SULPHIDISATION OF NICKEL OLIVINE AND AMMONIACAL LEACHING OF VAESITE (NiS_2)

by

ALFONSO BONILLA BONILLA

Chemical Engineer S. T. S. I. I. Madrid

A Thesis submitted for the degree of Doctor of Philosophy of the University of London and for the Diploma of Imperial College

November 1977

Dedicated to my parents

ABSTRACT

Two 'nickel olivine' compounds were synthesized, the first one containing a relatively large percentage of nickel oxide and the second consisting of almost pure nickel ortho-silicate containing small amount of α-Cristobalite as was shown by x-ray diffraction. The nickel contained in this second compound was determined gravimetrically.

The 'nickel olivine' compounds were submitted to a hydrothermal treatment using sulphur as a reactant and high air pressures and temperatures. Vaesite and a minor amount of nickel sulphate were identified as the products of the treatment. The temperature was found to have the strongest effect on the conversion of Ni_2SiO_4 to NiS_2 and $NiSO_4$ which was also affected by the amount of sulphur used and the time of reaction but to a lesser degree.

Vaesite was synthesized from nickel and sulphur. The x-ray diffraction pattern obtained for the synthetic nickel sulphide coincided with that given in A. S. T. M. 11-99 for vaesite. The composition was determined by gravimetric analysis as 47.5 wt % Ni and 52.5 wt % S.

The sulphide was oxidized in ammonia-ammonium sulphate solution using air under pressure as the oxidant. The mass transfer effects became very important at the temperature used. However, working at constant stirring speed throughout the experiments and using dilute solid concentration, it was found that NiS_2 dissolved in two stages. The apparent activation energy for the first stage indicated that the reaction rate was controlled by a mixed regime in which a surface chemical reaction, probably the oxidation of vaesite by air, had the main role. Nickel was probably leached faster than sulphur during

the fir st stage of leaching and a film was formed on the surface of the par ticles which had a great importance on the second stage of leaching. The nature of such film could not be clearly established.

Hydrolysis of the nickel hexa-ammine was found to occur at the temperature of the experiments. However the hydrolysis reaction was prevented by the addition of $(NH_4)_2SO_4$ the main role of which was to stabilize the complex.

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INTRODUCTION

The two main sources of Nickel in the world are the nickel sulphide ores and the nickel laterite ores. Although most of the actual production of nickel comes from nickel sulphide ores; the nickel laterites are becoming more and more important as a raw material for the production of nickel, according to some estimates[1], probably within the next decade, about 50 per cent of total nickel production will be obtained by processing such ores.

This thesis represents a new approach to the treatment of nickel laterite ores, although both nickel sulphide ores and nickel laterite could eventually be treated by the method which is proposed.

Nickel oxide ores, or nickel laterite, have been traditionally treated by pyrometallurgical methods, smelting to matte and smelting to ferronickel[2, 3, 4, 5, 6, 7, 8]. Hydrometallurgical methods are also being used, but these normally involve either a previous pyrometallurgical treatment in order to make the ore suitable for a selective leaching or a non selective leaching of the crude ore which will produce a leach liquor which needs to be purified subsequently.

The present approach for the treatment of the laterites ores proposes the use of a completely hydrometallurgical process which would be selective enough to avoid the need for a complicated process of purification after the leaching.

The mineralogy of the nickel laterite ores is complicated; an ore varies widely in composition so that more than one nickel bearing mineral is usually present and there may be four, five or six minerals making up the ore; so in order to avoid the complication that the presence

of so many minerals in the ore might have in an academic study, a synthetic mineral was used; this was nickel orthosilicate (Ni_2SiO_4) or nickel olivine.

The nickel olivine was synthesized and used as a model for the nickel silicates which form part of the nickel laterite ores. The nickel olivine was submitted to a hydrothermal treatment in the presence of sulphur. The thermodynamics of the process have been studied and are presented in the form of pH-E diagram for 200°C which indicates which of the stable species could be expected after the hydrothermal treatment.

The products of the hydrothermal treatment have been analysed qualitatively and quantitatively and the effects of the different variables in the conversion of Ni_2SiO_4 were also studied.

The second part of the thesis deals with the kinetic studies of the ammoniacal leaching of vaesite (NiS_2) which was shown to be the main solid compound obtained in the previous hydrothermal treatment of nickel olivine. However the NiS_2 used was synthesized from the pure elements to prevent any impurity effects that the use of NiS_2 produced by the hydrothermal treatment of Ni_2SiO_4 might have. The thermodynamics of the process have also been studied and presented as pH-E diagrams for 25°C which will show the areas of stability of nickel ammino-complexes and also in the form of $(NH_3) + (NH_4^+)$ versus pH diagrams for different $Ni(NH_3)_6^{++}$ concentrations and for different temperatures. The effect of the different variables in the rate of leaching has also been studied.

CHAPTER 1

LITERATURE SURVEY

1.1 HYDROMETALLURGY OF NICKEL OXIDE ORES

1.1.1 Leaching of Nickel Laterite Ores Submitted to a Previous Pyrometallurgical Treatment

The nickel oxide ores have the disadvantage that they cannot be submitted to a well established beneficiating technique such as flotation or magnetic separation due to the manner in which their nickel content is chemically disseminated. In a particular case screening might be used in order to reject the oversize which contains mainly less weathered fragments containing less nickel.

The nickel laterite ores have been, and still are, the subject of long studies by metallurgists very recently. Several reviews relating to the treatment and research going on in nickel laterite ores have been published[9, 10, 11, 12, 13, 14, 14, 16].

The nickel laterite ores can be submitted to the following pyrometallurgical treatments in order to make them suitable for a selective leaching: sulphation roast, reduction roast, segregation, chloridization roast.

Sulphation roast consists mainly of heating up the nickel laterite ores at 650°C to 750°C in the presence of either sulphur dioxide or sulphur trioxide and air which will make the ore suitable to water leaching.

Canterford[11] mentioned that the temperature of roasting should be carefully controlled in order to get a pregnant leach liquor almost totally free of iron.

Shunji et al[17] studied the selective sulphating roasting of nickel followed by water leaching in three different samples of a Philippine lateritic ore, they concluded that the NiO type of minerals in the ore will react as follows:-

$$NiO + SO_3 = NiSO_4$$

Other coexisting metallic oxides form sulphates simultaneously as follows:-

$$MeO + SO_3 = MSO_4$$

where Me = Fe, Al, Cr, Co, Mg, etc.

They pointed out that these reactions do not continue to unlimitedly high temperatures, and once a certain temperature is reached the reaction proceeds towards decomposition of the sulphate; they said that, in general, nickel is a little less readily converted to sulphate than iron which is present in greater quantity in the sample, but once formed nickel sulphate is more stable than iron sulphate at high temperature. Nevertheless if $NiSO_4$ coexists with Fe_2O_3, it is reported to decompose at lower temperature than pure $NiSO_4$, reaction being as follows:-

$$NiSO_4 + Fe_2O_3 \rightleftharpoons NiO.Fe_2O_3 + SO_3$$

The optimum temperature of roasting depends, of course, on the ore which is being treated, but they select $600 \pm 50^{o}C$ and $550 \pm 50^{o}C$ for two different ores. They also analysed the effects that the oxygen content and the SO_2 content in the roaster gas mixture have on the extraction. They found that the higher the oxygen and SO_2 content in the gas mixture the higher will be the nickel extraction in the water leach step.

Bainbridge[18] has studied the sulphation of nickeliferous laterites from Oregon and he has also pointed out the importance of the temperature. Generally these particular ores can be rapidly sulphated at temperatures

near 700°C with a partial pressure of sulphur trioxide near 0.2 atm. The sulphation rate falls off rapidly at temperatures above 750°C, but on the other hand, sulphation of iron can be kept to a low value at temperatures above 750°C, so he proposed a two-step process in which the Ni, Co and Fe are sulphated at temperatures near 700°C with 0.2 atmp. sulphur trioxide followed by rapid desulphation of iron at temperature near 780°C with 0.1 atm of sulphur trioxide.

Canterford[11] has studied the effect that some additives, such as chlorides and sulphates of sodium and potassium will have in promoting the sulphation reaction; he got the following results for nickel per cent extraction in the water leach process depending on the conditions of the sulphation roast process:-

	Ni	Mg	Fe
No addition	44.1	66.8	0.7
55% NaCl (w/w)	84.0	63.6	7.4

The atmosphere during cooling also has a large influence on the percent of extraction.

Sample cooled to 500°C	Ni	Mg	Fe
in SO_2/air	71.8	98.1	1.0
SO_2/air replaced by N_2 at 750°C	9.5	66.3	0

Another of the pyrometallurgical treatments that nickel laterite ore can be submitted to is reduction roasting.

The reduced ore can be leached either by ammoniacal leaching or by acid leaching.

The reduction roast followed by ammonia-ammonium carbonate leaching has been the subject of studies by hydrometallurgists since very early times. Caron studied it and the process was patented in the 1920's. The process was used in a large scale commercial operation at Nicaro (Cuba) in 1944 and it has been widely described[3, 9, 10, 11, 13, 22]. At the Nicaro plant the wet ore containing about 30 per cent moisture is first crushed, dried, milled to pass 100 mesh, and reductively roasted in multiple hearth furnace at 750°C for 90 minutes making the nickel amenable to ammoniacal leaching. Reduction is carried out using producer gas from the burning of anthracite coal. Combustion is carried out at about 50 per cent of theoretical air requirements to maintain a strongly reducing atmosphere. Hydrogen to water vapour, and carbon monoxide to carbon dioxide ratios have to be kept at 1:1. Heating of the ore is done at a fairly low rate to permit substantial reduction of nickel oxide to metal before the temperature reaches 750°C. At this temperature in a reducing atmosphere the serpentine fraction of the ore, $(Mg, Fe, Ni)_6 Si_4O_{10}(OH)_8$, undergoes an exothermic phase transformation to olivine $(Mg, Fe)_2SiO_4$. Any Nickel which has not been reduced will combine with the olivine and this is more difficult to reduce. On the other hand, it is essential that the ore be heated to, at least, 760°C in order to limit the amount of soluble magnesia in the product going to the leaching circuit.

The reduction reactions are as follows:

$$NiO + H_2 = Ni + H_2O$$

$$3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O$$

However, as much of the nickel in the ore is in solid solution with the iron-containing minerals, the end product of the reduction contains nickel as an iron-nickel alloy.

The reduced ore is cooled in an oxygen-free atmosphere, and leached counter currently with ammonia-ammonium carbonate solution using air as oxidant. The reaction is idealized in the following equation

$$FeNi + O_2 + 8NH_3 + 3CO_2 + H_2O = Ni(NH_3)_6^{++} + Fe^{2+} + 2NH_4^+ + 3CO_3^-$$

Ferrous iron is further oxidized to the ferric state and comes out of solution as a gelatinous precipitate that largely deposits on ore particles.

$$4Fe^{2+} + O_2 + 2H_2O + 8OH^- = 4Fe(OH)_3$$

After thickening and filtering the pregnant solution is steam heated to remove ammonia. During this process the nickel and cobalt are precipitated as basic carbonates according with the following reaction:

$$5Ni(NH_3)_6CO_3 = Ni(NH_3)_2CO_3 + 4NH_3$$

$$Ni(NH_3)_2CO_3 + 3H_2O = 3Ni(OH)_2 2NiCO_3 + 3CO_2 + 10NH_3$$

After filtration, the filter cake is dried and calcined

$$3Ni(OH)_2 2NiCO_3 = 5NiO + 3H_2O + 2CO_2$$

the nickel oxide calcine so formed is then sintered.

The final produce contained a considerable amount of cobalt and therefore could not meet various nickel alloy specifications, and in addition the overall cobalt recovery is low (50 to 60 per cent).

The reduction roast forms the pyrometallurgical precursor of other proposed leaching processes; the condition of the reduction roast has to be such that there is a maximum reduction of nickel and cobalt oxides and minimum formation of metallic iron.

The two points mentioned before (cobalt problem, maximum yield in roasting process) have been the subject of particular attention lately.

In 1976 Sherrit Gordon Mines Limited[23] patented a process which deals with the two points which have been mentioned earlier. In order to get the minimum reduction of iron to the metallic form, the water content of the reducing atmosphere should be kept at a level such that the water to hydrogen molar ratio should be of 0.4 to 0.5 and the retention time in the furnace would be less than 60 minutes; in most cases, from 5 to 45 minutes. The problem of the cobalt is solved including a new step after the ammonia ammonium carbonate leaching in the Nicaro process. In this step, cobalt in the leach solution is precipitated together with up to 1.5 moles of nickel per mole of cobalt by contacting the solution with a sulphidizing agent such as H_2S, $(NH_4)_2S$, Na_2S, NaHS; $(NH_4)_2S$ is preferred. In order to get a nickel to cobalt ratio greater than 1000:1 in the solution, the sulphide ion to cobalt molar ratio must be 3.5 to 4.5. The precipitation reaction is reported to be very rapid and is terminated in 5 to 10 minutes. In order to get good results the temperature of reaction has to be maintained below $40^{\circ}C$ and preferably at room temperature. The free ammonia is also important because if in excess of 100 grms per grm of cobalt or if it is less than 60 grms per gram of cobalt in solution it contributes to the formation of colloidal precipitates and complete removal of cobalt is prevented.

According to another patent[24] the extraction of cobalt from the reduced ore is substantially increased by controlling the initial cobalt content of the solution supplies to the leaching operation below 0.2 g.p.l by selectively removing cobalt from solution, using the method mentioned in the previous patent (Cobalt precipitation with H_2S), recycled to the leaching step to build up the nickel content of the solution to a desirable level, usually 10-15 g.p.l. Four different flow schemes of the process

are proposed in which the cobalt removal step is included, the use of one or another will depend on the various economic and operational factors relevant to the particular installation. The removal of the rest of the impurities is normally done after the precipitation of nickel carbonate which could be releached in ammonia-ammonium carbonate solution again; but the conditions of the leach are such that most of the nickel is removed without leaching Zn, Fe, Si and Mg. A similar process to the one described in the two patents mentioned is being used at the Townsville[25] plant of Queensland Nickel in Australia, and has been proposed by Sherrit Gordon for the Maurindique plant in the Philippines.

Brown and Mackin[26] and Shea et al[27] solved the problem of cobalt contamination in the Nicaro process by re-leaching the precipitate of nickel carbonate with ammonium carbonate and ammonium sulphate respectively and precipitating the cobalt as sulphide.

Considering the other point mentioned earlier in order to produce the maximum amount of nickel metal and the minimum amount of metallic iron in the reduction roast process, careful atmosphere and temperature control are necessary. However, it has been found that the optimum temperature, retention time, and composition of reductant often vary over a wide range, and it is not possible to operate under the same set of conditions for all the ores. In this respect, the effect that the addition of some compounds, such as sulphur compounds, halides or NaCl, will have in the maximum production of nickel metal with the minimum production of iron metal in the reduction roast process, has been analysed by various authors. They agreed that the addition of sulphur compounds, such as pyrite[22, 28, 29] will improve the extraction of nickel and diminish the extraction of iron. Siemens et al[31] studied the reduction of nickel laterites previous to leaching with ammonia-ammonium sulphate solutions.

They found that for their particular ore and for a 300 grm charge, optimum extraction was achieved after 40 minutes reduction, 600 ml per minute flow of carbon monoxide and a temperature range 350°C to 600°C. Like previous workers[32] they also found that nickel extraction can be significantly improved by addition of pyrite. They thought that if the ore has a magnesia content sufficiently high at a given reduction temperature, reduced nickel may be involved in a secondary reaction with magnesium and silicon which renders it inert in the subsequent leach. The sulphur from pyrite apparently impedes this secondary reaction. Illis A. et al[33] studied the roasting and selective reduction of some nickel-bearing pyrrhotites. During the roasting the nickel is converted to a nickeliferous iron oxide, mostly ferrite $NiFe_2O_4$, which is not suitable for ammoniacal leaching and has to be reduced; the reduction is done at 700°C to 870°C and by providing an atmosphere with CO_2:CO ratio 2:1, under these conditions the nickel ore will be reduced to a form suitable for ammoniacal leaching. Stevens et al[30] reported on the beneficial effects of the addition of small quantities of halide to the ore during reduction roast. Luper and Boingiu[34] found that adding one per cent NaCl to a low grade Rumanian serpentine ore, before reduction, gave the best nickel recovery (60 per cent). Shimakege et al[35-36] studied the reduction roast of nickel laterites with different reducing gas previously to ammonia pressure leaching. As in previous works they found that the recovery of nickel is mainly affected by the roasting time, temperature and flow rate. They used H_2, H_2-H_2O, CO, Co-CO_2 as reducing gases, and they pointed out that the reducing power of the gases used was in the order of: H_2 > CO > CO:CO_2(2:1) > H_2 - H_2O(3:7) > CO - CO_2 (1:1) > CO - CO_2(1:2) at the rate beyond the critical flow rate. They found that, for the particular ores that they were studying satisfactory reduction of the ores prior to pressure leaching could be obtained by roasting at 900°C for two hours under a flow of CO gas at the rate of 200 cc/min.

The Manganiferous Sea Nodules are in many ways similar to nickel laterite ores so it is not strange that similar techniques are being applied to extract the valuable metals from this raw material. Brooks P. et al[37-38] proposed a reduction roast followed by ammonia-ammonium carbonate leaching to extract Ni, Co, Mn, Cu from sea nodules. They achieved good extractability of manganese, nickel and cobalt by roasting for 80 minutes at 600°C using rich gas reductant, containing 8 per cent each of H_2 and CO, with the remainder N_2 and CO_2. Han K. N.[39] also studied the reduction roast and ammonia-ammonium leaching of deep-sea manganese nodules, they pointed out that because of the different mineralogy and geochemistry of the different nodules the recovery of the metals is very much dependent on the nodule being processed; this point is also very much emphasized in the recovery of metals from nickel laterite[31] ores. They concluded that the reduction step is very important but the adjustment of the different variables (temperature, composition of reduced atmosphere etc.) in this step in order to get the maximum yield is very much dependent on the characteristics of the nodules, but generally, they considered that a lower reduction temperature is required to obtain the same recoveries of Ni, Cu and Co from some manganese nodules in an ammonia-ammonium sulphate leach than is required in the ammonia-ammonium carbonate case.

Two processes to extract valuable metals from manganese nodules using reduction-roast and ammonia leaching have been patented[40-41].

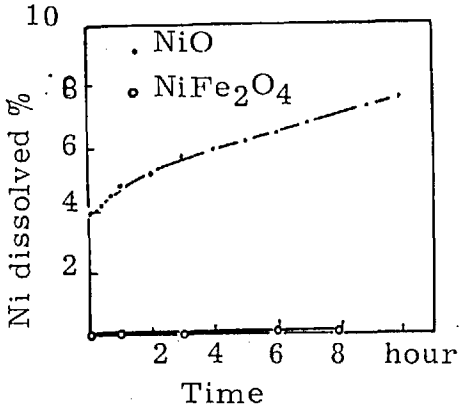
So far this discussion has been concerned with the reduction step in the processes involving reduction-roast ammonia leaching of nickel laterite ores. Several studies have been done on the ammonia ammonium carbonate leaching and ammonia ammonium sulphate leaching of a previously reduced nickel laterite.

Caron[19, 20, 21, 22] recommended that commercial leach liquors should have a reasonable amount of NH_3 (4 to 4.5 percent) and CO_2 in excess to keep the liquor sufficiently active. He also pointed out that very little nickel can be dissolved in pure ammonia solution free from CO_2. He further reported that free nickel oxide would be leached more easily than oxides combined with silica as water-free silicates. However, the nickel oxides in hydrated silicates could be extracted after reduction more easily than reduced water-free silicates. Shimakege et al[35] seem to agree with Caron where they reported that nickelferrite did not dissolve in ammonia solution under the conditions of pressure leaching (Fig. 1). The reason for this particular behaviour can be explained by a thermodynamic analysis of the process[39, 42]. Han K.N. et al[39] show the relative thermal stability of ionic species, metal oxides and metal ammoniun

Fig. 1 Solubility of nickelferrite and nickel oxide in ammonium solution.

Dissolution condition:

NH_3	3 mol/l
$(NH_4)_2SO_4$	1 mol/l
O_2 partial pressure	2 atm
Temperature	100°C
Stirring	500 rpm



complex in the form of Eh-pH diagrams (Fig. 2). They expressed the dissolution of divalent metal oxide MeO as follows.

$$MeO + nNH_4^+ = Me(NH_3)_n^{2+} + H_2O + (m-z)H^+$$

for the particular case of nickel they write the probable dissolution reaction and free energy in $Kcal_{/mol}$ as follows:

		ΔG° $Kcal_{/mol}$
(1.1)	$Ni + \frac{1}{2}O_2 + 4NH_3\ 2NH_4^+ = Ni(NH_3)_6^{2+} + H_2O$	-54.53
(1.2)	$NiO + 4NH_3 + 2NH_4^+ = Ni(NH_3)_6^{2+} + H_2O$	- 3.23
(1.3)	$Ni_3O_4 + 10NH_3 + 8NH_4 = 3Ni(NH_3)_6^{2+} + 3H_2O + \frac{1}{2}O_2$	+31.38

It can be seen that, in general, reactions which do not require oxidation have smaller values of the standard free energy of reaction than those which require oxidation; this implies that reactions involving oxidation are more favourable. The dissolution of Ni and NiO (reactions 1.1 and 1.2) is possible while that of Ni_3O_4 (reaction 1.3) requires a previous reduction under these conditions. Therefore to achieve thermodynamically favourable conditions, nickel oxides with higher oxidation states must be reduced to a lower oxidation state. Similar thermodynamic studies could be done for copper and cobalt and conclusions very much the same as that for nickel are reached. On the other hand, manganese and iron do not form stable ammonia complexes as observed in the Eh-pH diagrams. In other words thermodynamics favour manganese and iron to form the corresponding hydroxides or oxides in an ammonium solution under particular conditions. Therefore, it is possible to extract nickel, copper and cobalt preferentially over manganese and iron in an ammonia solution.

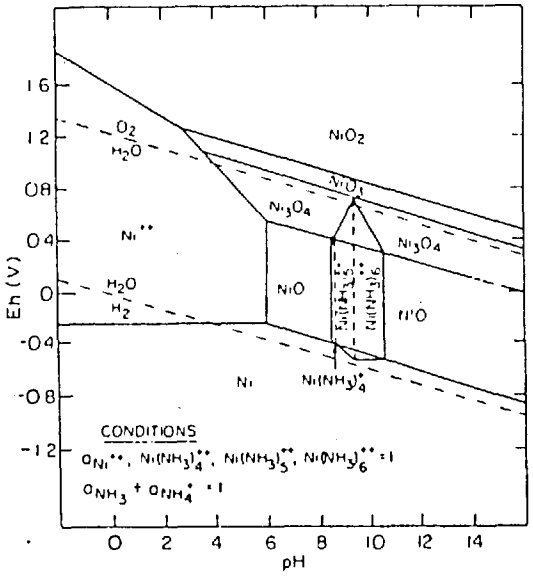


Fig. 2

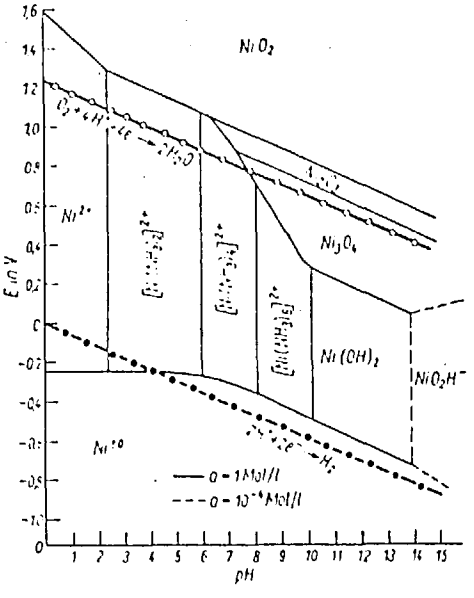


Fig. 3

Fig. 2 pH-Eh diagram showing the stable domain of nickel ammonium complexes calculated for an activity of all ionic species being unity - Temperature 25°C.

Fig. 3 pH-Eh diagram for the system $Ni/H_2O/NH_3$ activity of all ionic species being unity - Temperature 25°C.

However, although thermodynamic considerations show that it is possible to dissolve some ixides, such as NiO (reaction 1.2), the dissolution rate of Cu, Ni and Co oxides is, in general, very slow. Therefore, it is almost always necessary to reduce the oxides to metal to enhance the rate of dissolution. Schroder et al[42] gave another version of the Eh-pH diagram for the Ni-NH_3-H_2O system (Fig. 3). The diagram was drawn for ionic species activities of 1 mol/l and temperature of 25°C . They found that when NH_3 and NH_4^+ are absent, nickel (II) hydroxide appears at a pH value of 6. However when they are present, the formation of $Ni(OH)_2$ begins at a pH value of 10. They found that in order to keep the nickel in solution, the pH value must be below 10, and the solution must remain stable. Therefore, to maintain a 10M NH_3 solution at a pH value below 10 a salt must be added to form a buffer solution, such a salt could be $(NH_4)_2CO_3$ or $(NH_4)_2SO_4$. As can be seen in the Eh-pH diagram the formation of the simplest ammine complexes $Ni(NH_3)_2^{2+}$ began as low as pH = 2.5. However for pH = 8 to pH = 9 which are the most normal values for buffered solutions hexa-ammine complex seems to be the stable species. Ono and Matrushima[43] carried out experimental work to estimate the solubility of nickel in NH_3 solution, $(NH_4)_2CO_3$ solution and ammonia-ammonium carbonate solution. In the last case, solution of nickel in ammonia-ammonium carbonate, the authors concluded that the presence of CO_3^{2-} ions reduces the solubility of nickel ammines in the solution and that the solubility decreases with increase in CO_3^{2-} ion concentration. They also found that a reduction in NH_4^+ ion concentration also results in a lower solubility of nickel in solution. Illis et al[33] studied the ammonia-ammonium carbonate leaching of reducing nickel laterites; they reported that at a redox potential of about -500 mv the nickel and iron dissolve in solution (6-8 per cent NH_3 and 3-4 per cent CO_2) as Ni^{++} and Fe^{++} ions with the nickel rapidly forming a hexamine complex $Ni(NH_3)_6^{++}$ and the iron a ferrous ammonium carbonate complex $FeCO_3(NH_4)_2CO_3$. In the subsequent stages the redox potential is

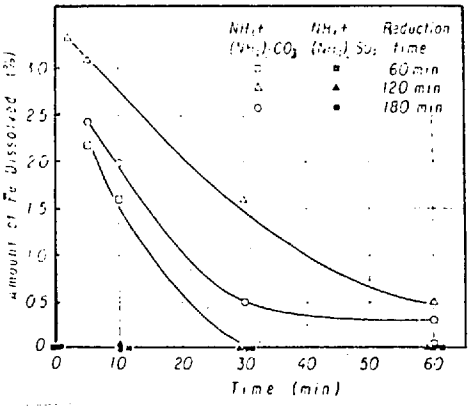
permitted to increase to about minus 150 mv which is sufficient to oxidize any sulphide form, if present, and convert the soluble ferrous carbonate to insoluble ferric hydroxide. Shimakege et al[35] used quite high temperature (100°C) and quite low stirring speed (500 rpm) when they leached with ammonia some reducing nickelferrites; under these conditions the use of a salt, such as $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$, is required for efficient extraction of nickel by way of preventing hydrolysis. They selected $(NH_4)_2SO_4$ because it has the additional advantage of keeping the leach solution without any iron (Fig. 4).

Fig. 4 Extraction and precipitation of iron from nickelferrite reduced to various extent in NH_3+ $(NH_4)_2SO_4$ and NH_3 + $(NH_4)_2CO_3$ solutions.

Reduction: H_2 gas, 100 cc/min, 700°C

Extraction:

NH_3	3 mol/l
$(NH_4)_2SO_4$ or $(NH_4)_2CO_3$	1 mol/l
O_2 partial pressure	2 atm
temperature	100°C
stirring	500 rpm



Shimakege et al[36] selected the following condition of leaching a previously reducing laterite ore in order to get maximum yield: temperature 100°C, oxygen partial pressure 2 atms, stirring speed 500 rpm, NH_3 concentration 3 mol/l, ammonium sulphate concentration 1 mol/l. Brooks et al[38] studied the ammonia-ammonium carbonate leaching of reduced manganese nodules. They found[38] that a solution nearly saturated with both ammonia and carbon dioxide but free of oxygen will dissolve manganous oxide as well as suitable iron from reductively roasted ore, whereas a weaker solution, such as they used to extract only

nickel and cobalt, is not effective. They also found that oxidation during leaching, accomplished by admitting air to the leach cell was necessary for maximum extraction of cobalt and nickel, whereas oxidation depressed extraction of manganese and iron. It is obvious that this behavious can be predicted by thermodynamic considerations as has been done by Han K. N. et al[39]. However it is interesting to note that they found iron extraction was influenced to a greater extent by aeration than was the extraction of manganese. Siemens et al[31] leached in ammonia-ammonium sulphate a previously reduced low-grade domestic laterite. As always, the leaching in the oxygenated NH_3 - $(NH_4)_2SO_4$ solution proceeds by a process of oxidation wherein the following reactions will take place.

$$Ni + \tfrac{1}{2}O_2 + NH_3 + H_2O + (NH_4)_2SO_4 = (Ni(NH_3)_6)SO_4(\text{soluble}) + 2H_2O$$

$$Fe + \tfrac{1}{2}O_2 + H_2O = Fe^{++} + 2(OH)^- \text{ (soluble)}$$

$$4Fe^{++} + O_2 + 2H_2O + 8OH^- = 4Fe(OH)_3 \text{ (insoluble)}$$

A minor amount of magnesium is also dissolved as a sulphate. They also pointed out that the $Fe(OH)_3$ precipitated will form a slime film, on the unleached particles containing Ni and Co preventing further dissolution. In order to avoid this inconvenience they proposed a controlled oxidation coupled with multistage leaching wherein the pulp was attritioned prior to each leach. On the other hand, as in the case of other ammonia leach processes, the oxidizing ammonia leach must be done in the presence of excess ammonia to prevent precipitation of nickel hydroxide. They obtained the best results using a concentration of ammonium hydroxide of 100 gr. p. l. and ammonium sulphate of 300 g. p. l. According to Hauf N. W.[44] ammonium sulphate or bisulphate solutions used at pH 8-10 will extract copper, nickel and cobalt from oxidixed ore under non-oxidising conditions and have the additional advantage of not dissolving manganese or alkali earth metals to any significant extent.

Although ammoniacal leaching is mainly applied after the reduction-roast of nickel laterite ores, acid leaching can also be used. Clarkson C.J.[45] studied the leaching of reduction-roasted garnierite in aerated sulphuric acid solution. He concluded that, although nickel laterite ores can be submitted to acid leaching without a previous pyrometallurgical treatment, if the reduction step is applied to a silicate ore, magnesium as serpentine is converted to olivine and nickel associated with serpentine is reduced to metal, allowing nickel to be more readily acid-leached than magnesium and minimizing acid consumption. He selected the following conditions of roasting: temperature 1000°C, time 2 hours, gas hydrogen and he obtained 96.8 per cent nickel reduction. His experimental leaching conditions (5 gr/l to 50 gr/l of acid at 30°C and 5 gr/l of acid at 30°C to 60°C) are consistent with nickel dissolution rates being controlled by rate of the cathode reaction occurring over the major part of the nickel platelets formed during reduction:

$$2H^{+} + \tfrac{1}{2}O_2 + 2e = H_2O$$

It is probable that cathode reaction rates are determined either by reactant diffusion through pores in particles or a chemical process at nickel surface.

Another pyrometallurgical process to which the nickel laterite ores can be submitted previously to a selective leaching is the segregation process. A review of the thermodynamics of the process has been done by Iwasaki[46], a survey of the process itself has also been published[47] and a detailed discussion on the mechanism has also been revised[48].

The segregation process is a method for treating oxidized ores in which the ore is heated with a reducing agent and a halide salt, generally a chloride for a certain time at temperatures between 700°C

and 1000°C. The addition of the salt results in the migration of metal as a chloride and its reduction to metal on the surface of the reducing agent rather than in the original matrix. The metal can be then recovered by a subsequent screening, leaching, magnetic separation or flotation operation. There appears to be general agreement that the three reactions of major importance occurring during segregation process are:-

a) Production of hydrochloric acid gas by reaction of certain ore components with the chloride salt,

b) Chlorination of the oxide minerals,

c) Reduction of the chloride to metal and regeneration of the hydrochloric acid gas.

Analysing the effects of the different kinds of chlorinating agents, it is generally agreed that $CaCl_2$ is the most effective reagent. Dor et al[48] and Hoover et al[49] pointed out that $CaCl_2$ is capable of generating higher partial pressures of HCl than NaCl and this is part of the reason why $CaCl_2$ has been found to be a more effective segregation reagent for the treatment of oxide nickel ores. The effects of moisture have been analysed by several workers and revised by Hoover et al[49], they reported that pre-dehydration of the ore by heating before segregation will reduce the evaluation of hydrochloric acid in the presence of solid chlorides and this generally means a substantially decreased recovery when the heating rate is too fast because the samples are dehydrated extremely rapidly. As has been mentioned earlier, the concentration of the segregated products is normally carried out by flotation or magnetic separation although leaching has also been used. Okamoto[50] studied the ammoniacal leaching of a previously segregated iron-rich laterite. The segregation was carried out at temperatures of 630°C to 850°C for 1h using chloride salts, and the ammoniacal leaching at 40°C for 30 to 60 minutes. He reported that the segregation roasting of iron laterites increased the extraction of nickel by ammonia leaching as compared to the ordinary reduction roasting.

Chloridization of nickeliferous laterites can be carried out using hydrogen chloride or chlorine in the gaseous phase or as an aqueous solution. Chloridization studies using chlorine in the gaseous phase were done by Lakschevitz[51]. The reduction was carried out in a rotary kiln at about 750/800°C using fine ore of less than 200 mesh. The following reaction took place:

$$NiO \times SiO_2 + CO/H_2 = Ni + x\,SiO_2 + CO_2/H_2O$$

$$3Fe_2O_3 + 3CO/H_2 = 3Fe_3O_4 + 3CO_2/H_2O$$

$$Fe_3O_4 + CO/H_2 = 3FeO + CO_2/H_2O$$

$$FeO + CO/H_2 = Fe + CO_2/H_2O$$

After the reduction the material was cooled down to 300°C whilst protected from oxidation and fed into a chloridization chamber, where chlorine was introduced and the following reaction took place:

$$Fe/Ni + Cl_2 = NiCl_2 + FeCl_2$$

$$FeCl_2 + \tfrac{1}{2}Cl_2 = FeCl_3$$

Afterwards the charge was cooled down to room temperature and leached with acid water at pH = 3. Heertjes and Jessarum[78] studied the chloridization of the nickel and cobalt compounds in a lateritic iron ore with gaseous HCl-H_2O mixtures. They claimed that working at a temperature of 220°C and with HCl/steam ratio between 25/75 kmol/kmol and 45/55 kmol/kmol, and without preroasting the lateritic ore, which lowers the nickel recovery, an enrichment factor of around 150 can be obtained. They pointed out that the chlorides formed during the chloridization process can be recovered by extraction with hot water (80°C) at pH = 3.25. Separation of the metals in the leach solution is possible by precipitation as their hydroxides at different pH values. Roorda H. S. and Queneau P. E.[52] have proposed a very interesting reduction/ chloridization process using chlorine in an aqueous solution. They

considered that their method has the following advantages:-

a) The superior reactivity of chlorine implies a sharp increase in reaction rates and corresponding decreases in extraction circuit costs. In laboratory tests 90 per cent extraction of Ni and Co can be achieved in 10 minutes.

b) The reaction products have high water solubility and the aqueous chloride solutions are outstandingly adaptable to solvent extraction for metal isolation.

c) The process does not depend on a large supply of fresh water since extraction can be carried out by use of sea water.

d) The iron content of the leached residue is present largely as magnetite.

The process discribed by Roorda and Queneau included reduction, selective oxidation-cooling and aqueous chlorination. The most favourable conditions for the reduction process were: temperature 750°C, gas composition three parts of N_2 to two parts of CO_2 and one part of H_2. The cooling was done by evaporation of direct water spray so controlled steam treatment reoxidizes a substantial part of the iron with only a small loss in nickel-cobalt extraction. The objective of the aqueous chlorination is the selective reaction of metallic nickel and cobalt with chlorine to form a soluble chloride, the process is easier to control and superior in selectivity with respect to iron than the one discribed previously.[51] Metal dissolution can be expressed as follows:-

$$Me(Ni,\ Co,\ Fe)_{solid} + Cl_2(aq) = MeCl_2\ (aq)$$

Thermodynamic conditions for the undesirable chlorination of MnO, Fe_3O_4, Mn_3O_4 are also favourable. However, providing that the pH and Eh are carefully controlled the only iron which goes into solution is that which

has been reduced to the metallic form. Moreover, kinetic factors reduce the chlorination of MnO, Fe_3O_4, Mn_3O_4 to a very low level during the short leaching time. They found that the best conditions of chlorination are:- temperature 30 to 80°C, Eh is approximately +1000 mv, pH is 1.5. Under these conditions more than 90 per cent of the nickel and cobalt is solubilized while only about 5 per cent of the total iron is in solution. The iron in solution is in the ferric state which makes the solution suitable for solvent extraction or ion exchange purification processes.

1.1.2 Direct Leaching of Nickel Laterite Ores

Another approach to the treatment of nickel laterite ores involves the direct non selective leaching of the ore followed by separation of the different metals from the leach liquor. This approach has not been considered attractive in the past either because it involves a rather high consumption of acid, as in the case of acid leaching or rich magnesium laterite ores (serpentine), or due to the lack to technology in the field of leach liquor purification; generally the two problems would appear together. However, the direct leaching of nickel laterite seemed to be attractive in the case of low magnesium content, high iron content, nickel laterite ores (limonite), as was the case of Moa Bay in Cuba. Studies in the Moa Bay limonitic type ores led to the construction of the Moa Bay plant which operated on an industrial scale. The Moa Bay process has been widely discribed[3, 53, 54] The Moa Bay process intended to produce impure NiS which would be sold for later refining. Basically the process included the following steps:

a) slurry preparation

b) Pressure leaching

c) Precipitation of chromium and reduction of ferric to ferrous state,

d) Neutralization

e) Pressure precipitation of NiS and MeS with H_2S.

We are mainly concerned with the pressure leaching step. The leaching was carried out in a Pachuca type autoclave reactor at 250°C, the slurry agitation was produced by injecting 610 p. si. steam into a 16 inch diameter draft tube of rolled titanium street; sulphuric acid of 98 per cent concentration was pumped into the first vassel in series. Under these conditions the formation of nickel ion by the attack of sulphuric acid on nickel oxide can be idealized as follows:-

$$NiO + H_2SO_4 = Ni^{++} + SO_4^{=} + H_2O$$

It has been reported that the acid-to-ore ratio was the principal variable in controlling the leach reaction. The Moa Bay process could be used to illustrate the importance which the mineralogical constitution of a particular deposit or even a particular ore within the deposit would have on the choice of a specific leaching process and, therefore, the importance of the mineralogical studies of the deposit, in particular, the identification of the minerals with which the nickel might be associated. In this way, Carlson and Simons[53] reported that the Cuban nickel ores in Moa Bay have the following mineralogical constitution: the major constituent of this ore is goethite, which could make up to 75% of the material. The alumina is present as the tri-hydrate, gibbite, which makes up some 10% of the ore. Serpentine and quartz is 5%. Finally some 10-15% of complex spinels. No nickel or cobalt minerals could be positively identified, they occur to some extent in the spinels, but the major part appeared to be associated with the goethite. Analysing the leaching rate it was found that at least three different nickel-mineral species would behave differently with regard to the rate of leaching:

a) the leaching was very rapid for one of them, in which about 60% of the nickel was contained. It has been

demonstrated that this species is associated with the goethite fraction of the ore.

b) The leaching rate is considerably slower for the second species and this is the rate that determines the extraction.

c) The leaching rate is very very slow for the third fraction where about 3 or 4% of the nickel is contained; presumably the last two species are associated with the complex spinels.

The particular point at which the ore contains a large amount of goethite and gibbsita, is also important in terms of choosing the leaching process. Under normal laboratory conditions (not using high temperatures), the great bulk of these ores is soluble in mineral acids making, in principle, the process non-selective, so that the consumption of acid would be high. However, when high temperatures are used the process has got a greater selectivity. At 230°C to 260°C excellent nickel and cobalt extraction (95% or better) can be achieved at low acid levels and treatment times. This is due to the fact that iron will hydrolyse and precipitate as Fe_2O_3 (anhydrous). It has been found[53] thst the transition from hydrous to anhydrous ferric oxide involves passing through the solution phase. Aluminium will also hydrolyse at the working temperature, and precipitate as possible di-hydrate of $Al_2O_3.SO_3$. The direct leaching of nickel laterite ores would be attractive providing the leach liquor could be purified and that the reactants, such as acid, can be regenerated and recycled; the wide use of solvent extraction to purify leach liquor has opened a new perspective to the treatment of nickel laterite ores; in this way the direct and non-selective leaching of nickel laterite seems to be the new approach of treatment of such ores. Panda S. E. et al[55] and Kanto Rao P.[56] have studied the sulphuric acid pressure leaching of certain low magnesia lateritic ores from India and have proposed a new flow-sheet for the treatment of such ores. They pointed out that the extraction of

nickel increases with increases in temperature of leaching (temperature range 160°C to 200°C) and, consequently, with the pressure of leaching. However, the extraction of cobalt remains almost constant within the temperature and pressure range studied. The free acid concentration decreases with increase in the contamination of iron. The extraction of nickel and cobalt as well as contamination of iron increases with increase in the amount of sulphuric acid used. The extraction of nickel and cobalt increase with increase in duration of leaching. They proposed two different flow-sheets, in both of them the magnesium is removed as magnesium sulphate and the iron and aluminium are recovered as oxides or hydroxides. In their first proposal sodium thiocyanate is added to the clear iron-magnesium-aluminium-free leach liquor and then cobalt is extracted in to methyl isobutyl ketone or tributyl phosphate in kerosene using solvent extraction. The cobalt in the organic phase is stripped and the cobalt thiocyanate is hydrolysed with sodium hydroxide; the cobalt hydroxide thus obtained is dried, calcined and reduced with hydrogen to get cobalt metal. The nickel and manganese in the raffinate are hydrolysed with NaOH, redissolved with H_2SO_4 and electrowon as Ni metal and battery grade MnO_2. In their second proposal NaOH is added to the iron-aluminium-magnesium-free leach liquor and pH 10 to 12 mixed hydroxides will be precipitated. Cobalt and manganese hydroxides in the precipitate are oxidized to MnO_2 and Co_2O_3 by heating the hydroxide slurry at 80°C and passing air at the rate of 3.5 lit/min. The slurry is treated with dilute sulphuric acid at pH of about 3, where Ni is dissolved and MnO_2 and Co_2O_3 remain in the residue; Ni in the leach liquor is hydrolysed with sodium hydroxide. the nickel hydroxide thus obtained is filtered, dried, calcined and reduced with hydrogen to produce nickel metal. The residue containing the oxides of manganese and cobalt is dissolved in hydrochloric acid solution of 320 gr/l. and then cobalt is extracted into tributyl phosphate in kerosene diluent using solvent extraction techniques. The cobalt is stripped, hydrolysed with NaOH, filtered, washed, dried, calcined and reduced with hydrogen to produce

cobalt metal. The following table will illustrate the efficiency of the process.

Constituent	Amount in gr. Present in 3 Kg.	Amount in gr. Present in LL	Leaching efficiency in %	Amount rec. in gr.
Nickel	24.00	22.32	93.00	21.66
Cobalt	1.50	1.40	93.00	1.33
Iron	921.60	18.43	2.00	18.43
Manganese	19.20	11.70	60.00	9.27

Constituent	Overall efficiency in %
Nickel	90.26 as very pure metal
Cobalt	88.88 as very pure metal
Iron	2.00 as very pure Fe_2O_3
Manganese	41.51 as battery grade gamma MnO_2

Sulphuric acid might be regenerated by using SO_2 produced by thermal decomposition of $MgSO_4 . H_2O$, and also the MgO produced could be used in the neutralization steps instead of $Na(OH)_2$. Using a very similar principle to the one discussed earlier; Kay. H.[57] has patented a process to recover nickel and cobalt from nickel laterite ores using sulphuric acid.pressure leaching and because sulphuric acid might be regenerated the process is not limited only to low acid consuming types of minerals (limonites) but can also be used for high acid consuming type minerals (serpentine) containing as much as 15% of Mg. The proposed process has got the following steps:-

a) After removal of the large pieces of the ore the remaining ore feed has a particle size of less than -400 mesh, and with this is formed a slurry of the ore which is leached with H_2SO_4 (93% H_2SO_4) at 204°C to 260°C and 450 psi. Under these conditions most of the Fe, Al, Si remains in the precipitate.

b) The leach liquor (pH = 1) is neutralized using MgO at 50° to 100°C until the pH is 3.5 to 4.5, under these conditions the remaining Fe, Al, Si in the leach liquor is precipitated but not Ni, Co, Mn, Mg.

c) The leach liquor from step two is treated with more MgO until the pH is 8 at 70°C to 95°C, under these conditions Ni, Co, Mn are precipitated as hydroxides.

d) Ni, Co, Mn hydroxides are dissolved in $(NH_4)_2SO_4$ - NH_3 solution and recovered by the H_2 precipitation.

e) The leach liquor after the hydroxide precipitation contains only $MgSO_4$ which is passed into a non evaporative crystallizer (an autoclave) where seed $MgSO_4$ crystals are present and where the solution is heated to 200°C at 237 psi; under these conditions $MgSO_4 . H_2O$ is precipitated, the final concentration of the solution being as low as 2.9 g.p.l.

f) The $MgSO_4 . H_2O$ is submitted in the presence of sulphur or pyrite to a thermal decomposition at 1350°F, under these conditions SO_2-SO_3 is formed which can be used to produce H_2SO_4 which is recycled, MgO is also formed in the thermal decomposition and can be used as a neutralizer and to produce seed $MgSO_4$; water is also produced in the thermal decomposition and can be recycled to the leach step.

Kay H.[57] claims that nickel and cobalt are recovered at 90% and 99% purity.

Researchers at Warren Spring Laboratory[58] have developed a new process for recovery Ni, Co, Mg, Mn from high magnesium nickel laterites (Fig. 5) which in many ways is very similar to the one proposed by Kay H. Oprolko et al[59] found that it is not necessary to add

sulphuric acid directly to the ore to leach out the nickel and cobalt contents, since it is possible to produce sulphuric acid in situ.

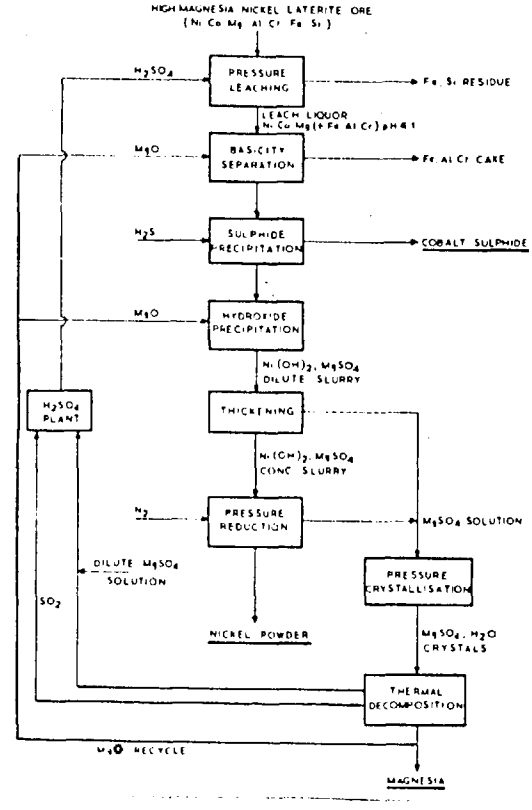


Figure 5

Warren Spring Laboratory Process for High Magnesium nickel laterites

This can be achieved by adding pyrite to a slurry of the ore, heating the mixture to above 200°C and treating with oxygen at an elevated pressure; under these conditions the pyrite is oxidized to establish and maintain a sulphuric and solution. Taminchi K.[60] studied the pressure leaching of garmerite ores using sulphuric acid under compressed air at different temperatures; using 20 gr. of ore and 300 ml of sulphuric and 90% of the nickel in the ore was leached out under the following conditions: sulphuric acid 10%, temperature 180°C, total pressure 10 Kgr/cm^2, time 2 hours, agitation speed 200 r.p.m. Figures 6 and 7 show the percentage of Ni and Fe in solution versus temperature. As we have mentioned earlier on nickel laterite ores are in many ways similar to the ocean manganese nodules, a

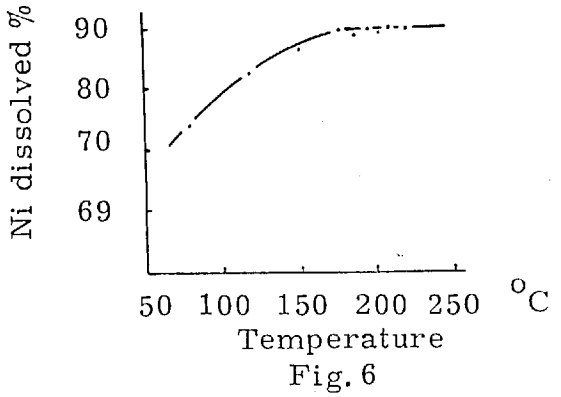


Fig. 6

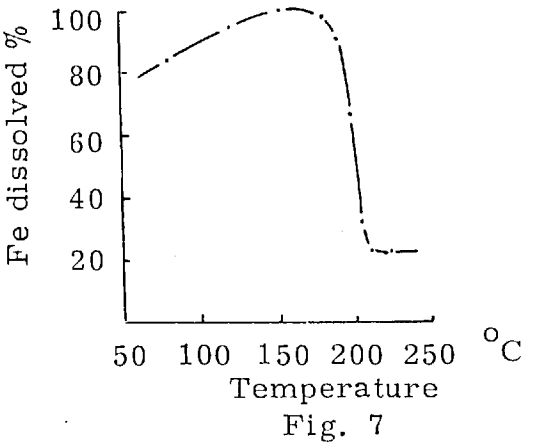


Fig. 7

Figure 6 Per cent of nickel dissolved on the sulphuric acid leaching under compressed air of garmerite versus temperature (Ref. 60).

Figure 7 Per cent of iron dissolved on the sulphuric acid leaching under compressed air of garmerite versus temperature (Ref. 60)

thermodynamic study of the acid leaching of ocean manganese nodules has been done by Hau K.N. and Fuerstenau D.W. [61] in terms of pH-E high temperature diagrams; this study can also illustrate the behaviour of metal, such as Ni, Co, Mn, Fe, Cu in the case of high temperature, oxygen pressure, acid leaching of nickel laterites. Figures 8, 9 and 10 represent the high temperature pH-E diagrams for the systems, $Ni\text{-}H_2O$, $Fe\text{-}H_2O$, $Mn\text{-}H_2O$, where the activities of the metal ionic species are taken to be unity. According to the diagrams the following conclusions can be pointed out:

a) Dissolution of metal oxides in acidic medium can be described by the following equations:-

(1) $Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O$

(2) $MnO_2 + 2H^+ = Mn^{2+} + H_2O + \frac{1}{2}O_2$

(3) $CuO + 2H^+ = Cu^{2+} + H_2O$

(4) $Ni_3O_4 + 6H^+ = 3Ni^{2+} + 3H_2O + \frac{1}{2}O_2$

(5) $Co_2O_3 + 4H^+ = 2Co^{2} + 2H_2O + \frac{1}{2}O_2$

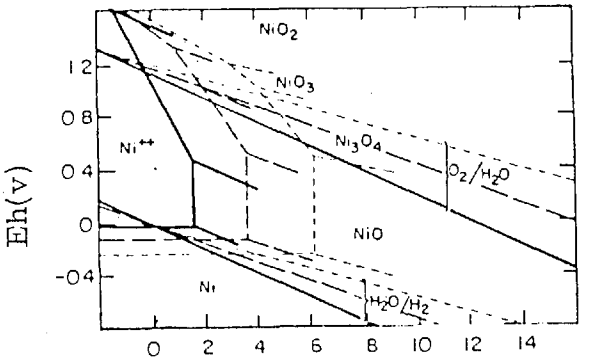


Fig. 8

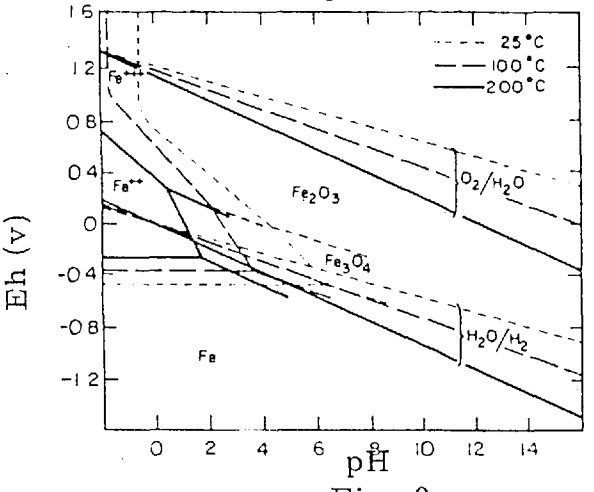


Fig. 9

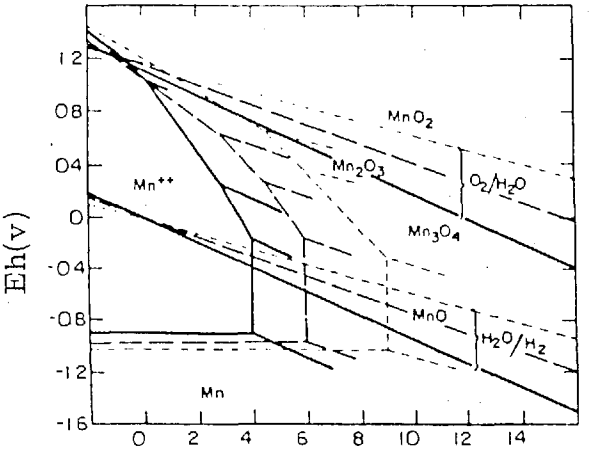


Fig. 10

Figure 8 pH-Eh diagram for the Ni-H_2O system at 25°C, 110°C and 200°C (Ref. 61)

Figure 9 pH-Eh diagram for the Fe-H_2O system at 25°C, 100°C and 200°C (Ref. 61)

Figure 10 pH-Eh diagram for the Mn-H_2O system at 25°C, 100°C and 200°C (Ref. 61).

b) Oxide phases, iron oxide and manganese oxide in particular, became increasingly stable as temperature increased. This point has been demonstrated by all the workers mentioned before, (see for instance Fig. 7 by Toninchi). The stability of the oxide phase follows the order Fe› Mn› Ni› Co› Cu.

c) Iron and Mn are very sensitive not only to temperature but also to oxygen pressure and will precipitate Fe_2O_3 and MnO_2 as temperature and O_2 pressure are increased.

d) Too high oxygen pressure will have an adverse effect in the dissolution of Ni and Co. (see Fig. 8 and equations (4) and (5)) However, if Ni occurs in part in a lower valence state (as NiO) dissilution would be less sensitive to oxygen pressure.

The leaching of lateritic ores with hydrochloric acid was studied quite a long time ago[62-63] under reflux conditions, but under these conditions much of the iron and magnesium is dissolved. Thus reagent consumption is high and recovery of nickel and cobalt presents a problem. However, very recently these two problems have been overcome because HCl can be recovered by pyrohydrolysis of acid[64] and nickel and cobalt can be separated using solvent extraction as in the Falconbridge Matte Leach Process[65].

Bearing these two points in mind Rice N.M. and Strong, L.W.[66-67] have studied the hydrochloric acid leaching of some nickel laterite ores and proposed a new flow-sheet. Their studies will point out again how important the careful mineralogical study of the ore is and how different the behaviour of the ores is in the leaching process depending on their mineralogy. Three different kinds of nickel laterite ores were studied: Serpentine(high magnesium content); Garnierite; Limonites (high iron, low magnesium content). The behaviour of the different kinds of nickel laterite ores according to the changes in the different variables of leaching is as follows:

a) Long times of reaction will normally increase the extraction of nickel and, in some cases, the iron in the serpentine type of ores but would not affect very much the extraction in the limonite type.

b) Acid strength increases the extraction of both metals, iron and nickel, and also the amount of gangue material taken into solution at low temperature; but the nickel and iron extraction would not be very much affected by the acid strength at high

temperature either for serpentine or limonite type of ores.

c) Analysing the effect of the temperature they concluded that for the serpentine type of ores, high temperature will favour considerably the extraction of nickel and magnesium, this is due to the fact that nickel might be associated with magnesium in these types of ores and the removal of nickel and magnesium is due to the rupture of weak Mg-O bonds while the stronger Si-O bonds remain intact in the silicate layer. For the garnierite type of ores high temperature will, in general, favour the extraction of nickel but in less degree than in the case of serpentine, this is due to the fact that the nickel is more tightly held in the silicate lattice. In the Limonitic type of ores nickel might substitute a Fe^{3+} in the goethite ($\alpha FeO(OH)$, $HFeO_2$, $Fe_2O_3.H_2O$) and this means that although at low pressure an increase in the temperature will favour the extraction of nickel it will also favour the extraction of iron both of these being very much related with the amount of goethite dissolved. The work described indicates that a promising process might be devised for hydrochloric acid leaching or serpentine type ores but that a preliminary reduction roasting may well be better for high iron laterites. In the flow-sheet that they proposed cobalt and iron are removed from the leach liquor using solvent extraction techniques[65] while nickel is recovered by hydrogen reduction of hydroxide after neutralizing the leach liquor with MgO recycled from the spray roasting for recovered HCl[64].

1.1.3 Previous Work on Hydrothermal Treatment of Nickel Laterite

Processes involving hydrothermal treatment are widely used in hydrometallurgy. In this context of hydrothermal treatment a great emphasis has been put in the study of high pressure hydrolysis or thermal precipitation[68-69] as a mean of purification of leach liquors.

Robins[70] main field of interest has been high pressure hydrolysis. However he has used the potential-pH diagrams to predict the reactions that will take place, not only by the high pressure hydrolysis, but also by any other type of hydrothermal process.

On the other hand, the thermodynamics of high temperature aqueous solution has received a great deal of attention in recent years, particularly in relation to geochemical studies of hydrothermal ore deposition[71]. It is now possible to predice with accuracy the behavious of hydrothermal solutions by means of pH-E diagrams.

Seidel D.C. and Fitzhugh E.T. developed a new process[72] for recovery of nickel from lateritic ores; the process involves the three following steps:-

a) Sulphidization wherein the lateritic ore is sulphidized by reacting with sulphur under hydrothermal conditions at 230°C to 240°C.

b) Oxidation wherein the reacted pulp is oxidized at 200°C with an air over-pressure of 1.3 MN/m^2.

c) Cementation wherein the acid pulp is then cemented directly with iron powder at 150°C to produce a nickel-iron product.

The process, which is known as HSO-HTCP (Hydrothermal Sulphidization-Oxidation-High Temperature Cementation in pulp) has now been patented[73]

and is under pilot plant operation[74]. The feed to the hydrothermal sulphidization step is a slurry, formed by an intimate mixture of the ore, elemental sulphur and water. Where comparative costs favour the use of pyritic sulphur rather than brimstone, about half the requirement may be added as pyrite or other compatible sulphide. The sulphidization reaction is carried out at 230°C-240°C and the associated pressure is between 380 and 480 p.s.i. Under these conditions most of the elemental sulphur is auto-reduced to sulphide ion which react to form nickel sulphides (mainly NiS and NiS_2), iron sulphides (mainly FeS_2) and mixed Ni and Fe Sulphides. The balance of the sulphur is auto-oxidized to sulphuric acid which is a major product of the sulphidization reaction, which immediately reacts with the acid-soluble constituents, such as nickel-magnesium silicates. We can write the main reactions of the hydrothermal sulphidization steps as follows:-

(1) $3NiSiO_3 + 4S + 4H_2O = 3NiS + 3H_2SiO_3 + H_2SO_4$

(2) $Fe_2O_3 + 5S + H_2O = 2FeS_2 + H_2SO_4$

(3) $(NiMg)SiO_3 + H_2SO_4 = (Ni\ Mg)SO_4 + H_2O + SiO_2$

They found that the sulphidization product liquor does not contain nickel; apparently any nickel that is solubilized during the acid attack on the garmerite and chlorite minerals is immediately reprecipitated as a nickel sulphide. The study of the effects of the different variables (reaction temperature, time and amount of elemental sulphur) in the degree of sulphidization was done by means of factorially designed experiment and the results are plotted in Figs. 11, 12 and 13. The following conclusions can be drawn from the results:

a) Bellow a certain temperature no sulphidization occurs but above this temperature the degree of sulphidization increases rapidly.

b) The optimum retention time is 3.5 hours.

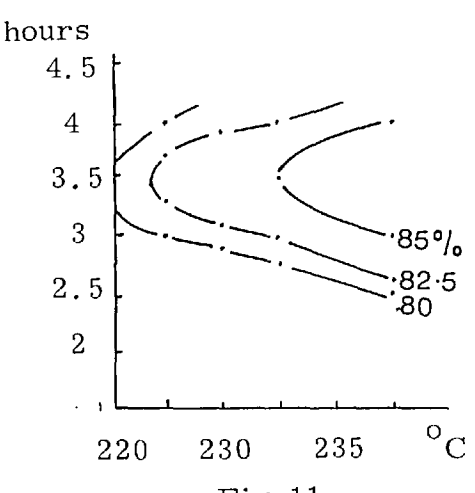


Fig. 11

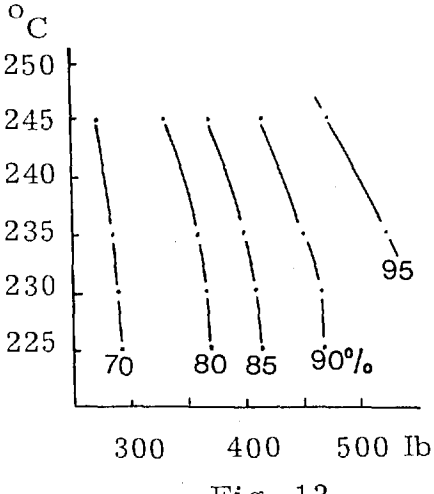


Fig. 12

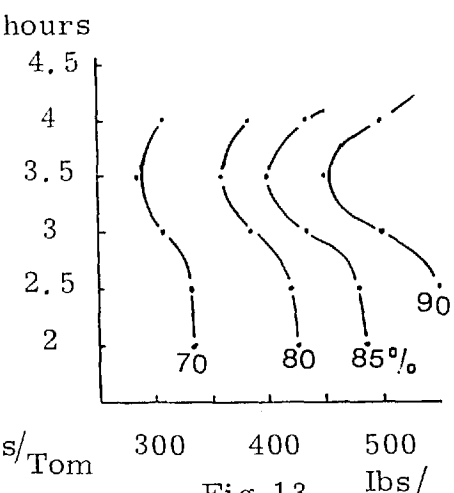


Fig. 13

Figure 11 A time vs temperature plot of the response contours for HSO nickel extraction with the addition of 400 lb per ton sulphur (Ref. 72).

Figure 12 A temperature vs sulphur addition plot of the response contours for HSO nickel extraction at 3.5 hours (Ref. 72).

Figure 13 A time vs sulphur addition plot of the response contours for HSO nickel extraction at 235°C. (Ref. 72).

c) The sulphur addition F. (11, 13) is probably the most significant variable of the three, since the adverse effect of non-optimum time and temperature conditions can be offset by increasing the sulphur addition. During the oxidation step the product of the sulphidization step is oxidized at 200°C and about 210 p. s. i. Under these conditions the following reactions will take place:

(4) Oxidation $NiS + 2O_2 = NiSO_4$

(5) Hydrolysis $4FeS_2 + 15O_2 + 8H_2O = 8H_2SO_4 + 2Fe_2O_3$

The H_2SO_4 produced reacts as in reaction (3) they found that fourty per cent of the total nickel extraction results from reaction (4) and sixty per cent from reaction (3). The last step includes the cementation of the acid pulp as has been mentioned earlier.

