

LITERATURE SURVEY

Chapter 2

- 2.1 Hydrometallurgy
- 2.2 Leaching
- 2.3 Sulphide minerals containing nickel, copper and cobalt
- 2.4 Familiar extracting and refining processes for nickel sulphides
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2.1 Hydrometallurgy

Hydrometallurgy will have an increasing role to play in the future regarding the extraction of valuable metals from sulphide minerals. It is unique in its application to low-grade ores, which cannot be beneficiated economically. It should be viewed as an alternative technology having high chemical specificity. In the following section the basic principles and fundamentals of hydrometallurgy are explained (Osseo-Asare & Miller, 1982:6).

2.1.1 Hydrometallurgy versus Pyrometallurgy

Whether a metal is extracted in a water environment or at high temperatures is, in principle, immaterial. Each extractive situation must be assessed on its own merits by the consideration of such factors as capital and operating costs and the environmental impact of the two different options that are available (Woollacott & Eric, 1994:213).

The more general characteristics of hydrometallurgy, which differ from pyrometallurgy are parameters such as low operating temperatures, low reaction rates, more environmental friendly, larger plant size for a given throughput of material, low unit costs and selective chemical reactions (Hayes, 1993:227).

According to Bautista (1984:v) the hydrometallurgical route for the recovery of a metal, where dissolution (leaching), separation, concentration and reduction to the metal is carried out at near ambient temperature, is becoming more competitive with the conventional high temperature processes used in the smelting of metals.

2.1.2 The basic principles of hydrometallurgy

When the chemical processing of metals is conducted in an aqueous environment, the technology employed is termed hydrometallurgy, which involves three distinct stages (Woollacott & Eric, 1994:321):

- The metal of interest must first be transferred from the solid feed material (ores, concentrates, etc.) into an aqueous solution.
- The condition of this metal-bearing solution (or solutions formed from it) must then be concentrated and purified.
- The metal must then be recovered from the purified solution in the solid state.

The transfer of the targeted metal from the solid feed material into an aqueous solution is accomplished by leaching. The dissolution of the solid material is more selective than the conventional smelting process, and the metal-bearing components dissolve, while the other components do not. A subsequent separation of the solution from the unaffected solids will then result in a separation of the metal from the unwanted components in the feed material.

The solution from a leaching process invariably contains impurities that need to be removed or reduced to as low as possible levels. In some cases, the concentration of the metal of interest is too low, and some form of concentration needs to be applied before the metal can be extracted economically. The concentration and/or purifying process of a metal-bearing solution can be accomplished in one of three ways.

- **Evaporation.** Boiling of a solution under reduced pressure achieves an increase in the concentration of the metal, because it removes water from the solution. Often this process is not economical on a large scale, and it does not purify the solution in any way.
- **Precipitation process.** The precipitation of one of the components from the solution occurs, which is then followed by the separation of the precipitate and the solution.

The technique can be used to refine a solution by the selective precipitation of an impurity.

- **Processes utilizing a carrier phase.** The selective removal of the metal from one aqueous phase and its transfer to a smaller volume of a second aqueous phase can be achieved without having to precipitate the metal from the solution. Instead, some convenient non-aqueous carrier phase can be used as a vehicle for the transfer. The metal is transferred from the first aqueous solution to the carrier phase. The solution and carrier phase is then separated. The carrier phase is mixed with a second aqueous solution. The refining action is achieved by ensuring that the transfer of metal from the first solution to the carrier phase is selective (Woollacott & Eric, 1994:328).

Some of the alternative routes for the chemical processing of materials using aqueous solution treatments are summerised in Figure 2.1 (Hayes, 1993:313).

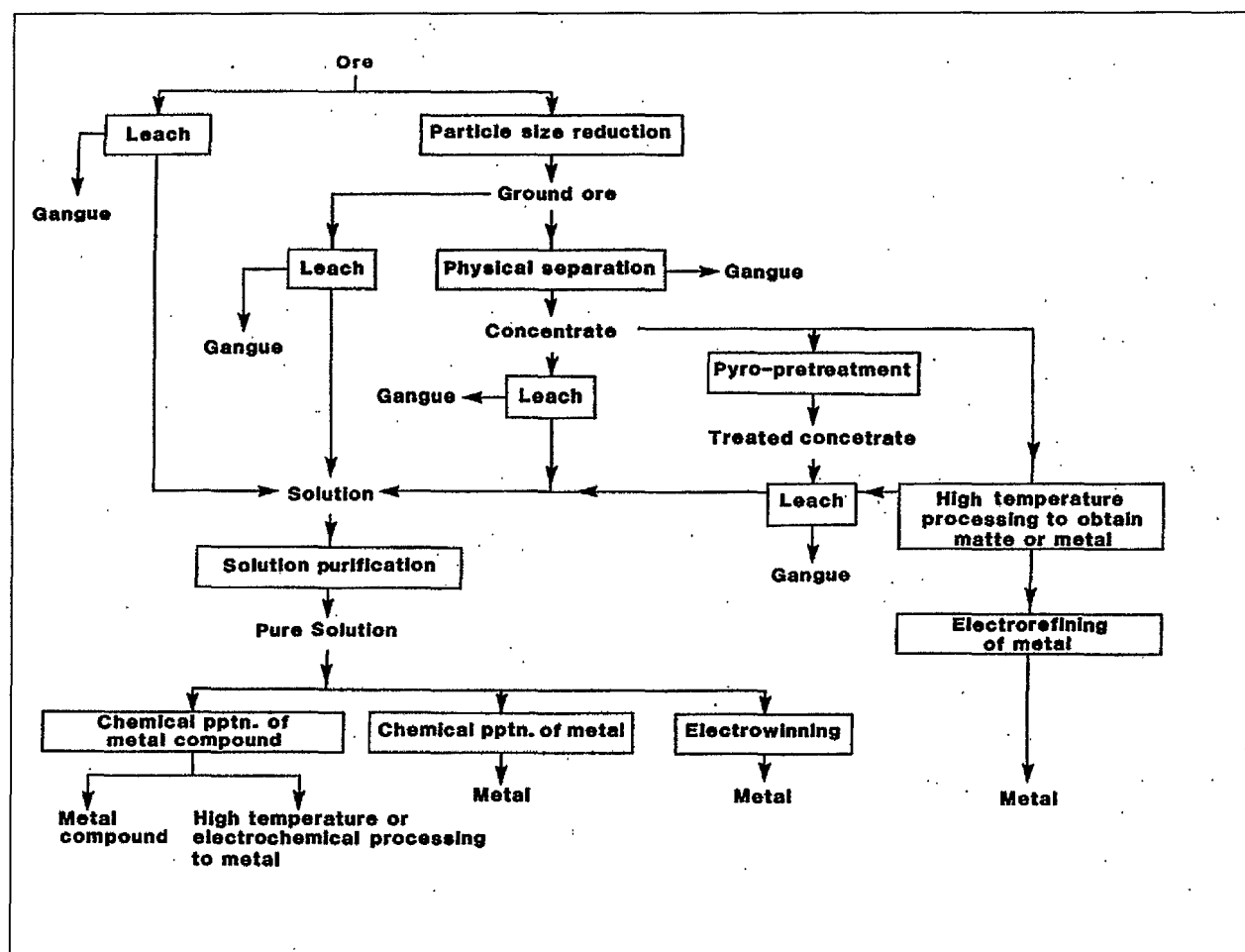


Figure 2.1 Schematic representation of alternative processing routes involving aqueous solution processing (Hayes, 1993:313)

2.1.3 The chemistry of hydrometallurgical processes

Hydrometallurgy is based on the chemistry of an aqueous solution. At first it may seem that this would severely restrict the range of processing options that can be exploited, however, this is misleading because a host of chemical reactions and processing possibilities become available if a metal can be taken up in an aqueous solution (Woollacott & Eric, 1994:322).

The difficulty of finding leaching reactions that will achieve, at reasonable cost, the rapid transfer of a metal from a mineral into an aqueous solution is, in fact, the greatest factor limiting the more widespread utilization of hydrometallurgical techniques. However, if suitable leaching reactions can be found, a wide range of water-based reactions can subsequently be exploited, and flexible processing options become available. The chemical environment in the solution can be accurately controlled to the extent that even only slight differences in the properties of similar metals can be exploited to effect their separation (Woollacott & Eric, 1994:322).

2.2 Leaching

The theory and practice of leaching, the removal of materials by dissolving them away from solids, is well developed and will be discussed in more detail in the following section.

