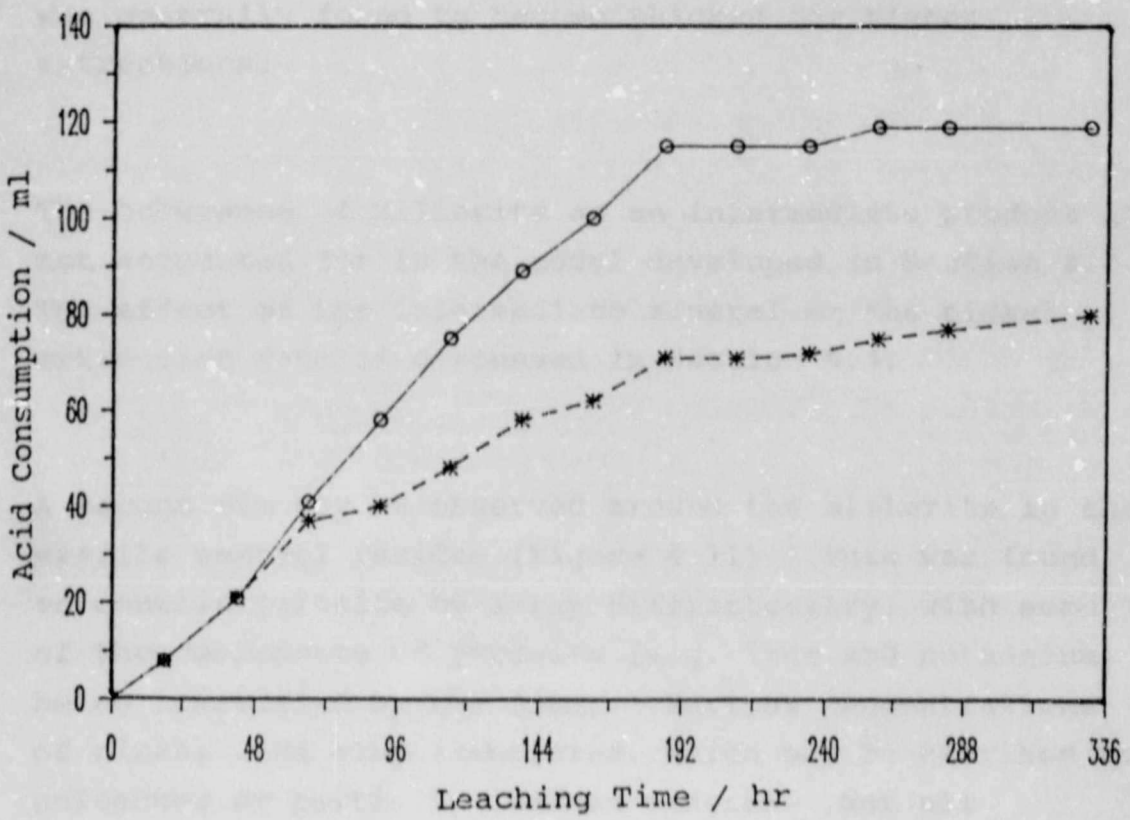
the system are capable of oxidizing reduced sulphur compounds. This is another feature one would expect if the bacteria contributed directly to the leaching of the mineral. As the leaching rate in the inoculated vessel was not enhanced, it could be questioned whether the bacteria only oxidized elemental sulphur that resulted from the chemical oxidation.

FIGURE 4.10.

Test C.5, Acid Consumptions (200 g/l 98% H_2SO_4) in Bioleaching of Ni_3S_2 and Parallel Sterile Control. (Experimental Conditions: Impellor Speeds 300 r.p.m.; 9 g/l Soluble Iron; pH Levels of 1,6 and Temperatures of 37°C.)



Key :

o Sterile System

* Inoculated System

4.3.6. ANALYSIS OF SOLID RESIDUES ARISING FROM LEACHING

Solid residues from the inoculated leach and from the sterile control were examined at various degrees of extraction. The photographs shown in Figures 4.11 and 4.12 were taken of polished sections of sterile and inoculated residues respectively at 70% nickel extraction in Test C.5. In both cases an unleached core Ni_3S_2 can be clearly observed. X-ray diffractometry showed these cores to be Heazlewoodite (Ni_3S_2), and the approximate stoichiometry was confirmed by the scanning electron microscope (SEM). Furthermore, a porous rim can also be observed around the unleached cores in both cases. This rim was identified to be Millerite (NiS), also by X-ray diffractometry, with the approximate stoichiometry again being confirmed by the SEM. The rim was generally found to become thicker for higher extractions.

The occurence of Millerite as an intermediate product is not accounted for in the model developed in Section 2.2. The effect of the intermediate mineral on the nickel extraction rate is discussed in Section 5.3.

A second rim may be observed around the millerite in the sterile control residue (Figure 4.11). This was found to contain jarosite by X-ray diffractometry, with some of the components of jarosite (e.g. iron and potassium) being identified by the (SEM). Various concentrations of nickel were also identified, which may be ascribed to unleached or partially leached mineral. Not all particles were found to have this type of rim. More jarosite was observed for particles which had been leached for a longer period. A very thin and diffuse

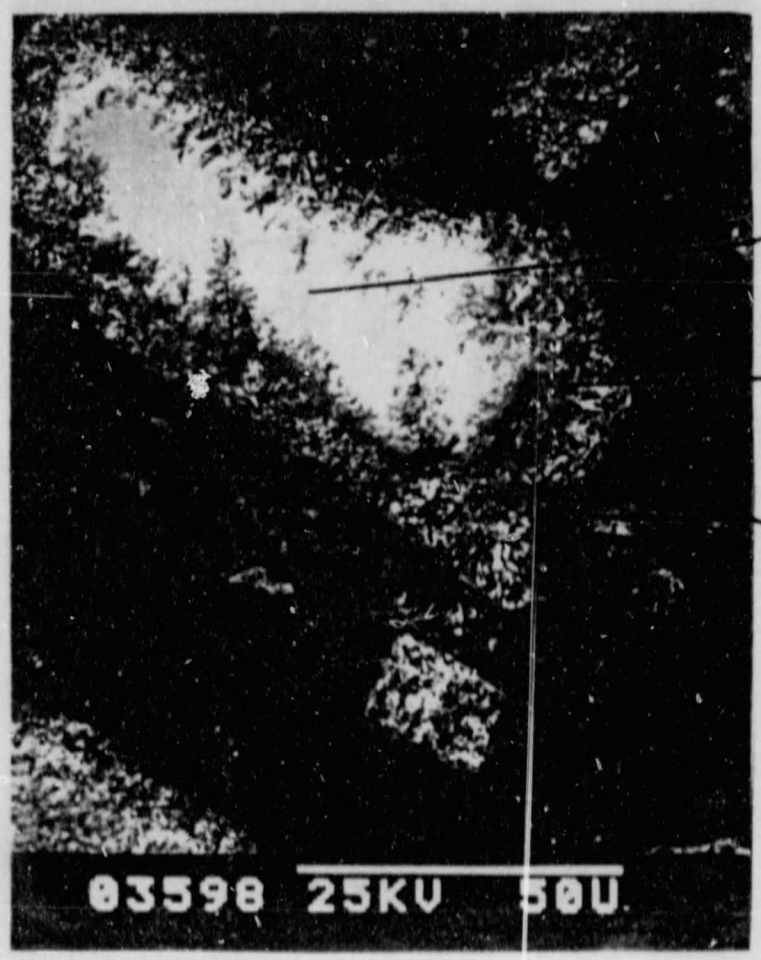
outer rim was also observed around this second rim, and seemed to have a high sulphur content by using the SEM. This rim is so faint that it cannot be observed on the photograph. The resin of the polished section around the sterile leached particles was also found to be rich in sulphur.

