It is suggested that the *Thiobacilli* possibly adapt to growth on glucose by shedding their envelope. The function of the cell envelope would then be to enable utilization of inorganic energy sources like ferrous ions.

Heterotrophic organisms (i.e. organisms which do require some organic matter) have been found to be present in mixed cultures. Groudev, Genchev and Gaidarjiev[38] identified heterotrophs in leach solutions, and found that by decreasing the pH level from 3,2 to 2,1 decreased the heterotrophic population from 24% of the total population to 3%.

It is speculated that these heterotrophic organisms obtain energy and nutrients from organic waste products of the rest of the bacterial population. The breaking down of waste products may well be benificial to the whole process. The proportion of heterotrophs in the system is suspected to be small under normal leaching conditions, considering the limited availability of organic material in a typical leaching system.

Dugan and Lungren[36] suggested that the envelope denies access by organic material to the cytoplasmic membrane of the cell, which results in organic material not being utilized as an energy source. In fact, organic compounds were suggested to block the transfer of sulphate and iron ions, by attaching to sulphate groups which complex the ferrous ions in the envelope layers of the cell.

Tuovinen and Kelly(4) reasoned that the remarkable resistance of *Thiobacillus ferrooxidans* to inhibition by other metals indicated that sites for binding of ferrous iron were not available to other cations.

GROWTH REQUIREMENTS

Thiobacillus ferrooxidans is widely reported to be most active at temperatures around 35°C, and acidity around a pH value of 2,5. For instance, Bryner, Walker and Palmer[39] have shown that, in the bacterial leachings of pyrite and chalcopyrite, maximum dissolution rates were obtained around a temperature of 35°C. Furthermore, the same authors found that as the temperature was increased further, a minimum was obtained around 55 to 65°C, after which the leaching rates increased again. One can thus conclude that the bacteria tended to die off above a temperature of 35°C, and that non-biological leaching resulted in the increasing leach rates observed above a temperature of 65°C.

In the literature, important nutrients have been found to be ammonium-nitrogen, phophorus, sulphate, and magnesium[33,40,41,42,43]. The growth medium which has been extensively utilized in bacterial leaching is the 9K nutrient medium of Silverman and Lungren[33]. "9K" refers to the 9 000 milligrams of ferrous iron present in the medium as an energy source for the bacteria. Reported minimum nutritional requirements for bacterial growth are given in Table A.1, where they are compared with the 9K medium.

TABLE A.1.

Nutritional Requirements of *Thiobacillus ferrooxidans*, Values are Given in Parts Per Million.

Element	Ref.[40]*	Ref.[41]*	Ref.[42]*	Ref.[43]*	Ref[33] 9K Med.
Ca	Trace	Trace	-	-	2,3
Mg	2	4	-	-	49,3
K	Trace	25	2,5	-	277
N	-	30	8	3	636
P	-	10	15	-	88,9
SO_4^{2-}	2 000	-	-	-	17 850

* : Minimum requirements

Dave, Natarajan and Bhat[44] found that 25% of the concentrations of the ingredients of the 9K medium was sufficient in sphalerite leaching at 5% pulp density. By completely omitting nitrogen from the medium, Tuovinen, Niemela and Gyllenberg[40] showed that oxidation of ferrous iron dropped by half. They pointed out, however, that an acidic medium is very effective in absorbing ammonia from the atmosphere, and that nitrogen could have been obtained by the bacteria in this way. Omitting phophorus reduced the oxidation rate by 20% after 13 transfers of a bacterial culture onto fresh phophorus-free growth medium.

It can be seen that the nutritional requirements of the bacteria have not yet been defined very closely. One of the dificulties involved is that nutritional require-

ments might well vary between different cultures of bacteria, and between cultures grown on various substrates. Also, a high bacterial concentration in a leaching system (due to a finely ground ore or a high solid density) will require a higher concentration of nutrients. The solid feed to a leaching system might also contain nutrients, in which case less nutrients would need to be supplied separately.

Approximately 50% of dried bacterial cells was found consist of carbon[45], and *Thiobacillus ferrooxidans* relies on dissolved carbon dioxide as its source of carbon. Hence no organic matter is required by the organism. In fact, organic molecules have been regarded as being toxic to the bacteria[36].