Bush P. D. [74] claims that the use of a sulphidization stage in processing nickel silicate ores has resulted in increase in nickel

extraction by as much as 5 to 20 percent as compared to an oxidation leach without sulphidization. However, this stage can be deleted from the overall processing of high iron laterites containing up to 2 per cent of magnesium.

As has been mentioned earlier the sulphur in the hydrothermal sulphidization step might be partly replaced by pyrite or other compatible sulphide. Apparently no attempt has been made to study the hydrothermal sulphidization using some of these compounds. However, Bussell N.[75] et al used pyrrhotite to precipitate Ni and Co from acid leach liquors as Ni and Co sulphides by a hydrothermal treatment. The main products of the treatment are: α-NiS, $(NiFe)_3S_4$ (violarite), $(NiFe)_9S_8$ (pentlandite) and Ni_3S_2 (heazlewoodite).

On the other hand Ewers[76] analysing the genesis of nickel-iron sulphide ores mentioned that pyrrhotite of any origin must be considered a potential sink for any nickel that is available in a mobile form. In this way, he pointed out that serpentinites commonly contain less nickel than the rocks from which they have formed, and some nickel has evidently dispersed in solution during serpentinization. Such nickel, at the temperature at which serpentinization occurs will be absorbed by available pyrrhotite. In the presence of plentiful sulphide the result would be a pentlandite-pyrrhotite association, if sulphide is rare, nickel displaces iron, and millerite or heazlewoodite results, depending on temperature.

It is clear that the research carried out by Bussell[75] and the phenomenon observed by Ewers[76] suggests that pyrrhotite, especially low nickel content pyrrhotites, might advantageously be substituted for sulphur in the hydrothermal sulphidization process described by Seidel[72].

On the other hand, it is interesting to mention that nickel sulphide can be obtained by the action of sulphur on heated nickel oxide[77] and also by heating one of the hydrated forms.

Nickel sulphide can also be formed when nickel oxide is heated with ferrous sulphide (pyrrhotite) in the presence of some slagging materials.[77]

1.2 AMMONIACAL LEACHING

1.2.1 Ammoniacal Leaching of Nickel and Copper Sulphides

The Sherritt Gordon[3-79-80] process for recovery of nickel, copper and cobalt from sulphide concentrate using ammoniacal leaching is well known. The process involves the leaching of pentlandite concentrates in an ammonia solution with air under pressure to produce soluble nickel ammine complexes, leaving behind the iron as hydrated iron oxide. The pregnant leach solution undergoes a boiling-off operation to remove copper followed by an 'oxydrolysis' process to oxidize and hydrolyse all the sulphur compounds to sulphate. Nickel is recovered as pure powder by hydrogen reduction of the nickel ammine solution. A by-product of the process is fertilizer grade ammonium sulphate.

The chemistry of the process has been described by Forward and Mackiw[81]; after studying the leaching reaction carried out under a variety of conditions, they concluded that the following reactions take place:

(1) $Ni{:}FeS + 3FeS + 7O_2 + 10NH_3 + 4H_2O = Ni(NH_3)_6SO_4 + 2Fe_2O_3.H_2O + 2(NH_4)_2S_2O_3$

(2) $2(NH_4)_2S_2O_3 + 2O_2 = (NH_4)_2S_3O_6 + (NH_4)_2SO_4$

(3) $(NH_4)_2S_3O_6 + 2O_2 + 4NH_3 + H_2O = NH_4SO_3NH_2 + 2(NH_4)_2SO_4$

The fact that reaction (1) is heterogeneous while reactions (2) and (3) are homogeneous and that the concentrate contains at least four sulphide minerals makes it extremely difficult to determine the rate controlling factor. However, the effect of the different variables on the rate and extent of leaching can be tested. Analysing the effect of temperature

Forward and Mackiw[81] concluded:

a) Higher temperatures tend to increase the reaction rate.

b) Higher temperatures tend also to increase NH_3 vapor pressure and to promote hydrolysis.

c) Under the conditions used industrially (80°C to 90°C and 100-150 p. s. i. air pressure[3]), pyrite does not react, it remains unaltered in the leach residue and any cobalt or nickel in the pyrite can not be dissolved during the leaching.

d) The effect of the temperature on the formation of lower oxyacids of sulphur is shown in Figure 14, which indicates the period of time in which the high concentrations of $S_3O_6^=$ $S_2O_3^=$ exist. The formation of these intermediate oxidised sulphur compounds will be examined later.

Analysing the effect of the oxygen pressure in the rate of leaching they found that during the early stage of a batch leach there is a high oxygen requirement for sulphide oxidation to sulphate and sulphamate. Under these conditions the rate is determined by the dissolution of oxygen at the gas-liquid interface which in turn depends on the oxygen partial pressure. However, as the leaching nears completion, other factors (no oxygen pressure) might be rate controlling.

On the other hand, increased oxygen pressure tends to decrease the maximum concentration and life of the $S_2O_3^=$ and $S_xO_6^=$ ions in the same way as these are affected by increased temperature (Fig. 14). Although analysing the effect of the unbound ammonia is very difficult due to the fact that ammonia present during leaching reacts in four ways; they generally agreed that increasing the free ammonia concentration increases both the rate of leaching and the per cent of Ni, Cu, Co recovery.

They pointed out that if the concentration of anions normally sulphate ion, in this process is too low, the leaching rate and ultimate metal recoveries are also low; however sufficient sulphur is normally dissolved from the sulphide concentrate to provide an adequate concentration of sulphate. Agitation will influence the dissolution of oxygen at the gas liquid interface, the transport of oxygen through the solution to the sulphide particles, and the removal of the concentrated leach solution from the liquid-solid interface. Due to the fact that one of these steps might be at one time or another the rate-controlling factor, the agitation is a vital factor and an increase in agitation normally means a substantial increase in the rate of leaching.

As mentioned before, during the ammoniacal leaching of nickel sulphide incompletely oxidised sulphur compounds are formed; the concentration and life of these intermediate sulphur compounds depends on the pressure and temperature (Fig. 14).

Peters E.[82] and Jansen N.L.[83] et al have used the pH-Eh diagram for the sulphur-water system to determine the range of metastability of these intermediate valence states. Jansen N.L. et al found that sulphate formation is promoted by a maximum of oxidant at pH› 2.5, and in many instances by high temperature. They also pointed out that although sulphamates are really formed during the ammoniacal leaching of some metal sulphides, the concentration of sulphamate is low when the concentration of ammonium ion is kept at a low level.

Nackiw V.N. et al[84] have also studied the change of $S_2O_3^=$ and $S_xO_6^=$ ions concentration with the temperature (Fig. 15) for pH› 5, and they concluded that at temperatures higher than 120°C $SO_4^=$ is the only species which exists. In order to clarify the reaction machanism of the oxidation of sulphide to sulphate in aqueous ammonia solution

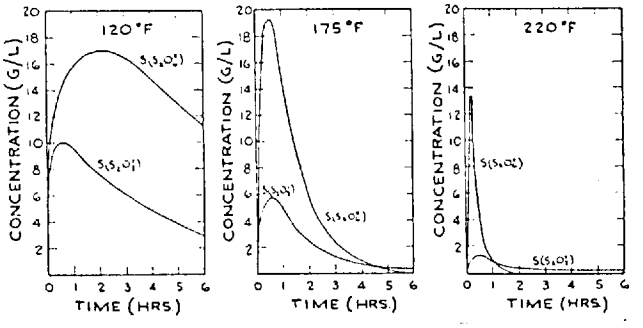


Fig. 14

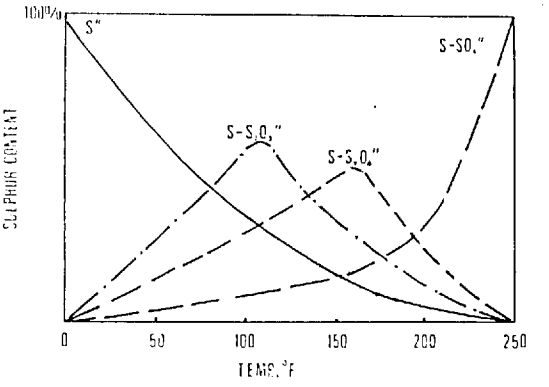


Fig. 15

Figure 14 Effect of the temperature on the concentration and life of $S_2O_3^=$ and $S_xO_6^=$

Figure 15 Effect of the temperature on the concentration of $S_2O_3^=$ and $S_xO_6^=$ during the oxidation of sulphides: pH> 5 $MeS/H_2O/O_2$

Shich et al[85] have used elemental sulphur suspended in aqueous ammonia as the starting material. They pointed out that thiosulphate is formed during the reaction but temporarily reaches a maximum and then gradually changes into sulphate and sulphamate. They found that the yield of sulphamate is improved when high ammonia concentration is used, it does not practically change with the oxygen pressure, and it is notably decreased with the temperature, probably because of the decomposition of trithionate to sulphate by hydrolysis. The sulphur leached from most metal sulphides behaves similarly. However, Burkin A. R.[86] pointed out that if pyrite is leached it gives only sulphate and none of the other oxyacids, so the sulphur must react differently at the solid-liquid interface. He reported that the different behaviour of pyrite is presumably due to the fact that it contains $S_2^=$ groups.

After the Sherritt Gordon method of ammoniacal leaching of Ni, Ca, Co sulphide concentrates with air under pressure was put

into industrial operation, the use of ammoniacal pressure leaching with similar kinds of ore has been studied by other workers.

Tandon D. S.[87] used ammonia and air under pressure to leach out Ni, Cu and Mo from Ni-Cu-Mo sulphides concentrate, their conclusions are very similar to those of Forward[81], however they found that although enough sulphur is normally dissolved from the concentrate to form the required $SO_4^=$ the use of $(NH_4)_2SO_4$ at the start of the reaction will considerably increase the rate of leaching of nickel and copper.

Fung H. and Glastanburg J.R.[88] used an electron-microprobe analyser to study the chemical and mineralogical constitution of some Australian nickel concentrates; they also used this technique to study the leach residues from pressure ammoniacal leaching of such a concentrate. After carefully selecting some pentlandite particles they studied the leach residue from these particles; they found that the reacting core model proposed by Forward[81] could be justified with some modification for removal of product layer by agitation and reaction within cleavages. However, they found that the iron oxide product was amorphous and therefore it is not pseudomorphic with the original mineral.

The Sherrit Gordon process can also be used to leach nickel mattes[89]. Pearce et al have studied the ammoniacal leaching of different kinds of nickel mattes with air under pressure. They considered that due to the fact that nickel mattes are normally low in sulphur content the used layer quantities of $(NH_4)_2SO_4$ in the feed solution will improve the nickel extraction.

Naboichenko et al[90] also studied the ammonia-ammonium sulphate leaching of some nickel mattes. Because of the complicated composition of the mattes the study was very difficult. Working at 100-110°C

and using an initial free ammonia concentration of 35-65 gr/l. together with 200 gr. /l. of $(NH_4)_2SO_4$, around 95% of the Ni can be extracted. It is interesting to note the following points:-

a) Increasing the ammonium sulphate concentration increased the metal extraction in solution.

b) Nickel isomorphously combined with iron sulphide is not extracted.

c) The use of higher temperatures than 100-110°C tends to promote hydrolysis and in order to avoid this it is necessary to increase the ammonium sulphate concentration.

In another article Noboichenko et al[91] further analysed the ammoniacal leaching of nickel mattes. They found that the pressure of iron as metal in the mattes is a disadvantage for the extraction of nickel due to the fact that it is rapidly oxidized, in this case an increase in $(NH_4)_2SO_4$ will be required to improve the nickel extraction. They reported that ferrous sulphide will affect the nickel to a lesser degree than iron metal. They also found that the best conditions in order to get a good nickel recovery are: $(NH_4)_2SO_4$ concentration 180-200 gr. /l., NH_3 concentration 35-65 gr. /l., temperature 100-110°C, partial oxygen pressure 6-7 atmos.

The same authors[92] have also studied the kinetics of the ammoniacal leaching of the lower sulphide of nickel, cobalt and copper with oxygen under pressure using a rotating disc method. The study was carried out using synthetic sulphide and it was determined by microscopic examination that there was only one phase in the sulphide. They analysed the effect of the different variables in the rate of leaching. They reported that when the concentration of ammonia was higher than 1 mol/l. (Fig. 16) there is a slight increase in the rate of leaching, but the rate of leaching decreased considerably with values of NH_3

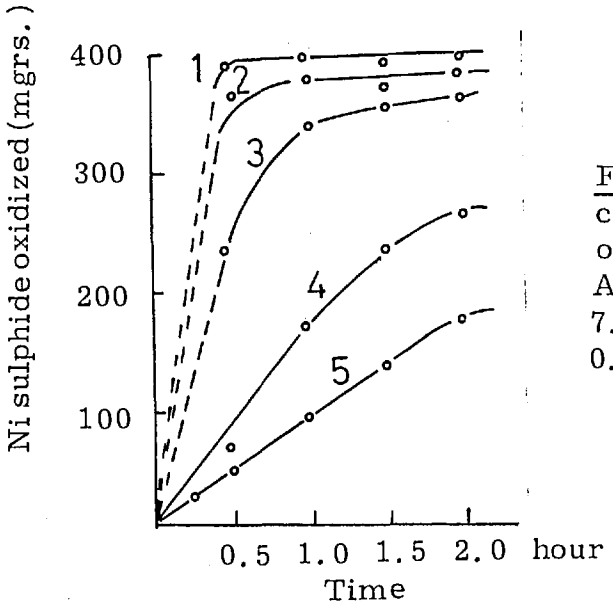


Figure 16 Effect of the ammonia concentration on the extraction of Ni from lower nickel sulphide. Ammonia concentration: 7.0(1), 5.0(2), 1.0(3), 0.7(4), 0.5(5) mol/l.

concentration less than 1 mol/l. They also pointed out that during the initial stages of the leaching the dependence of the quantity of nickel extracted on the time was linear, but they noticed a decrease of the reactivity with longer times. They thought that this is due to the fact that during oxidation of the sulphide a film is formed on the surface of the ore which has a great effect on the kinetics of the oxidation, however they could not identify the nature of such a film. Table 1 shows the dependence that they found between the rate of leaching and the concentration of $(NH_4)_2SO_4$ in the feed solution; it can be seen that the rate increases until the $(NH_4)_2SO_4$ concentration is 0.5 mol/l., further increases of the $(NH_4)_2SO_4$ concentration produced a decrease in the rate of reaction.

They found that the rate of leaching is directly proportional to the oxygen pressure and it is also proportional to the square root of the rotating speed; they calculated the energy of activation for the reaction to be 5.210 Kcal/mol. Bearing all this in mind they concluded that under the conditions of the experiment the controlling step of the oxidation is the difference of oxygen into the reaction zone. However, they pointed out that the rate control by oxygen difference only occurs during the first

TABLE 1

Concentration of $(NH_4)_2SO_4$ in mol/l	Concentration of NH_3 in mol/l.	Rate v in gr. ion/cm^2 sq.	log v
0.00	3.00	$2.17.10^{-8}$	7.669
0.25	3.00	$2.57.10^{-8}$	7.182
0.50	3.00	$2.47.10^{-7}$	6.590
0.60	3.00	$3.46.10^{-7}$	6.466
0.70	3.00	$3.15.10^{-7}$	6.509

part of the reaction because after some time has passed a film is formed on the surface of the sulphate which, as has been mentioned before, has a vital importance on the kinetics of leaching.

Mackiw V.N.[93] has patented a new process which he claims will considerably improve the Sherritt Gordon process because the reaction times in this process will be reduced and some of the Ni, Cu and Co which still remains in the residue after leaching in the Sherrit Gordon process will be recovered. His proposal involves reducing roasting of the leach residue that is produced by the ammoniacal leaching in the Sherritt Gordon process. During the reduction roasting Ni, Cu and Co sulphide from the leach residues are reduced to metals, while pyrite is reduced to FeS using H_2 or CO at 540°C to 900°C. The reduced metal-bearing material from the roasting step is ground and leached using ammonia-ammonium sulphate solution at 65 to 95°C and oxygen pressure of 20 to 50 p.s.i. Under these conditions the residue from the last leach operation will have around 0.04% of Ni, 0.02% of Co and 0.01% of Cu.

The ammoniacal leaching of nickel sulphides has been in industrial operation since 1954. Recently the Arbiter process has been put into operation.[94]

This uses ammoniacal low pressure leaching of various copper sulphide.

Much attention has been paid to the ammoniacal leaching of copper sulphide and a number of reviews relating to this subject have been published[82-84-95-100]. In addition, a good number of academic studies relating to the ammoniacal leaching of copper sulphide have also been published[102-110]. In as much as some of the phenomena observed in the ammoniacal leaching of sulphides are, according to some accounts, independent of the metal forming part of the sulphide, it is interesting to examine the ammoniacal leaching of copper sulphide.

Stanczyk and Rapacek[102] studied the effects of ammonia and ammonium sulphate concentration on the copper extraction of four different copper sulphides. The conditions of leaching were: temperature 200°C, pulp density 5 p. c. t. solids, oxygen partial pressure 100 p. s. i., reaction time 60 min., free NH_3 3 to 8 gr. per gr. of contained copper, NH_3 added as $(NH_4)_2SO_4$ 0.0 and 15 gr. per gr. contained copper. They found that the amount of free ammonia does not have a significant influence in the per cent of extraction. On the other hand, copper extraction was increased markedly by adding $(NH_4)_2SO_4$ except in the case of chalcopyrite which was affected only slightly.

Najima and Peters[103] studied the rate of oxidation of some sulphide minerals in different aqueous media. They found that the use of $(NH_4)_2SO_4$ together with free ammonia will considerably improve the extraction of Cu from sulphide. Using $((NH_4)_2SO_4) = 0.5M$ and $(NH_4OH) = 1M$, $Po_2 = 107$ p. s. i, T = 120°C and measuring the rate of

reaction in terms of oxygen consumption, the rate of leaching for the different sulphide varies as follows: Cu_2S > CuS > Cu_5FeS_4 > $CuFeS_2$. They also found that the oxidation rate of pyrite in an ammonia medium is quite low.

In the ammoniacal leaching of chalcopyrite, Fonseca[104] found that the copper dissolution by ammonia-oxidative pressure leaching is much more affected by an increase in temperature than by an increase in oxygen pressure and that increase in oxygen pressure has a much greater effect on copper dissolution at low temperature than at elevated temperature.

Tozawa K. et al[105] have studied the thermodynamics and kinetics of dissolution of copper sulphide (mainly chalcopyrite) concentrate. They pointed out that the increase in copper extraction noticed by Stanczyk[102] with the use of increased $(NH_4)_2SO_4$ concentration should be attributed rather to the buffering action of ammonia and ammonium ions than to an insufficient amount of $SO_4^=$ especially when working at elevated temperatures. They also found that increases of agitation intensity, oxygen partial pressure and leaching temperature led to increased leaching rate. They reported that adequate transport of oxygen to the surface of the mineral particles is very important especially when leaching minerals which require much more oxygen for their oxidation than other minerals of the same metal, as is the case with chalcopyrite in the copper sulphide family. On the other hand, they found that NH_3 concentration has no influence in the rate of leaching providing that enough NH_3 is supplied to form the metal complexes, either because enough free (NH_3) or enough (NH_3) + (NH_4^+) are present, where (NH_4^+) is usually supplied as $(NH_4)_2SO_4$ in the solution in order to form the metal complexes.

Reilly I.G. and Scott D.[106] studied the leaching of cupric sulphide in ammonia. They found that when some tests were done at different stirring speeds and at several temperatures, the mass transfer effects became important at temperatures above 100°C. They also found that at high temperatures it is not possible to recover 100 per cent of the copper; this is due to the hydrolysis of copper tetra-ammine. However, they pointed out that equilibrium concentrations show that the hydrolysis of tetra-ammine at high temperatures can be largely prevented by addition of ammonium ions. They proposed a mechanistic model and an empirical model in order to establish a useful expression for the rate of reaction. In another publication[107-108] the same authors further analysed the high temperature hydrolysis of the metal complexes. They found that the degree of hydrolysis is sensitive to the total ammonia present and less sensitive to the metal concentration, and also there exists a definite threshold amount of ammonium ion above which hydrolysis will be essentially zero.

Lately Becksted L.W. et al[109] have studied the ammoniacal oxidation leaching of chalcopyrite using a very high stirring speed and low solid phase concentration so that oxygen transport at the gas/liquid interface would not limit the rate. They proposed a catalytic electrochemical mechanism for the reaction and they reported that such a surface reaction controlled the reaction kinetics. The rate of reaction was shown to be independent of NH_3 concentration, one-half order dependent on oxygen pressure, hydroxide concentration and cupric ion concentration, which has a catalytic effect. In another publication[110] Beckstead has confirmed the electrochemical catalytic model for the leaching of chalcopyrite which he previously proposed. He pointed out that the reaction rate dependence on stirring speed, although similar to that which might be expected for systems in which the reaction rate is limited by mass transfer, is the result of surface

deposit effects and/or electrochemical site activation and is not a result of mass transfer control in the system.

The electrochemical model for sulphide oxidation in ammonia solutions was first proposed by Habashi[111]. He proposed the following electrochemical mechanism:-

Cathodic reaction:-

$$\tfrac{1}{2}O_2 + H_2O + 2e = 2OH^-$$

Anodic reaction:

$$MS = M^{2+} + S^o + 2e$$

$$M^{2+} + nNH_3 = M(NH_3)_n^{2+}$$

$$2S^o + O_2 + 2OH^- = S_2O_3^{=} + H_2O$$

$$S_2O_3^{=} + 2O_2 + 2OH^- = 2SO_4^{2-} + H_2O$$

He suggested by analogy with studies on the dissolution of metallic copper, where a similar electrochemical mechanism has been proposed, that the rate of solution can be expressed as:

$$\text{rate of solution} = \frac{2K_1K_2A(O_2)(NH_3)}{2K_1(O_2)+K_2(NH_3)}$$

However he did not test this equation for leaching of sulphides.

The ammoniacal leaching of copper and nickel sulphide under air or oxygen pressure involves, of course, dissolution of oxygen since only the dissolved oxygen reacts with the solid. The dependence of the solubility of O_2 in water on the temperature has been discussed by Pawlek. F.E.[112] and Himmelblau V.N.[113] (Fig. 17). On the other hand, the presence of other compounds dissolved in water, such as acids, bases or salt, decrease the solubility of oxygen[112-114-115].

Figures 18 and 19 represent the solubility of oxygen and hydrogen in aqueous solutions of $(NH_4)_2SO_4$ and NH_3 as a function of the concentration of $(NH_4)_2SO_4$ and NH_3. Not merely the solubilty of oxygen can limit the rate of leaching but also the way in which the oxygen is supplied can affect the rate of oxidation. Pawlek .F.E.[112] has analysed the effects of different types of stirrers and rotation speed on the amount of gas supplied and on the diameter of the bubbles produced. It is obvious that the rate of leaching could be affected by the size and shape of the autoclave, number and positions of baffles in the autoclave, size and shape of stirrers, etc. etc.

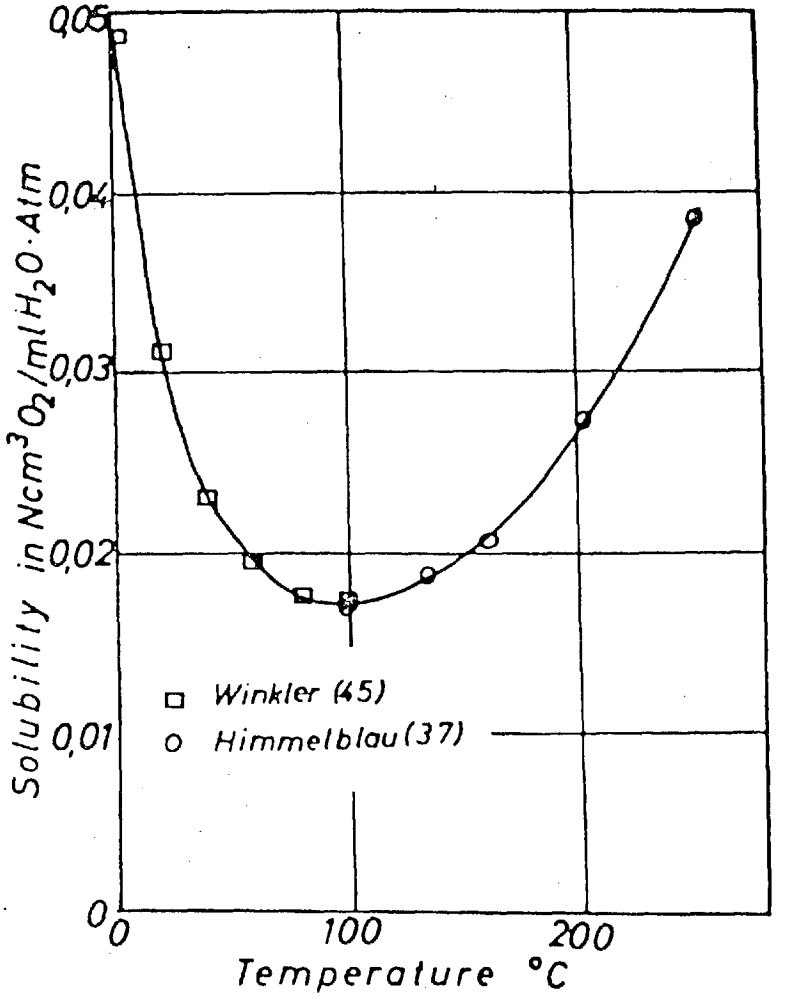


Figure 17 Solubility of O_2 in Water as a Function of Temperature

As mentioned before the use of high temperatures in the ammoniacal leaching of sulphide tends to promote hydrolysis of the metal complexes[81-105-107], so it is worthwhile to examine the research which has been done on high temperature hydrolysis for the system $NiSO_4$-H_2SO_4-H_2O. The system has been studied by Knok and Robins,[69] Marshall et al[116] and Manning D.G.[117] at 150°C and 200°C. At a temperature of 150°C and at high pH (adjusted with Na(OH)) they found three different types of compounds. When the pH was very high (maximum addition of Na(OH)) they all found that nickel hydroxide was precipitated; the other two compounds formed were not identified by Knok and Robines[69], using available x-ray diffraction data. However Manning D.G. thought that it might be a basic sulphate such as $Ni_5(SO_4)_2(OH)_6 \cdot nH_2O$ or $Ni_6(SO_4)_2(OH)_{10} \cdot nH_2O$.

$$v_1 = \frac{(O_2)_{(NH_4)_2SO_4}}{(O_2)_{H_2O}}$$

$$v_2 = \frac{(H_2)_{(NH_4)_2SO_4}}{(H_2)_{H_2O}}$$

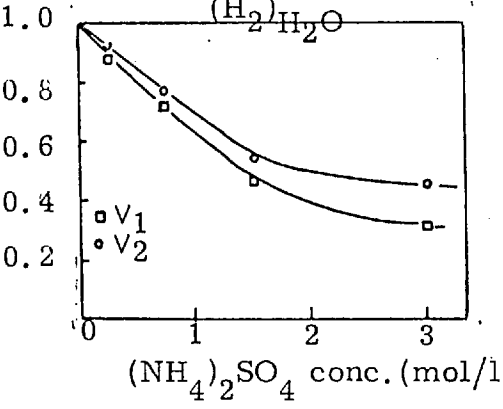


Fig. 18

$$v_3 = \frac{(O_2)_{NH_4O_4}}{(O_2)_{H_2O}}$$

$$v_4 = \frac{(H_2)_{NH_4OH}}{(H_2)_{H_2O}}$$

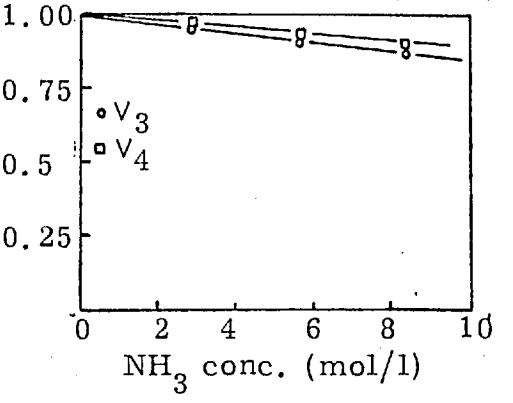


Fig. 17

Figure 18 Solubility of oxygen and hydrogen in aqueous solution of $(NH_4)_2SO_4$ as a function of the $(NH_4)_2SO_4$ concentration.

Figure 19 Solubility of oxygen and hydrogen in aqueous solution of NH_3 as a function of the NH_3 concentration.

He plotted the % wt. Ni precipitated versus the stoichiometric sodium hydroxide (%s Na) added to the nickel sulphate solution. He found that when a single solid phase was being precipitated from the solution the

% wt Ni precipitated with % sNa steadily increasing but when one solid phase was being converted into another solid phase (both in equilibrium with the solution simultaneously) by further addition of alkali the line showing % wt Ni versus % sNa shows an inflexion..

According to Mellor, J.N.[118] the nickel hexammine sulphate dissolves in water, forming a blue solution and a precipitate of green nickel metal.

1.2.2 Ammoniacal Leaching of Nickel Metal

Shimakeye et al[119] studied the ammoniacal leaching of nickel metal in the presence of oxygen under pressure. They proposed an electrochemical mechanism for the process as shown in the following scheme.

Anodic reaction:-

(1) $Ni = Ni^{2+} + 2e$

(2) $Ni^{2+} + 6NH_3 \rightleftharpoons Ni(NH_3)_6^{2+}$

Cathodic reaction:-

(3) $\frac{1}{2}O_2 + H_2O + 2e = 2OH^-$

(4) $2OH^- + 2NH_4^+ = 2NH_4OH = 2NH_3 + 2H_2O$

overall reaction

$$Ni + \tfrac{1}{2}O_2 + (n-2)NH_3 + 2NH_4^+ = Ni(NH_3)_m^{2+} + H_2O$$

They analysed the effects of the different variables on the rate of leaching. They found that the rate of leaching was decreased by the addition of $(NH_4)_2SO_4$ when the condition of leaching was: Oxygen pressure 28 p.s.i, temperature 100°C stirring velocity 700 r.p.m., NH_3 concentration 3 mol/l. and sample weight 10 gr; they pointed out that this is due to the decrease of the solubility of oxygen by the addition of $(NH_4)_2SO_4$[114-115]. On the other hand, they found that when the

concentration of $(NH_4)_2SO_4$ was low a yellowish-green precipitate was formed; they reported that this was due to the fact that OH^- in reaction (3) cannot be removed in reaction (4) and therefore hydrolysis of the nickel ammine complex ions occurred when the concentration of OH^- ions became sufficiently high. They also found that working at $(NH_4)_2SO_4$ concentrations between 0.1 and 2.25 mol/l. and the rest of the conditions similar to those described previously; the amount of nickel powder dissolved after a particular reaction time is about the same regardless of the ammonia concentration in the leach solution. They indicated that the maximum dissolution of nickel powder was obtained with $((NH_4)_2SO_4)$ = 0.5 mol/l. The rate of leaching was found to be proportional to the oxygen partial pressure and strongly dependent on the stirring speed. They reported that the rate is controlled by oxygen diffusion to the nickel surface.

1.3 PHASE RELATIONS AND CRYSTAL STRUCTURE

1.3.1 Composition and Structural Variation in Nickel Laterite Ores

In order to understand the composition and structure of nickel laterite ores better, it is worthwhile examining how the nickel laterite ores have been formed. They are the result of a process of serpentinization of ultramafic rocks and a process of weathering serpentinites. The most important nickel-bearing rock is peridotite of which a major constituent is olivine $(FeMg)_2SiO_4$ or Mg_2SiO_4, where the nickel may substitute for Fe or Mg; in addition another constituent such as orthopyroxene, plagioclase, may form part of the mafic rocks.

During the process of serpentinization the following reaction may occure:-

(1) $4Mg_2SiO_4 + 6H_2O = 2Mg_3Si_2O_5(OH)_4 + 2Mg(OH)_2$
(olivine) (serpentine) (brucete)

(2) $4Mg_2SiO_4 + 4MgSiO_3 + 8H_2O = 4Mg_3Si_2O_5(OH)_4$
(olivine) (orthopyroxene) (serpentine)

In the serpentine, Ni may also replace Mg or Fe.

Serpentinites are especially susceptible to weathering by acid-enriched ground water. During this process Mg, Fe, Ni are dissolved by water and silica forms a colloidal suspension; dissolved Fe oxidizes and precipitates mainly as goethite and remains in the upper zone. Nickel might remain associated with goethite (Nickeliferous limonite ores) or might be carried downwards and precipitated with the silica and some Mg as hydrous silicate (silicates or garnierites) when the ground water is neutralized by soil and rock (Fig. 20). Therefore during the formation of nickel laterite ores two different types of deposite are obtained: Nickeliferous limonites and hydrous silicates or garnierites.

Roorda et al[52] studied the mineralogical composition of some nickeliferous limonites. They found that goethite (∝- FeOOH) is the main constituent of the rock (at least 90%) and many of the minor elements are absorbed on the large surface of fine-grained mineral constituents. They pointed out that goethite is characterized by a poor degree of crystalinity and contains a considerable amount of adsorbed water. They also reported that part of the iron might be substituted by aluminium (Al OOH). In addition to goethite other minor components form part of the serpentine type ore, montmorillonite hematite, maghemite and chromite.

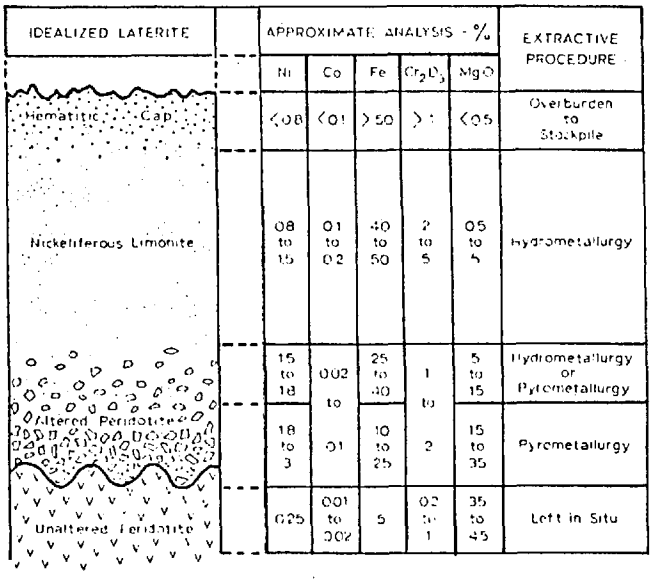


Figure 20 Idealized section through lateritic nickel deposit indicating variation in chemical and mineralogical analysis with depth and suggesting corresponding variation in method of treatment.

Kühnel R.A. et al[121] also pointed out that the degree of crystallinity of goethite is very poor, and changes with the depth of laterites profiles. They found that poorly crystalline minerals usually exhibits highly defective structures in which "strange elements" can be incorporated readily such as the nickel, chromium and aluminium in goethite.

Janot et al[122] Norrish and Taylor[123] and Nalavic and Pinta[124] have studied the problem of substitution of iron (FeOOH) by aluminium (Al OOH) in the nickeliferous limonites, and the incorporation of transition metals in such structures.

The structure of goethite (α- FeOOH) is isomorphous with diaspore and has been studied by Rice and Strong[66].

The second type of laterite ores are the so-called hydrous silicates or garnierites. Pecora et al[125] and Faust, G.[126] have published a review of the early history and nomenclature of such rocks. Lately Brindlay and Hang[127] concluded that garnierites are usually serpentine-group minerals or talc-like minerals or a mixture of these. They proposed the formula $((MgNi)_3Si_4O_{10}(OH)_2).H_2O$ for the talc-like minerals.

Springer, G.[128] has defined garnierites as nickel-magnesium hydrosilicates with or without alumina content, having x-ray diffraction patterns typical for serpentine, talc sepiolite chlorite, veriniculite or mixtures of these. He has sub-divided the garnierites

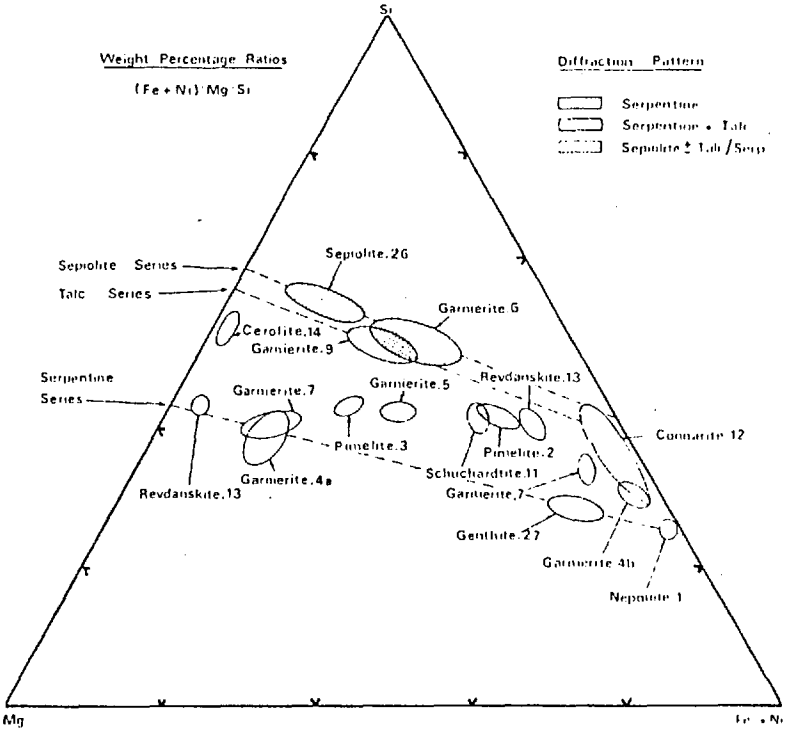


Figure 21 Measured (Fe + Ni) : Si : Mg ratios for garnierites with serpentine, talc or sepiolite-type x-ray diffraction patterns.

into three sub-groups:-

a) Nickel hydrosilicates with serpentine, talc or sepiolite-type structure (Fig. 21).

b) Chloritic nickel hydrosilicates which differ from "a" in their diffraction characteristics and in their composition (high alumina content).

c) Vermiculitic nickel hydrosilicates which are hydrosilicates with montmorillonitic and vermiculitic structure.

He has showed that for a given garnierite the determination of the exact varietal form is impossible because of low crystallinity or the presence of impurities.

1.3.2 Crystal Structure of Nickel-Olivine

Wells[129] has described the olivine structure as an assembly of SiO_4^{4-} groups with Ni^{2+} ions between them in holes between six oxygen atoms, or as infinite array of approximately close-packed oxygen atoms with Si in tetrahedral an Ni in octahedral holes (Fig. 22).

Wyckoff[130] gave the cell dimensions for Ni_2SiO_4 as follows: $a_o = 4.705\text{Å}$ $b_o = 10.11\text{Å}$, $c_o = 5.914\text{Å}$.

Taylor[131] found that nickel-olivine is orthorhombic, space group D_{2h}^{16} Pbnm and has given the following values for the lattice parameters: $a_o = 4.71\text{Å}$, $b_o = 10.13\text{Å}$ $c_o = 5.925\text{Å}$.

Studying the system NiO - SiO_2 - H_2O Pristorius[132] found that nickel olivine is the stable phase at 1000°C to 1400°C. He reported that the Ni_2SiO_4 is orthorhombic space group Pbnm - D_{2h}^{16} with the following cell parameters: $a_o = 4.725 \pm 0.04\text{Å}$,

b_o = 10.118 ± 0.08 Å, c_o = 5.908 ± 0.004Å. There are four formula weights per unit cell and the calculated density is 4.923 gr/cm^3 at 24°C. He calculated the unit cell dimensions at t°C as follows:

$$a_o = 4.724\,(1 + 9.31 \times 10^{-6}t + 3.5 \times 10^{-9}t^2)\ \text{Å}$$

$$b_o = 10.117\,(1 + 3.31 \times 10^{-6}t + 8.6 \times 10^{-9}t^2)\ \text{Å}$$

$$c_o = 5.907\,(1 + 1.20 \times 10^{-5}t)\ \text{Å}$$

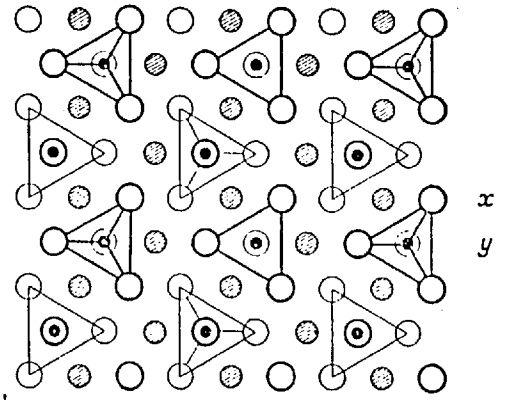


Figure 22 Plan of the structure of Ni_2SiO_4. Small black circles represent Si shaded circles nickel and open circles O atoms.

Lefebvre-Moreau[133] has given the following cell dimensions for the nickel-olivine a_o = 4.705Å, b_o = 10.11Å, c_o = 5.914Å.

1.3.3 Nickel-sulphur System, Phase-diagram

A review of the phase relations in the nickel-sulphur system has been lately published by Kelt[134]S.

The system was systematically studied by Kullerud G. and Yund R.[135] from 200°C to 1030°C, and a revision of this study for the sulphur-rich portion of the system (NiS-S system) for temperatures above 980°C has also been published[136].

Kullerud G. and Yund R.[135] (Fig. 23) reported that the compounds in the system are Ni_3S_2 (and a high temperature non-quenchable $Ni_3 \pm x\ S_2$ phase), Ni_7S_6, $Ni_{1-x}S$, Ni_3S_4, NiS_2. They showed that the high temperature $Ni_{3\pm x}\ S_2$ has a very large range of homogeneity; but even under the most rapid quenching, it decomposes to a mixture of Ni and Ni_3S_2 or Ni_3S_2 and Ni_7S_6 at room temperature. They found that Ni_3S_2 is the only condensed phase when nickel and sulphur in the 3:2 atomic ratio are heated at 200° to 500°C. The phases of composition Ni_7S_6 decompose above 573 ± 3°C and below this temperature two polymorphs exist. The high temperature form of α Ni_7S_6 has a very low symmetry, possible triclimic or monoclimic, and it shows some variation in composition. It transforms extremely slowly to β Ni_7S_6 at about 400°C. They reported that stoichiometric NiS grows from nickel and sulphur at 200°C to 700°C and inverts from millerite to the 'NiAs structure-type' somewhere between 300 and 400°C; however stoichiometric NiS is not stable at high temperatures; and NiS shows some solid solution on the sulphur side of the ideal composition $Ni_{1-x}S$ (nickel deficient). They found that vaesite (NiS_2) does not grow readily from Ni and S when these elements are heated together in the ratio of 1:2 at temperatures above 700°C this is due to the high vapour pressure of sulphur over NiS_2.

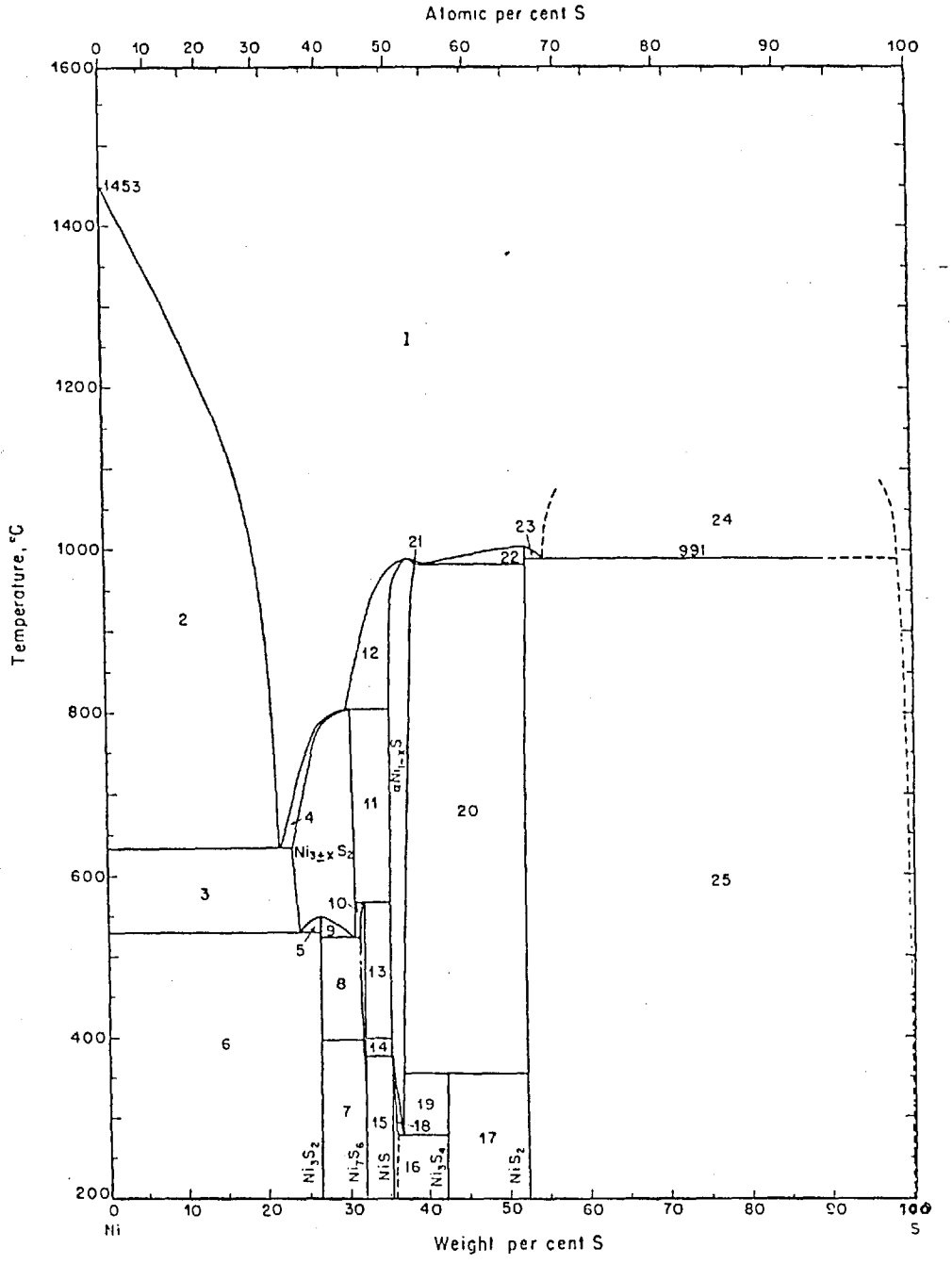


FIG 23 The 'condensed' diagram of the system Ni-S above 200° C. Vapor is present in all assemblages, and the pressure of the system is not constant. Phases present in addition to vapor in the numbered fields are as follows: 1, L; 2, $L + Ni_{ss}$; 3, $Ni_{ss} + Ni_{3\pm x}S_2$; 4, $L + Ni_{3\pm x}S_2$; 5, $Ni_3S_2 + Ni_{3\pm x}S_2$; 6, $Ni_{ss} + Ni_3S_2$; 7, $Ni_3S_2 + \beta Ni_7S_6$; 8, $Ni_3S_2 + \alpha Ni_7S_6$; 9, $Ni_3S_2 + Ni_{3\pm x}S_2$; 10, $Ni_{3\pm x}S_2 + \alpha Ni_7S_6$; 11, $Ni_{3\pm x}S_2 + \alpha NiS$; 12, $L + \alpha Ni_{1-x}S$; 13, $\alpha Ni_7S_6 + \alpha NiS$; 14, $\beta Ni_7S_6 + \alpha NiS$; 15, $\beta Ni_7S_6 + \beta NiS$; 16, $\beta Ni_{1\pm x}S + Ni_3S_4$; 17, $Ni_3S_4 + NiS_2$; 18, $\alpha + \beta Ni_{1-x}S$; 19, $\alpha Ni_{1-x}S + Ni_3S_4$; 20, $\alpha Ni_{1-x}S + NiS_2$; 21, $\alpha Ni_{1-x}S + L$; 22, $L + NiS_2$; 23, $NiS_2 + L$; 24, 2 liquids; 25, $NiS_2 + L$.

However vaesite is most efficiently synthesised when NiS and S are heated together in the 1:1 atomic ratio at 400°C to 800°C, providing that an excess (0.01 per cent by weight) of sulphur is added in order to compensate for the loss to the vapour phase. They showed that vaesite does not vary measurably from the stoichiometric NiS_2 composition and melts congruently at 1007°C $\pm$ 5°C. In the range 52 to 100 wt.% sulphur, NiS_2 was in contact with liquid sulphur. Kullerud and Yund[135] determined all the phase relations above 200°C but there is no evidence to suggest that new reactions occur below this temperature.

In contrast to Kullerud and Yung,[135] Arnold and Nalik[136] reported that vaesite melts incongruently, They found that NiS_2 melts syntectically at 1022$\pm$3°C to form two immiscible liquids, a nickel-rich liquid (L_1 52.2$\pm$1.8 wt % Ni) and a sulphur-rich liquid (L_2 0.5$\pm$wt% Ni). They found that disequilibrium crystallization causes the nickel-rich liquid to crystallize in the NiS-NiS_2 system (Fig. 24). They also reported that on cooling the two liquids proceed to crystallize independently of each other.

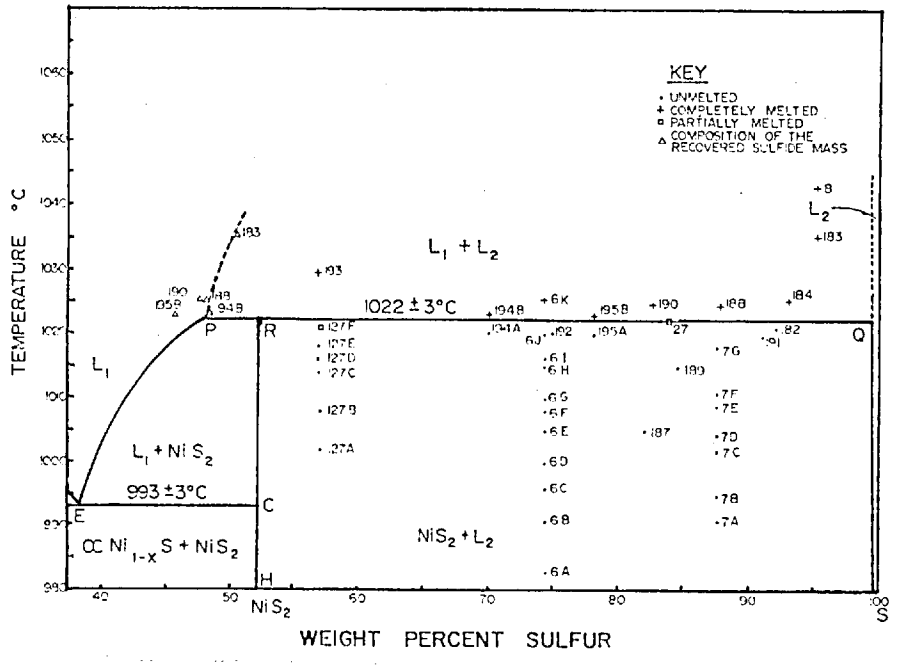


Figure 24 Phase diagram. The NiS_2-S portion of the NiS-S system.

1.3.4 Crystal Structure of Vaesite

Kerr P. F.[137] reported in 1947 the existence of a mineral in the Kesompi Mine in the Belgiam Congo approaching NiS_2 composition, he called it vaesite. He reported that the lattice constant for this natural NiS_2 is $a_o = 5.66787 \pm 0.00008$Å.

It has lately been reported that some vaesite (NiS_2) co-exists with violarite, pyrite and millerite in Black Swan nickel deposits[138] in Western Australia and also in the Vehinatai deposits[139] in Japan.

Povarennykh. A.[140] has included vaesite among minerals with the pyrite-type of structure. He reported that in these minerals, the array of units resembles that in NaCl (its crystals are cubic with four 'molecules' in a cell), the electropositive atoms replace the Na, while the centers of gravity of the S_2 pairs correspond to the position of the Cl atoms (Fig. 25). The bonds are essentially covalents with a small proportion of collectivized electrons which are responsible for the high hardness. He reported a cell dimension of $a_o = 5.67$Å, and a Ni-S interatomic distance of d(Ni-S) = 2.42Å, and S-S interatomic distance of d(S-S) = 2.09Å. The density of vaesite is 4.5.

Wyckoff R.[130] has given a cell dimension value of $a_o = 5.677$Å and Kullerud G. and Yund R.[135] have shown that $a_o = 5.689$Å.

Elliot N.[141] has studied the structure of FeS_2, CoS_2 and NiS_2 with special reference to the difference in the interatomic distances (N-S) of the three of them. He found that FeS_2, CoS_2 and NiS_2 have pyrite-type structure where the metal atoms are octahedrally surrounded by the sulphur atoms of six S_2 groups. The only difference

in the electron distribution of Fe, Co, Ni is in the '3d' sub-shells (Fe $3d^6$, Co $3d^7$, Ni $3d^8$). Elliot found that the 'd' orbitals split into two levels: lower energy (t2g) and higher energy (eg). He showed that the occupation, by one (Co) or two (Ni) electrons, of this 'eg' orbital lead to a progressive expansion of the unit cell from FeS_2 through CoS_2 to NiS_2. He reported that the cell dimension for vaesite is $a_o = 5.677\text{Å}$ and the interatomic distances d(S-S) = 2.065Å, d(Ni-S) = 2.396Å.

Nickel H. E.[142,143] reported that vaesite has the pyrite-type of structure where the octahedra (comprising one metal atom surrounded by six anions) share only corners (Fig. 26), which results in the metals being too far apart from each other for a significant degree of interaction. He has reported a Ni-Ni distance of d(Ni-Ni)=4.01Å. He showed that in NiS_2, consideration of either ionic or covalent bonding models lead to the conclusion that the eight '3d' electrons of nickel do not participate in the metal-sulphur banding. He pointed out that the structural stabilities of the disulphides of Fe, Co and Ni can be explained by the tendency of these compounds to crystallize in structures that permit the maximum spin-pairing of non-bonding electrons of the '3d' sub-shell of the metal. In the pyrite-type of

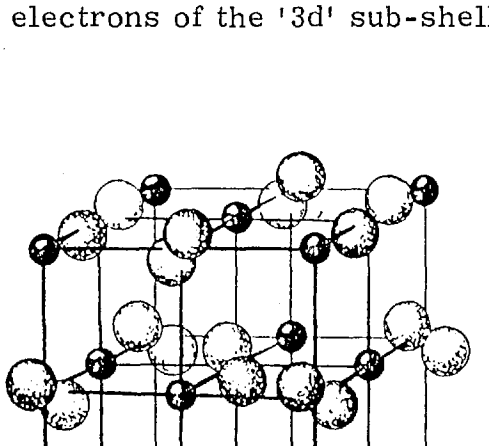


Figure 25 The NiS_2 (vaesite) structure.

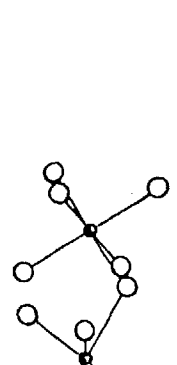


Figure 26 Combination of octahadra in vaesite

structures this can be done by complete occupancy of the t_{2g} level.

Table 1 gives the values of the lattice parameters and the interatomic S-S Ni-S and Ni-Ni distances given by different works.

TABLE 1

Unit Cell Dimensions and Interatomic Distances for NiS_2 - Cubic T_h^6 - Pa3 z = 4; 1

a_o(Å)	S-S Å	Ni-S Å	Ni-Ni Å	Reference
5.66787	-	-	-	Kerr (137)
5.67	2.09	2.42	-	Povarennykh (140)
5.677	-	-	-	Wyckoff (130)
5.689	-	-	-	Kullerud (135)
5.677	2.065	2.396	-	Elliot (141)
-	-	-	4.01	Nickel (142-143)
5.668	-	-	-	Ramdohn (144)

CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 SYNTHESIS

2.1.1 Synthesis of Nickel Olivine (Ni_2SiO_4)

The Ni_2SiO_4, nickel olivine or nickel ortho-silicate was prepared using a co-precipitation technique, the so called gel-method[145-146].

The gel-method involved the use of a high purity organic compound, tetraethyl ortho-silicate (T. E. O. S.), as the source of silica.

The required stoichiometric amount of nickel powder was dissolved in dilute nitric acid, to convert this element to nitrate; the solution was then evaporated to dryness (or nearly so) to remove excess nitric acid, the residue was re-dissolved in a small volume of water. This solution was then transferred into a beaker containing the required amount of T. E. O. S. dissolved in an equal volume of 95 per cent ethanol, more alcohol was used to rinse the beaker initially containing the nitrate solution to ensure quantitative transfer. The formation of the gel was accomplished by adding concentrated (0. 88 s. g.) ammonia solution dropwise to the solution while it was stirred continuously and the temperature was kept at about 50°C. The gel was allowed to stand overnight at room temperature to complete the gelling and then evaporated to dryness in an oven at 120°C. The completely dry gel was ground in an agate mortar and transferred to a porcelain dish where the green powder produced was ignited over a Bunsen flame to decompose the nitrate and to drive off residual water and ammonia. The ignited powder was transferred to an alumina crucible and placed in a furnace

where it was kept at 1300 to 1400°C for about 72 hours. The green powder produced was analysed using x-ray diffraction. The analysis revealed the existence of a considerable amount of NiO in the product, together with some Ni_2SiO_4 (Fig. 38, Table 7). This means that the synthesized product is a compound that lies in the area between zero weight per cent of Si and 28.68 wt % of SiO_2 in the equilibrium diagram for the system NiO-SiO_2 (Fig. 26). The described procedure was repeated several times but, in all the cases, x-ray diffraction analysis of the produced powder revealed the existence of NiO.

T.E.O.S. is a highly volatile compound; therefore it is quite likely that some SiO_2 might be lost by evaporation during the process of formation of the gel. When the process was carried out using 15 wt % in excess of the required amount of T.E.O.S., no NiO was detected by x-ray diffraction. However a very weak line having do = 4.05 Å in the x-ray film revealed the existence of some α-Cristobalite (Fig. 38, Table 8). Nevertheless the product obtained was considered adequate for the purpose of the experiment to be carried out.

Four samples (0.1 gr. each), two from NiO.Ni_2SiO_4 solid and another two from Ni_2SiO_4 solid, were dissolved in nitric acid using a method described in section (2.3.2). The solutions were analysed for Ni using atomic absorption and gravimetric methods as described in section (2.3.2).

The results of the different types of analysis are given in Table No. 2.

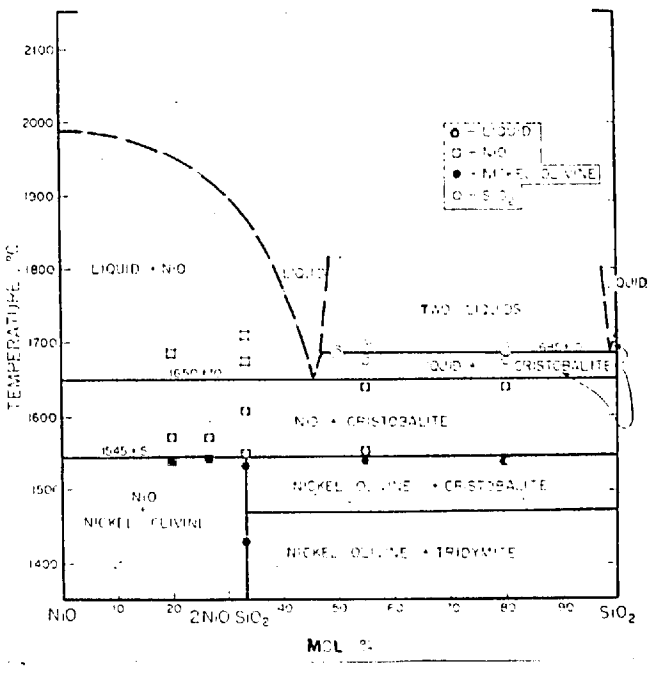


Figure 26 Equilibrium diagram for the system $NiO-SiO_2$

TABLE No. 2

	Solid 1	Solid 2
	Nickel oxide	α Cristobalita
X-ray diffraction	Nickel olivine	Nickel olivine
Atomic Absorption	Ni wt % = 67.0	Ni wt % = 50.7
Gravimetric	-	Ni wt % = 50.9

2.1.2 Synthesis of Vaesite

Vaesite (NiS_2) was synthesized by heating at 700°C a mixture of a previously synthesized NiS (or $Ni_{1-x}S$) with sulphur in excess of the amount required for NiS_2.

The technique used for the synthesis of NiS was identical to that described by Kelt[134], it involves the use of a two-compartment silica vessel. The required amount of sulphur was transferred into one of the compartments and melted. The required weight of nickel was placed into the second compartment. The silica vessel was evacuated using an oil-diffusion pump and, at the same time, sealed. The nickel used was previously reduced in a stream of hydrogen at 500°C.

The silica-vessel was then placed in a horizontal electric furnace. The heating was controlled by a transitol electronic controlled and the temperature was checked with a 13% Pt-Pt/Rh thermocouple, connected to a 'thermocouple potentiometer'. The temperature was slowly raised to 400°C and maintained there for two days to allow the sulphur to react with the metal in the vessel. The temperature was then increased to 700°C and the vessel was left in the furnace for two days. The vessel was then quenched. A sample from the solid was finely ground and analysed using x-ray diffraction. The x-ray diffraction pattern was identified as that of αNiS (Fig. 27, Table 4). Another sample from the same solid that had been kept at room temperature for six months was also finely ground and analysed using x-ray diffraction after this period of time. The x-ray pattern was identified as a mixture of αNiS and βNiS (Fig. 27, Table 4) as was expected (section 1.3.3).

Vaesite (NiS_2) was synthesized using a silica-vessel identical to the one described previously.

Two per cent excess of the amount required of sulphur was placed into the first compartment of the silica-vessel and melted. The required amount of NiS that was previously ground was transferred into the second compartment of the silica-vessel. As before the vessel was evacuated and sealed. The vessel was placed in the same horizontal furnace used previously. The temperature was slowly raised to 400°C and was kept there for two days; after this period of time the temperature was raised to 700°C and the vessel was maintained in the furnace for eight days. The solid formed was not melted due to the fact that NiS_2 melts into two immiscible liquids which crystallized separately on cooling (section 1.3.3). At the end of the eight days heating period the vessel was allowed to cool in the furnace.