2.2.1 Nature of leaching

Leaching is a primary extractive operation in hydrometallurgical processing, by which a metal of interest is transferred from naturally occurring minerals into an aqueous solution. In essence, it involves the selective dissolution of valuable minerals, where the ore, concentrate or matte is brought into contact with an active chemical solution known as a leach solution (Woollacott & Eric, 1994:329).

The transfer of a metal from the ore to the leach solution constitutes a transfer from a solid to a liquid phase. Because the dissolution is selective, most of the unwanted components in the ore are unaffected by the leaching process and remain in the solid state. Consequently, the metal is separated when the solids are separated from the solution after the leaching process has been completed, and the solution that is produced is termed a pregnant solution or leach liquor. The solid product is termed the residue or tailings (Woollacott & Eric, 1994:329). Furthermore, it is important that in the solution the waste minerals and compounds being rejected by the leaching reaction should have a solubility low enough to yield an acceptable separation of valuable and waste minerals during the leach, and to obtain a leach solution of acceptable purity for subsequent metal recovery (Weiss, 1985:13).

For the efficient leaching of metal from the metal-bearing species in an ore, use has to be made of an appropriate water-based chemical reaction that will yield a water-soluble metallic species. The thermodynamic characteristics of the reaction system will indicate the maximum possible extent to which the value-bearing mineral can be converted to a soluble species, as well as the solubility of that species in the aqueous solution. The degree to which such a transfer can be achieved is determined by the rate at which the reaction proceeds.

The following mechanisms, determining the overall leaching rate, are involved in a single stage leaching process (see Figure 2.2):

- The reagents must diffuse to the mineral surface.
- Reagents must adsorb on the surface.
- Chemical reaction must take place on the surface.
- Reaction products must desorb from the surface.
- Reaction products must diffuse from the surface vicinity to the bulk of the solution.

The rate of the slowest of these mechanisms controls the overall rate of the leaching process. Therefore, any effort to increase the rate at which one of these mechanisms occurs will be successful only if that step is rate-controlling.

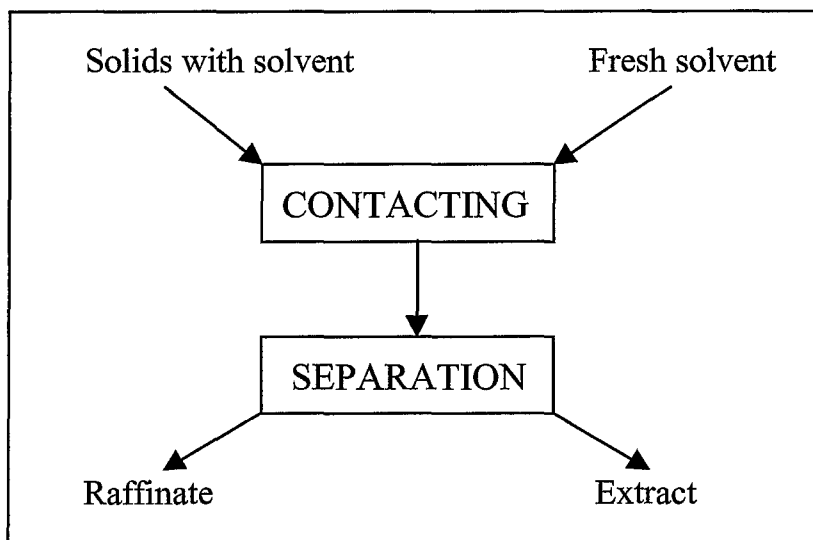


Figure 2.2 *Schematic diagram of a single stage leaching process* (Anon, 2000)

In a leaching process, attention is focused on the chemical reactions that result in the dissolution of the metallic species. The following three important factors influence the viability of a leaching operation:

- The degree of dissolution that can be achieved.
- The selectivity of the leaching reactions.
- The cost of the leach solution.
- The capital cost of the leach equipment

The degree of dissolution. For a high degree of metal extraction from an ore, the dissolution of the value metals must be as complete as possible, which is the primary consideration in the implementation of any leaching operation. Any valuable metal that remains unreacted in the ore, after leaching, constitutes a loss of the metal (Woollacott & Eric, 1994:329).

Selectivity of leaching. The second factor that affects the viability of leaching is the selectivity of the dissolution reactions. This factor is important because all ores contain a variety of minerals, other than those in which the metal of interest occurs. Inevitably, some of these will be attacked by the leach solution with the result that unwanted species are taken up in the leach liquor. The selectivity of the leaching reactions determines the

degree to which this happens and, consequently, the purity of the metal-bearing solution that is produced by the leach (Woollacott & Eric, 1994:329).

Cost of leach solutions. The cost of the leaching process is determined by the unit costs of the various reagents and the quantities used (Woollacott & Eric, 1994:329).

Capital cost of the leach equipment. The capital cost of leaching equipment can vary significantly, especially when considering the materials of construction which is dependant on the required operating conditions.

2.2.2 Leaching thermodynamics

A convenient way of examining the relative stabilities of compounds and how these change with temperature is on a ΔG° vs T plot, where at any given temperature, the relative stabilities of oxide and metal phases depend on the oxygen pressure of the system (Hayes, 1993:526).

Thus, at equilibrium

$$\Delta G^\circ = -RT \ln \frac{1}{P_{O_2}} \quad \dots\dots\dots(4)$$

from which the relative stabilities of oxide and metal phases can be determined. Another phase diagram, which also represents the relative stabilities of metals and metal compounds in aqueous solution, is the E_H -pH diagram or Pourbaix diagram, which indicates the predominant species present at equilibrium and are useful to portray the equilibria involved in the leaching of metal sulphide compounds. For the E_H -pH diagram that describes the ternary iron-nickel-sulphur system, it is particularly important to appreciate that the lines drawn on this diagram refer to specific reactions, whilst the concept of a field of stability for a predominating phase has to be treated within the context of these reactions. Figure 2.3 represents a E_H -pH diagram for the iron-nickel-sulphur aqueous system at a temperature of 25°C (Warner *et al.*, 1996:112).

The first stage in the selection of the leaching conditions for any material is to identify the various soluble species, which can form in any system. If the metal ions can dissolve in one or more forms in the solution, then the range of potentials, hydrogen ion concentrations and concentrations of the other ionic species over which the metal ions remain in solution should be identified (Hayes, 1993:235).