Some authors have reported on enriching the gas supply to leaching systems with carbon dioxide. Corrans[46] found that the leaching of pentlandite at pulp density of 20% was increased if the carbon dioxide concentration of the air in the system was increased to 1%. Little further increase in leach rate occurred by increasing the carbon dioxide concentration to 2%. Gormely[47] also found it necessary to increase the carbon dioxide concentration in his tests to 1%.

Torma, Walden, Duncan and Branion[48] found that bacteria were limited by the carbon dioxide concentration present in air when a pulp density of 12 g per 100 ml solution of zinc sulphide was exceeded. When enriching the air with 0,23% carbon dioxide, the pulp density could be increased to 24 g per 100 ml without decreasing the zinc extraction per unit surface area of solid. Above this pulp density, some other factor

became limiting, as further carbon dioxide enrichment did not allow an increase in pulp density without decreasing the leach rate per unit surface area of sulphide.

As was reasoned in the case of the nutrient supply, different cultures and different concentrations of bacteria will have different carbon dioxide requirements.

RATE OF GROWTH

A bacterium reproduces by growing, and then dividing into two separate identical bacteria, a process known as binary fission. The time elapsed from formation of the two bacteria to the next binary fission is known as the doubling time. McGoran, Duncan and Walden[49] found that the doubling time of *Thiobacillus ferrooxidans*, growing on ferrous iron, was between 6,5 and 10 hours. Doubling time on chalcopyrite varied from 14 to 17 hours.

It is thought that the doubling time is a function of the growth medium: sulphides less amenable to bacterial activity may result in very much longer doubling times. Different bacterial cultures may well exhibit different doubling times on the same energy source. The activity of the bacteria also plays a role here, as bacteria which have been subjected to unfavourable surroundings, e.g. cold temperatures and deprivation of energy or nutrient sources, will initially grow slowly.

This initial period, where conditions are favourable but growth is slow, is commonly known as a 'lag phase'. After this phase, the bacteria start to undergo regular binary fission at a faster rate. Plotting the log of the number of bacteria versus time will give a straight line, which led to this specific phase being called the 'log phase'. After some time, some nutrient or energy source may become limited, and stagnation of growth, and eventually death, occurs.

A.1.2. OXIDATION OF FERROUS IONS BY BACTERIA

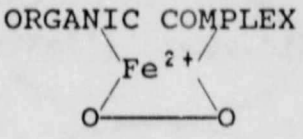
Lundgren and Tano[5] proposed that ferrous oxidation takes place according to the following two parallel reactions:

$$2\ e^- + \tfrac{1}{2}\ O_2 + 2\ H^+ \rightarrow H_2O \quad \ldots(A.1)$$

$$2\ Fe^{2+} \rightarrow 2\ Fe^{3+} + 2\ e^- \quad \ldots(A.2)$$

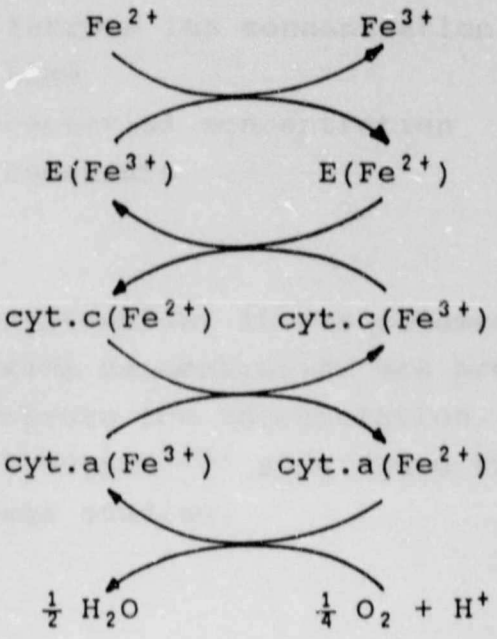
The first reaction was thought to take place within the inner (cytoplasmic) membrane, whereas the second reaction was thought to take place closer to the surroundings, in the periplasmic space or the outer membrane. Ingledew, Cox, Jones and Garland[50] suggested that it is very likely that the sites on bacteria which interacted with the ferrous ions would have to be exposed to the acidic surroundings. This was because spontaneous chemical oxidation of ferrous ions would result if these sites were situated at the high pH inside the cell.

