

The non-oxidative dissolution of nickel sulphides in aqueous acidic solutions

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SYNOPSIS

An account is given of a study on the non-oxidative dissolution in aqueous acidic solutions of nickel sulphides of different stoichiometric composition, in which a rotating ring-disc electrode was used. The rate of dissolution was found to depend on the potential of the sulphide and the nickel-to-sulphur stoichiometric ratio. A maximum rate for the dissolution of nickel from nickel sulphides containing an excess of nickel was recorded at potentials around $-0,2$ to $-0,3V$. The rate decreased markedly at more anodic potentials. For nickel-deficient nickel sulphides, the non-oxidative dissolution rate increased with a cathodic shift in potential. Under open-circuit conditions, a nickel sulphide of a composition approximating Ni_7S_6 reacted most rapidly. The dissolution rate was controlled by either a chemical or an electrochemical reaction at the electrode surface, had an activation energy of between 50 and 65 $kJ.mol^{-1}$, and was independent of stirring speed.

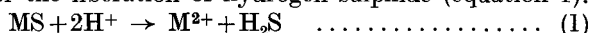
SAMEVATTING

'n Studie van die tempo van die nie-oksidatiewe oplossing van nikkelsulfiede met verskillende stoïgiometrië in waterige suuroplossings waarin 'n draairingskyfelektrode gebruik is, word beskryf. Daar is gevind dat die oplos-tempo van die potensiaal van die sulfied en van die stoïgiometriese nikkel-swawelverhouding afhang. 'n Maksimum tempo vir die oplossing van nikkel uit nikkelsulfiede wat 'n oormaat nikkel bevat, is by potensiale in die omgewing van $-0,2$ tot $-0,3V$ geregistreer. Die tempo het merkbaar afgeneem by meer anodiese potensiale. Vir nikkelsulfiede met 'n nikkeltekort het die nie-oksidatiewe oplos-tempo toegeneem met 'n katodiese verskuiving in die potensiaal.

In oopkringtoestande het 'n nikkelsulfied met 'n samestelling van ongeveer Ni_7S_6 die vinnigste gereageer. Die oplos-tempo is deur 'n chemiese of elektrochemiese reaksie op die oppervlak van die elektrode beheer en dit het 'n aktiveerings-energie van tussen 50 en 65 $kJ.mol^{-1}$ gehad en was onafhanklik van die roer tempo.

INTRODUCTION

The usual hydrometallurgical route for the extraction of metals from their sulphide ores requires the oxidation of the sulphide to either elemental sulphur or sulphate. The dissolved metal can then be separated from the residue and treated further. An alternative method for the dissolution of the more-soluble metal sulphides (e.g., NiS, FeS, and ZnS) is non-oxidative treatment with acid for the liberation of hydrogen sulphide (equation 1):



This method for the dissolution of metal sulphides has received little attention in the literature.

The Falconbridge matte-leaching process¹ is an example of non-oxidative leaching in commercial operation. A matte containing nickel and copper sulphides is subjected to a countercurrent leach at 70°C in 7,5M hydrochloric acid, and the nickel is dissolved selectively (98 per cent in 12 hours), leaving a copper sulphide residue that contains the platinum-group metals.

The non-oxidative dissolution of nickel-bearing concentrates in hydrochloric acid has been investigated by Van Weert *et al.*² and by Dyson and Scott³. Van Weert *et al.*² found that a nickeliferous pyrrhotite dissolved readily in a slight stoichiometric excess of hydrochloric acid at 60°C; 90 per cent of the iron was extracted in 3 hours, but the amount of nickel extracted varied from 10 to 70 per cent. An induction period prior to the evolution of hydrogen sulphide was observed, the period being longer in the experiments in which low concentrations of acids were used. Dyson and Scott³, in their study of the dissolution of nickel flotation concentrates in hydrochloric acid, found that the concentrates had to be activated before they were leached if a reasonable level of nickel extraction was to be obtained. The poor

extractions recorded when unactivated concentrates were leached were attributed to the formation of an inhibiting layer of sulphur.

A superficial investigation of the dissolution of heazlewoodite (Ni_3S_2) in hydrochloric acid has been reported by Sinev *et al.*⁴. It was suggested that beta nickel sulphide is formed on the partially reacted heazlewoodite, and that it retards the dissolution. This suggestion was substantiated by X-ray-diffraction and electron-microprobe analysis of the residual particles.

A fundamental investigation of the non-oxidative dissolution of iron sulphides has been reported⁵. The reaction mechanism proposed for the dissolution of iron involves the dissolution of stoichiometric iron sulphide. Iron-deficient iron sulphides ($Fe_{1-x}S$) had to be reduced to stoichiometric iron sulphide before the non-oxidative dissolution of iron from iron sulphides occurred at a measurable rate. The rate of non oxidative dissolution of iron from iron sulphides showed a maximum at around $-0,3V$ (SCE), and decreased with either an anodic or a cathodic shift in potential. This dependence of the rate on the potential was explained in terms of the rate-determining transfer of ions for potentials that are cathodic to the maxima while the rate is controlled by electron transfer at potentials that are anodic to the maxima. Since no comprehensive fundamental study of the dissolution of nickel sulphide has been reported, it was decided at the National Institute for Metallurgy (NIM) that such an investigation should be conducted into the non-oxidative dissolution of synthetic nickel sulphides. This would reveal whether their behaviour is similar to that of the iron sulphide system, and would explain the mechanism by which they react.

Apparatus

The electrochemical experiments were carried out in a thermostatted cell holding a rotating-disc electrode, a platinum counter electrode, a salt bridge containing a

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saturated calomel electrode, a gas bubbler, and a thermometer. The connection between the shaft of the rotating electrode and the cell was sealed with mercury. The working electrodes were connected to potentiostats: the disc to a P.A.R. model 371 potentiostat, and the ring to a potentiostat constructed at NIM.

The output from the potentiostat was recorded on an HP 7046 A x-y recorder. A triangular-waveform generator, constructed at NIM, was connected to the P.A.R. potentiostat.

The electrodes consisted of a silver ring and nickel sulphide discs. Araldite CW216 was used as the insulating material between the two electrodes, which were polished with grit 1000 silicon carbide paper prior to each run. Then, 50 ml of acid was pipetted into the reaction vessel, and was allowed to equilibrate to the required temperature while a slow stream of argon was passed through the solution to remove the oxygen. The reaction vessel was placed on the rotating-disc assembly, and the stirring was begun, the speed of rotation being controlled to within about 5 r/min. Samples of the solution were taken at appropriate times. All the potentials quoted in this paper are relative to the saturated calomel electrode.