A very distinct, compact rim can be seen to surround the Millerite rim of the inoculated particle shown in Figure 4.12. This rim was found to increase in definition as the leaching degree increased, and was observed around many of the particles. In Figure 4.13 a similar rim at 55% extraction of nickel is magnified, and small corridors can be seen to cross the rim. Analysis by the electron microprobe could not give a clear indication of the composition of this rim, as it is too thin for this purpose, but it did seem to have a high nickel content. It is speculated that this rim occurs as a result of bacterial activity, as it was not observed in the sterile leach residues. The presence of this rim could have been a major factor in inhibiting the leaching rate in the inoculated system. Unfortunately, elements like carbon and nitrogen cannot be identified by the electron micro-probe as their molecular mass is too low, so that any organic presence in the rim could not be proved.

An agglomertate of jarosite and partially leached mineral surrounds the distinct rim, was observed often without association with unleached mineral, and was not observed in the sterile leach residues. Perhaps the bacteria or bacterial products acted as a binding agent for loose particles in solution. No sulphur was detected in the resin around the residue particles of the inoculated system, confirming previous observations that bacteria oxidized reduced sulphur compounds.

FIGURE 4.11.

Test C.5, Residue of Parallel Sterile Control of Ni_3S_2 Leaching at 70% Ni Extraction. (Experimental Conditions: Impellor Speed 300 r.p.m.; 9 g/l Soluble Iron; pH Level of 1,6 and Temperature of 37°C.)



Bar Represents 50 Microns

Key :

a Core of Ni_3S_2

b Rim of NiS

c Rim Containing Jarosite

FIGURE 4.12.

Test C.5, Residue of Bioleaching of Ni_3S_2 at 70% Ni Extraction. (Experimental Conditions: Impellor Speed 300 r.p.m.; 9 g/l Soluble Iron; pH Level of 1,6 and Temperature of 37°C.)

Bar Represents 50 Microns

Key :

a Core of Ni_3S_2

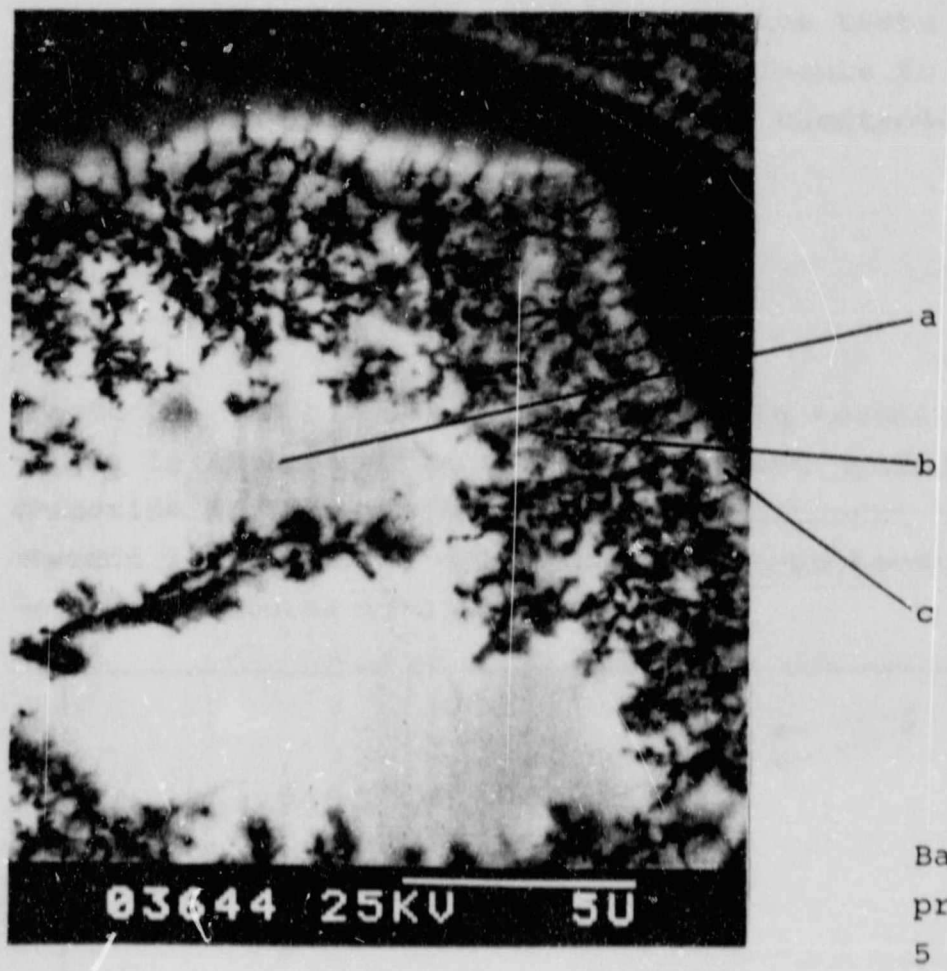
b Rim of NiS

c Thin, Compact Rim

d Agglomerate Containing Jarosite

FIGURE 4.13.

Test C.5, Residue of Bioleaching of Ni_3S_2 at 55% Ni Extraction. (Experimental Conditions: Impellor Speed 300 r.p.m.; 9 g/l Soluble Iron; pH Level of 1,6 and Temperature of 37°C.)



Bar Represents 5 Microns

Key :

