product with respect to number of recycle leach of the precipitates produced by the second iron removal and MHP2.

| $\mathrm{TE_{Ni}}$ | Number of Recycle Leach |
|---|---|
| 63.18 | 0 |
| 78.47 | 1 |
| 80.54 | 2 |
| 80.85 | 3 |
| 80.90 | 4 |

As can be seen from Table B.2 and Table B.3, the total extraction recovery of nickel increased as more recycle leaching of precipitates produced not only by the second iron removal but also MHP2. Therefore, continuous recycle leaching of the precipitates produced by both the second iron removal and MHP2 carried out in the study would improve significantly the nickel and also the cobalt extraction recoveries.