The kinetics and mechanism of the non-oxidative dissolution of some iron sulphides in aqueous acidic solutions

by M. J. NICOL*, Ph.D. (Wits.) and
P. D. SCOTT†, Ph.D. (Wits.) (Visitors)

SYNOPSIS

The kinetics of the non-oxidative dissolution in acids of the iron sulphides FeS, Fe–FeS, and Fe_9S_{10} were studied by the use of rotating-disc electrodes of the various compounds. It was found that the rates of dissolution vary by orders of magnitude with changes in surface potential. The dissolution rates depend on non-integral orders of hydrogen-ion concentration, which in turn vary with potential.

A mechanism based on the following premises is proposed to explain the kinetics of dissolution of the iron sulphides.

(1) Only an FeS compound that is exactly stoichiometric dissolves in accordance with the accepted theory of ionic charge transfer.

(2) Any non-stoichiometric iron-deficient iron sulphides must be reduced to exactly stoichiometric FeS before spontaneous non-oxidative dissolution can occur. The dissolution of Fe_9S_{10} and slightly iron-deficient FeS compounds under open-circuit conditions occurs only when an oxidation reaction (usually the oxidation of hydrogen sulphide to elemental sulphur) can provide the electrons necessary for the production of exactly stoichiometric FeS. The establishment of such a mixed-potential system is the reason for the induction period that occurs during the dissolution of pyrrhotites in acids.

SAMEVATTING

Die kinetika van die nie-oksidatiewe oplossing van die ystersulfiede Fes, Fe–FeS, en Fe_9S_{10} in sure is bestudeer met gebruik van draaiskyfelektrodes van die verskillende verbindings. Daar is gevind dat die oplostempo's met grootte-ordes wissel met veranderinge in die oppervlakpotensiaal en dat hulle afhang van nie-integraalordes van die waterstof-ioonkonsentrasie wat op hul beurt met die potensiaal wissel.

'n Meganisme wat op die volgende veronderstellings gebaseer is, word voorgestel om die oploskinetika van die ystersulfiede te rasionaliseer.

(1) Slegs 'n FeS-verbinding wat presies stoïgiometries is, los volgens die aanvaarde ioonladingoordragteorie op.

(2) Nie-stoïgiometriese ystersulfiede met 'n ystertekort moet gereduseer word tot FeS wat presies stoïgiometries is voordat spontane nie-oksidatiewe oplossing kan plaasvind. Die oplossing van Fe_9S_{10} en FeS-verbindings met 'n geringe ystertekort onder oopkringtoestande vind slegs plaas wanneer 'n oksidasiereaksie (gewoonlik die oksidasie van waterstofsulfied tot elementale swawel) die elektrone kan voorsien wat nodig is vir die produksie van FeS wat presies stoïgiometries is. Die daarstelling van so 'n stelsel met gemengde potensiale is die rede vir die induksieperiode wat tydens die oplossing van pirrotiete in sure voorkom.

Introduction

The dissolution of a solid can be defined as non-oxidative when the formal oxidation states of the solute species are identical both in the solution and in the solid states. Oxidative dissolution takes place when one or more of the solute species exist in different oxidation states in the solid and solution phases. Non-oxidative dissolution of mineral sulphides has been proposed as a means of leaching metals from sulphide ores[1]. There is evidence to suggest that the rates of the oxidative dissolution of zinc sulphide ores, under conditions typical of some hydrometallurgical processes, are at least partially limited by non-oxidative dissolution processes[2, 3].

The non-oxidative dissolution of copper–nickel–iron mattes, which consist in part of metal sulphides, is practised on a considerable scale. For these reasons, it is important that the mechanisms governing the rates of dissolution reactions, for example,

$$FeS + 2H^+ \rightarrow Fe^{2+} + H_2S \qquad \ldots \ldots \ldots \ldots (1)$$

should be fully understood.

Parsons and Ingraham[4] have published a review of the work to 1970 that is related to the generation of hydrogen sulphide from base-metal sulphides. Therefore,

only recent work will be reviewed here, with the emphasis on iron sulphides.