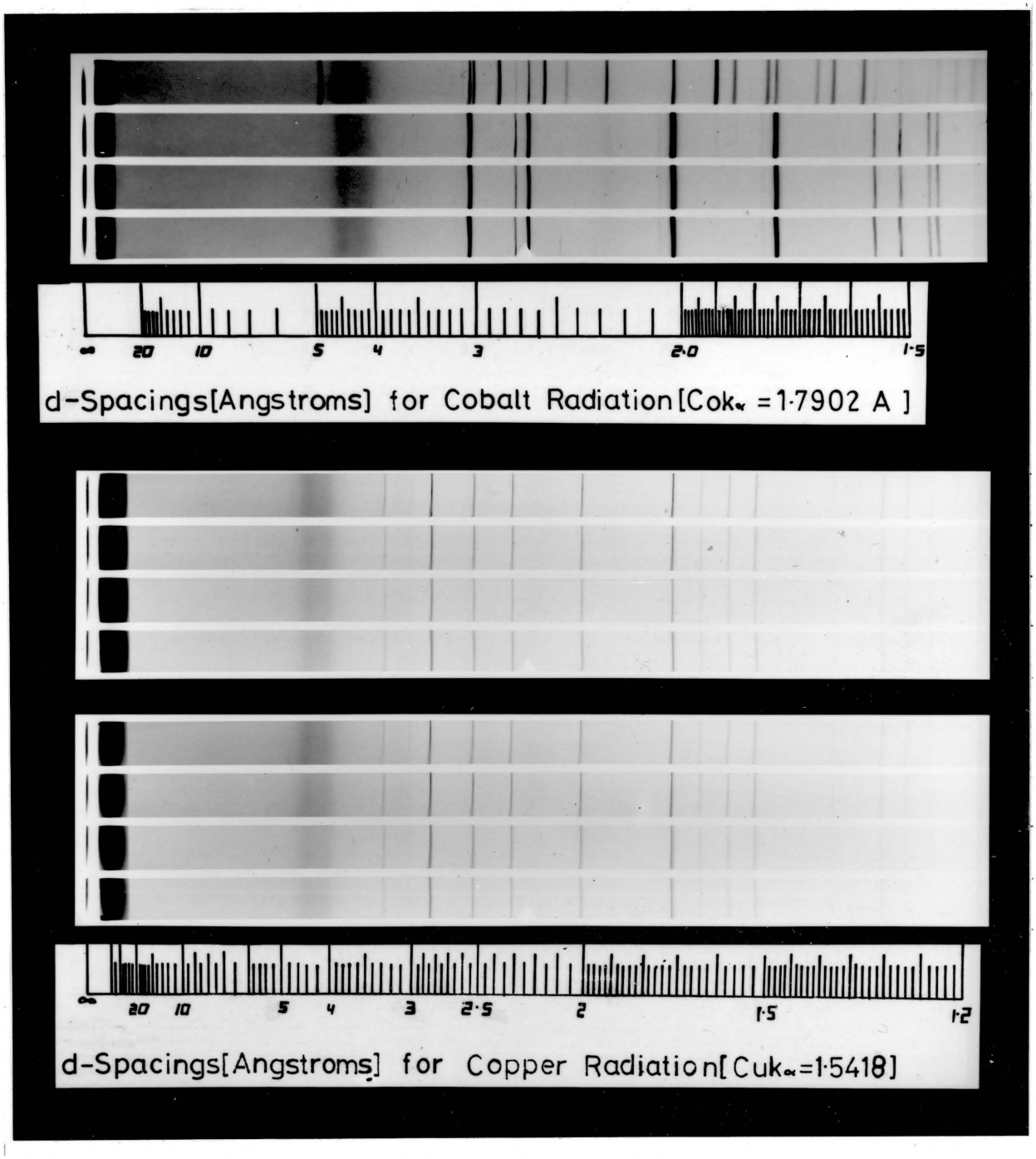


Fig. 27: X-Ray Patterns of the Synthetic NiS and NiS_2

(X-ray Diffraction Data are given in Table 4)

(1) NiS three months after being synthesized (Mixture of NiS + NiS)
(2) Synthetic NiS
(3) Synthetic NiS
(4) Synthetic NiS
(5)-(12) Synthetic NiS_2 samples taken from different parts of the material.

TABLE 4

X-Ray Diffraction Data for the Synthetic Sulphides

-NiS ASTM 12-41		- NiS ASTM 2-1280		NiS_2 ASTM 11.99		Sulphide No. 1		Sulphide No. 2		Sulphide No. 3	
d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I	d(Å)	I	d(Å)	I
4.81	60	2.96	80	3.27	20	4.8	w	2.95	s	3.28	w
2.946	40	2.58	70	2.83	100	2.95	w	2.65	m	2.84	s
2.777	100										
2.513	65	1.97	100	2.54	40	2.93	w	2.58	s	2.54	w
2.406	12	1.71	80	2.32	40	2.75	s	1.98	vs	2.32	w
2.228	55	1.52	30	2.00	50	2.58	w	1.71	s	2.01	w
1.8631	95	1.48	30	1.892	5	2.50	w	1.52	w	1.70	s
1.8178	45	1.42	30	1.707	80	2.38	m	1.48	w	1.64	w
1.7372	40	1.33	30	1.634	20	2.23	w	1.44	vm	1.57	w
1.6340	18	1.29	60	1.570	30	1.97	s	1.42	w	1.52	w
1.6037	35	1.21	20	1.514	30	1.85	s			1.30	m
1.5470	25	1.13	10	1.375	10	1.82	w			1.265	m
1.3884	8	1.12	10	1.336	5	1.72	w			1.235	m
1.3343	4	1.09	30	1.304	20	1.705	w				
1.3008	10	1.05	50	1.268	20	1.62	vw				
1.2560	8	1.03	50	1.234	20	1.59	w				
1.2023	6	1.00	10	1.208	10	1.54	w				
1.1283	4			1.158	30	1.52	vw				
1.1447	6			1.133	5	1.475	m				
1.1133	16			1.113	5	1.42	m				
				1.091	60	1.40	m				
						1.37	m				

When the silica-vessel was taken out of the furnace, it was observed that part of the excess sulphur was condensed in one of the vessel compartments. The sulphide formed was in the other compartment and it appeared as a single mass having a grey colour.

Several samples from different parts of the solid formed were finely ground and analysed using x-ray diffraction (Fig. 27 Table 4); the x-ray diffraction pattern revealed the existence of only NiS_2 without any residual $Ni_{1-x}S$. The solid was crushed under acetone and annealed in the presence of more sulphur at $700^{o}C$ for five days. The ground product was again analysed using x-ray diffraction. The x-ray diffraction pattern revealed again the existence of only NiS_2.

Several other analyses were made to check the homogeneity and composition of the material.

The microscopic examination on polished sections revealed that the particles inspected were all pale grey 'metallic' with many pits or dark spots. Only one phase was apparently present.

Electron-probe microanalysis confirmed the homogeneity of the material and the existence of topographic effects revealed the existence of many particles with pits (Fig. 28). The average composition of the NiS_2 was determined using CdS and Ni metal as standards. The results were as follows:- S(57.1 wt %, 70.9 at %), Ni (42.9 wt %, 29.1 at %). This seemed to indicate that the content of sulphur determined by this method was higher than that for NiS_2 (52.2 wt %).

Three samples of the synthesized material (0.1 gr each) were dissolved in a mixture of hydrochloric and nitric acid as described

in section (2.3.2), and analysed using atomic absorption spectrophotometry. The results were, in Ni wt %: Sample 1: 46.50 wt %, Sample 2: 47.00 wt %, Sample 3: 47.00 wt %, that is a Ni weight per cent average of 46.80 wt % Ni.

Nickel in the solid form was also determined gravimetrically, using an alcoholic solution of dimethyl-glyoxime as precipitating agent, as described in section (2.3.2). This method gave a result in better agreement with the theoretical weight per cent of nickel in NiS_2 (47.8 wt % Ni). The results were, in Ni wt %: Sample 1: 47.5 wt %, Sample 2: 47.2 wt %, Sample 3: 47.6 wt %. The average value is 47.5 wt %, Ni, this value was considered to be the real nickel content of the solid ($NiS_{2.06}$).

Table 3 gives the wt % of Ni and S using different methods of analysis.

TABLE 3

Determination of the Composition of NiS_2

	Ni wt %	S wt %	Formula
Electron-microprobe	42.9	57.1	$NiS_{2.43}$
Atomic-absorption	46.8	53.1	$NiS_{2.07}$
Gravimetric	47.5	52.5	$NiS_{2.06}$
Stochiometric	47.8	52.2	NiS_2

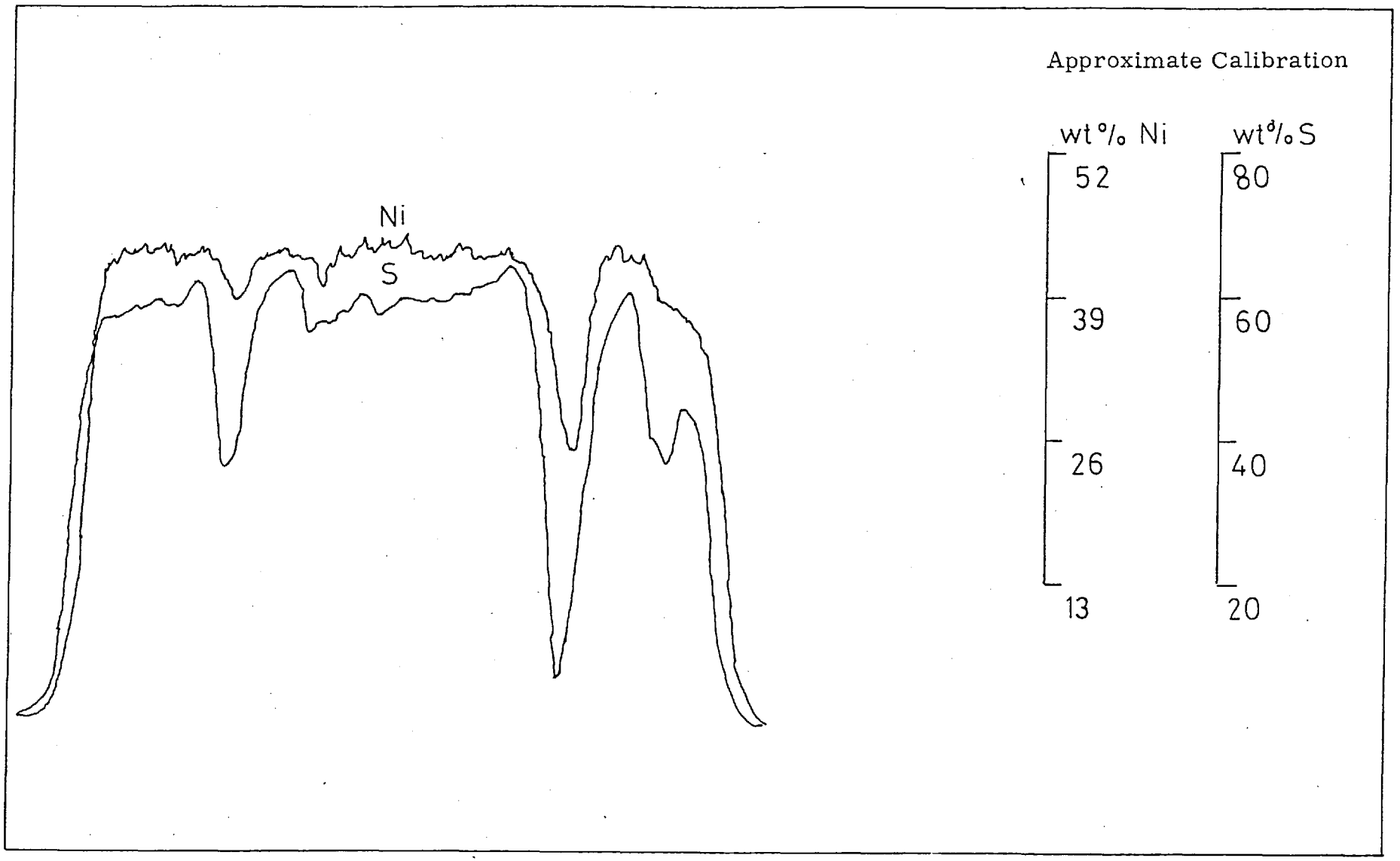


Fig. 28 Electron Microprobe Trace Showing the Variation of Nickel and Sulphur Composition of the Original Vaesite

2.2 APPARATUS AND EXPERIMENTAL PROCEDURE

2.2.1 Hydrothermal Treatment

A required amount of nickel olivine (0.5 gr.) and a variable weight of recrystallized sulphur were mixed together and placed in a narrow-necked ampoule; 3cc of distilled water was added to the ampoule using a pipette. The ampoules were previously made by heating thick-walled pyrex test-tubes. The ampoules were sealed with an oxygen torch and the sealed tubes were manually shaken and heated at the required temperature during the required period of time in a one gallon autoclave that was two-thirds filled with water to balance the internal vapor pressure within the tubes. The heating was controlled by a transistol electronic controller and the temperature inside the autoclave was controlled by an iron-constantan thermocouple that was introduced by means of a thermowell in the autoclave.

The tubes were kept inside the autoclave for the required period of time and the autoclave was then switched off. On cooling the tubes were taken out of the autoclave. Figure 29 shows the ampoules before and after the reaction for different reaction conditions. The ampoules were then cut open and the contents filtered. The green liquid obtained (presumably $NiSO_4$) was analysed using the atomic absorption method. The solid was washed with water and acetone and dried. Unreacted sulphur in the solid was dissolved in CS_2 using a Soxhlet extractor apparatus with single thickness 10 x 50 cellulose extraction thimbles for holding the solid product. The solid obtained was analysed using x-ray diffraction as described in sections 2.4.1 and 2.4.2.

No attempt was made to carry out the hydrothermal treatment directly inside the autoclave without the use of ampoules because of fears of corrosion troubles.

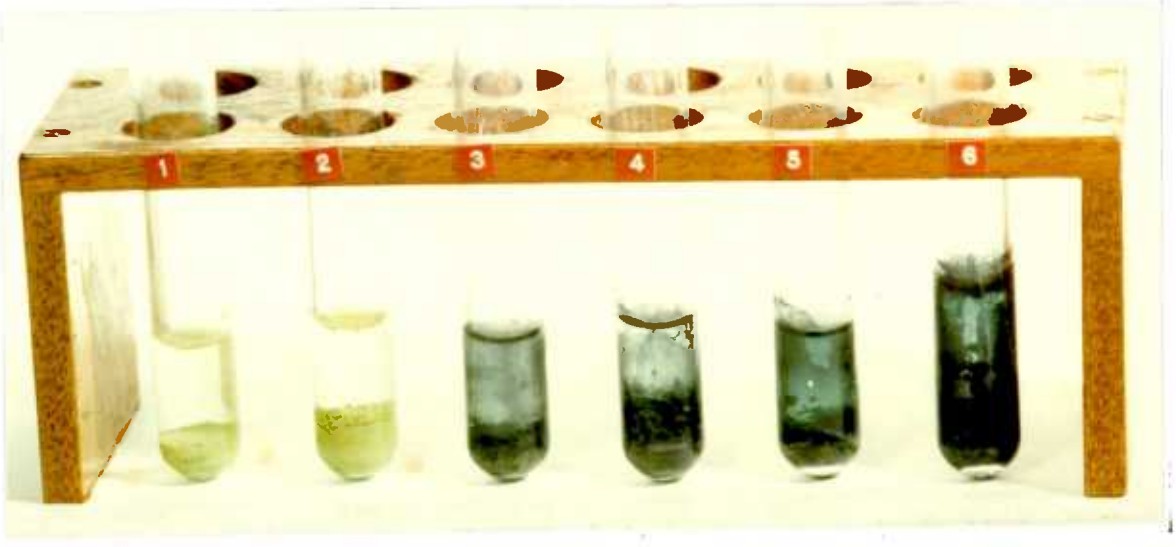


Fig. 29 Photograph showing the Ampoules before 1-2) and after (3-6) the hydrothermal treatment

(1) Ampoule containing: 0.5 gr of Ni_2SiO_4, 0.2 gr of S and 3cc H_2O

(2) Ampoule containing: 0.5 gr. of Ni_2SiO_4, 1.8 gr. of S and 3 cc of H_2O

(3) Ampoule (1) after the hydrothermal treatment (2 hours, 200°C)

(4) Ampoule (2) after the hydrothermal treatment (2 hour, 200°C)

(5) Ampoule (1) after the hydrothermal treatment (6 hour, 240°C)

(6) Ampoule (2) after the hydrothermal treatment (6 hour, 240°C)

Some experiments were also carried out in order to determine the degree of hydrolysis of nickel hexa-ammine. Ten cubic centimetres of a solution with the required concentration of Ni (which was obtained by dissolving a required weight of $NiSO_4$ in NH_3 solution), NH_3 and $(NH_4)_2SO_4$ were placed in a narrow-necked ampoule, which was made as previously described, and the ampoule was sealed. The tubes were heated in an autoclave in the same way that has previously been reported. On cooling the ampoules containing a visible precipitate were cut open and the contents filtered. The solid product was washed with water and acetone and dried. The solids were analysed using x-ray diffraction as described in section 2.4.1. The liquid was analysed by atomic absorption as described in section 2.3.1.

2.2.2 Leaching Apparatus

All leaching experiments were carried out in a stainless steel autoclave of 300 ml. Stirring was provided by a magnetic assembly known commercially as a 'magnedrive' unit; it was mainly made up of a four blade impeller combined with one baffle (Fig. 30). The impeller shaft was hollow, with openings at the impeller end and at the top of the shaft. This design improved the mixing between the gas and the liquid phases and therefore improved the rate of mass transfer.

The autoclave, as well as the needle valves, cross pieces, impeller, baffles, filter and pipes were supplied by Autoclaves Engineers of Pensylvania, U.S.A. The material of construction used was 316 stainless steel.

A cylindrical heater was fitted tightly around the body of the autoclave to heat it to its working temperature. The temperature was controlled by a temperature controller designed by Eurotherm. This received its signal from an iron-constantan thermocouple which was placed in a thermocouple sheath bolted to the head of the autoclave.

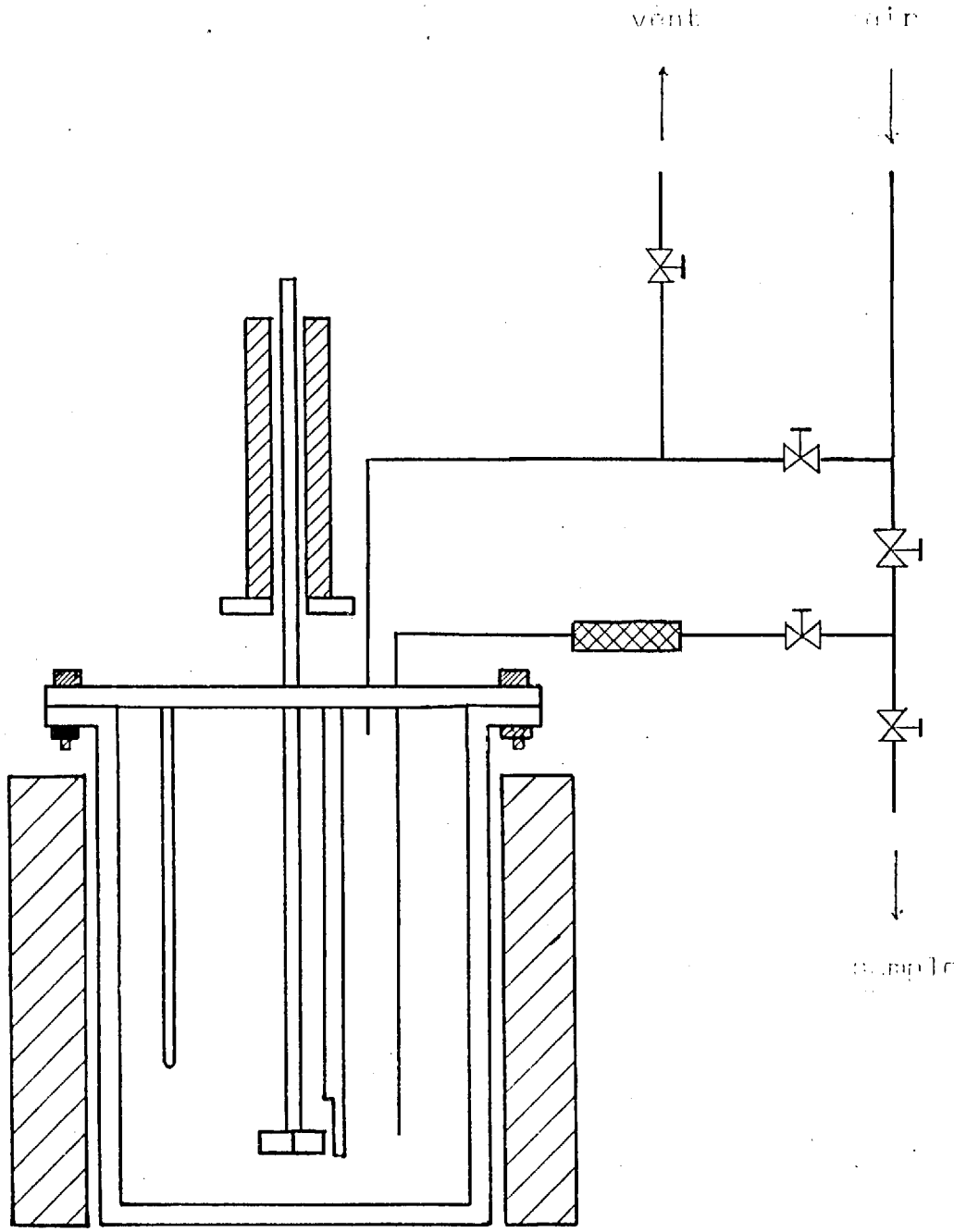


Figure 30 - Schematic drawing of the autoclave used in the leaching experiments

The impeller was driven by a compressed air motor. The air was provided by a compressor. The volume of air delivered to the motor determined its speed and it was controlled by a metering valve in the line. The stirring speed was measured by the use of a tachometer. The signal was provided by a magnetic 'pick-up' which slipped over the stationary part of the 'magnedrive' unit immediately adjacent to and flush with the top of the rotating magnets. Sometimes the stirring speed was also checked with a stroboscope.

The pressure in the autoclave was controlled by a pressure gauge capable of measuring from 10 p.s.i. to 2000 p.s.i.

The experimental procedure was carried out as follows:-

After the autoclave was charged with the 'reactant' materials, other than oxygen, the head of the autoclave was tightened down to the main body of the autoclave. A torque wrench was used to deliver 35 ft lbs to each of the eight bolts, which were tightened by opposites in clockwise rotation. This procedure was followed in order to prevent undue distortion of the gasket.

The main line leading from the gas cylinders to the pressure control valve was flushed with nitrogen. The gas was then released from the line by means of a line 'vent' valve. The autoclave was then flushed with nitrogen three times; each time the system was pressure tested. Once this was pressure tight, the gas was released by opening the 'autoclave vent' valve and the 'line vent' valve. All the valves were then closed, the power was switched on and the heating current adjusted to 2 amps while the motor speed was adjusted to a nominal value of 150 r.p.m. When the working temperature of the autoclave was attained, the motor speed was adjusted to the working value, the valve on the

air cylinder was opened, the air was introduced into the autoclave by the 'inlet valve' and the pressure adjusted to the required value.

Aliquots of the leach solution were extracted periodically through a filter on a condenser. The amount of solution remaining in the pipes and the filter after each sample was obtained was injected back into the autoclave by opening the 'sample flush valve' and the pressure was again adjusted to the required value.

At the end of the leaching run the compressed air motor and the heating system were switched off and the autoclave was allowed to cool down. It was then opened and its contents were filtered to separate the leach liquor from the solid residue. The latter was washed with distilled water and acetone and dried. It was, then analysed using x-ray diffraction, microscopic examination and electron-probe microanalysis.

2.3 ANALYSIS OF SOLUTIONS

2.3.1 Atomic Absorption Spectrophotometry

The nickel concentration in the leach samples as well as the nickel concentration in the solutions from the hydrothermal treatment were determined by the atomic absorption method.

The apparatus used was a Perkin-Elmer 290E with a graphical read-out on a Perkin-Elmer 56 pen recorder. The analyses were made using a multi-element hollow cathode lamp (either for the elements Ag-Cu-Fe-Ni-Cr or for the elements Fe-Cu-Ni). The wavelength used was 2320Å. The technique described in the Perkin Elmer methods manual[148] for the determination of nickel was followed. Calibration curves of deflection versus concentration were drawn using standards prepared from 1000 ppm stock solution. All the samples were diluted with 0.1M HCl using a variable diluter. The standard solutions were also prepared using 0.1M HCl solution for the dilution. Linearity for the calibration curve was obtained in the range 0 to 5 ppm. The working range was 0 to 7 ppm.

The required dilutions range from 20 times to 200 times, so the diluter was used in the range of 0.05 ml to 0.5 ml samples.

2.3.2 Gravimetric Determination of Nickel

The amount of nickel in the two synthesized solids, Ni_2SiO_4 and NiS_2 was determined by gravimetric means using an alcoholic solution of dimethyl-glyoxime as precipitating agent.

The two synthesized solids were first dissolved as follows:

a) The dissolution of Ni_2SiO_4 was carried out using a method described by Lewis and Ott[149]. 0.1 gr. of solid was

treated with nitric acid and allowed to stand for a few minutes. The solution was treated until red fumes were expelled and a few crystals of potassium chlorate were added continuously from time to time. When decomposition appeared to be complete, the solution was evaporated to dryness and dissolved in HCl, it was again evaporated to dryness and redissolved in HCl. The solution was diluted and filtered. After the residue was washed, the residue and filter-paper were ignited and fused with sodium carbonate. The cooled melt was dissolved in HCl and added to the original solution for analysis.

b) NiS_2 was dissolved using a method described by Kelt[134]. 0.1 gr. of nickel sulphide was digested in a Kjeldahl flask with concentrated nitric acid, bromine and carbon-tetrachloride. The flask was heated continuously until the bromine had been driven off. It was then evaporated to dryness and dissolved in concentrated hydrochloric acid, again evaporated to dryness and redissolved in dilute HCl to the required volume.

The gravimetric determination of nickel was carried out using a method described by Vogel[150]. The process required to adjust the pH of the solution to 7.5 to 8 using ammonia solution. The pH of the solution was measured using a glass electrode with a PYE pH meter. The electrode was standardized using buffer solution tablets at pH = 4.00 and pH = 6.99 at 25°C.

2.3.3 Qualitative Analyses of the Sulphur Species in the Leach Solution

It has been reported that during the ammoniacal leaching of metal sulphides under oxygen pressure the following oxyacids of

sulphur might be formed: Thiosulphates $S_2O_3^=$, Thionates $S_xO_6^=$ (x = 3, 4, 5, 6) Amidosulphates or sulphamates $NH_2SO_3^-$, sulphates $SO_4^=$. The presence in the leach solutions of some of these compounds was tested qualitatively using a method proposed by Karchmer[151]. Three different types of qualitative test were carried out. Test 1 was carried out in order to test for the presence of thiosulphates ($S_2O_3^=$) in the leach solutions. Test 2 was carried out in order to determine whether polithionates were present. Test 3 was performed to test for the presence of sulphamates and sulphates.

Test 1 - 0.5 gr. of sodium azide are dissolved in 50 ml of 0.1N iodine solution. A drop of the solution to be tested is mixed with a drop of iodine-azide solution. If the sample contains $S_2O_3^=$ bubbles will develop due to the catalysis of the reaction.

$2NaN_2 + I_2 = 2NaI + 3N_2$ by traces of $S_2O_3^=$.

Test 2 - The presence of trithionates, tetrathionates, pentathionates and hexathionates is tested using mercurous nitrate solution. With trithionate mercurous nitrate gives a black precipitate, the other thionates produce a yellow precipitate.

Test 3 - The presence of $SO_4^=$ in the solution is tested using barium chloride solution. If $SO_4^=$ is present in the solutions to be tested a white precipitate will appear when these solutions are mixed with a solution of barium chloride. After filtering the mixture, the clean solutions are treated with a mixture of barium chloride and sodium nitrite, a white precipitate will be obtained if amidosulphate is present.

A solution containing $S_2O_3^=$, $NH_2SO_3^-$ and $SO_4^=$ as well as free ammonia was prepared in order to confirm tests 1, 2 and 3 before

treating the leach samples. This solution was treated with iodine in order to convert part of $S_2O_3^{=}$ into $S_4O_6^{=}$, so that the final solution will contain $S_2O_3^{=}$, $S_4O_6^{=}$, $NH_2SO_3^{-}$, $SO_4^{=}$ and free NH_3. The results of tests 1, 2 and 3 in this solution as well as in the leach solution are given in section 4.1.9.

Ammonia was found to interfere in test 2 because it gives a black precipitate with mercurous nitrate. In order to avoid this interference, ammonia in the solutions was eliminated by heating the solutions until the gases produced no longer turned the litmus paper blue, before test 2 was carried out.

2.3.4 Quantitative Analyses of Sulphate in the Leach Solution

The existence of sulphate in the leach solutions was confirmed by test 3 described in section 2.3.3.

The analyses were made using a method described in Kelt[134]. The process involves the indirect determination of sulphate by atomic absorption analysis using barium chloride.

A number of standard sulphate solutions were prepared. A known amount of standard solution of barium chloride was added to the standard solutions of sulphate. This amount was sufficient to react with all the amount of the sulphate present in the solutions of sulphate. The amount of barium remaining in the solution was measured by atomic absorption analysis and the readings were plotted directly against the initial sulphate concentrations.

A nitrous oxide/acetylene flame was used for the determination of barium. Such a flame will cause partial ionisation of barium and,

in order to overcome this problem a large amount of potassium chloride was added to the solutions, the potassium being preferentially ionized.

The preparation of the standard solutions for the calibration curve for the analysis of the sulphate was carried out as follows:- 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 0.9cc of standard potassium sulphate solution containing 1000 ppm of $SO_4^{=}$ were pipetted into different 50 cc flasks; 2 cc of standard Ba^{++} solution containing 500 ppm of barium and 20 gr/l of potassium chloride were added to the flasks and the solutions were made up to the mark. Figure 31 represents the calibration curve used for the determination of sulphate by atomic absorption.

Different amounts of leach solution, varying from 2.5 cc to 0.05 cc depending on the leach solution sample, were pipetted into different 25 cc flasks. 1 cc of standard barium solution containing 500 ppm of Ba^{++} and 20 gr/l of potassium chloride were added to the flasks, and the solutions were made up to the mark. These solutions and the standard sulphate solution were shaken and allowed to stand for 24 hours to complete the precipitation of barium sulphate. All the solutions were centrifuged at 4000 r.p.m. for 15 minutes in an M.S.E. centrifuge.

The clear solutions were analysed for barium using a Perkin Elmer 290E spectrophotometer.

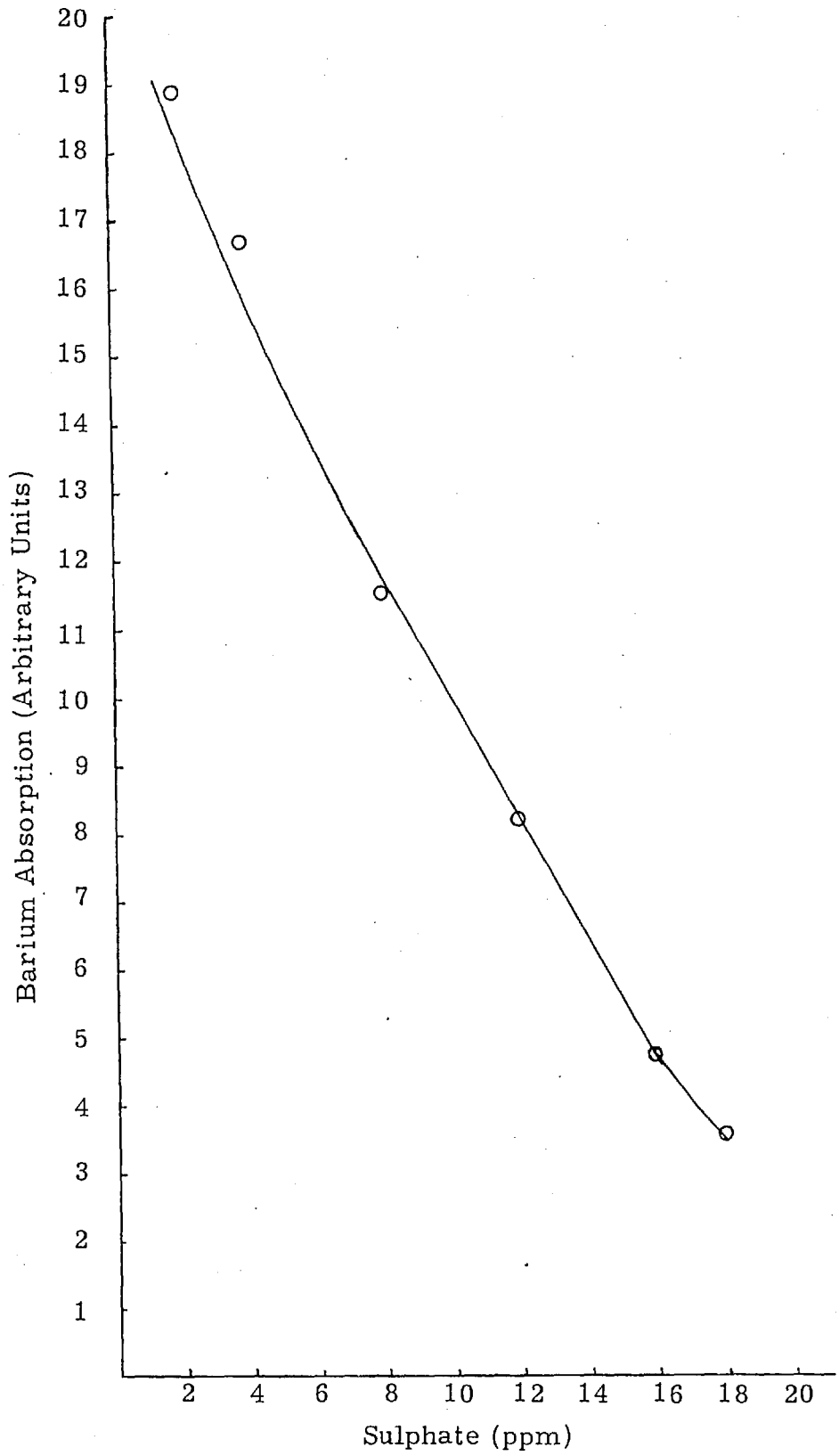


Fig. 31 Calibration Curve for the Determination of Sulphate by Atomic Absorption Spectrophotometry

2.4 ANALYSIS OF SOLIDS

2.4.1 X-Ray Diffraction Analysis

For the identification of the compounds present in the starting materials, after the hydrothermal treatment and in the leach residues the x-ray powder diffraction method was used.

The analyses were carried out in a Guinier de Wolff camera of the focussing type with a focussing monochromator. The monochromator is a quartz slab cut at $4\frac{1}{2}^{o}$ to the (101) planes and bent assymetrically to approximate to a logarithmic spiral, this may be adjusted for various source wavelengths, but does not provide perfect focussing. Since the monochromator provides a line focus with a broad x-ray source, four samples can be stacked above one another if a crystal with a large vertical dimension is used.

The Guinier de Wolff camera used has the following advantages over the Debye-Scherrer camera:

a) Four samples can be photographed at the same time,

b) The x-ray pattern produced by the camera is equivalent to that produced by a Debye-Scherrer camera with a diameter twice as large,

c) The monochromator eliminates sufficiently the white radiation in the beam so that the x-ray patterns have a low background intensity; this allows even very weak lines, such as superstructure lines to be observed. One disadvantage of the Guinier de Wolff camera is that it records reflections contained in the range 0^{o}-40^{o} of Bragg angle, reflections whose angles are greater than 40^{o} cannot be observed.

Four powder samples which were obtained by finely grinding a small amount of the material to be analysed were placed in a divided flat holder and secured by cellotape. Cellotape itself gives two diffraction bands which can easily be recognized and ignored. On the other hand, due to the fact that the depth of the particles through which the beam passed was very thin compared to the width, the sample holder was oscillated in its own plane to reduce any spottiness in the reflections caused by preferentially orientated crystals. The infinity line for the x-ray beam was found by removing the lead shutter from the beam path for four seconds while the generator power was at minimum.

The exposure time was variable from one hour to three hours. The exposure time influences the intensity of the lines, and therefore it was carefully controlled in order to get an intensity value which fitted inside the graph paper when a suitable scale was used for the measurement of the intensity by microphotometric techniques. The x-ray generator was operating at 30 Kv and 20 ma. Both copper and cobalt radiations were used, the wavelength of the copper radiation was 1.5418$\mathring{A}$ and that of the cobalt 1.7902$\mathring{A}$.

The specified radius for the camera is 5.7 cm. Two types of special rules, one for copper radiation and another for cobalt radiation, which were designed so as to take account of the fact that the radius of the camera is 5.7 cm, were used to measure the 'd spacing'. This method was considered good enough for the purpose of identification of the powder speciments, therefore no attempt was made to calibrate the films, which would have allowed us to cover any mistakes due to miscalculation of the camera radius, bad alignments, film shrinkage and other problems.

The intensities of the x-ray patterns were estimated visually, except in the cases when quantitative analysis was carried out, when the measurements were made using a Joyce Lobel microdensitometer with a graphical output. The relative intensities of the lines were estimated by comparing the heights of the peaks.

2.4.2 Quantitative Analysis by x-ray Diffraction Methods

Quantitative analysis by x-ray diffraction is based on the fact that the intensity of the diffraction pattern of a particular phase in a mixture of phases is proportional to the amount of that phase present in the mixture (except for an absorption correction). Therefore for a mixture of two components a calibration curve (per cent of a component in the mixture versus intensities ratio for two selected diffraction lines, one for each component) can be plotted. This method of analysis is not very accurate since the intensity of a selected diffraction line depends not only on the concentration of a particular component but also on its density, mass absorption coefficient as well as the mass absorption coefficient of the mixture. On the other hand, a number of other factors influence the results and therefore they also are sources of error in the measurement of intensity by microphotometric techniques. Despite these facts, quantitative analysis by x-ray diffraction methods was carried out by reference to a calibration curve prepared from synthetic mixture of the two components.

The required amounts of NiS_2 and Ni_2SiO_4 that were previously synthesized as has been described in sections 2.1.1 and 2.1.2 were finely ground (size less than 45 microns which seemed to be enough to provide patterns with smooth lines), weighed and mixed

together in a glass vial. Ten standard samples were prepared in this way. The weight per cent of NiS_2 and Ni_2SiO_4 in each one of the standard samples is shown in Table 5.

A Guinier de Wolff camera was used to obtain the x-ray powder diffraction patterns of the standard samples and the samples to be analysed. The exposure timewas from 1-10 to 2.30 hours and the x-ray generator was operating at 30 kv and 20 ma. Figure 32 shows the x-ray powder diffraction patterns for the standard samples. Table 6 shows the x-ray diffraction data for the standard samples, the intensities were visually stimated.

The intensities of the x-ray patterns were estimated using a Joyce Lobel double beam microdensitometer. Figure 33 shows the graphical output of the x-ray diffraction pattern for the standard No.4 (68.12 wt %, NiS_2, 31.88 wt % Ni_2SiO_4 obtained using a microdensitometer with the scale used (2:1) it covered a 'd spacing' range from 14Å to 4.0Å.

In theory any couple of diffraction lines, one for each component of the mixture, can be used to calculate the intensity ratio but the use of the stronger lines and the lines whose intensities are not too different improves the accuracy[153, 152]. The diffraction lines of 'd spacing' values I_1= 2.32Å, I_2 = 2.83Å were selected for NiS_2 and the diffraction lines of 'd spacing' values I_1^1 = 2.430Å, I_2^1 = 2.488Å, I_3^1 = 2.740Å were selected for Ni_2SiO_4. Considering this selection of diffraction lines a different scale (4:1) can be used in the microdensitometer. Figure 34 represents the graphical output of the x-ray diffraction pattern for the standard No. 4 obtained using

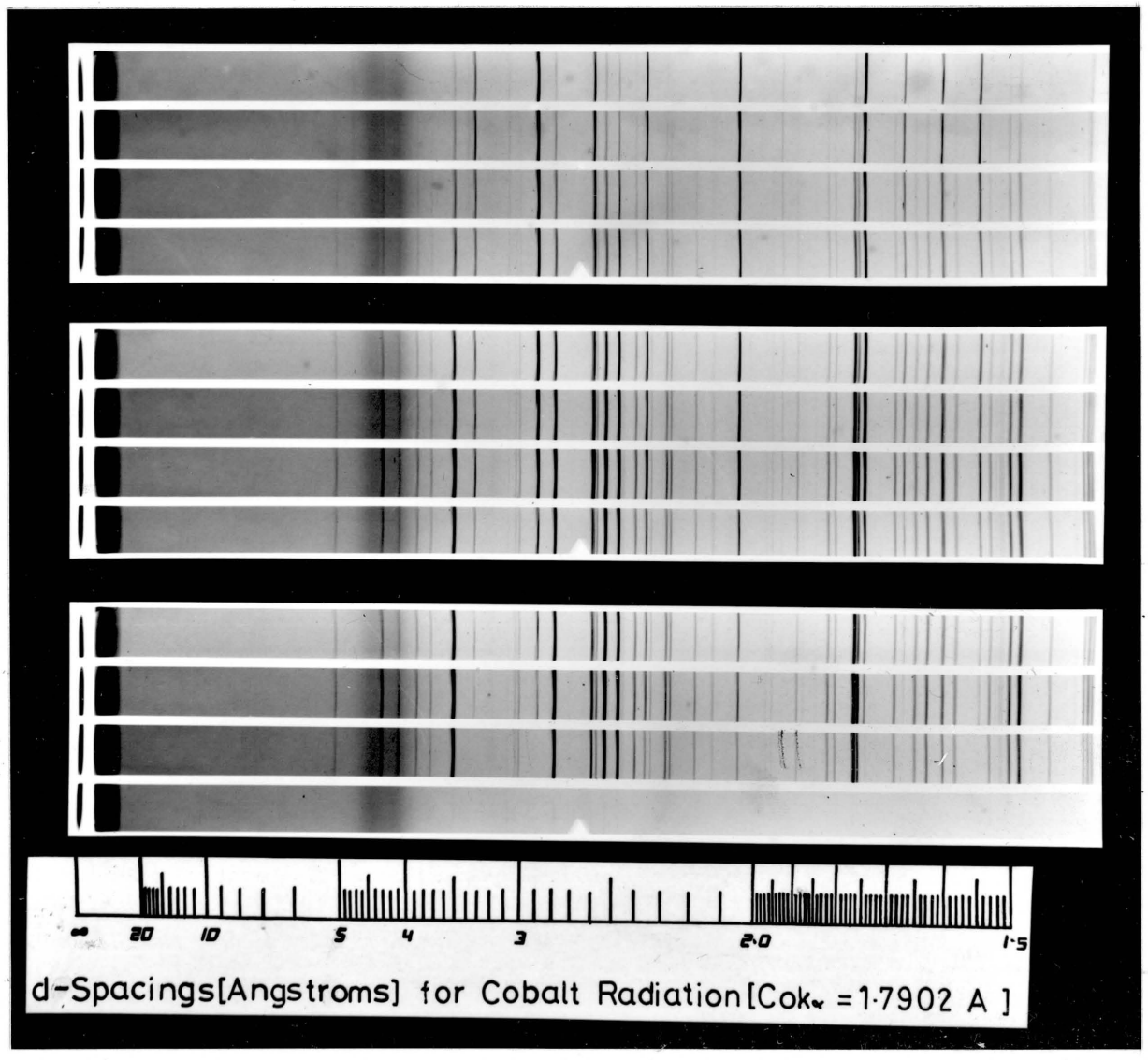
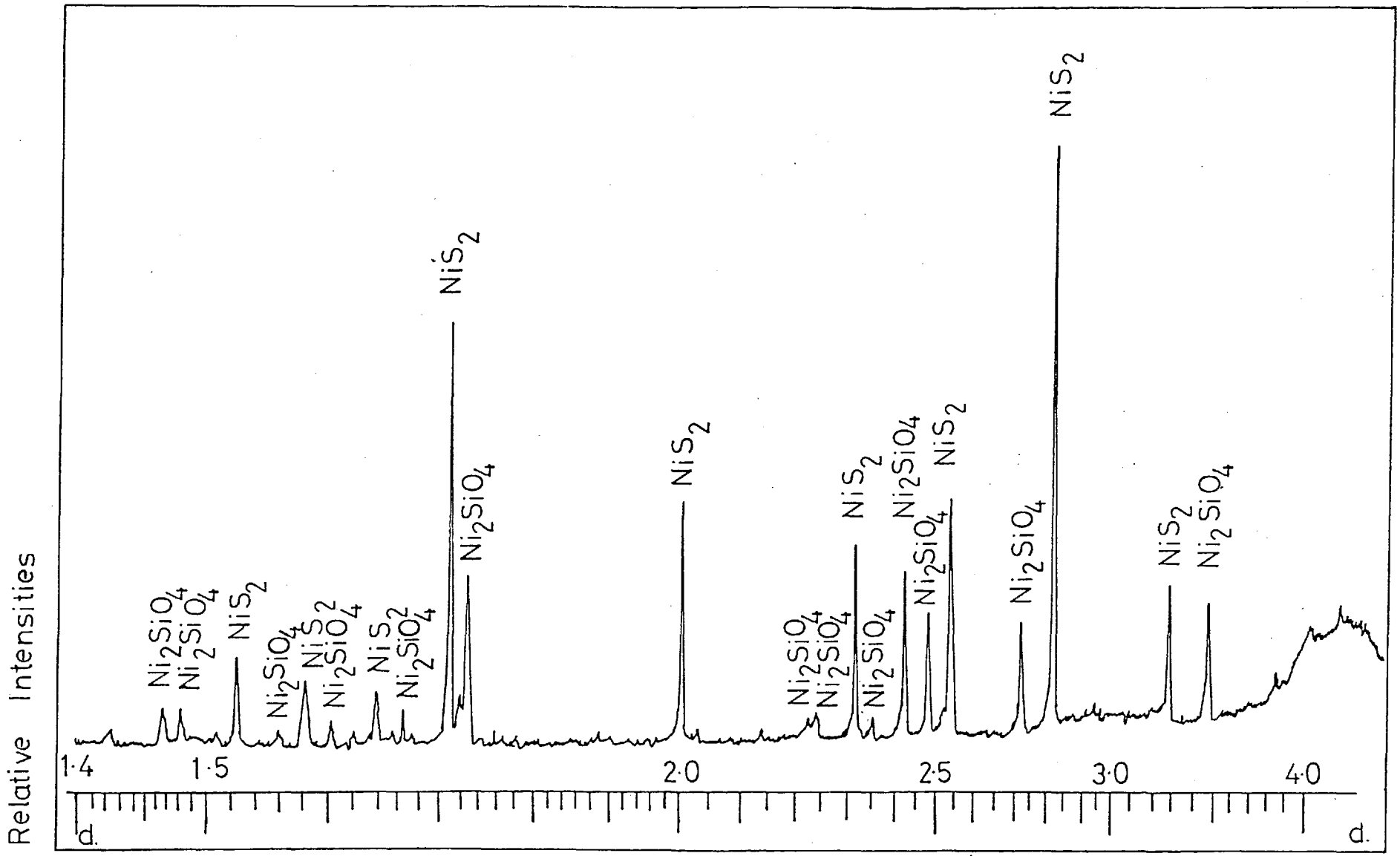


Fig. 32: X-Ray Patterns of the Ni_2SiO_4-NiS_2 mixture (standard samples) used in the Quantitative Analysis by X-Ray Diffraction Methods

(1)	94.93 wt % NiS_2	5.07 wt % Ni_2SiO_4
(2)	89.92 wt % NiS_2	10.08 wt % Ni_2SiO_4
(3)	80.04 wt % NiS_2	19.96 wt % Ni_2SiO_4
(4)	68.12 wt % NiS_2	31.88 wt % Ni_2SiO_4
(5)	59.90 wt % NiS_2	40.10 wt % Ni_2SiO_4
(6)	50.59 wt % NiS_2	49.41 wt % Ni_2SiO_4
(7)	40.75 wt % NiS_2	59.25 wt % Ni_2SiO_4
(8)	30.00 wt % NiS_2	70.00 wt % Ni_2SiO_4
(9)	20.25 wt % NiS_2	79.75 wt % Ni_2SiO_4
(10)	9.72 wt % NiS_2	90.28 wt % Ni_2SiO_4
(11)	0 wt % NiS_2	100 wt % Ni_2SiO_4



d =Spacings(Angstroms) for Cobalt Radiation (Cokα = 1·7902 A)

Fig33 X-Ray pattern of the solid (NiS_2=68·1%-Ni_2SiO_4=31·9%)

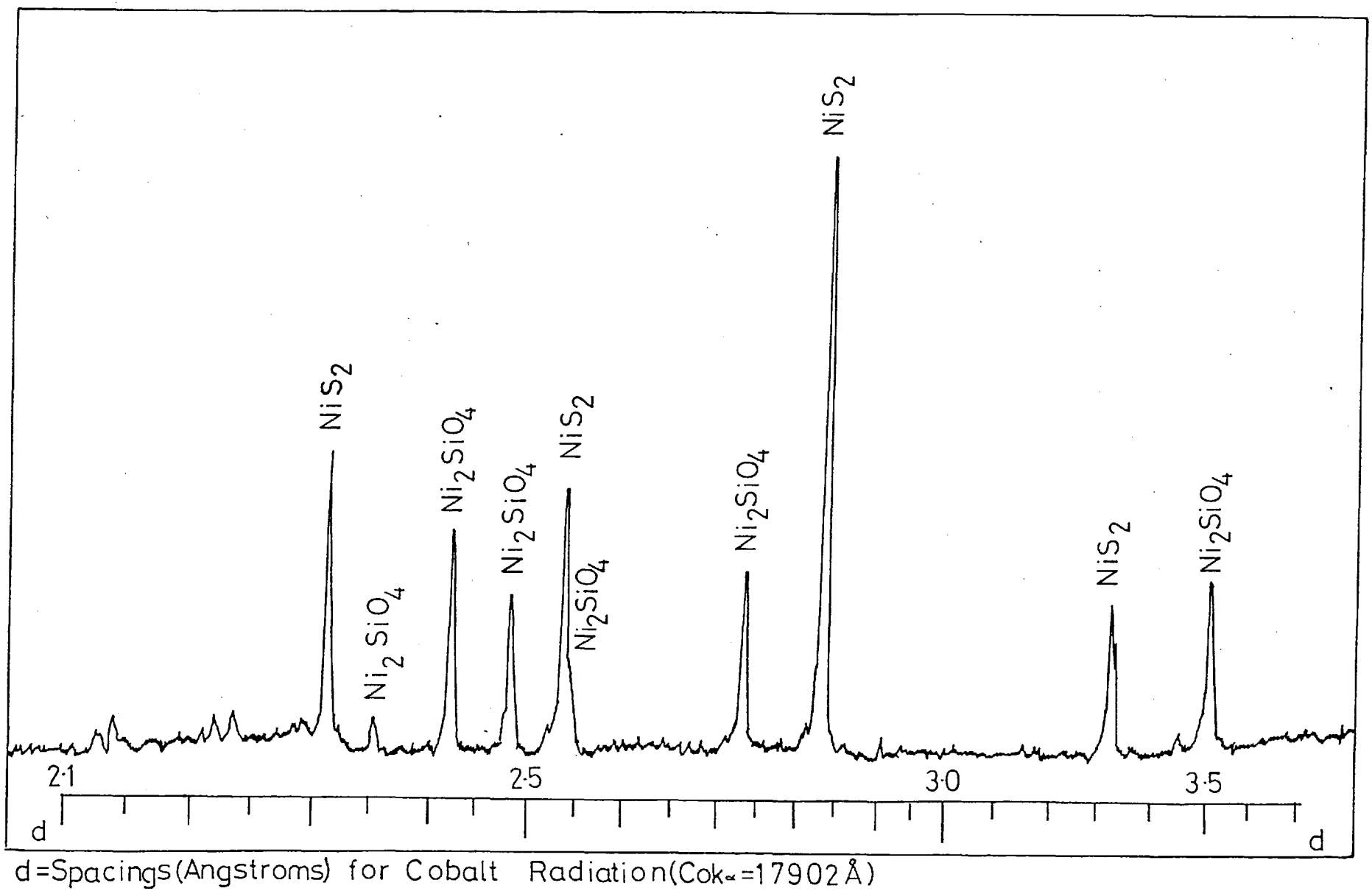


Fig 34 X-Ray pattern of the solid (NiS_2=68·1%Ni_2SiO_4=31·9 %)

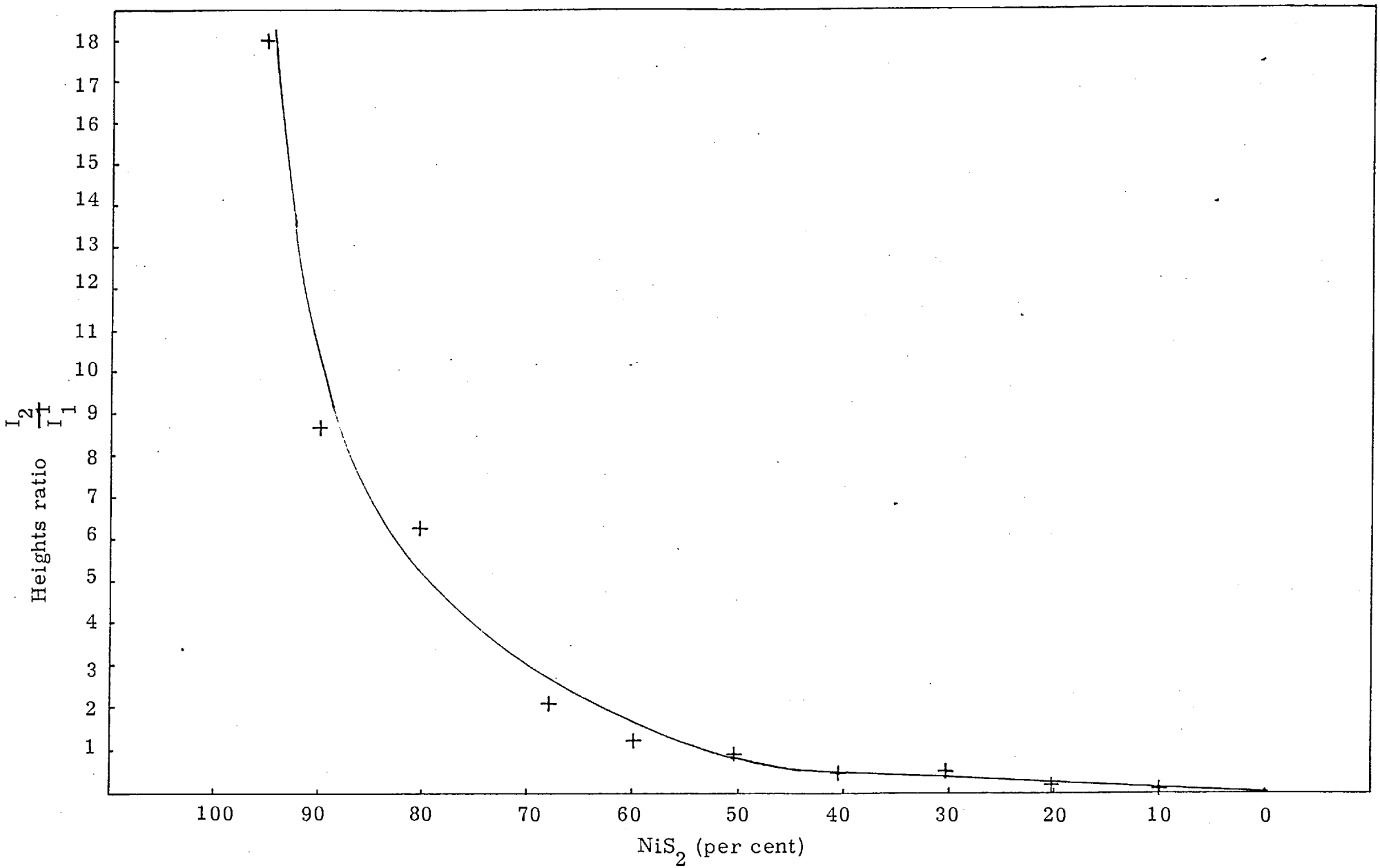


Fig. 35 Calibration Curve Used for the Quantitative Analysis by X-Ray Diffraction Methods

a microdensitometer where the scale was 4:1. Both the standard and the unknown samples were analysed in the microdensitometer using the scale 4:1 which covered a 'd spacing' from 2.1Å to 3.6Å.

The intensities of the lines were estimated by measuring the heights of the selected peaks and the ratios of intensities were obtained by calculating the ratios of the heights.

Of the selected lines I_2 = 2.83Å, I_1^1 = 2.430Å, I_3^1 = 2.74Å were used to plot the calibration curves ($\frac{I_2}{I_1^1}$ and $\frac{I_2}{I_3^1}$ versus per cent NiS_2 of Ni_2SiO_4). With the values selected no interference and superposition between lines seemed to be obtained; and concentration values for the unknown compounds with very big and obvious deviation from the majority were not obtained. Table 5 shows the $\frac{I_2}{I_1^1}$ and $\frac{I_2}{I_3^1}$ ratios for the standards samples. Figures 35-36 show the calibration curve ($\frac{I_2}{I_1^1}$ versus % wt NiS_2) used for the calculations.

TABLE No. 5

Values Used for the Standards - Quantitative Analysis by X-ray Diffraction Methods

Sample No.	wt% NiS_2	wt% Ni_2SiO_4	$\frac{I_2}{I_1^1}$ calibration curve	$\frac{I_2}{I_3^1}$
1	94.93	5.07	18	30
2	89.92	10.08	8.68	10.85
3	80.04	19.96	6.36	7.56
4	68.12	31.88	2.15	2.72
5	59.90	40.10	1.28	1.52
6	50.59	49.41	0.94	1.14
7	40.75	59.25	0.45	0.55
8	30.00	70.00	0.55	0.68
9	20.25	79.75	0.24	0.30
10	9.72	90.28	0.18	0.18

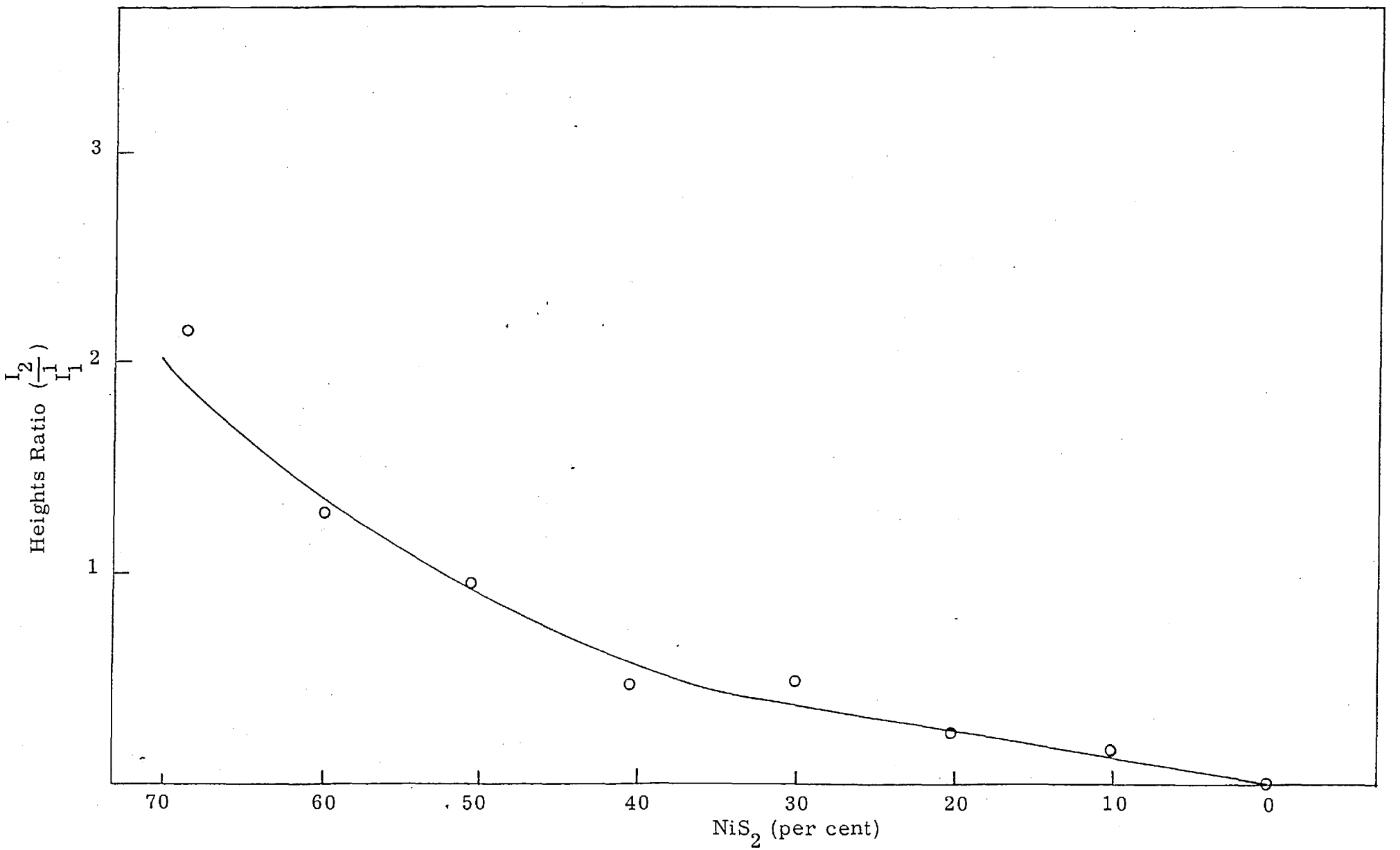


Fig. 36 Calibration Curve Used for the Quantitative Analysis by X-ray Diffraction Methods

TABLE 6

X-RAY DIFFRACTION DATA FOR THE STANDARDS SAMPLES

Standard Sample No. 1		Standard Sample No. 2		Standard Sample No. 3		Standard Sample No. 4		Standard Sample No. 5		Standard Sample No. 6		Standard Sample No. 7		Standard Sample No. 8		Standard Sample No. 9		Ni_2SiO		Ni_2SiO_4 p. s. t. m. 15.388		NiS_2 A. S. T. M. 11.99	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I/I_1	d(Å)	I/I_1
-		-		5.00	vm	5.00	vm	5.00	m	5.00	m	5.00	m	5.00	m	5.00	vw	5.00	vw	5.058	12	-	-
-		4.25	vm	4.25	vm	4.25	m	4.25	vw	4.24	vw	4.25	w	4.25	w	4.25	w	4.25	w	4.281	25	-	-
-		-		4.05	vvm	4.05	m	4.05	m	4.05	m	4.05	m	4.05	m	4.05	m	4.05	m	-	-	-	-
-		3.82	vvm	3.82	m	3.82	m	3.82	vw	3.82	vw	3.82	vw	3.82	vw	3.82	w	3.83	w	3.84	16	-	-
-		-		-		3.68	vm	3.68	m	3.68	m	3.68	m	3.68	m	3.68	m	3.68	m	2.69	8	-	-
3.45	m	3.45	m	3.45	vw	3.45	w	3.45	w	3.45	s	3.45	s	3.45	s	3.45	s	3.45	s	3.47	90	-	-
3.27	w	3.27	w	3.27	w	3.27	w	3.27	w	3.27	w	3.27	w	3.27	vw	3.27	m	-		-	-	3.27	20
3.00	vm	3.00	vm	3.00	vm	3.00	vm	2.97	vm	2.97	m	2.97	m	2.97	m	2.97	m	2.97	m	2.98	4	-	-
-		-		-		2.95	vm	2.95	vm	2.95	m	2.95	m	2.95	m	2.95	vw	2.95	vw	2.95	8	-	-
2.83	s	2.83	s	2.83	s	2.83	s	2.83	s	2.83	s	2.83	s	2.83	w	2.83	w	-		-	-	2.83	100
2.74	m	2.74	m	2.74	m	2.74	vw	2.74	w	2.74	w	2.74	s	2.74	s	2.74	s	2.74	s	2.74	85	-	-
-		2.55	vvm	2.55	m	2.55	m	2.55	vw	2.55	vw	2.55	w	2.55	w	2.55	w	2.55	w	2.55	40	-	-
2.54	s	2.54	s	2.54	s	2.54	s	2.54	w	2.54	w	2.54	w	2.54	vw	2.54	m	-		-	-	2.54	40
-		-		2.53	vvm	2.53	vm	2.53	m	2.53	m	2.53	vw	2.53	vw	2.53	w	2.53	w	2.53	12	-	-
2.48	vw	2.48	vw	2.48	w	2.48	w	2.48	w	2.48	s	2.48	s	2.48	s	2.48	s	2.48	s	2.48	80	-	-
2.43	vw	2.43	vw	2.43	w	2.43	w	2.43	w	2.43	s	2.43	s	2.43	s	2.43	s	2.43	s	2.43	100	-	-
-		-		2.36	vm	2.36	m	2.36	m	2.36	vw	2.36	vw	2.36	w	2.36	w	2.36	w	2.36	16	-	-
2.32	s	2.32	s	2.32	s	2.32	s	2.32	w	2.32	w	2.32	w	2.32	vw	2.32	m	2.30	vw	2.32	10	2.32	40
-		-		-		-		2.30	vm	2.30	m	2.30	m	2.30	m	2.30	m	2.24	w	2.30	8	-	-
2.24	vm	2.24	vvm	2.24	vvm	2.24	m	2.24	m	2.24	vw	2.24	vw	2.24	vw	2.24	vw	2.24	w	2.24	16	-	-
2.23	vm	2.23	vm	2.23	vm	2.23	vm	2.23	m	2.23	vw	2.23	vw	2.23	vw	2.23	vw	2.23	w	2.22	14	-	-
-		-		2.14	vvm	2.14	vm	2.14	vm	2.14	m	2.14	m	2.14	vw	2.14	vw	2.14	vw	2.14	6	-	-
-		-		2.08	vvm	2.08	vm	2.08	vm	2.08	vm	2.08	vm	2.08	m	2.08	m	2.08	m	2.01	10	-	-
2.01	s	2.01	s	2.01	s	2.01	s	2.01	s	2.01	s	2.01	s	2.01	w	2.01	vw	-		-	-	2.00	50
-		-		-		1.92	vm	1.92	vm	1.92	vm	1.92	vm	1.92	vm	1.92	m	1.92	m	1.92	2	-	-
1.89	vw	1.89	vw	1.89	m	1.89	m	1.89	m	1.89	m	1.89	m	-		-		-		-	-	1.89	5
-		-		-		1.86	vvm	1.86	vvm	1.86	vm	1.86	vm	1.86	m	1.86	m	1.86	m	1.86	6	-	-
1.78	vvm	1.78	vvm	1.78	vm	1.78	vm	1.78	vm	1.78	m	1.78	m	1.78	m	1.78	m	1.78	vw	1.79	10	-	-
1.77	vvm	-		-		1.77	vvm	1.77	m	1.77	m	1.77	m	1.77	m	1.77	m	1.77	m	1.77	6	-	-
1.73	m	1.73	m	1.73	vw	1.73	w	1.73	w	1.73	s	1.73	s	1.73	s	1.73	s	1.73	s	1.73	60	-	-
-		1.72	vm	1.72	vm	1.72	m	1.72	m	1.72	vw	1.72	w	1.72	w	1.72	w	1.72	w	1.72	-	-	-
1.705	s	1.705	s	1.71	s	1.71	s	1.71	s	1.71	s	1.71	s	1.71	w	1.71	w	-		-	-	1.71	80
-		-		1.65	vvm	1.65	vm	1.65	vm	1.65	m	1.65	m	1.65	m	1.65	vw	1.65	vw	1.65	8	-	-
1.64	w	1.64	w	1.64	w	1.64	w	1.64	w	1.64	w	1.64	w	1.64	vw	1.64	m	-		-	-	1.63	20
-		-		-		1.60	vm	1.60	m	1.60	m	1.60	vw	1.60	vw	1.60	w	1.60	w	1.60	14	-	-
1.57	s	1.57	s	1.57	s	1.57	s	1.57	s	1.57	w	1.57	w	1.57	vw	1.57	m	-		1.57	12	1.57	30
-		-		1.55	vm	1.55	m	1.55	m	1.55	vw	1.55	vw	1.55	vw	1.55	w	1.55		1.55	18	-	-
1.51	s	1.51	s	1.51	s	1.51	s	1.515	s	1.515	w	1.515	w	1.515	m	1.515	m	-		-	-	1.51	30
-		-		-		-		1.50	vm	1.50	vm	1.50	m	1.50	m	1.50	m	1.50		1.50	6	-	-
-		-		-		-		1.495	vm	1.495	vm	1.495	vm	1.495	vm	1.495	vm	1.495	vm	-	-	-	-
-		-		-		-		1.485	vvm	1.485	vm	1.485	vm	1.485	vm	1.485	vm	1.485	vm	-	-	-	-
-		-		-		-		1.483	vvm	1.483	vvm	1.483	vm	1.483	vm	1.483	vm	1.483	vm	-	-	-	-
1.47	vm	1.47	vm	1.475	m	1.475	m	1.475	m	1.475	vw	1.475	w	1.475	w	1.475	w	1.475	w	1.47	20	-	-
1.46	vm	1.46	m	1.46	m	1.46	m	1.46	m	1.46	m	1.46	w	1.46	w	1.46	s	1.46	s	1.46	20	-	-
-		-		-		1.42	vm	1.42	vm	1.42	m	1.42	m	1.42	m	1.42	m	1.42	m	1.42	6	-	-
-		-		-		1.385	vm	1.385	vm	1.385	vm	1.385	m	1.385	m	1.385	m	1.385	m				
-		-		-		1.38	vm	1.38	vm	1.38	vm	1.38	vm	1.38	m	1.38	m	1.38	m				
1.37	m	1.37	m	1.37	m	1.37	m	1.375	m	1.375	m	1.375	m	-		-		-					

2.4.3 Electron-probe Microanalysis

Electron-probe microanalysis of the unleached synthetic material and leach residues was carried out on a JEOL model JXA-3A made in 1967, fitted with scanning facilities. Some of the specifications of the apparatus are:-

- Probe diameter: 1 micron
- Scanning area: Square varying from 40 x 40 to 120 x 120 microns
- Magnifications: 300 x to 2400 x
- Resolution (electron image): 1 micron
- Resolution (x-ray image) = between 4 and 5 microns
- Range of elements: From sodium to uranium (atomic numbers 11 to 92).
- Accuracy for quantitative analysis: $\pm$1% for amounts of elements greater than 10 weight per cent.