Dugan and Lungren[36] demonstrated that ferrous ions are complexed before being oxidized by bacteria. A complex structure, consisting of some organic complex, the ferrous ion and a bound oxygen molecule was proposed, and can be represented as follows:



It was further suggested that this complex structure is attached to the outside of the cell envelope or dissolved in the growth medium. The complex was shown to enter the cell envelope and attach to the cell wall or membrane. Attached complexes could then be acted on by iron oxidase, an enzyme which causes the release of an electron. It was also suggested that sulphate ions are involved in the initial transfer of electrons between the iron and the cell. The electron could then be transferred to an electron deficient sulphate group which is bound to the cell surface, at a site adjacent to the enzyme. Alternatively the electron could be transferred directly to a flavoprotein. Following the isolation of a quinone of coenzyme Q6 and cytrochrome c from an extract of *Thiobacillus ferrooxidans*, the electron was deduced to be transported by means of a typical electron transport system.

Silver[51] summarized the available literature on metabolic mechanisms in ferrous ion oxidation as shown in the following transport system:



In the scheme, E = an enzyme (i.e. a biological catalyst), and cyt.c and cyt.a are complex biological molecules. This enzyme and these complexes contain iron in a ferrous or ferric state, indicated in the scheme above by the ion in brackets. At each stage in the diagram (represented by the arrows touching) an electron is transferred. During this whole process, ATP, a form of biological energy storage, is produced from the energy liberated by the oxidation of the ferrous ion. Silver also suggested that the oxidation of iron in insoluble sulphide could proceed in the same way as that for dissolved ferrous ions. Blaylock and Nason[52] supplied evidence of the mentioned electron transport system in *Thiobacillus ferrooxidans*.

Lacy and Lawson[53] found, using iron solutions of approximately 9 g/l concentrations, that bacterial oxidation followed Michaelis-Menten kinetics:

$$\frac{d[Fe^{2+}]}{dt} = \frac{-\mu\,[Fe^{2+}]X}{Y(K + [Fe^{2+}])} \qquad \ldots(A.3)$$

where $[Fe^{2+}]$ = ferrous ion concentration
t = time
X = bacterial concentration
μ, Y, K = constants

To obtain this expression, it was assumed that the change in bacterial concentration was proportional to the change in ferrous ion concentration. Schnaitman, Korczynsky and Lundgren[54] also found this type behaviour in their studies.

Jones and Kelly[55] used Michaelis-Menten kinetics (i.e. Equation A.3), and found that under some conditions, bacterial growth rates were inhibited by the ferrous and/or ferric ions. They found that the way in which oxidation was inhibited depended on the previous history of the bacterial cultures used. They suggested that conditions such as pH level and potassium ion concentration might also have influenced the way in which a bacterial culture was inhibited. Such observations serve as an indication of the complexities that could arise when dealing with living organisms.

Ferrous oxidation thus seems to be dependent on the condition and type of bacteria, while the influence of the environment might also be of importance.

A.1.3. DISCUSSION OF SOME OF THE LITERATURE ON IMPORTANCE OF DIRECT AND INDIRECT MECHANISM

Duncan, Landesman and Walden[11] bacterially leached chalcopyrite and pyrite minerals, and used inhibitors to inhibit the sulphide and ferrous oxidation reactions selectively. A cycochrome inhibitor was used to depress the oxidation of ferrous ions and a thiol-binding agent to depress sulphide oxidation.

On using a bacterial strain adapted to and growing on chalcopyrite, Duncan et.al.[11] found that 68 to 74% of the oxygen uptake was due to sulphide oxidation, while 25 to 30% was due to iron oxidation. With the same bacterial strain growing on pyrite, all the oxygen uptake was associated with sulphide oxidation. These, and subsequent observations were made during the first 70 minutes of leaching.

Further, using a bacterial culture which had been adapted to growing on ferrous iron, gave different results. Here 80 to 90% of the oxygen consumption in the first 10 minutes of the leaching of chalcopyrite was found to be due to ferrous oxidation. This initial oxidation was found to be quite fast. (The authors postulated that the bacteria preferentially oxidized the readily available ferrous iron, present at the initial stages.) After this initial period, similar results were obtained as for the chalcopyrite-adapted bacteria.

They also found that ferrous-adapted bacteria oxidized pyrite faster than chalcopyrite bacteria. Here only ±20% of the oxidation was found to be due to sulphide oxidation, with the remainder being due to ferrous oxidation.

