inhibitors of sulphide and ferrous oxidation. The relative rates of sulphur and iron oxidation seemed to depend on the mineral and the bacterial culture employed. Beck and Brown[12] did work on the same minerals, and found that the indirect mechanism dominated the leaching behaviour. Duncan and Walden[13] observed that the addition of ferric ions in the bioleaching of chalcopyrite, chalcocite, covellite and marmatic zinc sulphide had no observable positive effects, and concluded that ferric ions are not a necessary component in bioleaching. The results of these authors[11,12,13] and possible interpretations are presented in Appendix A.1.3.

Madgwick and Ralph[14] observed apparent inhibition of the direct mechanism at low pH in the leaching of low-grade copper ore. Tuovinen and Kelly[4] mentioned that certain cations inhibit bacterial development on thiosulphate. It is reasoned therefore, that certain cations could possibly inhibit sulphide oxidation.

From the literature one can conclude that there still is uncertainty over the relative importance of the direct and the indirect mechanisms. It could be that the relative importance depends on the mineral type, on the physical conditions (e.g. pH and certain metal ion concentrations) and on the bacterial culture used.

1.2.4. MODELLING DEVELOPMENTS IN BIOLEACHING

A number of papers dealing with growth models have recently been published. Two of the papers (by Gormely, Duncan, Branion and Pinder[15], and Sanmugasunderam,

Branion and Duncan[16]) dealt with a zinc sulphide concentrate. This concentrate contained little iron, and no account was taken of the indirect mechanism. The emphasis in these papers was on the growth rates and concentrations of bacteria, and the absorption and desorption of bacteria onto and from the solid. The latter process was proposed to be a dynamic equilibrium between absorbed and desorbed species. Bagdigian and Meyerson[17], working on coal containing pyrite, proposed that some of the bacteria were irreversibly attached to surfaces.

The growth of bacteria on pyrite was investigated by Chang and Meyerson[18] and they found that the growth rate of attached bacteria depended on factors such as ferrous ion concentration, solid surface concentration and dilution rate in the reactor. No mention was made of the indirect mechanism.

Blancarte-Zurita, Branion and Lawrence[19] presented a shrinking particle model to describe the effect of bioleaching an iron poor zinc sulphide concentrate.

1.3. BACTERIAL BY-PRODUCTS

The main inorganic by-product commonly found in bacterial leaching is jarosite[13,20], a mineral which can be represented by the formula $AFe_3(SO_4)_2(OH)_6$[13], where A is most frequently K^+, NH_4^+, or H_3O^+. Lazaroff, Sigal and Wasserman[21] inferred that bacteria produce a soluble precursor before actual precipitation of jarosite takes place. They suggested that it consisted of a hydroxo-bridged polymer which contained sulphate ions in outer coordination.

Agate, Korcynski and Lundgren[22] identified a cellular complex produced by *Thiobacillus ferrooxidans*, which was liberated into solution. These types of complexes could help bacteria to attach to sulphide surfaces. Mild physical or chemical treatments resulted in the release of another substance, lipopolysaccharide, from the surface of the bacteria. Goodman, Babij, and Ritchie[23] observed that bacteria secreted stringy, thread-like material, which adhered to the ore particles that were being leached.

It therefore seems that bacterial by-products may have an effect on leaching in a given system. For example solids could be covered by jarosites, inhibiting leaching and removing nutrients from the solution. The solution characteristics might also be changed by e.g. the excretion of organic matter by the bacteria.

1.4. GALVANIC INTERACTIONS

Galvanic interactions between minerals in electrical contact could well be of importance in leaching. If two minerals are in electrical contact, the mineral with the lower electropotential will tend to dissolve more rapidly, while the other mineral is passivated. Mehta and Murr[24] and Ahonen, Hiltunen and Tuovinen[25] investigated galvanic effects with chalcopyrite and pyrite. They found galvanic effects to be very important in bioleaching. It is presumed that the importance of galvanic interactions depends on the type of material being leached.