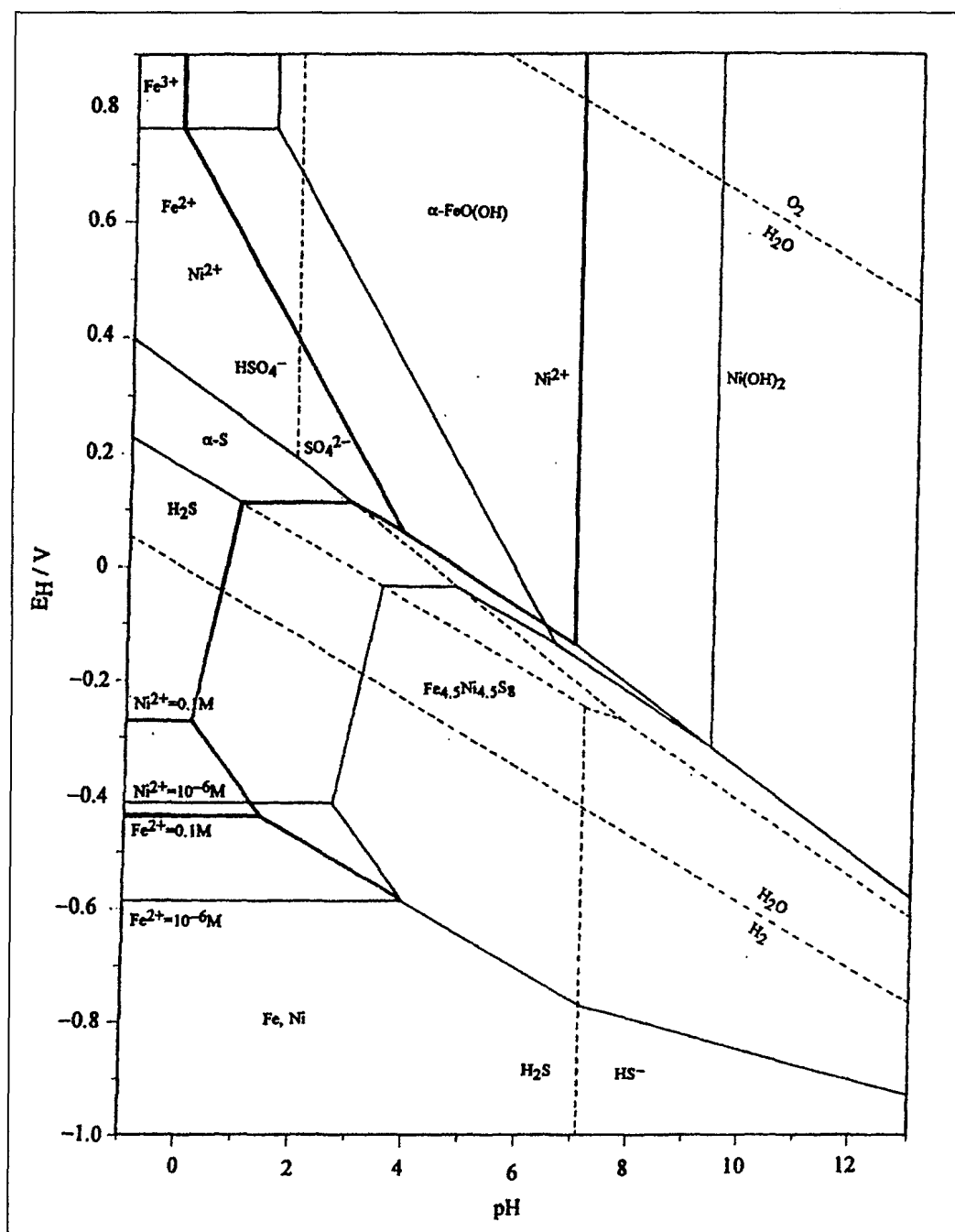


Figure 2.3 The E_H -pH diagram for the Fe-Ni-S aqueous system at 25°C. Activities of aqueous sulphur species = 0.1 mol/dm³. Activities of aqueous nickel and iron species = 0.1 mol/dm³ (bold line) and 10⁻⁶ mol/dm³ (fine line) (Warner et al., 1996:114)

The leaching reaction can be described by the following reaction:



where MA represents the mineral in which the metal, M , is found.

The leach solution enhances this reaction by providing a favorable aqueous environment. For the leaching reaction to be feasible, the reaction must be shifted to the right, i.e. the concentration of MA in the solid phase must be negligibly small once an equilibrium condition has been reached. Qualitatively, it can be said that the solubility of MA in the leach solution should be high, and for the leaching process to be selective, the above reaction should be feasible only for the targeted metal-bearing mineral (Woollacott & Eric, 1994:331).

2.2.3 Leaching kinetics

Leaching economics, especially the capital costs of leaching plants, is to some extent a function of leaching rates due to the effect of equipment on process efficiencies.

The minerals to be leached, can contain the dissolving valuable mineral or compound in at least three physical forms (Weiss, 1985:3), namely as:

- Free, 'pure' particles.
- 'Middling' multiphase particles in which the valuable mineral is exposed on at least one side to the leach solution.
- Dispersed material, surrounded by gangue material and either inaccessible or not readily accessible to the leach solution.

Leaching is in general a slow process. Consequently, the extent to which the targeted mineral is leached, is determined not only by the thermodynamics of the system, but by kinetic factors as well. What becomes important is how long it takes for the leaching system to approach the equilibrium condition, and how much time the operation allows

for it to do so. In some cases, equilibrium is not possible. Any grain of a targeted mineral that is not exposed on the surface of an ore particle (or by means of cracks and fissures in the particle) will not come into physical contact with the leach solution and so cannot be leached at all. Dissolution must therefore start at the surface of a particle and progress inwards (Woollacott & Eric, 1994:331).

Weiss (1985:13) stated that, for diffusion controlled reactions (activation energy about 4 kcal per mole) the effect of a temperature increase over a limited temperature range is often to increase the reaction rate more or less linearly. For reactions which are chemically controlled at ambient temperature (e.g., oxidation of sulphides with activation energies about 15-20 kcal per mole) an increase in temperature gives an exponential increase in reaction rate and the reaction becomes diffusion controlled. Figure 2.4 displays the effect of some process variables on the leaching rate.

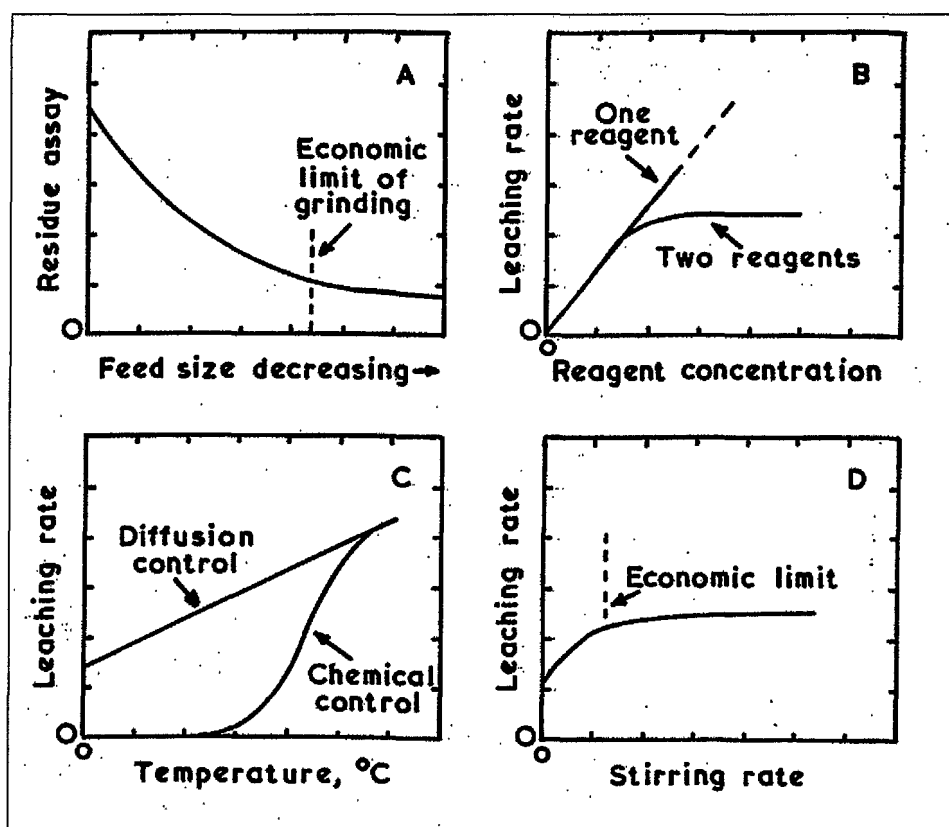


Figure 2.4 Graph indicating the effect of some process variables on the leaching rate of sulphide ores (Weiss, 1985:13)

Based on an understanding of the kinetics, decisions about the most suitable operating conditions can be made in a rational manner. The following parameters in a leaching process are of importance (Woollacott & Eric, 1994:332); (Habashi, 1970:19) and (Weiss, 1985:13):

- **Particle size.** The ore or concentrate particles must be small enough for the valuable metals they contain, to be exposed physically to the leach solution, and it does not matter if the mineral is not completely liberated. What is of importance is the degree of exposure of the mineral to ensure complete leaching of a mineral grain in an ore. The degree of exposure influences the rate at which leaching proceeds. Generally the rate of leaching increases with decreasing particle size.
- **Diffusion rates.** The rate of diffusion of reactants or products can control the rate of a leaching process. When the diffusion of a species in the solution phase to and from the mineral surface is slow, an increase in the degree of agitation of the solution will increase the rate at which the species diffuse. If the rate-controlling mechanism is the diffusion of some species through a porous layer around the mineral particles, or through fissures in the particles, the degree of agitation does not influence the rate of leaching very much. In such cases, the options available for increasing the leaching rate are either to decrease the size of the particles or to increase either the temperature or the concentration of the reagents in the leach solution. On the other hand if it is chemically-controlled then it will not be influenced by agitation; provided that enough agitation is done to prevent the solids from settling.
- **The rate of chemical reaction.** In some situations, the rate at which the leaching reactions proceed at the mineral surface determines the kinetics of leaching. To increase the chemical reaction rate, the degree of exposure of the valuable metal can be increased, the temperature or pressure of the leaching system can be increased, or a catalyst can be employed. For a diffusion-controlled process the increase in the leaching rate due to an increase in temperature is much less remarkable than for a chemically controlled process.
- **Leach agent concentration.** The rate of leaching increases with increasing concentration of the leaching agent.