Ingraham, Parsons, and Cabri[5] measured the dissolution rates of suspensions of particles of monoclinic and hexagonal pyrrhotite concentrates ($FeS_{1,1-1,2}$) in hydrochloric acid solutions over an acid concentration range of 1,5 M to 10 M, and at temperatures between 30 °C and 90 °C. The kinetic data were characterized by two important features.

(a) The initial parts of the graphs showing extent of dissolution versus time demonstrated that the rate of dissolution increased with time until a dissolution of approximately 50 per cent was reached. After that, the rate of dissolution decreased with time.

(b) The rates of dissolution in the initial stages were found to exhibit a half-order dependence on stirrer speed, a dependence on acid concentration of less than first order, and an activation energy of approximately 7 kcal.mol⁻¹.

Van Weert, Mah, and Piret[6] investigated the kinetics of dissolution of pyrrhotite concentrates in 6 M to 8 M hydrochloric acid at temperatures between 60 °C and 90 °C. They found that relatively rapid dissolution in accordance with equation (1) was preceded by an 'induction period' during which no hydrogen sulphide was evolved, although some iron dissolved slowly. The

*National Institute for Metallurgy, Randburg, Transvaal.
†Formerly National Institute for Metallurgy; now Darling & Hodgson Ltd, Sandton, Transvaal.

length of the induction period decreased at higher acid concentrations and at higher temperatures. They prepared mixtures of the pyrrhotite concentrate in ferrous chloride solutions saturated with hydrogen sulphide, and placed a platinum electrode in these mixtures. Its potential was then measured against that of a standard calomel electrode while hydrochloric acid was added to the mixture. When the acid was added, the potential of the platinum electrode rapidly increased from about $-0,15$ V to about $+0,35$ V. The potential then decreased slowly during the induction period to about zero, at which stage hydrogen sulphide began to evolve. They also found that the rate of dissolution increased with increasing acid concentration. They suggested that the induction period could be attributed to the presence of ferric ions produced by the dissolution of the 8 to 10 per cent magnetite (Fe_3O_4) found in their pyrrhotite samples. However, their explanation of the cause of the induction period, in terms of the oxidation of hydrogen sulphide to elemental sulphur by ferric ions, is of doubtful validity, since they did not detect elemental sulphur on the surfaces of the pyrrhotite particles. Their results could equally well be explained on the assumption that only the magnetite dissolved during the induction period.

A recent, more fundamental, study[7] of the kinetics of the dissolution of synthetic iron sulphide (troilite) in sulphuric acid solutions of varying pH showed that the rate of the reaction was not mass-transport controlled and was proportional to the acid concentration. A mechanism was proposed in which H^+ adsorbs at the surface on the anionic sites, forming a bond with S. This then decomposes as HS^-, which further reacts rapidly with H^+ to form H_2S. In a recent paper, Henry et al.[8] found that several synthetic iron-deficient sulphides could be reduced electrochemically, and measurements of the amount of electricity corresponding to the reduction and the amount of iron(II) appearing in the solution could be correlated with the deviations of the solids from stoichiometry.

In a detailed investigation of the acid decomposition of various iron and nickel sulphides, Jibiki[9] found that the dissolution rate was strongly dependent on the electrochemical potential of the sulphides. In addition, the parameters that were found to promote the dissolution of pyrrhotite were a low excess of sulphur in the pyrrhotite, a high concentration of both acid and chloride ions in solution, and a high temperature.

Various mechanisms have been proposed to explain the experimental finding of each of the above investigations. However, no single theory can accommodate all the data. This paper summarizes the results of a detailed study of the kinetics of dissolution of various iron sulphides, and these results, together with the above published data, are explained in terms of a common mechanism of dissolution.

Experimental Method

Materials

Three types of iron sulphide were used.

A synthetic iron sulphide (Maybaker) was shown by chemical analysis to have a 1,33 to 1 stoichiometric ratio

of iron to sulphide. X-ray analysis by Guinier diffractometer showed that the compound consisted of a mixture of an iron phase and a troilite (stoichiometric) phase. This material is designated Fe–FeS in this paper.