1.5. OBJECTIVE AND SCOPE OF THE PRESENT STUDY

The direct and indirect mechanisms have been identified in bacterial leaching using bacteria of the Thiobacillus ferrooxidans type. The direct mechanism is considered in this dissertation to occur when bacteria attach to a sulphide mineral surface, and, using biological catalysts (enzymes), oxidize sulphide ions in the crystal lattice directly to soluble sulphate ions. The indirect mechanism is considered to occur when soluble ferric ions oxidize the mentioned sulphide ions to sulphur molecules, while at the same time reverting to their ferrous state. The bacteria indirectly promote this oxidation by catalysing the re-oxidation of the ferrous ions back to their ferric state. In this dissertation, it is hypothesized that the biological leaching of a mineral in the presence of soluble iron is largely a function of the indirect leaching mechanism, and that the direct leaching mechanism can be considered to contribute very little to the leaching rate.

A pure synthesized mineral , Ni_3S_2, is used in the experiments in order to avoid the galvanic interactions that would arise on using impure minerals. One of the objectives of the present study is to demonstrate that the leaching behaviour of this mineral by the indirect mechanism can be modelled using an electrochemical model described in detail in Section 2.2. This model has been used by Dry[9] and Verbaan and Crundwell[10].

According to the model, leaching is a function of the redox potential in the system, so that the prediction of

redox potential is of great importance. This study therefore includes as an objective the prediction of redox potential under typical bacterial leaching conditions (in this work a pH level 1,6; temperature of 37°C; and total iron concentration of 9 g/l and less are used). The effects of addition of nutrients and oxygen, both required for bacterial growth, on redox potential are also investigated. Since bacteria can excrete organic substances, the effect of the presence of bacteria on the redox potential in solution is also established.

The main testwork in this dissertation is inoculated and sterile control leaching experiments performed in parallel. Batch experiments are conducted in order to observe the different phases of bacterial activity. In the sterile control experiments, no bacteria are present, and the redox potential in solution is continuously adjusted, by means of addition of an oxidizing agent, to the level in the inoculated vessels. If the chemical leaching rate in the parallel sterile control experiment is found to be equal to the bio-leaching rate in the inoculated experiment, the hypothesis would have been proved, and the direct bacterial action on the mineral can be considered to contribute little to the leaching rate.

In Table 1.1 the types of experiments performed in this study and their aims are presented. Table 1.2 shows where in this dissertation material relevant to the different types of experiments may be obtained.

TABLE 1.1.		
Categories of Experiments, with Descriptions and Aims		
	Description	Aim(s)
A	Experiments utilizing an acidic iron sulphate solution (with various ferrous/ferric ion ratios) in absence of nickel sulphide.	To determine effects of nutrients, oxygen and bacteria on redox potential, and generate data for modelling of redox potential and pH.
B	Leaching experiments performed at various (fixed) redox potentials, sterile (in absence of bacteria).	To determine the electrochemical model constants of the nickel sulphide system.
C	Bioleaching of Ni_3S_2 and parallel sterile control. Redox potential in sterile control is kept at that in bioleach system by addition of hydrogen peroxide.	To determine whether the bioleaching behaviour of Ni_3S_2 may be explained i.t.o. chemical leaching (controlled by solution redox potential).
D	Leaching experiments performed without the addition of hydrogen peroxide, sterile (no bacteria).	To deduce whether the addition of hydrogen peroxide affects leaching of Ni_3S_2 in Type B and Type C experiments.

TABLE 1.2.				
Location of Material Relevant to Types of Experiments				
Cat.	Theoretical Modelling	Experimental Procedure	Experimental Results	Modelling of Results
A	Sec. 2.1. p 13	Sec. 3.6.1. p 37	Sec. 4.1. p 44	Sec. 5.1. p 69
B	Sec. 2.3. p 22	Sec. 3.6.2. p 38	Sec. 4.2. p 47	Sec. 5.2&3. p 74 & 77
C	Sec. 2.4. p 26	Sec. 3.6.3. p 39	Sec. 4.3. p 49	Sec. 5.3. p 74
D	Sec. 2.4. p 26	Sec. 3.6.4. p 42	Sec. 4.4. p 68	Sec. 5.2&3. p 74 & 77

2. THEORETICAL ANALYSIS AND MODELLING

In Section 2.1 the calculation of redox potential and pH level in an acidic iron sulphate solution is described.