Materials

The nickel sulphides were produced from Specpure nickel powder and Specpure sulphur powder that had been heated in an evacuated silica tube. Each sample was melted to yield a compact nickel sulphide block suitable for the construction of electrodes, and was then annealed at a lower temperature. Chemical analyses and mineralogical descriptions of the materials are given in Table I. A diamond drill was used to produce a cylindrical sample suitable for the construction of electrodes. The silver used for the silver ring of the electrode was of more than 99.9 per cent purity. A sample of natural pyrite was used for the construction of the pyrite electrode.

TABLE I
A DESCRIPTION OF THE DISC MATERIALS USED IN THIS STUDY

| Sample No. | Stoichiometry | Mineralogical description |
|------------|----------------------|--|
| 1 | Ni | Nickel metal |
| 2 | Ni _{1.54} S | Ni ₃ S ₂ (heazlewoodite) + Ni metal |
| 3 | Ni _{1.45} S | Heazlewoodite + α -Ni ₇ S ₆ |
| 4 | Ni _{1.20} S | α -Ni ₇ S ₆ + heazlewoodite |
| 5 | Ni _{0.95} S | α -Ni _{1-x} S |
| 6 | Ni _{0.45} S | NiS ₂ (vaesite) + α -Ni _{1-x} S |

Acids of various concentrations were prepared from concentrated A.R.-grade acids and distilled water. The concentrations of the acids were standardized against sodium hydroxide.

Analyses

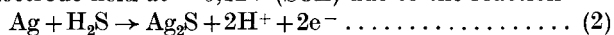
Nickel

Aliquot portions of the solution were taken at intervals during the experiments, and were analysed by atomic-absorption spectrophotometry. Allowance was made for the decreased volume of solution when samples were taken for analysis.

Hydrogen sulphide

The rate of hydrogen sulphide production was moni-

tored by measurements of the current at the silver-ring electrode held at $-0.12V$ (SCE) due to the reaction

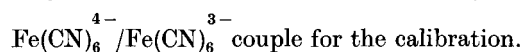


At this potential, the rate of silver oxidation due to the reaction



is negligible at 60°C and chloride ion concentrations of less than 3M.

The collecting efficiency of the rotating-ring electrode was calculated, from data given by Albery and Hitchman⁶, to be 0.41 ± 0.01 . This was confirmed experimentally for several of the electrodes by use of the



At lower rotation speeds, the rate of hydrogen sulphide production for the more-reactive sulphides is faster than its rate of dissolution in the solvent. Thus, a bubble of hydrogen sulphide forms on the nickel sulphide, and alters both the surface area of the disc and the collecting efficiency of the ring. This problem was not apparent at 1500 r/min, except when the hydrogen sulphide formation rates exceeded $10^{-8} \text{ mol. cm}^{-2} \cdot \text{s}^{-1}$.

General Results

The kinetic reactions in the dissolution of the nickel sulphides that were tested were linear after an initial period of about 3 minutes, during which the rate was faster (Fig. 1). The production rate of hydrogen sulphide as measured by the ring current was usually fast at first, and it decayed more slowly than the dissolution rate of nickel to a steady-state value (Fig. 1).

Thus the rates for the dissolution of nickel and hydrogen sulphide are not rigidly proportional during the reaction. Rate constants for the nickel dissolution were calculated from the linear section of the kinetic plot (on the assumption that the surface is smooth), and are quoted in units of $\text{mol. cm}^{-2} \cdot \text{s}^{-1}$. They are considered reproducible to within about 10 per cent. The rates for the production of hydrogen sulphide, calculated from the average ring current over the reaction period, are considered reproducible to about 30 per cent.

Experiments were conducted on the effect of a number of variables on the rate of production of nickel and hydrogen sulphide from the nickel sulphides. This was done first at fixed potentials, and then at the open-circuit potential.

Experiments at Fixed Potentials

Dependence on Potential

The first variable to be investigated was the dependence of the dissolution rate on the potential at which the nickel sulphide disc was held. The rates of nickel dissolution are plotted as a function of potential in Fig. 2 for samples 1 to 4, and in Fig. 3 for samples 5 and 6. The rate constants (k_{Ni}) shown in this diagram represent the sum of the oxidative and non-oxidative dissolution rates for nickel.

If the oxidation of nickel sulphide is a two-electron process for each dissolved nickel ion, the oxidation current can be converted to an oxidative dissolution rate (k_{ox}) by the application of Faraday's law. Thus, the component of the total nickel-dissolution rate that is