It is thought that the following reactions are relevant in analyzing the findings of Duncan et.al.[11], presented above:

$$CuFeS_2 + 4\ O_2 \xrightarrow{B} Cu^{2+} + Fe^{2+} + 2\ SO_4^{2-} \quad \ldots(A.4)$$

$$CuFeS_2 + \tfrac{5}{4}\ O_2 + 5\ H^+ \xrightarrow{B} Cu^{2+} + Fe^{3+} + 2\ S^0 + \tfrac{5}{2}\ H_2O \quad \ldots(A.5)$$

$$Fe^{2+} + \tfrac{1}{4}\ O_2 + H^+ \xrightarrow{B} Fe^{3+} + \tfrac{1}{2}\ H_2O \quad \ldots(A.6)$$

$$S^0 + \tfrac{3}{2}\ O_2 + H_2O \xrightarrow{B} SO_4^{2-} + 2\ H^+ \quad \ldots(A.7)$$

$$CuFeS_2 + 4\ Fe^{3+} \rightarrow Cu^{2+} + 5\ Fe^{2+} + 2\ S^0 \quad \ldots(A.8)$$

$\xrightarrow{B}$ Implies that the reaction is catalysed by bacteria.

Equation A.4 results when the bacteria attack only the sulphide ions of the mineral. Iron is liberated in the ferrous form. In Equation A.5, the ferrous iron of the mineral is shown to be oxidized to ferric iron by the bacteria. Presumably Duncan et.al.[11] referred to equations similar to A.4 and A.5 when writing about ferrous and sulphide oxidation. Equation A.6 shows the oxidation of ferrous ions in solution being catalysed by bacteria, while equation A.7 shows the oxidation of elemental sulphur being catalysed by bacteria. In Equation A.8 the occurence of the indirect, abiotic

leaching of the mineral is shown. Adding multiples of Equations A.6, A.7 and A.8 gives Equation A.4, while adding multiples of Equations A.6 and A.8 gives Equation A.5.

From the discussion above, it could be deduced that leaching of the sulphide as such could have been purely chemical (Equation A.8), with the oxidation of the leaching products (ferrous iron and elemental sulphur) being catalysed by bacteria (Equations A.6 and A.7 respectively). To complicate matters even further, the chemical, abiotic oxidation of ferrous to ferric ions is known to be catalysed significantly in the presence of copper ions. A set of equations similar to Equations A.4 to A.8 can be written for pyrite, and a similar conclusion could be drawn. Furthermore, it is also not known whether these results will hold for more extended leaching periods than the 70 minutes investigated by Duncan et.al.[11]

Beck and Brown[12] deduced from efficiency values (ratio of carbon dioxide fixed as carbon in the bacteria and oxygen absorbed by bacteria) that the indirect mechanism was more important (under the conditions they used). This is because they found that these efficiency values for pyrite and chalcopyrite oxidation (5,5 and 7,0 respectively, in the given units) were closer to that of iron (found to be approximately 2,3) than sulphur (around 21). The same observations mentioned above apply to this work, i.e. is the sulphur oxidized as elemental sulphur or as sulphide ions in the mineral crystal lattice?

Duncan and Walden[13] investigated the effect of the addition of ferric ions (varying between 15 and 50 g/l) in the leaching of chalcopyrite, chalcocite, covellite and marmatitic zinc sulphide (or (Zn Fe)S) in shake flasks. They found that the addition of ferric ions in sterile control experiments (i.e. experiments in the absence of bacteria) increased leaching in all cases except for chalcocite. Here the leaching was not enhanced even though ferrous ions were formed (suggesting that ferric leaching had taken place). Apparently acid leaching of chalcocite (which presumably took place in the test where no ferric ions were added) occurred at a similar rate to ferric leaching (in the test where ferric ions were added).

Further, the addition of ferric ions to inoculated shake flasks (i.e. where bacteria were added) was found to have only little effect on the leaching rates obtained, except in the case of chalcopyrite. Here the copper extraction was only 50% of that in the inoculated flask without added ferric ions. The authors did not offer any explanation for the apparent inhibition of bacterial activity in this case (perhaps a ferric precipitate inhibited bacterial access to the mineral).

The authors also found that in all cases the presence of bacteria increased leaching, except in the case of covellite where leaching in the presence of ferric ion was not affected. They suggested that the chemical ferric leaching of covellite is much faster than its bacterial leaching.