The electrochemical model utilized is discussed in Section 2.2. In Section 2.3 the method used for the calculation of the electrochemical model constants for the present sulphide system is presented.

The means by which nickel dissolution during leaching may be predicted given the variation of redox potential with time is described in Section 2.4.

2.1. REDOX POTENTIAL AND pH PREDICTION

The prediction of redox potential has been described by Dry[9]. An indication of his method is given in this section. The computer program utilized in the predictions and a flow diagram of the calculation procedure are detailed in Appendix A.5.1.

Several complexes are of interest in the prediction of redox potential and pH levels in the present system, as their presence contributes to these values. These are $FeSO_4^+$, $FeHSO_4^{2+}$, $FeSO_4^0$, $FeHSO_4^+$, HSO_4^-, $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$, $Fe(SO_4)_2^-$, and $NiSO_4^0$. Equilibrium constants for the first four of these complexes have been determined by Dry[9]. Constants for the

remaining complexes have been obtained from Smith and Martell[26]. There has been some controversy over whether the complex $Fe(SO_4)_2^-$ is important in determining redox potential[9]. One equation can be written for each of these complexes, e.g. for $FeSO_4^+$ the equilibrium constant, K, is given by

$$K = \frac{(FeSO_4^+)}{(Fe^{3+})\ (SO_4^{2-})} \quad ...(2.1)$$

where (i) = activity of species i (mol l^{-1})

Other ions in the system are Fe^{3+}, Fe^{2+}, H^+ , OH^- and SO_4^{2-}. One can determine the total concentrations of ferrous, ferric and sulphate ions experimentally, which gives three more equations. Hydrogen and hydroxide ions are related by the following equilibrium relationship:

$$K_w = 1/((H^+)\ (OH^-)) \quad ...(2.2)$$

In the above expression, the value for Kw is obtained from Smith and Martell[26]. The total amount of hydrogen ions in the system may be calculated as follows:

$$[H^+]_t = 2\ [SO_4^{2-}]_t - 3\ [Fe^{3+}]_t - 2\ [Fe^{2+}]_t - 2\ [Ni^{2+}]_t + [FeOH^{2+}] + 2\ [Fe(OH)_2^+] + 2\ [Fe_2(OH)_2^{4+}] + [OH^-] \quad ...(2.3)$$

$[i]_t$ = total concentration of ion i (mol l^{-1})

$[i]$ = concentration of ion i (mol l^{-1})

Expressions 2.2 and 2.3 are two more equations that are available. We therefore end up with one equation for each species in solution, and thus the concentrations of all the species may now be calculated. Activities can be calculated using activity coefficients:

$$(i) = \gamma_i\ [i] \quad \ldots(2.4)$$

where (i) = activity of ion i (mol l^{-1})
γ_i = activity coefficient of i (dimensionless)
$[i]$ = concentration of i (mol l^{-1})

Provided that the formation of complex ions is taken into account[9], the activity coefficients may be estimated using the extended Debye Huckel form[27]:

$$\log \gamma_i = \frac{-A\ z(i)^2 \sqrt{I}}{1 + A_0\ B\sqrt{I}} \quad \ldots(2.5)$$

where A = constant ($l^{1/2}$ $mol^{-1/2}$)
B = constant ($l^{1/2}$ $angstroms^{-1}$ $mol^{-1/2}$)
Both A and B are dependent on temperature and the type of solution, and are obtained from Hame[28]
A_0 = ion size parameter of species i, obtained from Oblad[29] and Barner and Scheuerman[30] (angstroms)
z(i) = charge of the ion of which the activity coefficient is being calculated (dimensionless)