Samples of the unleached starting material and the leach residues were mounted in araldite, made up from 9 parts of Araldite epoxy resin MY753 to 1 part of Araldite hardner MY951. The samples were ground on a Metaserv rotary pregrinder, and were then polished on a Kent Mark II automatic polisher using six micron and three micron cloths in turn. Hyprez spray diamond-yellow was used for the six micron cloth and Hyprez spray diamond-green was used for the three micron cloth.

The surfaces of the samples were carbon coated, to confer conductivity on the particles and on the mounting plastic.

The standards used were pure element in the case of nickel, while CdS was used in the case of sulphur. After adjustment for the background radiation, the 'raw count' data was processed by a computer

program which calculated the atomic and weight per cent, after correcting for the following effects:

a) Absorption effect: due to the fact that the standard and specimen absorb the emitted radiation by different amounts.

b) Atomic number effect: because of the differences in the percentage of electrons back scattered by the standard and specimen and the difference in electron retardation and x-ray production efficiency due to the difference in atomic number.

c) Characteristic fluorescence factor: to allow for the production of radiation of another wavelength.

The instrument was used for quantitative measurement of the elements at a number of fixed spots on the surface of the specimens. It was also used to investigate the homogenity in the unleached solid and any change of distribution of the elements in the leach residues.

2.4.4 Microscopic Analysis

For the microscopic analysis samples of the leach residues and unleached starting material were mounted in araldite in exactly the same form as for electron micro-probe analysis except that they were not carbon coated. The polished samples were observed with Reichert microscope using reflected light, under both normal and polarising conditions.

2.5 MATERIAL AND SPECIFICATION OF THE MATERIALS

For the synthesis of the Ni_2SiO_4 and NiS_2 spectrographically pure elements were used. The analysis of these elements gave the following estimation of the quantity of impurities.

a) Nickel sponge - (Spec-pure). Johnson Matthey.
Impurities present (ppm): Iron 10; Aluminium 1, Calcium 1; Sodium 1; Copper and Magnesium less than 1.

b) Sulphur powder - (Spec-pure) Johnson Matthey
Impurities present (ppm): Aluminium 0.5; Sodium 0.2; Zinc 0.2; Barium 0.1; Nickel 0.1; Copper 0.05; Titanium 0.05; Magnesium 0.03; Manganese 0.03; Silver 0.03; Boron 0.01; Calcium, Iron and Silicon each less than 1.

In addition the following compounds were also used for synthesis.

a) Tetraethyl ortho-silicate (TEOS) $(C_2H_5O)_4Si$ manufactured by Eastman Kodak company.

b) Ethanol 68. James Burrough Ltd. Ethyl Alcohol 96% v/v 93.87% mass min. Maximum limits of impurities in weight per cent: Total acid as acetic 0.005%; Fixed acid as acetic 0.001%; Alkalinity nil; Alclehydes and Ketones as acetaldehyde 0.01%.

c) Nitric acid. Analytical Reagent. BDH Chemicals Ltd., Poole England. Nitric acid (HNO_3) sp. gr. 149. Assay 69.0 to 71.0% HNO_3. Maximum limits of impurities in weight per cent: Non-volatile matter 0.001%; Chloride (Cl) 0.00005%; Phosphate (PO_4) 0.0001%; Silicate (SiO_2) 0.00005%; Sulphate (SO_4) 0.0002%; Arsenic (As) 0.000001%; Iron (Fe) 0.00002%; Heavy metals (Pt). 0.00002%, Manganese (Mn) 0.00004

The specification of the compounds used in the hydrothermal treatment and in the leaching experiments are:-

a) Sulphur recrystallized. General purpose reagent. Manufactured by Hopkin-Williams.

b) Ammonia solution (about 35% NH_3). Analytical reagent. BDH Chemical Ltd., Poole England. Ammonia solution sp. gr. 0.88. Maximum limits of impurities in weight per cent: non-volatile matter 0.002%; Chloride (Cl) 0.00005%; Carbonate (CO_3) 0.002%; Sulphide 0.00001%; Phosphate 0.0001%; Silicate 0.001%; Sulphate 0.0002%; Arsenic 0.000005%; Calcium group and Magnesium 0.0004%; Copper 0.00001%; Iron 0.00002%; Heavy Metals (Pb) 0.00004%; Oxygen Absorbed (0) 0.0008%; Pyridine and Homologus 0.002%.

c) Ammonium sulphate. General purpose reagent - recrystallized. Assay 98.5 wt % min. Maximum limits of impurities in weight per cent: non -volatile matter 0.1%; Chloride (Cl) 0.01%; Lead (Pb) 0.001%.

The calibration curves for atomic absorption spectrophotometry were obtained by using solutions of different concentrations prepared from nickel standard solution (Hopkin and Williams), containing 1000 ppm w/v of nickel in 0.1N $HClO_4$. Metal content is within 0.5% of the nominal value. Solutions for the calibration curve for the sulphate analysis were prepared using potassium sulphate analytical reagent (Hopkin-William Ltd.) and barium standard solution (Hopkin and William) containing 1000 ppm w/v of barium in 0.1N $HClO_4$. Metal content is within 0.5% of the nominal value.

CHAPTER 3

RESULTS AND DISCUSSION - SULPHIDISATION OF NICKEL OLIVINE (Ni_2SiO_4)

3.1 X-RAY DIFFRACTION IDENTIFICATION OF THE PRODUCT OF THE SULPHIDISATION PROCESS

The two compounds (NiO-Ni_2SiO_4 and Ni_2SiO_4), which were synthesized as has been described in section 2.1.1 were hydrothermally treated as described in section 2.2.1.

An experiment was carried out using NiO-Ni_2SiO_4 synthetic material. The conditions of the experiment were:-

Amount of NiO-Ni_2SiO_4 in each tube	1 gr.
Temperature	240°C
Time of reaction	4 hours
Amount of sulphur	Variable from 0.4 gr. to 3.2 gr.

The x-ray diffraction patterns are shown in Figure 37, and the 'd spacing' in Table 7 in Appendix 2.

The x-ray powder diffraction patterns showed the existence of a new phase which appeared together with the two other phases previously identified (NiO and Ni_2SiO_4). This new phase was identified as NiS_2 or vaesite. The intensities of the diffraction lines of vaesite seemed to increase when the amount of sulphur in the 'reaction tubes' was increased and, at the same time, the intensities of the diffraction lines of NiO and Ni_2SiO_4 decreased. This indicated that both NiO and Ni_2SiO_4 took part in the hydrothermal reaction. Due to this fact

quantitative analysis of the solids, as has been described in section 2.4.2, which referred to a mixture of two components, could not be done.

A set of experiments was planned using Ni_2SiO_4 as the starting material. These were planned in accordance with a 'factorial design' to test the influence of three variables (amount of sulphur, temperature, time of reaction). However, due to the obvious limitations in the quantitative analysis of the solid by x-ray diffraction (section 2.4.2) and the high accuracy in analysis that factorial design requires; a complete analysis of the results using 'factorial design techniques' was not carried out. Nevertheless, some of the results which are analysed below are presented in a way which is familiar in 'factorial design' because it is clearer in order to appreciate the influence of the different variables in the conversion of Ni_2SiO_4 to $NiSO_4$ and NiS_2. This, of course, does not imply that a factorial analysis was carried out.

The conditions of the experiments were:

Amount of Ni_2SiO_4	0.5 gr.
Temperature	200°C (low value)
	240°C (high value)
Time of reaction	2 hours (low value)
	6 hours (high value)
Amount of sulphur	Variable from 0.2gr. (low value) to 1.8gr. (high value)

The x-ray diffraction patterns are shown in figure 38 and the x-ray diffraction data in table 8 in Appendix 2.

As was expected the x-ray powder diffraction results showed the existence of a new compound which was identified as NiS_2 or vaesite. It was observed that the intensity of the diffraction lines of NiS_2 seemed to increase only very slightly when the amount of sulphur in the 'reaction ampoules' was increased (S1, S2, S3, S4), but the intensity seemed to increase in a clearer way when the time of reaction (S3) and the temperature (S2, S4) were increased; in this case the increase in intensity of the 'diffraction lines' of NiS_2 was clearly combined with a decrease in intensity of the 'diffraction lines' of Ni_2SiO_4 (S3, S4). These visual observations were later confirmed when the intensities of the 'diffraction lines' were measured by microdensitometer techniques in order to carry out the quantitative analysis.

3.2 SULPHIDISATION RESULTS

3.2.1 Effect of the Amount of Sulphur

Figure 29 shows the ampoules used for the hydrothermal treatment before and after the hydrothermal process. A change of colour had occurred in the solid as well as in the solution, x-ray diffraction data (section 3.1) indicated that NiS_2 and $NiSO_4$ were formed during the treatment.

The influence of the high and low levels of sulphur in the per cent of nickel converted to $NiSO_4$ and NiS_2 at low and high levels of the variables time and temperature is given in tables 9, 10, 11, 12. The interactions of amount of sulphur and temperature and the amount of sulphur and time, calculated according to Duckworth[154] are given in tables 13 to 16.

The complete results for the hydrothermal treatment are given in tables 17 to 20 in Appendix 2.

TABLES 9 & 10

% Ni Extracted as NiS_2 for Different Conditions

Table 9

Amount of Sulphur	Time = 2 hours Temperature	
	low level (200°C)	high level (240°C)
low level 0.2 gr.	18.0	56.0
high level 1.8 gr.	21.8	80.5

Table 10

Amount of Sulphur	Time = 6 hours Temperature	
	low level (200°C)	high level (240°C)
low level 0.2 gr.	50.0	47.0
high level 1.8 gr.	58.2	79.3

TABLES 11 & 12

% Ni Extracted as $NiSO_4$ for Different Conditions

Table 11

Amount of Sulphur	Time = 2 hours Temperature	
	low level (200°C)	high level (240°C)
low level 0.2 gr.	0.5	12.2
high level 1.8 gr.	5.3	17.1

Table 12

Amount of Sulphur	Time = 6 hours Temperature	
	low level (200°C)	high level (240°C)
low level 0.1 gr.	5.9	9.6
high level 1.8 gr.	8.0	17.7

TABLES 13 & 14

Interactions Between Variables. % Ni Extracted as NiS_2

Table 13

Amount of Sulphur	Temperature	
	low level (200°C)	high level (240°C)
low level 0.2 gr.	34.0	51.5
high level 1.8 gr.	40.0	79.9

Table 14

Amount of Sulphur	Time	
	low level (2h)	high level (6h)
low level 0.2 gr.	37.0	48.5
high level 1.8 gr.	51.6	68.8

TABLES 15 & 16

Interaction between variables. % Ni extracted as Ni_2SiO_4

Table 15

Amount of Sulphur	Temperature	
	low level (200°C)	high level (240°C)
low level 0.2 gr.	3.2	10.9
high level 1.8 gr.	6.5	17.4

Table 16

Amount of Sulphur	Time	
	low level (2 h)	high level (6 h)
low level 0.2 gr.	6.4	7.8
high level 1.8 gr.	11.2	12.9

Examining tables 9, 10, 11, 12, 15, 16, 17, 18, the following conclusions can be drawn:-

a) An increase in the amount of sulphur tended to increase both the the percent of nickel extracted as $NiSO_4$ which was always very small, and the percent of nickel obtained as NiS_2.

b) At 'low level' of temperature the percent of nickel converted to NiS_2 increased with the amount of sulphur used, although this increase was very small and fell well within the limits of accuracy of the quantitative analysis by x-ray diffraction.

c) At 'high level' of temperature there was a definitive increase in the percent of nickel converted to NiS_2 with the amount of sulphur used.

These observations seemed to be independent of the time of reaction.

Similar conclusions can be drawn considering the interaction tables 13 to 16. The interaction (Tables 13 and 15) shows that the increase in Ni% conversion of Ni_2SiO_4 to NiS_2 and $NiSO_4$ by a hydrothermal treatment, with the amount of sulphur was more marked when the temperature was high. The interaction (Table 14 and 16) shows that the increase in Ni % conversion of Ni_2SiO_4 to NiS_2 and $NiSO_4$ by a hydrothermal treatment, with the amount of sulphur was more marked when the time was high. However in this case the increase fell well within the limits of accuracy of the analysis and the conclusions drawn from tables 14 and 16 are not very reliable.

3.2.2 Effect of Time of Reaction

In order to find the influence of the time of the reaction on the per cent of Ni converted to $NiSO_4$ and NiS_2 it is again convenient

to consider Tables 9 to 12 and 17 to 20 and the interaction effects in tables 14 - 16, 20-21.

TABLES 20 & 21

Interaction between Variables. Ni % extraction as NiS_2 (Table 20) and as $NiSO_4$ (Table 21)

Table 20			Table 21		
Time	Temperature		Time	Temperature	
	Low level (200°C)	high level (240°C)		low level (200°C)	high level (240°C)
low level 2h	19.9	68.3	low level 2 h	2.9	14.7
high level 6h	54.1	63.2	high level 6 h	7.0	13.7

Considering tables 9 to 12 and 17 to 20, the following conclusion can be drawn.

a) At 'high level' of temperature the conversion of Ni_2SiO_4 to NiS_2 and $NiSO_4$ seemed to be very rapid and independent of the time of reaction.

b) At 'low level' of temperature an increase in the time of reaction seemed to increase slightly the nickel extraction as $NiSO_4$ but there was a definitive increase in the nickel conversion to NiS_2.

This observation seemed to be true independently of the amount of sulphur used.

Considering now the interaction effects (Tables 20-21 and 14-16) the following conclusion can be drawn:-

a) The interaction effects shown in Table 20-21 indicate that the increase in Ni% conversion from Ni_2SiO_4 to NiS_2 and $NiSO_4$ by a hydrothermal treatment, with the time of reaction was more marked when the temperature was low.

b) The interaction effects shown in Tables 14 and 16 show that the increase in Ni% conversion from Ni_2SiO_4 to NiS_2 and $NiSO_4$ with the time of reaction is more marked when the amount of sulphur is high. Here again, the increases fall well within the limits of accuracy of the analysis and therefore the conclusion drawn from Tables 14 and 16 is not very reliable.

3.2.3 Effect of Temperature

The temperature seemed to be the main controlling factor in the conversion of Ni_2SiO_4 to $NiSO_4$ and NiS_2 by a hydrothermal treatment. When the temperature was kept at its 'low level' the per cent Nickel conversion was also low. Working at high level of temperature improved both the percent nickel converted to NiS_2 and the percent nickel converted to $NiSO_4$.

Considering the interaction tables (Table 13-15 and 20-21) it can be concluded that:-

a) The interaction effects shown in Tables 13-15 show that the increase in Ni % conversion to NiS_2 and $NiSO_4$ with the temperature was more marked when the amount of sulphur was high.

b) The interaction effects shown in Tables 20-21 show that the increase in Ni % conversion to NiS_2 and $NiSO_4$ with the temperature was more marked when the time of reaction was low.

3.3 Discussion and Comparison with other Work

During the experimental study of the factors which affect the sulphidization of Ni_2SiO_4, it was seen that the change of colour in the solid as well as in the solution, and x-ray diffraction data indicated that NiS_2 and $NiSO_4$ were formed during the hydrothermal treatment. Accordingly, it can be concluded that during the hydrothermal treatment part of the sulphur was oxidized and part was reduced. The following half-cell reaction can be written:-

$$\begin{aligned} S &= S^{6+} + 6e^- \\ 3S + 6e^- &= 3S^{=} \\ \hline 4S &= S^{6+} + 3S^{=} \end{aligned} \qquad (3.3.1)$$

Since water was present, the following set of reactions may also be written:-

$$\begin{aligned} S &= S^{6+} + 6e^- \\ S^{6+} + 4H_2O &= SO_4^{=} + 8H^+ \\ 3S + 6e^- &= 3S^{=} \\ \hline 4S + 4H_2O &= 3S^{=} + SO_4^{=} + 8H^{=} \end{aligned} \qquad (3.3.2)$$

The products of this reaction were thought to attack the nickel olivine according to the following reaction.

$$2Ni_2SO_4 + 7S + 2H_2O = 3NiS_2 + NiSO_4 + 2H_2SiO_3 \qquad (3.3.3)$$

Considering the condition under which the experiments were performed (they were carried out using sealed tubes and agitation was not used); it was likely that, at the temperature used the mother sulphur would react directly with the silicate to give NiS_2. In addition, another part

of the sulphur would go into the solution with simultaneous oxidation to give sulphuric acid which in turn would react either with NiS_2 already formed or with Ni_2SiO_4 to form a minor amount of sulphate.

Considering reaction (3.3.2) it was possible that part of the nickel sulphate which had been formed might precipitate as a nickel sulphide by reaction with the $S^{=}$. This would be NiS_2 since this has been the only sulphide identified by x-ray diffraction or there could have been a minor amount of NiS present which could not be detected by x-ray diffraction.

The temperature seemed to be the main controlling factor of the sulphidization process. At low level of temperature reaction (3.3.3) seemed to occur only in a minor degree. In this case the sulphidization improved considerably with the time of reaction, but the amount of sulphur present had very little influence. Providing that the temperature was kept at its high level ($240^{o}C$), the sulphidization seemed to be nearly complete independent of the time of reaction in the range used but, in this case, the sulphidization improved with the amount of sulphur present.

Most of the results in this work are in good agreement with that in the work by Seidel and Fitzhugh[72]. However they found that NiS_2 and NiS were formed during the process and no $NiSO_4$ was present; it seems that these disagreements were due to the different ways in which the experiments were carried out, since they carried out the experiments directly in an autoclave using agitation and we carried out the experiments using sealed tubes and without agitation, $NiSO_4$ was not observed in their work but was found in this work. This was probably due to the different nickel content in the two ores (Seidel and Fitzhugh 2.3 wt % Ni, this work 50.9 wt % Ni) and also to the different manner in which the experiments were carried out.

They also concluded that the most significant factor in the sulphidization was the amount of sulphur used; but in the present work, we concluded that this seemed to be true only if the temperature was kept at a 'high level' to allow the sulphidization to be carried out.

CHAPTER 4

RESULTS AND DISCUSSION - AMMONIACAL LEACHING OF VAESITE

4.1 AMMONAICAL LEACHING: KINETICS RESULTS

4.1.1 Shape of the Leaching Rate Curve

Vaesite was leached in ammonia-ammonium sulphate solutions. The effects of the different variables on the leaching rate were investigated.

The variations in the leaching conditions used are shown in Table 22.

TABLE 22

Variation of Leaching Conditions for NiS_2

Variables	Most Common Conditions	Range of Variation
Weight of NiS_2	0.5 gr.	0.5 - 1 gr.
NH_3 concentration	60 gr/l	0 - 60 gr/l
$(NH_4)_2SO_4$ concentration	1 mol/l	0 - 1 mol/l
Temperature	150°C	100 - 150°C
Air Pressure	800 p.s.i.	200 - 1200 p.s.i.
Particle size	-180 + 125 μ	-53^{+}-54μ/-425+300μ
Stirring speed	550 r.p.m.	350 - 1000 r.p.m.
Initial amount of solution	200 cc	200 cc
Time of a leaching run	8 hours	5 to 8½ hours

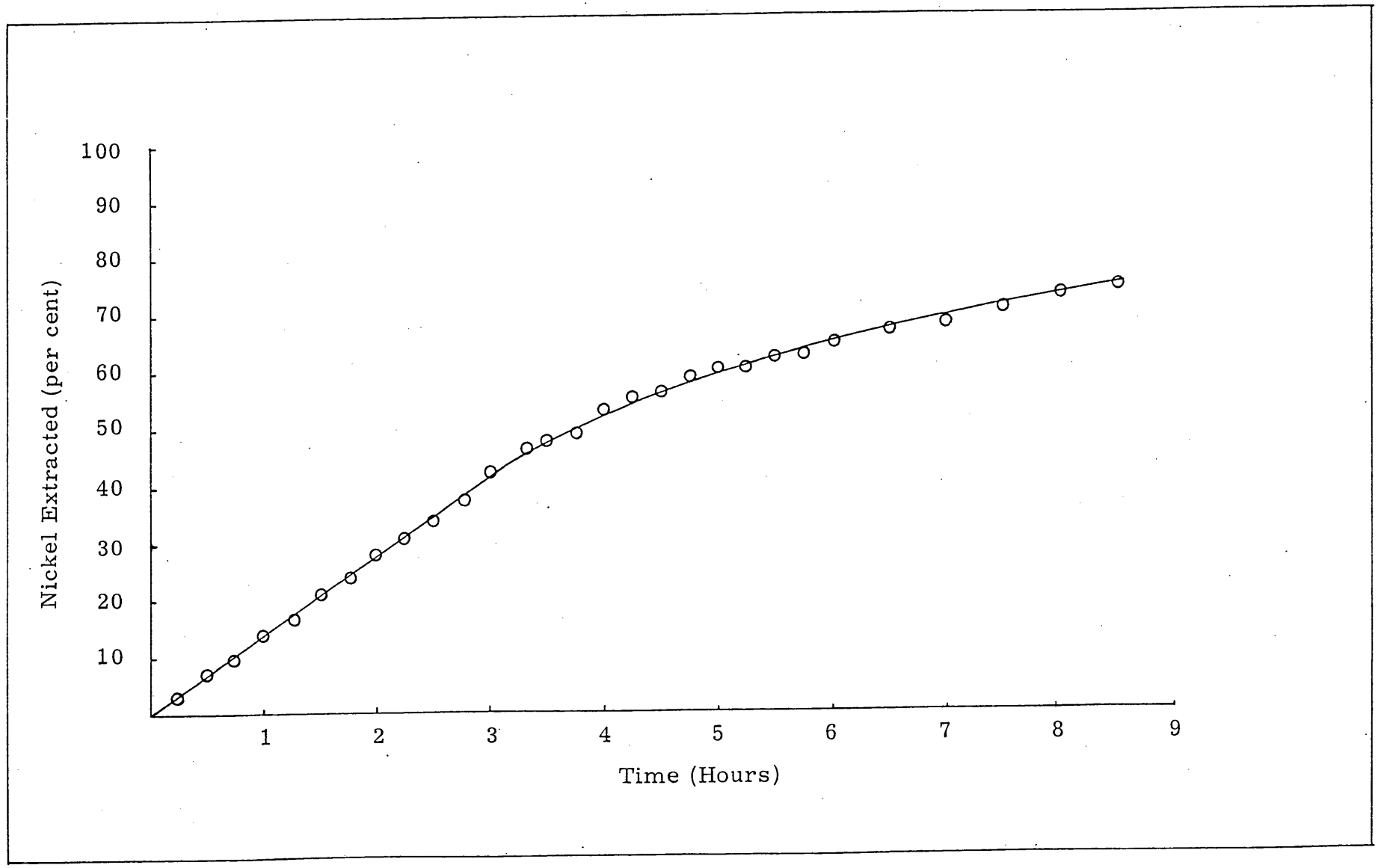


Fig. 39 Characteristic Shape of the Leach Curve of NiS_2

The results for the dissolution show that the ammoniacal leaching of NiS_2 took place in two stages (Fig. 39). Initially there was a linear increase of the per cent nickel extracted with the time, up to 45% nickel leached after three hours leaching. After this the leaching rate fell; so that after eight hours around 80% of the nickel had been extracted. The extraction rate was very slow at the end of the experiment (after six hours of leaching) and the results of the analysis after this period shows random fluctuations in the nickel extraction.

Most of the runs were carried out for eight hours in order to study better the phenomena which occurred during the last part of the leaching process.

The effects of the following variables in the leaching rate were investigated: particle size and sample weight, air pressure, temperature, stirring speed, free ammonia and ammonium sulphate concentrations.

4.1.2 Effect of Temperature

The effect of the temperature on the rate of leaching of vaesite was studied using five different temperatures. The conditions and results of the leaching runs are given in Tables (A-1), (A-2), (A-3), (A-4), (A-5), in appendix No. 2. The percentage of nickel extracted versus time at different temperatures is represented in Figure 40.

Vaesite proved to be a very difficult mineral to leach in an ammoniacal medium under the conditions used even using temperatures rather high for ammoniacal leaching ($100^{o}C$) only 15% of the nickel in the solid was dissolved after eight hours. However, of the variables studied, the temperature had the greatest effect on the rate of leaching.

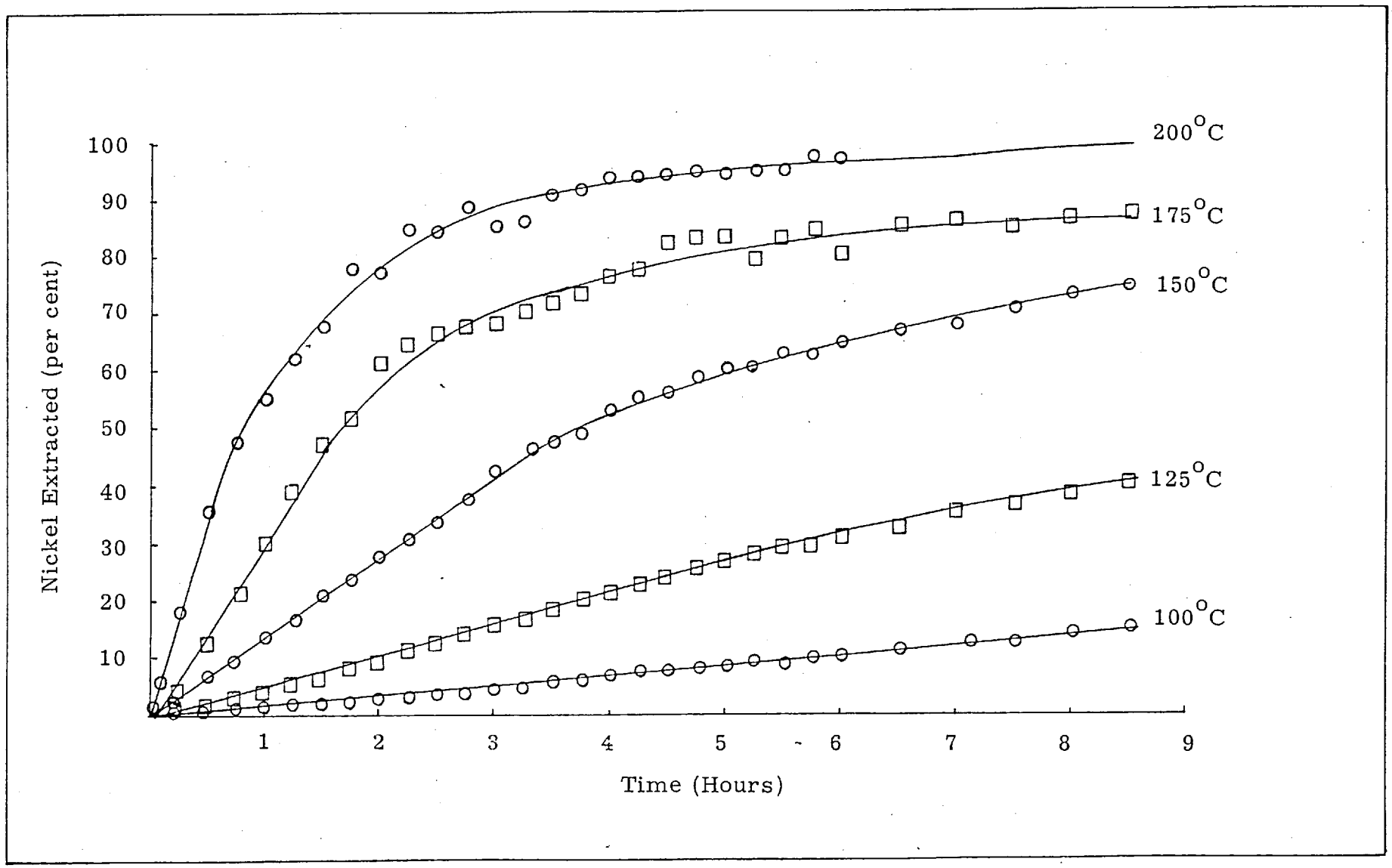


Fig. 40 Effect of the Temperature on the Leaching Rate

Thus 80 wt % of nickel was extracted in two hours at 200°C, but 30 wt % of nickel was extracted at 150°C and only 5 wt % at 100°C during the same period.

It can be seen in Figure 40 that, of the two stages in which the leaching of NiS_2 was divided (section 4.1.1) the first seems to be the predominant one at low temperature; in fact, at 100°C it seems to be the only one. It seemed that the second stage did not exist until a certain percentage of nickel was extracted.

The apparent activation energy for the first stage of the reaction was calculated using the Arrhenious equation

$$E_o = RT^2 (d(\ln K)/dT)$$

$$\ln K = -\frac{Ea}{R}\frac{1}{T} + C$$

where K = rate constant. The rate for the nickel dissolution was determined as the rate at the time when a specific amount of nickel had been dissolved. The apparent activation energy for this part of the reaction (0 to 45 wt % nickel extracted) was calculated as 10.9 ± 0.2 Kcal per mol (Fig. 41). Some attempts were made to calculate the apparent activation energy for values of 'nickel extracted' greater than 45 wt % but the 'Arrhenious plot for these cases was not very accurate. Nevertheless, in this case, the slope of the 'Arrhenious plot' was such that the apparent activation energy was slightly smaller than the one calculated for the first stage of leaching (around 9 Kcal mol). These values of the apparent activation energy of the two stages of leaching were both too high for entirely transport controlled reaction, about 4 Kcals mol^{-1} and too small for chemical control, about 20 Kcals mol^{-1}. Therefore it seemed likely that there was a 'mixed control' controlling mechanism in the two stages proposed.

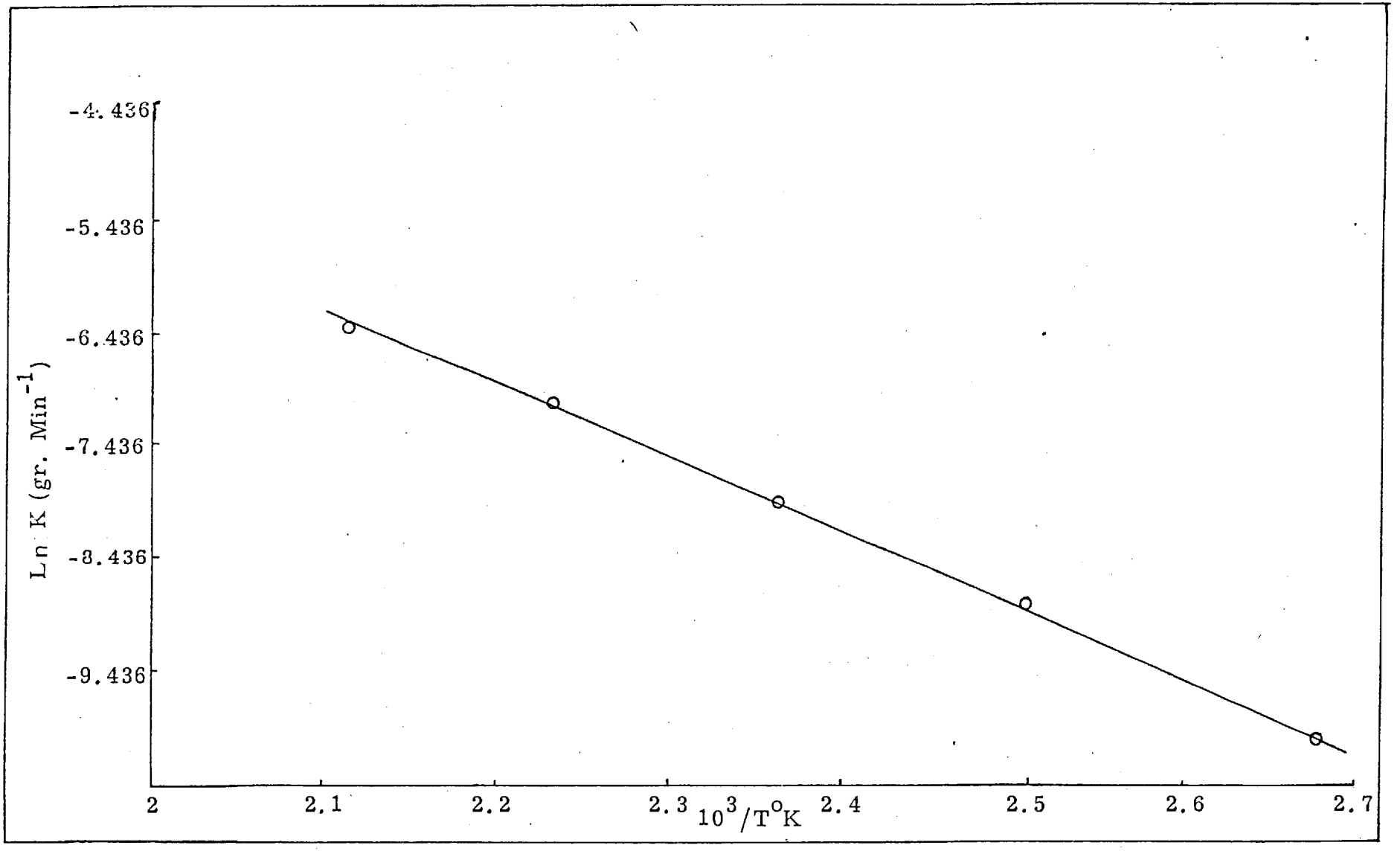


Fig. 41 Determination of the Apparent Activation Energy for the Dissolution of Nickel during the First Stage of Leaching NiS_2

The limitation of the kinetics studies to high temperatures presented some problems. First of all, the vapour pressure of ammonia solutions increased considerably with the temperature. This presents a problem in practice since the leaching reactors must withstand the high pressure at elevated reaction temperatures, and accordingly the construction cost of reactors will increase with increasing temperature. On the other hand, the use of high temperature tended to promote hydrolysis of the nickel hexa-ammine. However, it can be seen in Figure 40 that even at temperatures as high as 200°C no diminution of the percent nickel extracted was obtained. In addition, the x-ray diffraction results from the residues did not show the existence of any other solid phase than that of vaesite whose structure seemed to be maintained. Therefore the hydrolysis of the hexa-ammine did not seem to happen even at temperatures as high as 200°C. It will be seen later (section 4.1.9 and Appendix 1) that the hydrolysis of the hexa-ammine was largely prevented by the addition of large amounts of $(NH_4)_2SO_4$ (1 mole/l) the main role of which in the leaching reaction was to stabilize the nickel complex.

4.1.3 Effect of Air Pressure

Two sets of runs were carried out in order to test the effects of the pressure in the rate of leaching.

The first one was carried out for an ammonium sulphate concentration of 1 mole/l and a stirring speed of 550 r.p.m. The results of these runs are given in tables (A-6), (A-7), (A-8), (A-9), (A-10) (A-11) and the percent nickel extracted versus time at different pressures is represented in Figures 42 and 43. The second one was carried out for an ammonium sulphate concentration of 0.1 mole/litre and a stirring speed of 850 r.p.m. The results of these runs are given

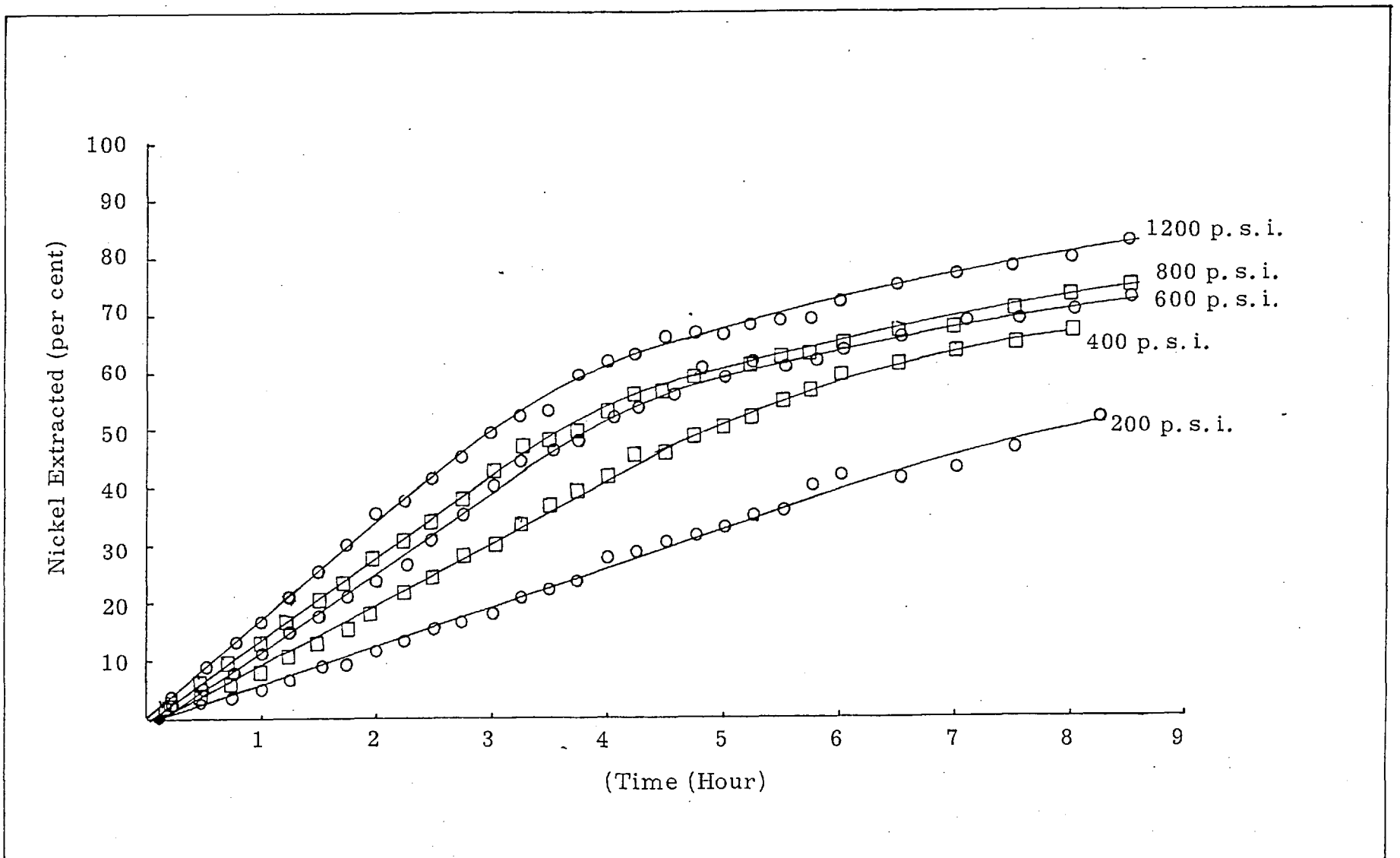


Fig. 42 Effect of the Air Pressure on the Leaching Rate

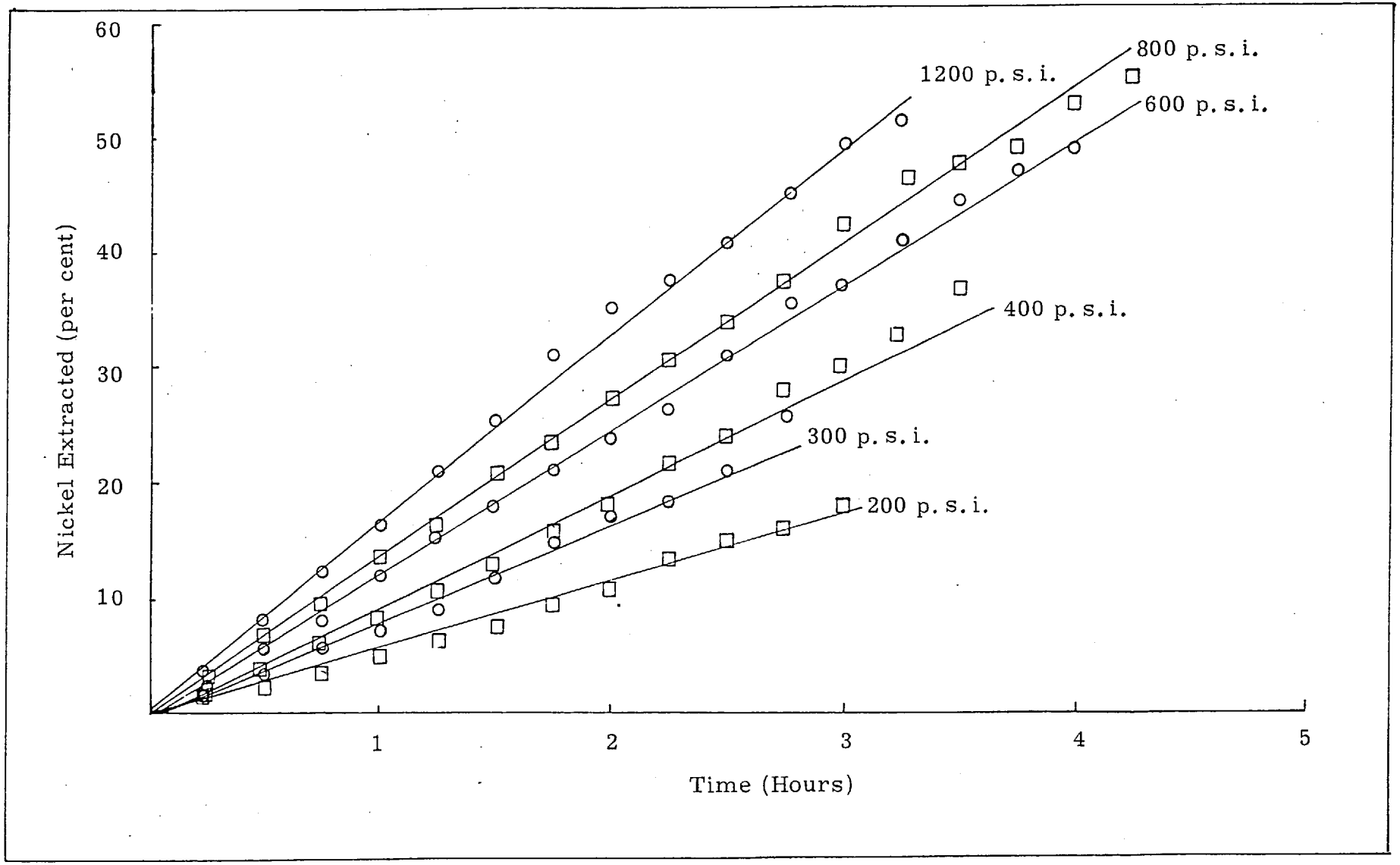


Fig. 43 Effect of the Air Pressure on the Leaching Rate

in Tables (A-12), (A-13), (A-14), (A-15), (A-16). The percentage of nickel extracted versus time for different pressures is represented in Figure 44. The pressure seemed to have a considerable effect on the rate of leaching, mainly during the first stage of the leaching. Thus 50 wt % nickel was extracted after three hours of leaching at an air pressure of 1200 p. s. i. but only 20 wt % of nickel was extracted after the same period of time when the air pressure was 200 p. s. i. (Fig. 42).

During the first thirty minutes of the leaching experiment a drop in the pressure was observed, although the pressure was adjusted to its original value each fifteen minutes when the samples were taken, this drop in pressure seemed to indicate that during the initial period of leaching there was a clear demand for oxygen, obviously in order to oxidise the sulphur in NiS_2 to $SO_4^{=}$ and convert the nickel to $Ni(NH_3)_6^{++}$. Therefore, it seemed that during the first stage of leaching the oxidation rate depended, at least partly, on the supply of oxygen which, in turn, depended on the oxygen pressure.

An empirical expression for the dependence of the rate of leaching on the oxygen pressure was obtained for the first stage of leaching by plotting the logarithm of the initial rate of reaction (logr.) versus the logarithm of the oxygen pressure (log PO_2). This was done for ammonium sulphate concentration of 1 mole/1. stirring speed 550 r. p. m and ammonium sulphate concentration of 0.1 mol/1. and stirring speed 850 r. p. m. (Fig. 45 and Table 23).

Considering Figure 45 the following empirical expression can be obtained.

Conditions 1:

$$r = K_1 P_{O_2}^{0.55}$$

Conditions 2:

$$r = K_2 P_{O_2}^{0.59}$$

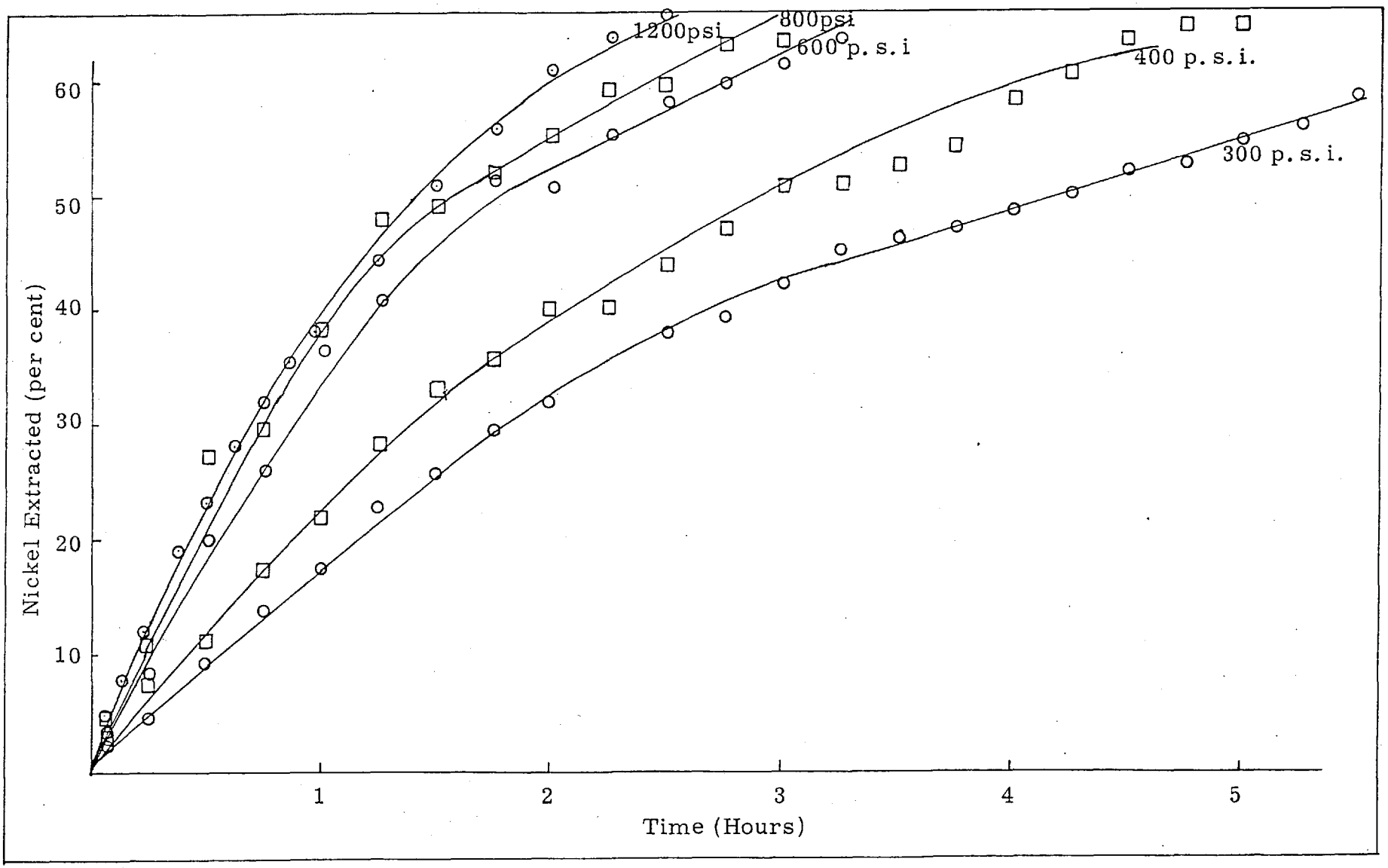


Fig. 44 Effect of the Air Pressure on the Leaching Rate

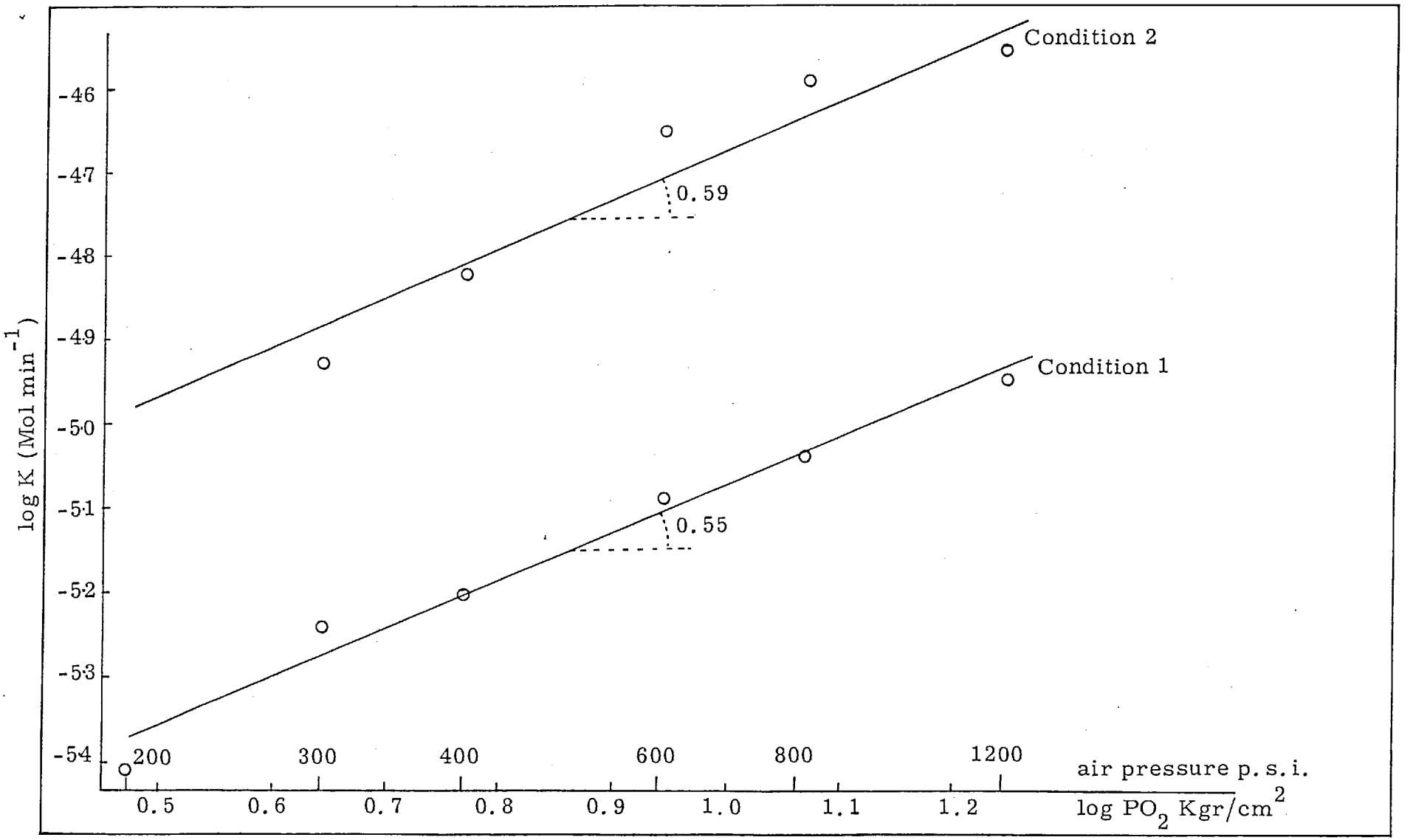


Fig 45 Effect of the Air Pressure on the Leaching Rate

TABLE 23

- Conditions of leaching -
- Free ammonia concentration - 60 gr/l
- Temperature 150°C
- Particle size -180$\pm$125 μ
- Amount of NiS_2 0.5 gr.

				$(NH_4)_2SO_4$ 1 mole/l stirring speed 550 r.p.m.	$(NH_4)_2SO_4$ 0.1 mole/l stirring speed 850 r.p.m.
Air Pressure p.s.i.	O_2 Pressure Kgr/cm^2	log P_{O_2} p.s.i.	log P_{O_2} Kgr/cm^2	log r_1 mole/min	log r_2 mole/min
200	2.95	1.62	0.47	-5.41	-
300	4.43	1.80	0.65	-5.24	-4.93
400	5.91	1.92	0.77	-5.20	-4.83
600	8.86	2.10	0.95	-5.09	-4.65
800	11.81	2.23	1.07	-5.04	-4.59
1200	17.72	2.40	1.25	-4.95	-4.53

It can be seen that independently of the stirring speed and ammonium sulphate concentration (conditions 2 are more favourable since the values of $(NH_4)_2SO_4$ and stirring speed favoured the mass transfer), The rate of leaching was about half order dependent on the oxygen pressure.

4.1.4 Effect of Stirring Speed

The effect of the stirring speed in the rate of leaching was studied for stirring speed values between 300 r.p.m. and 1000 r.p.m.

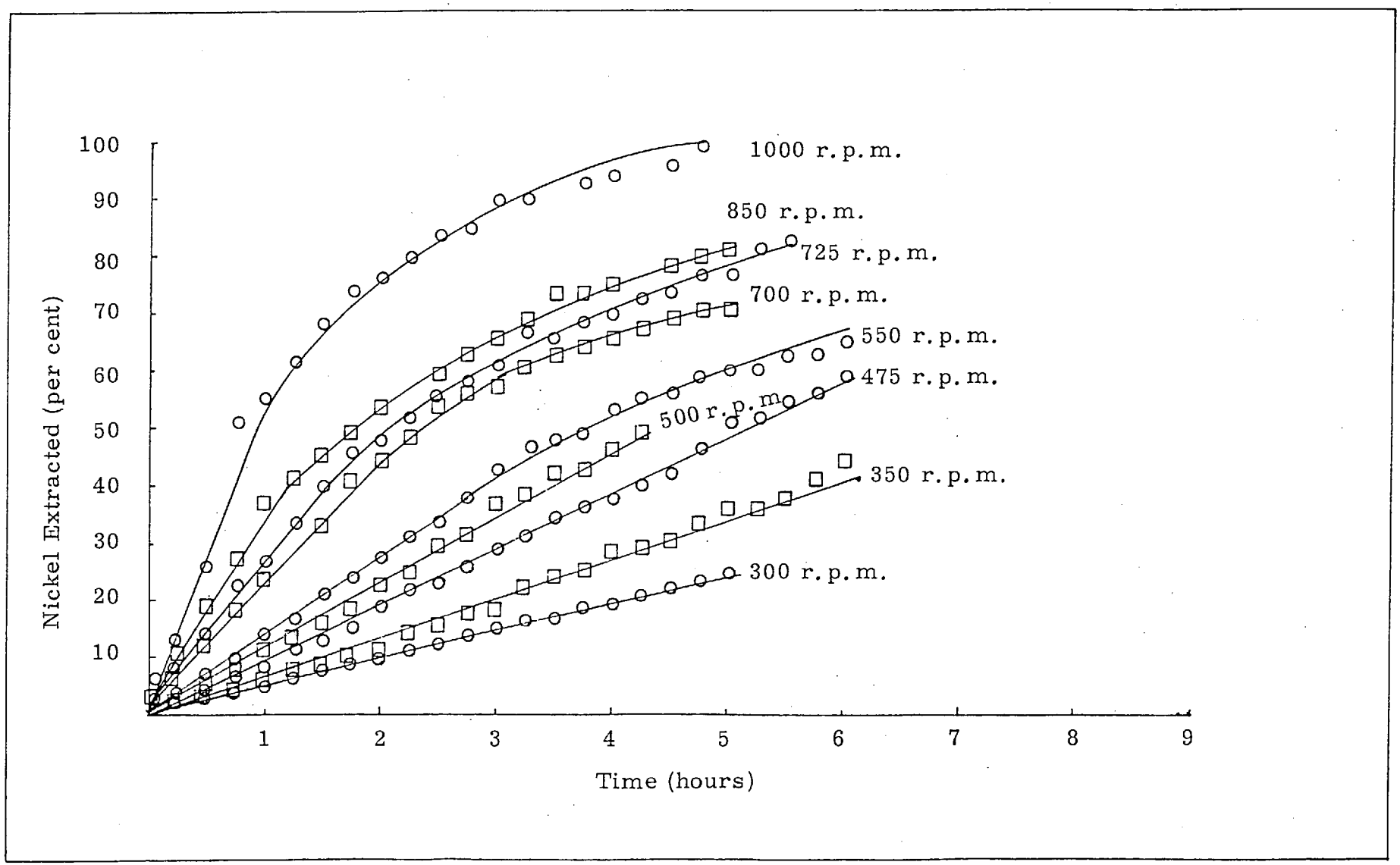


Fig. 46 Effect of Stirring Speed on the Leaching Rate

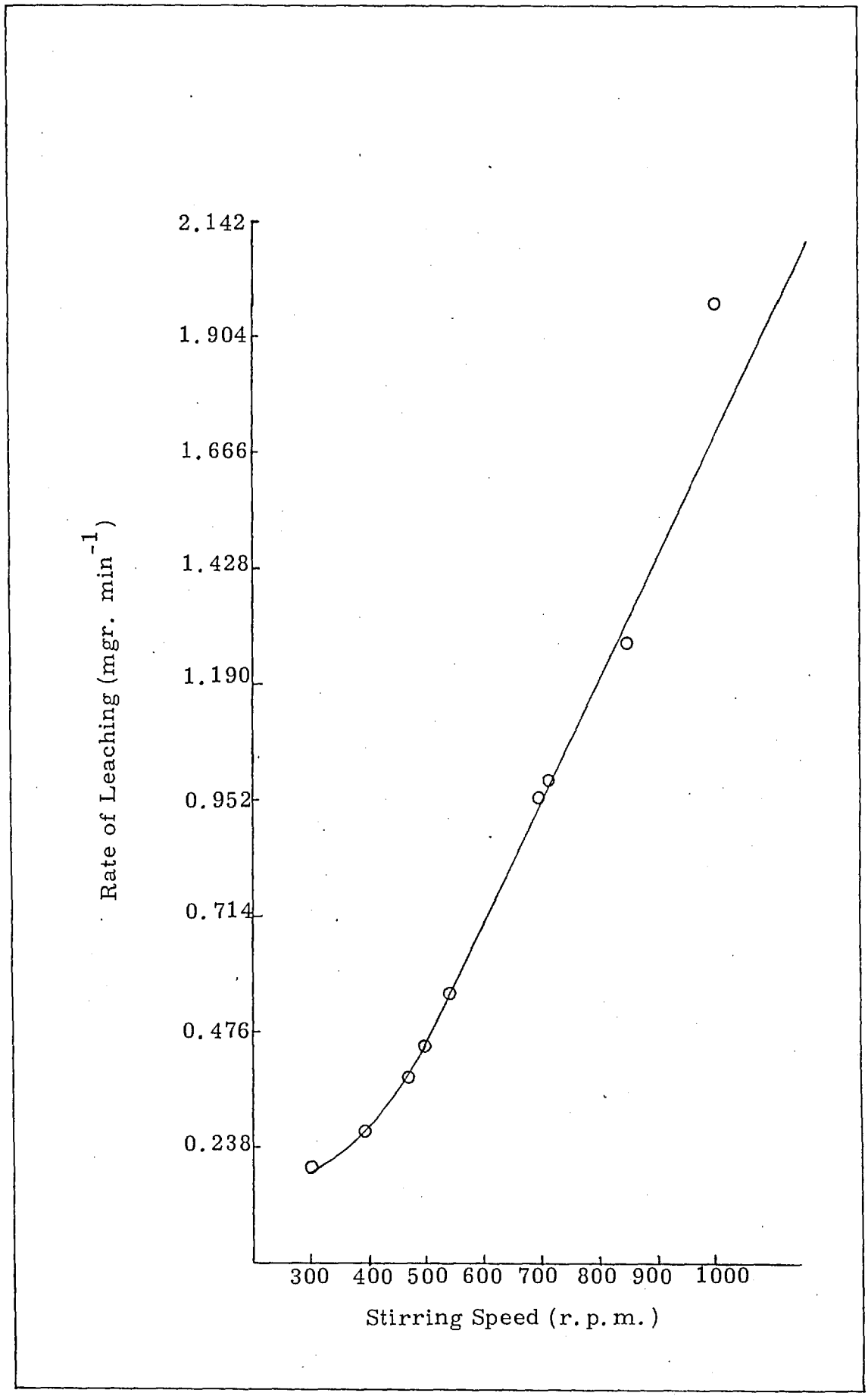


Fig. 47 Effect of Stirring Speed on the Leaching Rate

The results are given in Tables (A-17) to (A-25) and the percent nickel extracted for different stirring speed, versus time is represented in Figure 46. The rate of leaching versus stirring speed is represented in Figure 47.