a Core of Ni_3S_2

b Rim of NiS

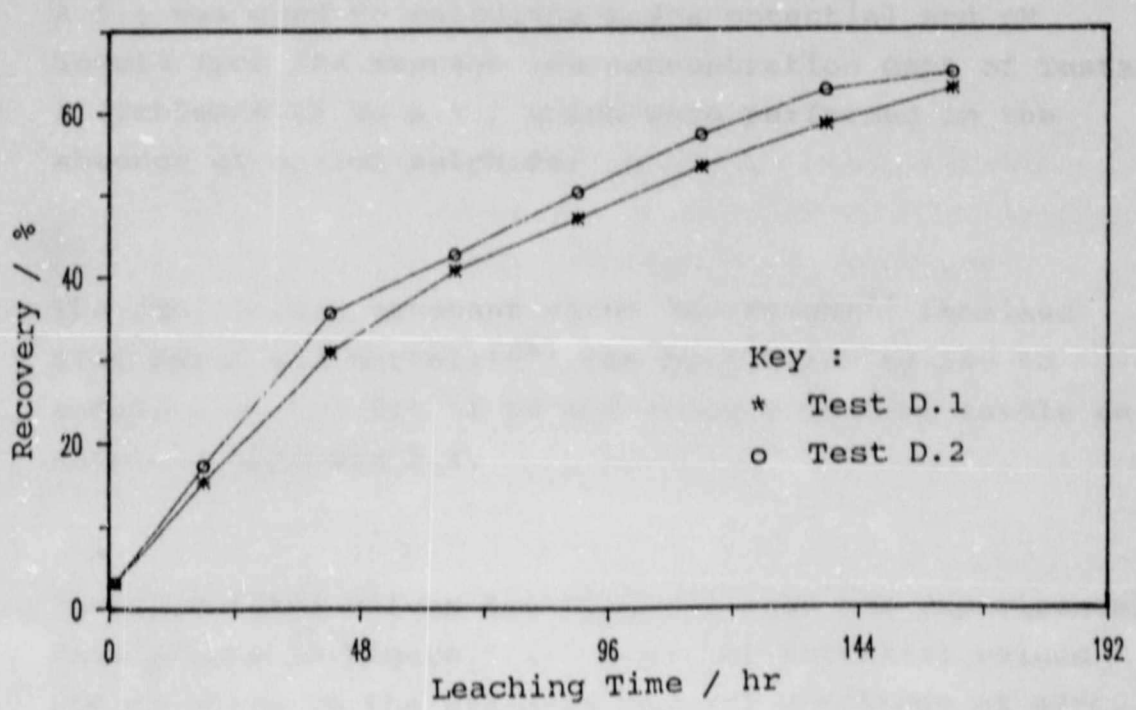
c Thin, Compact Rim

4.4. NICKEL SULPHIDE LEACHING CHARACTERISTICS WITHOUT HYDROGEN PEROXIDE ADDITION IN ABSENCE OF BACTERIA

The results for the two sterile leaches of Type D performed in the absence of hydrogen peroxide addition can be found in Appendix A.3.4 (Tables A.44 and A.45). The leaching results of the two tests are given in Figure 4.14. The redox potential in the tests varied from 580 mV at the start of the experiments to just above 400 mV (vs the standard calomel electrode at 37°C) at the end of the tests.

FIGURE 4.14.

Tests D.1 and D.2, Nickel Recoveries in Leaching of Ni_3S_2 in Absence of Bacteria and Without Hydrogen Peroxide Addition. (Experimental Conditions: Impellor Speeds 300 r.p.m.; 9 g/l Soluble Iron; pH Levels of 1,6 and Temperatures of 37°C.)



5. MATHEMATICAL MODELLING OF EXPERIMENTAL RESULTS

Modelling of the redox potential in tests of Types A and C is discussed in Section 5.1. Estimation of electrochemical model constants is done in Section 5.2, using data obtained from Types B and D experiments. These constants are used in Section 5.3 in modelling the bioleaching of Ni_3S_2 and the parallel sterile control (Type C tests) and chemical leaching of the Ni_3S_2 without hydrogen peroxide addition (Type D Tests).

5.1. MODELLING OF REDOX POTENTIAL AND pH IN ABSENCE AND PRESENCE OF NICKEL SULPHIDE

In this section, the theory outlined in Section 2.1 is utilized. The values of the equilibrium constants for the complexes in solution were chosen to be those shown in Table 5.1. The computer program given in Appendix A.5.1 was used to calculate redox potential and pH levels from the average ion concentration data of Tests A (Tables A.14 to A.17) which were performed in the absence of nickel sulphide.

The equilibrium constant value for $Fe(OH)^{2+}$ obtained from Smith and Martell[26] was multiplied by 160 to obtain a better fit of pH and redox potential levels as shown in Appendix A.4.

The calculated values are compared with the experimental data points in Figure 5.1. Here the potential values are relative to the standard calomel electrode at 37°C.

TABLE 5.1.

Equilibrium Constant Values @ 37°C of Complexes Used in Calculation of Redox Potential and pH Levels in Solutions of Experiments of Type A

Constant no	Complex	Equilibrium Constant
K(1)*	$FeSO_4^+$	13 538
K(2)*	$FeHSO_4^{2+}$	6 203
K(3)**	$FeOH^{2+}$	$9,04 \times 10^{13}$
K(4)***	$Fe(OH)^{2+}$	$2,00 \times 10^{22}$
K(5)***	$Fe_2(OH)_2^{4+}$	$4,37 \times 10^{24}$
K(6)*	$Fe(SO_4)_2^-$	0
K(7)*	$FeSO_4$	178
K(8)*	$FeHSO_4^+$	1 321
K(9)***	HSO_4^-	138
K(10)****	$NiSO_4$	230

* Values from Dry[9]

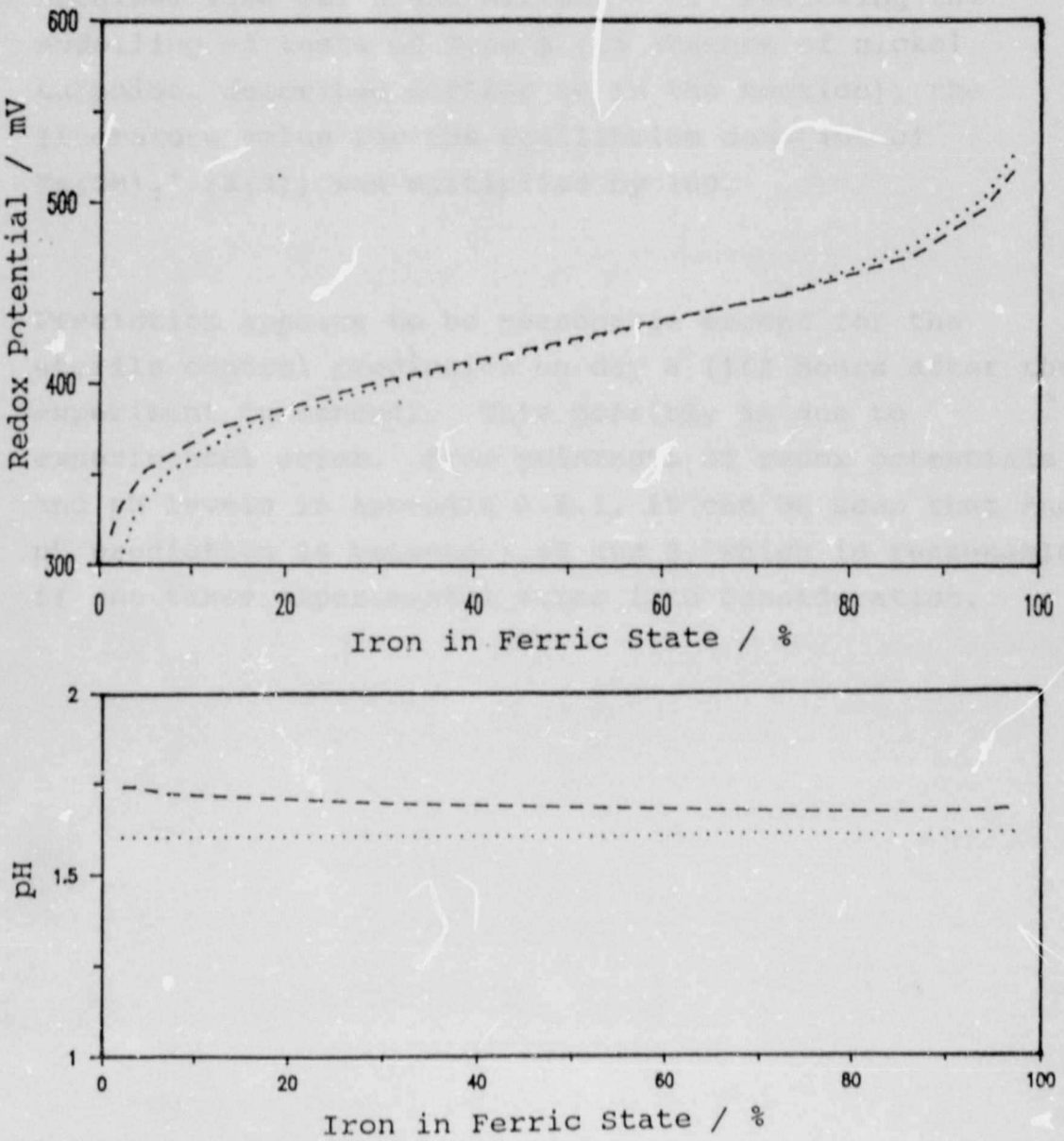
** Value obtained by multiplying Smith and Martell's[26] value for the constant by 160.