The ionic strength, I, is given by the following expression:

$$I = \frac{1}{2} \sum_{1} [j]\, z(j)^2 \quad \ldots(2.6)$$

where [j] = concentration of j (mol l^{-1})
z(j) = charge of ion j

Activity coefficients are thus a function of the ionic concentrations in solution. As there is one equation for each species in solution, and no further unknowns, the activities and concentrations of the different species can be calculated. Assuming that the ferrous/ ferric couple dominates the redox reaction, the potential may now be calculated from the Nernst Equation:

$$E = E^0 - \frac{R\,T}{F} \ln \left[\frac{(Fe^{2+})}{(Fe^{3+})} \right]$$

$$= 785{,}28 - 26{,}7276 \ln \left[\frac{(Fe^{2+})}{(Fe^{3+})} \right] \quad \ldots(2.7)$$

where E = redox potential of the solution vs the Standard Hydrogen Electrode (SHE) (mV)
R = universal gas constant (mJ K^{-1} mol^{-1})
T = absolute temperature (K)
E^0 = redox potential of a solution with unity ferrous and ferric ion activity at temperature T, also vs the SHE (mV)
(i) = activity of i (mol l^{-1})

The value for E^0 at 37°C is obtained by integrating dE^0/dt = 1,19 mV/K, with E^0 = 771 mV at 25°C[31]. To obtain the potential of the Standard Calomal Electrode (SCE), one needs to subtract 236,3 mV, the potential of the SCE at 37°C[32] vs the SHE.

The pH level can be calculated from the well-known expression:

$$pH = -\log(H^+) \quad ...(2.8)$$

Thus the redox potential and the pH level in solution may be calculated, and these are compared with experimentally obtained values in Section 5.1.

2.2. ELECTROCHEMICAL MODEL FOR PREDICTION OF LEACH RATE OF NICKEL SULPHIDE

The electrochemical model applied by Dry[9] and by Verbaan and Crundwell[10] is discussed in this Section. The presentation of the model is largely based on Dry's work.

It is proposed that the dissolution of Ni_3S_2 may be represented by the following anodic reaction:

$$Ni_3S_2 \rightarrow 3Ni^{2+} + 2S^0 + 6e- \quad ...(2.9)$$

The anodic current for the dissolution is given by the anodic term in the Butler-Volmer equation[9]:

$$i = i_0 \exp\left\{(1 - \beta)(E - E_e)\left(\frac{F}{RT}\right)\right\} \quad ...(2.10)$$

where i = current density ($C\ hr^{-1}\ m^{-2}$)
i_0 = exchange current density ($C\ hr^{-1}\ m^{-2}$)
β = symmetry factor (Dimensionless)
$E - E_e$ = overpotential = potential with current flowing - open circuit potential (no current) (mV)
F = Faraday constant ($C\ mol^{-1}$)
R = Universal Gas Constant ($mJ\ K^{-1}\ mol^{-1}$)
T = absolute temperature (K)

The current at the particle (or electrode) surface is related to the dissolution of the sulphide as follows:

$$\frac{1}{a}\frac{dm}{dt} = 6\ F\ I \qquad \ldots(2.11)$$

where a = particle (or electrode) surface area (m^2)
m = number of moles of sulphide of the particle (dimensionless)

Substituting Equation 2.10 in 2.11 and rearrangement gives:

$$\frac{dm}{dt} = -\ 6\ a\ F\ i_0\ \exp\left\{(1 - \beta)(E - E_e)\left(\frac{F}{R\ T}\right)\right\} \qquad \ldots(2.12)$$

For a given reaction, the symmetry factor, β, is constant. Also, for a given sulphide and a given solution, E_e and i_0 are also constant at a given temperature. Under these circumstances, only E varies for a given leach process, and Equation 2.12 may be written as follows:

$$\frac{dm}{dt} = -\ a\ K\ \exp(k_2\ E) \qquad \ldots(2.13)$$

here $K = 6\ F\ i_0\ \exp\left\{-(1 - \beta)E_e\left(\frac{F}{R\ T}\right)\right\}$ $\quad (mol\ m^{-2}\ hr^{-1})$