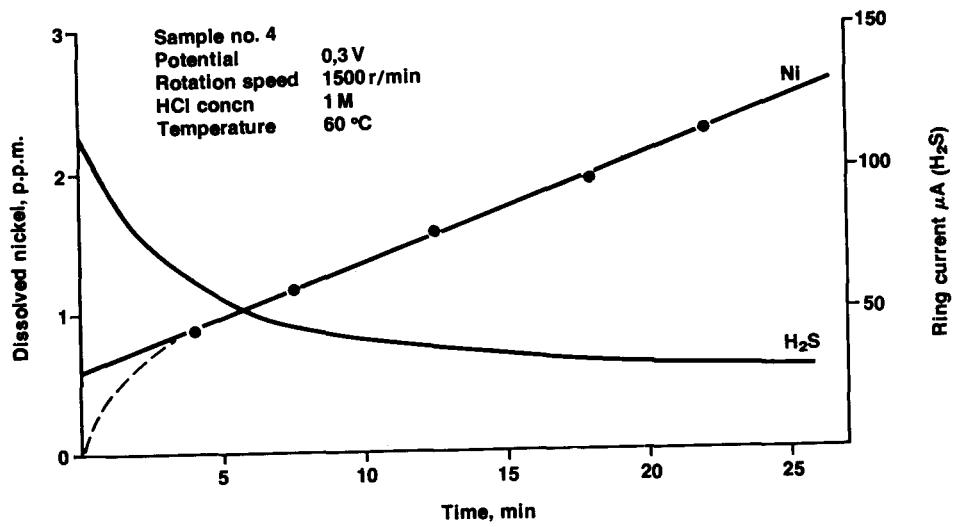


Fig. 1—Dissolution rates of nickel and hydrogen sulphide

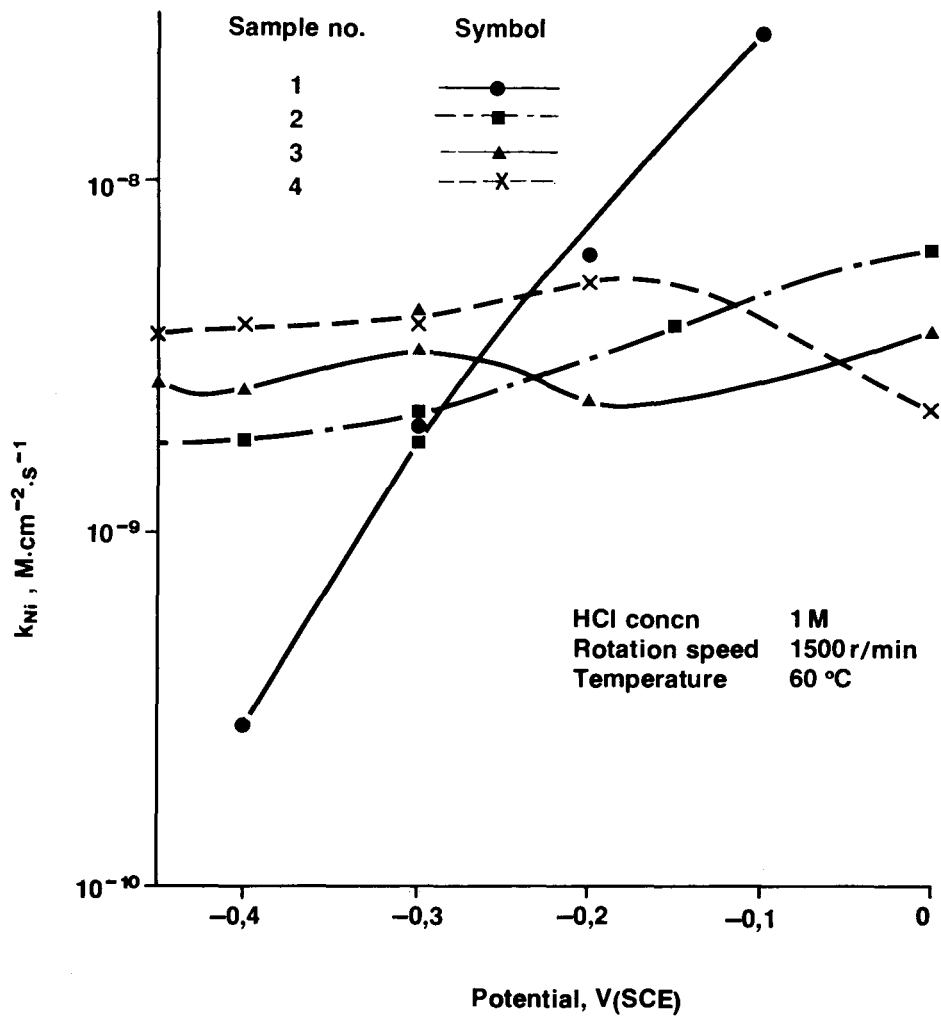


Fig. 2—Rate of nickel dissolution versus potential

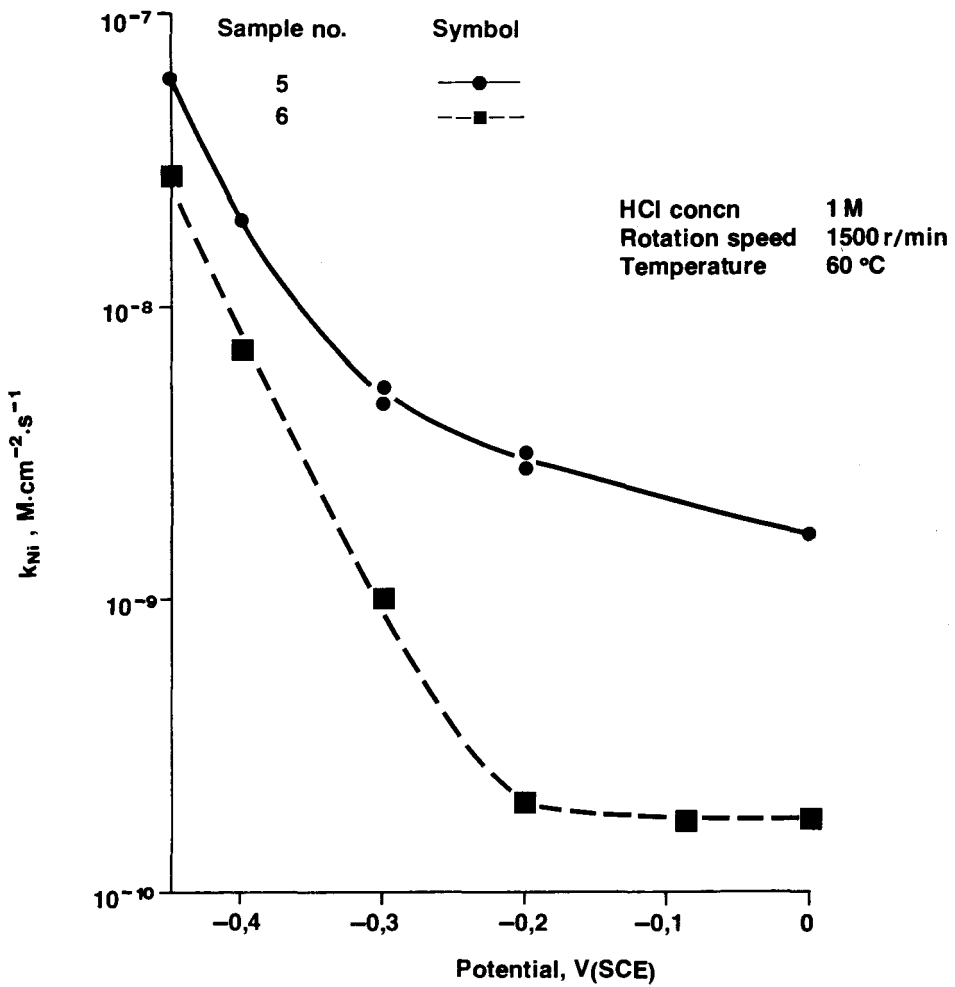


Fig. 3—Rate of nickel dissolution versus potential

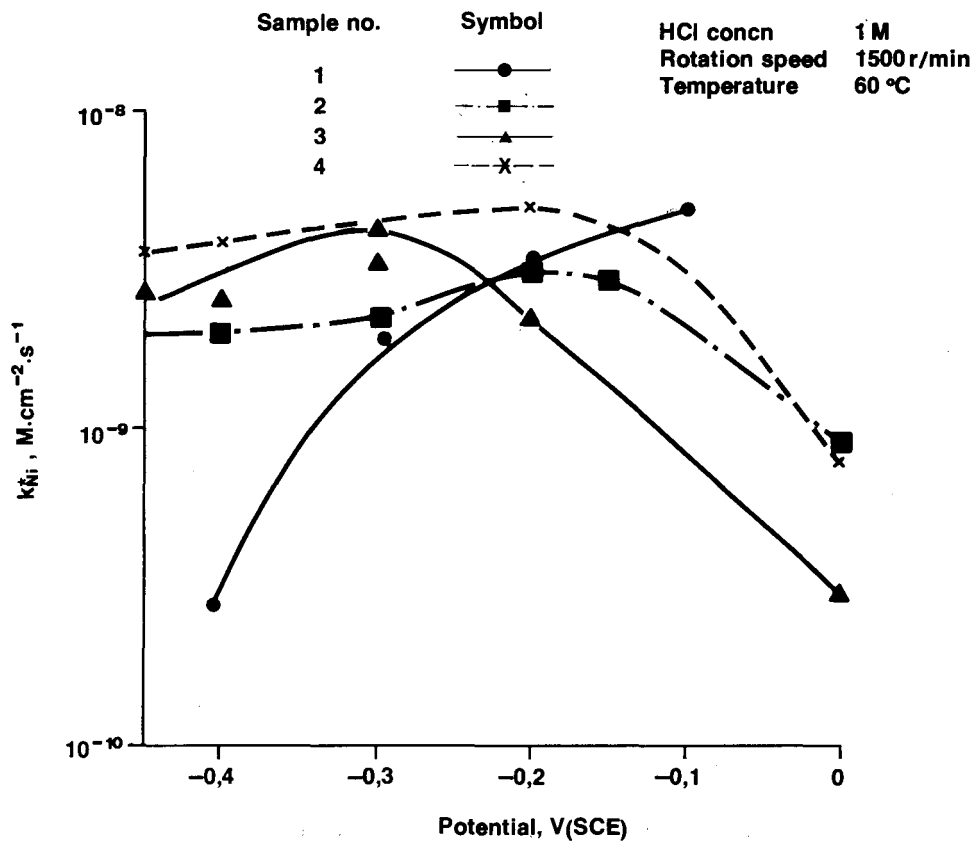


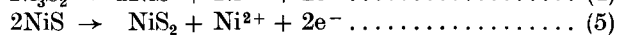
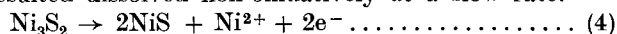
Fig. 4—Rate of non-oxidative nickel dissolution

due to non-oxidative nickel dissolution (k_{Ni}^*) (i.e., reactions of the type $NiS + 2H^+ \rightarrow Ni^{2+} + H_2S$ and $Ni + 2H^+ \rightarrow Ni^{2+} + H_2$) can be calculated. The dependence of k_{Ni}^* on the potential is plotted in Figs. 4 and 5.

The rate of the non-oxidative dissolution of samples 2 to 4 follows a dependence similar to that observed by Nicol and Scott⁵ for iron sulphides – a maximum rate at around $-0,3V$, decreasing slightly with a shift in either anodic or cathodic potential. However, the two nickel-deficient nickel sulphides (samples 5 and 6) exhibit markedly different behaviour, in that the rate increases with a more-cathodic shift in potential.

At more-anodic potentials (greater than $-0,1V$), all the samples except sample 6 were oxidized at a measurable rate. This was attributed to reactions like those

shown in equations 4 and 5. Such reactions are thermodynamically feasible at a potential of $-0,1V$ (Table II). The surface of the nickel-deficient nickel sulphide that resulted dissolved non-oxidatively at a slow rate.



At cathodic potentials of less than $-0,4V$, reduction of the nickel-deficient nickel sulphide occurs. The current recorded at this potential is due principally to the evolution of hydrogen sulphide, but also to the evolution of hydrogen and the reduction of residual oxygen. A cyclic voltammogram (Fig. 6) of sample 6 shows a reduction at around $-0,4V$ with a ring current indicating the formation of hydrogen sulphide. A similar curve for current versus potential was obtained for sample 5, but samples 2 to 4 did not exhibit any reduction that led