The stirring speed had, under the condition used, a very great effect on the rate of leaching. Thus 53 wt% of nickel was extracted after 1 hour of leaching when the stirring speed was 1000 r.p.m. but only 15 wt % nickel was extracted when the stirring speed was 550 r.p.m. This seemed to indicate that mass transfer effects were very important. In fact, the type of curve shown in Figure 46 is typical of systems in which the reaction rate is limited by gas-liquid mass transfer. However, one-half dependence of oxygen pressure at 850 r.p.m. as well as 550 r.p.m. and an apparent activation energy of approximately 11 Kcal/mol. did not support gas-liquid mass transfer as the rate limiting process. In fact, as has been mentioned earlier, there probably was a 'mixed control' controlling mechanism; but it is believed that during the first stage of the process the 'diffusion of oxygen' had some degree of influence. The fact that the apparent activation energy was higher in such a type of rate controlling mechanism (diffusion control), apart from the fact that we think that the rate of leaching was controlled by a mixed mechanism, was probably due to the fact that the oxygen dissolution increased considerably with the temperature[112] (Fig. 17) altering the oxygen concentration in the bulk of the solution, and this generally means an increase in the slope of the Arrhenious plot. Although there were some reasons to believe that the diffusion of oxygen might have had some degree of influence in the rate of leaching nevertheless considering that kinetic studies have been carried out at constant stirring speed, dilute solid concentration (0.5 gr. of solid in 200 cc), relatively high oxygen pressure (11.81 Kg/cm^2) and

considering also the value of the apparent activation energy and the influence of oxygen pressure on the rate of leaching, it is very unlikely that the diffusion of oxygen was the main rate controlling factor.

4.1.5 Effect of the Particle Size and the Sample Weight

To investigate the effect of particle size on the leaching rate, experiments were carried out using the following particle size:- -53 + 45 μ, -90 + 60 μ, -180 + 125 μ, -300 + 212 μ, -425 + 300 μ. The different conditions under which the runs were carried out and the results are given in Tables (A-26) to (A-31) and Figures 48 and 49.

It can be seen in Figure 48 that the leaching rate increased when the particle size was changed from -180 + 125 u to -53 + 45 u. However, when the experiments were carried out using particles larger than -180 + 125 μ the rate of leaching also increased. This result was puzzling so the run using particle size -425 + 300 μ was repeated three times, the results are given in table (A-31) and it can be seen that the results were not reproducible. In order to test the reproductivity of the results in general the run using particle -180 + 125 μ was also repeated. The results are given in Table (A-32) and, in this case, they were reproducible. There could be two explanations of the results shown in Figures 48 and 49:

a) The particles contained many agglomerates of small size particles, the percentage of agglomerates being considerably higher in the particles theoretically selected as 'large' (-425 + 300 μ, -300 + 212 μ) than in the particles selected as 'small' (-53 + 45 μ, -90 + 60 μ, -180 + 125 μ). This misjudgment of the true size of the particles would affect

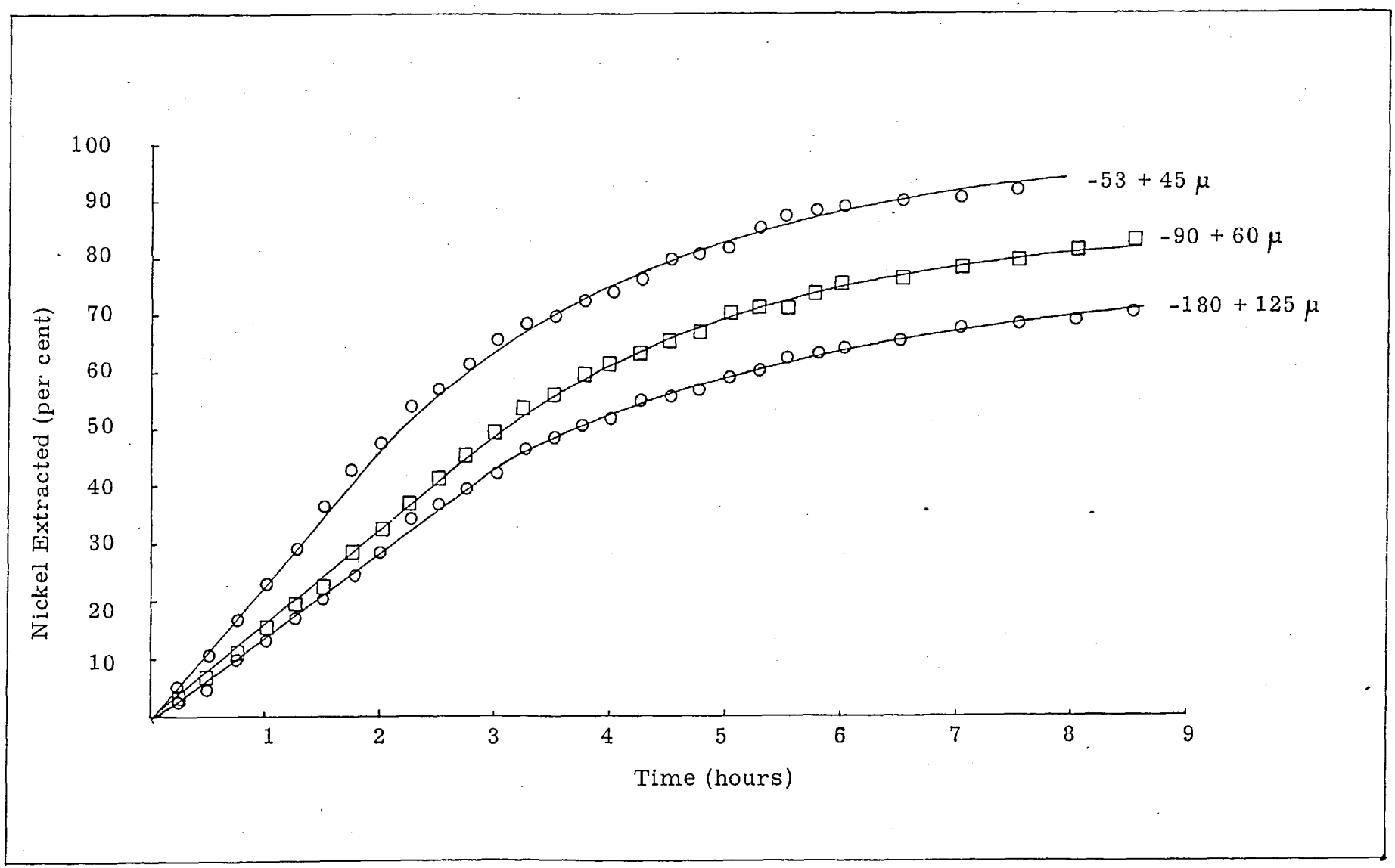


Fig. 48 Effect of the Particle Size on the Leaching Rate

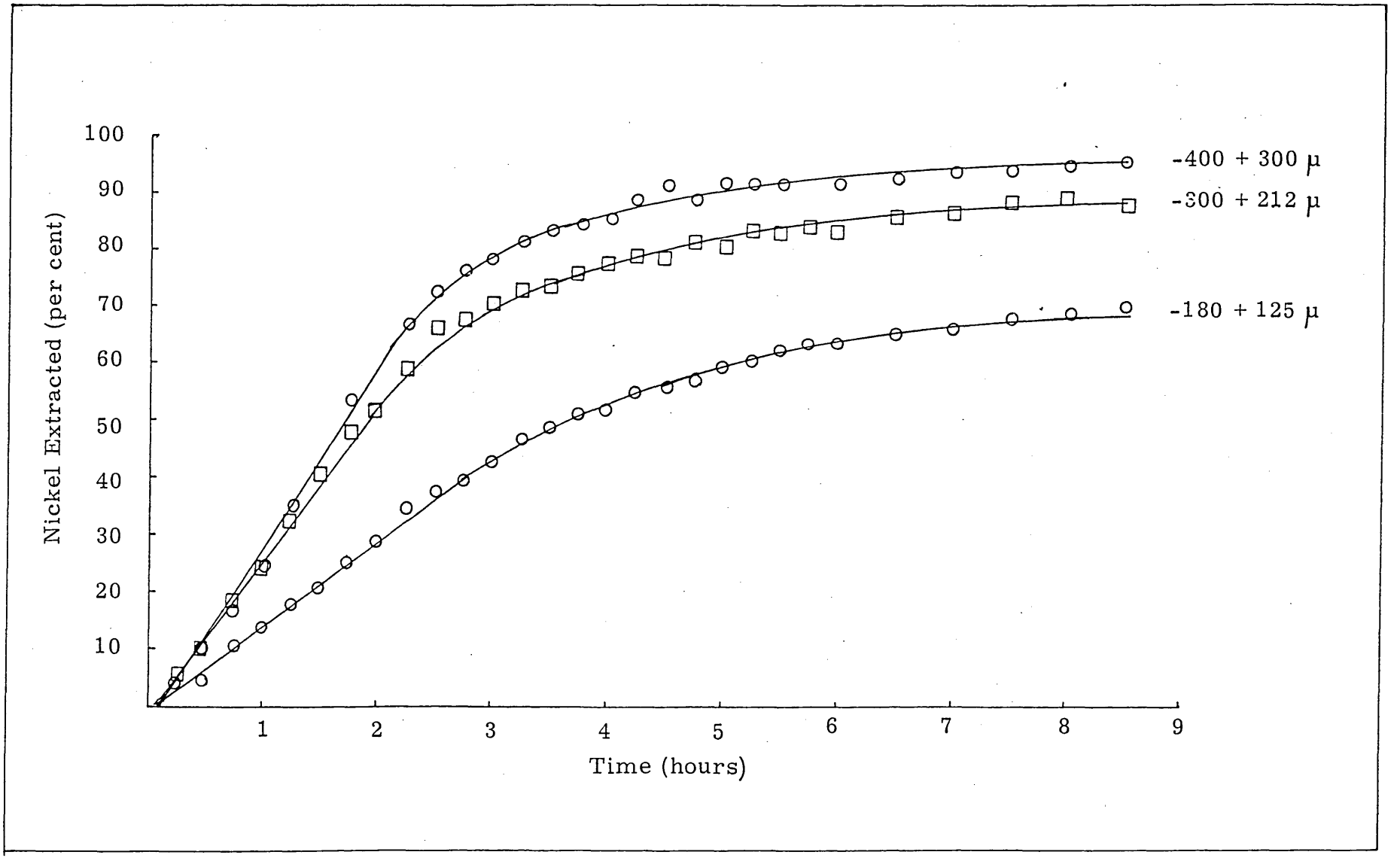


Fig. 49 Effect of the Particle Size on the Leaching Rate

the rate of leaching. Since as the percentage of agglomerates was higher in the particles selected as 'large' than in the 'small', the rate of leaching for the 'large' particles would be faster than for the 'small' particles.

b) The amount of holes on the 'large' particles was greater than on the 'small' ones. This would mean an increase in the surfacearea of the 'large' particles which, in turn would mean an increase in the rate of leaching at the beginning of the experiment and possibly the 'breaking down' of the particles when a certain degree of leaching had been achieved and this would further increase the rate of leaching.

Since the microscopic examination of the synthetic vaesite revealed the existence of many pits or holes (section 2.1.2) the explanation (b) seemed to be the more likely one.

The increase in the leaching rate with decreasing particle size was consistent with a reaction rate controlled by a surface reaction, but also with a reaction controlled by the diffusion of one of the reactants to the solid surface.

Two experiments were carried out using 0.5 gr. and 1 gr. of NiS_2 in order to find the effect of the amount of solid on the rate of leaching. The condition under which the experiments were carried out and the nickel extracted in percent are given in Tables (A-33) and (A-34). The milligrams of nickel extracted versus time are represented in Figure 50 and the rate of leaching in milligrams min^{-1} versus the amount of NiS_2 is shown in Figure 51. These results indicated that the extraction rate increased linearly with the increasing surface area of the solid, therefore

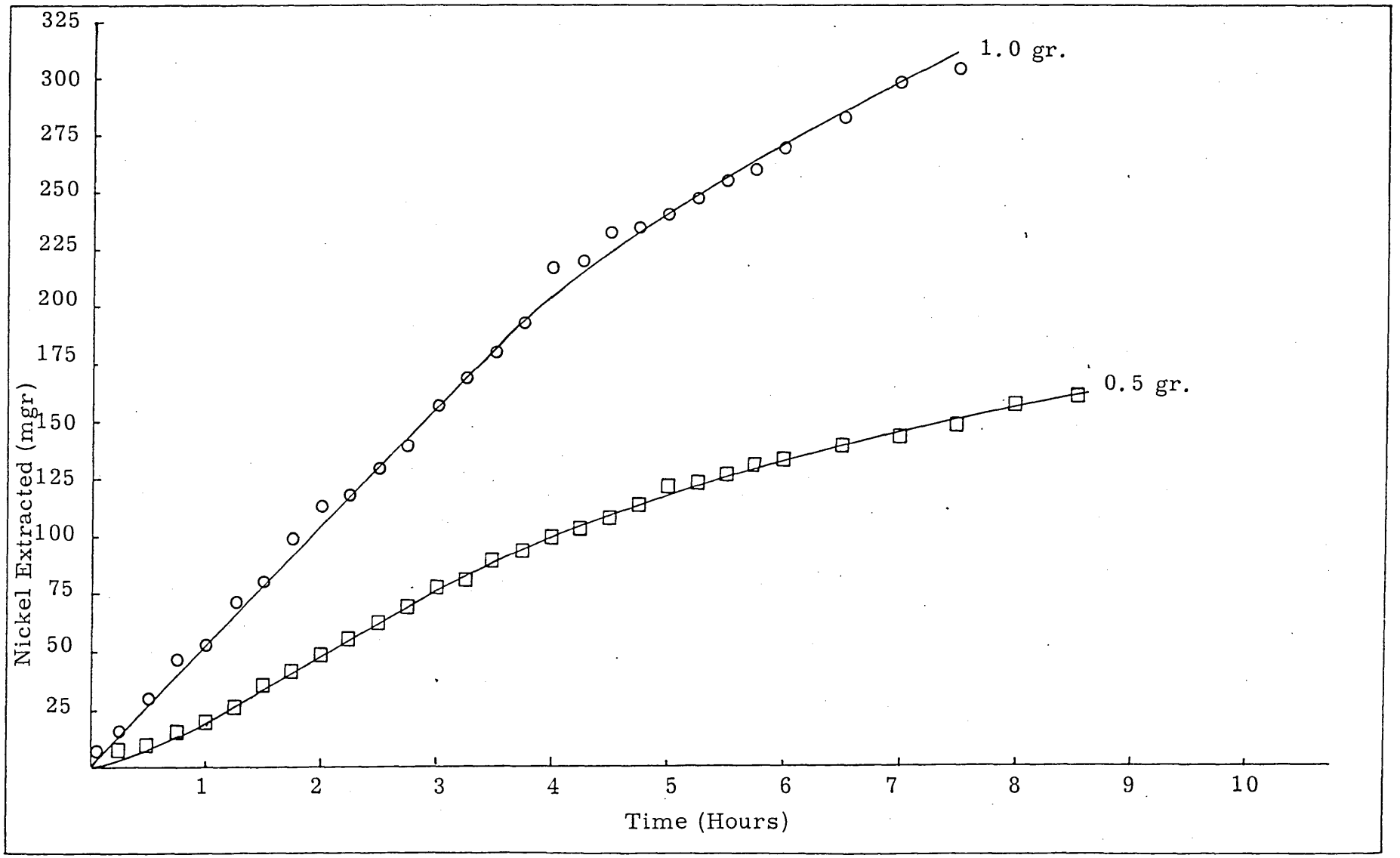


Fig. 50 Effect of the Sample Weight on the Leaching Rate

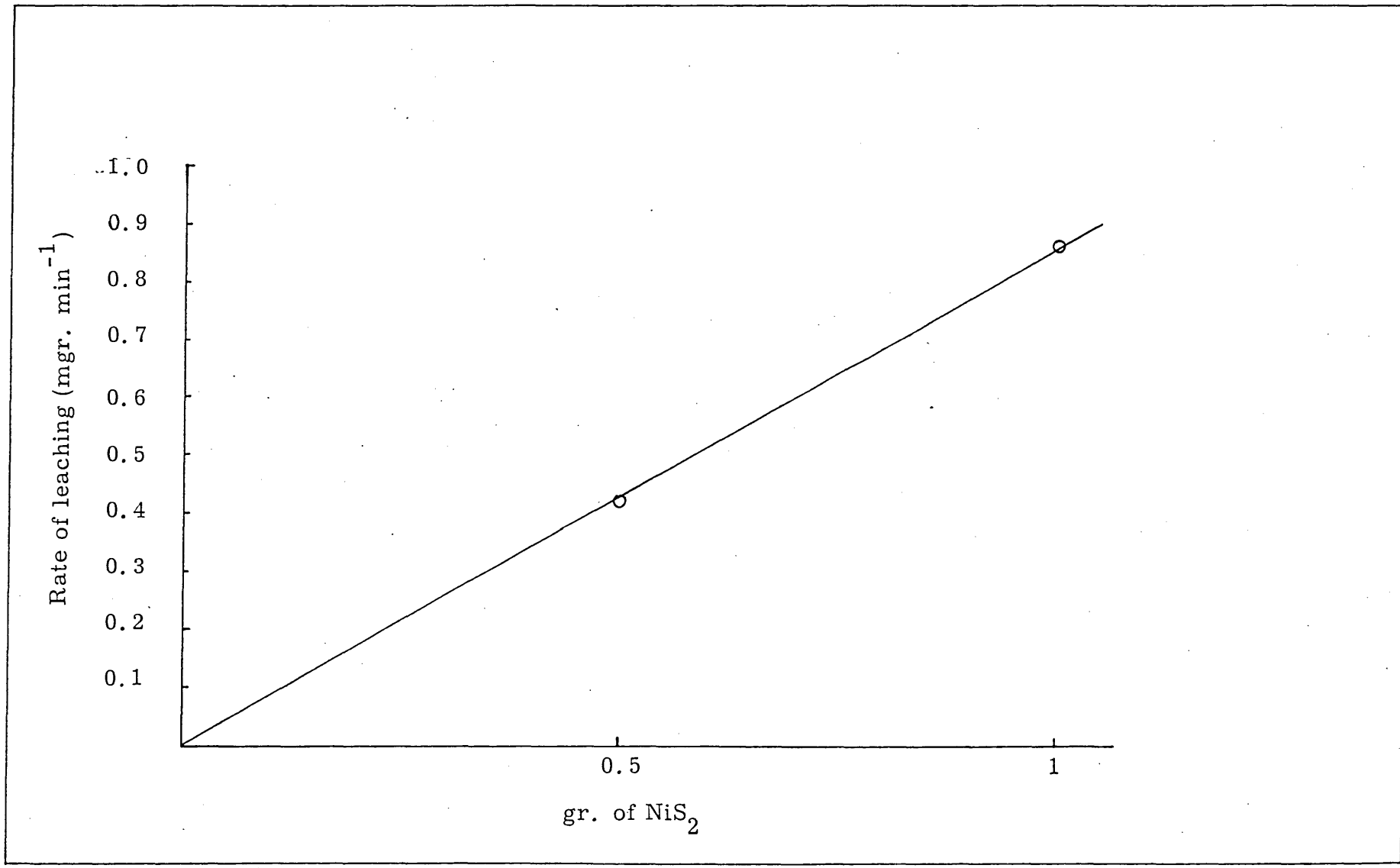


Fig. 51 Effect of the Sample Weight on the Leaching Rate

the leaching of NiS_2 during the first stage could be considered as a heterogeneous reaction which took place on the surface of NiS_2.

The results obtained in this section seemed to indicate that although a mixed controlling mechanism was probably involved the chemical surface reaction had the main effect and not some molecular transport step in the process.

Figure 52 shows the data given in Tables (A-33) and (A-34) plotted as $1-(1-x)^{\frac{1}{3}}$, where x is the fraction reacted at time 't'. The data fitted the function quite well until 45 wt% nickel extraction. This could be an indication that the rate was mainly controlled by a surface reaction with a shrinking core model. On the other hand, the equality of the function $1-(1-x)^{\frac{1}{3}}$ shown in Figure 52 at equal reaction times for different surface area/liquid volume ratios indicated that the reaction rate per unit area of solid was the same in each case, suggesting that during this first stage mass transfer from liquid to solid surface was not a significant rate-determining factor.

A further indication of the small importance of any molecular transport step in the process can be seen in Figure 53 where the function $1-(1-x)^{\frac{1}{3}}$ has been plotted versus time for the particles size -53+45μ, -90+60μ, -180+125μ and -38μ (the results and characteristics of the run carried out with particle size of -38μ are given in Table (A-35)). The high rate of reaction shown by the -38μ fraction of NiS_2 relative to that of -180+125μ and -90+60μ is further evidence that the rate of reaction was mainly controlled by a surface chemical reaction.

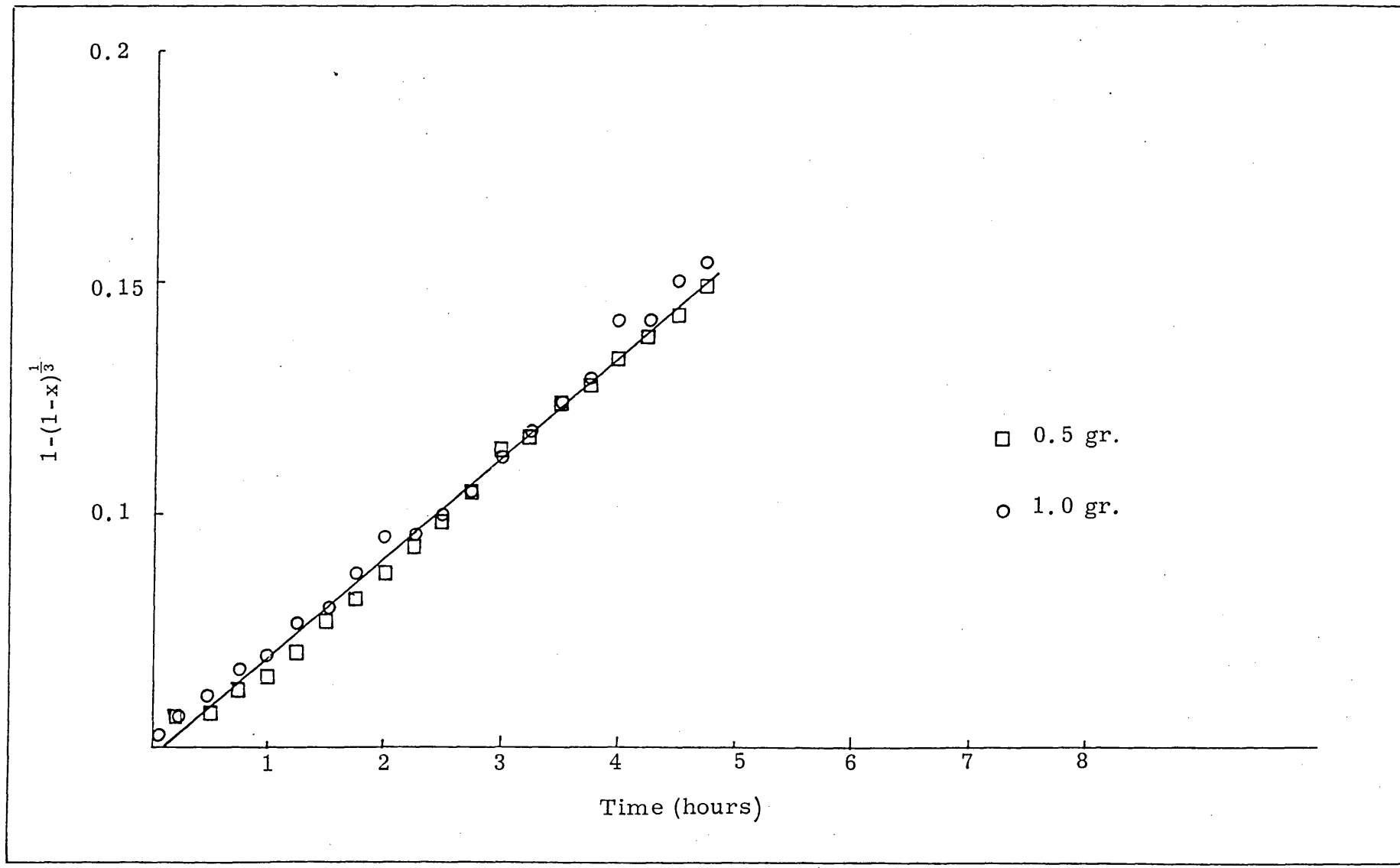


Fig. 52 Conversion as a Function of Sample Weight

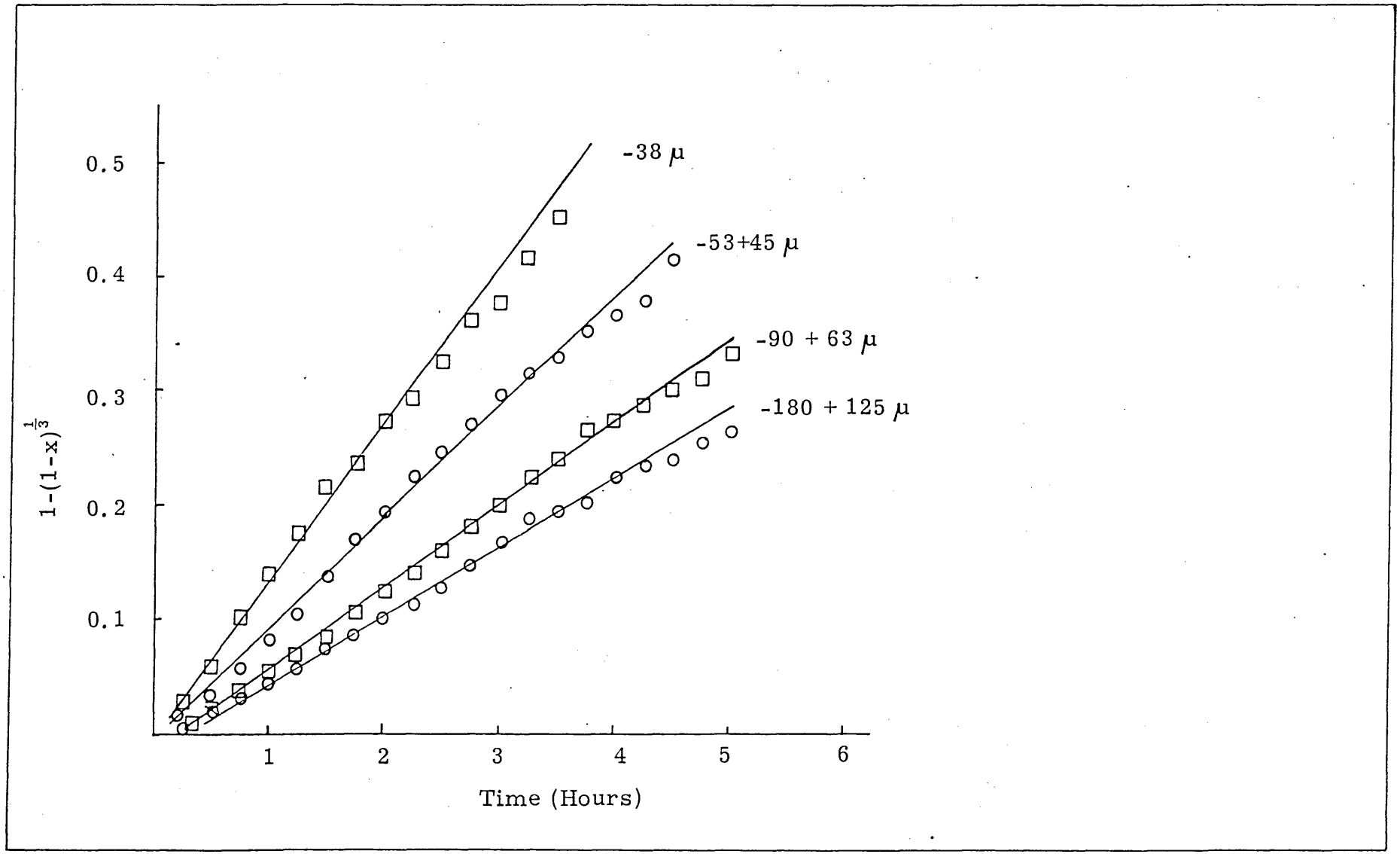


Fig. 53 Conversion as a Function of Particle Size

4.1.6 Effect of Ammonia Concentration

Two sets of experiments were carried out in order to test the effect of the concentration of ammonia in the rate of leaching. The first one was carried out at an ammonium sulphate concentration of 1 mole/l and stirring speed of 550 rpm; the second one was carried out at an ammonium sulphate concentration of 0.1 mole/l and a stirring speed of 850 r.p.m.

The ammonia concentration was varied from 5 gr/l to 60 gr/l. In each case the ammonia concentration was in excess of that required to form the nickel hexa-ammine if reaction were to go to completion. The condition and results of these experiments are given in Tables (A-36) to (A-42) and are represented in Figures 54 and 55. It can be seen that the reaction rate was not significantly influenced by the free ammonia concentration. In fact, the rate of leaching was slightly smaller at high ammonia concentration than at low ammonia concentration. This was thought to be due to the slight decrease in the solubility of oxygen when the concentration of ammonia was increased (Fig. 19). On the other hand, when the ammonium sulphate concentration was 0.1 mole/l and the ammonia concentration was kept at low value (5 gr/l and 10 gr/l), there was a clear decrease in the per cent nickel extracted once a certain degree of extraction was achieved. This was due to the hydrolysis of the nickel hexa-ammine which was not stable under these conditions. It was thought that the amount of ammonia available in most of the experiment (60 gr/l) was so larger in comparison with the amount of oxygen that the rate of leaching became independent on the ammonia concentration and dependent on the concentration of oxygen, which in turn depended on the ammonium sulphate concentration and, to a smaller extent, on the ammonia concentration (Fig. 18 and 19) and the rate of transport of oxygen to the surface which, in turn, depended on the stirring speed.

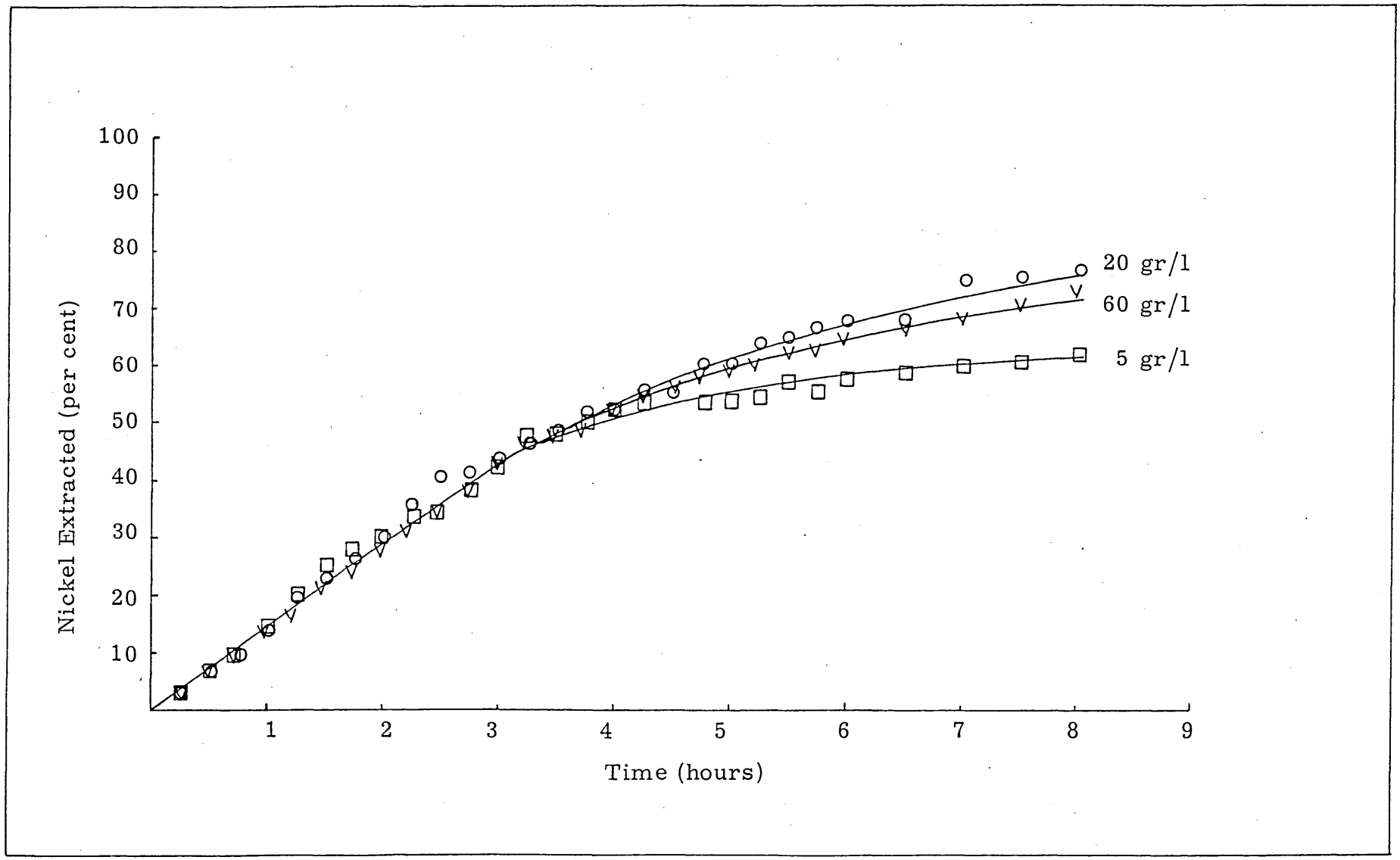


Fig. 54 Effect of NH_3 Concentration on the Leaching Rate

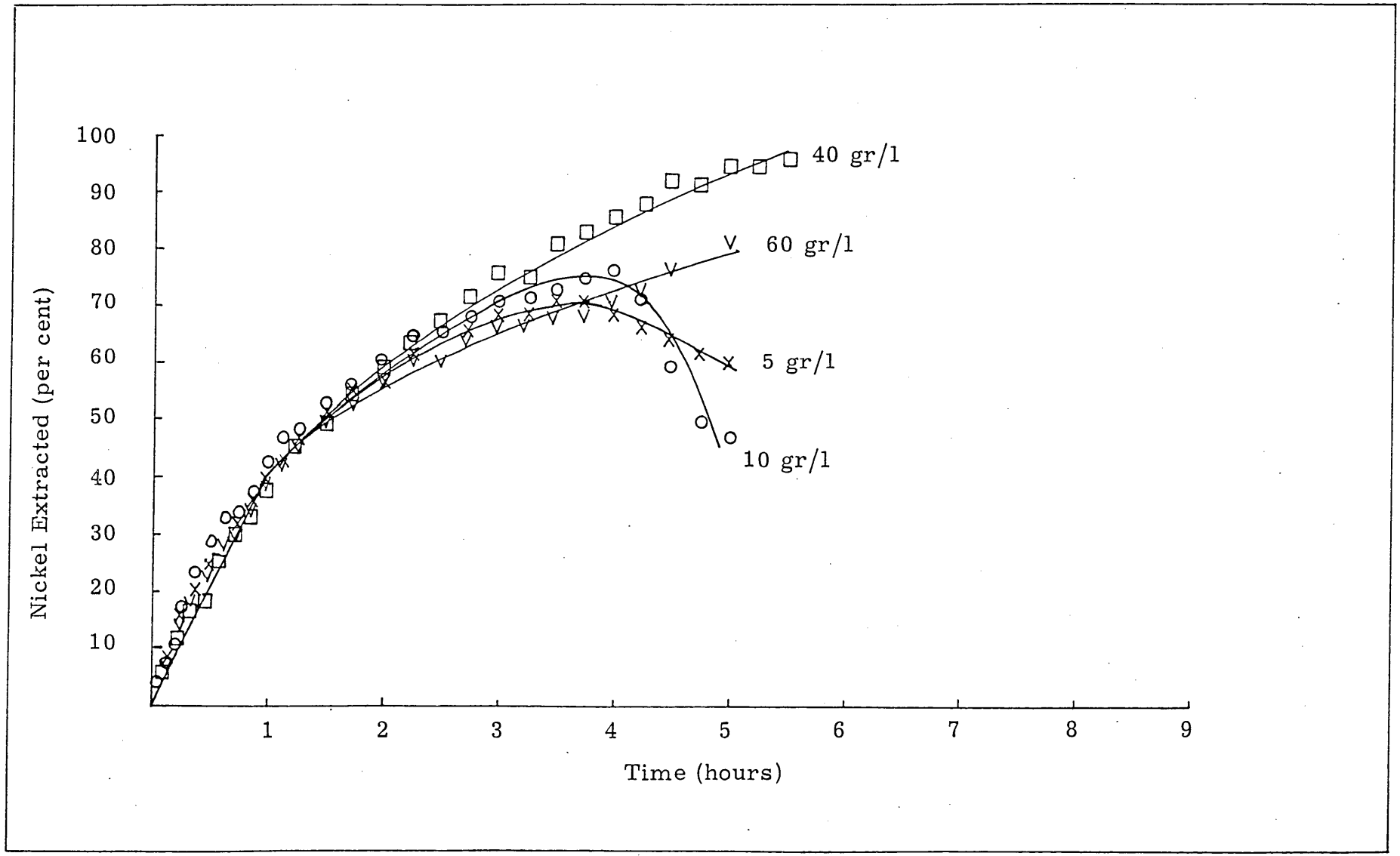


Fig. 55 Effect of NH_3 Concentration on the Leaching Rate

4.1.7 Effect of the Ammonium Sulphate Concentration

In order to study the effect of the concentration of ammonium sulphate on the rate of leaching a set of experiments was carried out in which the concentration of ammonium sulphate was varied from 0 mole/l to 1 mole/l. The conditions and results of the experiments are given in Tables (A-43) to (A-49). The percentage of nickel extracted for different ammonium sulphate concentrations, versus time is represented in Figures 56 and 57, and the rate of leaching in terms of mgr min^{-1} versus ammonium sulphate concentration is represented in Figure '58a'. It can be seen that the rate of leaching increased when the concentration of ammonium sulphate was increased up to a certain value (around 0.1M of $(NH_4)_2SO_4$) but it decreased if the concentration of ammonium sulphate was further increased. It was thought that the ammonium sulphate did not intervene directly in the leaching process but it was obvious that its presence in moderate concentrations (0.1 to 0.2 mol/l) favoured both the rate of leaching and the percentage of nickel extracted. The low rate of extraction and the low percentage of nickel extracted when ammonium sulphate was not present or when its concentration was very low was not due to an insufficient amount of $SO_4^=$ in solution, since enough sulphur from NiS_2 was oxidized to form $Ni(NH_3)_6SO_4$ as it will be seen in section 4.1.9, but rather to the instability of the nickel hexa-ammine in unbuffered solutions ($pH \leq 12$). The main role of the ammonium sulphate was due to the buffering action of ammonia-ammonium ion because the nickel hexa-ammine became stable in buffered solutions ($pH \leq 10$). A thermodynamic study of the stability of nickel hexa-ammine complex ion in aqueous solution is given in Appendix 1 and in section 4.1.8. Further evidence of the high temperature hydrolysis of the hexa-ammine when the $(NH_4)_2SO_4$ concentration was low will be added in section 4.1.9 and 4.2.

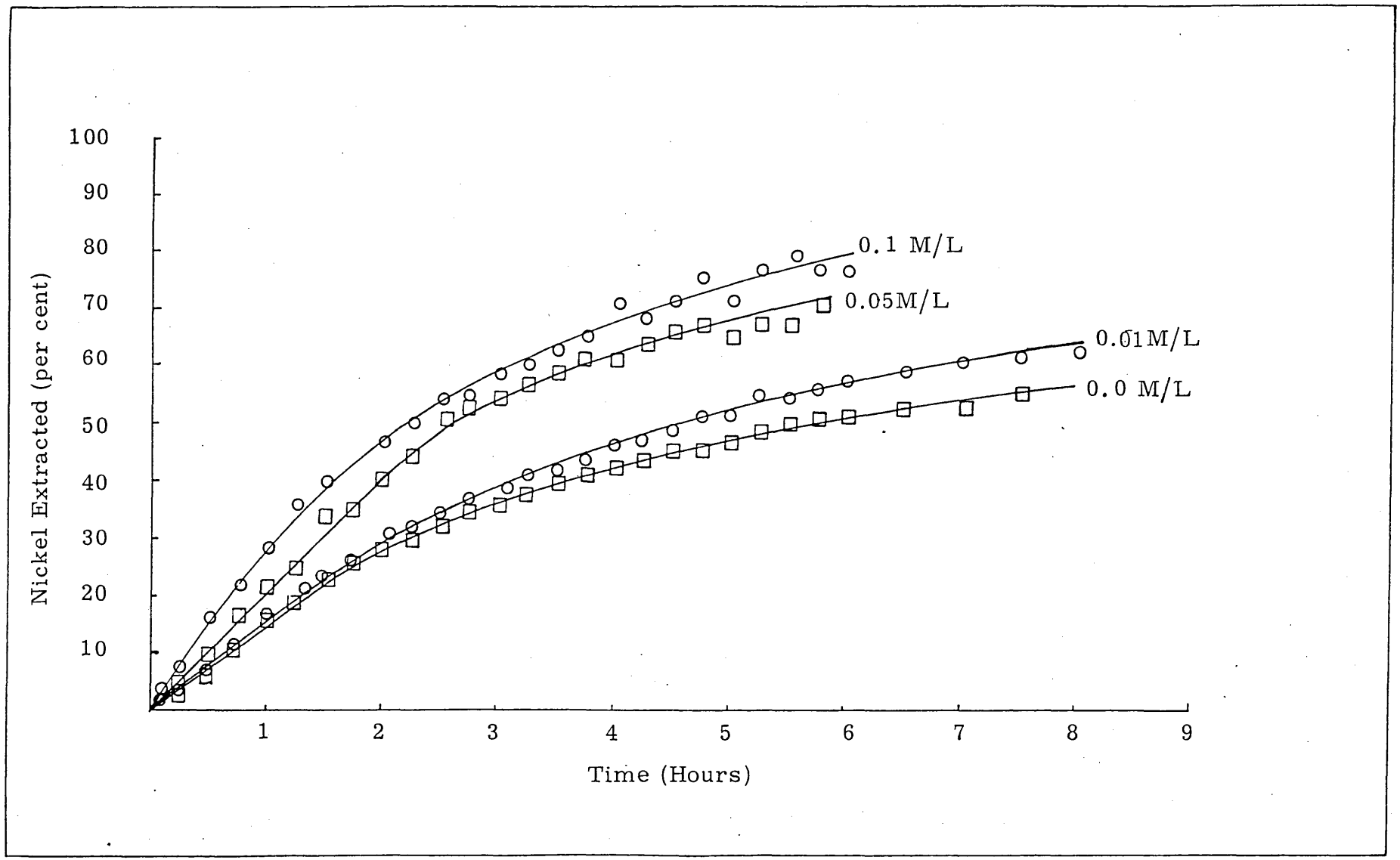


Fig. 56 Effect of $(NH_4)_2SO_4$ Concentration on the Leaching Rate

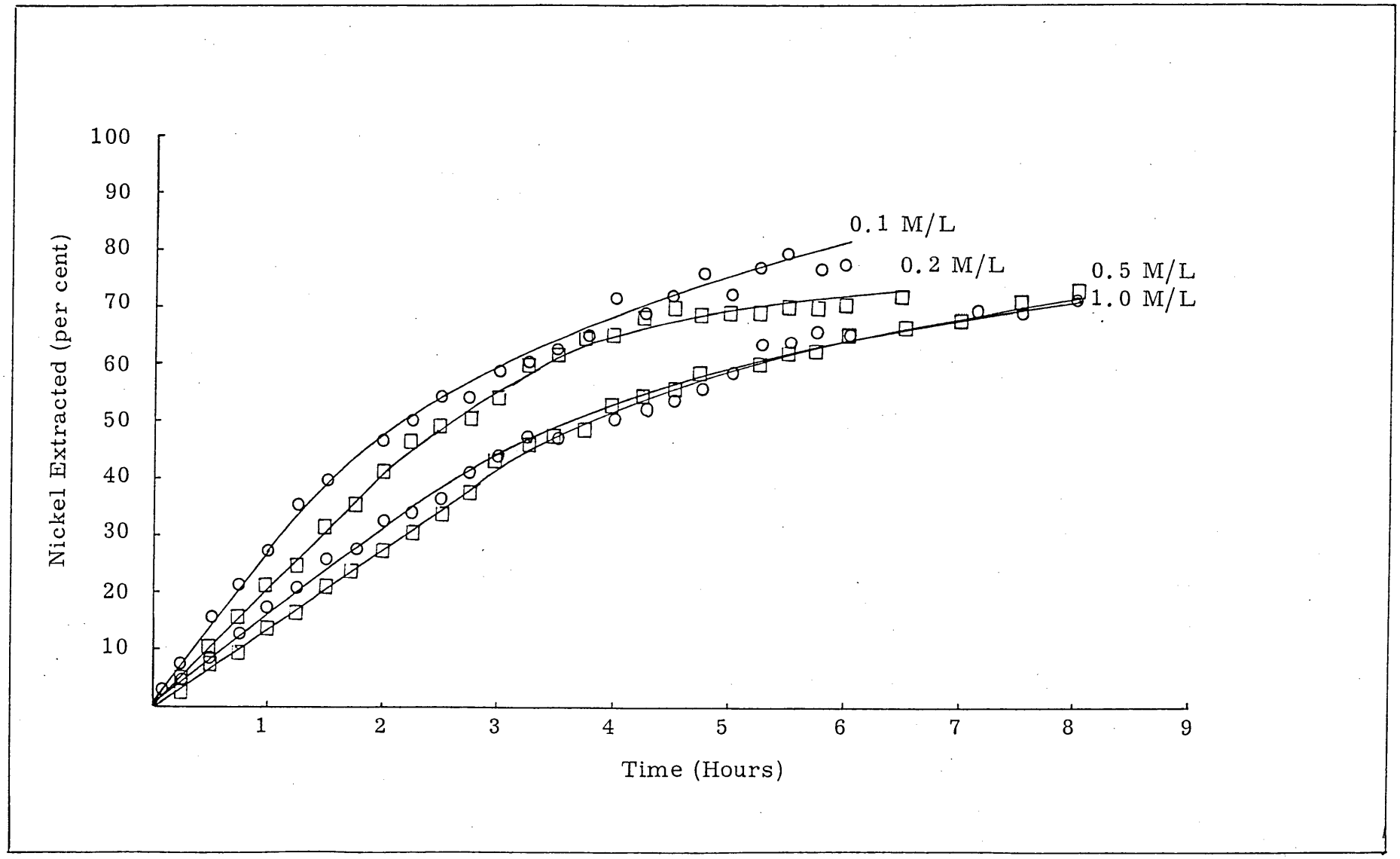


Fig. 57 Effect of $(NH_4)_2SO_4$ Concentration on the Leaching Rate

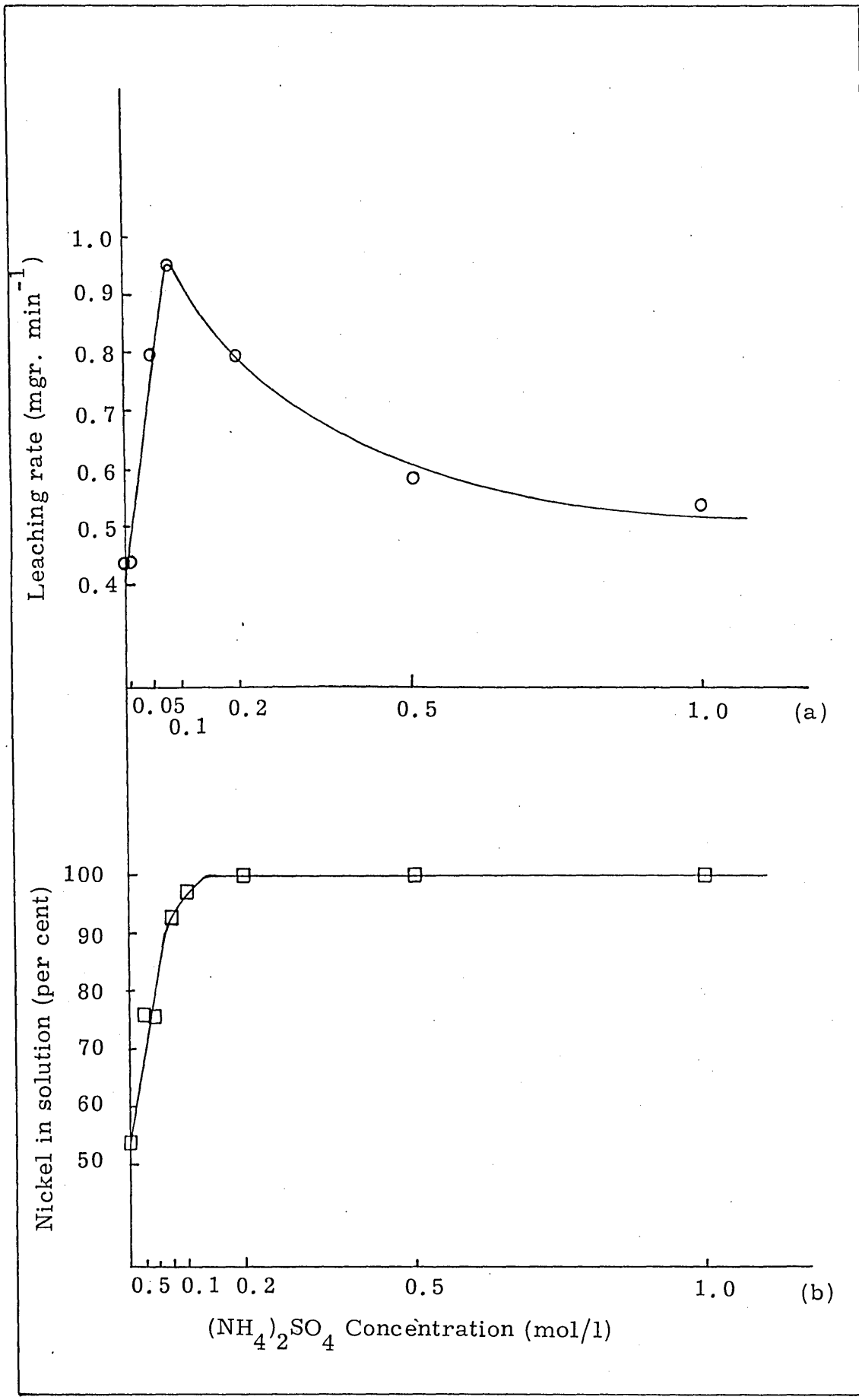


Fig. 58a Effect of the $(NH_4)_2SO_4$ concentration on the leaching rate.

Fig 58b Effect of the $(NH_4)_2SO_4$ concentration on the degree of hydrolysis

On the other hand, when the ammonium sulphate concentration was higher than 0.1 mole/l the rate of leaching decreased (Fig. 58). This was due to the decrease in the solubility of oxygen in the solution when the concentration of ammonium sulphate increased (Fig. 18) and since the availability of oxygen has been demonstrated to be very important in the leaching process the decrease in the solubility of oxygen caused a decrease in the rate of leaching.

4.1.8. The Hydrolysis of Nickel Hexa-ammine

In preliminary leaching runs using unbuffered solution and solution to which ammonium sulphate was added, it was apparent that higher yields of soluble nickel and higher rates of leaching were obtained in the buffered solutions. A side reaction was considered to be a possibility, reducing the maximum obtainable yield and the rate of leaching in unbuffered experiments. One reaction known to occur as has been reported by Mellor[118], is the hydrolysis of the nickel hexa-ammine, presumably according to the reaction:-

$$Ni(NH_3)_6^{++} + 2H_2O \rightleftharpoons Ni(OH)_2 + 4NH_3(aq) + 2NH_4^+ \qquad (4.1.8.1)$$

The equilibrium relationship can be expressed as:

$$K = KcKy$$

with

$$Kc = \frac{(M + 2Cx)^2(N + 4Cx - 6C)^4}{C(1-x)(W-2Cx)^2} \qquad (4.1.8.2)$$

where

x = fraction of $Ni(NH_3)_6^{++}$ decomposed at equilibrium

N = moles/l of NH_3 originally present

W = moles/l of H_2O originally present

M = moles/l of NH_4^+ originally present

C = moles/l of Ni originally present

and

$$K_y = \frac{y_N^4 \; y_M^2}{y_C \; y_W^2}$$

where

y_N = activity coefficient for aqueous NH_3
y_M = mean ion activity coefficient of $(NH_4)_2SO_4$
y_C = mean ion activity coefficient of $Ni(NH_3)_6SO_4$
y_W = activity coefficient of water

The value of'K'can be calculated from data in the literature. Using the free energy data given in appendix (1), the following free energy can be estimated for 25°C, 100°C, and 150°C:

$25^oC \quad \Delta G_R = -99.224 + 4(-6.35) + 2(-18.97)+61.2+2(56.687) = 12.01$ Kcal/mol

$100^oC \quad \Delta G_R = -111.99+4(-8.42)+2(21.30)+68.27+2(58.1) = -3.8$ Kcal/mol

$150^oC \quad \Delta G_R = -114.26+4(-9.88)+2(-23.12)+72.27+2(59.2) = -9.35$ Kcal/mol

Using these values the following values for the equilibrium constant can be obtained: $K_{25^oC} = 1.55 \times 10^{-9}$, $K_{100^oC} = 1.7 \times 10^{2}$, $K_{150^oC} = 6.9 \times 10^{4}$. For a typical leaching run in an unbuffered system the concentration of the reactants were as follows: W = 52.2 moles/l, N = 3.5 moles/l, M = 0 moles/l, C = 0.0203 mole/l (supposing that all the nickel in 0.5 gr. of NiS_2 was dissolved as $Ni(NH_3)_6^{++}$). On the other hand, in this system the relationship between activities and concentration was unknown, so that as a first approximation, activity coefficients can be taken as unity. Bearing this in mind and substituting the values of W, N, M, C, and K in the formula (4.1.8.2) the value of the degree of hydrolysis, x, could be estimated at 25°C, 100°C and 150°C. The values were x = o for 25°C, x = 0.99 for 100°C and x = 0.9999 for 150°C. The value obtained for the degree of hydrolysis

at 25°C seemed to be the true one since the hydrolysis did not occur at 25°C. However considering that for unbuffered solutions around 50 wt % of nickel was dissolved at 150°C it was obvious that the degree of hydrolysis at 100°C and 150°C estimated using thermodynamic data was too large. It is interesting to point out that some of the thermodynamic data used for the calculation of the equilibrium constant at high temperature cannot be considered very reliable, for instance, the high temperature free energy for $Ni(NH_3)_6^{++}$ was estimated using 'Criss and Cobble's Correspondence Principle'[155-156]. Since a small free energy change of reaction calculated in this way was subject to very large percentage errors and hence theoretical calculations, when combined with the difficulty of estimating activity coefficient, would not yield accurate values for the extent of the hydrolysis. Nevertheless, these thermodynamic values will be used to calculate the $Ni(NH_3)_6^{++}$ stable region and it will be clearly seen that an unstable region can exist. The degree of hydrolysis was also checked experimentally. An experiment was carried out as indicated in section 2.2.1. The amount of nickel sulphate was such that the concentration of nickel in solution was the same as that obtained when 0.5 grs. of vaesite were completely dissolved (100 wt % nickel recovery) in a leaching experiment. The concentration of $(NH_4)_2SO_4$ was different for each ampoule. The experiment was carried out at 150°C. The conditions under which the experiment was carried out and the degree of hydrolysis obtained (x) are given in Table 24.

Table 24

Conditions:

N = 3.5 moles/l

C = 0.0203 moles/l

W = 52.2 moles/l

T = 150°C

$(NH_4)_2SO_4$ concentration moles/l	Degree of hydrolysis	X-ray Diffraction
0	0.45	$Ni(OH)_2$
0.025	0.24	possible $Ni_6Si_4O_{10}(OH)_8$
0.05	0.24	possible $Ni_6Si_4O_{10}(OH)_8$
0.075	0.07	-
0.1	0.02	-

The solid products obtained were analysed by x-ray diffraction and the results of the analysis are given in section 4.2.

It is interesting to point out that, as expected, hydrolysis of the hexa-ammine did not occur at 25°C. Nevertheless, as some hydrolysis had to occur at this temperature the degree of hydrolysis was considered to be 0.01, this value was used in the calculation subsequently.

It can be seen (Table 24) that the hydrolysis of the hexa-ammine seemed to take place when the concentration of ammonium sulphate was low but when the concentration was higher than 0.1 moles/l the hydrolysis reaction did not occur at the temperature which we were concerned (150°C).

The value of the degree of hydrolysis x, obtained at 150°C and the value estimated at 25°C for unbuffered solutions ($(NH_4)_2SO_4$ concentration = 0) were used in the equation 4.1.8.2 and this in turn was used to calculate the free energy change (Table 25).

TABLE 25

Calculation of Free Energy Change for Ammine Hydrolysis

	T = 25°C	T = 150°C
M	0	0
N	3.5	3.5
C	0.0203	0.0203
W	52.2	52.2
X	0.01	0.45
K = equilibrium constant	$3.9\ 10^{-7}$	$1.5\ 10^{-3}$
ΔG^{o} = Free energy change cal/mol	8734	5469

The values for the equilibrium constant were calculated using concentration (Formula 4.1.8.2), this was not thermodynamically correct since the activity coefficients in this system were not unity. However, lacking information on these values for all components, it was not possible to obtain a thermodynamically correct value of the equilibrium constant. All the same these values can be used to predict equilibrium compositions at other conditions than those used experimentally. Using a relationship of the form $\Delta G^{o}_{T} = A + BT$, the data shown in Table 22 can be used to obtain the standard free energy change.

$$\Delta G_1 = 16517.8 - 26.12T$$

This equation was used to calculate the degree of hydrolysis of the nickel hexa-ammine at a variety of conditions, these results are summarized in Figure 59 and 60. Examining this figure the following conclusions can be drawn:

a) It can be seen in Figure 59 that for an unbuffered solution ($(NH_4^+) = O$), the degree of hydrolysis at a given temperature and at constant metal concentration decreases as the initial concentration of free ammonia increases.