$k_2 = (1 - \beta)\left(\frac{F}{R\ T}\right)$ $\quad (mV^{-1})$

In order to obtain the surface area (a) in terms of the number of moles of the mineral in a given particle, it is necessary to define an average characteristic particle size in each size range as follows:

Let $a = SF\ d^2 = 4\ SF\ r^2$ ...(2.14)

here SF = some shape factor (dimensionless)
d = average characteristic particle size (m) in a given size range
r = average characteristic particle radius (m) in a given size range

The volume of a certain Ni_3S_2 particle in a given size range may be calculated by the following integration:

$$v = \int_0^r 4\ SF\ r^2\ dr$$

$$v = \frac{4}{3}\ SF\ r^3 = \frac{1}{6}\ SF\ d^3 \quad ...(2.15)$$

where v = volume of an average particle in a given size range (m^3)

The volume of a Ni_3S_2 particle containing m moles of the sulphide can also be calculated using the density of the mineral as follows:

$$v = 0{,}24025\ m/\rho \quad ...(2.16)$$

0,24025 = molecular mass of Ni_3S_2 ($kg\ mol^{-1}$)
ρ = density of the mineral ($kg\ m^{-3}$)

Combination of Equations 2.14, 2.15 and 2.16 allows the calculation of the surface area of a given particle (a) in terms of the number of moles in the particle (m) as follows:

$$a = SF^{1/3} \ (1,4415/\rho)^{2/3} \ m^{2/3} \quad ...(2.17)$$

If it is assumed that all particles leach according to the shrinking core model, the shape factor (SF) will stay constant as the leaching progresses. Therefore one may substitute Equation 2.17 in Equation 2.13:

$$\frac{dm}{dt} = - k_1 \exp (k_2 E) \ m^{2/3} \quad ...(2.18)$$

where $k_1 = SF^{1/3} \ (1,4415/\rho)^{2/3} \ K$ = constant (mol hr^{-1})

If the ferrous/ferric exchange current density is much larger than the anodic current due to mineral dissolution, then the redox potential may be used to approximate the surface potential of the particles (E).

2.3. DETERMINATION OF ELECTROCHEMICAL MODEL CONSTANTS FOR NICKEL SULPHIDE SYSTEM

To obtain the values of k_1 and k_2 in Equation 2.18 for the mineral Ni_3S_2, sterile experiments of Type B (at various constant redox potentials) were conducted. In this section it is shown how the data generated by these experiments may be used in the calculation of the electrochemical model constants.

$$M = Nm \quad ...(2.19)$$

where M = total number of moles of sulphide in a given size range (moles)

N = number of particles in the same size range (dimensionsless)

m = number of moles in a given particle of the size range (moles)

The number of particles in a given size range (N) stays constant during leaching, until the particles are completely leached, when it becomes zero. N may be determined using the volume of a particle (Equation 2.15) and the density of the mineral:

$$N = \frac{6x(\text{mass in size range})}{SF\ d^3} \quad ...(2.20)$$

where d = average size in the size range (m)

The mass in a given size range may be read off the size distribution curve (given in Section 3.1).

Substituting Equation 2.19 in Equation 2.18 and rearrangement gives:

$$\frac{dM}{dt} = -k_1 \exp(k_2 E) N^{1/3} M^{2/3} \quad \ldots(2.21)$$

If the solution potential (i.e. E) is held constant during a given experiment, then

$$k_1 \exp(k_2 E) = k_3 = \text{constant} \quad \ldots(2.22)$$

Substituting Equation 2.22 into Equation 2.21 gives:

$$\frac{dM}{dt} = -k_3 N^{1/3} M^{2/3} \quad \ldots(2.23)$$

Integration of Equation 2.23 from time t_1 to time t_2 (corresponding to M_1 and M_2 moles of sulphide respectively) and rearrangement gives:

$$M_2 = (M_1^{1/3} - \tfrac{1}{3} k_3 N^{1/3} (t_2 - t_1))^3 \quad \ldots(2.24)$$

here
M_2 = moles of sulphide in a given size range at time t_2
M_1 = moles of sulphide in a given size range at time t_1

The total amount of moles left in the mineral may be calculated from experimental data. For each size, we have a term for M_2 (Equation 2.24). A value for k_3 in Equation 2.24 can be determined for the given constant redox potential (E) of the experiment, such that the addition of the M_2 terms for all the size ranges gives the total amount of moles left in the mineral.