*** Values from Smith and Martell[26]

**** The Equilibrium Constant for this Complex is Required in Redox Potential Prediction for Experiments of Type C, and was also Obtained from Smith and Martell[26]

FIGURE 5.1.

Modelling Redox Potential and pH Levels in Tests of Type A by Multiplying the Literature Value of K(3) by 160. (Experimental Conditions: No Sulphide Mineral; 9 g/l Soluble Iron; pH Levels of 1,6 and Temperatures of 37°C.)



Key :

··· Average of Tests A.1 - A.4

- - Calculated Values

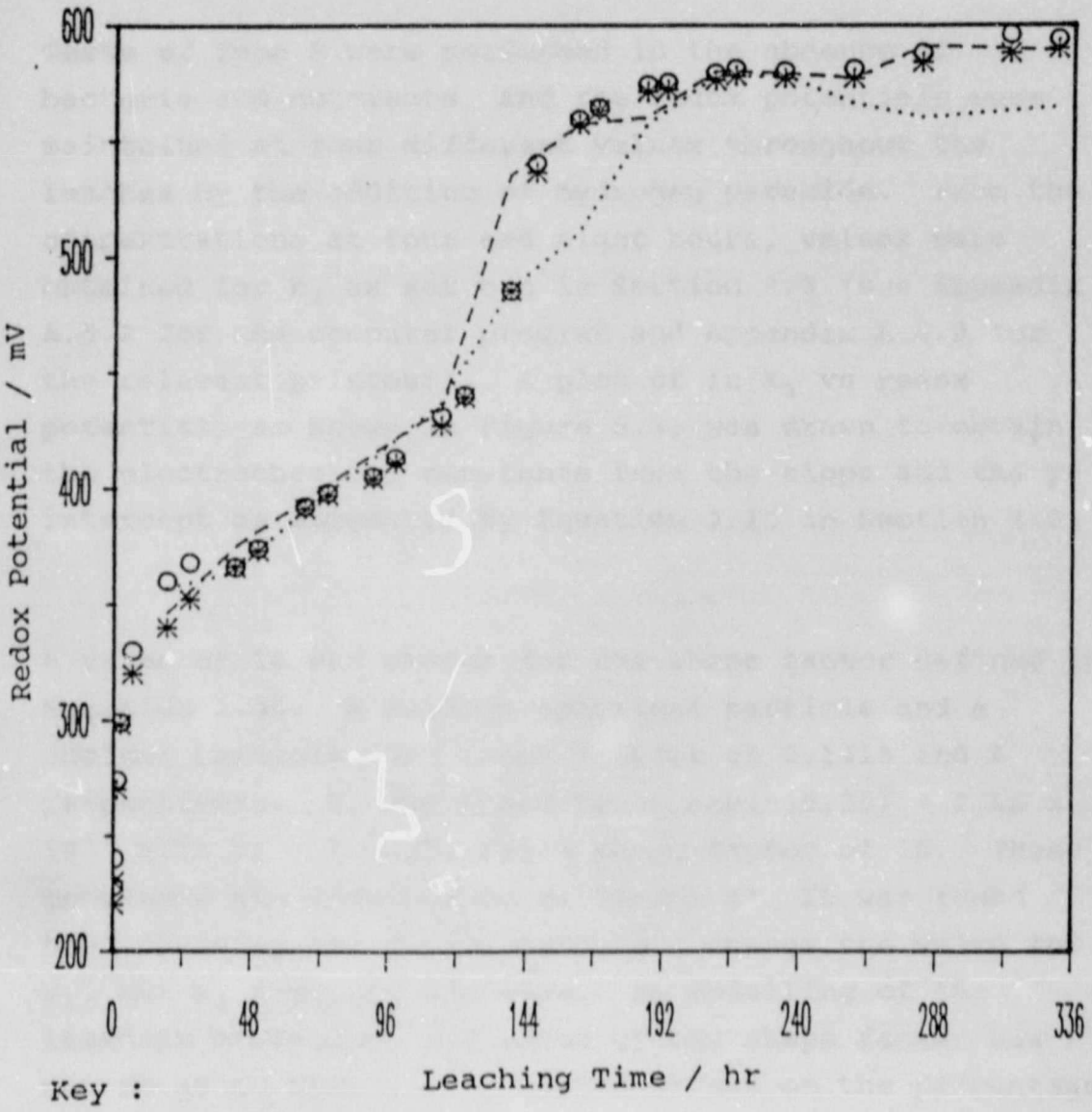
In Figure 5.2 the redox potential in the sterile and inoculated system in Test C.5 are predicted using the experimental data (ferrous, ferric, sulphate and nickel analyses given in the Appendix, Tables A.39 and A.40), and the redox potential and pH predicting program in Appendix A.5.1.

The equilibrium constant for the complex $NiSO_4$ was obtained from Smith and Martell[26]. Following the modelling of tests of Type A (in absence of nickel sulphide, described earlier on in the section), the literature value for the equilibrium constant of $Fe(OH)_2^+$ (K(3)) was multiplied by 160.

Prediction appears to be reasonable except for the sterile control prediction on day 8 (162 hours after the experiment commenced). This possibly is due to experimental error. From printouts of redox potentials and pH levels in Appendix A.6.1, it can be seen that the pH prediction is between 1.65 and 2, which is reasonable if one takes experimental error into consideration.

FIGURE 5.2.

Test C.5, Modelling of Redox Potential in Bioleaching of Ni_3S_2 and Parallel Sterile Control by Multiplying the Literature Value of K(3) by 160. (Experimental Conditions: Impellor Speeds 300 r.p.m.; 9 g/l Soluble Iron; pH Levels of 1,6 and Temperatures of 37°C.)



Key :

o Sterile System Data

* Inoculated System Data

··· Modelling of Sterile System

- - Modelling of Inoculated System

5.2. ESTIMATION OF ELECTROCHEMICAL MODEL CONSTANTS FOR NICKEL SULPHIDE LEACHING

The results of the tests of Types B and D are used in the calculation of these constants.