- **Pulp density.** The rate of leaching increases with decreasing pulp density. In the case of high pulp densities, low quantities of solution and high concentrations exist, this will cause the equilibrium to shift and reaction rates will decrease.
- **Insoluble products.** If an insoluble reaction product is formed during leaching, then the rate will depend on the nature of this product. If it forms a non-porous layer, the rate of leaching will greatly decrease. If, however, the solid product is porous, it will slightly or not at all affect the rate.

2.3 Sulphide minerals containing nickel, copper and cobalt

In this section the formation and close relationship between the sulphide minerals containing nickel, copper and cobalt will be described.

2.3.1 Nickel, copper and cobalt occurrence

There are two types of nickel ores which can be mined economically and which are classified as either sulphide or lateritic type ores. The sulphide deposits currently account for most of the nickel produced in the world (Kirk & Othmer, 1984:796). The most common nickel sulphide is pentlandite, $(\text{Ni,Fe})_9\text{S}_8$, which is almost always found in association with chalcopyrite, CuFeS_2 , and pyrrhotite, Fe_{1-x}S . According to Klein & Hurlbut (1993:360) pentlandite commonly contains small amounts of cobalt. Other much rarer nickel sulphides include millerite, NiS , heazlewoodite, Ni_3S_2 , and the sulphides of the linnaeite series, $(\text{Fe,Co,Ni})_3\text{S}_4$ (Kirk & Othmer, 1984:796).

The nickel sulphides were formed deep below the surface of the earth, due to the reaction of sulphur with nickel bearing rocks. Ores in which the nickel is in the sulphide form are found in, or close to, bodies of rather special types of intrusive igneous rocks that are high in iron and magnesium and relatively low in silicon. The rock types range from gabbro, the variety of gabbro known as norite, to peridotite. They have ascended from depth, molten or as mush, and forced their way up among rocks closer to the surface where these intrusions form masses with irregular shapes. The common and close association of nickel sulphide ore with rocks of this type leads to the conclusion that the

nickel was a constituent of the molten rock, and that the nickel bearing sulphides have been derived from it, either during or subsequent, to the cooling period (Weiss, 1985:17). The grade of the sulphide ores typically is 0.4-2.0% nickel, 0.2-2.0% copper, 10-30% iron, and 5-20% sulphur. Major sulphide ore bodies occur in Canada, the Soviet Union, the Republic of South Africa, Australia, Zimbabwe, and Finland. (Kirk & Othmer, 1984:796).

In contrast to the sulphide ores, the lateritic ores were formed over long periods of time as a result of weathering of exposed nickel containing rocks. The lateritic weathering process results in nickel solutions that were redeposited elsewhere in the form of oxides or silicates. The continued chemical and mechanical action of air, water and temperature changes, breaks the rock down to soil or clay. One type of laterite is limonitic or a nickeliferous iron laterite which consists primarily of hydrated iron oxide in which the nickel is dispersed in solid solution (Kirk & Othmer, 1984:796). Figure 2.5 displays a simplified example of the laterite ore body on the surface with the sulphide ore body in depth.

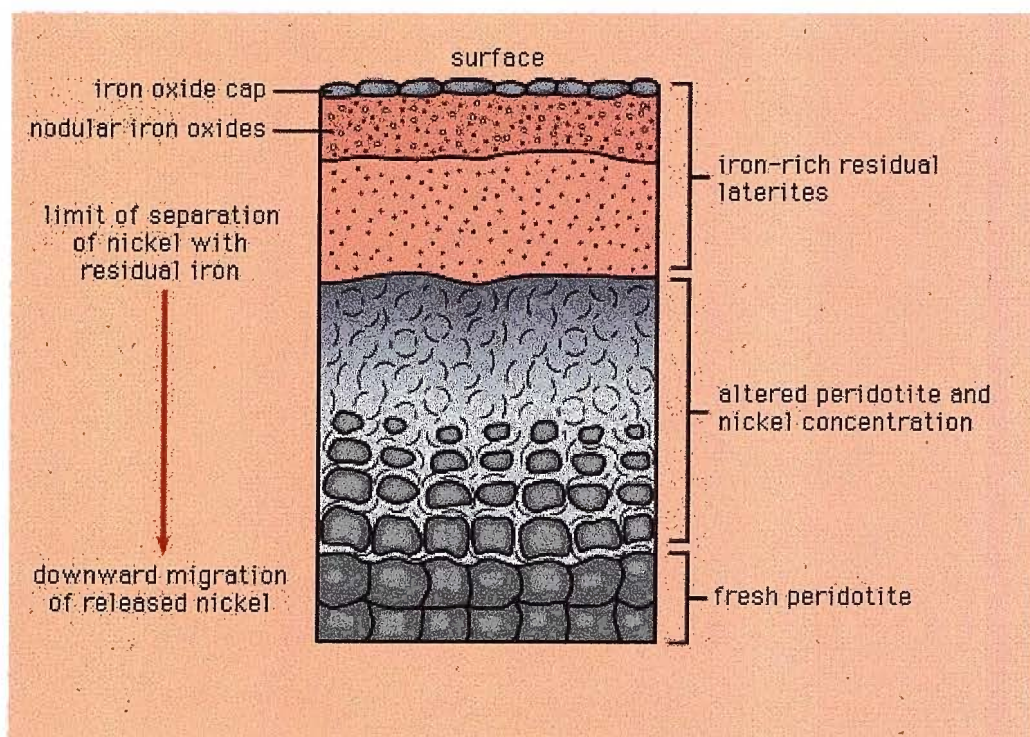


Figure 2.5 *Schematic view of a typical nickel bearing ore body* (Anon., 2000)

2.4 Extracting and refining processes for nickel sulphides

The different extracting and refining routes of nickel sulphides have been investigated and modified frequently during the past. A general overview of two processes used to extract and refine nickel sulphides is presented in the following section.

2.4.1 Introduction

Typically the sulphide ores are crushed and ground in order to liberate the nickel minerals, containing between one and four percent nickel. The next step involves the concentration and separation of the valuable metal from the waste materials by selective flotation, where the ore is mixed with special reagents and agitated by mechanical and pneumatic devices to produce air bubbles. As these rise through the mixture, the sulphide particles adhere to their surfaces and are collected as a concentrate containing six to twelve percent nickel. Because some nickel bearing sulphides are magnetic, magnetic separators can be used in place of, or in conjunction with, the selective flotation process. (Anon., 2000).

The nickel concentrates can be leached with sulphuric acid, ammonia or chlorine, or the concentrates can be dried and smelted in flash and bath processes, as is the case with copper concentrates. Nickel concentrates, however, requires temperatures in the range of 1350°C in order to produce an artificial nickel iron sulphide, known as matte, which contains 25 to 45% nickel. The nickel matte can be treated in an ammonia pressure leach, in which nickel is recovered from solution using hydrogen reduction, and the sulphur is recovered as ammonium sulphate, or the matte may be roasted to produce high-grade nickel oxides which are then subjected to a pressure leach, and the solution is electro- and carbonyl refined (Anon., 2000).

In Figures 2.6 and 2.7 two of the most generally used process flowsheets to refine nickel from sulphide ores are shown:

2.4.2 The Sherrit Gordon process

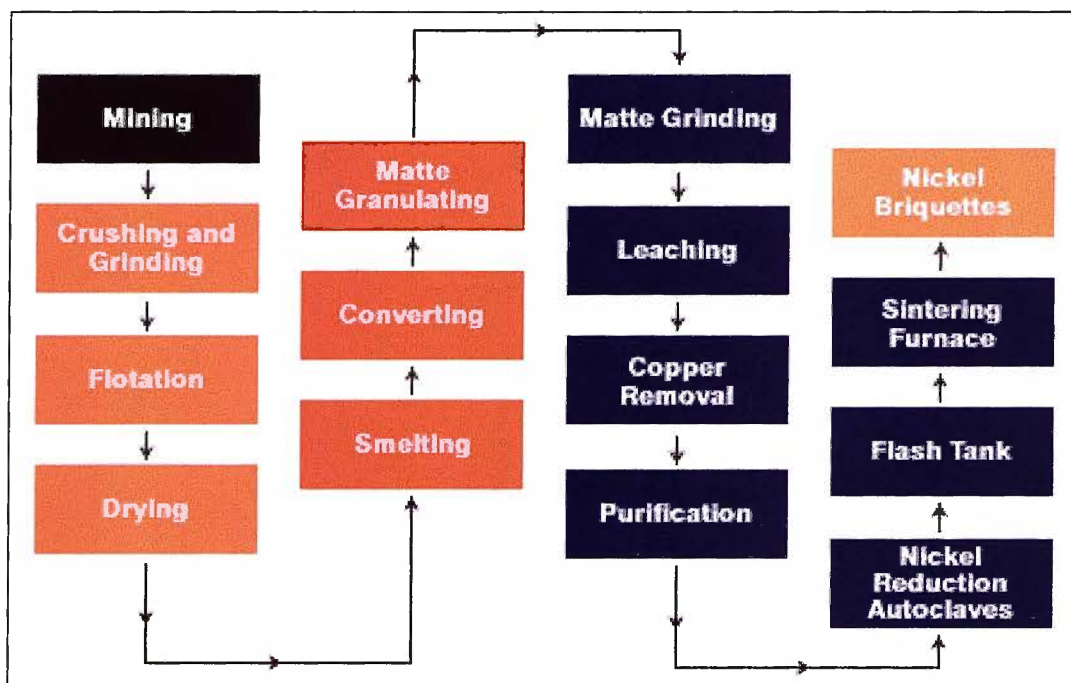


Figure 2.6 Basic flowsheet of the Sherrit Gordon process

The sulphide ore is crushed and ground to the desired particle size and the liberated ore is then floated with xanthate and frother (chemical reagents) to a concentrate with 8-12% nickel, which is then filtered to about 6% moisture. The smelters produce a nickel iron sulphide matte, which contains 25 to 45% nickel. In the next step, the iron in the matte is converted to an oxide, leaving a matte with 70 to 75% nickel. The nickel matte is then crushed and ground to liberate the nickel minerals and pumped into autoclaves where the concentrate is leached under pressure with ammonia. The leach solution contains the dissolved nickel, copper and cobalt as amine complexes. The copper in the solution is then removed by adding ammonia and hydrogen to ensure precipitation. The nickel cobalt solution is purified in two steps namely oxidation and hydrolysis, which removes the thiosulphate and the polythionates. The purified nickel cobalt solution, with a high ammonium sulphate concentration, then passes to the hydrogen reduction stage where batchwise reduction in autoclaves produces a high purity nickel powder, which is finally briquetted.

2.4.3 Carbonylation

Carbon monoxide at atmospheric pressure contacts active nickel crudes at temperatures between 40 and 95°C, where the nickel is volatilized as a carbonyl. This compound decomposes to nickel metal and carbon monoxide when heated to the temperature range of 150 to 315°C. Under the mild conditions employed for reaction at atmospheric pressure the impurities in crude nickel metal do not enter the gas phase. Iron forms a volatile carbonyl, $\text{Fe}(\text{CO})_5$ and the cobalt can form tetracarbonyl, $\text{Co}_2(\text{CO})_8$, and tricarbonyl, $\text{Co}_4(\text{CO})_{12}$, but both these solids have low volatility. The refined nickel is produced in pellet form (Weiss, 1985:17).

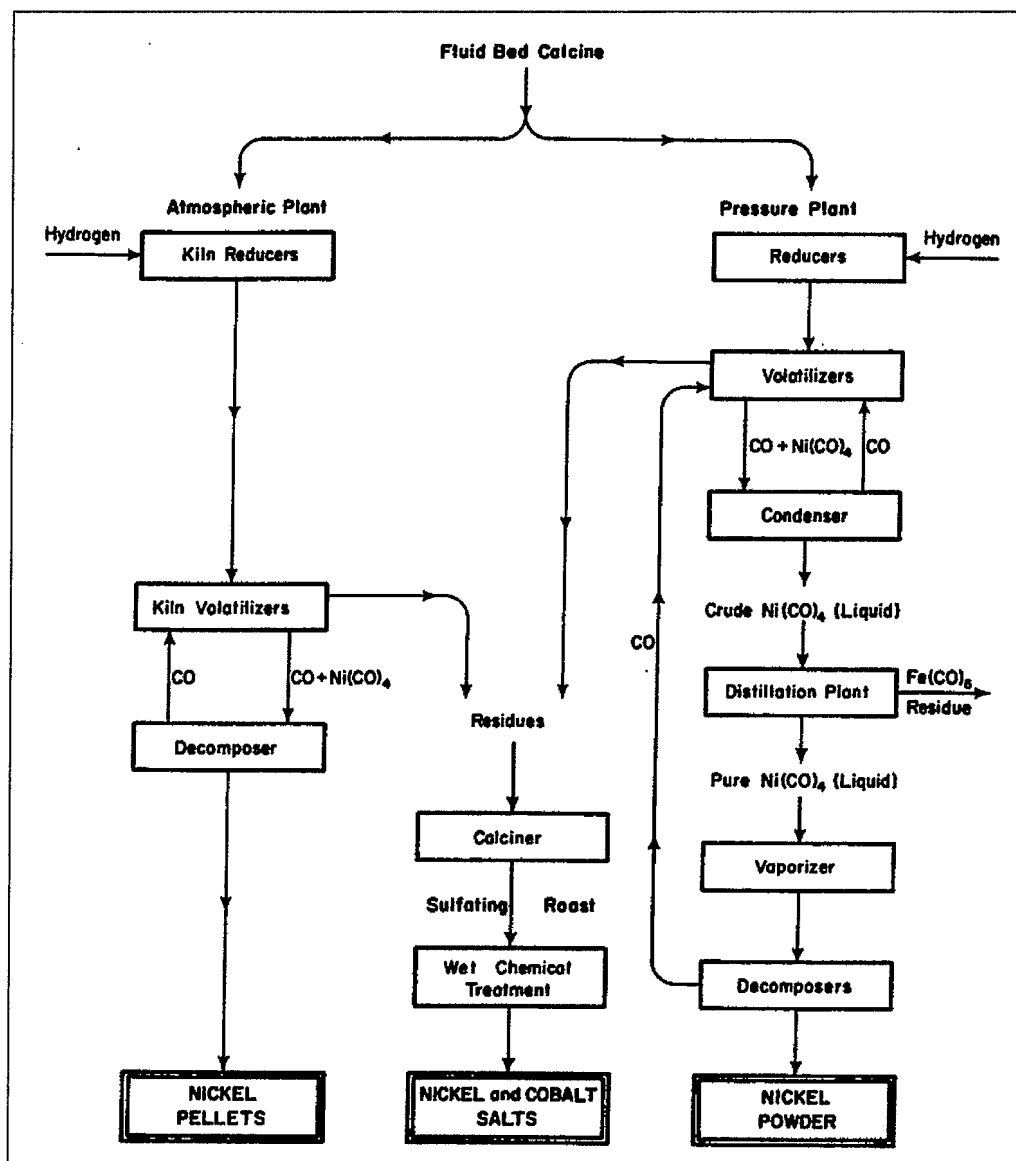


Figure 2.7 Basic flowsheet representing the extraction of nickel by the carbonyl process (Weiss, 1985:17)

2.5 Fundamentals of sulphide leaching

The leaching of metal sulphides, under the specific conditions studied in this investigation, is an electrochemical process, which consists of selective chemical reactions. In this section, the leaching kinetics and behavior of specifically sulphide minerals are investigated.

2.5.1 Introduction

Aspects of sulphide mineralogy, of particular importance in hydrometallurgy, include the nature and mechanism of phase transformations, since solid state transformations are known to occur during leaching. Also of importance is the phenomenon of nonstoichiometry, whether deviations from the 'ideal' formula are small or large. Such variations can affect electrical properties of the materials and also their electrochemical behaviour (Bautista,1984:21).

Metal sulphides are practically insoluble in water, even at temperatures as high as 400°C, but in the presence of oxygen, they are solubilised as sulphates. Pressure leaching of sulphides is an exothermic process and cooling rather than heating is needed. The desired residue product from the oxidation of the sulphides is elemental sulphur and sulphates, and not only sulphates (Habashi, 1970:103).

The two decisive factors, when considering the leaching of sulphides, are the temperature and pH at which leaching take place. Depending on these factors, the following possibilities present themselves (Habashi, 1970:103):

- Both metal and sulphur will be obtained in soluble form. This is the process mostly used at present for treating nickel, copper and cobalt sulphide ores. Sulphur is recovered in the form of ammonium sulphate or sodium sulphate.
- The metal is obtained in a soluble form and the sulphur in elemental form. This method is used in cases when economical necessity implies the recovery of sulphur in the elemental form.

- Both metal and sulphur are obtained in an insoluble form. This is the case when ferrous sulphide or pyrrhotite is treated. Sulphur is recovered in the elemental form, and the iron as a ferric oxide.