In the above tests, chalcopyrite, chalcocite, covellite and marmatic zinc sulphide were leached for 160, 250,

250, and 130 hours respectively. In chalcocite leaching, the iron concentration in solution was found to be less than 0,5 g/l. From their work, the authors concluded that ferric ions are not a necessary component in bacterial leaching, although it is an active component.

There are two possible ways of analyzing the results of Duncan and Walden[13], presented above. One could accept that the indirect chemical leaching of sulphide minerals is proportional to the ferric ion concentration (as postulated by Corrans[46] for total iron concentrations less than 0,1 molar). It then would seem that ferric ions play a very small role in bacterial leaching. Secondly, it is possible that the chalcocite and covellite used in the tests contained iron impurities. Also, calcopyrite and marmatitic zinc sulphide contain iron. In the leaching process this iron goes into solution, and in the presence of an active bacterial culture, soluble iron will be predominantly in the ferric form. Therefore, if the rate of leaching is a function of the ferric to ferrous ion ratio (as suggested by Dry[9], see Section 2 in the present work) one would have to consider the ferric to ferrous ion ratio. Then the conclusion might be that the ratio of ferric to ferrous ions is of importance in bioleaching, and not the amount of ferric ions as such.

APPENDIX A.2. EXPERIMENTAL DETAILS

In Section A.2.1 details of the preparation and characterization of the Ni_3S_2 mineral used in the work are provided. In Section A.2.2, the preliminary experiments performed in order to decide what aqueous medium to use are presented.

The development of the two bacterial cultures used in this work is discussed in Section A.2.3. Additional details of the experimental procedures followed in tests of Types C and D (see Section 3.5) are provided in Section A.2.4.

In Section A.2.5, the calibration and maintenance of the electrodes in the various types of experiments are described.

A.2.1. NICKEL SULPHIDE PREPARATION AND CHARACTERIZATION

The precipitation of nickel sulphide is discussed in detail in the first section, and details of the melting and recrystallization of the precipitate obtained are given in the second section. Details of the sulphide sizing appear in Section A.2.1.3.

A.2.1.1. PRECIPITATION OF NICKEL SULPHIDE

It was known that dissolved metal species could be precipitated by bubbling hydrogen sulphide gas through a solution containing free nickel ions. The following equilibrium reaction was presumed to take place:

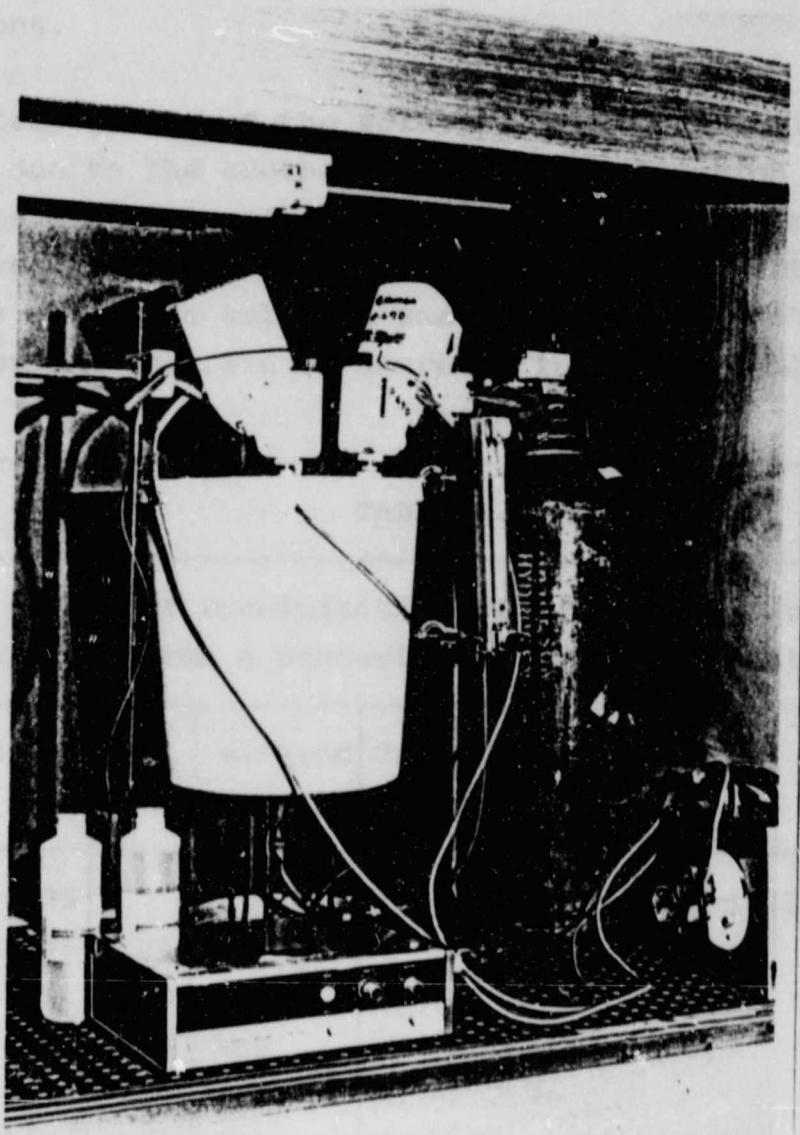
$$Ni^{2+} + H_2S = NiS + 2H^{+} \quad ...(A.9)$$