The leach rate in the first hour of the experiments is fast and seems to be independent of the redox potential in solution (see Section 4.2). It is assumed that a nickel poor layer is formed around each particle in the first hour of leaching. Theoretically this can be accounted for by assuming a small decrease in the sizes of all the particles in the first hour. This decrease is shown in Section 5.2 to be very small, and the above assumptions therefore do not significantly affect the value obtained for k_3. A program to determine a value for k_3 for a given experiment along with its logic diagram is presented in Appendix A.5.2.

A number of experiments of Type A were conducted, each at a given redox potential (E). Therefore a number of values for k_3 were determined, each corresponding to a redox potential. Dividing Equation 2.22 (the expression for k_3) by k_1, taking logs and rearrangement gives:

$$\ln k_3 = k_2 E + \ln k_1 \quad \ldots(2.25)$$

Plotting the log of the k_3 values (determined as shown above) against the redox potentials corresponding to each value of k_3 should therefore result in a straight line. The value for k_1 may then be obtained from the

intercept (which is equal to ln k_1) and the value for k_3 may be obtained from the slope (= k_2).

Another way of calculating the values for k_1 and k_2, is by performing a sterile leach (as Tests D in the absence of bacteria) and choosing the values for the constants by trial and error until the leaching progress is adequately modelled. This method is also used in determining the constant values in Section 5.2.

2.4. PREDICTING LEACH RATE OF NICKEL SULPHIDE FOR VARYING REDOX POTENTIALS

Having obtained the values for k_1 and k_2 by plotting $\ln.k_3$ vs E, the course of any sterile leach can now be predicted. The program to do this is presented in Appendix A.5.3. The decrease in diameter of the particles in the first hour (independent of the redox potential) is included in the program. It is assumed that the redox potential in solution can be adequately approximated by a straight line between the consecutive experimental readings, i.e.

$$E = k_4\ t + k_5 \quad \ldots(2.26)$$

k_4 and k_5 are constants for the period of time between two consecutive readings. This expression is thought to be accurate within the limits of experimental error.

Substituting Equation 2.26 in Equation 2.21 (the rate of decrease of the number of moles) and expanding gives:

$$\frac{dM}{dt} = [-k_1\ \exp(k_2\ k_5)N^{1/3}]\ \exp(k_2\ k_4\ t)M^{2/3} \quad \ldots(2.27)$$

The expression in square brackets is constant in the given time span. Integrating Equation 2.27 from time t_1 (time at one experimental redox potential reading) to time t_2 (time at the next experimental reading) gives the following result:

$$M_2 = \left[M_1^{1/3} + \frac{X\ (\exp\ (k_2 k_4 t_2) - \exp(k_2 k_4 t_1))}{3\ k_2\ k_4} \right]^3 \quad \ldots(2.28)$$

where X = constant in square brackets in Equation 2.27
$= -k_1 \exp(k_2\ k_5) N^{1/3}$

M_1 = total number of moles in a given size range at the one experimental reading (at time t_1)

M_2 = total number of moles in a given size range at the next experimental reading (at time t_2)

In Equation 2.28, k_1 and k_2 are known, and k_4 and k_5 can be calculated from the redox potential readings. Thus, for each size range, the moles of sulphide remaining after each experimental reading can be calculated. The total nickel coming into solution can be calculated by addition of the contributions of all the size fractions. This is then compared with experimentally obtained concentrations in Section 5.3. The program written to perform these calculations is given in Appendix A.5.3.

3. EXPERIMENTAL

In Section 3.1 and Section 3.2 the nickel sulphide and aqueous media utilized in the experiments are discussed respectively. A description of the apparatus used is given in Section 3.3. Section 3.4 is a description of the analytical methods employed in determining concentrations in solution, while the characterization of nickel sulphide residues is discussed in Section 3.5.