It is not possible at any pH value to get sulphur in the elemental form when leaching is conducted above 120°C, the melting point of sulphur. The reason for this is that the reaction,



is very slow below 120°C, and is greatly accelerated with increasing temperature. In high temperature leaching (above 120°C) the pH has no influence on the products of the reaction, whilst at low temperatures the reaction products depend greatly on the pH of the medium (Habashi, 1970:104). Rygaert *et al.* (1959:19) studied the aqueous oxidation of synthetic CuS in an alkaline, neutral and acid medium in the temperature range 50-80°C. They found from their experiments that in a neutral or alkaline medium no elemental sulphur can be formed, although leaching was carried out below 120°C. In some cases, in an acid medium, elemental sulphur was not formed, although leaching was carried out below 120°C which is the case when a metal sulphide in a lower valency state undergoes oxidation to a higher valency.

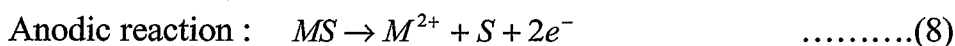
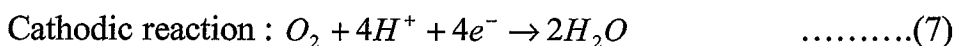
Apart from temperature and pH dependence of the leaching system, the pressure applied in the system or autoclave also affects the thermodynamics and kinetics of the leaching process. In this case, the rate of leaching depends on the oxygen partial pressure and not the total pressure (Habashi, 1970:103).

2.5.2 Possible leaching mechanisms

The mechanisms suggested for aqueous oxidation of sulphides were classified into five different categories by Habashi (1970:108):

- **Adsorption complexes mechanisms.** The mechanism include the adsorption and dissociation of oxygen on the metal sulphide surface, the hydration of the oxygen atom adsorbed on the metal sulphide surface and the formation of the reaction products.
- **H₂S as intermediate product.** The H₂S which formed as an intermediate product will be oxidised to elemental sulphur and the metal sulphate is oxidised to a higher valency (ferrous to ferric), where the higher valency sulphate will form a metal oxide and H₂SO₄.
- **Oxide and elemental sulphur as intermediate products.** The metal sulphide is oxidised directly to an oxide and elemental sulphur and further product formation depend on the medium.
- **Oxide and SO₂ as intermediate products.** The metal sulphide is oxidised to a metal oxide and SO₂. Further products depend on the medium.
- **The electrochemical mechanism.** The metal sulphide reacts with O₂ and H₂SO₄ to form a metal sulphate and elemental sulphur.

The last mechanism is typical for the leaching of sulphide minerals and according to the electrochemical mechanism, (assumed to be the mechanism followed in the present experimental investigation), the leaching of sulphides can therefore be represented by the following reactions:



2.6 Previous investigations on nickel, copper and cobalt sulphide leaching

The leaching of specifically nickel sulphide minerals has received limited investigation over the past few years although it has become one of the most popular processes for treating nickel sulphide ores. In the following sections a brief discussion of previous investigations on the leaching of nickel, copper and cobalt sulphide ores is given.

2.6.1 Investigation of the direct hydrometallurgical processing of mechanically activated complex sulphide ore

Amer (1995:225) studied the effect of the mechanical treatment on the extraction of nickel, copper and cobalt from complex sulphide ores. A typical massive sulphide ore was treated with sulphuric acid at a temperature between 50 and 110°C in an oxygen pressure of 5 to 20 bars for periods ranging from 15 to 150 minutes. He found that 90% and 87% of the nickel and copper respectively can be transferred at 110°C into the solution in a 90 minutes leaching period, after the sulphide ore was ground for three hours. For an unground sample the maximum dissolution of nickel and copper was 69% and 37%, respectively, thus indicating that the grinding to ultra fine particles is of importance, as was discussed in section 2.2.3. The leaching rate for both nickel and copper increased as the oxygen partial pressure increased from 5 to 20 bar. An increase in sulphuric acid concentration to above 6M had practically no effect on improving the nickel and copper extraction.

For the determination of the empirical rate constant of leaching, k , Amer (1995:230) applied the following equation:

$$\ln(1 - E) = -kt \quad \dots\dots\dots(9)$$

where, E = extent of extraction of metal into solution by weight; t = the time of leaching.

To determine the apparent activation energy for both nickel and copper, Arrhenius plots resulted in apparent activation energies for nickel and copper as 25 kJ/mol K and 27 kJ/mol K, respectively. Amer (1995:234) concluded that a method comprising mechanical pre-treatment of a nickel and copper sulphide ore and its subsequent oxidative direct leaching at low temperatures (around 110°C) has advantages and that the oxygen partial pressure as well as the sulphuric acid concentration is of importance to ensure maximum recoveries.

2.6.2 The leaching behaviour of a nickel concentrate in an oxidative sulphuric acid solution

Bredenhann & Van Vuuren (1999:687) investigated the oxidative leaching of a nickel sulphide concentrate in a sulphuric acid solution, where a millerite-linnacite-catierite ore was leached by means of a nitrate and ferric iron solution. Their experiments were conducted at a temperature of 90°C in a two liter vessel at atmospheric pressure.

The sulphide concentrate was leached at a much faster rate (factor of five) using sodium nitrate instead of a ferric sulphate solution as leaching agent, and the optimum concentration of sodium nitrate, to obtain the maximum leaching rate, was 30 g/l. They suggested that the disadvantage of the sulphur formation was the decrease in the leach rate as the sulphur layer forms.

Bredenhann & Van Vuuren (1999) assumed that the rate of dissolution can be described initially by a shrinking particle model followed by diffusion through the product layer. The formulae used are given as:

The shrinking particle model : $1 - (1 - X)^{\frac{1}{3}} = kt$ (10)

and:

Diffusion through product layer model : $1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = kt$ (11)

Where $k = \text{constant (min}^{-1}\text{)}$
 $t = \text{reaction time (min)}$
 $X = \text{conversion (fraction of nickel dissolved)}$

According to Bredenhann & Van Vuuren (1999) the oxidative dissolution of a nickel sulphide concentrate, using nitrate as leaching agent in an acid medium, takes place with the formation of sulphur. The rate of the reaction is controlled by a surface chemical reaction during the initial stages of the reaction but changes into a diffusion controlled mechanism towards the end of the reaction. The activation energy for nickel of the initial dissolution process was found to be 88 kJ/mol K, much higher than the value found by

Amer (1995:231) and can be contributed to the fact that a different nickel mineral was investigated or that a different empirical model was used to calculate the reaction rates.

2.6.3 Application of attrition grinding in acid leaching of nickel sulphide concentrate.

Ximming *et al.* (1997:142) studied the acid leaching of fine ground nickel sulphide concentrate containing pyrrhotite, pentlandite and chalcopyrite under atmospheric pressure in a sulphuric acid and ferric sulphate medium.

The experimental results showed that the leaching rate of the nickel sulphide concentrate was remarkably accelerated after 80 minutes of fine grinding, to a particle size $< 10 \mu\text{m}$. The recovery of the metals was increased initially with the leaching time, but there was no exceptional change after a leaching time of 3 hours. The elevation of temperature had a significant effect on the copper extraction and a linear relationship was found between a temperature of 60 to 90°C for the copper extraction, while a more parabolic curve was observed for the nickel and cobalt extraction with increasing temperatures. High sulphuric acid concentrations did not greatly improve the extraction of valuable metals under the specific conditions.

Ximming *et al.* (1997:146) found a linear relationship for the extraction of elemental sulphur *versus* the change of the specific surface area of the particles leached. This means that the formation of elemental sulphur effected the leaching process by adhering to the surface of the sulphide minerals and provided a diffusion barrier, which blocks the inner-surface of the mineral particles.

They concluded that the leaching rate of nickel sulphide concentrate was remarkably accelerated after 80 minutes of fine grinding. The formation of elemental sulphur affected the leaching process, and the elevation of temperature was favorable to the extraction of valued metals with the formation of elemental sulphur. The leaching rate of the pentlandite can be described by the diffusion through a product layer kinetic model and the apparent activation energy for the leaching of nickel from pentlandite was found to be 92 kJ/mol K.

2.6.4 Passivation of chalcopyrite during oxidative leaching in sulphate media.

Hackl *et al.* (1995:25) stated that high copper extractions are not attainable in a reasonable residence time, unless the leaching temperature exceeds 200°C (oxygen pressure leaching) or chalcopyrite is 'activated' by a pretreatment method prior to leaching. The objective of this study was to gain further insight into the chalcopyrite passivation phenomenon and how it impacts the leaching kinetics.