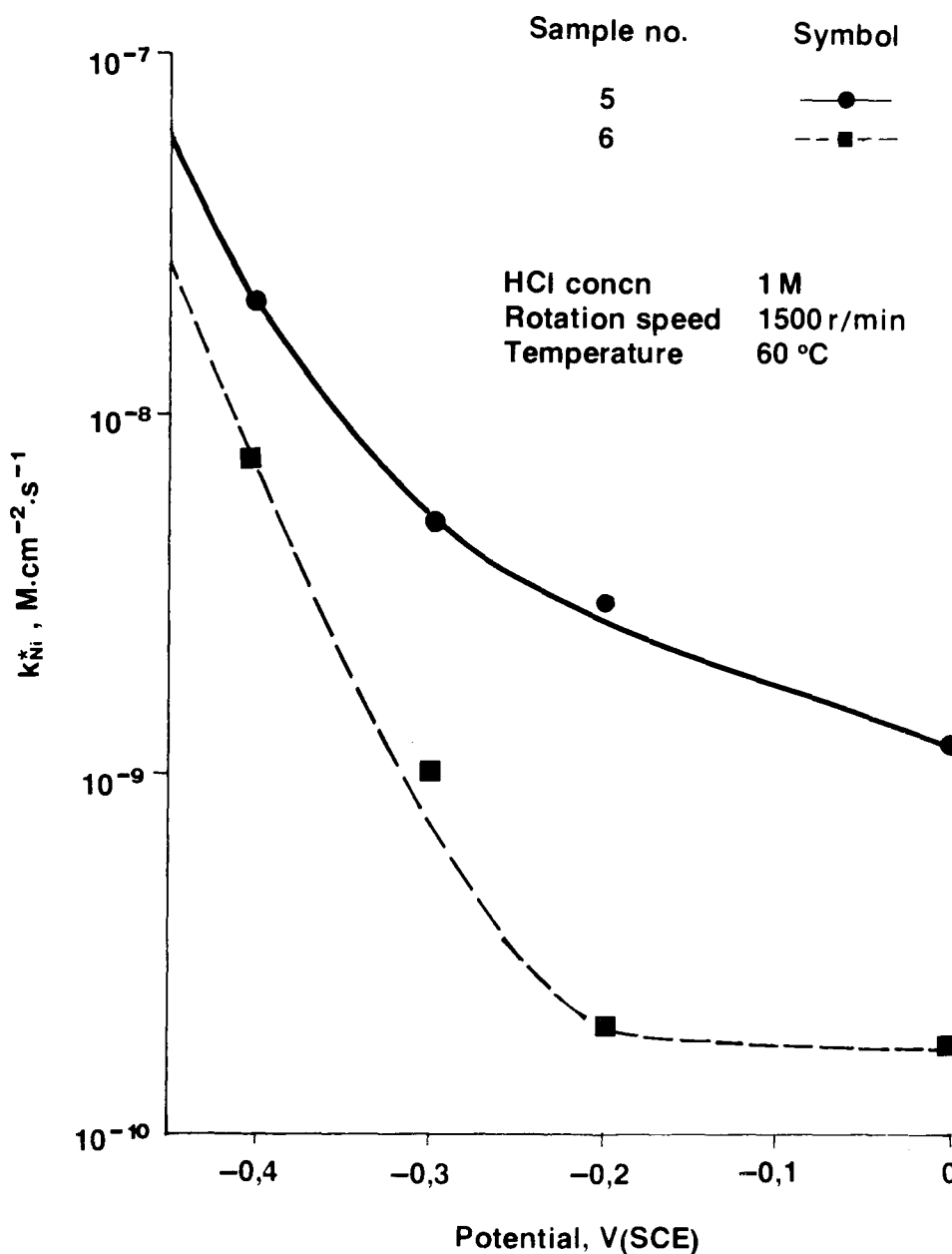


Fig. 5—Rate of non-oxidative nickel dissolution

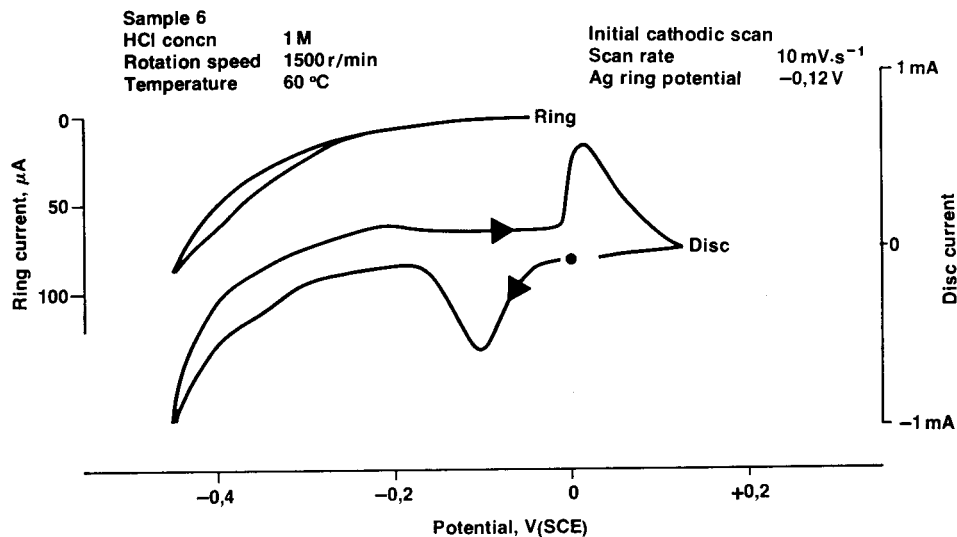


Fig. 6—Cyclic voltammogram of sample 6 indicating the formation of hydrogen sulphide at cathodic potentials

to the formation of hydrogen sulphide within this range of potential. This indicates that reduction occurs only for nickel-deficient sulphides. Equations (7) and (8) describe the reactions that are possible:

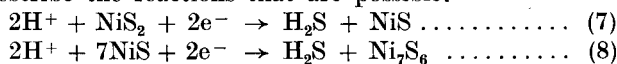


TABLE II

THERMODYNAMIC POTENTIALS FOR NICKEL SULPHIDE REACTIONS (AS CALCULATED FROM VALUES GIVEN BY MILLS⁷)

| Reaction | $\Delta G^\circ, \text{kJ}$ | $E^\circ, \text{V(SCE)}$ |
|--|-----------------------------|--------------------------|
| $\text{NiS}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NiS} + \text{H}_2\text{S(g)}$ | +11 | -0,3 |
| $3\text{NiS} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Ni}_3\text{S}_2 + \text{H}_2\text{S(g)}$ | +91 | -0,7 |
| $3\text{Ni}_7\text{S}_6 + 8\text{H}^+ + 8\text{e}^- \rightarrow 7\text{Ni}_3\text{S}_2 + 4\text{H}_2\text{S(g)}$ | +480 | -0,85 |
| $7\text{NiS} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Ni}_7\text{S}_6 + \text{H}_2\text{S(g)}$ | +50 | -0,5 |
| $\text{Ni}_3\text{S}_2 - 2\text{e}^- \rightarrow 2\text{NiS} + \text{Ni}^{2+}$ | +39 | -0,45 |
| $2\text{NiS} - 2\text{e}^- \rightarrow \text{NiS}_2 + \text{Ni}^{2+}$ | -18 | -0,15 |

The reduction of NiS to Ni₃S₂ is not possible thermodynamically (Table II) at these potentials. Thus, at cathodic potentials, non-oxidative dissolution occurs in samples 2 to 4 from essentially unaltered sulphide surfaces, and this follows the behaviour observed for iron sulphides (i.e., a maximum non-oxidative dissolution rate of around -0,3V). For samples 5 and 6, the electrode surface appears to be reduced to a stoichiometry that favours rapid non-oxidative dissolution. The rate of nickel dissolution appears to be dependent on the rate of reduction of the sulphide, becoming faster as the potential shifts cathodically. The reason for the greater reactivity of the freshly reduced nickel-deficient sulphides, compared with that of the metal-rich sulphides, could be a surface-area effect. Similar behaviour (i.e., increased dissolution rate with cathodic shift in potential) was also found for the dissolution of pyrite (Fig. 7). Thus, compounds containing a large excess of sulphur must be reduced prior to rapid non-oxidative dissolution. The relationship between cathodic currents and dissolution rates found by Nicol and Scott⁵ for the non-oxidative dissolution of slightly metal-deficient iron sulphides was also apparent for pyrite, indicating that

the dissolution rate of iron was limited by the reduction of FeS₂ to FeS prior to non-oxidative dissolution. A numerical relationship between the dissolution rate of nickel and cathodic current was not apparent for the non-oxidative dissolution of nickel sulphides. This was attributed to the presence of more than one phase in the nickel sulphides, and larger errors associated with the slower dissolution of the sulphides. The concurrent reduction of residual oxygen, for example, can lead to errors of this type.

It can be concluded that any metal-deficient sulphide with a surface that has resulted from oxidation or bulk stoichiometry dissolves non-oxidatively more slowly than a metal sulphide that contains an excess of metal greater than a 1 : 1 stoichiometry. Further evidence to support this conclusion is presented towards the end of this paper.

An increased non-oxidative dissolution rate for nickel metal at potentials anodic of the mixed potential (-0,32V) is shown in Fig. 5. Since the dissolution is controlled by the rate of nickel oxidation and proton reduction, the rate would be expected to be a maximum at the mixed potential. However, the apparent enhancement of the rate that is observed at greater anodic potentials could be due to an increase in the surface area of the nickel electrode resulting from the concurrent electrochemical oxidation.

Dependence on Temperature

Activation energies were calculated from Arrhenius

TABLE III

THE DEPENDENCE OF THE DISSOLUTION RATE ON TEMPERATURE

| Sample no. | Apparent activation energy, kJ.mol ⁻¹ |
|------------|--|
| 1 | 65 ± 5 |
| 2 | 65 ± 5 |
| 3 | 54 ± 5 |
| 4 | 52 ± 5 |
| 5 | 66 ± 5 |
| 6 | 60 ± 10 |

plots of the log of the nickel-dissolution rates against the inverse of the temperature, and are shown in Table III for different nickel sulphides. The apparent activation energy of the nickel and nickel sulphide dissolution appeared to be independent of the stoichiometry, and is indicative of a chemically-controlled reaction.