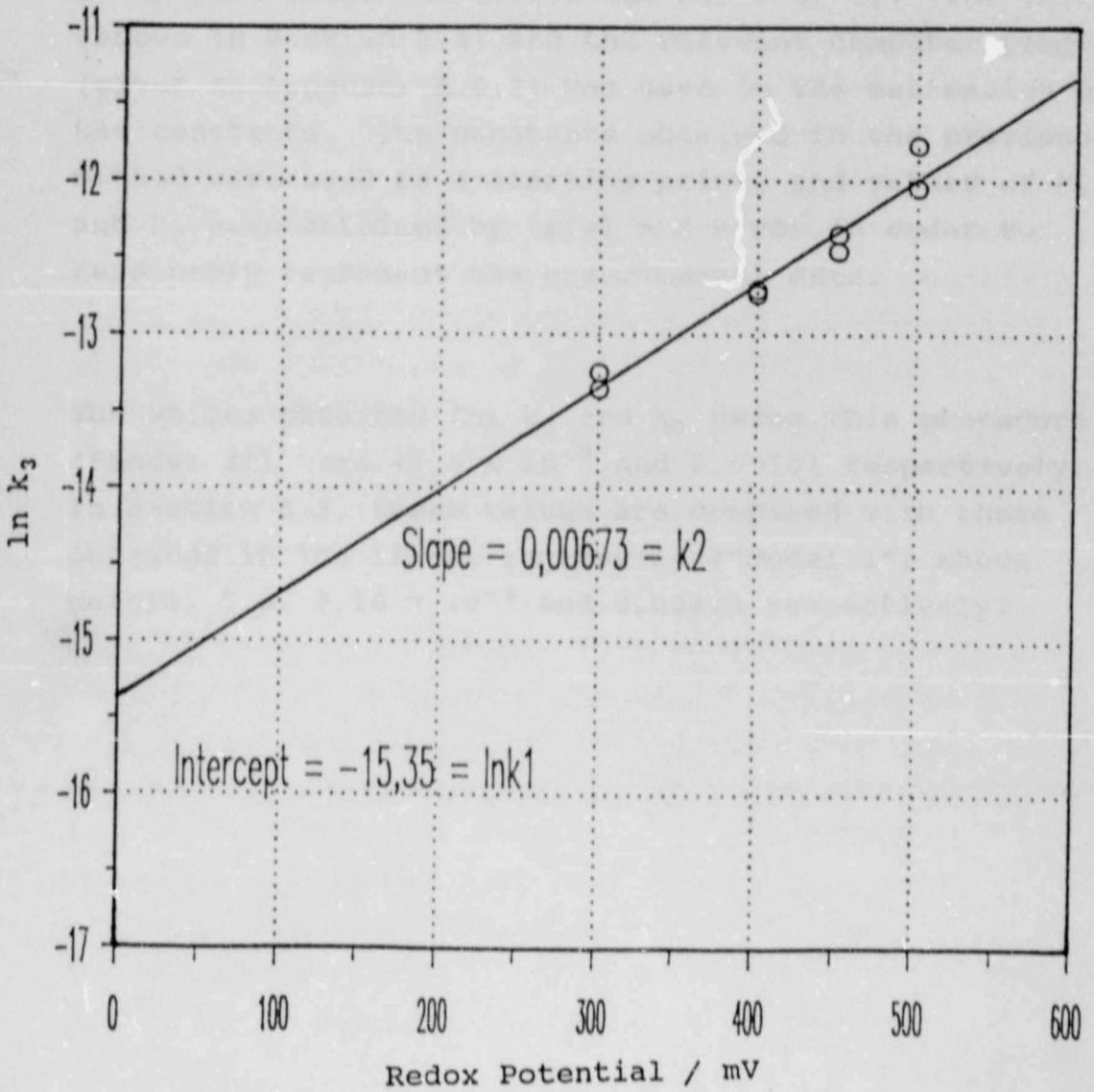
Tests of Type B were performed in the absence of bacteria and nutrients, and the redox potentials were maintained at four different values throughout the leaches by the addition of hydrogen peroxide. From the concentrations at four and eight hours, values were obtained for k_3 as set out in Section 2.3 (see Appendix A.5.2 for the computer program and Appendix A.6.2 for the relavant printout). A plot of ln k_3 vs redox potential, as shown in Figure 5.3, was drawn to obtain the electrochemical constants from the slope and the y-intercept as suggested by Equation 2.15 in Section 2.2.

A value of 10 was chosen for the shape factor defined in Equation 2.14. A perfect spherical particle and a cubical particle have shape factors of 3,1416 and 6 respectively. k_1 was found to be $\exp(-15,35) = 2,16 \times 10^{-7}$ with $k_2 = 0.00673$ for a shape factor of 10. These constants are referred to as "Model 1". It was found that changing the shape factor did change the value for k_1, but k_2 remained the same. In modelling of the leaching behaviour, the value of the shape factor was not found to have a very marked effect on the percentage extraction after a given time, therefore only modelling results obtained with a shape factor of 10 are reported in this work.

The values for ln k_3 in Figure 5.3 can be seen to lie on a reasonably straight line, which implies that the electrochemical model is adequate to describe the leaching behaviour under the given conditions for up to 8 hours.

FIGURE 5.3.

Linear Regression of Data from Tests of Type B, in Order to Obtain Values for the Electrochemical Model Constants k_1 and k_2 for a Shape Factor of 10. (Experimental Conditions: Impellor Speeds 300 r.p.m.; 9 g/l Soluble Iron; pH Level of 1,6 and Temperatures of 37°C.)



The data obtained in Tests of Type D (chemical leaching in the absence of bacteria and with no hydrogen peroxide addition) were also used in calculating the electrochemical model constants (these constants are referred to as "Model 2"). These experiments had a time span of 7 days, and therefore could be used to check that the leaching behaviour in the first 8 hours (as determined in tests of Type B above) was continued over a longer period of time. Also, it was thought that any possible different leaching behaviour due to the absence of hydrogen peroxide could also have been observed.

The redox potential in the tests varied from above 500 mV to just above 400 mV (vs the SCE @ 37°C). The theory (shown in Section 2.4) and the relevant computer program (given in Appendix A.6.3) was used in the estimation of the constants. The constants obtained in the previous method were used as a starting point, and values of k_1 and k_2 were obtained by trial and error in order to reasonably represent the experimental data.

The values obtained for k_1 and k_2 using this procedure ("Model 2") were $47,5 \times 10^{-7}$ and 0,00101 respectively. In Section 5.3, these values are compared with those obtained in the linear regression ("Model 1") shown before, i.e. $2,16 \times 10^{-7}$ and 0,00673 respectively.