A chalcopyrite concentrate was ground to a mean particle size of 14.5 µm and then leached with sulphuric acid and ferric iron at pressures of 7 to 13.8 bar and a temperature of 110°C. After 6 hours of leaching, the copper extraction had reached a level of 69% leaching at a temperature of 110°C and a pressure of 13.8 bar. According to Hackl *et al.* (1995:25) oxygen pressure leaching of chalcopyrite at low temperatures is slow and ineffective. The formation of sulphur and sulphate product barriers was blamed for the slow reaction rate. It was concluded that the reaction rate is ultimately controlled by a passivating mechanism unrelated to elemental sulphur formation.

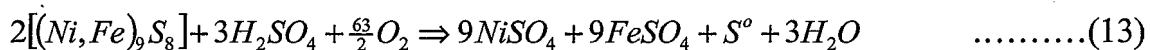
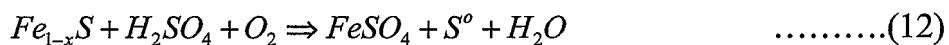
Initially, the kinetics revealed a parabolic extraction rate and the rate was controlled by ion diffusion through a thickening passivating layer. However, the passivating layer decomposed, but at a much slower rate than for CuFeS₂, so it eventually reached a steady state. The mechanism then reverted to a chemical reaction control where the rate was controlled by the rate at which the passivating layer decomposed. Surface studies suggested that the passivating layer was a copper rich polysulphide of composition CuS_n (n>2), which forms as a result of solid state changes that occur in the mineral during leaching.

2.6.5 Summary of previous investigations on nickel, copper and cobalt sulphide leaching

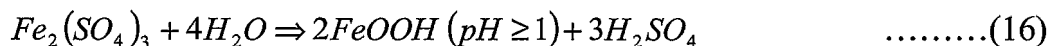
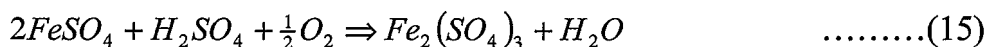
From the preceding study of the relevant literature a summary regarding the leaching of nickel, copper and cobalt sulphide minerals can be made.

The extraction of nickel, copper and cobalt from a sulphide ore by means of pressure-acid leaching is viable under specific conditions. Copper dissolution from chalcopyrite, however, requires longer retention times and higher temperatures to ensure complete extraction due to the passivation of the mineral surface. The leaching efficiency depends greatly on the specific process variables such as temperature, pressure, pH, particle grain size and leach reagent. An increase in temperature and pressure enhances the reaction rate which leads to smaller retention times required for complete dissolution. High leach reagent concentrations such as sulphuric acid, does not greatly improve the extraction of the valuable metal but only influences the by-product formation. Mechanical activation by means of ultra fine milling offers significant advantages for the extraction of the valuable metals from sulphide ores.

The oxidising of the minerals pyrrhotite ($Fe_{1-x}S$), pentlandite $(Ni,Fe)_9S_8$ and chalcopyrite ($CuFeS_2$), at a oxygen partial pressure of 10 bar and a temperature of $110^\circ C$ in the presence of sulphuric acid, can be described by means of the following process reactions:



The iron hydrolysis and precipitation that occur during the leaching of these minerals can be described by the following reactions:



The activation energy deduced for the extraction of nickel and copper from the sulphide ore ranged between 20 and 100 kJ/mol K, and no apparent activation energy value was found for the extraction of cobalt from pentlandite.

2.7 Mössbauer spectroscopy

The recoilless emission of gamma radiation, followed by its resonant absorption by a sample, was discovered by Rudolf Mössbauer in 1958 and is now known as the Mössbauer Effect.

2.7.1 An introduction to Mössbauer spectroscopy

According to Cohen (1976:2), the Mössbauer effect is the recoilless emission by radioactive nuclei and resonant reabsorption of γ -rays, which arises from the nuclear excited states. These γ -rays are electromagnetic radiation and have no electrical charge and are absorbed or scattered by energetic collisions when passing through matter. The very small energy changes can be measured by the Mössbauer effect to give information about the surroundings of the nucleus. In Figure 2.8, a schematic representation of the nuclear decay and excitation process is given.

In Figure 2.8 the horizontal lines represent nuclear energy levels of the source and absorber. The source nucleus decays from the excited state to the ground state, emitting a γ -ray. The γ -ray is subsequently absorbed in the absorber, thus raising the absorber nucleus to its excited state. Since every isotope has absorption energy in a different energy region, γ -rays of each nucleus (e.g. ^{57}Fe) can only be reabsorbed by nuclei of the same type.

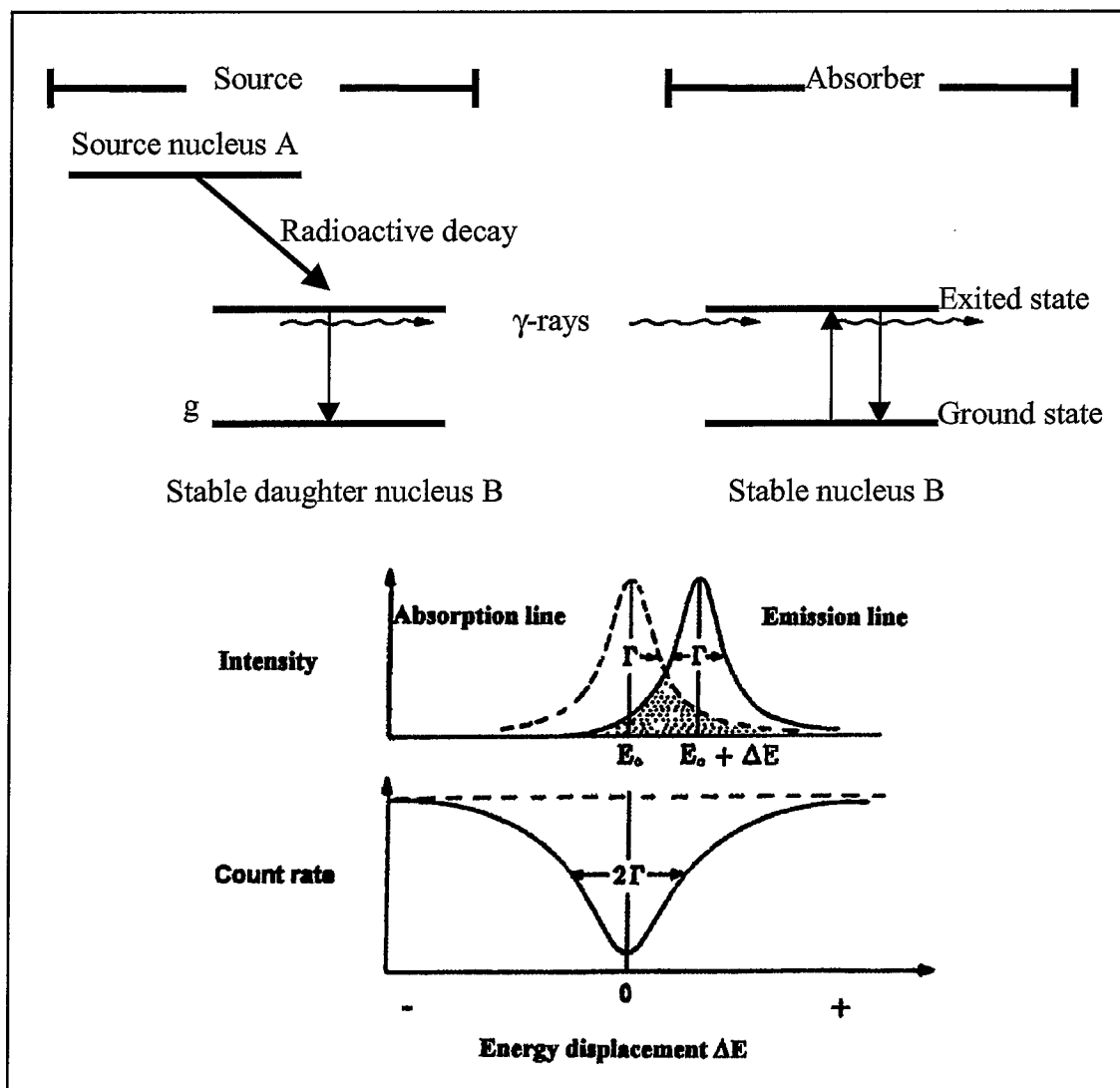


Figure 2.8 *Schematic representation of the events occurring in Mössbauer spectroscopy* (Cohen, 1976:3)

Small perturbations in the energy of nuclear levels in the absorber can be measured by observing the change in γ -ray energy required for the γ -ray to be resonantly absorbed. These measurements are usually performed by scanning the gamma-ray energy, using the Doppler shift, produced by moving the source with known velocities.