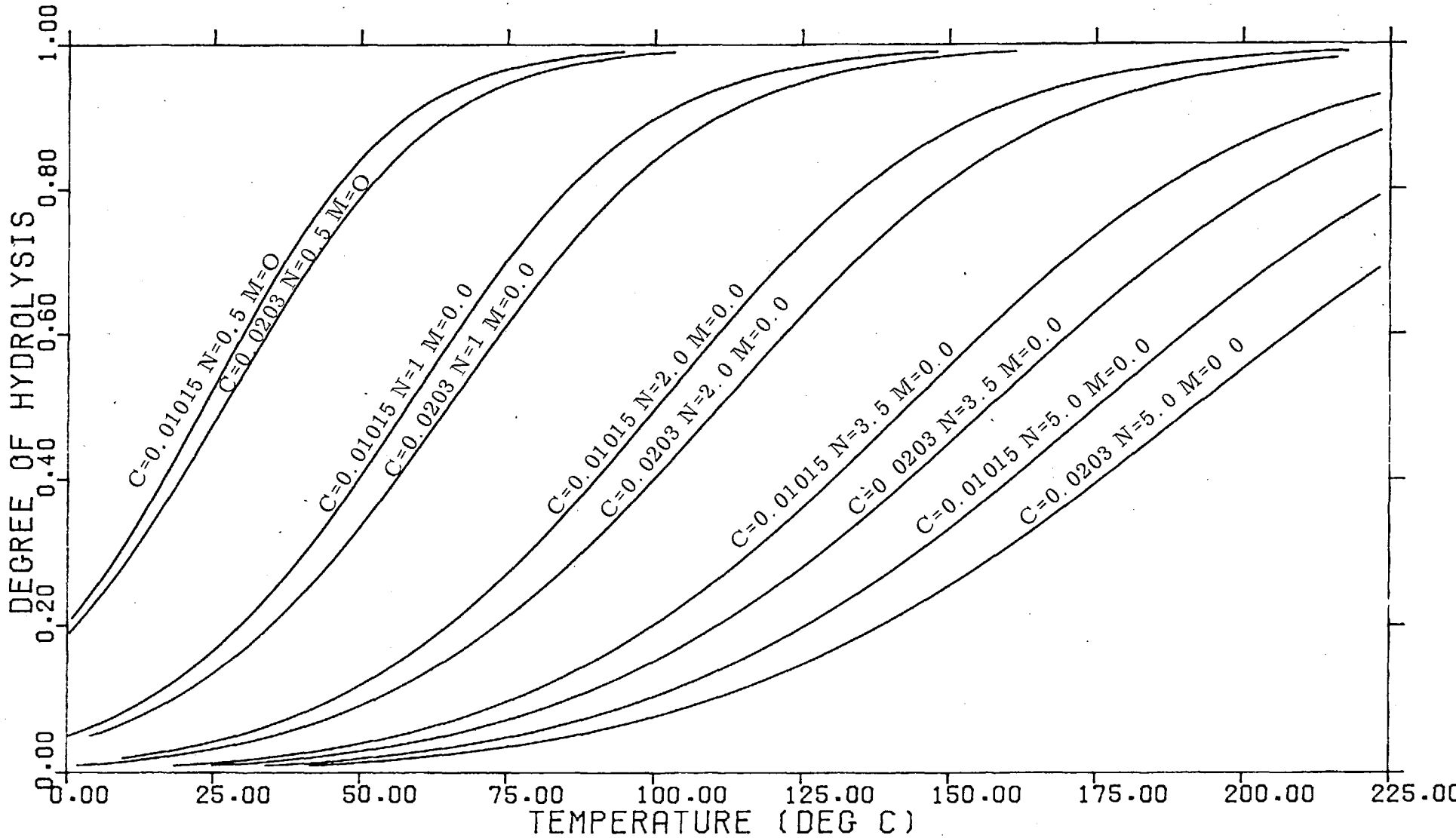


Fig. 59 Hydrolysis of Nickel Hexa-ammine

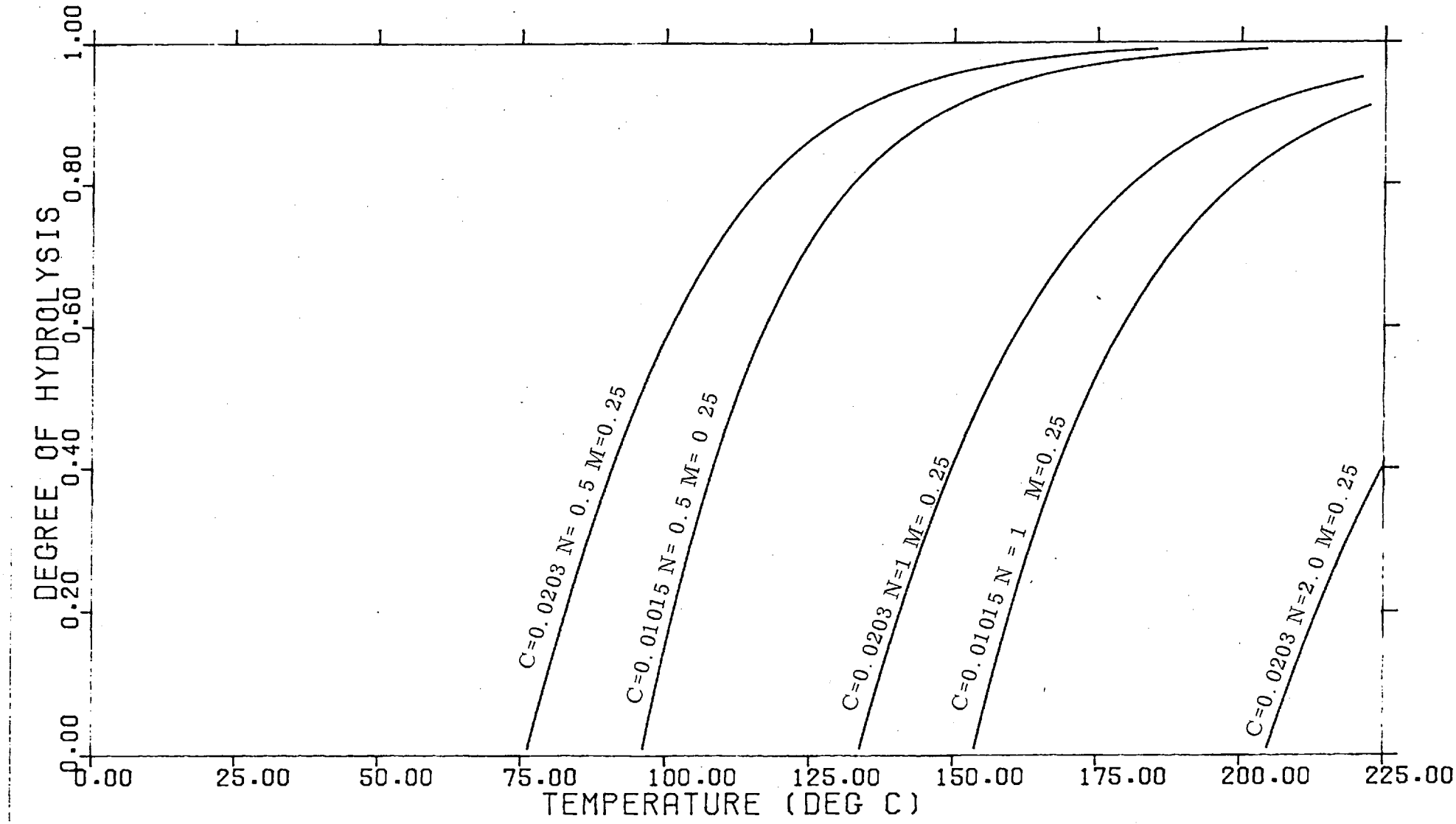


Fig. 60 Hydrolysis of Nickel Hexa-ammine

b) For an unbuffered solution (Fig. 59), the absolute amount of nickel in solution also affects the equilibrium since the degree of hydrolysis at a given temperature and at constant free ammonia concentration, increases slightly when the concentration of nickel in solution decreases.

c) It can be seen in Figure 60 that, for a buffered solution ((NH_4^+) = 0.25 M/L), the hydrolysis reaction only takes place when the free ammonia concentration is low (1 M/L or less) and therefore the presence of NH_4^+ in solution, even in moderate concentration has a major effect in preventing hydrolysis of the metal complexes.

d) It can be seen in Figure 60 that at a given temperature and at low concentration of free ammonia the degree of hydrolysis increases considerably with the concentration of metal in solution and it can be that at a given temperature and a given value of metal concentration, the degree of hydrolysis is 0.60 whereas when the concentration of metal in solution is half the value previously considered the hydrolysis reaction does not occur. This could explain the sudden drop in the metal concentration observed for certain concentrations of ammonia in Figure 55, because when a certain concentration of nickel in solution is reached the hydrolysis reaction can be expected to occur.

4.1.9 Qualitative Analysis of the Intermediate Partially Oxidized Sulphur Species and Quantitative Analysis of Sulphate in the Leach Solution

The presence of large amounts of ammonium sulphate such as were present in the buffered solutions where the typical concentration of ammonium sulphate was 1 mole/l, would have made it very difficult

to determine the $SO_4^=$ or other oxidized sulphur compounds, due to their relatively small concentration. Such compounds, would be products of the oxidation of only 0.5 grs. of NiS_2, in the leach liquor. Therefore an experiment was carried out in which the initial ammonium sulphate concentration was 0 mole/l (unbuffered system) in order to analyse qualitatively and quantitatively the sulphur species in samples taken periodically. The conditions under which the experiment was carried out as well as the results of the run are given in Table (A-50). The qualitative analysis of the different sulphur species was performed in samples taken after 15, 30, 45 and 60 minutes of leaching as well as in the so-called 'test solution' according with the procedure described in section (2.3.3). Test 1, 2 and 3 were positive when performed in the 'test solution' but thiosulphates, polithionates and sulphamates were not detected in the leach liquor samples. However $SO_4^=$ was present in all the leach liquor samples. It seemed that under the conditions used the sulphur was oxidized only to sulphate. Quantitative analysis of the sulphate in the leach solutions was also carried out according with the procedure described in section 2.3.4. The results of the analysis are given in Table (A-50) and in Figures 61 and 62. It can be seen that the rate of extraction of sulphur was greater than the rate of extraction of nickel. Since the chemical equation for the oxidation of vaesite in ammoniacal medium may be written:-

$$NiS_2 + 8NH_3 + \frac{7}{2}O_2 + H_2O = Ni(NH_3)_6^{++} + 2SO_4^= + 2NH_4^+$$

It seemed logical to suppose that the rate of extraction of sulphur would be equal to the rate of extraction of nickel. The fact that the rate of extraction of nickel was smaller than the rate of extraction of sulphur seemed to be due to the hydrolysis of the nickel hexa-ammine and the subsequent precipitation of $Ni(OH)_2$ according to the reaction:

$$Ni(NH_3)_6SO_4 + 2H_2O = Ni(OH)_2 + 4NH_3(aq) + (NH_4)_2SO_4$$

It seemed that in unbuffered solution the precipitation of $Ni(OH)_2$ occurred as soon as some $Ni(NH_3)_6^{++}$ was formed.

Further indication of this has been reported in section 4.1:8 where it has been demonstrated that the degree of hydrolysis for unbuffered solutions increases when the concentration of metal in solution decreases.

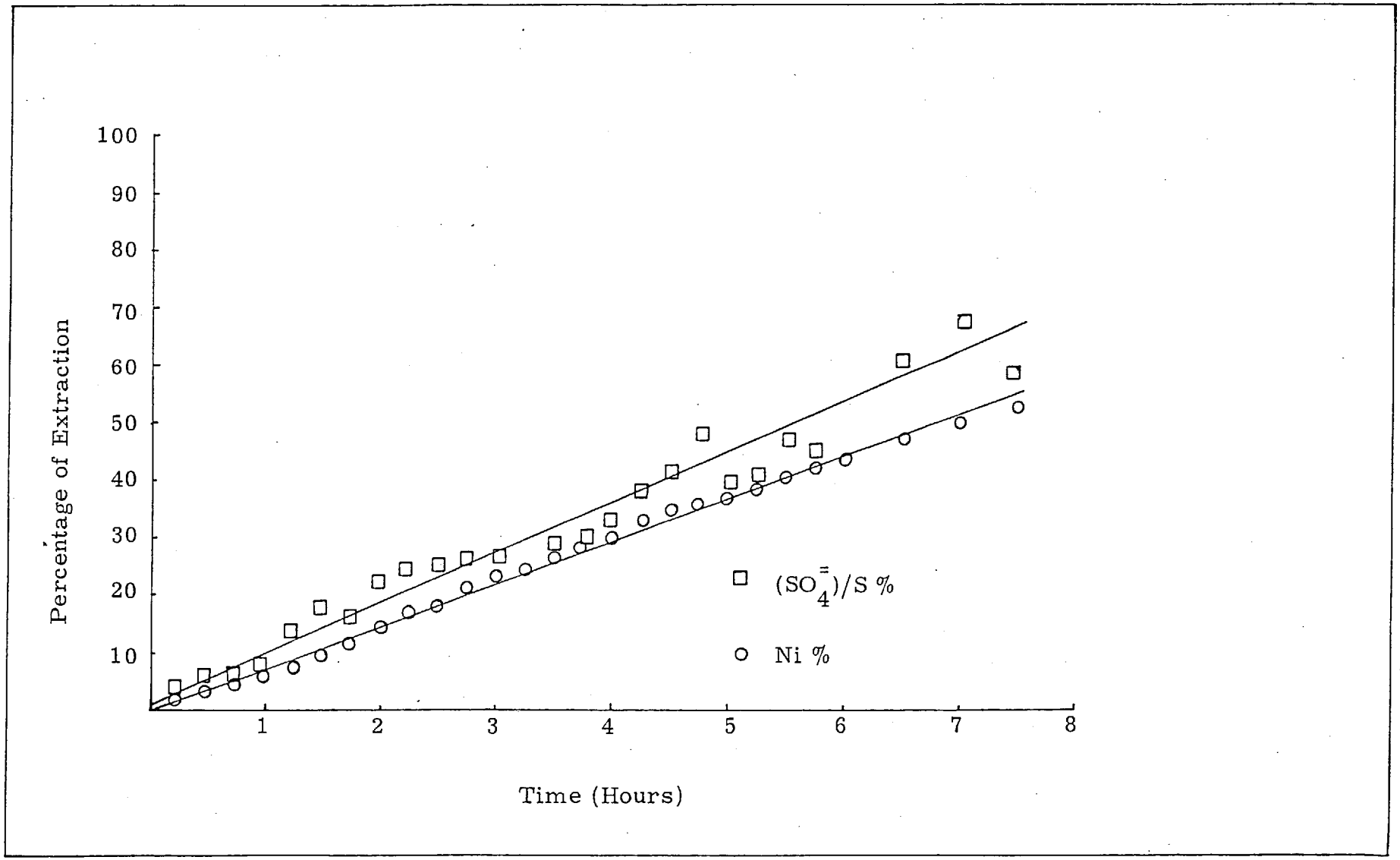


Fig. 61 Sulphate Analysis of the Leach Samples of NiS_2

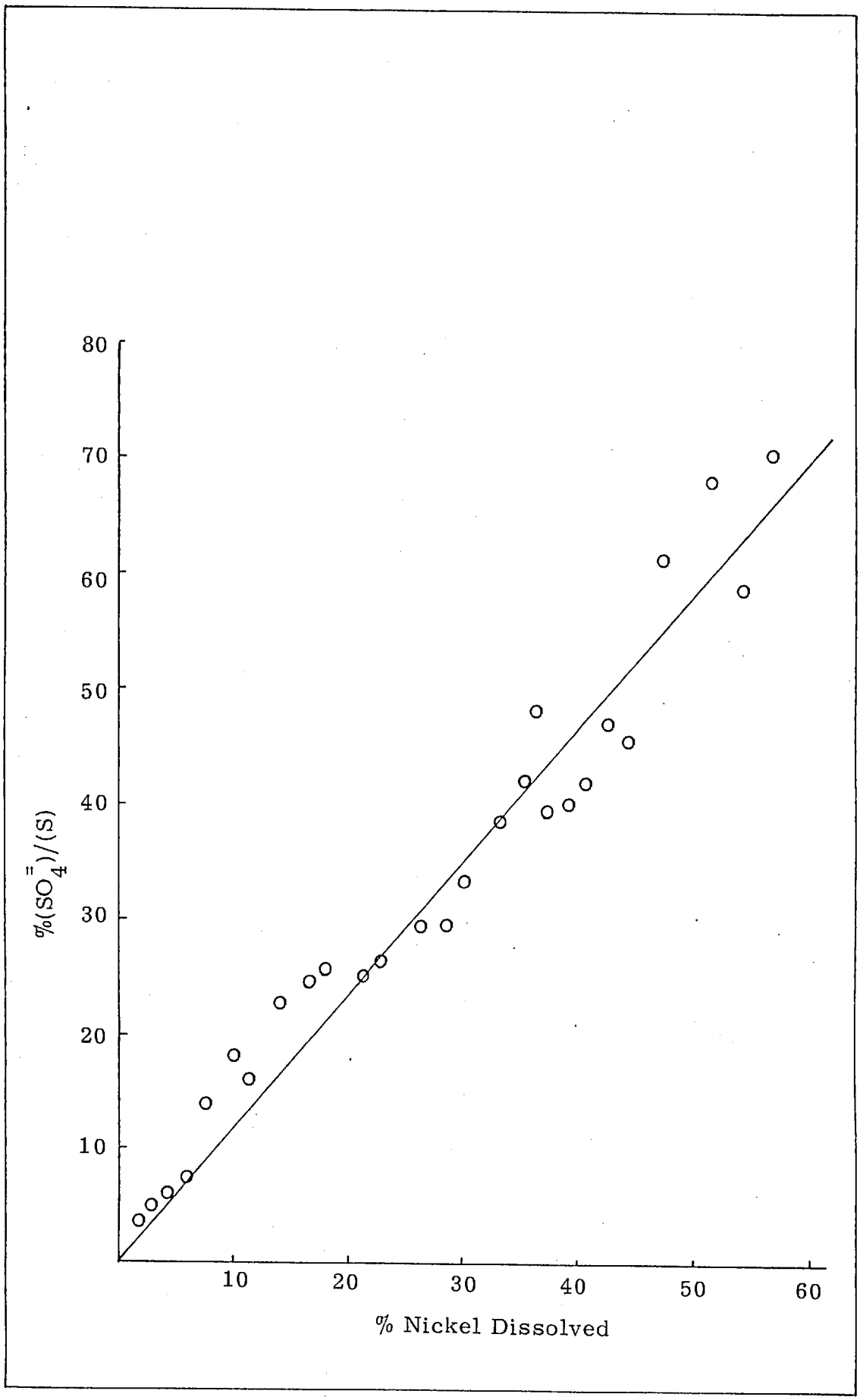


Fig. 62 Sulphate Analysis of the Leach Samples of NiS_2

4.2 X-RAY DIFFRACTION RESULTS

The solid residues from the leaching experiments were analysed by x-ray diffraction, using the techniques described in section 2.4.1. As mentioned earlier, the x-ray pattern for the initial solid was comparable with that given in A. S. T. M. index for NiS_2.

Since the ammoniacal leaching of vaesite seemed to take place in two stages (section 4.1.1), it was thought that some sort of film might be formed after three hours of leaching (first stage) which seemed to modify the characteristics of the solid and, therefore, the kinetic of the ammoniacal leaching of NiS_2.

The results of the x-ray diffraction analysis of the residues are given in Table 23 and Figure 63.

The only solid product, besides NiS_2 identified by x-ray diffraction was $Ni(OH)_2$ which was present when leaching had been carried out in unbuffered solution ($(NH_4)_2SO_4$ concentration = 0), for $(NH_4)_2SO_4$ concentration 0.05 moles/l, the x-ray diffraction pattern of $Ni(OH)_2$ was not so clearly identified, but the existence of a very weak line in d = 2.7Å and d = 2.37 Å seemed to indicate that $Ni(OH)_2$ was also formed under these conditions.

The nickel hydroxide was produced by re-deposition from solution and not directly by reaction on vaesite. Therefore, supposing that some new compound was produced which altered the characteristics of the solid, this was not identified by x-ray diffraction techniques. Thus the new solid might be pseudomorphic with the original material. The only way of determining the nature of the film would be to analyse the solid residue using Electro-Microprobe.

The x-ray diffraction patterns for the solid products of the hydrothermal treatment of the nickel hexa-ammine are also given in Table 23 and Figure 63. A clear pale green precipitate was obtained in an unbuffered solution and it was readily identified as $Ni(OH)_2$, but where the ammonium sulphate concentration was 0.025 and 0.05 moles/l the precipitate was not so obvious and a fibrous green solid was obtained which adhered to the wall of the tube. The lines obtained for the x-ray diffraction pattern of this 'fibrous green solid' was very diffuse and could not be identified with any of the basic sulphates that may be formed. However the product was identified as poorly crystalline synthetic nickel serpentine $Ni_6Si_4O_{10}(OH)_8$, A.S.T.M. 22-754. According with PiChong Kong and Swaddle[157], silica is quite soluble in superheated water. Therefore, it seemed that the $Ni(OH)_2$ precipitated when the ammonium sulphate concentration was 0.025 moles/l and 0.05 moles/l reacted with the silica dissolved from the tubes to form $Ni_6Si_4O_{10}(OH)_8$.

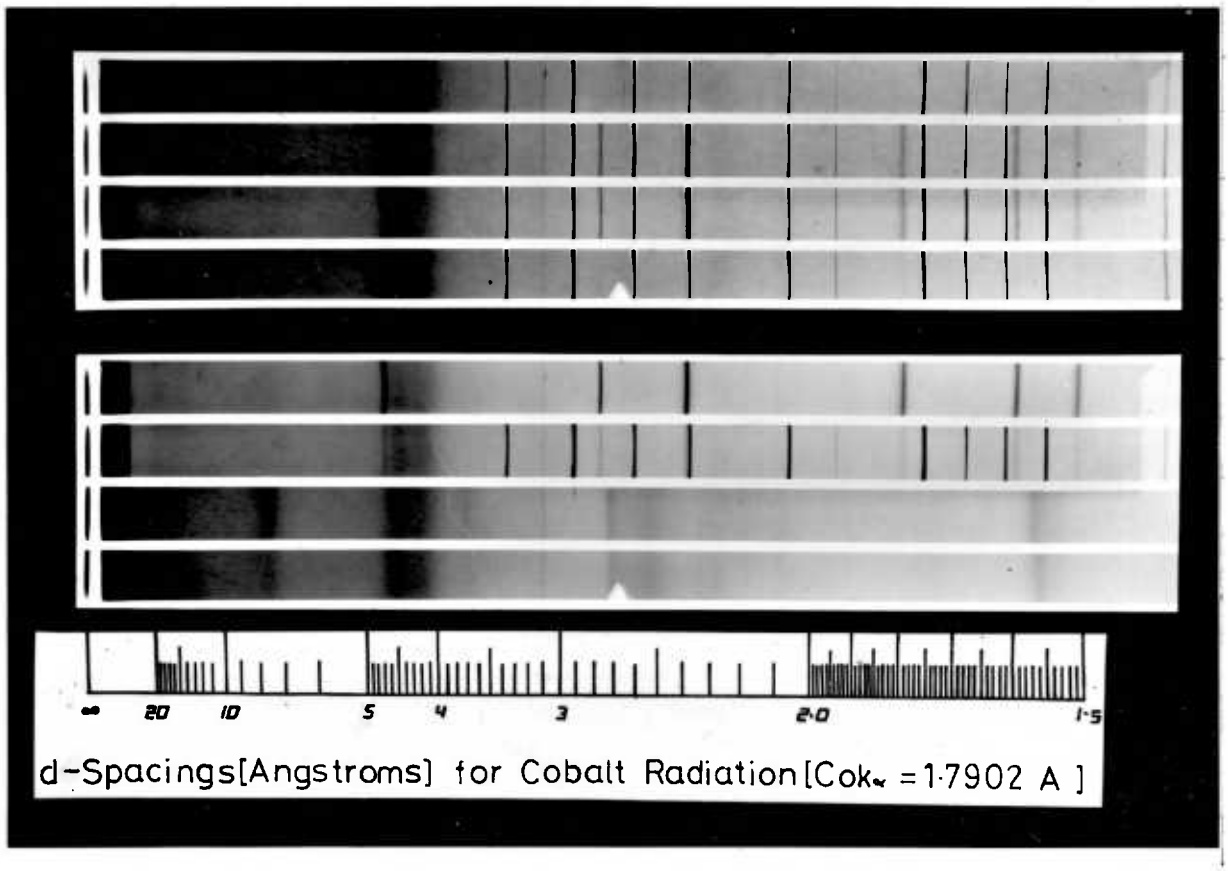


Fig. 63 X-ray Patterns of the Solid Samples Taken after the Leach Runs A-49 and A-47 (2, 3, 4, 6) and X-ray Patterns of the Solid Products obtained after the Hydrolysis of Nickel Hexa-ammine (5, 7, 8)

(1) Unleached vaesite NiS_2

(2), (3), (6) X-ray pattern of the solid residue obtained after leach run A-49

(4) X-ray pattern of the solid residue obtained after leach run A-47

(5), (7), (8) X-ray pattern of the solid products obtained after the Hydrolysis of nickel hexamine

Conditions of the Hydrolysis Treatment

	Temperature	(Ni)	(NH_3)	((NH_4)$_2SO_4$)	Identification of Solids
(5)	150°C	0.0205 mol/l	60 gr/l	0.0 mol/l	$Ni(OH)_2$
(7)	150°C	0.0205 mol/l	60 gr/l	0.025 mol/l	$Ni_6Si_4O_{10}(OH)_8$
(8)	150°C	0.0205 mol/l	60 gr/l	0.05 mol/l	$Ni_6Si_4O_{10}(OH)_8$

TABLE 26

X-RAY DIFFRACTION DATA FOR THE SOLID RESIDUES OBTAINED AFTER RUNS A-48 AND A-49 (2, 3, 4, 6)/X-RAY DIFFRACTION DATA FOR THE SOLID PRODUCTS OF HYDROLYSIS (5, 7, 8)

(1) Unleached NiS_2		(2) Residue Run A		(3) Residue Run A		(4) Residue Run A		(5) Product of Hyd.		(6) Residue Run A		(7) Product of Hyd		(8) Product of Hyd.		NiS_2 A.S.T.M. 11:99		$Ni(OH)_2$ A.S.T.M. 14-117		$Ni_6Si_4O_{10}(OH)_8$ A.S.T.M. 22-754	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I/I_1	dÅ	I/I_1	dÅ	I/I_1
-	-	-	-	-	-	-	-	-	-	-	-	7.5	-	7.5	-	-	-	-	-	7.43	100
-	-	4.6	w	4.6	w	-	-	4.6	s	4.6	w	-	-	-	-	-	-	4.60	100		
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.50	60
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.66	80
3.26	w	3.26	w	3.26	w	3.26	w	-	-	3.26	w	-	-	-	-	3.27	20	-	-	-	-
2.83	s	2.83	s	2.83	s	2.83	s	-	-	2.83	s	-	-	-	-	2.83	100	-	-	-	-
-	-	2.69	w	2.69	w	2.69	vm	2.70	w	2.69	w	-	-	-	-	-	-	2.707	45	-	-
-	-	-	-	-	-	-	-	-	-	-	-	2.65	-	2.65	-	-	-	-	-	2.62	60
2.54	s	2.54	s	2.54	s	2.54	s	-	-	2.54	s	-	-	-	-	2.54	40	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	2.47	-	2.47	-	-	-	-	-	2.447	50
-	-	2.33	s	2.33	s	2.33	vm	2.33	s	2.33	w	-	-	-	-	-	-	2.334	100	-	-
2.31	w	2.31	s	2.31	s	2.31	s	-	-	2.31	s	-	-	-	-	2.32	40	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.302	2	-	-
2.00	s	2.00	s	2.00	s	2.00	s	-	-	2.00	s	-	-	-	-	2.00	50	-	-	-	-
1.88	m	1.88	m	1.88	m	1.88	m	-	-	1.88	m	-	-	-	-	1.89	s	-	-	-	-
-	-	1.75	w	1.75	w	-	-	1.75	w	1.75	2	-	-	-	-	-	-	1.754	35	-	-
1.705	s	1.705	s	1.705	s	1.705	s	-	-	1.705	s	-	-	-	-	1.707	80	-	-	-	-
1.63	w	1.63	w	1.63	w	1.63	w	-	-	1.63	2	-	-	-	-	1.634	20	-	-	-	-
1.565	w	1.565	w	1.565	w	1.565	w	-	-	1.565	w	-	-	-	-	1.570	30	-	-	-	-
-	-	1.56	w	1.56	w	-	-	1.56	w	1.56	w	-	-	-	-	-	-	1.563	25	-	-
-	-	-	-	-	-	-	-	-	-	-	-	1.53	-	1.53	-	-	-	-	-	1.529	80
1.51	w	1.51	w	1.51	w	1.51	w	-	-	1.51	w	-	-	-	-	1.514	30	-	-	-	-
-	-	1.475	w	1.475	w	-	-	1.475	w	1.475	w	-	-	-	-	-	-	1.430	16	-	-
1.37	m	1.37	m	1.37	m	1.37	w	-	-	1.37	m	-	-	-	-	1.375	10	-	-	-	-

4.3 ELECTRON MICROPROBE ANALYSIS

The electron probe microanalysis was carried out using the techniques described in section 2.4.3. The results of the analysis for the unreacted vaesite are given in section 2.1.2.

The electron probe microanalysis for the leached particles was carried out in the residues from two runs. The leaching experiments were carried out with buffered solutions ($NH_4)_2SO_4$ concentration 1 mole/l) and for height hours.

Unfortunately the results from the electron microprobe analysis of the residues were not very accurate and, clearly not reproducible. For instance, the analysis carried out in particles from the first leaching experiment showed that ten or eleven of the sixteen particles analysed had a thin layer of material of distinctly high sulphur content on one or both of the edges (Fig. 64), but when the analysis was repeated by counting this was not found when the analysis was performed using the leach residues from a second experiment which was carried out under identical condition to the first, it was seen that some of the particles showed a very thin layer of high sulphur at one of the edges, usually the one 'favouring' the S - spectrometer (Fig. 65), this was thought to be due to topographical effects of the edges. However this effect was not observed in the original vaesite (Fig. 28).

Many topographical effects were observed in both the unreacted material and the leached residues, (more in the unreacted vaesite) due to the existence of many holes in the solid.

The uncertainty of the electron microprobe analysis left us with only the possibility of speculating about the possible nature of the film formed. It might be possible that a 'very thin layer' of a sulphur rich compound NiS_x ($x > 2$) was formed. Thus the nickel might be leached

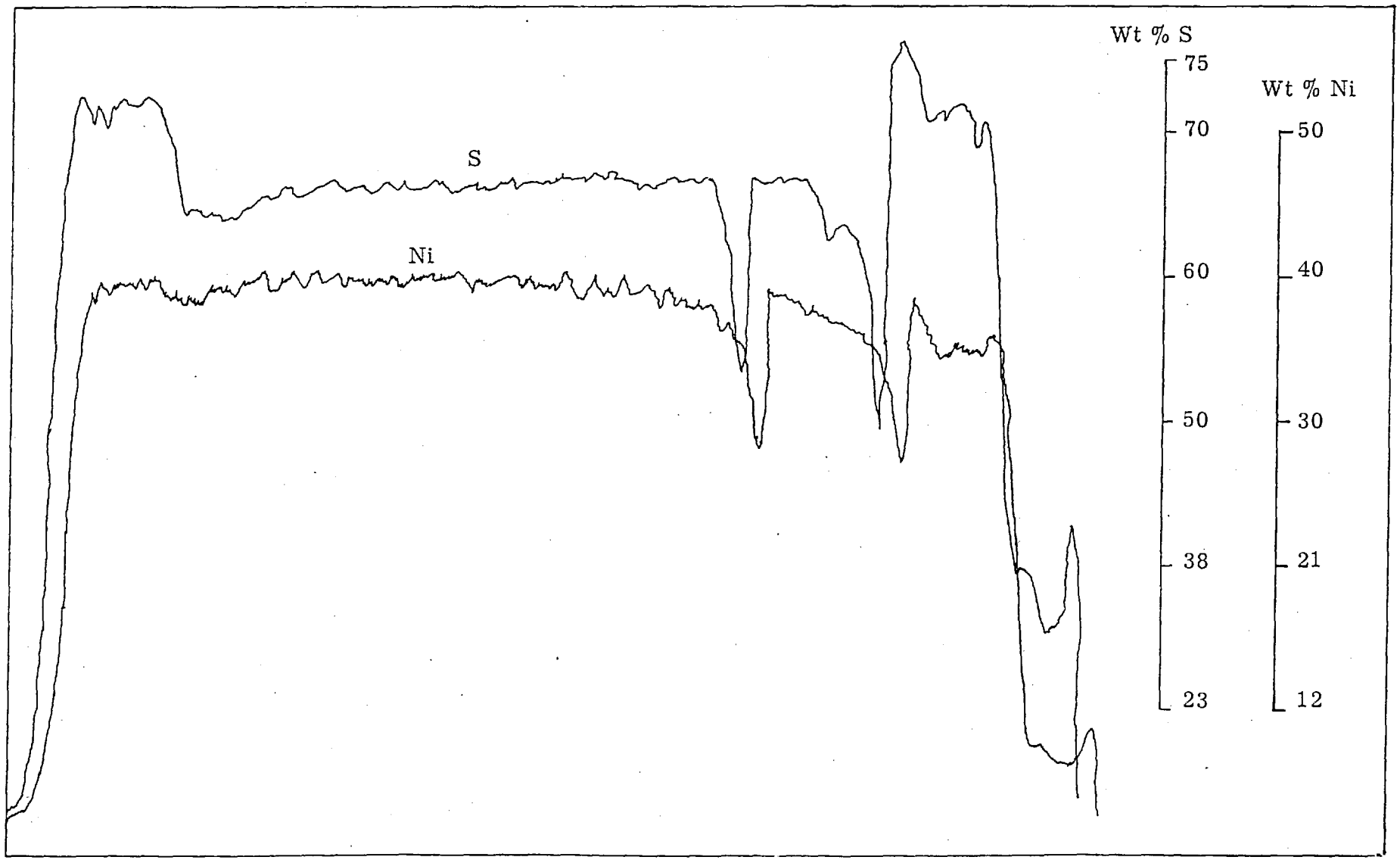


Fig. 64 Electron Microprobe Trace Showing the Variation of Nickel and Sulphur Composition of the Leached Vaesite(NiS_2)

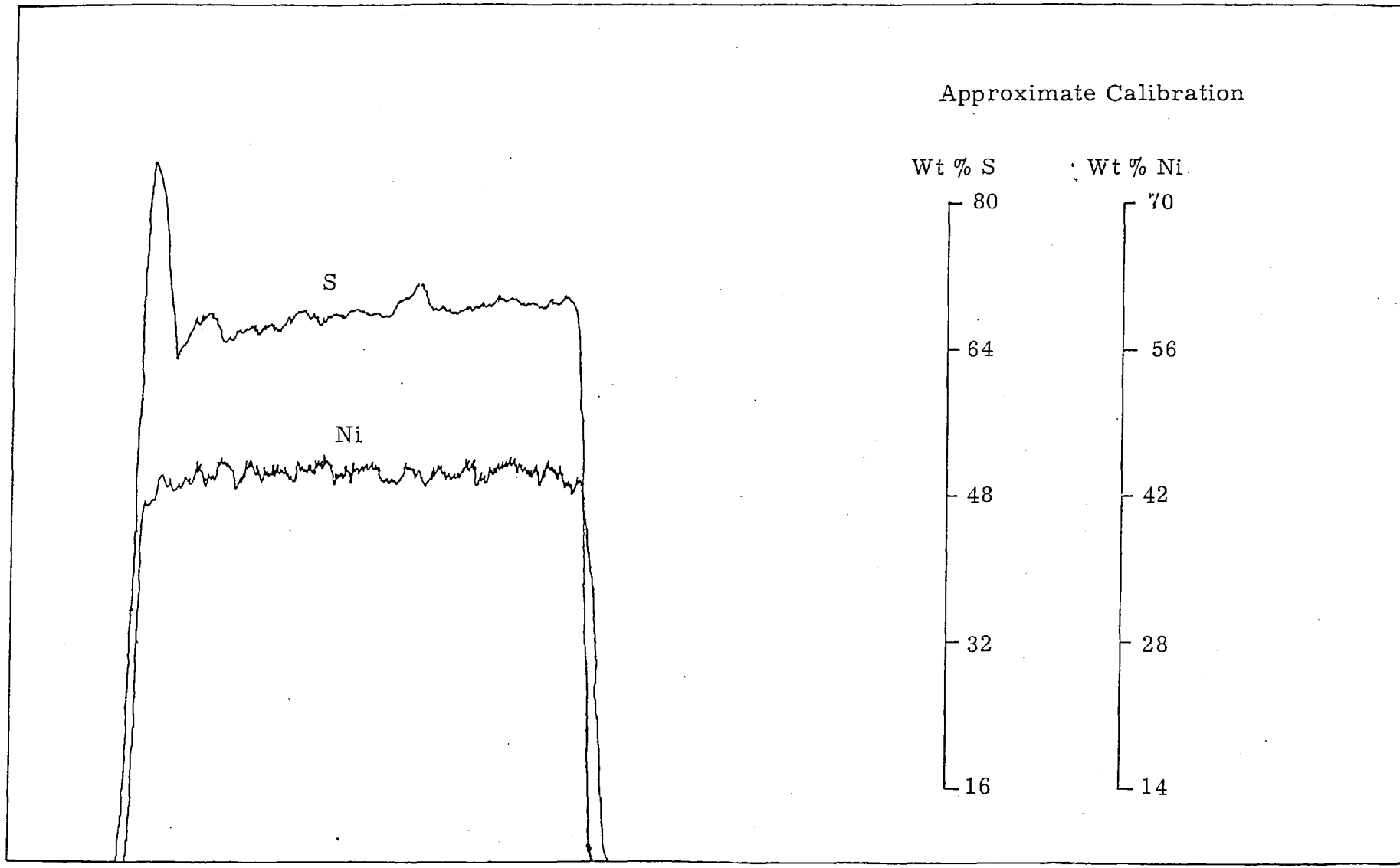


Fig. 65 Electron Microprobe Trace Showing the Variation of Nickel and Sulphur Composition of the Leached Vaesite (NiS_2)

out faster than the sulphur (a slight decrease in the nickel distribution at the edge of some of the particles together with an increase in the sulphur distribution seemed to indicate this). However, since a new compound was not observed by x-ray diffraction it was impossible to say what NiS_x was, but if NiS_x ($x > 2$) was formed this might well modify the kinetic of leaching. It is possible that the S-S bonds might be responsible for this particular behaviour and, therefore, it could be that some other compounds with S-S bonds might behave similarly. It seemed that the only way of knowing the nature of the film and the behaviour of these compounds during the leaching was to use a single crystal which was not available.

4.4 DISCUSSION AND COMPARISON WITH OTHER WORK

It seemed that the ammoniacal leaching of vaesite was carried out accroding with the following reaction:-

$$NiS_2 + 8NH_3 + \frac{7}{2}O_2 + H_2O = Ni(NH_3)_6^{++} + 2SO_4^{=} + 2NH_4^{+} \quad (4.4.1)$$

Similarly for the other two nickel sulphides (heazlewoodite Ni_3S_2 and millerite NiS) considered in appendix 1, the following reactions may be written:

$$Ni_3S_2 + \frac{9}{2}O_2 + 6NH_3 + 2NH_4^{+} = 3Ni(NH_3)_6^{++} + 2SO_4^{=} + H_2O \quad (4.4.2)$$

$$NiS + 2O_2 + 6NH_3 = Ni(NH_3)_6^{++} + SO_4^{=} \quad (4.4.3)$$

Considering now the free energy values given in appendix No. 1 the following 'free energy change' values can be calculated for reaction (4.4.1),(4.4.2) and (4.4.3) at 25°C

$$\Delta G_1 \text{ (reaction (4.4.1))} = -317.423 \text{ Kcal/mol}$$

$$\Delta G_2 \text{ (reaction (4.4.2))} = -406.437 \text{ Kcal/mol}$$

$$\Delta G_3 \text{ (reaction (4.4.3))} = -179.13 \text{ Kcal/mol}$$

It seemed that all three reactions were, in principle, thermodynamically favourable at 25°C. In fact, reactions which required a greater amount of oxidant ((4.4.1) and 4.4.2)) were more thermodynamically favourable than the reaction which required a smaller amount of oxidant (4.4.3). This was also observed by Han K.N. et al [39] when examining the ammoniacal leaching of nickel oxides. Therefore, there was not any thermodynamic reason why vaesite should have been more difficult to leach under ammoniacal conditions than either of the other nickel sulphides, providing that enough oxygen was supplied to oxidize NiS_2, the demand for oxygen being quite high in this case. It was obvious

that we had been obliged to use high temperatures in order to get reasonable rates of leaching due to the inadequate supply of oxidant. These two factors, temperature and supply of oxidant, were the most important ones in the kinetics of leaching.

It appeared that the ammoniacal leaching of vaesite carried out at high temperature and moderate condition of agitation took place in two stages. During the first stage, according to the 'apparent activation energy' derived from the study of the effect of the temperature, the dissolution was controlled by a mixed regime of a chemical reaction and a transport controlled mechanism.

It has been demonstrated that at the temperature used mass transfer effects became very important, and the rate of leaching during the first stage was strongly dependent on the stirring speed. However considering that, the agitation was kept constant throughout the experiments, that the experiments were carried out using dilute solid concentrations, and considering also the effect of the particle size, oxygen pressure and weight of the sample in the rate of leaching, it can be concluded that at the beginning (first stage of leaching) a chemical reaction, probably the reaction of NiS_2 with oxygen was the main rate determining factor. On the other hand, the kinetic data for the first stage of leaching fitted rather well with the function $1-(1-x)^{\frac{1}{3}}$ which seemed to indicate further that during this first stage the rate of dissolution was mainly controlled by a surface chemical reaction.

It has been proved that the rate of leaching during the first stage was independent of the ammonia concentration providing that enough ammonia was present to form the complex. In fact, in most

of the experiments the amount of ammonia was so large in comparison with the available oxygen that the rate of leaching became independent of ammonia and dependent only on the other variable (oxygen). During the second stage of leaching the rate became dependent on the ammonia concentration, mainly at low ammonium sulphate concentration since, in this case the stability of the nickel hexa-ammine became clearly dependent on the amount of ammonia.

It has been found that the ammonium sulphate did not intervene directly on the leaching process but its indirect intervention played a major role in the leaching process, since in its absence (unbuffered solutions pH = 12) the nickel hexa-ammine became unstable and hydrolysed according with the reaction (4.4.4).

$$Ni(NH_3)_6SO_4 + 2H_2O = Ni(OH)_2 + 4NH_3(aq) + (NH_4)_2SO_4 \qquad (4.4.4)$$

Reaction (4.4.4) appeared to occur as soon as the hexa-ammine was formed, not only in the case of unbuffered solutions but also when the concentration of ammonium sulphate was kept at a low level (less than 0.1 moles/l); this affected both the rate of leaching and the maximum amount of nickel extracted. Further indications of the hydrolysis of the hexa-ammine were obtained in the 'Hydrolysis Studies' (section 4.1.8). On the other hand high concentrations of ammonium sulphate affected oxygen solubility and this, in turn, affected the rate of leaching.

The only oxidized sulphur compound found in the leach liquor was $SO_4^=$. It appeared that even if some thiosulphate, polythionate or sulphamate were formed, their concentration was very low and their life very short since they seemed to oxidize to $SO_4^=$ almost immediately. Some other oxidized forms of sulphur, as for example, elemental sulphur, were not observed. Sulphur was not, of course, stable under

ammoniacal conditions; however it might exist in a metastable state. Nevertheless even its existence as a metastable compound was impossible at the temperature used.

A decrease in the rate of leaching after some degree of leaching was achieved was apparent even when the experiments were carried out at quite high stirring speeds (1000 r.p.m.). It has been demonstrated that this was not produced by re-deposition from the solution (hydrolysis of the nickel hexa-ammine) providing that the ammonium sulphate concentration was kept at theadequate level section (4.1.7) which was the case in buffered solutions (1 mole/l) in fact, the hydrolysis of the hexa-ammine did not seem to occur even at high temperature (200^{o}C, section 4.1.2) providing that the ammonium sulphate concentration was kept large enough. Therefore it appeared that the decrease in the reaction rate during the second stage must be due to some reaction which might have previously occurred on the vaesite, altering the characteristics of the edges of the particles after some degree of leaching had occurred. On the other hand, a decrease in the apparent activation energy for this second stage of leaching seemed to indicate that diffusion effects rather than a chemical surface reaction became more important. It was very unlikely that this was due to some transport process in the gas-liquid interface.

Unfortunately, the analysis of the solids carried out on the leach residues were not very informative. The x-ray diffraction pattern of the solid residues at the end of the leaching run carried out using buffered solution, did not show the existence of any phase except vaesite and the result from the electron probe microanalysis were confused. Nevertheless, according to these results and as mentioned in section 4.3, it could be possible that a very thin layer of a sulphur-rich compound (NiS_x, $x > 2$) was formed on the vaesite affecting the rate of leaching.

The results obtained in this work agreed in the main points with the results obtained by Forward and Mackiw [81], Tandon [87] Fung H. and Stastambur [88], Pearson [89] and Noboichenko et al [90]. However, these authors' studies were carried out using, either nickel concentrates (81, 87, 88) or nickel mattes (89, 90) and they were intended to study the chemistry of the process rather than the kinetics of leaching. However, the following points can be considered common between these studies and the present one:-

a) Higher temperature increased the rate of leaching,

b) Higher temperature promoted hydrolysis of the hexa-ammine.

c) During the early stage of leaching there was a high oxygen requirement for oxidation of sulphide to sulphate.

The previously mentioned authors also pointed out that for low concentration of anions ($SO_4^=$) the leaching rate and the metal recoveries were low. On this line, Stanczyk and Rapacek [102] found that when leaching different copper sulphides, including chalcopyrite, at rather high temperatures (200°C) the rate of leaching and the extraction of metal improved when $(NH_4)_2SO_4$ was added, they explained that the low rate of extraction and the small amount of copper extracted when $(NH_4)_2SO_4$ was not added was due to the insufficient amount of anions ($SO_4^=$) in solution.

Tozawa K. et al [105] and Reilly I. G. [106-107] pointed out that although the insufficiency of $SO_4^=$ in solution caused a low rate of extraction and a low percentage of extraction of metal when not enough $SO_4^=$ could be produced by oxidation of the sulphides (as was the case when leaching some concentrates and mattes) to form $Ni(NH_3)_6SO_4$ or $Cu(NH_3)_4SO_4$, the low rate of metal extraction and low percentage of extraction when enough $SO_4^=$ could be produced by oxidation of the sulphides (as was the case when leaching chalcopyrite) had to be attributed to the instability of the complexes in unbuffered solutions (pH = 12) at high temperature.

On the other hand, Shimakaye et al[119] attributed the low nickel yield when leaching nickel metal in the absence of $(NH_4)_2SO_4$ to the hydrolysis of the nickel hexa-ammine.

The results obtained in this work for nickel are similar to the results reported by Tozawa K. et al[105] and Reilly I. G.[106-107] for copper, in the sense that the low rate of leaching and the low percentage of nickel extracted in the absence of $(NH_4)_2SO_4$ was attributed to the instability of the nickel hexa-ammine in unbuffered solution (pH = 12) at high temperature rather than to the lack of $SO_4^=$. On the other hand, the results reported by Shimakaye et al[119] must be attributed rather to the lack of $SO_4^=$ than to the instability of the hexa-ammine; the fact that they leached part of the nickel even in the absence of $SO_4^=$ had to be attributed to the formation of $Ni(NH_3)_6CO_3$ where the CO_2 was dissolved from the air, and not to the formation of $Ni(NH_3)_6SO_4$.

As far as the formation of the incompletely oxidized sulphur compounds is concerned the results obtained in this work did not coincide with the results reported by Forward and Mackiw[81] (Fig. 14), in the sense that no $S_2O_3^=$, $S_xO_6^=$ or $NH_3SO_3^-$ were appreciated in the leach liquor. However, the results reported in this work agreed with those reported by Jansen[83], Mackiw[84] and Shich[85] and also with the observation pointed out by Forward and Mackiw[81] in the sense that the only compound that could be expected on the ammoniacal oxidation of sulphides at high temperature was $SO_4^=$ (Fig. 15). Burkin A. R.[86] had also reported that during the oxidation of FeS_2 only $SO_4^=$ and none of the other oxyacids were formed. Since vaesite has the same structure as pyrite it could be expected to behave similarly.

Noboichenko et al[92] reported that the rate of leaching was independent of the ammonia concentration for values of $(NH_3) > 1$ mole/l.

They found that under the conditions used the ammoniacal leaching of nickel sulphides was carried out in two stages, during the first stage the rate of leaching was controlled by oxygen diffusion and a film was formed in the surface of the sulphide which had a great importance on the rate of leaching during the second stage. The results obtained in this work coincided with the results reported by Noboichenko in the sense that providing that enough NH_3 was present the rate of leaching was independent of the ammonia concentration. However, under the conditions used the rate of leaching during the first stage was controlled by a mixed mechanism in which the surface chemical reaction had the main role. As in their studies a film was thought to be formed during the first stage which had a great influence on the kinetics of leaching during the second stage.

Tozawa K. et al[105] reported that the rate of leaching of chalcopyrite was independent of the ammonia concentration providing that enough ammonia was supplied to form the complex. It has been demonstrated in this work that the rate of leaching of vaesite under the conditions used was also independent of the ammonia concentration providing that enough ammonia was supplied to form the nickel complex. They also reported that the supply of oxygen became a very important factor especially when treating ores which required large amounts of oxygen to be oxidized (chalcopyrite), this has also been confirmed in this work.

Reilly I. G. and Scott D[106] demonstrated that mass transfer effects became important at high temperature, this has been confirmed in this work.

The results obtained by Becksted L. W. et al[109] for the ammoniacal leaching of chalcopyrite coincided in many points with the results obtained in this work so that the electrochemical reaction mechanism that they proposed might well fit the ammoniacal leaching

of vaesite. They found that the rate of reaction was controlled by electrochemical surface reaction during the first stage of leaching, the decrease in the rate of reaction during the second stage of leaching was due to the decrease of the anodic area due to the formation of Fe_2O_3 on the anodic region. It could be considered that such a formation of a new solid might also have occurred during the ammoniacal leaching of vaesite, the new solid being NiS_x, $x > 2$; but the new solid would not cause, in principle, the passivity of some particular areas on the anodic zone, as Fe_2O_3 did, however it could have modified the kinetics of leaching. Nevertheless we did not consider that a single mechanism was involved but rather a mixed mechanism. Even in the case of the chalcopyrite leaching studies carried out by Becksted[108] it was rather unlikely that a single mechanism was involved since the 'apparent activation energy' calculated in their case was 10 Kcal/mol.

On the other hand, the electrochemical mechanism proposed by Habashi[111] for the ammoniacal leaching of sulphides by analogy with a similar mechanism proposed for the ammoniacal leaching of copper metal did not seem to fit in with the results obtained in this work.

CHAPTER 5

CONCLUSION

6.1 SUMMARY OF THE RESULTS

6.1.1 Sulphidisation of Nickel Olivine

Two 'nickel olivine' compounds, the first one containing significant percentage of nickel oxide and the second one being nearly pure nickel ortho-silicate but containing a very small percentage of α-Cristobalite and containing 51 wt % of nickel, were synthesized.

The two compounds were submitted to a hydrothermal treatment using sulphur as a reactant and high pressure and temperatures. Vaesite (NiS_2) was identified as the main solid product of the treatment with, in addition, a minor amount of nickel transformed to nickel sulphate during the process.

Temperature was found to be the most important variable affecting the nickel conversion to vaesite and nickel sulphate during the treatment since when the temperature was kept at a low value the percentage of nickel converted to NiS_2 and $NiSO_4$ was also low, but the conversion in this case, improved with the time of reaction. At the higher level of temperature the conversion of nickel to sulphide and sulphate was nearly complete and independent of the time of reaction in the range used but it improved when the amount of sulphur used was increased.

The products obtained during the hydrothermal treatment were suitable for ammoniacal leaching. Since the vaesite could be oxidized to $Ni(NH_3)_6SO_4$ during the ammoniacal leaching using air under pressure as the oxidant and the nickel sulphate could be converted to $Ni(NH_3)_6SO_4$ by direct action of ammonia.

6.1.2 Ammoniacal Leaching of Vaesite

Vaesite was synthesized containing 47.5 % wt of nickel. The x-ray diffraction pattern obtained for vaesite was similar to that given in A. S. T. M. 11-99.

The oxidation of vaesite in ammonia-ammonium sulphate solution using air as the oxidant took place in two stages. The value of the apparent activation energy for the dissolution of nickel indicates that the reaction rate was controlled by a mixed mechanism.

The rate of leaching was found to be strongly dependent on the stirring speed which indicated that a mass transfer effect became important at the temperature used. However, considering that the stirring speed was kept constant throughout the experiment, the experiments were carried out using dilute solid concentration, the rate of leaching was independent of the ammonia concentration, the rate of leaching was half order dependent on the oxygen pressure and considering also the dependence of the rate of leaching on the particle size and the sample weight it could be concluded that, under the condition used, the surface chemical reaction (which may be the surface oxidation of NiS_2) played the main role during the first stage of the mixed mechanism proposed.

During the first stage of leaching a film was formed on the surface of the particles which had a major role in limiting the rate of leaching during the second stage of leaching. The nature of such a film could not be clearly established.

Nickel hexa-ammine complex was the main product of the leaching reaction. However the nickel hexa-ammine was not stable under certain conditions of leaching and it was found to hydrolyse to precipitate $Ni(OH)_2$. The hydrolysis of the hexa-ammine affected both the rate of leaching and the maximum yield of metal.

It was found that ammonium sulphate did not intervene directly in the leaching process but its presence at moderate concentrations was necessary to stabilize the nickel hexa-ammine. On the other hand, when the concentration of ammonium sulphate was too high the solubility of oxygen in the solution decreased and therefore the rate of leaching also decreased.

ACKNOWLEDGMENT

The author wishes to express his sincere thanks to his supervisor Dr A.R. Burkin for his invaluable help and advice throughout the course of this work.

The author also wishes to express his gratitude to all the members of the Hydrometallurgy Group, especially to Mr. J.E.A. Burgess for his practical advice and Mr. J.G. Phillis for his help in the computer work. Thanks are also due to Dr. G.D. Manning and Dr. N. Hamster for their constant advice during this work.

The author would like to express his gratitude to the Analytical Service Laboratory for the electron probe microanalyses, to the photographic section for the reproduction of the photographs and to Mrs. M. Smit for her excellent typing.

Acknowledgment is also due to the E.N. Adaro, Spain for their financial assistance during the last three years.

Finally, the author sincerely wishes to thank all his friends, specially the ones inside the College and at 'Netherhall House' students hostel, for their kindness and companionship during the period of this work.

APPENDIX 1

THERMODYNAMIC STUDIES

E-pH Diagrams:-

The E-pH diagrams for the systems Nickel-Sulphur-water and Nickel-Sulphur-ammonia-water have been drawn at 25°C and ionic activities of (10^{-3}) (Fig. 4) (10^{-1})(Fig. 5) and (1) (Fig. 6). The high temperature E-pH diagram for the system Nickel-Sulphur-water has also be en drawn for ionic species activities of (10^{-3}) (Fig. 1), (10^{-1}) (Fig. 2) and (1) (Fig. 3).

- Introduction

The E-pH diagrams contain a great deal of thermodynamic data collected in a form which shows equilibrium relationships among the various ionic and solid species in aqueous systems.

The stable products which can be expected in a hydrothermal treatment of oxidized nickel ores such as the sulphidization of nickel olivine studied in this work, can be predicted by E-pH diagrams at high temperature, such as the E-pH diagram for the Ni-S-H_2O system.

On the other hand, E-pH diagrams can be used to show the area of stability of the ionic species, and therefore, they are useful instruments to predict the ionic species which can be expected in the leach liquor when the leaching experiments are carried out under certain conditions. For instance, in the E-pH diagram for the system Ni-S-NH_3-H_2O the area of stability of the nickel ammonia complexes can be predicted.

Thus E-pH diagrams can give us very useful thermodynamical information, on the behaviour of certain ores, submitted to hydrothermal treatment and also on the behaviour of the ores during the leaching process. However,E-pH diagrams do not give us any information on the kinetic aspects of the problem.

- E-pH Relationship

The following reactions can be considered:-

a) Redox Reactions:-

Half-cell reaction:

$$aA + bB + ze = cC + dD \qquad (A\text{-}1)$$

which can be written as a full-cell reaction:-

$$aA + bB + ze = cC + dD$$
$$\frac{z}{2} H_2 = zH^+ = ze$$
$$aA + bB + \frac{z}{2} H_2 = cC + dD + zH^+$$

For the half-cell reaction the electrode potential is given by the Nernst equation:-

$$E_T = E_T^o - \frac{RT}{zF} \ln \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

as $E_T^o = - \frac{\Delta G_T^o}{zF}$ and considering $B = H^+$ and $D = H_2O$.

The Nernst equation can be written

$$E_T = - \frac{\Delta G_T^o}{zF} - 2.303 \frac{RT}{zF} b\, pH_T - 2.303 \frac{RT}{zF} \log \frac{(a_C)^c}{(a_A)^a}$$

where: a_A, a_B, a_C, a_D, a_{H_2O} are the activities of the respective species and $a_{H_2O} = 1$.

b) Reactions which do not involve electrons

$$aA^- + xH^+ = bB + cH_2O$$

$$\Delta G_T = -2.303\ RT \log \frac{(a_B)^b (a_{H_2O})^c}{(a_{A^-})^a (H^+)^x}$$

$$\Delta G_T = -2.303RT \left(\log \frac{(a_B)^b}{(a_{A^-})^a} + xpH\right)$$

$$pH = -\frac{\Delta G_T}{2.303RTx} - \frac{1}{x} \log \frac{(a_B)^b}{(a_{A^-})^a}$$

where a_B, a_{A^-}, a_{H_2O} are the activities of the respective species and $(a_{H_2O}) = 1$.

c) Reactions for the stability of water

The reactions:

$$2H^+ + 2e^- = H_2$$

and

$$O_2 + 4H^+ + 4e^- = 2H_2O$$

express the stability of water under reducing and oxidizing conditions.

The Nerst equation for these reactions can be written:-

$$E_{1T} = E^o_{1T} - 2.303 \frac{RT}{F} pH_T - 2.303 \frac{RT}{2F} \log P_{H_2}$$

$$E_{2T} = E^o_{2T} - 2.303 \frac{RT}{F} pH_T + 2.303 \frac{RT}{4F} \log P_{O_2}$$

When the partial pressures $P_{H_2} = P_{O_2} = 1$ atm, these equations determine the limits of thermodynamic stability of water under the standard state conditions.

- Calaculation of ΔG_T at Elevated Temperatures

ΔG_T has been calculated using the following relationships.

$$\Delta G^o_{T_2} = \Delta H^o_{T_2} - T_2 \Delta S^o_{T_2}$$

$$\Delta H^o_{T_2} = \Delta H^o_{T_1} + \int_{T_1}^{T_2} \Delta C^o_p \, dT$$

$$\Delta S^o_{T_2} = \Delta S^o_{T_1} + \int_{T_1}^{T_2} \frac{\Delta C^o_p}{T} \, dT$$

Considering

$$\int_{T_1}^{T_2} \Delta C^o_p \, dT = \overline{\Delta C}^o_p \Big|_{T_1}^{T_2} (T_2 - T_1)$$

$$\int_{T_1}^{T_2} \frac{\Delta C^o_p}{T} \, dt = \overline{\Delta C}^o_p \Big|_{T_1}^{T_2} \ln \frac{T_2}{T_1}$$

where $\overline{\Delta C}^o_p \Big|_{T_1}^{T_2}$ is the average value of the heat capacities at temperatures T_2 and T_1.

The $\Delta G^o_{T_2}$ can be written:-

$$\Delta G^o_{T_2} = \Delta G^o_{T_1} - \Delta S^o_{T_1} (T_2 - T_1) + \Delta C^o_p \Big|_{T_1}^{T_2} (T_2 - T_1 - T_2 \ln \frac{T_2}{T_1})$$

The $\Delta C^o_p \Big|_{T_1}^{T_2}$ values for no ionic species were estimated using existing data.

The $\Delta C_p^o\Big|_{T_1}^{T_2}$ values for ionic species were estimated using a method developed by Criss and Cobble[155-156]. The Criss and Cobble method rests on what is called "Correspondence Theory of Ionic Entropy'. They showed that if a standard state is chosen properly by fixing the entropy of H^+ (aq) at each temperature, then the ionic entropies at one temperature are linearly related to their corresponding entropies at 25°C. Their choice of standard state at 298°K corresponded to an entropy for the hydrogen ion of -5.0 cal $mole^{-1}$ $^oK^{-1}$ which is in agreement with the values for the 'absolute' ionic entropy of H^+ (aq) suggested by other authors.

Normalizing the entropy values to the absolute scale

$$\bar{S}^o_{298}\,(i\ abs) = S^o_{298}\,(i,\ comv) - 5.0\ z$$

where $\bar{S}^o_{298}(i,\ abs)$ = absolute entropy

$S^o_{298}(i,\ comv)$ = conventional entropy

z = ionic charge (with sign)

The conventional scale is based on $S^o(H^+) = 0$. The concept of 'absolute entropy' can be extended to any temperature:-

$$\bar{S}^o_{T_2}\,(i, abs) = S^o_{T_2}\,(i,\ comv) - S^o_{T_2}\,(H^+,\ abs)z$$

According to Criss and Cobble's 'Correspondence Principle of Ionic Entropy'

$$\bar{S}^o_{T_2}\,(i, abs) = a(T_2) + b(T_2)\,\bar{S}_{298} \qquad (A\text{-}2)$$

where $a(T_2)$ and $b(T_2)$ are constants dependent on the class of ions (cations, anions, oxyanions and acidoxyanions) and on the temperature.

The basis for equation (A-2) rests on Criss and Cobble's analysis of the available experimental data. Considering that

$$\Delta C_p^o \Big|_{T_1}^{T_2} = \frac{\overline{S}^o_{T_2} - \overline{S}^o_{T_1}}{\ln \frac{T_2}{T_1}} \qquad \text{(A-3)}$$

and (A-2) for $\overline{S}^o_{T_1}$ (i, abs) = $\overline{S}^o_{298}$ (i, abs)

(A-3) may be written

$$\Delta C_p^o \Big|_{298}^{T_2} = \alpha_{T_2} + \beta_{T_2} \overline{S}^o_{298}(i, abs)$$

where α_{T_2} and β_{T_2} are constants dependent on the class of ions and are related to the constants a_{T_2} and b_{T_2}.

- Observation:-

Considering reaction (A-1) and

$$H^+(aq) + e^- = \tfrac{1}{2}H_2(g)$$

The full-cell reaction can be written:-

$$aA + bB + \frac{zH_2}{2} = cC + dD + zH^+ \qquad \text{(A-4)}$$

The electrode potential relationship being:

$$E^o_{298}(\text{full cell}) = E^o_{298}\ (\text{half-cell}) - E_{298}\ (\text{SHE})$$

at 298 ^oK and $a_{H^+} = 1$ $P_{H_2} = 1$

$$E_{298}(\text{SHE}) = O$$

and $E_{298}(\text{full-cell}) = E_{298}(\text{half-cell})$

therefore the reaction (A-1) can be considered to calculate ΔG^{o}_{298} and $E^{o}_{298} = \frac{\Delta G^{o}_{298}}{zF}$ but at T_2, being $T_2 > 298^{o}K$ $E_{298}(\text{SHE}) \neq O$ and the reaction (A-4) has to be considered to calculate $G^{o}_{T_2}$ and $E^{o}_{T_2} = -\frac{\Delta G^{o}_{T_2}}{zF}$

TABLE OF THE THERMODYNAMIC DATA				
Species	ΔG_{298} Kcal mol^{-1}	ΔH_{298} Kcal $mole^{-1}$	S^{o}_{298} Cal K^{-1} $mole^{-1}$	Cp cal K^{-1} mol^{-1}
O_2	0	0	49.00	$Cp = 7.16+10^{-3}T - 0.4x10^{5}T^{-2}$
H_2	0	0	31.21	$Cp = 6.52+0.78x10^{-3}T+0.12x10^{5}T^{-2}$
H_2O	-56.687	-68.317	16.75	$Cp = 17.17+2.56x10^{-3}T+0.08x10^{5}T^{-2}$
H^+	0	0	0	
S	0	0	7.62	$Cp = 3.53+5.75x10^{-3}T+0.174x10^{5}T^{-2}$
H_2S	-8.02	-4.93	49.16	$Cp = 6.93+0.86x10^{-3}T+0.48x10^{5}T^{-2}$(b)
$S^{=}$	20.5	7.9	-3.5	
$SO_4^{=}$	-177.97	-217.32	4.8	
HSO_4^-	-180.69	-212.08	31.5	
HS^-	2.88	-4.2	15.0	
Ni	0	0	7.4	$Cp = 4.06+7.04x10^{-3}T$
Ni^{2+}	-10.9	-12.9	-30.8	
NiO	-50.6	-57.3	9.09	$Cp = -4.99+37.58x10^{-3}T+3.89x10^{5}T^{-2}$(c)
Ni_3O_4	-170.15		35.66(d)	$Cp = 30.84+17.08x10^{-3}T-5.72x10^{5}T^{-2}$(d)
Ni_2O_3	-112.27	-117.0	21.5(d)	$Cp = 23.49+18.60x10^{-3}T-3.55x10^{5}T^{-2}$
NiO_2	-51.42		12.68(d)	$Cp = 16.6+2.44x10^{-3}T-3.88x10^{5}T^{-2}$
$NiHO_2^-$	-83.465		10(e)	
Ni_3S_2	-50.23	-51.60	32.01	$Cp = 3x(7.766+5.39x10^{-3}T)$(b)
NiS	-21.94	-22.5	12.66	$Cp = 9.30+6.40x10^{-3}T$
NiS_2	-30.17	-32.0	16.2	$C_{p400} = 18.91$ $C_{p500} = 19.57$
$Ni(NH_3)_4^{2+}$	-47.4(f)	-104.9	61.8	
$Ni(NH_3)_5^{2+}$	-54.5(g)			
$Ni(NH_3)_6^{2+}$	-61.2(g)			
NH_3(aq)	-6.35	19.19	26.6	
NH_4^+ (aq)	-18.97	-31.67	27.1	

Species	C_{p298} cal. $K^{-1} mol^{-1}$	$Cp\,\Big|_{298}^{473}$ cal. $K^{-1} mol^{-1}$	ΔG_{473} Kcal mol^{-1}
O_2	7.016	7.233	-8.89
H_2	6.889	6.916	5.76
H_2O	17.995	18.20	-60.41
H^+	0	35[a]	-1.52
S	3.538	4.933	-1.55
H_2S	7.72[b]	7.636[b]	-16.96
$S^=$		-65.26[a]	23.95
$SO_4^=$		-114[a]	-173.85
HSO_4^-		-18[a]	-185.42
HS^-		-66[a]	3.13
Ni	6.23	6.81	-1.54
Ni^{2+}		75.70	-8.81
NiO	10.59[c]	12.55[c]	-52.74
Ni_3O_4		32.93[d]	-177.823
Ni_2O_3		27.87[d]	-117.245
NiO_2		14.49[d]	-54.27
$NiHO_2^-$		-88.4[a]	-81.455
Ni_3S_2	9.37[b]	29.53[b]	-57.12
NiS	11.261[b]	11.79[b]	-24.67
NiS_2	18.04[b]	18.7[b]	-32.19
$Ni(NH_3)_4^{2+}$			
$Ni(NH_3)_5^{2+}$			
$Ni(NH_3)_6^{2+}$			
NH_3(aq)			
NH_4^+ (aq)	19.1		

-Values for non-ionic species obtained from selected values of Chemical Thermodynamic Properties N. B. S.

N^{o} 270-3 and N^{o}270-4 [158-159] and other publications[160-167]

(a) Ionic heat capacities from Cecil N. Criss and J. W. Cobble[155-156]

(b) From thermodynamic data for inorganic sulphides, selemides and tellurides[168].