Dependence on Stirring Rate

The speed at which the ring-disc electrode was rotated had no significant effect on the rate of dissolution of the nickel or the production of hydrogen sulphide from any of the nickel sulphides that were potentiostatted at $-0,3V$ in 1M hydrochloric acid at $60^{\circ}C$. It was concluded that the rate-determining reaction in the non-oxidative dissolution of nickel sulphides is not the diffusion of the reactants or products through the solution – a conclusion that is in agreement with the activation energies that were calculated.

Dependence on Acid

The rates at which nickel is dissolved from nickel metal and nickel sulphides were determined for three different acids. In all instances, the dissolution rate in hydrochloric acid was faster than in perchloric acid, and the dissolution rate in sulphuric acid was slowest (Table IV).

TABLE IV

DEPENDENCE OF THE DISSOLUTION RATE OF NICKEL ON THE TYPE OF ACID

Conditions: Potential $-0,3V$ Temperature $60^{\circ}C$
Rotation speed 1500 r/min

| Sample no. | 1 M HCl ($\text{mol.cm}^{-2}\text{s}^{-1}$) $\times 10^{10}$ | 1 M HClO ₄ ($\text{mol.cm}^{-2}\text{s}^{-1}$) $\times 10^{10}$ | 0,5 M H ₂ SO ₄ ($\text{mol.cm}^{-2}\text{s}^{-1}$) $\times 10^{10}$ |
|------------|--|--|---|
| 1 | 20 | 10 | 7 |
| 2 | 20 | 13 | 6 |
| 3 | 38 | 22 | 16 |
| 4 | 39 | 12 | 6 |
| 5 | 49 | 26 | 13 |

That the dissolution is fastest in hydrochloric acid is thought to be because the chloride ions facilitate a transfer of the charge across the interface between the solid and the solution. It should be noted that nickel(II) forms a weak complex with chloride ions and will thus allow for a greater concentration of nickel in equilibrium. However, thermodynamic limitations are not thought to be rate-controlling at such low pH values. The dissolution of nickel is faster in perchloric acid than in sulphuric acid only because the sulphuric acid has a higher pH value. The pH value at $60^{\circ}C$ of 1M hydrochloric acid was 0,10; that of 1M perchloric acid was 0,12, and that of 0,5M sulphuric acid was 0,67.

The effect of the concentration of hydrochloric acid on the rate of nickel dissolution was also studied. The acid dependence can be described by a power expression,

$$k_{N1}^* = A [HCl]^x,$$

where k_{N1}^* is the non-oxidative dissolution rate and A is a constant for hydrochloric acid concentrations of 0,1 to 5M. The values of x for the nickel sulphides are shown in Table V. The dependence of the dissolution rate of nickel from nickel metal (sample 1) and from nickel-rich heazlewoodite (sample 2) on the concentration of the acid is different from that of the other

nickel sulphides. This indicates a change in rate-determining step between those species containing nickel metal and those which are less rich in nickel. It is possible that the rate of dissolution of nickel from nickel sulphides containing metal is limited by the rate of dissolution of the nickel metal, which is dissolved relatively slowly by a mixed-potential mechanism. This observation is substantiated by the results given in Table VI.

TABLE V

DEPENDENCE OF THE NON-OXIDATIVE DISSOLUTION RATE ON THE CONCENTRATION OF HYDROCHLORIC ACID

Conditions: Potential $-0,3V$ Temperature $60^{\circ}C$
Rotation speed 1500 r/min

| Sample no. | $x \pm 0,05$ |
|------------|--------------|
| 1 | 0,4 |
| 2 | 0,45 |
| 3 | 0,8 |
| 4 | 0,8 |
| 5 | 0,75 |
| 6 | 0,7 |

TABLE VI

DEPENDENCE OF THE DISSOLUTION RATE OF NICKEL ON THE CONCENTRATION OF ACID

C Sample 1 Sample 2

Conditions: Potential for sample 1
Potential $-0,4V$ for sample 1
Potential $-0,3V$ for sample 2
Temperature $60^{\circ}C$
Rotation speed 1500 r/min

| Solution | Sample 1 ($\text{mol.cm}^{-2}\text{s}^{-1}$) $\times 10^{-10}$ | Sample 2 ($\text{mol.cm}^{-2}\text{s}^{-1}$) $\times 10^{-9}$ |
|-------------------------------|--|---|
| 1 M HCl | 3 | 2,0 |
| 0,1 M HCl and 0,9 M NaCl | 3 | 2,4 |
| 0,01 M HCl and 0,99 M NaCl | 4 | 2,4 |

The rate of nickel dissolution from samples 1 and 2 at $-0,4V$ and $-0,3V$ respectively is independent of the concentration of hydrogen ions at a constant concentration of chloride ions, as would be expected if the rate of dissolution were controlled by a mixed-potential mechanism. The dissolution rates of samples 3 to 6 are dependent on the concentration of both hydrogen and chloride ions, showing that the process is dependent on the transfer of either ionic or electron charges⁵.

The dependence of the rate of nickel-dissolution on the concentration of hydrochloric acid exhibited by samples 3 to 6 is similar to that of iron sulphides under similar conditions.

Experiments under Open-circuit Conditions

Nickel sulphide electrodes were rotated in acid solutions under open-circuit conditions, and the rate of nickel dissolution, hydrogen sulphide evolution, and their open-circuit potentials were recorded. The open-circuit potential of the nickel sulphides, which was usually constant (about 20mV) after the first five minutes of reaction, altered by 200mV in this initial period. This shift was irreproducible, and was thought to be dependent on the polishing of the electrode surface. The constant open-circuit potential is given in Table VII,