The resultant spectrum is normally displayed as a spectrum of count rate versus γ -ray energy shift (see Figure 2.8). The nuclear resonance will cause an increased absorption at γ -ray energies, matching the possible excitation energies in nuclei in the absorber and will result in an absorption line. This dip (or series of dips) is known as a Mössbauer spectrum. The energy shifts, at which resonant absorption occurs, as well as the relative

line intensities, are the principal measured parameters in most Mössbauer spectroscopy experiments and are determined by electronic effects on the nuclear energy levels.

The energy shift arises from the interactions of electrons with the nuclei, and these measurements allow various conclusions to be drawn about the electronic structure of the material being studied. These effects, called "hyperfine parameters", are the isomer (chemical) shift, δ , (electric) quadrupole splittings, Δ , and the magnetic hyperfine Zeeman splitting. The isomer shift and quadrupole splitting are expressed as a value with units of mm.s^{-1} and the magnetic hyperfine Zeeman splitting in terms of the magnetic field strength measured in Tesla.

In the present investigation use was made of a ^{57}Co -source emitting λ -rays of 14.4 keV energy, decaying to ^{57}Fe , of which the energy level diagram is shown in Figure 2.9

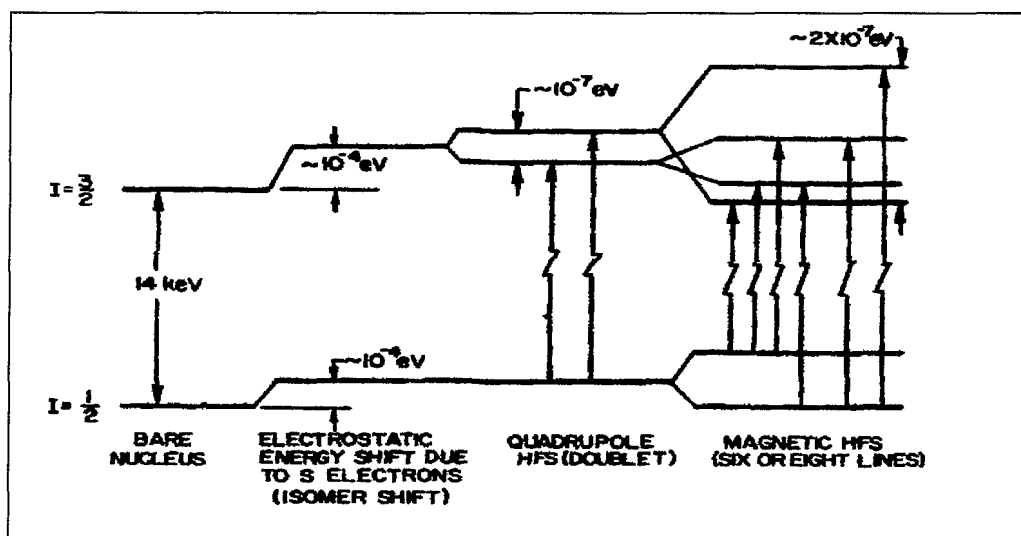


Figure 2.9 Energy level diagram for ^{57}Fe (Cohen, 1976:5)

2.7.2 Isomer shift (δ)

The total electron density on the Mössbauer atom is measured by the isomer shift (see Figure 2.10). Strictly, it is the electron density at the nucleus that is important and it is measured relative to that in a standard material. The nucleus interacts with the electrons in a manner, which raises the energy levels by an amount that is proportional, both to the size of the nucleus and to the magnitude of the electron density.

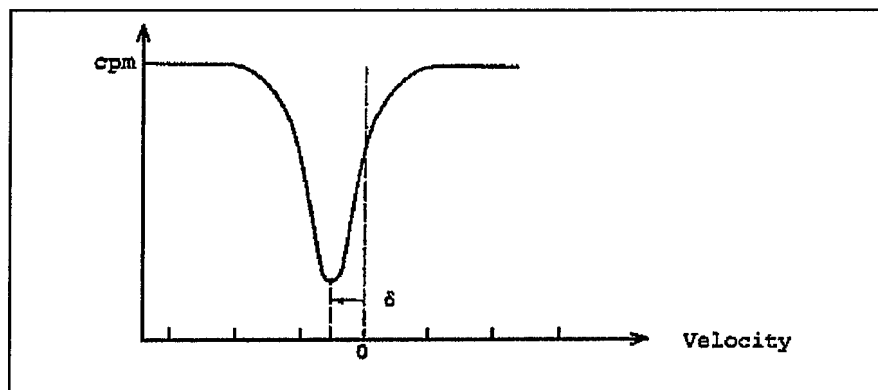


Figure 2.10 *Characteristic parameter of a Mössbauer spectra: isomer shift (singlet)*

According to Greenwood (1967:56), the isomer shift is determined by the interaction between the nucleus and the charge distribution of electrons in the region of the nucleus. The isomer shift depends on the fact that the spacing of the nuclear energy levels depend on the chemical environment of the nucleus.

2.7.3 Quadrupole interactions (Δ)

Cohen (1976:10) stated that a Mössbauer nucleus can be used as an 'observer' or probe to get information about site symmetries and field gradients within a crystal and to give details of imbalance of *p* and *d* electrons. The nuclear energy levels, represented by the electric quadrupole and magnetic dipole hyperfine interactions, may be split, in addition to energy level changes, produced by the isomer shift. This splitting leads to a number of possible absorption energies, resulting in a number of absorption lines. According to Armstrong *et al.* (1981:515), a split between the nuclear excited state ($I=3/2$) and ground state ($I=1/2$) of ^{57}Fe -nucleus results in the formation of two absorption lines, namely a doublet. This type of interaction is illustrated in Figure 2.11.

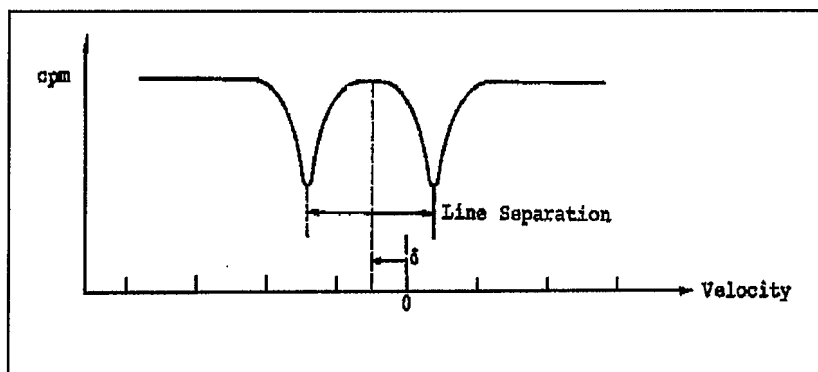


Figure 2.11 *Characteristic parameter of Mössbauer spectra: electric quadrupole splitting (doublet)*

2.7.4 Hyperfine magnetic interactions (Zeeman splitting)

The third of the major types of interaction that can be investigated by Mössbauer spectroscopy is the hyperfine magnetic interactions (Zeeman splitting) of the nuclear energy levels in a magnetic field, resulting in a sextet (six lines) as illustrated in Figure 2.12. Cohen (1976:13) stated that the magnetic hyperfine interaction arises from the coupling of the nuclear magnetic moment with effective magnetic fields at the nucleus and results in splitting of the nuclear ground and excited states if they have a nuclear spin larger than zero.

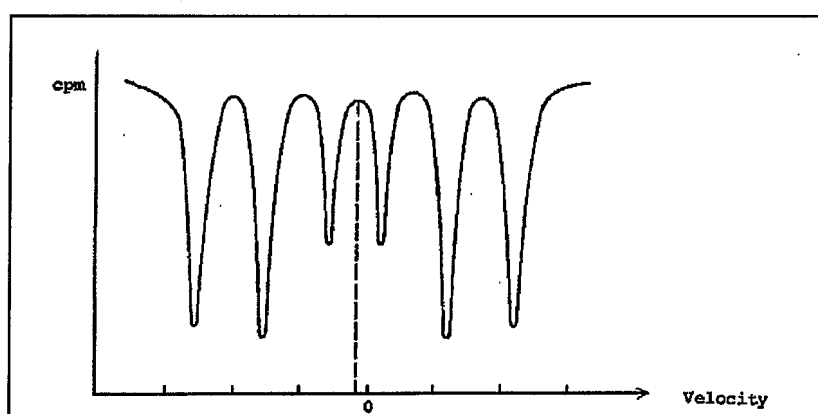


Figure 2.12 *Characteristic parameter of Mössbauer spectra: nuclear Zeeman splitting (sextet)*