Another iron sulphide was prepared in the laboratory, according to the method of Dutrizac and MacDonald[2], from spectrographically pure iron and sulphur. The product was ground and melted at 1490 K in a sealed and evacuated silica tube to produce cylindrical samples of iron sulphide, which were shown by chemical analyses to have a 1-to-1 stoichiometric ratio of iron to sulphur. X-ray-diffraction studies showed that this iron sulphide was troilite, designated FeS in this paper.

A hexagonal pyrrhotite of composition Fe_9S_{10} was prepared[10] from spectrographically pure iron and sulphur. The product was ground and melted at 1490 K in a sealed and evacuated silica tube, which produced cylindrical samples. X-ray-diffraction analysis confirmed the structure of this compound as 5C hexagonal pyrrhotite of composition Fe_9S_{10}.

Reagent-grade chemicals and triply distilled water were used in the preparation of all the solutions.

Apparatus and Method

The cylindrical samples of the iron sulphides were encased in Teflon holders that left a disc of the material exposed. These holders were fitted to vertical-drive shafts that could be rotated at any one of a series of constant speeds between 120 r/min and 2400 r/min. The shafts were also in electrical contact with the back of the iron sulphide samples, so that they acted as rotating-disc electrodes (RDE). The solutions were contained in a 125 ml water-jacketed reaction vessel fitted with a lid containing inlets for a Luggin capillary, an auxiliary platinum electrode separated from the solution by a sintered-glass frit, a nitrogen bubbler, a device for the extraction of hydrogen sulphide, a sampling tube, and the RDE. Water from a constant-temperature waterbath maintained the temperature in the reaction vessel. A saturated calomel electrode (SCE) with a bridge of sodium chloride (in electrical contact with the solution through the Luggin capilliary) was used as a reference electrode.

The surfaces of the RDE were prepared by being ground on coarse and on fine silicon carbide papers. In some instances, the electrodes were also polished with $0,5$ μm alumina paste.

At intervals during any dissolution experiment, the solution was aspirated directly into an atomic-absorption spectrophotometer, and the concentration of iron in solution was measured.

The potential of the RDE relative to the SCE could be controlled by a potentiostat. Both the potential of the RDE and the current flowing in it were measured by digital voltmeters. All the potentials are quoted relative to the SCE.

A triangular-wave potential sweep-generator was connected to the potentiostat, and a cyclic voltammogram of the RDE in each solution was made on an X–Y recorder.

Results

Induction Periods and Open–circuit Dissolution

When a polished RDE of FeS was placed in either hydrochloric or perchloric acid of concentrations up to 3 M, the potential of the RDE assumed positive values in the range 0,1 V to 0,4 V and no measurable dissolution occurred. These positive potentials assumed in acid solutions by the FeS RDE were shown to be characteristic of induction periods in the dissolution reactions. For example, in 3 M hydrochloric acid after 3,75 hours, the potential of an RDE surface had drifted from +0,3 V to +0,15 V and no dissolution had occurred. Suddenly, during the space of a minute, the potential decreased to −0,08 V, and very rapid dissolution occurred. In 5 M hydrochloric acid, the induction period was only 3 to 5 minutes. During an induction period, the reaction could be initiated by the passing of a cathodic pulse to potentials of less than −0,100 V for as little as 10 seconds. However, an anodic pulse, or a stream of air or oxygen, made the electrode potential positive and inhibited the dissolution reaction.

Once dissolution had begun under open-circuit conditions, the potential of the RDE fluctuated around its mean value by about 0,03 V, making it impossible to obtain reproducible measurements of the dissolution rate. The mean dissolution potential was also a function of hydrogen-ion concentration, so that a valid comparison of the kinetic effects of acid concentration could not be made. Consequently, the kinetic effects of hydrogen- and chloride-ion concentrations and of temperature on the dissolution rates of FeS were measured at fixed RDE potentials. Under these conditions, the graphs of dissolved iron against time were linear, the slopes yielding rate constants characteristic of the reaction conditions.