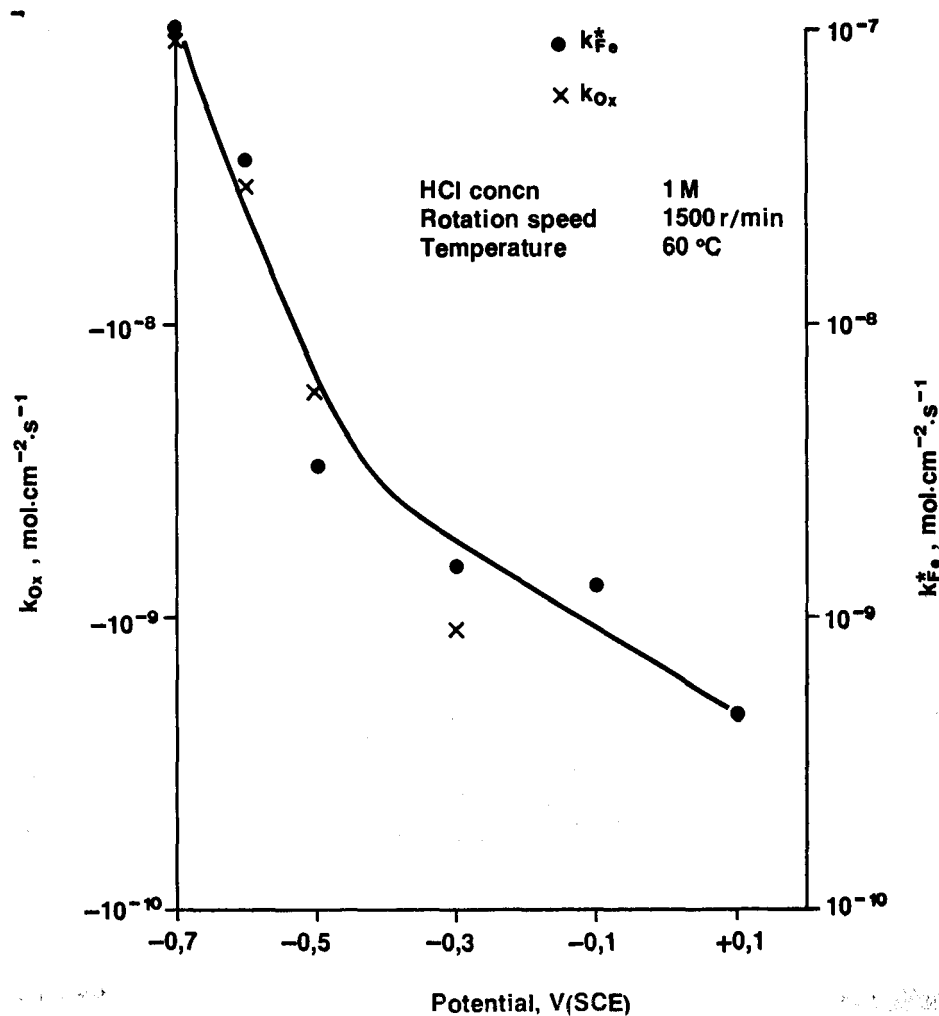


Fig. 7—Potential dependence of iron dissolution from FeS₂

along with the rate constants for nickel dissolution and the average production rate of hydrogen sulphide. Predicted values for the non-oxidative nickel-dissolution rate, based on Figs. 4 and 5 and the open-circuit potential, are also given.

TABLE VII

THE OPEN-CIRCUIT DISSOLUTION OF NICKEL SULPHIDES

Conditions: HCl concentration 1M Rotation speed 1500 r/min
Temperature 60 °C

| Sample no. | E_{OC} V (SCE) | $10^{10}k_{Ni}^*$ | $10^{10}k_{Ni}^{\dagger}$ | $10^{10}k_{H_2S}$ |
|------------|---------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| | | mol.cm ⁻² .s ⁻¹ | mol.cm ⁻² .s ⁻¹ | mol.cm ⁻² .s ⁻¹ |
| 1 | -0,35 | 11 | 9,0 | — |
| 2 | -0,42 | 22 | 20 | 18 |
| 3 | -0,28 | 20 | 30 | 15 |
| 4 | -0,25 | 30 | 40 | 20 |
| 5 | -0,12 | 7 | 20 | 7,2 |
| 6 | +0,20 | 0,7 | — | <5 |

† Predicted value

The open-circuit potential of the nickel sulphides shifts anodically as the stoichiometric ratio of nickel to sulphur decreases. This is to be expected in view of the more-oxidized nature of the nickel-deficient sulphides.

The rate of nickel dissolution reaches a maximum for sample 4, and becomes very slow as the nickel-to-sulphur ratio becomes less than 1. The production rate of hydrogen sulphide follows a similar pattern. It appears therefore that Ni₇S₆ is the most rapidly dissolved nickel sulphide under open-circuit conditions. Heazlewoodite (Ni₃S₂) is only slightly slower, but, once the nickel-to-sulphur ratio is decreased to less than 1 (i.e., Ni_{1-x}S and NiS₂), the non-oxidative dissolution is very slow. This is in agreement with results presented earlier in this paper, which showed that nickel sulphides that were oxidized at 0,0V dissolved more slowly non-oxidatively. However, the non-oxidative dissolution of nickel-deficient nickel sulphides did not require an induction period prior to the reaction, contrary to what was reported⁵ for iron-deficient iron sulphides. From this it can be concluded that, unlike the iron-sulphur system, nickel-deficient nickel sulphides react spontaneously in acid solutions. If any surface reduction is required prior to dissolution, as was postulated for iron sulphides, it occurs virtually instantaneously.

It can also be noted from Table VII that the rate at which nickel sulphides react under open-circuit potentials can be predicted approximately from constant-potential experiments simply by the reading off of the

nickel-dissolution rate at the open-circuit potential. Thus, to maximize the rate of non-oxidative dissolution for a particular nickel sulphide, a graph of rate versus potential similar to Figs. 4 and 5 can be constructed. The nickel sulphide can then be held at its optimum leaching potential either by the application of an external electrical potential to the system, or by the introduction of redox reagents for the adjustment of the mixed potential to the optimum value.

The addition of approximately 10^{-2} M hydrogen sulphide to the solution in which the nickel sulphide electrode dissolves is illustrated in Table VIII. The open-circuit potential was shifted anodically for the

TABLE VIII
THE OPEN-CIRCUIT DISSOLUTION OF NICKEL SULPHIDES IN ACIDIC
SULPHIDE SOLUTION

Conditions: HCl concentration 1M H₂S concentration 10^{-2} M
Temperature 60°C Rotation speed 1500 r/min

| Sam- ple no. | E_{OC} V (SCE) | $10^{10}k_{Ni}^*$ | $10^{10}k_{Ni}^{\dagger}$ | $k_{Ni}^*(HCl/H_2S) \ddagger$ |
|--------------------|---------------------|---------------------------------------|---------------------------------------|-------------------------------|
| | | mol.cm ⁻² .s ⁻¹ | mol.cm ⁻² .s ⁻¹ | $k_{Ni}^*(HCl)$ |
| 1 | -0,25 | 21 | 22 | 4,4 |
| 2 | -0,20 | 31 | 30 | 1,4 |
| 3 | -0,22 | 20 | 30 | 1,0 |
| 4 | -0,30 | 41 | 40 | 1,4 |
| 5 | -0,18 | 7,6 | 30 | 1,1 |
| 6 | -0,00 | 0,5 | 1,8 | 0,7 |

† Predicted value

‡ Ratio of k_{Ni}^* in the presence and absence of H₂S

nickel-richer sulphides, and cathodically for the nickel-deficient sulphides. The addition of hydrogen sulphide also resulted in an increase in the rate of nickel dissolu-

tion, particularly for nickel metal. Because of a mass-action effect, one would expect the rate to slow down if there were any thermodynamic rate limitation on the dissolution process. However, the oxidation of nickel is considerably enhanced by the addition of hydrogen sulphide (Fig. 8), and it is feasible that a similar process occurs for the nickel sulphides. It can be concluded that the non-oxidative leaching of nickel-rich nickel sulphides should be carried out under conditions in which an overpressure of hydrogen sulphide is maintained.