5.3. MODELLING LEACHING OF NICKEL SULPHIDE IN PRESENCE AND ABSENCE OF BACTERIA

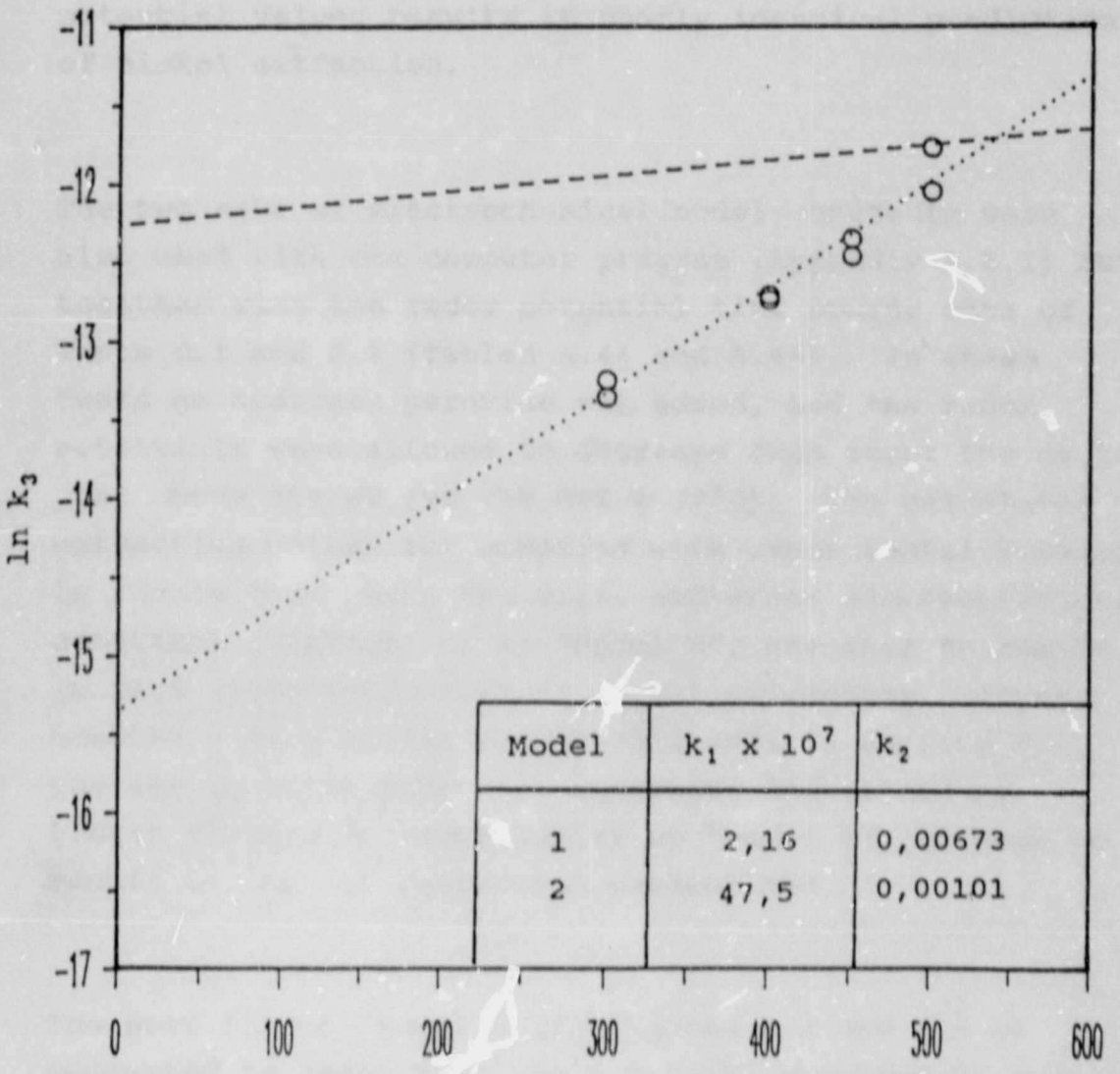
The modelling of Types B, C and D tests is discussed in this Section.

The data points shown in Figure 5.3 of Section 5.2 (obtained from Type B experiments) were used to determine k_2 (the value of the slope) and ln k_1 (the value of the intercept). The data points in the figure were obtained from the leaching of Ni_3S_2 at four different constant redox potentials in the absence of bacteria. In Figure 5.4, the same plot is given, but showing the effect of changing the model constants to those determined by the trial-and-error method ("Model 2"). The graph representing "Model 2" is seen to be a poor approximation to the experimental data obtained in Tests B. "Model 1" represents the values for k_1 and k_2 which were determined by linear regression of the data points in Section 5.2.

In tests of Type C Ni_3S_2 was bioleached, and a parallel sterile control was performed at the same time. The redox potential in the sterile control was maintained at the same level as that in the inoculated system at any given time by the addition of hydrogen peroxide. The two sets of electrochemical model constants determined in Section 5.2 were used in the computer program (Appendix A.5.3) together with the sterile redox potential time course data of Test C.5 (Table A.36). The effect of using the redox potential for the sterile system as calculated from solution composition (in

FIGURE 5.4.

Comparing Data from Tests of Type B with the Graph Obtained Using the Trial-and-Error Electrochemical Constants k_1 and k_2 ("Model 2"). (Experimental Conditions: Impellor Speeds 300 r.p.m.; 9 g/l Soluble Iron; pH Levels of 1,6 and Temperatures of 37°C.)



Model	$k_1 \times 10^7$	k_2
1	2,16	0,00673
2	47,5	0,00101

Key :

o Data from Tests B

''' Model 1

- - Model 2

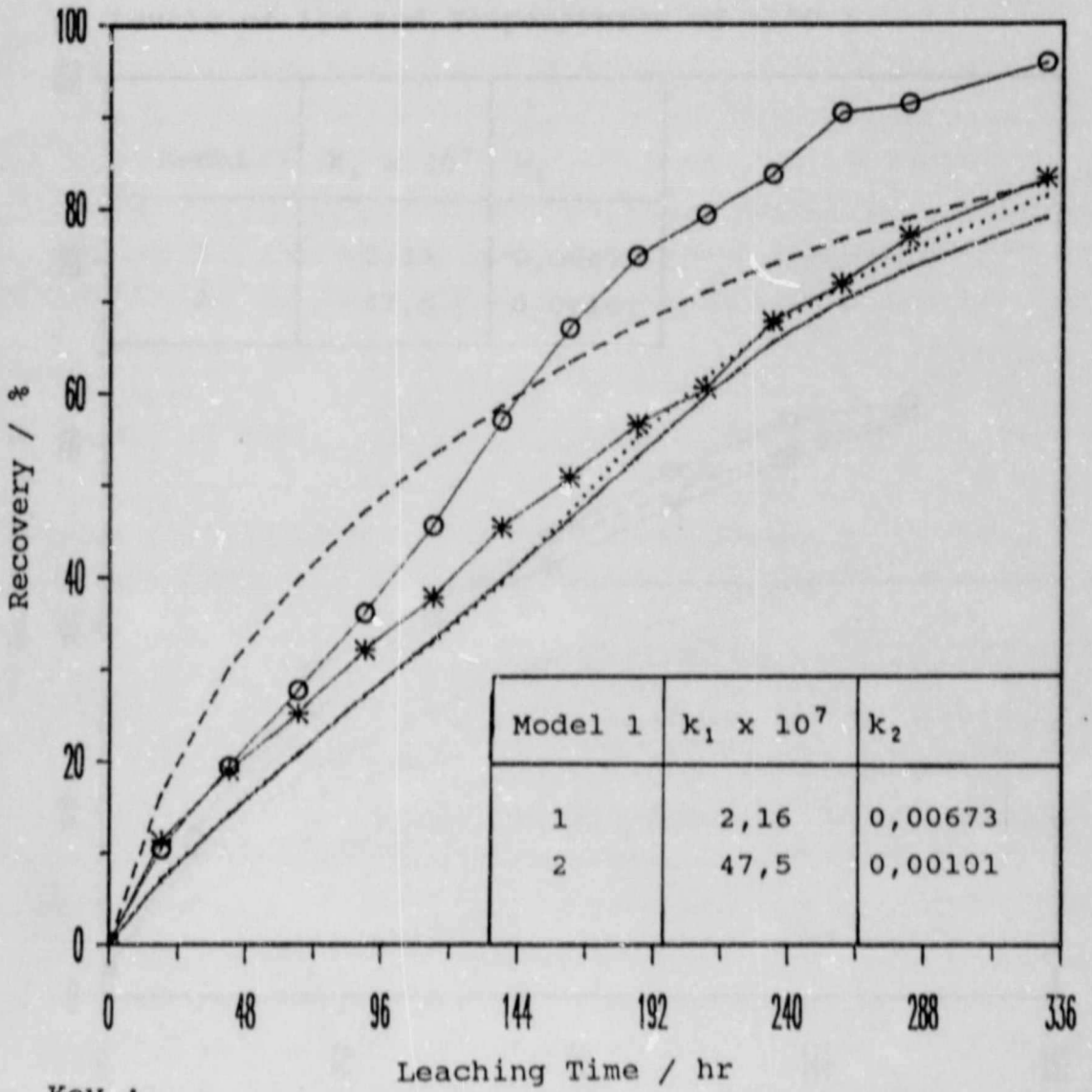
Section 5.1) was also investigated. The calculated extraction values are compared with experimental results in Figure 5.5. In the figure, "Model 2", which represents the trial-and-error model constants, does not fit the data of either the sterile or the inoculated system. Using the constants obtained by the linear regression, "Model 1", results in a prediction similar to the inoculated system, but significantly lower than the sterile system towards the end of the leach. It can also be seen that, in this case, using calculated redox potential values results in nearly identical prediction of nickel extraction.