In Section 3.6 procedures for the different types of experiments are discussed. Calibration and maintenance of electrodes is described in Appendix A.2.5.

3.1. NICKEL SULPHIDE MINERAL UTILIZED

It was decided to use a pure mineral in order to have a clearly defined system to work on, and to eliminate the possibility of galvanic interactions. At the inception of the present project, most of the work in bacterial leaching at the Council for Mineral Technology (Mintek) involved the leaching of base metals. It was therefore decided to use a pure nickel sulphide for this study.

Efforts were made to purchase the mineral NiS from overseas organisations such as the Wards institute in New York, U.S.A, and Electronic Space Products, Los Angeles, U.S.A. These efforts proved fruitless. Consequently it was decided to produce a pure mineral synthetically at Mintek.

It was decided to use a sulphide which contained only sulphide and nickel ions. Although many natural sulphides contain iron, it was reasoned that soluble ferrous ions could be added to the leaching system as desired, thus making up for the lack of iron in the sulphide. A reason for not including iron in the sulphide was that its inclusion would have complicated the sulphide preparation procedure.

NiS was precipitated by bubbling hydrogen sulphide gas through a concentrated nickel sulphate solution. The precipitate obtained was very fine, and therefore not suitable for leaching experiments. Consequently it was decided to melt and recrystallize the precipitate in an induction furnace to obtain a more crystalline sulphide. An effect of the melting process was the driving off of some of the sulphur from the sulphide system. A mixture of Ni_3S_2 and Ni_7S_6 was obtained initially, but after repeated meltings a pure Ni_3S_2 product was obtained. The precipitation process and the melting and recrystallization stages are described in more detail in Appendices A.2.1.1 and A.2.1.2 respectively.

The mineral was milled and sized using sieves and a Malvern 3600 type particle size analyser. It was decided to use the screening results, coupled with the Malvern results (for sizes less than 38 microns). Sizing data and the resulting size distribution curves are discussed in Appendix A.2.1.3. For modelling purposes, the size distribution was divided in 100 equal mass fractions, an amount which is believed to result in adequate representation of the whole size distribution. The average size for a given fraction is also given in Appendix A.2.1.3 (Table A.10).

3.2. AQUEOUS MEDIA UTILIZED

The medium which has been widely used in bioleaching tests by numerous investigators, is the so-called 9K medium of Silverman and Lundgren[33]. Therefore the media used in these tests were based on this medium, which is given in the following table:

TABLE 3.1.

9K Medium: amounts per litre

$(NH_4)_2SO_4$	3,00 g	Nutrients
KCl	0,10 g	
K_2HPO_4	0,50 g	
$MgSO_4.7H_2O$	0,50 g	
$Ca(NO_3)_2$	0,01 g	
$FeSO_4.7H_2O$	44,80 g	- Energy Source
H_2SO_4 (98%)		- To Adjust pH Level

Bacteria require the 'Nutrients' for growing, because substances such as nitrogen, potassium, phosphorus, etc. form part of the microorganism structure. After some preliminary tests, presented in Appendix A.2.2, it was decided to use $1/10^{th}$ of the nutrient concentrations in the 9K medium, and to adjust the pH levels to 1,6. In some sterile leaches, nutrients were not included at all in order to try and limit jarosite precipitation. In all tests, 44,8 g/l of ferrous sulphate was utilized (i.e. 9 g/l of ferrous ions in solution).

3.3. APPARATUS

The main experiments were performed in stirred reactors. The reactors consisted of two litre glass vessels, equipped with a temperature controller and a pH controller, a calomel and platinum electrode for millivolt redox readings, and a 4 (flat) bladed impellor rotating at 300 r.p.m. Sampling was done using a verticle tube with the bottom end bent at 90 degrees. In this way the flow of the stirred pulp was more or less into the tube during sampling.