This reaction results in an increase in acidity, which had to be neutralized. Failure to do this would have resulted in decreasing of the reaction rate according to Le Chatelier's equilibrium principle. A few preliminary tests were carried out on a small scale to establish that Reaction A.9 occurred at a reasonable rate. A sodium hydroxide solution was added to the nickel sulphate solution in order to neutralize acid produced by Reaction A.9. Care had to be taken that the pH did not rise too high, as it was found that the pH continued to increase some time after addition had stopped. Allowing the pH to rise too high would have lead to the precipitation of nickel hydroxide.

Following the successful small scale preliminary precipitation experiments, a large scale precipitation was carried out in a 20 litre container, set up as shown in Figure A.1. The nickel sulphate solution was made up close to saturation, in order to speed up Reaction A.9. Therefore 12 kg of $NiSO_4.7H_2O$ was dissolved in 19,3 litres of deionized water. Hydrogen sulphide gas was metered through a rotameter and introduced into the

FIGURE A.1.

Apparatus Used in the Large Scale Precipitation of Nickel Sulphide from a Concentrated Nickel Sulphate Solution by Bubbling Hydrogen Sulphide Through the Solution.



concentrated nickel sulphate solution via a sintered glass disk, used to disperse the gas. Two stirrers were employed to ensure adequate mixing in the system, one stirring just above the sintered glass disk and the other in the bulk of the solution. The pH level was monitored with a pH meter, the pH being corrected at intervals with a very concentrated sodium hydroxide solution (800 g/l was used in order to minimize dilution of the nickel sulphate solution). The complete apparatus was set up in a fume cupboard for obvious reasons.

The temperature of the solution was found to increase to 55°C due to the exothermic nature of Reaction A.9. The course of the precipitation is presented in Table A.2. The reaction was considered to be complete after four hours, when the solution was seen to have lost its green colour and the rate of decrease in pH level slowed.

TABLE A.2.

Time Course of Precipitation of NiS by Bubbling Hydrogen Sulphide Through a Concentrated Nickel Sulphate Solution

Time	T °C	pH	ml NaOH 800 g/l	Comments
07h30	25			Fill reactor with 18 l solution
08h00	25	2,28	100	
08h05		2,88	-	
08h10		2,50	100	pH increases to 2,7
08h15		2,50	200	pH -> 2,76
08h26		2,50	100	pH -> 6,22 (has NaOH absorbed
08h35		5,57	-	onto probe? Ensure that future
08h45		2,50	200	additions mix before contact.)
08h55		1,34	200	pH -> 1,50

TABLE A.2. (Continued...)