No induction periods were observed for the Fe–FeS samples, and several dissolution experiments were conducted in which the potential of the Fe–FeS RDE was not controlled by potentiostat, but was monitored during dissolution in perchloric acid. In 0,1 M perchloric acid, the potential of the RDE changed from about −0,4 V at the start of the reaction to about −0,5 V after approximately 10 minutes of dissolution. During dissolution in 1 M perchloric acid, similar changes in potential occurred, although their range was much narrower, i.e., −0,4 V to −0,42 V. Graphs showing the amount of iron dissolved against time in these experiments were not linear over the period during which the potential of the RDE changed. These graphs were wholly reproducible only under identical conditions of constant potential during the dissolution processes. Subsequently, the potential of the RDE was controlled by potentiostat during all the experiments. Under these conditions, the graphs of dissolved iron against time were reproducible and linear.

In 0,1 M and 1,0 M hydrochloric acid and in 0,5 M sulphuric acid, no measurable dissolution of Fe_9S_{10} was observed under open-circuit conditions. The open-circuit potentials were typically greater than +0,1 V. Contrary to what occurs with stoichiometric FeS, cathodic pulses did not initiate the dissolution of Fe_9S_{10}. However, at higher concentrations of acid, open-circuit dissolution occurred (e.g., 3 M hydrochloric acid and 5 M sulphuric

acid, at potentials of −0,02 V and +0,02 V respectively). A cathodic pulse was required to begin open-circuit dissolution in 5 M sulphuric acid, but in 3 M hydrochloric acid the potential drifted spontaneously from anodic potentials of about +0,1 V to −0,02 V and dissolution began.

It was found that the dissolution of Fe_9S_{10} in dilute acids could be achieved by the construction of an electrochemical cell made of iron wire dipped into acid solution and connected, by an external electrical circuit, to the Fe_9S_{10} RDE. In one such experiment, 0,5 M sulphuric acid was used and the Fe_9S_{10} dissolved at a potential of about −0,3 V.

Changes in the rotation speeds of the RDE in the range 120 r/min to 2400 r/min did not have any effect on the potentiostatic experiments designed to show the influence of hydrogen- and chloride-ion concentration, of potential, and of temperature on the dissolution rates of FeS and Fe_9S_{10}.

Rate as a Function of Acidity and Chloride Concentration

Fig. 1 gives graphs of the rate constants for the dissolution of various iron sulphides against the pH values of the reactant solutions at 25 °C for perchlorate media at potentials of both −0,2 V and −0,5 V. The slopes of the lines in Fig. 1 can be used to show that the kinetic order of the dissolution rate with respect to the hydrogen-ion concentration is approximately 1 at −0,2 V but less than unity at −0,5 V. (Actual values are shown in parentheses on the lines.)

The rate of dissolution of all three sulphides was found to increase only slowly with the concentration of chloride
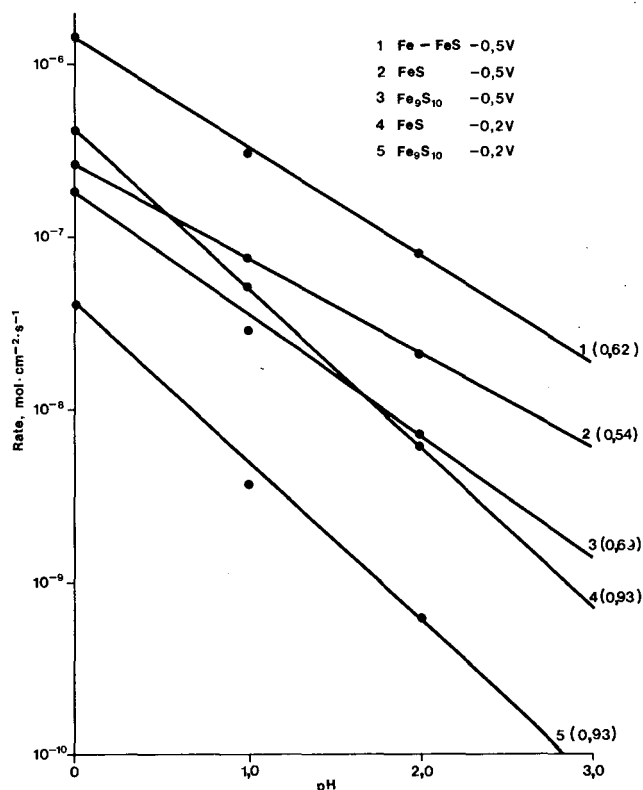

Fig. I—The rates of dissolution of various iron sulphides in 1,0 M perchlorate solutions at 25 °C as a function of pH

in the range 10^{-3} M to 1 M, the rate for FeS only doubling over this range. A more rapid increase occurs at concentrations above 1,0 M. The rate of dissolution of Fe_9S_{10} at a potential of $-0,2$ V in 0,5 M sulphuric acid was found to be almost identical to that in 1 M hydrochloric acid under the same conditions.