The sampling tube also served as an aeration tube when no samples were being taken. The air feed was humidified before being fed into the reactor using a humidifier. This consisted of a bottle filled with de-ionized water and fitted with a sintered glass gas disperser. If required, the temperature of the water in the humidifier was maintained at a temperature of 37°C by means of an infrared lamp. The airflow out of the reactor was by means of a ring opening around the impellor shaft. Approximate dimensions of the apparatus were:

Vessel: diameter = 130 mm, height = 200 mm
Impellor blades each 45 mm x 20 mm (x 4)
Distance of blades from bottom: 6 mm

A schematic representation of the reactors used in the tests is given in Figure 3.1. A photograph of the two reactors used in the parallel leaching tests of Type C as described in Section 3.6.3, is shown in Figure 3.2.

FIGURE 3.1.

Schematic Representation of Apparatus Used in Main Experiments

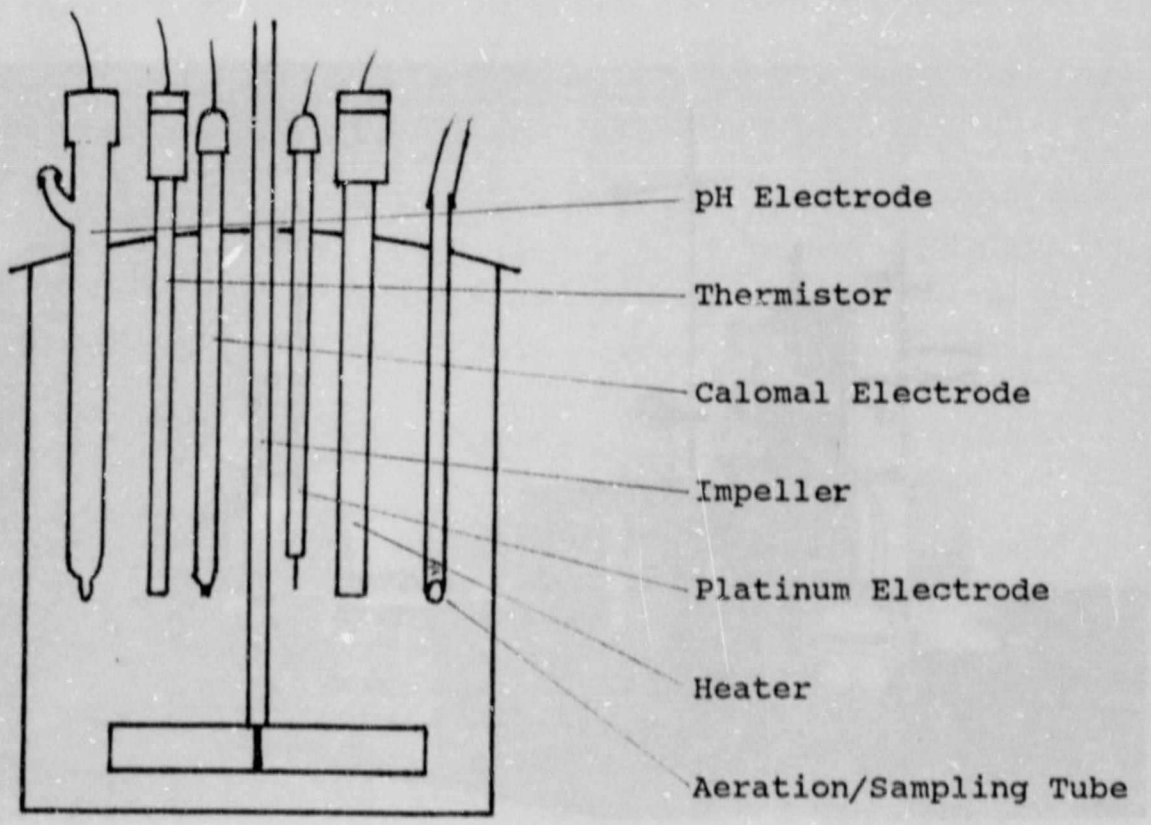

FIGURE 3.2.

Photograph of Apparatus Used to Determine Bioleaching Behaviour of Ni_3S_2, Showing the Parallel Inoculated and Sterile Control Systems.