Time Course of Precipitation of NiS by Bubbling Hydrogen Sulphide Through a Concentrated Nickel Sulphate Solution

Time	T °C	pH	ml NaOH 800 g/l	Comments
09h00		1,50	200	pH -> 1,78
09h08	44	1,69	200	pH -> 2,20
09h20		1,82	200	pH -> 1,85
09h30	48	1,75	200	pH -> 2,20
09h40	50	1,80	200	pH -> 1,98
09h50		1,85	100	Reactor full. Remove 2 l slurry
10h00		1,63	200	pH -> 1,82
10h10	50	1,63	200	pH -> 1,80
10h20		1,63	200	pH -> 1,80
10h30		1,63	200	pH -> 1,79
10h40		1,62	200	pH -> 1,77
10h50		1,63	200	pH -> 1,80
11h00	55	1,67	200	pH -> 1,82
11h15		1,74	100	pH -> 1,82 Reaction seems to be complete (solution colourless). Remove 4 l solution, add 1,3 l of remaining $NiSO_4$ solution and the 2l solution removed at 09h50.
11h30	50	1,64	200	pH -> 1,81
11h40		1,66	300	pH -> 2,10
12h00		1,88	-	Stop

Mass of $NiSO_4.7H_2O$: 12 kg
Volume of Solution: 19,3 l (initially)
Mass of precipitate: 3 940g
Analysis of precipitate: Ni : 64 mass %, S : 34 mass %

The precipitate was dried in a bottle placed in an oven at 70°C, with nitrogen gas being passed into the bottle to limit sulphide oxidation and to remove water vapour. The solid was found to contain 34% sulphur and 64% nickel, i.e. pure NiS as far as experimental analysis could ascertain. Approximately four kilograms of precipitate was recovered, i.e. close to 100% recovery was obtained. This precipitate was found to be very fine, and therefore unsuitable for leaching experiments. Consequently it had to be converted to a more crystalline form. This was achieved by melting the precipitate and recrystallizing it.

A.2.1.2. MELTING AND RECRYSTALLIZATION OF NICKEL SULPHIDE

Initial investigations were performed in an induction furnace, under an argon atmosphere, using the sulphide samples that were obtained in the small scale precipitation tests. It was found that sulphur was rapidly driven off in the initial stages of melting. This lead to the recrystallization of a more sulphur deficient nickel sulphide than NiS. Mineralogical examination showed that at least two phases were present. This was unacceptable as a single pure phase was required.

With the help of the High Temperature Mineralogy Work Group at Mintek, a series of more controlled melting tests were performed. This was done to try and obtain an initial estimate of the conditions required in an induction furnace to produce a single pure nickel sulphide phase on recrystallization. These tests were performed in a silicon carbide furnace, using alumina

crucibles. Temperatures varied from as low as 700°C (using a NaCl:KCl flux) to 1300°C, and for times varying from 1 hour to 3 days.

The purpose of using a flux was to allow fusion to take place at a lower temperature than the melting temperature of the sulphide. It was hoped that sulphur loss would be minimized to such an extent as to obtain stoichiometric NiS. Some fusion did accur in the presence of the flux, but the mineral still had a granular appearance. Also, regardless of the lower temperatures, sulphur was driven off, so that apparently there was no advantage in using a flux. Another way which is commonly used to overcome the loss of sulphur, is to seal the melting system so that no sulphur gas can escape. For melting on such a large scale, however, no vessel was readily obtainable to be able to withstand the high sulphur pressures at the melting temperature of the sulphide.

Some of the samples in the above tests were quenched in water, but most were cooled slowly. Results of these tests are tabulated in Table A.3. Mostly mixtures of Ni_7S_6 and Ni_3S_2 were formed, but in two cases only Ni_3S_2 was formed and in another two cases mixtures of Ni_3S_2 and Ni metal were obtained.

The results indicated that with increasing time spent in the molten state, and with increasing temperature, more sulphur was driven off from the system. Thus it was shown that a pure mineral (Ni_3S_2) could indeed be formed, provided that the correct temperature and corresponding time in the molten state could be found, so that the correct amount of sulphur could be driven

off. It was only after this fact had been established that a decision was made to proceed with the large scale precipitation and recrystallization of the nickel sulphide.

TABLE A.3.

Recrystallization of NiS on Small Scale in Alumina Crucibles. All Tests Were Performed Under an Argon Atmosphere.