Rate as a Function of Potential

The rate of dissolution of the sulphides in 0,1 M hydrochloric acid at 25 °C is shown as a function of the potential in Fig. 2. In each case, the rate increases with decreasing potential to a maximum at about $-0,3$ V, below which it decreases slowly with decreasing potential. Over the range of potentials in which measurable nonoxidative dissolution occurs, small steady-state cathodic currents flow in the electrodes. It was assumed that these currents were the result of a two-electron reduction process. The calculated rates of this process are shown for FeS and Fe_9S_{10} in Fig. 2. In the case of FeS, at no potential does the rate of the cathodic process constitute more than 2 per cent of the dissolution rate. However, the cathodic currents and the dissolution rates vary with potential in a similar manner.

This direct proportionality between the measured dissolution rates and the cathodic currents is also apparent in Fig. 2 for Fe_9S_{10}. The higher cathodic currents in this instance enabled a more accurate estimate to be made of the ratio of the dissolution rate to that of the two-electron reduction process. For a total of twenty-five experiments in hydrochloric, perchloric, and sulphuric acid solutions, a value of 9,06 (with a standard deviation of 0,34) was obtained for this ratio.

Similar measurements could not be made with the Fe–FeS sample because of the simultaneous anodic dissolution of the free iron at potentials anodic to $-0,5$ V, and the cathodic evolution of hydrogen at more negative results.

Cyclic Voltammetry

Steady-state cyclic voltammograms, obtained with the various iron sulphide electrodes in dilute acid solutions over the potential ranges in which dissolution occurs, are shown in Fig. 3. Shown for comparison is the voltammogram obtained with an iron electrode in the presence of dissolved hydrogen sulphide. It is apparent in all instances that well-defined anodic and cathodic processes occur about the open-circuit dissolution potentials. For the FeS, a cathodic peak at $-0,28$ V and a corresponding anodic peak at $-0,06$ V indicate that processes requiring a limited charge are involved. An anodic peak at about 0 V occurs with Fe_9S_{10}, and a shoulder occurs at $-0,5$ V for Fe–FeS. For both these sulphides, however, no cathodic peaks or plateaux are apparent in the range of potentials shown.

Steady-state voltammograms for FeS and Fe_9S_{10} in solutions of varying acidity are shown in Figs. 4 and 5 respectively. For the FeS, the cathodic peak becomes smaller and shifts to more cathodic potentials with increasing pH, whereas the anodic peak shows little change of position. Similar trends are apparent in the cathodic behaviour of Fe_9S_{10}, but the anodic peak becomes more intense and well-defined in solutions of high acidity. The anodic shift of about 0,07 V in the position of the peak in 6 M hydrochloric acid can be atrributed, at least in part, to an increased liquid-junction potential. Also apparent is a cathodic peak at $-0,15$ V in this solution. Voltammograms made under quiescent and stirred conditions showed only small differences.