The two sets of electrochemical model constants were also used with the computer program (Appendix A.5.3) but together with the redox potential time course data of Tests D.1 and D.2 (Tables A.44 and A.45). In these tests no hydrogen peroxide was added, and the redox potentials were allowed to decrease from about 580 mV to just above 400 mV (vs the SCE @ 37°C). The calculated extraction values are compared with experimental results in Figure 5.6. Here the trial-and-error electrochemical constants (represented by "Model 2") are seen to result in reasonable prediction of nickel extraction. (These constants were chosen to fit this data in Section 5.2.) The set of electrochemical constants determined by linear regression (represented by "Model 1") is seen to result in too low extraction predictions.

The poor fit of "Model 2" in Figures 5.4 and 5.5 is suggested to imply that the constants obtained by trial-and-error are totally inadequate to describe the leaching behaviour.

FIGURE 5.5.

Test C.5, Modelling of Nickel Extraction in Bioleaching of Ni_3S_2 and Parallel Sterile Control Using the Two Sets of Electrochemical Model Constants. (Experimental Conditions: Impellor Speeds 300 r.p.m.; 9 g/l Soluble Iron; pH Levels of 1,6 and Temperatures of 37°C.)



Key :

o Data from Sterile System

* Data from Inoculated System

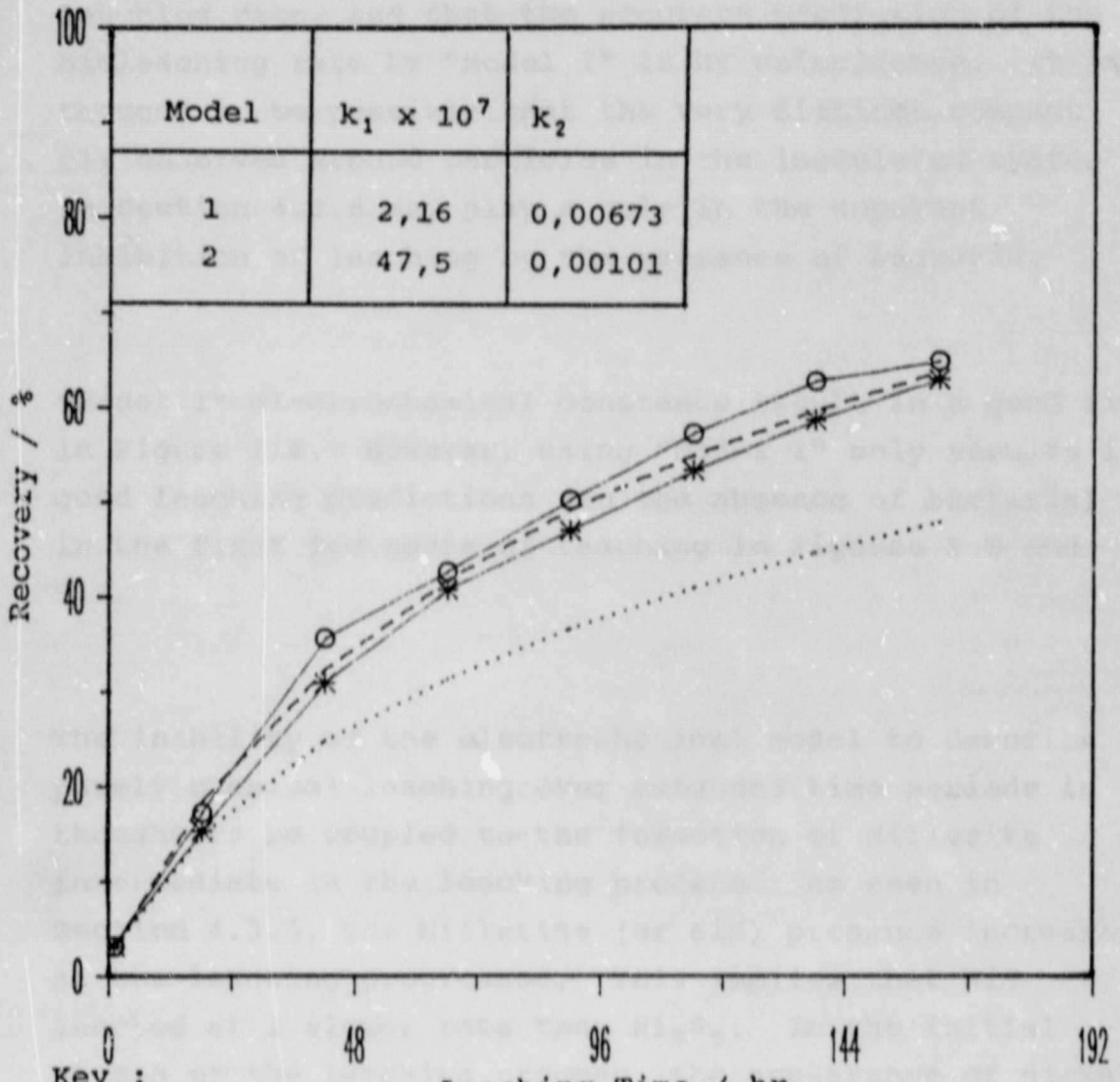
··· Model 1 Using Experimental Data from Sterile System

--- Model 1 Using Calculated Redox Potentials

– – Model 2 Using Sterile System Data

FIGURE 5.6.

Tests D.1 and D.2, Modelling of Nickel Extraction in Leaching of Ni_3S_2 in Absence of Bacteria and Without Hydrogen Peroxide Addition Using the Two Sets of Electrochemical Model Constants. (Experimental Conditions: Impellor Speeds 300 r.p.m.; 9 g/l Soluble Iron; pH Levels of 1,6 and Temperatures of 37°C.)



Key :

* Data from Test D.1

o Data from Test D.2

··· Values Calculated with Model 1

– – Values Calculated with Model 2

If "Model 1" accurately predicted extractions, one could possibly deduce that the bioleaching of Ni_3S_2 in Figure 5.5 may be explained purely in terms of an electrochemical mechanism. The increased leaching rate observed in the sterile control could be thought to be due to direct action of peroxide radicals in the mineral. However, it can be seen from Figure 5.6 that "Model 1" predictions in the absence of hydrogen peroxide prediction are also too low. It therefore seems that the presence of bacteria in the bioleaching system somehow decreased the leaching rate, and that the accurate prediction of the bioleaching rate by "Model 1" is by coincidence. It is thought to be possible that the very distinct compact rim observed around particles in the inoculated system in Section 4.3.6 may play a role in the apparent inhibition of leaching by the presence of bacteria.