Run	Temp °C	Time hrs	Procedure	Results	
1.*	700	48	Cooled slowly.	No melting.	Ni_3S_2+Ni_7S_6
2.	1 000	1	Quenched.	Melted.	Ni_3S_2+Ni_7S_6
3.	1 000	15	Quenched.	Melted.	Ni_3S_2+Ni_7S_6
4a.	1 000	1	Quenched. Crushed under acetone for use in 4b.	Melted.	Ni_3S_2+Ni_7S_6
4b.*	700	72	Cooled slowly.	No melting.	Ni_3S_2+Ni_7S_6
5a.	1 000	24	Cooled slowly. Crushed under acetone for use in 5b.	Melted.	Ni_3S_2+Ni_7S_6
5b.	1 000	24	Cooled slowly.	Melted.	Ni_3S_2
6.	1 300	5	Cooled slowly.	Melted.	Ni + Ni_3S_2
7.	1 300	1	Cooled slowly.	Melted.	Ni + Ni_3S_2
8a.	1 200	1	Cooled slowly. Crushed under acetone for use in 8b.	Melted.	Ni_3S_2+Ni_7S_6
8b.	1 200	1	Cooled slowly.	Melted.	Ni_3S_2

* : implies that a NaCl:KCl flux has been used

The four kilogram precipitated powder sample was melted down in one kilogram batches at 1200°C, each for one hour. This took place in a fire clay crucible placed in an induction furnace purged with argon gas. Typical time course data is given in Table A.4:

TABLE A.4.

Recrystallization of 1 kg Batch of NiS Precipitate in an Induction Furnace Under an Argon Atmosphere.

Time	Temp (°C)	MF Power (kW)	Ar Rotameter	Comments
08h45	25	10	0	Commence
09h15	365	15	20	
09h45	960	15	20	Vapour emission
10h15	1 200	8	20	''
10h20	1 208	7,5	20	''
10h30	1 185	15	20	''
10h35	1 209	8	20	''
10h45	1 199	8	20	''
11h00	1 204	8	20	''
11h15	1 202	0	20	''
11h30	1 092	0	20	'' diminishes
12h03	887	0	20	
14h00	490	0	20	
15h00	305	0	0	Open furnace

Mass of powder in crucible : 1 000,00 g
Mass of recrystallized solid : 899,39 g

The resulting sulphide lost about 10% mass, from which a stoichiometry of $Ni_3S_{2,15}$ could be deduced. As expected, the sample was a mixture of Ni_7S_6 and Ni_3S_2.

The recrystallized samples were then combined, and remelted three times at 1200°C for times varying from half an hour to one hour, but in each case the mass loss was less than 0,5%, so that Ni_7S_6/Ni_3S_2 mixtures were obtained. The solid was then split into two parts with the one part melted for one hour, and the other for two hours at 1400°C. Mass loss of 1,8% and 2,4% was found respectively. Examination of a polished section showed that approximately 10% Ni_7S_6 remained. The samples were combined and melted for two hours at 1450°C. During this run the crucible broke and approximately 40% of the solid was lost. The remaining solid was slightly tarnished, but it was found that the tarnish could be removed with sulphuric acid. Polished section showed the sample to be very pure (approximately 99% Ni_3S_2).

The solid was crushed, leached in sulphuric acid to remove the tarnish, and re-melted by allowing the temperature to go up to 1 350 degrees, before cooling again. The end product was found to be almost pure Ni_3S_2. The X-ray diffraction pattern obtained was typical of alpha-Ni_3S_2.

Thus a solid suitable for the purposes of this project was obtained. The solid then had to be prepared and characterized for the leaching tests. The density of the Ni_3S_2 was found to be 5,94(±0,04) g/ml by measuring the volumes displaced by, and the mass of, four samples of the mineral (as chunks of crystallized material).

A.2.1.3. SIZING OF NICKEL SULPHIDE

The block of recrystallized mineral was broken up in largish chunks, and then pulverized for one minute in a vibratory mill. Sizing was initially performed by dry screening of a 40 g representative sample. The masses of solid in the various size fractions were measured periodically over two hours. Little material was found to be larger than 212 microns. Basic experimental data are given in Tables A.5 and A.6. The results are presented in Figure A.2, which shows that the screening was more or less complete after two hours had elapsed.

TABLE A.5.

Screening Masses of Pulverized Nickel Sulphide Recorded in Various Size Fractions with time.

Time (min.)	< 38 Microns	38 -> 45 Microns	45 -> 53 Microns	53 -> 75 Microns	75 -> 106 Microns
20	11,41	2,67	6,58	7,13	4,60
30	12,99	1,89	7,42	5,84	4,62
40	15,40	2,30	5,16	5,39	4,62
60	17,10	3,35	2,88	5,02	4,62
90	17,77	3,61	2,28	4,96	4,62
120	18,10	3,57	2,12	4,05	4,54