(c) From thermodynamic properties of 65 elements their oxides, halides, carbides and nitrates.[159]

(d) From the thermodynamics and electrode kinetic behaviour of nickel and solution in the temperature range 25°C to 300°C[169].

(e) From entropy of aqueous oxy-anions[170]

(f) ΔG has been calculated using S and ΔH and the reactions:

$$4NH_4^+ + Ni = Ni(NH_3)_4^{2+} + H_2 + 2H^+$$

$\Delta G_{Ni(NH_3)_4^{++}}$ = -104.9x1000+4(31.67x1000-298(61.8+31.208-4x27.1-7.4) + 4(-18.97)x1000 = -47.4 Kcal mol^{-1}

(g) Calculated using stability constants[171]

- Reaction in the Ni-S-H_2O System at High Temperature (200°C)

- Reactions involving water stability

1 $2H^+ + 2\,e = H_2$

2 $O_2 + 4H^+ + 4e = 2H_2O$

- Reactions involving solids:-

3 $NiO + 2H^+ + 2e = Ni + H_2O$

4 $NiO + 2H^+ = Ni^{2+} + H_2O$

5 $NiHO_2^- + H^+ = NiO + H_2O$

6 $NiHO_2^- + 3H^+ + 2e = Ni + 2H_2O$

7 $NiO_2 + 4H^+ + 2e = Ni^{2+} + 2H_2O$

8 $2NiO_2 + 2H^+ 2e = Ni_2O_3 + H_2O$

9 $Ni_2O_3 + 6H^+ + 2e = Ni^{2+} + 3H_2O$

10 $3Ni_2O_3 + 2H^+ + 2e = 2Ni_3O_4 + H_2O$

11 $Ni_3O_4 + 8H^+ + 2e = 3Ni^{2+} + 4H_2O$

12 $Ni_3O_4 + 2H^+ + 2e = 3NiO + H_2O$

13 $Ni_3O_4 + 2H_2O + 2e = 3NiHO_2^- + H^+$

14 $Ni_2O_3 + H_2O + 2e = 2NiHO_2^-$

15 $NiO_2 + H^+ + 2e = NiHO_2^-$

16 $Ni_3S_2 + 4H^+ + 2e = 2H_2S + 3Ni$

17 $Ni_3S_2 + 2H^+ + 4e = 2HS^- + 3Ni$

18 $Ni_3S_2 + 4e = 2S^= + 3Ni$

19 $3NiHO_2^- + 2S^= + 9H^+ + 2e = Ni_3S_2 + 6H_2O$

20 $3NiHO_2^- + 2SO_4^= + 25H^+ + 18e = Ni_3S_2 + 14H_2O$

21 $3NiO + 2SO_4^= + 22H^+ + 18e = Ni_3S_2 + 11\,H_2O$

22 $NiO + SO_4^{=} + 10H^{+} + 8e = NiS + 5H_2O$

23 $Ni^{2+} + 2HSO_4^{-} + 14H^{+} + 14e = NiS_2 + 8H_2O$

24 $Ni^{2+} + HSO_4^{-} + 7H^{+} + 8e = NiS + 4H_2O$

25 $NiO + HSO_4^{-} + 9H^{+} + 8e = NiS + 5H_2O$

26 $NiS_2 + 2H^{+} + 2e = NiS + H_2S$

27 $NiS_2 + H^{+} + 2e = NiS + HS^{-}$

28 $NiS_2 + 2e = NiS + S^{=}$

29 $NiS + SO_4^{=} + 8H^{+} + 6e = NiS_2 + 4H_2O$

30 $NiS + HSO_4^{-} + 7H^{+} + 6e = NiS_2 + 4H_2O$

31 $Ni_3S_2 + SO_4^{=} + 8H^{+} + 6e = 3NiS + 4H_2O$

32 $3NiS + 2e = Ni_3S_2 + S^{=}$

33 $3NiS + 2H^{+} + 2e = Ni_3S_2 + H_2S$

34 $3NiS + H^{+} + 2e = Ni_3S_2 + HS^{-}$

35 $3NiO + 2S^{=} + 6H^{+} + 2e = Ni_3S_2 + 3H_2O$

- Reactions involving the S-H_2O System:-

36 $SO_4^{=} + H^{+} = HSO_4^{-}$

37 $HSO_4^{-} + 7H^{+} + 6e = S^{o} + 4H_2O$

38 $S + 2H^{+} + 2e = H_2S$

39 $HS^{-} + H^{+} = H_2S$

40 $SO_4^{=} + 9H^{+} + 8e = HS^{-} + 4H_2O$

41 $S^{=} + H^{+} = HS^{-}$

42 $SO_4^{=} + 8H^{+} + 8e = S^{=} + 4H_2O$

43 $SO_4^{=} + 10H^{+} + 8e^{-} = H_2S + 4H_2O$

44 $HSO_4^{-} + 9H^{+} + 8e = H_2S + 4H_2O$

- Equations Relating E_T - pH and Activity in the Ni-S-H_2O System at 200°C

Equation	Activity	E_T/pH Relationship
1	1	E = - 0.0939 pH
	10^{-1}	"
	10^{-3}	"
2	1	E = 1.149 - 0.0939 pH
	10^{-1}	"
	10^{-3}	"
3	1	E = 0.075 - 0.0939 pH
	10^{-1}	"
	10^{-3}	"
4	1	pH = 3.105
	10^{-1}	pH = 3.605
	10^{-3}	pH = 4.605
5	1	pH = 13.94
	10^{-1}	pH = 12.94
	10^{-3}	pH = 10.94
6	1	E = 0.729 - 0.1409 pH
	10^{-1}	E = 0.682 - 0.1409 pH
	10^{-3}	E = 0.588 - 0.1409 pH
7	1	E = 1.443 - 0.1878 pH
	10^{-1}	E = 1.490 - 0.1878 pH
	10^{-3}	E = 1.584 - 0.1878 pH
8	1	E = 1.374 - 0.0939 pH
	10^{-1}	"
	10^{-3}	"

Equation	Activity	E_T/pH Relationship
9	1	E = 1.513 - 0.2817 pH
	10^{-1}	E = 1.607 - 0.2817 pH
	10^{-3}	E = 1.795 - 0.2817 pH
10	1	E = 1.27 - 0.0939 pH
	10^{-1}	"
	10^{-3}	"
11	1	E = 1.634 - 0.3756 pH
	10^{-1}	E = 1.775 - 0.3756 pH
	10^{-3}	E = 2.057 - 0.3756 pH
12	1	E = 0.76 - 0.0939 pH
	10^{-1}	"
	10^{-3}	"
13	1	E = -1.203 + 0.047 pH
	10^{-1}	E = -1.062 + 0.047 pH
	10^{-3}	E = -0.7805 + 0.047 pH
14	1	E = -0.379
	10^{-1}	E = -0.285
	10^{-3}	E = -0.097
15	1	E = 0.498 - 0.047 pH
	10^{-1}	E = 0.544 - 0.047 pH
	10^{-3}	E = 0.639 - 0.047 pH
16	1	E = -0.326 - 0.0939 pH
	10^{-1}	"
	10^{-3}	"
17	1	E = -0.729 - 0.047 pH
	10^{-1}	E = -0.682 - 0.047 pH
	10^{-3}	E = -0.588 - 0.047 pH

Equation	Activity	E_T/pH Relationship
18	1	E = -1.147
	10^{-1}	E = -1.100
	10^{-3}	E = -1.006
19	1	-
	10^{-1}	-
	10^{-3}	E = 3.777 - 0.423 pH
20	1	-
	10^{-1}	-
	10^{-3}	E = 0.521 - 0.13 pH
21	1	E = 0.380 - 0.115 pH
	10^{-1}	E = 0.370 - 0.115 pH
	10^{-3}	E = 0.349 - 0.115 pH
22	1	E = 0.401 - 0.117 pH
	10^{-1}	E = 0.389 - 0.117 pH
	10^{-3}	E = 0.365 - 0.117 pH
23	1	E = 0.296 - 0.0939 pH
	10^{-1}	E = 0.276 - 0.0939 pH
	10^{-3}	E = 0.236 - 0.0939 pH
24	1	E = 0.274 - 0.0821 pH
	10^{-1}	E = 0.250 - 0.0821 pH
	10^{-3}	E = 0.202 - 0.0821 pH
25	1	E = 0.347 - 0.1056 pH
	10^{-1}	E = 0.335 - 0.1056 pH
	10^{-3}	E = 0.311 - 0.1056 pH
26	1	E = 0.08 - 0.0939 pH
	10^{-1}	"
	10^{-3}	"

Equation	Activity	E_T/pH Relationship
27	1	E = -0.323 - 0.047 pH
	10^{-1}	E = -0.276 - 0.047 pH
	10^{-3}	E = -0.182 - 0.047 pH
28	1	E = -0.741
	10^{-1}	E = -0.694
	10^{-3}	E = -0.600
29	1	E = 0.397 - 0.125 pH
	10^{-1}	E = 0.381 - 0.125 pH
	10^{-3}	E = 0.350 - 0.125 pH
30	1	E = 0.325 - 0.1096 pH
	10^{-1}	E = 0.309 - 0.1096 pH
	10^{-3}	E = 0.278 - 0.1096 pH
31	1	E = 0.465 - 0.125 pH
	10^{-1}	E = 0.449 - 0.125 pH
	10^{-3}	E = 0.418 - 0.125 pH
32	1	E = -0.945
	10^{-1}	E = -0.898
	10^{-3}	E = - 0.804
33	1	E = - 0.1234 - 0.0939 pH
	10^{-1}	"
	10^{-3}	"
34	1	E = - 0.526 - 0.047 pH
	10^{-1}	E = -0.479 - 0.047 pH
	10^{-3}	E = -0.385 - 0.047 pH
35	1	E = 2.519 - 0.2817 pH
	10^{-1}	E = 2.425 - 0.2817 pH
	10^{-3}	-

Equation	Activity	E_T/pH Relationship
36	1	pH = 4.64
	10^{-1}	pH = 4.64
	10^{-3}	pH = 4.64
37	1	E = 0.282 - 0.1096 pH
	10^{-1}	E = 0.266 - 0.1096 pH
	10^{-3}	E = 0.235 - 0.1096 pH
38	1	E = 0.209 - 0.0939 pH
	10^{-1}	"
	10^{-3}	"
39	1	pH = 8.58
	10^{-1}	pH = 7.58
	10^{-3}	pH = 5.58
40	1	E = 0.217 - 0.1056 pH
	10^{-1}	"
	10^{-3}	"
41	1	pH = 8.92
	10^{-1}	"
	10^{-3}	"
42	1	E = 0.113 - 0.0939 pH
	10^{-1}	"
	10^{-3}	"
43	1	E = 0.318 - 0.117 pH
	10^{-1}	E = 0.306 - 0.117 pH
	10^{-3}	E = 0.283 - 0.117 pH
44	1	E = 0.263 - 0.106 pH
	10^{-1}	E = 0.251 - 0.106 pH
	10^{-3}	E = 0.228 - 0.106 pH

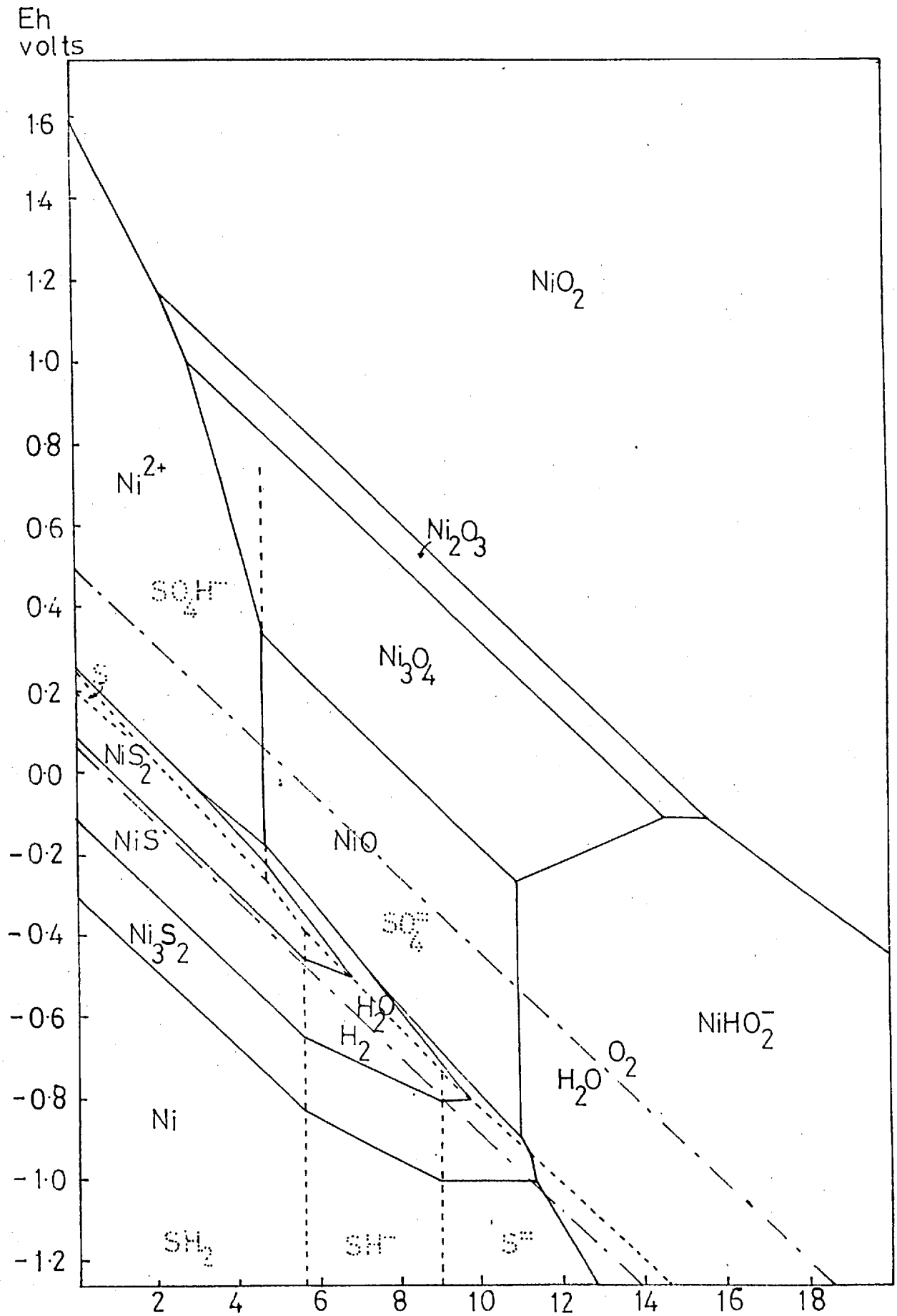


FIG.1 Eh-pH DIAGRAM FOR THE Ni-S-H_2O SYSTEM T 200°C

activity of ionic species -10^{-3}-

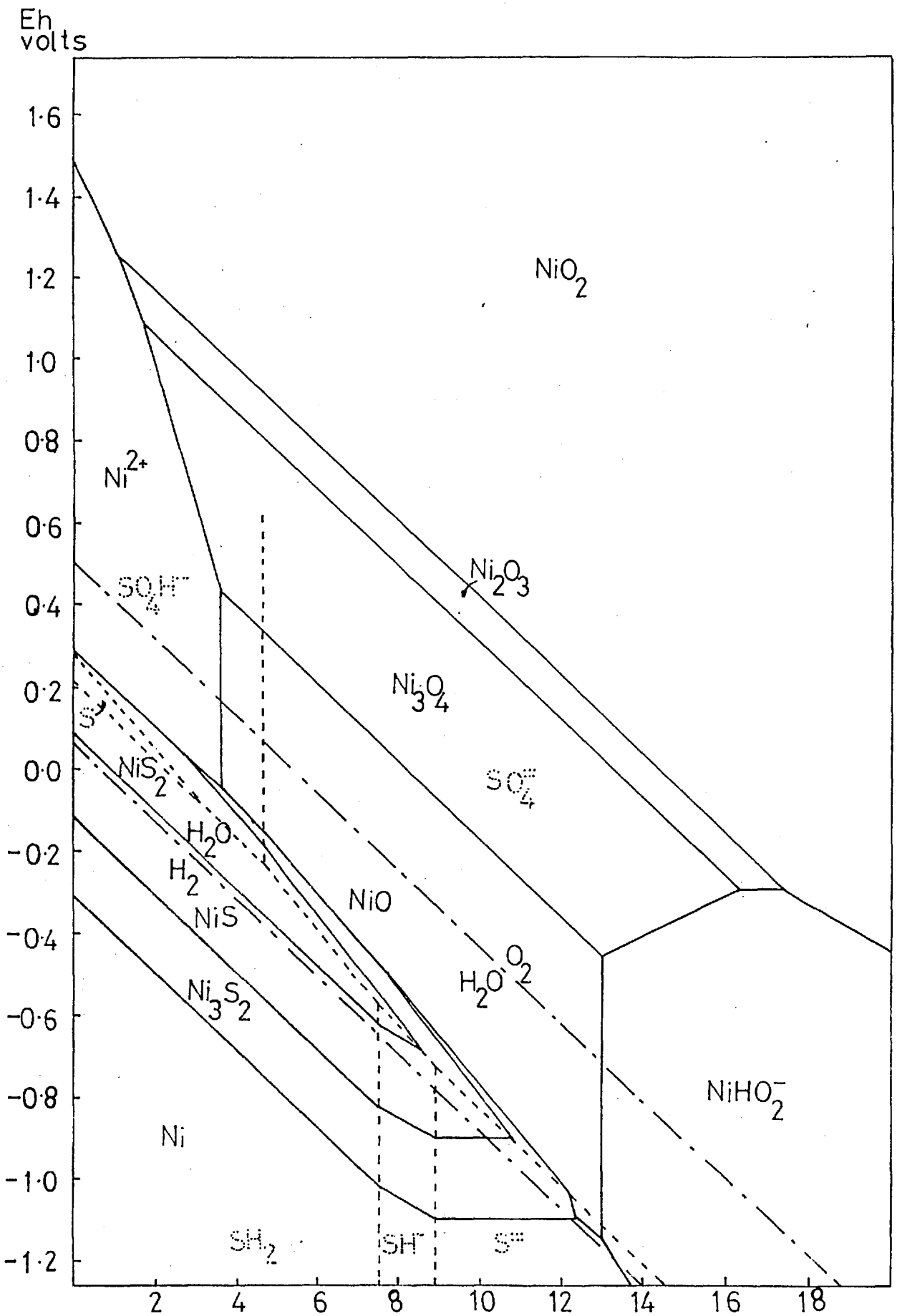


FIG.2 Eh-pH DIAGRAM FOR THE Ni-S-H_2O SYSTEM T 200°C

activity of ionic species $-10^{-1}-$

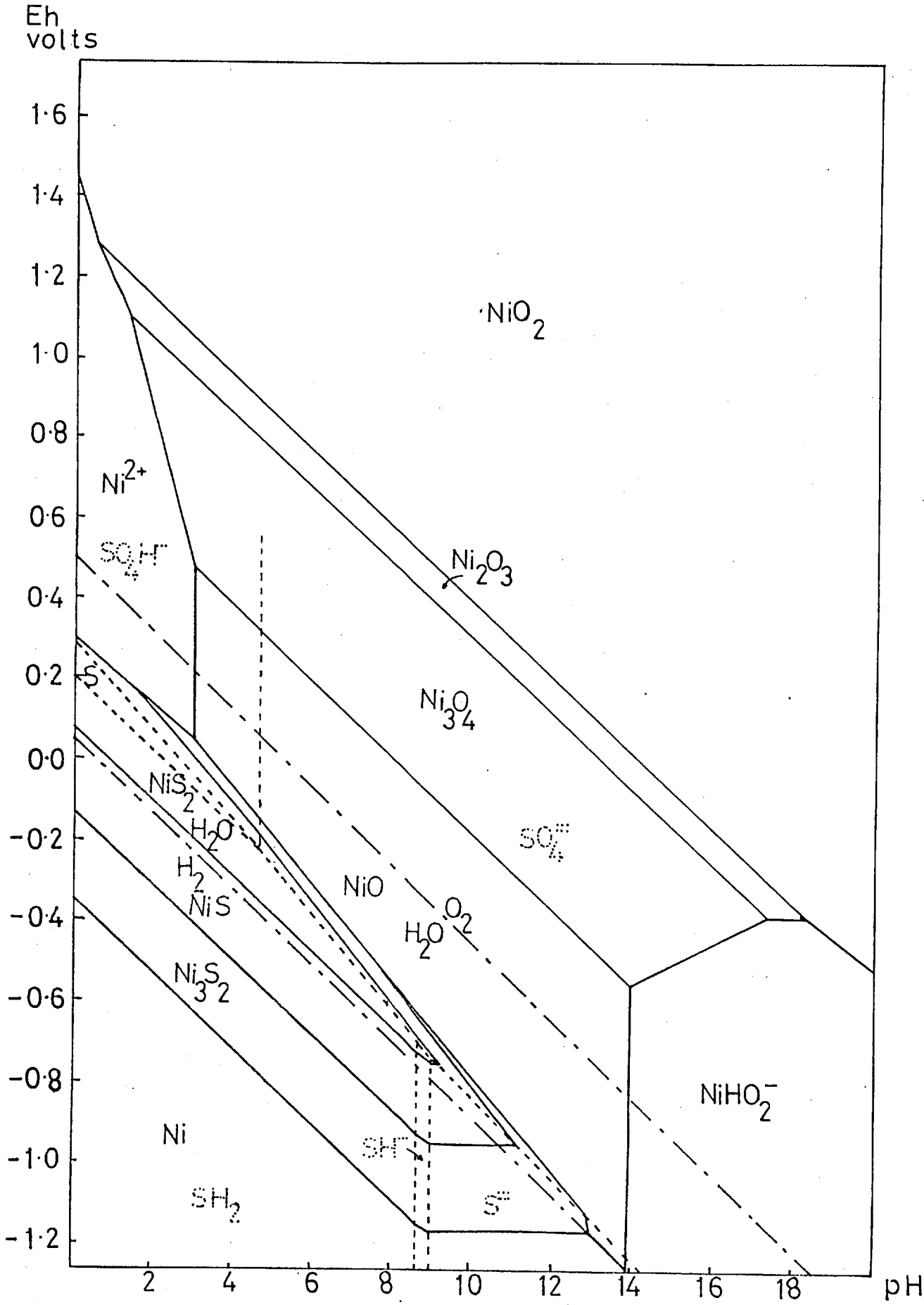


FIG.3 Eh-pH DIAGRAM FOR THE Ni-S-H_2O SYSTEM T 200°C

activity of ionic species -1-

E -pH Diagram for the Ni-S-NH_3-H_2O System

The E-pH diagrams for the system Ni-S-NH_3-H_2O have been drawn at 25°C and ionic activities of (10^{-3}), (Fig. 4), (10^{-1}), (Fig. 5) and (1), (Fig. 6). In order to draw the E-pH diagram for this system the equilibrium reaction (A-5) has to be considered.

$$NH_3 + H^+ = NH_4^+ \qquad \text{(A-5)}$$

The free energy change for this reaction at 25°C can be calculated according to the data given on the 'Table of thermodynamic data':

$$\Delta G_{A-5} = \Delta G_{NH_4^+} - \Delta G_{NH_3} - \Delta G_{H^+} = -12.62$$

and the equilibrium constant at 25°C can be calculated as follows:-

$$-12.62 = -\frac{1.987 \times 298 \times 2.303}{1000} \log \frac{(NH_4^+)}{(NH_3)(H^+)}$$

$$\log \frac{(NH_4^+)}{(NH_3)(H^+)} = 9.25 \qquad \text{(A-6)}$$

when $(NH_3) = (NH_4^+)$ pH = 9.25

In order to plot the E-pH diagram for this system, two types of approach can be considered:-

a) Considering the equation (A-6)
and $(NH_3) + (NH_4^+) = 1$

we can write:

$$(NH_4^+) = f_1(pH) \quad \text{or} \quad (NH_3) = f_2(pH) \qquad \text{(A-6)}$$

Considering, now that for pH values smaller than pH = 9.25 NH_4^+ is involved in the different reactions and that for pH values above pH = 9.25 NH_3 is involved in the different reactions and writing the different Nerst's equations for the different reactions we will obtain that:

For pH < 9.25 $E_1 = f_3((NH_4^+), pH)$

pH > 9.25 $E_2 = f_4((NH_3), pH)$

considering (A-6) $E_1 = f_5(pH)$

$E_2 = f_6(pH)$

b) Considering that for pH values smaller than pH = 9.25 NH_4^+ is involved, being $(NH_4^+) = 1$ and $(NH_3) = O$ and that for pH values bigger than 9.25 NH_3 is involved, with $(NH_3) = 1$ and $(NH_4^+) = 0$. The Nerst's equations for the different reaction can be written as:

$$E_1^1 = f_2(pH), \quad E_2^1 = f_8(pH)$$

The E-pH diagram for the Ni-S-NH_3-H_2O system at 25°C are drawn in accordance with the approach (b) since, although the approach (a) is the correct one, the small difference obtained using approach (a) does not justify the extra mathematical work necessary in using this approach.

- Reaction in the Ni-S-NH_3-H_2O System (Temperature 25°C)

- Reactions involving Water stability:-

1 $2H^+ + 2e = H_2$

2 $O_2 + 4H^+ + 4e = 2H_2O$

- Reactions involving solids

3 $Ni_3O_4 + 2H^+ + 2e = 3NiO + H_2O$

4 $3Ni_2O_3 + 2H^+ + 2e = 2Ni_3O_4 + H_2O$

5 $2NiO_2 + 2H^+ + 2e = Ni_2O_3 + H_2O$

6 $Ni_3O_4 + 8H^+ + 2e = 3Ni^{2+} + 4H_2O$

7 $Ni_2O_3 + 6H^+ + 2e = 2Ni^{2+} + 3H_2O$

8 $NiO_2 + 4H^+ + 2e = Ni^{2+} + 2H_2O$

9 $NiO + 2H^+ = Ni^{2+} + H_2O$

10 $NiHO_2^- + 3H^+ + 2e = Ni + 2H_2O$

11 $NiHO_2^- + H^+ = NiO + H_2O$

12 $Ni_3O_4 + 2H_2O + 2e = 3NiHO_2^- + H^+$

13 $Ni_2O_3 + H_2O = 2e = 2NiHO_2^-$

14 $NiO_2 + H^+ + 2e = NiHO_2^-$

15 $Ni_3S_2 + 4H^+ + 2e = 2H_2S + 3Ni$

16 $Ni_3S_2 + 2H^+ + 4e = 2HS^- + 3Ni$

17 $Ni_3S_2 + 4e = 2S^= + 3Ni$

18 $3NiS + 2H^+ + 2e = Ni_3S_2 + H_2S$

19 $NiS_2 + 2H^+ + 2e = NiS + H_2S$

20 $3NiS + H^+ + 2e = Ni_3S_2 + HS^-$

21 $NiS_2 + H^+ + 2e = NiS + HS^-$

22 $3NiS + 2e = Ni_3S_2 + S^{=}$

23 $3NiHO_2^- + 2S^{=} + 9H^+ + 2e = Ni_3S_2 + 6H_2O$

24 $3NiHO_2^- + 2SO_4^{=} + 25\ H^+ + 18e = Ni_3S_2 + 14H_2O$

25 $3NiO + 2SO_4^{=} + 22H^+ + 18e = Ni_3S_2 + 11H_2O$

26 $NiO + SO_4^{=} + 10H^+ + 8e = NiS + 5H_2O$

27 $Ni^{2+} + SO_4^{=} + 8H^+ + 8e = NiS + 4H_2O$

28 $Ni^{2+} + 2SO_4^{=} + 16H^+ + 14e = NiS_2 + 8H_2O$

29 $Ni^{2+} + 2HSO_4^- + 14H^+ + 14e = NiS_2 + 8H_2O$

30 $Ni_3S_2 + SO_4^{=} + 8H^+ + 6e = 3NiS + 4H_2O$

31 $NiS + SO_4^{=} + 8H^+ + 6e = NiS_2 + 4H_2O$

Reactions involving NH_3 and NH_4^+

32 $Ni(NH_3)_4^{++} + H_2O + 2H^+ = NiO + 4NH_4^+$

33 $Ni_2O_3 + 12NH_4^+ + 2e = 2Ni(NH_3)_6^{++} + 3H_2O + 6H^+$

34 $Ni_3O_4 + 18NH_4^+ + 2e = 3Ni(NH_3)_6^{++} + 4H_2O + 10H^+$

35 $Ni_3O_4 + 12NH_4^+ + 2e = 3Ni(NH_3)_4^{++} + 4H_2O + 4H^+$

36 $Ni(NH_3)_4^{++} + SO_4^{=} + 12H^+ + 8e = NiS + 4NH_4^+ + 4H_2O$

37 $Ni(NH_3)_6^{++} + SO_4^{=} + 14H^+ + 8e = NiS + 6NH_4^+ + 4H_2O$

38 $Ni_3O_4 + 15NH_4^+ + 2e = 3Ni(NH_3)_5^{++} + 4H_2O + 7H^+$

39 $Ni(NH_3)_5^{++} + SO_4^{=} + 13H^+ + 8e = NiS + 5NH_4^+ + 4H_2O$

40 $Ni(NH_3)_5^{++} + H^+ = Ni(NH_3)_4^{++} + NH_4^+$

41 $Ni(NH_3)_6^{++} + H^+ = Ni(NH_3)_5^{++} + NH_4^+$

42 $Ni(NH_3)_4^{++} + 4H^+ = Ni^{2+} + 4NH_4^+$

43 $Ni(NH_3)_6^{++} + SO_4^{=} + 8H^+ + 8e = NiS + 6NH_3 + 4H_2O$

44 $Ni(NH_3)_6^{++} + H_2O = NiO + 6NH_3 + 2H^+$

45 $Ni_3O_4 + 18\ NH_3 + 8H^+ + 2e = 3Ni(NH_3)_6^{++} + 4H_2O$

46 $3Ni(NH_3)_6^{++} + 2SO_4^{=} + 16H^+ + 18e = Ni_3S_2 + 18NH_3 + 8H_2O$

47 $Ni_2O_3 + 12NH_3 + 6H^+ + 2e = 2Ni(NH_3)_6^{++} + 3H_2O$

- Reactions involving the S-H_2O system:-

48 $SO_4^{=} + H^+ = HSO_4^-$

49 $HSO_4^- + 7H^+ + 6e = S + 4H_2O$

50 $SO_4^{=} + 8H^+ + 6e = S + 4H_2O$

51 $S + 2H^+ + 2e = H_2S$

52 $S + H^+ + 2e = HS^-$

53 $S^{=} + H^+ = HS^-$

54 $HS^- + H^+ = H_2S$

55 $SO_4^{=} + 8H^+ + 8e = S^{=} + 4H_2O$

56 $SO_4^{=} + 9H^+ + 8e = HS^- + 4H_2O$

- Equations relating E_T-pH and Activity in the Ni-S-NH_3-H_2O System at 25°C

Equation	Activity	E_T/pH Relationship
1	1	E = -0.0591 pH
	10^{-1}	"
	10^{-3}	"
2	1	E = 0.615 - 0.0591 pH
	10^{-1}	"
	10^{-3}	"
3	1	E = 0.831 - 0.0591 pH
	10^{-1}	"
	10^{-3}	"
4	1	E = 1.305 - 0.0591 pH
	10^{-1}	"
	10^{-3}	"
5	1	E = 1.434 - 0.0591 pH
	10^{-1}	"
	10^{-3}	"
6	1	E = 1.936 - 0.236 pH
	10^{-1}	E = 2.025 - 0.236 pH
	10^{-3}	E = 2.203 - 0.236 pH
7	1	E = 1.726 - 0.177 pH
	10^{-1}	E = 1.785 - 0.177 pH
	10^{-3}	E = 1.903 - 0.177 pH
8	1	E = 1.580 - 0.118 pH
	10^{-1}	E = 1.609 - 0.118 pH
	10^{-3}	E = 1.668 - 0.118 pH

Equation	Activity	E_T/pH Relationship
9	1	pH = 6.13
	10^{-1}	pH = 6.73
	10^{-3}	pH = 7.73
10	1	E = 0.648 - 0.0887 pH
	10^{-1}	E = 0.618 - 0.0887 pH
	10^{-3}	E = 0.558 - 0.0887 pH
11	1	pH = 17.47
	10^{-1}	pH = 16.47
	10^{-3}	pH = 14.47
12	1	E = -0.718 + 0.03 pH
	10^{-1}	E = -0.629 + 0.03 pH
	10^{-3}	E = -0.451 + 0.03 pH
13	1	E = -0.044
	10^{-1}	E = 0.015
	10^{-3}	E = 0.133
14	1	E = 0.695 - 0.03 pH
	10^{-1}	E = 0.725 - 0.03 pH
	10^{-3}	E = 0.785 - 0.03 pH
15	1	E = -0.371 - 0.591 pH
	10^{-1}	"
	10^{-3}	"
16	1	E = 0.607 - 0.03 pH
	10^{-1}	E = 0.577 - 0.03 pH
	10^{-3}	E = 0.517 - 0.03 pH
17	1	E = -0.989
	10^{-1}	E = -0.959
	10^{-3}	E = -0.899

Equation	Activity	E_T/pH Relationship
18	1	E =-0.164 - 0.0591 pH
	10^{-1}	"
	10^{-3}	"
19	1	E = -0.005 - 0.591 pH
	10^{-1}	"
	10^{-3}	"
20	1	E = -0.400 - 0.03 pH
	10^{-1}	E = -0.370 - 0.03 pH
	10^{-3}	E = -0.310 - 0.03 pH
21	1	E = -0.241 - 0.03 pH
	10^{-1}	E = -0.211 - 0.03 pH
	10^{-3}	E = -0.151 - 0.03 pH
22	1	E = -0.783
	10^{-1}	E = -0.753
	10^{-3}	E = -0.693
23	1	E = 3.924 - 0.266 pH
	10^{-1}	E = 3.776 - 0.266 pH
	10^{-3}	E = 3.481 - 0.266pH
24	1	E = 0.572 - 0.082 pH
	10^{-1}	E = 0.556 - 0.082 pH
	10^{-3}	E = 0.523 - 0.082 pH
25	1	E = 0.400 - 0.72 pH
	10^{-1}	E = 0.393 - 0.072 pH
	10^{-3}	E = 0.380 - 0.072 pH
26	1	E = 0.416 - 0.074 pH
	10^{-1}	E = 0.409 - 0.074 pH
	10^{-3}	-

Equation	Activity	E_T/pH Relationship
27	1	E = 0.324 - 0.0591 pH
	10^{-1}	E = 0.309 - 0.0591 pH
	10^{-3}	E = 0.280 - 0.0591 pH
28	1	E = 0.362 - 0.068 pH
	10^{-1}	E = 0.349 - 0.068 pH
	10^{-3}	E = 0.324 - 0.068 pH
29	1	E = 0.345 - 0.591 pH
	10^{-1}	E = 0.332 - 0.0591 pH
	10^{-3}	E = 0 307 - 0.0591 pH
30	1	E = 0.465 - 0.079 pH
	10^{-1}	E = 0.455 - 0.079 pH
	10^{-3}	E = 0.436 - 0.079 pH
31	1	E = 0.412 - 0.079 pH
	10^{-1}	E = 0.402 - 0.079 pH
	10^{-3}	E = 0.382 - 0.079 pH
32	1	pH = 8.21
	10^{-1}	pH = 7.71
	10^{-3}	-
33	1	-
	10^{-1}	-
	10^{-3}	E = -0.852 + 0.117 pH
34	1	E = -2.196 + 0.296 pH
	10^{-1}	E = -2.107 + 0.296 pH
	10^{-3}	E = -1.930 + 0.296 pH
35	1	E = -0.625 + 0.1182 pH
	10^{-1}	E = -0.536 + 0.1182 pH
	10^{-3}	E = -0.359 + 0.1182 pH

Equation	Activity	E_T/pH Relationship
36	1	E = 0.538 - 0.089 pH
	10^{-1}	E = 0.523 - 0.089 pH
	10^{-3}	E = 0.494 - 0.089 pH
37	1	E = 0.669 - 0.103 pH
	10^{-1}	E = 0.654 - 0.103 pH
	10^{-3}	E = 0.625 - 0.103 pH
38	1	E = -1.397 + 0.207 pH
	10^{-1}	E = -1.308 + 0.207 pH
	10^{-3}	E = -1.131 + 0.207 pH
39	1	E = 0.602 - 0.096 pH
	10^{-1}	E = 0.587 - 0.096 pH
	10^{-3}	E = 0.558 - 0.096 pH
40	1	pH = 8.70
	10^{-1}	"
	10^{-3}	"
41	1	pH = 9.00
	10^{-1}	"
	10^{-3}	"
42	1	-
	10^{-1}	-
	10^{-3}	7.22
43	1	E = 0.258 - 0.0591 pH
	10^{-1}	E = 0.243 - 0.0591 pH
	10^{-3}	E = 0.214 - 0.0591 pH
44	1	pH = 10.7
	10^{-1}	pH = 11.2
	10^{-3}	pH = 12.2

Equation	Activity	E_T/pH Relationship
45	1	E = 2.730 - 0.236 pH
	10^{-1}	E = 2.819 - 0.236 pH
	10^{-3}	E = 2.996 - 0.236 pH
46	1	E = 0.189 - 0.053 pH
	10^{-1}	E = 0.173 - 0.053 pH
	10^{-3}	E = 0.140 - 0.053 pH
47	1	-
	10^{-1}	-
	10^{-3}	E = 2.432 - 0.177 pH
48	1	pH = 1.99
	10^{-1}	"
	10^{-3}	"
49	1	E = 0.333 - 0.069 pH
	10^{-1}	E = 0.323 - 0.069 pH
	10^{-3}	E = 0.303 - 0.069 pH
50	1	E = 0.353 - 0.079 pH
	10^{-1}	E = 0.343 - 0.079 pH
	10^{-3}	E = 0.323 - 0.079 pH
51	1	E = 0.174 - 0.0591 pH
	10^{-1}	"
	10^{-3}	"
52	1	E = -0.062 - 0.03 pH
	10^{-1}	E = -0.032 - 0.03 pH
	10^{-3}	E = -0.028 - 0.03 pH
53	1	pH = 12.92
	10^{-1}	"
	10^{-3}	"

Equation	Activity	E_T/pH Relationship
54	1	pH = 7.99
	10^{-1}	pH = 6.99
	10^{-3}	pH = 4.99
55	1	E = 0.153 - 0.059 pH
	10^{-1}	"
	10^{-3}	"
56	1	E = 0.249 - 0.067 pH
	10^{-1}	"
	10^{-3}	"

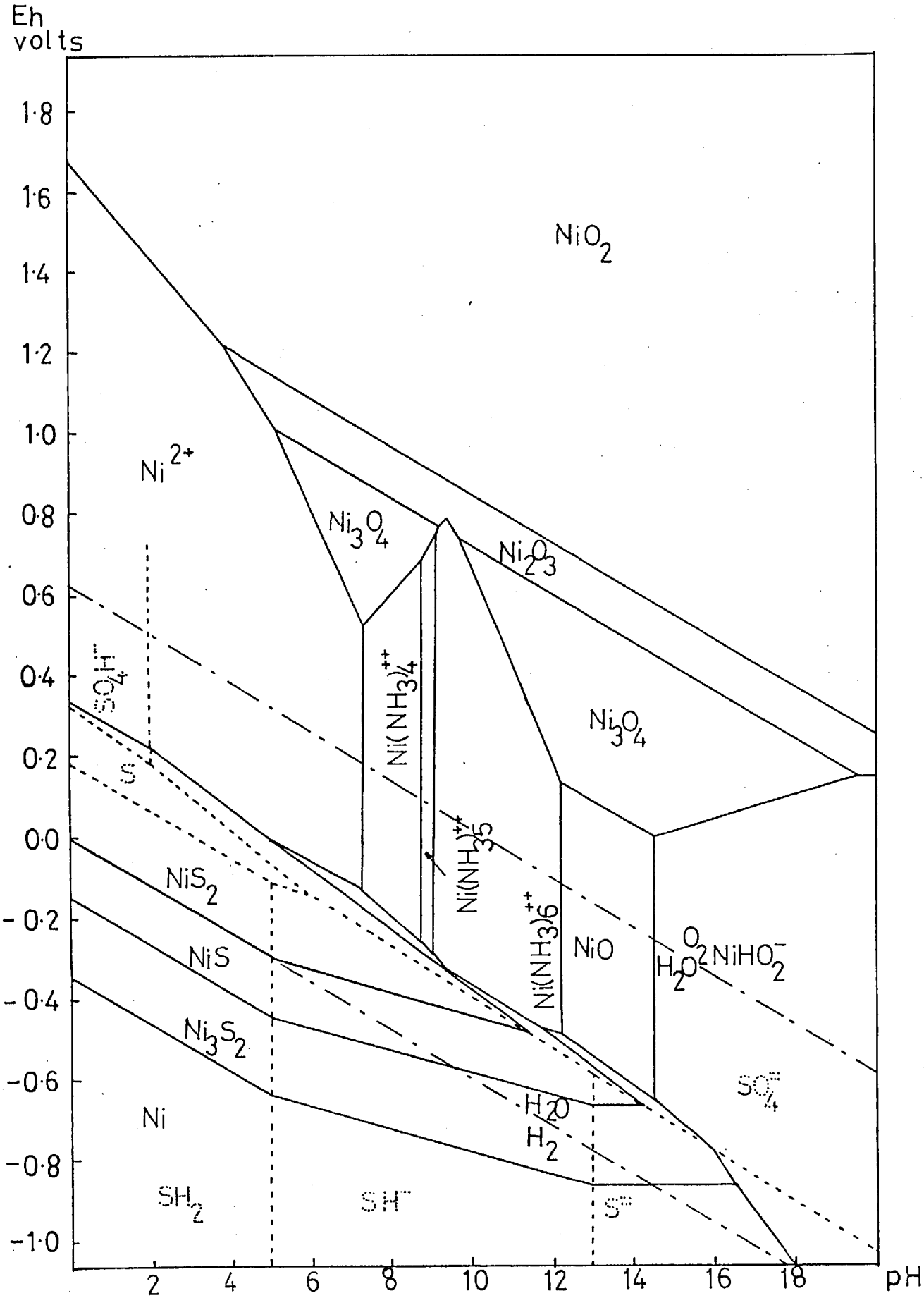


FIG.4 Eh-pH DIAGRAM FOR THE Ni-S-NH_3-H_2O SYSTEM T 25°C

$[NH_3]+[NH_4^+]$=1. activity of ionic species-10^{-3}-

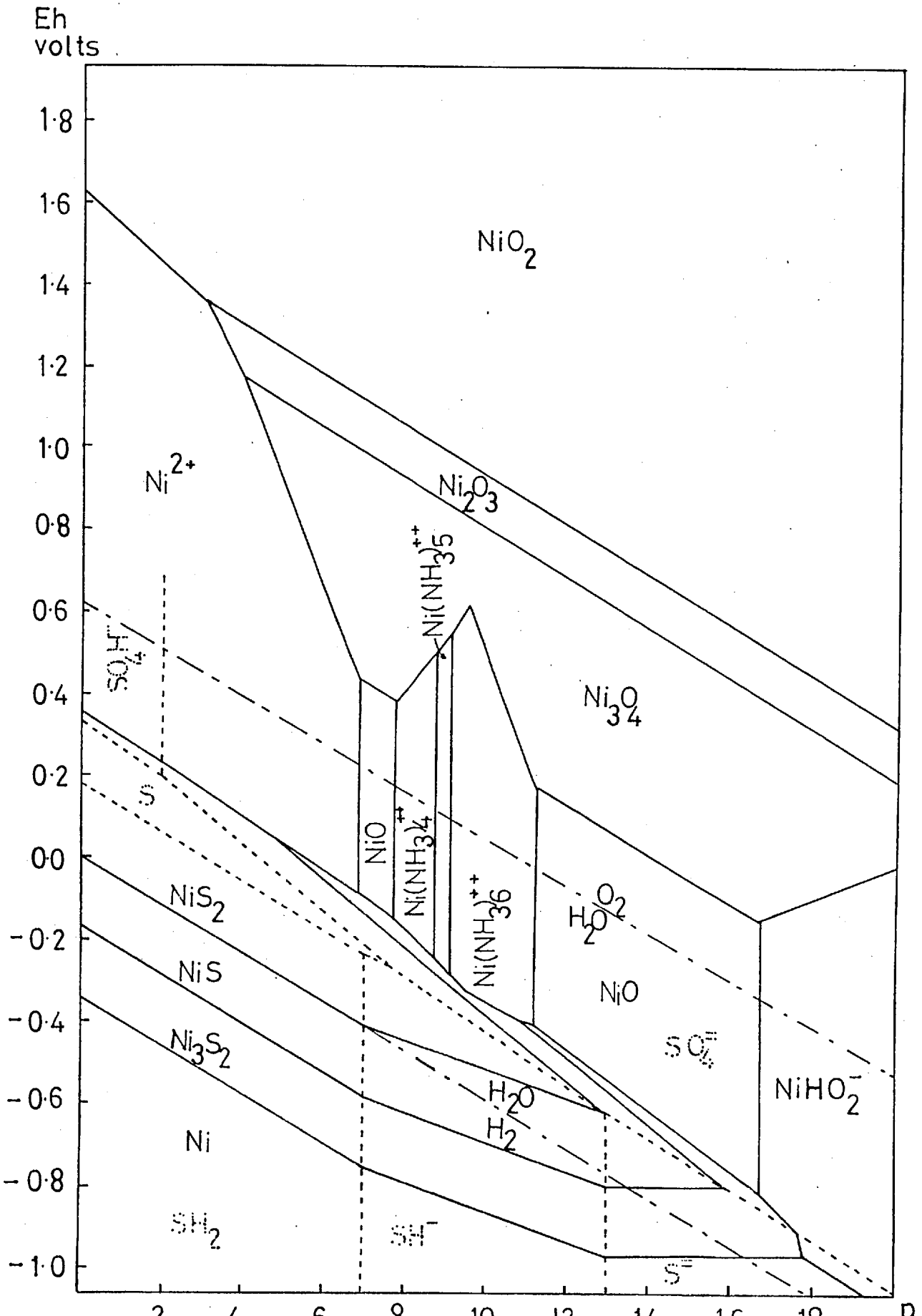


FIG.5 Eh-pH DIAGRAM FOR THE Ni-S-NH_3-H_2O SYSTEM T 25°C

$[NH_3]+[NH_4^+]$=1. activity of ionic species-10^{-1}-

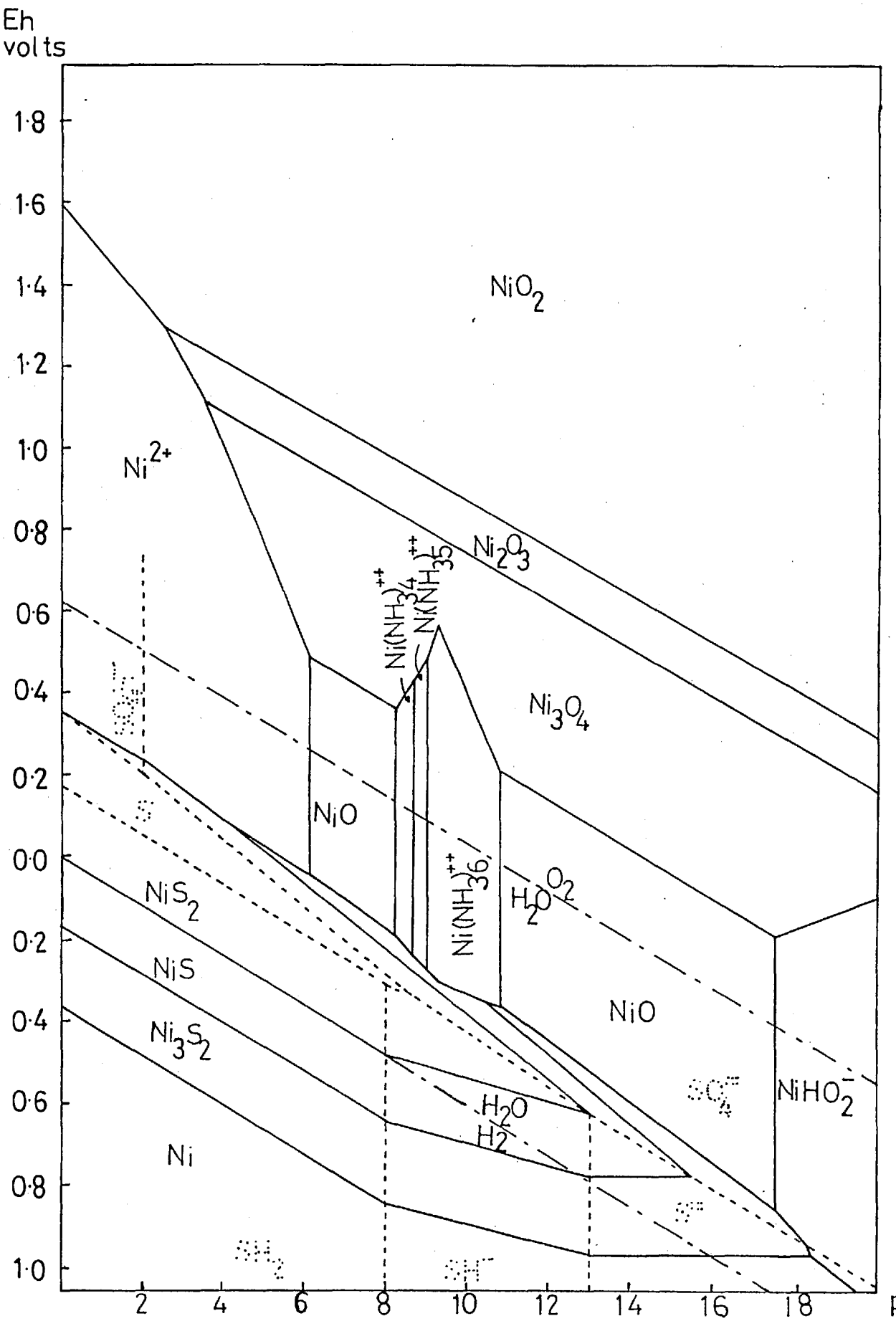


FIG.6 Eh-pH DIAGRAM FOR THE Ni-S-NH_3-H_2O SYSTEM T 25°C

$[NH_3]+[NH_4^+]=1$ activity of ionic species -1-

- Conclusions

The potential/pH diagrams constructed using E-pH relationships established above are shown in Figures 1 to 6. The diagrams shown in Figures 1, 2 and 3 are the E-pH diagrams for the system S-Ni-H_2O at 200°C, having the activity of the ionic species 10^{-3}, 10^{-1} and 1. The diagrams shown in Figures 5, 6 and 7 are the E-pH diagrams for the system Ni-S-NH_3-H_2O at 25°C, having the activity of the ionic species 10^{-3}, 10^{-1} and 1.

Among the possible nickel sulphides that can exist only three have been considered. NiS_2, NiS and Ni_3S_2 were the sulphides taken into account.

The area of stability of sulphur becomes smaller when the temperature is increased and so does the area of stability of the sulphides and Ni^{2+}, but the area of stability of $NiHO_2^-$ becomes bigger with an increase in temperature.

Considering the E-pH diagrams for the system Ni-S-H_2O at 200°C (Fig. 1, 2, 3) it can be seen that the area of stability of sulphur and sulphides becomes bigger when the activity of the ionic species is increased but the areas of stability of Ni^{2+} and $NiHO_2^-$ decrease when the activity of the ionic species is increased.

Ni_3S_2 seems to be the most stable sulphide under reducing and acid conditions but can be oxidized to NiS and this can be further oxidized to NiS_2 and Ni^{2+} (Fig. 1 to 6).

The E-pH diagrams for the system Ni-S-NH_3-H_2O have been drawn considering (NH_3) or (NH_4^+) = 1. It can be seen in figures 5 and 6 that NiO and Ni_3O_4 exist in alkaline and acidic conditions with their stability domains interrupted by stability domains

of nickel ammine complexes. For low activity of the ionic species (Fig. 4) the domains of stability of $Ni(NH_3)_6^{2+}$ and $Ni(NH_3)_4^{2+}$ increase and NiO is not stable under acidic conditions. It is interesting to note that the area of stability of NiO_2 and Ni_2O_3 is not altered when the nickel complexes are considered, and the area of stability of Ni_3O_4 is only slightly altered under the same conditions.

For all the activities of the ionic species considered (1, 10^{-1} and 10^{-3}) the area of stability of the nickel complexes lies around the equilibrium pH for the reaction (A-5).

- Thermodynamic Conditions for the Hydrolysis of Nickel Hexa-ammines ($(NH_3) + (NH_4^+)$) - pH diagrams

In the thermodynamic estimation of the stability of $Ni(NH_3)_6^{++}$ the following equilibrium reactions should be taken into account:

$$NH_4^+ = NH_3 + H^+ \qquad (A-7)$$

$$Ni(NH_3)_6^{2+} = Ni^{2+} 6NH_3 \qquad (A-8)$$

$$Ni(NH_3)_6^{2+} + 2H_2O = Ni(OH)_2 + 6NH_3 + 2H^+ \qquad (A-9)$$

In addition the following free energy values at 25°C (ΔG_{298}), 100°C (ΔG_{373}), 150°C (ΔG_{423}) and 200°C (ΔG_{473}) should be considered.

Species	ΔG_{298} Kcal mol^{-1}	ΔG_{373} Kcal mol^{-1}	ΔG_{423} Kcal mol^{-1}	ΔG_{473} Kcal mol^{-1}
$Ni(NH_3)_6^{++}$	-61.2	-68.27 (1)	-72.27 (1)	-77.57 (1)
NH_3	-6.35	- 8.42 (2)	- 9.88 (2)	-11.40 (2)
NH_4^+	-18.97	-21.30 (1)	-23.12(1)	-25.24 (1)
H_2O	-56.687	-58.1	-59.2	-60.42
H^+	0	- 0.281(1)	- 0.76 (1)	- 1.52 (1)
Ni^{2+}	-10.9	- 9.19 (1)	- 8.67 (1)	- 8.81 (1)
$Ni(OH)_2$	-99.224(3)	-111.99(3)	-114.26(3)	116.40 (3)

(1) Calculated according with Criss and Cobble's 'Correspondence principle'.(155-156)

(2) Calculated using data reported by N.J. Sheridan(172).

(3) Calculated using data for the stability constant for the reaction $Ni(OH)_2 = Ni^{2+} + 2OH^-$ reported by Robins(173).

Considering the equilibrium constant for reactions (A-7), (A-9) and (A-10) and the values of the free energy given in the previous table the following relationships may be written

$$\log K_1 = \log \frac{(NH_3)(H^+)}{(NH_4^+)} = - \frac{\Delta G_{1T} \times 1000}{1.987 \times 2.303 \times T} \quad \text{(A-10)}$$

$$\log K_2 = \log \frac{(Ni^{2+})(NH_3)^6}{(Ni(NH_3)_6^{++})} = \frac{-\Delta G_{2T} \times 1000}{1.987 \times 2.303 T} \quad \text{(A-11)}$$

$$\log K_3 = \log \frac{(NH_3)^6(H^+)^2}{(Ni(NH_3)_6^{++})} = \frac{-\Delta G_{3T} \times 1000}{1.987 \times 2.303\ T} \quad \text{(A-12)}$$

where ΔG_{1T}, ΔG_{2T} and ΔG_{3T} are the free energy charge for the reaction (A-7), (A-8) and (A-9).

From expression (A-10) and (A-12) the following equation may be written:

$$\log((NH_3 + (NH_4^+)) = \frac{1}{6} \log (Ni(NH_3)_6^{2+}) - \log K_1 + \frac{1}{6} \log K_3 - \tfrac{2}{3}\ pH + $$

$$+ \log (1 + 10^{\log K_1 + pH}) \quad \text{(A-13)}$$

considering $(Ni(NH_3)_6^{2+}) = 1$ mol/l or 0.1 mol/l or 0.01 mol/l and the free energy change for reaction (A-7) (A-8) and (A-9) at 25°C calculated in accordance with the ΔG values given in the previous table equation (A-13) may be written as follows:-

For $(Ni(NH_3)_6^{++}) = 1\ M/_L$

$$\log ((NH_3) + (NH_4^+)) = 4.70 - \tfrac{2}{3}\ pH + \log (1 + 10^{pH\ -9.25}) \quad \text{(A-14)}$$

For $(Ni(NH_3)_6^{++}) = 0.1\ M/_L$

$$\log ((NH_3) + (NH_4^+)) = 4.53 - \tfrac{2}{3} pH + \log (1 + 10^{pH\ -9.25}) \quad \text{(A-15)}$$

For $(Ni(NH_3)_6^{++} = 0.01\ M/L$

$$\log ((NH_3) + (NH_4^+)) = 4.37 - \tfrac{2}{3}\,pH + \log (1 + 10^{pH-9.25}) \qquad (A-16)$$

According with the equations (A-14), (A-15) and (A-16) the Figure 7, which represents $(NH_3) + (NH_4^+)$ versus pH for different $Ni(NH_3)_6^{++}$ concentration at T = 25°C, can be drawn

Considering, now $(Ni(NH_3)_6^{++}) = 1$ and the free energy charge for reaction (A-7), (A-8), (A-9) at 25°C, 100°C, 150°C and 200°C calculated using the ΔG_T values given in the previous table, equation (A-13) may be written as follows:-

For T = 25°C

$$\log ((NH_3) + (NH_4^+)) = 4.70 - \tfrac{2}{3}pH + \log (1 + 10^{pH-9.25}) \qquad (A-17)$$

For T = 150°C

$$\log ((NH_3) + (NH_4^+)) = 5.29 - \tfrac{2}{3}\,pH + \log (1 + 10^{pH-7.38}) \qquad (A-18)$$

For T = 150°C

$$\log ((NH_3) + (NH_4^+)) = 5.11 - \tfrac{2}{3}pH + \log (1 + 10^{pH\,-\,6.45}) \qquad (A-19)$$

For T = 200°C

$$\log ((NH_3) + (NH_4^+)) = 4.88 - \tfrac{2}{3}pH + \log (1 + 10^{pH\,-\,5.70}) \qquad (A-20)$$

Using the relationships (A-17), (A-18), (A-19) and (A-20) the figure 8, which represents $(NH_3) + (NH_4^+)$ versus pH for different temperatures for $(Ni(NH_3)_6^{++}) = 1$ M/L can be drawn.

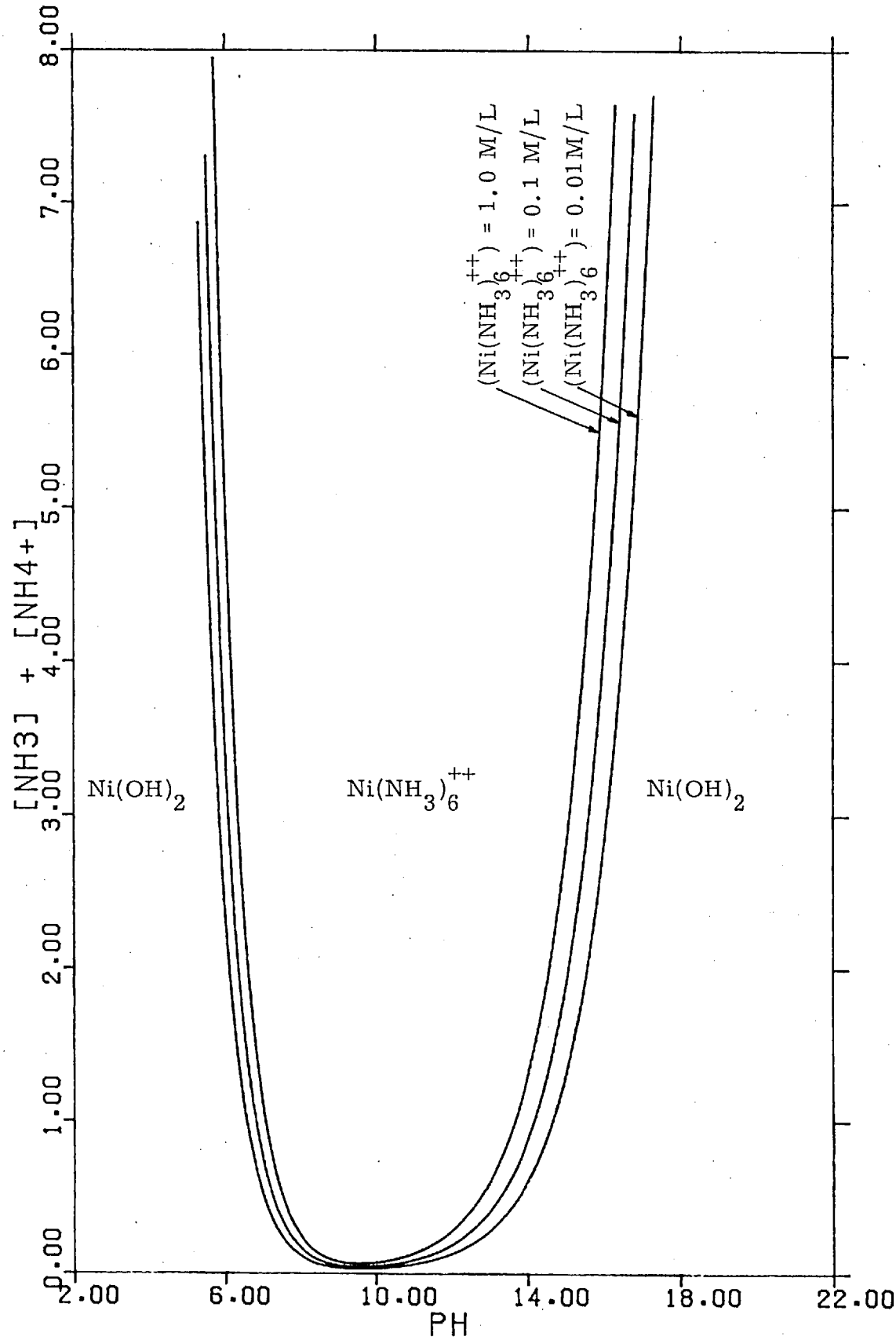


Fig. 7 $Ni(NH_3)_6^{2+}$ - Stable Region at 25°C

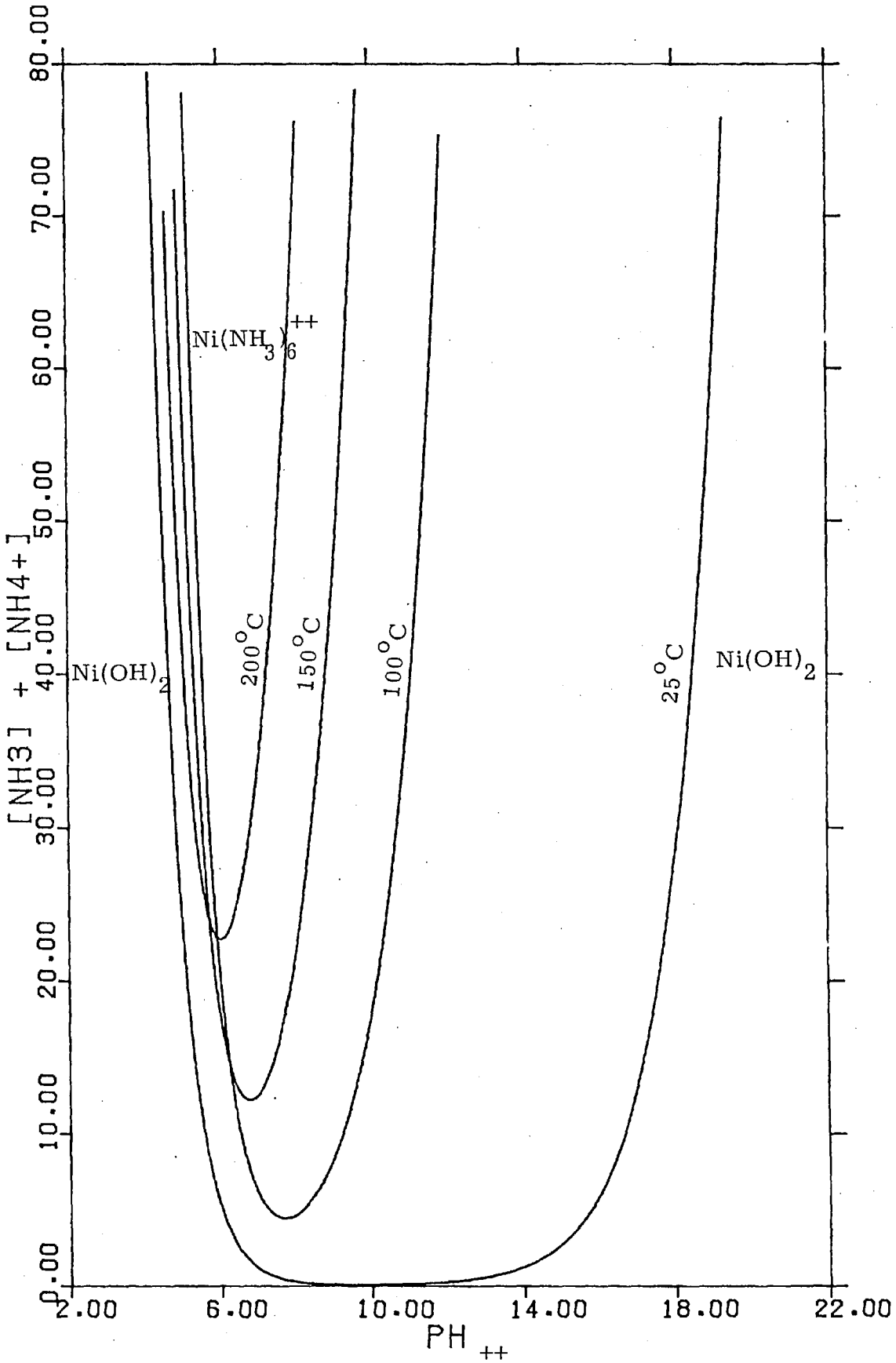


Fig. 8 Variation of $Ni(NH_3)_6^{++}$ - Stable Region with Temperature ($Ni(NH_3)_6^{++}$) = 1M/L

- Conclusion

Considering figures 7 and 8 the following conclusion can be drawn:

It can be seen in Figure 7 that the stable region of $Ni(NH_3)_6^{++}$ at 25°C covers a wide range of pH, from pH = 6 to pH = 14.

b) The stability area of $Ni(NH_3)_6^{++}$ at 25°C decreases slightly as the concentration of $Ni(NH_3)_6^{++}$ increases.

c) It can be seen in Figure 8 that the stable region of $Ni(NH_3)_6^{++}$ at a given concentration of $Ni(NH_3)_6^{++}$ decreases considerably when the temperature is increased. Thus at 100°C, 150°C and 200°C $Ni(NH_3)_6^{++}$ is not stable at pH = 12 (unbuffered solutions) or at pH = 10 (buffered solutions) even when the $(NH_3) + (NH_4^+)$ values are extremely high.