For the Fe_9S_{10}, it was observed that open-circuit dis-
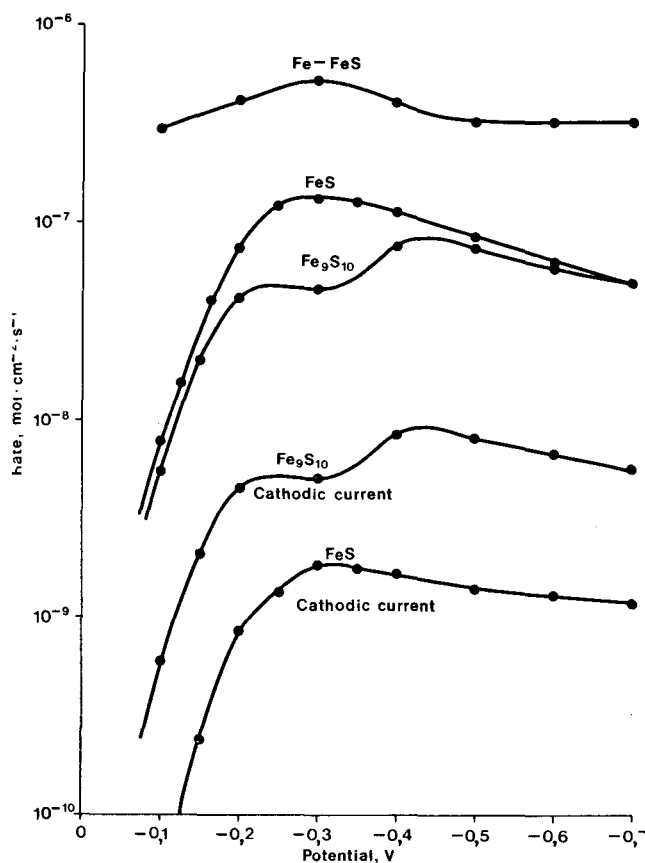

Fig. 2—The rates of dissolution of various iron sulphides in 0,1 M hydrochloric acid at 25 °C as a function of potential. Also shown are the corresponding steady-state cathodic currents (converted to dissolution rates on the assumption of a two-electron process)
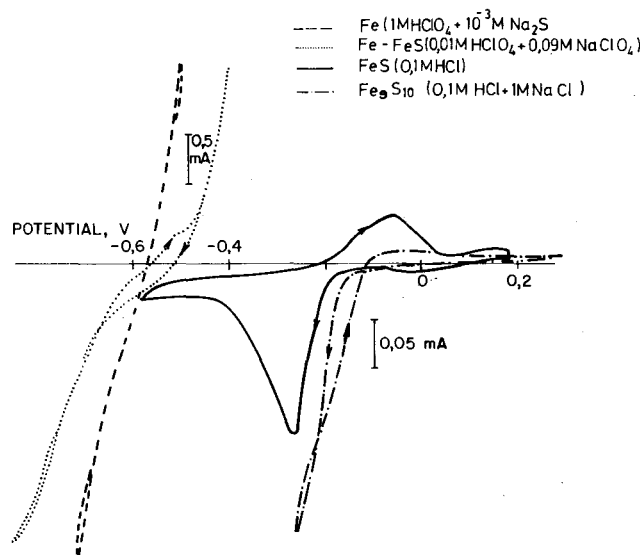

Fig. 3—Cyclic voltammograms (25 mV/s) for rotating discs of the various sulphides

solution was possible only in acid solutions that give rise to the well-defined anodic peak close to 0 V on the cyclic voltammograms. The following experiments were carried out in the hope that they would provide an explanation of this phenomenon.

By potentiostatic control of the stationary disc at the open-circuit potential (approximately 0,0 V) in strong acid (6 M hydrochloric acid), a bubble of hydrogen sulphide of continually increasing radius was grown on the disc. When the potential was changed to +0,050 V (the position of the peak of the anodic process), the
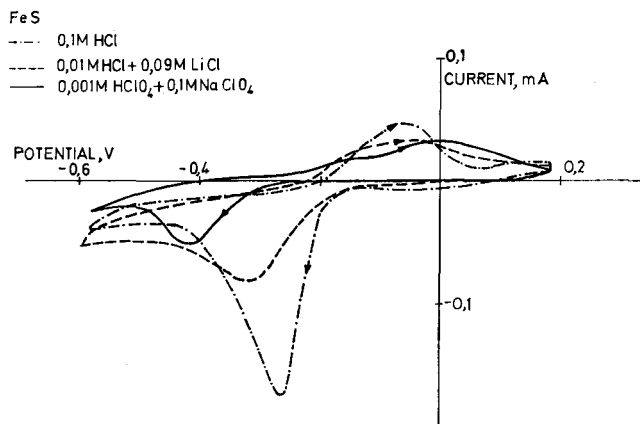