"Model 1" electrochemical constants result in a good fit in Figure 5.4. However, using "Model 1" only results in good leaching predictions (in the absence of bacteria) in the first few hours of leaching in Figures 5.5 and 5.6.

The inability of the electrochemical model to describe purely chemical leaching over extended time periods is thought to be coupled to the formation of Millerite intermediate in the leaching process. As seen in Section 4.3.6, the Millerite (or NiS) presence increased as the leaching progressed. This implies that NiS leached at a slower rate than Ni_3S_2. In the initial stages of the leaching process, the appearance of nickel in solution may be ascribed mainly to the loss of nickel from Ni_3S_2 in the formation of NiS. However, as the leaching process progressed, the Millerite presence increased substantially, therefore more of the nickel

that came into solution can be attributed to NiS leaching. It is suggested that this additional portion of nickel that came into solution is not accounted for in "Model 1". Possibly one could postulate that the leaching of Ni_3S_2 to NiS, and the subsequent leaching of NiS are both electrochemical processes. The determination of the relevant electrochemical constants in such a system is obviously more complicated than a system where no intermediate species form. A complicating factor is that the NiS intermediate does not hinder further leaching of the Ni_3S_2. Some of the leaching of Ni_3S_2 could conceptually occur without the formation of a NiS intermediate. Further testwork to investigate these aspects, however, was thought to lie outside the scope of this project.

6. DISCUSSION AND CONCLUSIONS

IMPORTANCE OF DIRECT AND INDIRECT MECHANISMS:

Bacteria in the culture utilized seemed to attach to the solid particles in the system. Conceptually this is one of the requirements for the direct mechanism. It has also been shown that the bacterial culture developed oxidized reduced sulphur compounds, as could be seen by the increased production of sulphuric acid in the inoculated system. Leaching in the sterile control (with redox potential made equal to that in the inoculated system), proceeded at a faster rate than in the presence of bacteria. One could conclude that the bacteria, and/ or bacterial products, inhibit the ferric leaching in some way. A thin compact layer of material which was found to form only around particles in the inoculated system is thought to be as a result of bacterial activity. It is thought that this layer could have played a major role in the apparent inhibition of leaching in the inoculated system. One could argue that the inhibiting factor is actually larger than is observed, and that the bacteria make up the difference by directly oxidizing the mineral. At this stage, however, it is felt that this possibility is unlikely, and that the direct action of bacteria does not occur significantly.

The beneficial aspect of the bacteria in the given system therefore seems to be restricted to re-oxidation of ferrous ions. Oxidation of reduced sulphur species may also be regarded as beneficial for certain applications.

MODELLING OF LEACHING BEHAVIOUR:

Constants used in prediction of redox potential and pH levels in solution are given in Table 5.1. It was found that multiplying the equilibrium constant for $FeOH^{2+}$ which was reported in the literature by 180 gave the best results for pH and redox potential prediction. It was found that these calculated redox potentials could be used instead of the measured redox potentials in the prediction of nickel extraction. Prediction of leaching solution composition as a function of time, however, would be difficult due to the precipitation of ferric species and the oxidation of sulphur by ferric ions, which then also has to be modelled.

k_1 and k_2 in the electrochemical leach rate expression $dm/dt = -k_1 \exp(k_2 E)\ m^{2/3}$ (Equation 2.18) used in modelling the leaching of Ni_3S_2 were found to be $2{,}16 \times 10^{-7}$ and 0,00673 respectively, by linear regression of data obtained from experiments of Type B (with various constant redox potentials). These constants (referred to as "Model 1" in this work) were found to predict reasonably leaching rates only in the initial stages of all the leaching tests. Sterile leaching therefore did seem to depend on the redox potential of the solution, but did not follow the shrinking core model. This is thought to have been due to the formation of Millerite (NiS) as an intermediate of the leaching process. More work would be required on the modelling side of this specific bioleaching process for leaching rates to be accurately predicted over longer time spans.

The constants k_1 and k_2 obtained by the trial-and-error fitting of data from Type D tests (performed with decreasing redox Potentials) were found to be $47{,}5 \times 10^{-7}$

and 0,00101 respectively. These constants, referred to as "Model 2" were found not to predict leaching rates in tests of Types B and C at all satisfactorily.

7. RECOMMENDATIONS

In view of the fact that bioleaching processes are on the verge of commercial application, it is felt that the mechanism by which bacterial leaching occurs is of great importance in modelling applications. The method employed in this project was found to elucidate successfully the importance of the indirect mechanism in the bioleaching of synthetic Heazlewoodite in the presence of soluble iron at a concentration of 9 g/l. This was even though the leaching did not follow the ideal shrinking core model. It is suggested that further tests be performed on natural minerals using the same bioleaching procedure with parallel sterile controls running at the same time under conditions of controlled redox potential. Where shrinking core behaviour is observed, it is suggested that an attempt be made to predict the leaching behaviour using an electrochemical model.

APPENDICES

APPENDIX A.1.

In Section A.1.1, the nature and growth requirements of the bacterium involved in bioleaching is discussed. In Section A.1.2, oxidation of ferrous ions by this bacterium is discussed in detail.

A discussion of literature on the importance of the direct and the indirect mechanisms appears in Section A.1.3.

A.1.1. NATURE AND REQUIREMENTS OF *Thiobacillus ferrooxidans*

GENERAL

Bacterial leaching of metal sulphides has been associated with several types of bacteria, e.g. *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans*[35]. These bacteria catalyse the oxidation of ferrous ions and/or reduced sulphur compounds in acidic iron sulphate solutions. By these oxidations, bacteria obtain energy to survive and multiply. In the process metals are dissolved and the sulphide sulphur is eventually oxidized to sulphate.

Thiobacillus ferrooxidans, the most prominent type of bacterium, is an autotrophic, chemolithic, and acidophilic organism. This means that the bacterium

obtains its nutrients (e.g. nitrogen, potassium, phosphorus and magnesium) and energy for growth processes from inorganic sources, and lives under acidic conditions.

Dugan and Lundgren[36] reported that the examination of the fine structure of *ferrobacilli* showed that *Thiobacillus ferrooxidans* is surrounded by a complex envelope structure typical of gram-negative bacteria. Lundgren and Tano[5] provided a description of the envelope surrounding gram-negative bacteria. It consists of an outer membrane, an inner membrane and a periplasmic space in between the two membranes. The outer membrane controls the movement of ions and molecules into and out of the periplasmic space. Enzymes, present in the periplasmic space, are thus protected from the harmful acidity and high metal ion concentrations associated with the surroundings of the bacteria. Enzymes are complex, sensitive biological catalysts and those of interest are the ones involved in the oxidation of ferrous ions and reduced sulphur compounds. The inner, or cytoplasmic membrane, was thought[5] to prevent toxic products of the inorganic oxidation from reaching the cytoplasm, which makes up the largest part of the bacterium.

Apparently it is this envelope that gives *Thiobacillus ferrooxidans* some of its destinguishing features. Remsen and Lundgren[37] found that cells grown on an iron sulphate medium were inhibited by most organic compounds, but could in time adapt to glucose as an energy source. They also found that brief exposure of cells to sonic energy for the purpose of removing the envelope material left cells capable of growth on glucose, but not on iron.