The values obtained in this study and therefore the conclusion drawn from Figures 7 and 8 are not quantitatively correct because there are obvious limitations in the thermodynamic values used in the calculations, moreover activity coefficients have not been taken into account. Nevertheless, these calculations (Equations A-14 to A-20, Figure 7 and 8) do demonstrate the thermodynamic behaviour of the hydrolysis reaction, and show clearly that a region of instability can exist, expecially at high temperature, in the pH range used in this work.

APPENDIX 2

X-RAY PATTERNS OF NICKEL OLIVINE (Ni_2SiO_4)

SULPHIDISATION

TABLE 7

X-RAY DIFFRACTION DATA FOR THE DIFFRACTION PATTERNS IN FIGURE 37

Pattern (1)		Pattern (2)		Pattern (3)		Pattern (4)		Pattern (5)		Pattern (6)		Pattern (7)		Ni_2SiO_4 A.S.T.M. 15.388		NiO A.S.T.M. 4.0835		NiS_2 A.S.T.M. 11.99	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	d(Å)	I/I_1	dÅ	I/I_1	dÅ	I/I_1
-	-	5.00	vvm	-	-	-	-	-	-	-	-	5.00	vvm	5.058	12	-	-	-	-
-	-	4.30	m	4.3	vvm	4.3	vvm	4.3	vvm	-	-	4.3	vvm	4.281	25	-	-	-	-
-	-	-	-	-	-	-	-	-	-	3.8	vm	3.8	vm	3.845	16	-	-	-	-
-	-	-	-	-	-	-	-	-	-	3.65	vvm	3.65	vvm	3.69	8	-	-	-	-
-	-	3.45	w	3.45	vw	3.45	vw	3.45	vw	3.45	m	3.45	vm	3.469	90	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.45	-	-	-	-	-
-	-	-	-	3.27	vw	3.27	vw	3.27	w	3.25	s	3.25	s	-	-	-	-	3.27	20
-	-	-	-	-	-	-	-	-	-	2.96	vvm	2.96	vvm	2.98	4	-	-	-	-
-	-	-	-	-	-	-	-	-	-	2.94	vvm	2.98	vvm	2.95	8	-	-	-	-
-	-	-	-	2.84	s	2.84	s	2.83	vs	2.83	vs	2.83	vs	-	-	-	-	2.83	100
-	-	2.73	w	2.735	w	2.735	vw	2.735	vw	2.73	vw	2.73	vw	2.74	85	-	-	-	-
-	-	2.55	w	2.54	m	2.54	m	2.54	vm	-	-	-	-	2.55	40	-	-	-	-
-	-	-	-	2.53	vw	2.53	vw	2.54	w	2.54	s	2.54	vs	-	-	-	-	2.54	40
-	-	2.53	m	-	-	-	-	-	-	-	-	2.53	vm	2.53	12	-	-	-	-
-	-	2.48	ws	2.48	m	2.48	m	2.48	m	2.48	vw	2.48	vw	2.48	80	-	-	-	-
-	-	2.43	ws	2.42	m	2.42	m	2.43	m	2.43	vw	2.43	vw	2.43	100	-	-	-	-
2.40	-	2.40	s	2.40	s	2.40	s	2.40	s	2.40	w	2.40	w	-	-	2.41	91	-	-
-	-	2.35	vm	2.35	vvm	2.35	vvm	2.35	vvm	2.35	vm	2.35	vm	2.36	16	-	-	-	-
-	-	2.32	m	2.32	w	2.32	w	2.32	w	2.32	s	2.32	s	2.32	10	-	-	2.32	40
-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.30	8	-	-	-	-
-	-	2.23	vm	2.23	vvm	2.23	vvm	2.23	vvm	2.23	vvm	2.23	vvm	2.24	16	-	-	-	-
-	-	2.22	vm	2.22	vvm	2.22	vvm	2.22	vvm	2.22	vvm	2.22	vvm	2.23	14	-	-	-	-
-	-	-	-	-	-	-	-	-	-	2.14	vvm	2.14	vvm	2.14	8	-	-	-	-
2.08	-	2.08	s	2.08	s	2.08	s	2.08	s	2.08	w	2.08	w	-	-	2.088	100	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.01	10	-	-	-	-
-	-	-	-	2.00	w	2.00	w	2.00	w	2.00	s	2.00	s	-	-	-	-	2.00	50
-	-	-	-	-	-	-	-	-	-	1.92	vvm	-	-	1.92	2	-	-	-	-
-	-	-	-	1.89	vvm	1.89	vvm	1.89	vvm	1.89	m	1.89	m	-	-	-	-	1.89	5
-	-	-	-	-	-	-	-	-	-	1.85	vvm	1.85	vvm	1.86	6	-	-	-	-
-	-	1.78	vm	-	-	-	-	-	-	1.78	vvm	1.78	vvm	1.79	10	-	-	-	-
-	-	1.77	vm	-	-	-	-	-	-	1.77	vvm	1.77	vvm	1.77	6	-	-	-	-
-	-	1.72	w	1.73	vw	1.73	vw	1.73	m	1.72	vvm	1.72	vvm	1.73	60	-	-	-	-
-	-	1.71	m	1.72	vm	1.72	vm	1.72	vm	-	-	-	-	1.72	-	-	-	-	-
-	-	-	-	1.705	s	1.705	s	1.705	s	1.705	vs	1.705	vs	-	-	-	-	1.71	80
-	-	1.65	vm	1.64	vm	1.64	vm	1.64	vvm	1.65	vvm	1.65	vvm	1.65	8	-	-	-	-
-	-	-	-	1.63	m	1.63	m	1.63	vw	1.63	s	1.63	s	-	-	-	-	1.63	20
-	-	1.59	w	1.59	m	1.59	m	1.59	m	1.59	m	1.59	m	1.60	14	-	-	-	-
-	-	1.57	m	1.57	w	1.57	w	1.57	w	1.57	s	1.57	s	1.57	12	-	-	1.57	30
-	-	1.54	m	-	-	-	-	-	-	1.55	vvm	1.55	vvm	1.55	18	-	-	-	-
-	-	-	-	1.51	w	1.51	w	1.51	w	1.51	s	1.51	s	-	-	-	-	1.51	30
-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.50	6	-	-	-	-
1.465	-	1.465	s	1.47	s	1.47	s	1.47	s	1.47	w	1.47	vw	-	-	1.476	57	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.47	20	-	-	-	-
-	-	1.45	m	1.46	m	1.46	m	1.46	m	1.46	m	1.46	m	1.46	20	-	-	-	-
-	-	-	-	-	-	-	-	-	-	1.42	m	1.42	vm	1.42	6	-	-	-	-

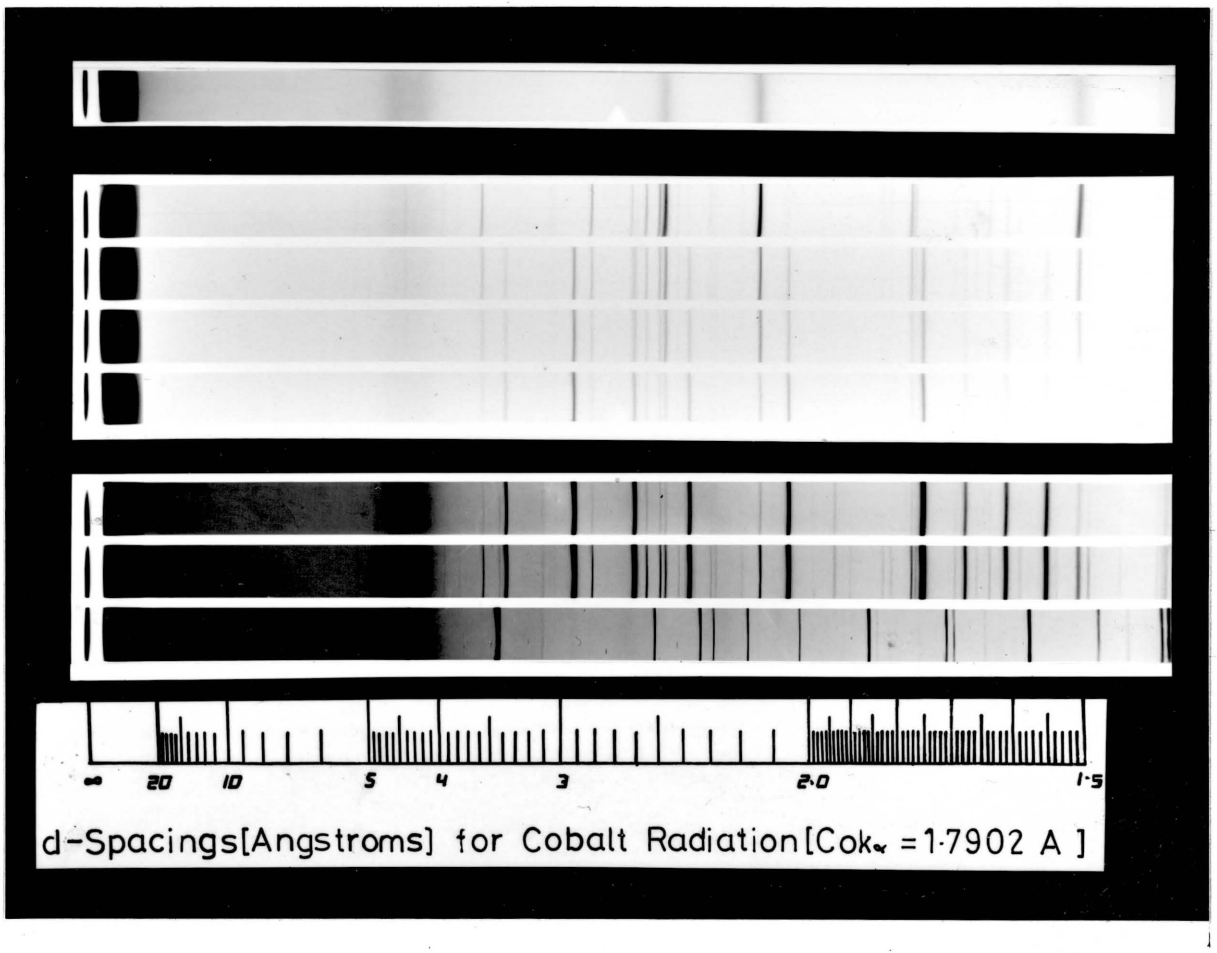


Fig. 37 X-Ray Patterns of the Solid Products Obtained after the Hydrothermal Treatment of Synthetic $NiO-Ni_2SiO_4$ Material

(1) X-ray pattern of the ignited powder (Section 2.1.1)

(2) X-ray pattern of synthetic $NiO-Ni_2SiO_4$ material

(3)-(7) X-ray patterns of the solid products obtained after hydrothermal treatment of (2)

Conditions used in the Hydrothermal Treatment

	Temperature	Time	Amount of Sulphur	Amount of (2)
(3)	240°C	4 hours	0.4 gr.	1 gr.
(4)	240°C	4 hours	0.8 gr.	1 gr.
(5)	240°C	4 hours	1.6 gr.	1 gr.
(6)	240°C	4 hours	2.4 gr.	1 gr.
(7)	240°C	4 hours	3.2 gr.	1 gr.

(8) X-ray pattern of SiO_2

TABLE 8

X-RAY DIFFRACTION DATA FOR THE DIFFRACTION PATTERNS IN FIGURES 38(a) - 38(b)

Pattern (1)		Pattern (2)		Pattern (3)		Pattern (4)		Pattern (5)		Pattern (6)		Pattern (7)		Pattern (8)		Pattern (9)		Pattern (10)	
5.00	m	5.00	m	5.00	m	5 01	vm	5.01	vm	5.01	vm	5.01	vm	5.01	vvm	5.01	vvm	5.01	vvm
4.30	m	4.30	m	4.30	m	4.30	m	4.30	m	4.30	m	4 30	m	4.30	m	4.30	m	4.30	m
-	-	-	-	4.05	w	4.05	m	4.05	m	4.05	m	4.05	m	4.05	m	4.05	m	4.05	m
3.80	m	3.80	m	3.80	m	3.84	m	3.84	m	3.84	m	3.84	m	3.84	m	3.84	m	3.84	m
3.65	m	3.65	m	3.65	m	3.67	vm	3.67	vm	3.67	vm	3.67	vm	3.67	vm	3.67	vm	3.67	vm
3.45	s	3.45	s	3.45	vs	3.45	s	3.45	s	3.45	s	3.45	s	3.45	s	3.45	s	3.45	s
-	-	-	-	-	-	3.28	vm	3.28	vm	3.28	vm	3.28	vm	3.28	w	3.28	w	3.28	w
2.97	vvm	2.97	vvm	2.97	vm	2.97	vvm	2.97	vvm	2.97	vvm	2.97	vvm	2.97	vvm	2.97	vvm	2 97	vvm
2 94	vvm	2.94	vvm	2.94	vm	2.94	vvm	2.94	vvm	2.94	vvm	2.94	vvm	2.94	vvm	2 94	vvm	2.94	vvm
-	-	-	-	-	-	2.84	w	2.84	w	2.84	w	2.84	w	2 84	s	2.84	s	2.84	s
2.73	s	2.73	s	2.73	vs	2.73	s	2.73	s	2.73	s	2.73	s	2.73	s	2.73	s	2.73	s
-	-	-	-	-	-	2.55	w	2.55	w	2.55	w	2.55	w	2.55	s	2.55	s	2.55	s
2.54	s	2.54	s	2.54	s	2.54	s	2.54	s	2.54	s	2.54	s	2.54	s	2.54	s	2.54	s
2.53	w	2.53	w	2.53	w	2.53	m	2.53	m	2.53	m	2.53	m	2.53	m	2.53	m	2.53	m
2.47	s	2.47	s	2.47	vs	2.47	s	2.47	s	2.47	s	2.47	s	2.47	s	2.47	s	2.47	s
2.43	s	2 43	s	2.43	vs	2.43	s	2.43	s	2.43	s	2.43	s	2.43	s	2.43	s	2.43	s
2.40	vs	2.40	w	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2.35	m	2.35	m	2.35	m	2.36	m	2.36	m	2.36	m	2.36	m	2.36	m	2.36	m	2.36	m
2.32	m	2.32	m	2.32	m	2.32	w	2.32	w	2.32	w	2.32	w	2.32	s	2.32	s	2.32	s
2.28	vm	2.28	vm	2.28	vm	2.28	vvm	2.28	vvm	2.28	vvm	2.28	vvm	2.28	vvm	2.28	vvm	2.28	vvm
2.23	m	2.23	m	2.23	m	2.23	m	2.23	m	2.23	m	2.23	m	2.23	m	2.23	m	2.23	m
2.22	m	2.22	m	2.22	m	2.22	m	2.22	m	2.22	m	2.22	m	2.22	m	2.22	m	2.22	m
2.13	m	2.13	m	2.13	m	2.14	m	2.14	m	2.14	m	2.14	m	2.14	m	2.14	m	2.14	m
2.08	vs	2.08	w	2.08	vm	2.08	vm	2.08	vm	2.08	vm	2.08	vm	2.08	vm	2.08	vm	2.08	vm
2.00	w	2.00	w	2.00	w	2.01	w	2.01	w	2.01	w	2.01	w	2.01	s	2.01	s	2.01	s
1.93	vm	1.93	vm	1.93	vm	1.93	vvm	1.93	vvm	1.93	vvm	1.93	vvm	1.93	vvm	1.93	vvm	1.93	vvm
1.91	vm	1.91	vm	1.91	vm	1.92	vvm	1.92	vvm	1.92	vvm	1.92	vvm	1.92	vvm	1.92	vvm	1.92	vvm
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.85	m	1.85	m	1.85	m	1.85	m	1.85	m	1.85	m	1.85	m	1.85	m	1.85	m	1.85	m
1.78	w	1.78	w	1.78	w	1.79	m	1.79	m	1.79	m	1.79	m	1.79	m	1.79	m	1.79	m
1.765	w	1.765	w	1.765	w	1.77	m	1.77	m	1.77	m	1.77	m	1.77	m	1.77	m	1.77	m
1.725	s	1.725	s	1.725	vs	1.73	s	1.73	s	1.73	s	1.73	s	1.73	s	1.73	s	1.73	s
1.72	m	1.72	m	1.72	m	1.72	m	1.72	m	1.72	m	1.72	m	1.72	m	1.72	m	1.72	m
-	-	-	-	-	-	1.71	w	1.71	w	1.71	w	1.71	w	1.71	s	1.71	s	1.71	s
1.70	w	1.70	w	1.70	w	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.65	w	1.65	w	1.65	w	1.66	m	1.66	m	1.66	m	1.66	m	1.66	m	1.66	m	1.66	m
-	-	-	-	-	-	1.655	m	1.655	m	1.655	m	1.655	m	1.655	w	1.655	w	1.655	w
1.61	w	1.61	w	1.61	w	1.615	w	1.615	w	1.615	w	1.615	w	1.615	w	1.615	w	1.615	w
1.59	w	1.59	w	1.59	w	1.59	w	1.59	w	1.59	w	1.59	w	1.59	w	1.59	w	1.59	w
-	-	-	-	-	-	1.57	w	1.57	w	1.57	w	1.57	w	1.57	s	1.57	s	1.57	s
1.565	w	1.565	w	1.565	w	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.55	w	1.55	w	1.55	w	1.55	w	1.55	w	1.55	w	1.55	w	1.55	w	1.55	w	1.55	w
-	-	-	-	-	-	1.515	w	1.515	w	1.515	w	1.515	w	1.515	s	1.515	s	1.515	s
1.495	m	1.495	m	1.495	m	1.50	m	1.50	m	1.50	m	1.50	m	1.50	m	1.50	m	1.50	m
1.485	vm	1.485	vm	1.485	vm	1.49	vvm	1.49	vvm	1.49	vvm	1.49	vvm	1.49	vvm	1.49	vvm	1.49	vvm
1.48	vm	1.48	vm	1.48	vm	1.48	vvm	1.48	vvm	1.48	vvm	1.48	vvm	1.48	vvm	1.48	vvm	1.48	vvm
1.475	vm	1.475	vm	1.475	vm	1.48	vvm	1.475	vvm	1.475	vvm	1.475	vvm	1.475	vvm	1.475	vvm	1.475	vvm
1.465	vs	1.465	s	1.465	s	1.47	s	1.47	s	1.47	s	1.47	s	1.47	s	1.47	s	1.47	s
1.45	s	1.45	s	1.45	vs	1.46	w	1.46	w	1.46	w	1.46	w	1.46	w	1.46	w	1.46	w
1.42	w	1.42	w	1.42	w	1.425	w	1.425	w	1.425	w	1.425	w	1.425	w	1.425	w	1.425	w
1.378	w	1.378	w	1.378	w	1.38	w	1.38	w	1.38	w	1.38	w	1.38	w	1.38	w	1.38	w
1.373	w	1.373	w	1.373	w	1.377	w	1.377	w	1.377	w	1.377	w	1.377	w	1.377	w	1.377	w
-	-	-	-	-	-	1.375	w	1.375	w	1.375	w	1.375	w	1.375	w	1.375	w	1.375	w
1.368	vm	1.368	m	1.368	m	-	-	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 8

X-RAY DIFFRACTION DATA FOR THE DIFFRACTION PATTERNS IN FIGURES 38(a)-38(b)

Pattern (11)		Pattern (12)		Pattern (13)		Pattern (14)		Pattern (15)		Pattern (16)		Pattern (17)		Pattern (18)		Pattern (19)		Ni_2SiO_4 A.S.T.M. 15.388		NiS_2 A.S.T.M. 11.99		NiO A.S.T.M. 4.0835		-Cristobalite SiO_2 11.695	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I/I_1	d(Å)	I/I_1	dÅ	I/I_1	dÅ	I/I_1
5.01	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5.058	12	-	-	-	-	-	-
4.30	m	4.30	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.281	25	-	-	-	-	-	-
4.05	m	4.05	m	4.05	m	4.05	m	4.05	m	4.05	m	4.05	m	4.05	m	4.05	m	-	-	-	-	-	-	4.05	100
3.84	m	3.84	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.845	16	-	-	-	-	-	-
3.67	vm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.69	8	-	-	-	-	-	-
3.45	s	3.45	w	3.45	w	3.45	w	3.45	w	3.45	m	3.45	m	3.45	m	3.45	m	3.469	90	-	-	-	-	-	-
3.28	w	3.27	w	3.27	w	3.27	w	3.27	w	3.27	w	3.27	w	3.27	w	3.27	w	-	-	3.27	20	-	-	-	-
2.97	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.98	4	-	-	-	-	-	-
2.94	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.95	8	-	-	-	-	-	-
2.84	s	2.84	s	2.84	s	2.84	s	2.84	s	2.84	s	2.84	s	2.84	s	2.84	s	-	-	2.83	100	-	-	-	-
2.73	s	2.74	m	2.74	m	2.74	m	2.74	m	2.74	m	2.74	m	2.74	m	2.74	m	2.74	85	-	-	-	-	-	-
2.55	s	2.54	s	2.54	s	2.54	s	2.54	s	2.54	s	2.54	s	2.54	s	2.54	s	-	-	2.54	40	-	-	-	-
2.54	s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.55	40	-	-	-	-	-	-
2.53	m	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.53	12	-	-	-	-	-	-
2.47	s	2.48	w	2.48	w	2.48	w	2.48	w	2.48	m	2.48	m	2.48	m	2.48	m	2.48	80	-	-	-	-	-	-
2.43	s	2.43	w	2.43	w	2.43	w	2.43	w	2.43	m	2.43	m	2.43	m	2.43	m	2.43	100	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.41	91	-	-
2.36	m	2.35	vvm	2.35	vvm	2.35	vvm	2.35	vvm	-	-	-	-	-	-	-	-	2.36	16	-	-	-	-	-	-
2.32	s	2.32	s	2.32	s	2.32	s	2.32	s	2.32	s	2.32	s	2.32	s	2.32	s	2.32	10	2.32	40	-	-	-	-
2.28	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.30	8	-	-	-	-	-	-
2.23	m	2.23	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.24	16	-	-	-	-	-	-
2.22	m	2.22	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.23	14	-	-	-	-	-	-
2.14	m	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.14	8	-	-	-	-	-	-
2.08	vm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.088	100	-	-
2.01	s	2.01	s	2.01	s	2.01	s	2.01	s	2.01	s	2.01	s	2.01	s	2.01	s	2.01	10	2.00	50	-	-	-	-
1.93	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.92	2	-	-	-	-	-	-
1.92	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	1.89	vvm	1.89	vvm	1.89	vvm	1.89	vvm	-	-	-	-	-	-	-	-	-	-	1.89	5	-	-	-	-
1.85	m	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.85	6	-	-	-	-	-	-
1.79	m	1.785	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.79	10	-	-	-	-	-	-
1.77	m	1.77	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.77	6	-	-	-	-	-	-
1.73	s	1.73	w	1.73	w	1.73	w	1.73	w	1.73	m	1.73	m	1.73	m	1.73	m	1.73	60	-	-	-	-	-	-
1.72	m	1.72	m	1.72	m	1.72	m	1.72	m	1.72	vm	1.72	vm	1.72	vm	1.72	vm	1.72	-	-	-	-	-	-	-
1.71	s	1.71	s	1.71	s	1.71	s	1.71	s	1.71	s	1.71	s	1.71	s	1.71	s	-	-	1.71	80	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.66	m	1.66	vvm	1.65	vvm	1.65	vvm	1.65	vvm	-	-	-	-	-	-	-	-	1.65	8	-	-	-	-	-	-
1.655	w	1.645	w	1.645	w	1.645	w	1.645	w	1.645	w	1.645	w	1.645	w	1.645	w	-	-	1.63	20	-	-	-	-
1.615	w	1.615	m	1.615	vm	1.615	vm	1.615	vm	-	-	-	-	-	-	-	-	1.60	14	-	-	-	-	-	-
1.59	w	1.59	m	1.59	vvm	1.59	vvm	1.59	vvm	-	-	-	-	-	-	-	-	1.57	12	-	-	-	-	-	-
1.57	s	1.57	w	1.57	w	1.57	w	1.57	w	1.57	s	1.57	s	1.57	s	1.57	s	-	-	1.57	30	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.55	18	-	-	-	-	-	-
1.55	w	1.55	vm	1.55	vvm	1.55	vvm	1.55	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.515	s	1.51	w	1.51	w	1.51	w	1.51	w	1.51	s	1.51	s	1.51	s	1.51	s	-	-	1.51	30	-	-	-	-
1.50	m	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.50	6	-	-	-	-	-	-
1.49	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.48	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.475	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.47	s	1.47	m	1.47	vm	1.47	vm	1.47	vm	1.47	vvm	1.47	vvm	1.47	vvm	1.47	vvm	1.47	20	-	-	-	-	-	-
1.46	w	1.46	m	1.46	vm	1.46	vm	1.46	vm	1.46	vvm	1.46	vvm	1.46	vvm	1.46	vvm	1.46	20	-	-	-	-	-	-
1.425	w	1.42	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.38	w	1.38	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.377	w	1.375	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.325	w	1.373	vvm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

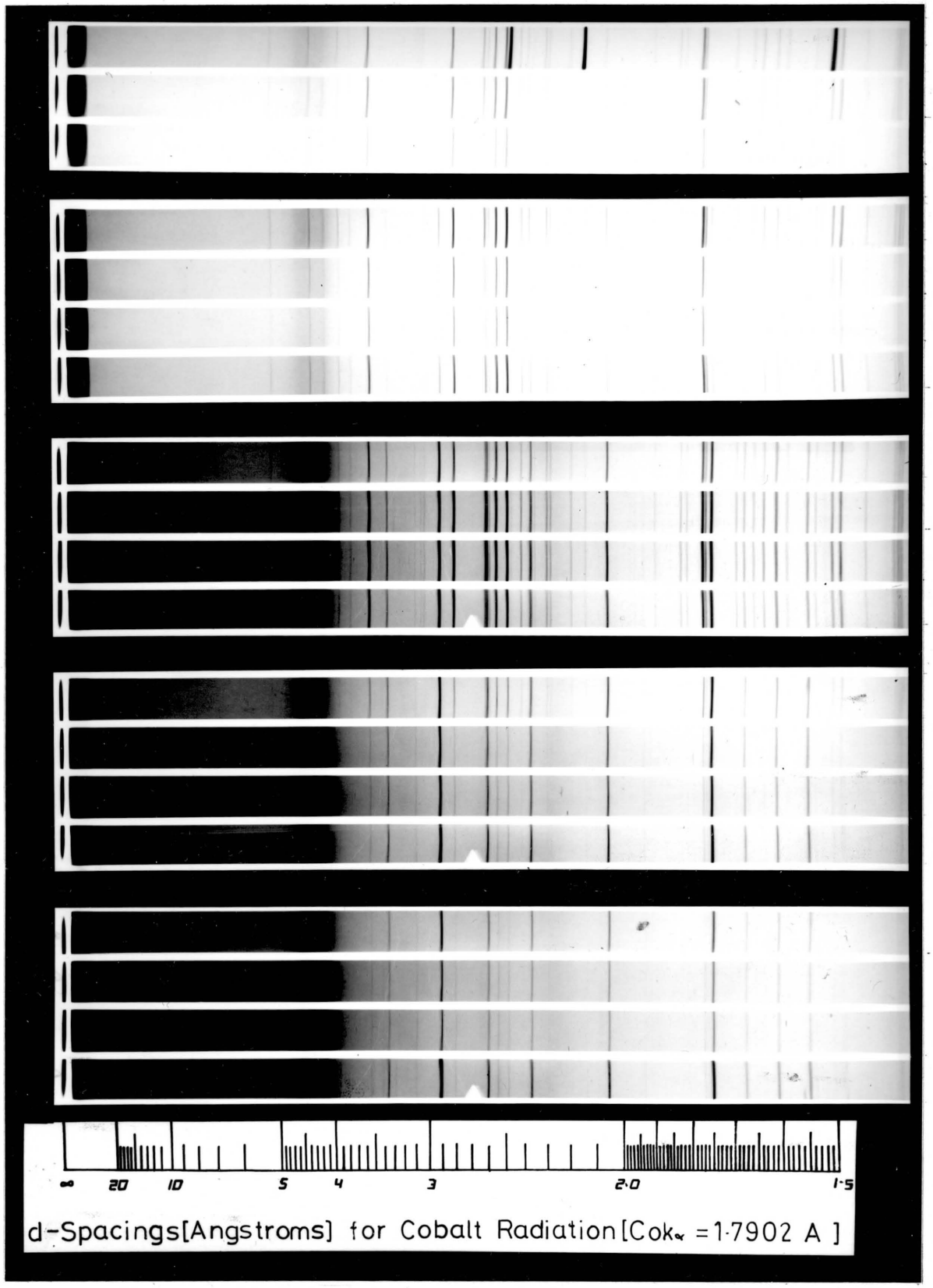


Fig. 38 X-ray Patterns of the Solid Products Obtained After the Hydrothermal Treatment of Synthetic Ni_2SiO_4 Material

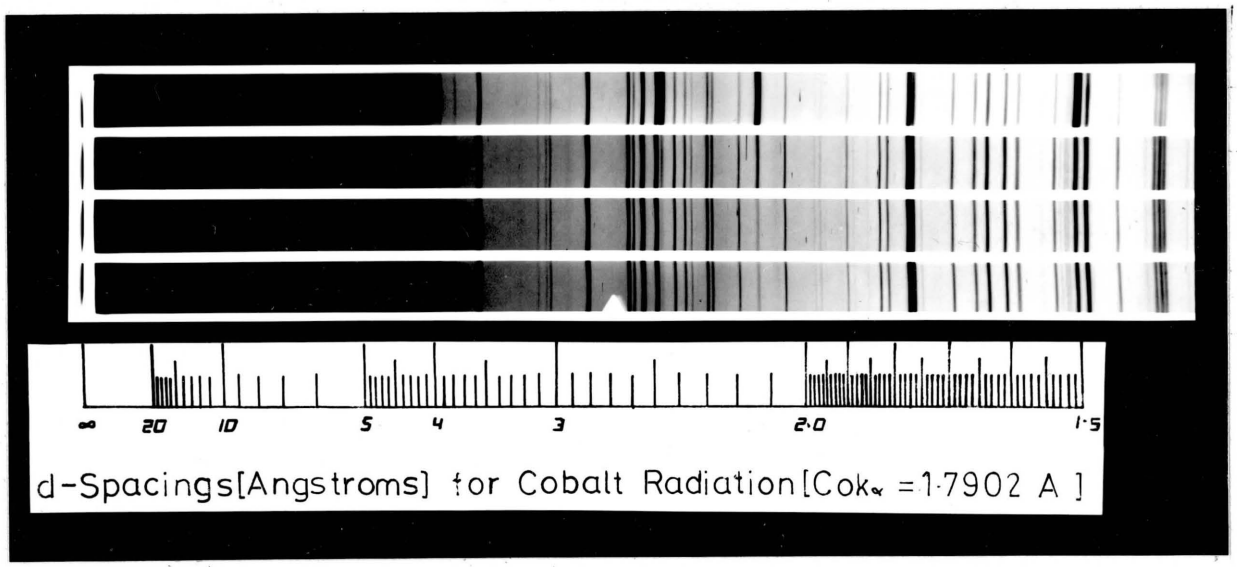


Fig. 38 X-Ray Patterns of the Solid Products Obtained after the Hydrothermal Treatment of Synthetic Ni_2SiO_4 Material

(1) X-ray pattern of Synthetic NiO-Ni_2SiO_4 Material No. 1.

(2) X-ray pattern of synthetic NiO-Ni_2SiO_4 material No. 2

NiO content in synthetic material No 2 Ni content in synthetic material No. 1.

(3) X-ray pattern of synthetic Ni_2SO_4 material

(4)-(19) X-ray patterns of the solid products obtained after the hydrothermal treatment of (3)

Conditions used in the Hydrothermal Treatment

	Temperature	Time	Amount of Sulphur	Amount of (3)
(4)	200°C	2 hours	0.6 gr.	0.5 gr.
(5)	200°C	2 hours	0.8 gr.	0.5 gr.
(6)	200°C	2 hours	1.0 gr.	0.5 gr.
(7)	200°C	2 hours	1.2 gr.	0.5 gr.
(8)	200°C	6 hours	1.0 gr.	0.5 gr.
(9)	200°C	6 hours	1.2 gr.	0.5 gr.
(10)	200°C	6 hours	1.4 gr.	0.5 gr.
(11)	200°C	6 hours	1.6 gr.	0.5 gr.
(12)	240°C	2 hours	1.4 gr.	0.5 gr.
(13)	240°C	2 hours	1.6 gr.	0.5 gr.
(14)	240°C	2 hours	1.8 gr.	0.5 gr.
(15)	240°C	2 hours	2.0 gr.	0.5 gr.
(16)	240°C	6 hours	1.4 gr.	0.5 gr.
(17)	240°C	6 hours	1.6 gr.	0.5 gr.
(18)	240°C	6 hours	1.8 gr.	0.5 gr.
(19)	240°C	6 hours	2.0 gr.	0.5 gr.

- Sulphidisation of Nickel Olivine (Ni_2SiO_4) Results

- Amount of Ni_2SiO_4 - SiO_2 (wt % Ni) .... 0.5 gr.

- Amount of water in the ampoule ..... . 3 cc

TABLE 17			TABLE 18		
Temperature		200°C	Temperature		240°C
Time of reaction		2 hours	Time of reaction		2 hours
Amount of S	Ni % Extracted as NiS_2	$NiSO_4$	Amount of S	Ni % Extracted as NiS_2	$NiSO_4$
0.2 gr.	17.9	0.5	0.2 gr.	56.0	12.2
0.4	19.2	1.4	0.4 gr.	56.0	9.2
0.6 gr.	17.1	2.2	0.g gr.	59.7	12.2
0.8 gr.	17.1	2.5	0.8 gr.	63.4	10.4
1.0 gr.	22.1	3.0	1.0 gr.	63.4	9.4
1.2 gr.	24.8	2.8	1.2 gr.	68.4	12.4
1.4 gr.	22.3	3.2	1.4 gr.	8.1.9	10.9
1.6 gr.	22.7	3.2	1.6 gr.	76.0	17.4
1.8 gr.	21.8	5.3	1.8 gr.	80.5	17.0

TABLE 19

Temperature	200°C
Time of reaction	6 hours

Amount of S	Ni % Extracted as NiS_2	Ni % Extracted as $NiSO_4$
0.2 gr.	50.0	5.9
0.4 gr	46.5	5.9
0.6 gr.	53.7	7.1
0.8 gr.	53.9	7.5
1.0 gr.	55.5	7.5
1.2 gr.	51.5	8.0
1.4 gr.	50.6	8.0
1.6 gr.	55.2	8.0
1.8 gr.	58.2	8.0

TABLE 20

Temperature	240°C
Time of reaction	6 hours

Amount of S	Ni % Extracted as NiS_2	Ni % Extracted as $NiSO_4$
0.2 gr.	47.0	9.6
0.4 gr.	53.7	12.7
0.6 gr.	55.8	14.6
0.8 gr.	60.4	16.9
1.0 gr.	66.3	21.8
1.2 gr.	80.8	17.1
1.4 gr.	77.1	17.1
1.6 gr	-	17.8
1.8 gr.	79.3	17.7

LEACHING OF VAESITE (NiS_2) RESULTS

Leaching of Vaesite NiS_2	Table A-1 Temp: 150°C		Table A-2 Temp: 100°C		Table A-3 Temp:. 125°C		Table A-4 Temp: 175°C		Table A-5 Temp: 200°C	
	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved
NH_3 concentration: 60 gr/l	15	3.0	15	1.01	15	0.6	15	4.42	5	5.8
$(NH_4)_2SO_4$ conc.: 1mole/l	30	7.0	30	0.74	30	1.5	30	12.44	15	18.1
Air pressure: 800 p.s.i.	45	9.4	45	1.04	45	3.0	47	21.71	30	35.8
Particle size -180+125μ	60	13.7	60	1.28	60	4.1	60	30.44	45	47.3
Amount of NiS_2 0.5 gr.	75	16.2	75	1.62	75	5.7	75	39.01	60	55.0
Initial volume 200 cc	90	20.9	90	1.85	90	6.5	90	47.85	75	62.0
Stirring speed 550 r.p.m.	105	23.4	105	2.26	105	8.4	105	51.65	90	67.2
	120	27.3	120	3.05	120	9.5	120	61.00	105	77.9
	135	30.4	135	2.91	135	11.3	135	64.30	120	76.9
	150	33.7	150	3.45	150	12.4	150	66.10	135.	85.1
	165	37.3	165	3.79	165	14.7	165	67.51	150	84.1
	180	42.4	180	4.53	180	15.9	180	68.20	165	88.4
	198	46.4	195	4.56	195	17.2	195	70.91	180	84.9
	210	47.6	210	5.62	212	18.7	210	71.57	195	85.8
	225	48.5	225	5.93	225	20.4	225	73.50	210	90.4
	240	53.0	240	6.63	240	21.5	240	76.67	225	91.6
	255	54.9	255	7.49	255	23.3	255	77.59	240	93.4
	270	55.5	270	7.49	270	24.0	270	83.19	255	93.4
	285	58.3	285	8.06	285	25.5	285	83.93	272	93.4
	300	59.8	300	8.28	300	26.4	300	83.20	285	94.2
	315	59.8	318	9.28	315	28.6	315	79.64	300	93.4
	330	62.2	330	8.49	330	29.7	330	83.13	315	94.4
	345	62.2	345	9.77	345	29.3	345	84.84	330	95.2
	360	64.2	360	10.14	360	31.0	360	79.68	345	97.4
	390	66.3	390	11.11	390	32.4	390	85.68	360	96.9
	420	67.6	420	12.41	420	35.2	420	86.32		
	450	70.5	450	12.64	450	36.6	450	85.09		
	480	73.0			480	38.2	480	86.29		
	510	74.5			510	40.3	510	86.87		

Leaching of Vaesite NiS_2	Table A-6 Air Press: 800p. s. i		Table A-7 Air Press:1200p.s.i		Table A-8 Air Press: 600 p.s.i		Table A-9 Air Press: 400 p.s.i		Table A-10 Air Press: 300 p.s.i	
	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved
NH_3 concentration 60 gr/l	15	3.0	15	2.9	15	2.86	15	1.8	15	1.85
$(NH_4)_2SO_4$ conc. 1 mole/l	30	7.0	30	8.3	30	5.58	30	3.7	30	3.53
Temperature 150°C	45	9.4	45	12.3	45	7.98	45	5.5	45	5.58
Particle size: -180+125μ	60	13.7	60	16.4	60	11.88	60	8.1	60	7.38
Amount of NiS_2 0.5 gr.	75	16.2	75	21.0	75	15.52	75	10.5	75	8.90
Initial volume 200cc	90	20.9	90	25.6	90	17.79	90	12.9	90	11.72
Stirring speed 550 r.p.m.	105	23.4	105	30.8	105	21.12	105	15.5	105	15.13
	120	27.3	120	35.2	120	23.66	120	18.0	120	17.01
	135	30.4	137	37.3	135	26.16	135	21.8	135	18.39
	150	33.7	150	40.8	150	30.70	150	23.8	150	20.82
	165	37.3	167	45.0	167	35.49	165	28.1	165	26.52
	180	42.4	180	49.4	180	37.16	180	30.0	180	31.18
	198	46.4	195	51.7	195	40.76	195	32.8	195	32.86
	210	47.6	210	52.6	210	44.60	210	36.8	210	36.31
	225	48.5	225	59.3	225	47.72	225	38.9	225	40.95
	240	53.0	240	61.8	240	48.94	240	41.2	240	42.67
	255	54.9	255	62.7	255	52.21	255	45.0	255	43.90
	270	55.5	272	65.6	270	54.25	270	44.7	270	45.11
	285	58.3	285	66.2	285	57.66	285	48.0	285	49.46
	300	59.8	300	66.3	300	61.23	300	49.7	300	51.43
	315	59.8	315	67.9	315	60.70	315	52.0	315	51.99
	330	62.2	330	68.1	330	63.33	330	54.4	330	52.59
	345	62.2	345	68.1	345	62.04	345	54.9	345	54.90
	360	64.2	360	71.9	360	62.55	360	56.1	360	54.64
	390	66.3	390	74.7	390	64.26	390	59.5	390	58.12
	420	67.6	420	76.6	427	66.38	420	60.4	430	59.56
	450	70.5	450	77.6	450	68.68	450	63.5	450	62.13
	480	73.0	480	79.4	480	70.69	480	64.8	480	64.61
	510	74.5	510	82.6	510	72.41	510	66.5	510	66.33

Table A-11 Air Press:200p.s.i		Leaching of Vaesite NiS_2	Table A-12 Air Press:400 p. s. i.		Table A-13 Air Press:600p. s. i.		Table A-14 Air Press:800p. s. i.		Table A-15 Air Press:1290p.s.i.	
Leaching time min	Wt % Ni dissolved		Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved
15	1.6	NH_3 concentration 60 gr/l	5	2.06	5	3.15	5	4.20	5	4.2
30	2.6		16	7.45	15	8.32	15	10.40	10	7.71
45	3.7	$(NH_4)_2SO_4$ conc. 0.1 mol/l	30	11.19	30	20.09	30	-	15	11.37
60	5.1		45	17.42	45	26.06	45	29.47	30	23.06
75	6.2		61	21.88	60	36.78	60	38.46	37.5	28.05
90	7.5	Temperature 150°C	75	24.53	75	41.18	75	48.03	45	31.82
105	9.1		90	33.38	92	55.83	90	49.92	52.5	35.51
120	11.5	Particle size -180+125u	105	35.94	105	51.78	105	52.16	60	37.32
135	13.4		120	40.10	120	50.70	120	55.46	75	44.09
150	15.1		135	40.10	135	55.63	135	59.80	90	51.43
165	16.1	Amount of NiS_2 0.5 gr.	150	44.11	150	58.40	150	59.80	110	56.90
180	17.9		165	47.02	165	60.09	165	63.63	120	61.24
195	20.2	Initial volume 200 cc	180	51.22	182	61.75	180	66.03	135	63.53
210	22.2		195	51.88	195	63.70	195	66.03	150	66.40
225	23.5		210	53.15	210	68.15	210	67.66	165	68.90
240	27.5	Stirring speed 850 r.p.m.	225	54.40	225	68.15	225	67.66	180	72.55
255	28.6		240	58.68	240	79.41	240	70.15	195	74.35
270	29.9		255	61.08	255	74.34	255	72.28	210	76.08
285	31.2		270	64.61	270	74.34	270	76.14	225	78.35
300	32.9		285	65.19	285	76.05	285	85.77	240	80.57
315	34.4		300	65.19	300	81.86	300	80.35	255	82.46
330	35.3									
345	40.1									
360	41.5									
390	40.6									
420	42.6									
450	46.8									
490	51.2									

Table A-16 Air Press:300p. s. i.		Leaching of Vaesite NiS_2	Table A-17 St. Speed:200r. p. m.		Table A-18 St. Speed:350r. p. m.		Table A-19 St. Speed:475r. p. m.		Table A-20 St. Speed:500r. p. m.	
Leaching time min.	Wt % Ni dissolved		Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved
5	2.3	NH_3 concentration 60 gr/l	5	0.95	15	1.48	15	2.40	5	1.58
15	4.79		15	1.77	30	3.09	30	4.40	15	3.17
30	9.44	$(NH_4)_2SO_4$ conc. 1 mole/l	30	2.98	45	4.17	45	6.99	30	5.64
45	13.62		45	3.74	60	5.64	60	8.28	45	8.10
60	17.52	Air pressure: 300 p. s. i.	60	4.75	75	7.17	75	11.26	60	11.64
75	23.06		75	6.32	90	8.49	90	12.91	75	13.84
90	25.88		90	7.36	105	9.79	105	15.10	90	15.44
105	29.58	Particle size: -180+125μ	105	8.66	120	10.88	120	18.99	105	18.58
120	32.12		120	9.85	135	14.43	135	21.55	120	22.74
135	-		135	11.02	150	15.81	150	22.26	135	24.71
150	38.39	Amount of NiS_2 0.5 gr.	150	11.97	165	17.82	165	25.41	150	29.78
165	39.39		165	13.45	180	18.48	180	28.49	165	31.50
180	42.63		180	14.80	195	22.30	195	31.02	180	36.94
195	45.50	Initial volume 200 cc	195	16.12	210	24.16	210	34.48	195	38.61
210	46.44		210	16.77	225	25.70	225	35.81	210	42.38
225	47.36		225	17.72	240	28.70	240	37.36	225	42.25
240	49.16	Temperature 150°C	240	18.95	255	29.57	255	39.87	240	45.91
255	50.63		260	20.47	270	30.71	270	41.71	255	49.04
270	52.36		270	21.95	285	33.49	285	46.50		
285	52.93		285	22.96	300	36.20	300	51.18		
300	55.15		300	24.55	315	36.20	315	51.74		
315	56.50				330	38.03	330	54.20		
330	59.13				345	41.63	345	55.78		
345	60.66				360	43.91	360	56.55		
					390	48.00	390	59.79		
					420	50.65	420	63.21		
					450	55.86	450	67.12		
					480	59.93	480	67.22		
							495	65.88		

Table A-21 St. Speed:550r. p. m.		Table A-22 St. Speed:700r. p. m.		Table A-23 St. Speed:725r. p. m.		Table A-24 St. Speed:850r. p. m.		Table A-25 St. Speed:1000r. p. m.	
Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved
15	3.0	5	3.28	15	6.10	5	2.98	5	5.25
30	7.0	15	7.55	30	13.88	15	10.38	15	12.66
45	9.4	30	12.33	52	22.40	30	18.98	30	25.59
60	13.7	45	18.28	60	26.16	45	26.99	45	50.14
75	16.2	60	23.96	75	33.24	60	36.90	60	54.78
90	20.9	75	-	90	39.82	75	41.45	75	61.61
105	23.4	90	33.10	105	45.13	90	45.17	90	67.89
120	27.3	105	40.72	120	47.36	105	49.18	105	73.66
135	30.4	120	44.89	135	51.01	120	53.12	120	76.14
150	33.7	135	48.63	150	54.60	135	66.75	135	79.60
165	37.3	150	53.97	165	57.10	150	59.20	150	83.67
180	42.4	165	55.93	180	60.23	165	62.56	165	84.79
198	46.4	180	56.89	195	67.13	180	65.52	180	89.48
210	47.6	195	60.31	210	64.76	195	68.42	195	89.48
225	48.5	210	63.06	225	68.06	210	73.77	210	-
240	53.0	225	64.26	240	69.69	225	73.77	225	92.24
255	54.9	240	65.71	255	72.58	240	74.68	240	93.14
270	55.5	255	67.41	270	73.21	255	-	255	99.50
285	58.3	270	69.62	285	76.62	270	78.82	270	95.27
300	59.8	285	70.70	300	76.62	285	79.98	285	98.04
315	59.8	300	70.18	315	81.65	300	80.54	300	-
330	62.2			330	82.52				
345	62.2			345	83.94				
360	64.2			360	85.32				
390	66.3			390	87.50				
420	67.6			420	89.36				
450	70.5			450	90.92				
480	73.0			480	92.69				
510	74.5								

Leaching of Vaesite NiS_2	Table A-26 Part.size:-180+125μ		Table A-27 Part.size:-90+63μ		Table A-28 Part. size:-53+45μ		Table A-29 Part. size:-300+212μ		Table A-30 Part. size:-425+300μ	
	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved
NH_3 concentration: 60 gr/l	15	3.0	18	3.78	15	4.0	15	4.93	15	4.20
$(NH_4)_2SO_4$ conc: 1 mole/l	30	7.0	30	6.92	30	9.9	30	10.83	30	9.88
Air pressure: 800 p.s.i.	45	9.4	45	10.88	45	16.4	45	17.47	45	15.28
Amount of NiS_2: 0.5 gr.	60	13.7	60	15.84	60	22.9	60	24.80	60	20.10
Temperature: 150°C	75	16.2	75	19.49	75	28.9	75	32.58	75	26.65
Initial volume: 200cc	90	20.9	90	23.25	90	36.2	90	40.21	90	33.07
Stirring speed: 550 r.p.m.	105	23.4	105	28.92	105	42.9	105	47.34	105	38.75
	120	27.3	120	32.86	120	47.4	135	51.02	120	44.85
	135	30.4	135	37.01	135	53.5	135	58.62	135	49.55
	150	33.7	150	41.40	150	57.0	150	65.74	150	54.68
	165	37.3	165	45.38	165	61.2	165	67.14	165	60.54
	180	42.4	180	49.56	180	65.2	180	70.57	180	64.68
	198	46.4	195	53.35	195	67.9	195	72.60	195	68.68
	210	47.6	210	56.18	210	69.5	210	73.60	210	71.66
	225	48.5	225	60.32	225	72.6	225	75.55	225	74.56
	240	53.0	240	61.39	240	74.1	240	77.79	240	79.02
	255	54.9	255	63.74	255	75.9	255	78.73	255	79.56
	270	55.5	270	65.79	270	79.9	270	78.11	270	80.89
	285	58.3	285	67.02	285	81.1	285	81.76	285	83.68
	300	59.8	300	70.40	300	81.3	300	80.57	300	84.68
	315	59.8	315	71.10	315	85.1	315	83.61	315	85.39
	330	62.2	330	71.11	330	87.0	330	82.92	330	87.01
	345	62.2	345	73.78	345	88.0	345	84.06	345	87.89
	360	64.2	360	75.52	360	88.5	360	82.94	360	87.00
	390	66.3	390	75.94	390	90.2	390	86.21	390	87.41
	420	67.6	420	78.81	420	89.9	420	86.21	420	89.02
	450	70.5	450	79.40	450	91.1	450	88.30	450	89.41
	480	73.0	480	81.51			480	89.03	480	90.49
	510	74.5	510	82.80			510	87.32	510	91.86

Table A-31. Part. size -425+300μ		Leaching of Vaesite NiS_2	Table A-32 Temp. 150°C		Leaching of Vaesite NiS_2	Table A-33 Amount NiS_2:1.0gr		Table A-34 Amount NiS_2:0.5gr	
Leaching time min.	Wt % Ni dissolved		Leaching time min.	Wt % Ni dissolved		Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved
15	4.2	NH_3 concentration 60 gr/l	15	2.52	NH_3 concentration 60 gr/l	5	1.58	15	3.58
30	9.6		30	4.37		15	3.24	30	4.50
45	16.38	$(NH_4)_2SO_4$ conc. 1 mole/l	45	10.40	$(NH_4)SO_4$ conc. 1 mole/l	30	6.42	45	2.23
60	24.29		60	13.16		45	9.98	60	9.00
75	30.82		75	17.22		60	11.28	75	11.72
90	34.92	Air pressure 800 p.s.i.	90	20.24	Temperature 150°C	75	15.41	90	15.13
105	52.37		105	24.90		92	16.96	105	17.71
120	59.85	Particle size -180+125 μ	120	28.52	Air pressure 800 p.s.i.	105	20.97	120	20.00
135	66.72		135	34.74		120	24.53	135	23.78
150	72.13		150	37.15		137	24.90	150	26.55
165	76.13	Amount of NiS_2 0.5 gr.	165	39.18	Particle size -180+125μ	150	27.07	165	29.93
180	77.93		180	42.49		165	29.21	180	33.55
195	81.13	Initial volume 200 cc	195	46.69	Initial volume 200 cc	180	33.07	197	34.84
210	83.40		210	48.58		195	35.49	210	38.32
225	84.22		225	50.43		210	38.21	225	39.55
240	85.30	Stirring speed 550 r.p.m.	240	51.64	Stirring speed 490 rpm	225	40.37	240	42.55
255	88.40		255	54.27		240	45.69	255	43.72
270	91.15		272	55.13		258	46.09	270	46.01
285	88.49		285	56.52		270	48.87	285	48.23
300	91.53		300	58.96		285	50.44	300	51.74
315	91.08		315	60.02		300	50.83	315	52.26
330	91.08		330	62.07		315	51.95	330	53.53
345	91.08		345	62.82		330	53.80	345	55.49
360	92.12		360	63.06		345	54.53	360	56.92
Table (A-31) Part.size:-425+300μ			390	64.91		360	56.67	390	59.23
15	4.00		420	65.81		390	59.67	420	61.04
30	8.30		450	67.56		420	62.51	450	62.78
45	14.6		480	68.40		450	63.81	480	66.74
60	17.7		510	69.01				510	69.34
75	22.7		540	69.21					
90	26.9								
105	31.5								
120	37.4								

Leaching of vaesite NiS_2	Table A-35 Part.size: -38 μ		Leaching of Vaesite NiS_2	Table A-36 NH_3 conc: 60 gr/l		Table A-37 NH_3 conc: 20 gr/l		Table A-38 NH_3 conc: 5 gr./l	
	Leaching time min.	Wt % Ni dissolved		Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved
NH_3 concentration 60 gr/l	15	7.5	$(NH_4)_2SO_4$ conc. 1 mol/l	15	3.0	15	3.36	15	4.67
	30	17.6		30	7.0	30	6.89	30	7.61
	45	28.7		45	9.4	45	10.67	45	10.72
$(NH)_4SO_4$ conc. 1 mol/l	60	36.3	Air pressure 800 p.s.i.	60	13.7	60	14.13	60	14.95
	75	43.5		75	16.2	75	20.24	75	21.07
	90	51.9		90	20.9	90	23.43	90	25.22
Air Pressure 800 p.s.i.	105	55.5	Particle size -180+125μ	105	23.4	105	27.13	105	28.17
	120	62.3		120	27.3	120	30.58	120	30.69
Temperature 150°C	135	64.4	Amount of NiS_2 0.5 gr.	135	30.4	135	36.87	138	34.15
	150	69.1		150	33.7	150	40.92	150	34.91
	165	73.8		165	37.3	165	41.85	165	38.64
Amount of NiS_2 0.5 gr.	180	75.8	Initial volume 200 cc	180	42.4	180	44.01	180	43.42
	195	80.2		198	46.4	195	47.57	195	48.14
Initial volume 200 cc	210	83.2	Stirring speed 550 r.p.m.	210	47.6	210	48.97	210	48.85
	225	83.2		225	48.5	225	52.08	225	50.62
	240	83.2		240	53.0	240	52.42	240	52.71
Stirring speed 550 r.p.m.	255	82.7		255	54.9	255	55.43	255	53.74
	270	84.4		270	55.5	270	55.43	270	53.74
				285	58.3	285	60.29	287	53.74
				300	59.8	300	60.93	300	54.67
				315	59.8	315	64.07	315	57.41
				330	62.2	330	65.30	330	55.64
				345	62.2	345	67.41	345	57.68
				360	64.2	360	68.01	360	58.82
				390	66.3	390	68.06	390	59.90
				420	67.6	420	75.16	420	60.22
				450	70.5	450	75.72	450	62.42
				480	73.0	480	77.10		
				510	74.5	510	79.81		

Leaching of Vaesite NiS_2	Table A-39 NH_3 conc. 60 gr/l		Table A-40 NH_3 conc. 40 gr/l		Table A-41 NH_3 conc. 10 gr/l		Table A-42 NH_3 conc. 5 gr/l	
	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved
$(NH_4)_2SO_4$ conc. 0.1 mol/l	5	4.20	7.30	5.88	7.5	9.67	7.5	8.28
	15	10.40	15	11.83	15	17.03	15	15.35
	30	-	22.5	16.98	22.5	23.78	22.5	20.77
Air pressure 800 p.s.i.	45	29.47	30	18.56	30	29.13	30	24.79
	60	38.46	37.5	25.05	37.5	33.82	37.5	28.34
	75	48.03	45	30.46	45	38.47	45	33.95
Particle size: -180 + 125 μ	90	49.92	52.5	33.10	52.5	43.59	52.5	38.42
	105	52.16	60	37.21	60	46.95	60	39.60
Amount of NiS_2 0.5 gr.	120	55.46	67.5	47.55	67.5	48.96	67.5	43.84
	135	59.80	75	45.08	75	52.93	75	47.47
	150	59.80	90	49.52	90	55.75	90	51.92
Initial volume 200 cc	165	63.63	105	54.56	105	60.61	105	55.42
	180	66.03	120	58.67	120	64.69	120	56.28
Stirring speed 850 r.p.m.	195	66.03	135	67.38	135	65.36	138	61.36
	210	67.66	150	66.35	150	68.63	150	66.03
	225	67.66	165	65.70	165	71.84	165	64.73
Temperature 150°C	240	70.15	180	71.73	180	71.84	180	67.95
	255	72.28	195	73.61	195	73.69	195	67.95
	270	76.14	210	76.67	210	-	210	71.09
	285	85.77	225	78.46	225	75.81	225	70.17
	300	80.35	240	83.03	240	76.40	240	68.06
			255	82.48	255	70.36	255	66.31
			270	85.21	270	58.52	270	64.30
			285	85.21	285	49.73	285	61.79
			300	86.76	300	47.59	300	60.44

Leaching of Vaesite NiS_2	Table A-43 $((NH_4)_2SO_4)$:1mol/l		Table A-44 $((NH_4)_2SO_4)$:0.5mol/l		Table A-45 $((NH_4)_2SO_4)$:0.2mol/l		Table A-46 $((NH_4)_2SO_4)$:0.1mol/l		Table A-47 $((NH_4)_2SO_4)$:0.05mol/l	
	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved
NH_3 concentration 60 gr/l	15	3.0	15	3.45	15	4.92	5	3.00	5	1.98
	30	7.0	30	7.73	30	11.54	15	7.32	15	4.34
	45	9.4	45	12.21	45	16.06	30	15.84	30	9.88
Air pressure 800 p.s.i.	60	13.7	60	17.44	60	21.30	45	21.4	45	16.48
	75	16.2	75	20.41	75	24.68	60	28.18	60	20.28
Temperature: 150°C	90	20.9	90	25.86	90	32.06	75	35.44	75	24.22
	105	23.4	105	27.60	105	35.74	90	39.54	90	33.96
	120	27.3	120	31.94	120	41.42	105	-	105	35.10
Particle size -180+125μ	135	30.4	135	33.79	135	47.12	120	46.86	120	40.20
	150	33.7	150	35.62	150	49.68	135	49.72	135	44.38
Amount of NiS_2 0.5 gr.	165	37.3	165	40.28	165	50.76	150	53.92	152	47.78
	180	47.4	180	43.11	180	54.68	165	53.24	165	51.10
	198	46.4	195	46.61	195	60.64	180	58.64	180	52.92
Initial volume 200 cc	210	47.6	210	46.61	210	62.72	195	59.96	195	54.72
	225	48.5	225	48.64	225	65.08	210	62.28	210	56.86
Stirring Speed 550 r.p.m.	240	53.0	240	49.64	240	65.72	225	65.02	225	58.62
	255	54.9	255	51.28	255	68.32	240	71.50	240	61.06
	270	55.5	270	5292	270	69.60	255	68.44	255	61.06
	285	58.3	285	54.85	285	68.36	270	71.46	270	64.12
	300	59.8	300	58.33	300	68.36	285	75.56	285	66.12
	315	59.8	315	58.63	315	68.36	300	71.58	300	67.12
	330	62.2	330	63.85	330	68.94	315	77.16	315	64.81
	345	62.2	345	63.85	345	68.36	330	79.16	330	67.10
	360	64.2	360	65.32	360	68.36	345	76.28	345	67.16
	390	66.3	390	65.33	390	71.62	360	76.32	360	71.46
	420	67.6	420	-	420	73.2				
	450	70.5	450	69.82	450	81.76				
	480	73.0	480	72.77	480	79.52				
	510	74.5			510	81.66				

Table A-48 $(NH_4)_2SO_4$ 0.01 mol/l		Table A-49 $(NH_4)_2SO_4$ 0.0 mol/l		Leaching of Vaesite NiS_2	Table A-50 Temperature 150°C		
Leaching time min.	Wt % Ni dissolved	Leaching time min.	Wt % Ni dissolved		Leaching time min.	Wt % Ni dissolved	$\frac{(SO)^{2-}}{(S)}$ %
15	3.78	15	4.20	NH_3 concentration 60 gr/l	15	1.98	3.72
30	6.99	30	7.26		30	2.99	4.92
45	10.86	45	10.91	$(NH_4)_2SO_4$ conc. 0 gr/l	45	4.24	5.87
60	16.41	60	15.89		60	5.92	7.30
78	21.02	75	18.72		75	7.47	13.91
90	22.90	93	22.48	Air pressure 800 p.s.i.	90	9.63	18.12
105	25.84	105	25.51		105	11.38	16.10
124	30.68	120	27.92	Particle size -180+125 μ	120	13.90	22.50
135	31.63	135	30.02		135	16.44	24.53
150	34.28	150	32.64		150	18.06	25.61
165	36.70	165	34.86	Amount of NiS_2 0.5 gr.	165	21.23	25.04
185	38.55	180	35.60		180	23.07	26.31
195	40.23	195	36.48	Initial volume 200 cc	195	24.26	-
210	41.45	210	39.54		212	26.28	29.36
225	43.23	225	40.59		225	28.25	29.36
240	46.05	240	42.49	Stirring Speed	240	29.90	33.29
255	46.74	255	43.53		255	33.10	38.44
270	48.80	270	45.04		270	35.18	42.14
285	51.19	285	45.04		285	36.19	48.11
300	51.19	300	46.51		300	37.18	39.50
315	54.52	315	48.60		315	39.10	40.17
330	54.52	330	49.71		330	40.50	41.83
345	55.86	345	51.09		345	42.31	46.94
360	57.12	360	51.27		360	43.31	45.41
390	59.02	390	51.27		390	46.99	61.13
420	60.28	420	52.75		420	50.64	68.25
450	61.52	450	52.75		450	53.71	58.31
480	62.13	480	52.75		480	56.30	70.13

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