FeS
--·-- 0,1M HCl
---- 0,01M HCl + 0,09M LiCl
—— 0,001M HClO₄+0,1MNaClO₄

Fig. 4—Cyclic voltammograms (20 mV/s) for a rotating disc
of FeS in various media

Fe₉S₁₀
··—·· 0,001 M HCl + 1 M NaCl
········ 0,01 M HCl + 1 M NaCl
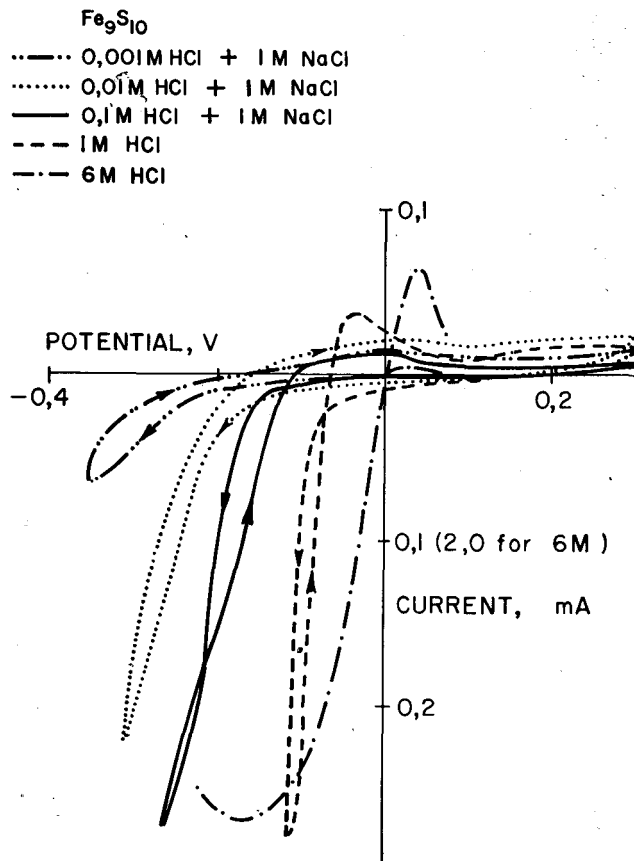—— 0,1 M HCl + 1 M NaCl
--- 1 M HCl
—·— 6 M HCl

Fig. 5—Cyclic voltammograms (20 mV/s) for a rotating disc of
Fe₉S₁₀ in various solutions

bubble shrank rapidly to a steady-state size. The steady-state radius was apparently independent of the initial radius of the bubble, and remained unchanged even after periods of up to an hour. Steady-state currents of 0,8 mA were recorded. When the disc potential was increased to the anodic extremity of the peak on the cyclic voltammogram, +0,1 V, the bubble disappeared from the surface of the disc and the steady-state current dropped to 0,06 mA.

The variation of potential with time for a rotating Fe_9S_{10} electrode in 1 M hydrochloric acid under various conditions was studied. After the potential had been held at +0,1 V for twenty seconds and the electrode then open-circuited, the potential decayed to about 0,02 V, at which point no dissolution occurs. The addition of sodium sulphide, to produce a solution of 5×10^{-3} sulphide, resulted in an immediate decrease of the potential into the active region ($-0,02$ V). A subsequent anodic pulse to +0,2 V was unable to restore the electrode, when it was open-circuited, to the inactive state. A cathodic pulse to $-0,1$ V caused an even more active open-circuit potential.

Discussion

Under the experimental conditions used, the dissolution rates of the iron sulphides in acid solutions were not controlled by the rates of mass transport of the reactant species towards the iron sulphide surfaces, or of the products away from them. The finding that the rates of dissolution depend on several constituents of the solution excludes the possibility of rate control by a solid-state process alone.

Consequently, the rates of dissolution must be limited by the transfer of the reactant species across the electrochemical-potential barrier at the solid–solution phase boundary, i.e., a process of 'ionic charge transfer'[11]. The mechanism involved in ionic charge transfer has been applied to the dissolution reactions of several ionic compounds[12], and is also applicable to covalent compounds such as the iron sulphides[13]. For the iron sulphides, the results indicate that some cathodic process is a prerequisite for dissolution involving ionic charge transfer, and the following mechanism appears to explain the experimental observations.