Electrical contact between the rotating nickel sulphide disc and a nickel metal sheet that was immersed in the solution resulted in a shift in open-circuit potential towards the region of -0,25 to -0,3V (Table IX). The value of k_{Ni}^* recorded for all the nickel sulphides was considerably higher than predicted owing to the dissolution of the nickel metal in an acidic sulphide solution. A comparison of the dissolution rates of hydrogen sulphide from nickel sulphides in contact with nickel metal and those not in contact with nickel metal shows that the dissolution rate of the nickel-deficient sulphides is generally increased. This can be attributed to the shift in mixed potential to a more cathodic value, at which non-oxidative dissolution is faster. For samples 3 and 4, the shift in potential was small, and the difference in rate was therefore within the limits of experimental accuracy.

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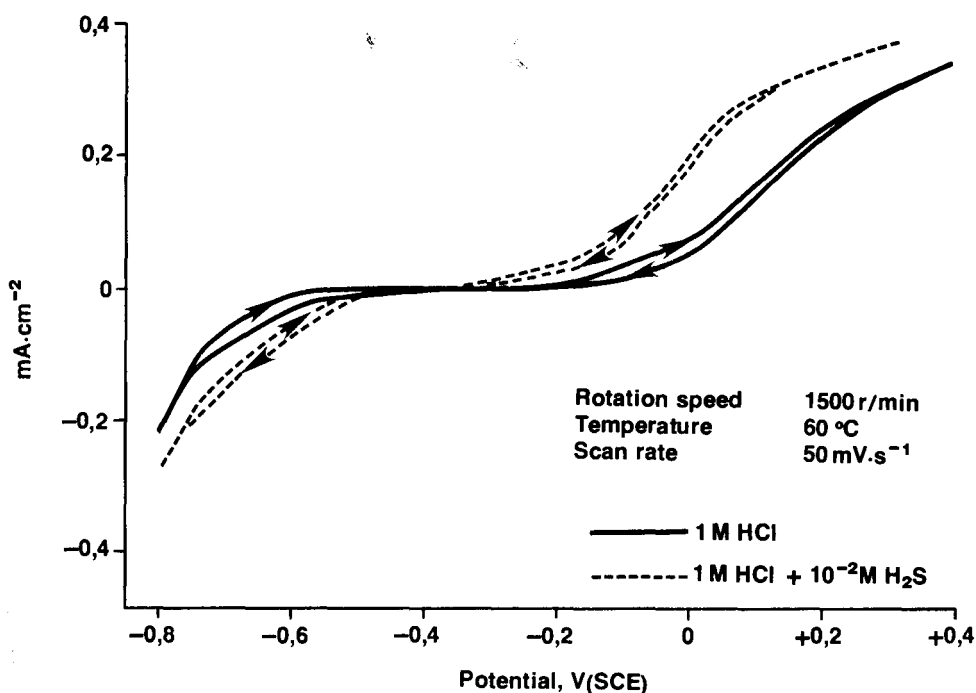


Fig. 8—Effect of hydrogen sulphide on the cyclic voltammogram of nickel metal

TABLE IX
THE OPEN-CIRCUIT DISSOLUTION OF NICKEL SULPHIDES IN CONTACT WITH NICKEL METAL

Conditions:

HCL concentration 1M
Rotation speed 1500 r/min

Temperature 60°C
NiS in electric contact with Ni metal

| Sample no. | E_{OC} V(SCE) | $10^{10}k^*_{Ni}$ mol.cm ⁻² .s ⁻¹ | $10^{10}k^*_{Ni}†$ mol.cm ⁻² .s ⁻¹ | $10^{10}k_{H_2S}$ mol.cm ⁻² .s ⁻¹ | $\frac{k_{H_2S(Ni)}‡}{k_{H_2S}}$ |
|------------|--------------------|--|---|--|----------------------------------|
| 1 | -0,35 | 20 | 20 | — | — |
| 2 | -0,30 | 230 | 20 | 30 | 1,6 |
| 3 | -0,27 | 160 | 40 | 13 | 0,9 |
| 4 | -0,30 | 190 | 40 | 16 | 0,8 |
| 5 | -0,25 | 140 | 40 | 13 | 2 |
| 6 | -0,20 | 220 | 40 | 8 | > 5 |

† Predicted value.

‡ Ratio of k_{H_2S} with and without contact with nickel metal.

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Coal-mining charts

Six new wall charts in colour have been published by Industrial Training Branch of the National Coal Board. Five of them show typical layouts and support methods for different face-end systems, bringing out, with colour, the various operational zones, e.g. face, packhole, stable, roadhead, heading, T-junction, roadway pack, and goaf. The sixth chart shows in some detail the structure, functions, and operation of the hydraulic prop. The

charts are based on illustrations in the manual *Underground Support Systems*. The charts were designed as aids for use in mining and mining-engineering training.

The charts can be purchased at £12 a set of six from HQ Purchasing and Stores Department, National Coal Board, Hobart House, Grosvenor Place, SW1X 7AE. Further information can be obtained from Training Aids Section, Industrial Training Branch at the same address.

Hellenic arc and trench

An International Symposium on the Hellenic Arc and Trench will be held in Athens from 8th to 10th April, 1981. The Symposium is being organized by the National Technical University of Athens and research teams working on the Hellenic Arc and Trench. It is being held under the auspices of the Ministry of Culture and Science of Greece and is also sponsored by the Geophysical Committee of Greece. It is co-sponsored by the International Union of Geological Sciences.

The Symposium will be concerned with the formation and evolution of the Hellenic Arc and Trench from land- and sea-based studies, and their relation to the tectonics of the adjacent areas. Comparisons with similar geotectonic structures in the world, especially the Tyrrhenian

Sea and Pannonian Basin, will be made.

The H.E.A.T. Symposium is a contribution to the new Lithosphere programme, and elements of that programme will be presented at the meeting. Results of new oceanographic and space techniques, and a discussion of deep lithospheric and asthenospheric processes responsible for the dynamics of the area will be emphasized.

For further information, write to Prof S. S. Augustithis, International Symposium on the Hellenic Arc and Trench, National Technical University, Department of Mineralogy-Petrography-Geology, P.O. Box 1006, Athens, Greece.