(a) Only an FeS compound that is exactly stoichiometric dissolves in acid solutions by the mechanism of ionic charge transfer.

(b) The FeS that is apparently stoichiometric is, in fact, a slightly non-stoichiometric iron-deficient compound (in this report designated $Fe_{1-x}S$). Such iron-deficient iron sulphides having the formula $Fe_{1-x}S$, where x is very small, are known to occur.[10]

Such a mechanism suggests that the initial rapid increase in dissolution rate of FeS in 0,1 M hydrochloric acid between potentials of $-0,1$ and $-0,2$ V (see Fig. 2) would be determined by the potential dependence of the reduction of $Fe_{1-x}S$ to FeS in accordance with equation (2):

$$Fe_{1-x}S+2xe+2xH^+\rightarrow(1-x)FeS+xH_2S. \quad . \quad . \quad . \quad (2)$$
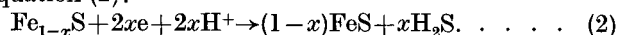
At potentials between $-0,2$ and $-0,35$ V, the rate of dissolution would be governed by both the reduction

process of equation (2) and the ionic charge transfer described by equation (3):

$$FeS+2H^+\rightarrow Fe^{2+}(aq)+H_2S. \qquad \ldots\ldots\ldots (3)$$
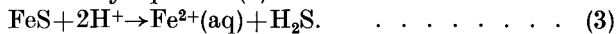
Finally, at potentials cathodic to $-0,35$ V, the rate of dissolution is controlled by the rate of ionic charge transfer alone.

The fact that the rate of dissolution of Fe_9S_{10} is exactly nine times greater than the rate of the reduction process under all the experimental conditions establishes that Fe_9S_{10} is transformed into FeS in accordance with equation (4):

$$Fe_9S_{10}+2e+2H^+\rightarrow 9FeS+H_2S. \qquad \ldots\ldots\ldots (4)$$

The FeS formed then dissolves. At potentials between $-0,1$ and $-0,2$ V, the rate of dissolution in 0,1 M hydrochloric acid is limited by the rate of the reduction reaction. At potentials cathodic to $-0,45$ V, the dissolution of FeS by the ionic transfer mechanism is rate-limiting, whereas both processes are rate-determining at potentials between $-0,2$ and $-0,45$ V. Fig. 2 shows the similarity between the rates of dissolution of FeS and Fe_9S_{10} at potentials cathodic to $-0,45$ V.

The presence of Fe in Fe–FeS ensures that the FeS does not occur as a sulphur-rich or iron-poor stoichiometric compound, so that both the excess iron and the exactly stoichiometric FeS dissolve. Although pure iron dissolves in 0,1 M hydrochloric acid about a hundred times more slowly than Fe–FeS, the dissolution rate of iron is greatly enhanced by hydrogen sulphide[14] (see Fig. 3). Consequently, the fact that the dissolution rate of Fe–FeS is about three times that of stoichiometric FeS over the range of disc potentials can be ascribed in part to the oxidative dissolution of the Fe in Fe–FeS. Other factors, such as differences in surface roughness, could contribute to the differences in the measured dissolution rates of stoichiometric FeS and Fe–FeS.

The mechanisms proposed for the dissolution kinetics of Fe–FeS, FeS, and Fe_9S_{10} are similar to those suggested by Engell[15] in rationalizing his kinetic data for the dissolution of FeO and Fe_3O_4 in acids. Engell apparently expected that the potential dependencies of the dissolution rates of ionic compounds might be modelled wholly by the ionic charge transfer theory that he developed. However, the dissolution kinetics of FeO and Fe_3O_4 could not be explained by this theory alone. Vermilyea[16], by making different assumptions from those of Engell, derived a similar ionic charge transfer model to predict the potential dependence of the rate of dissolution of an ionic compound. Unlike Engell, Vermilyea considered the influence exerted by the adsorption of the reactant species on the dissolution kinetics of an ionic compound. However, Vermilyea's ionic charge transfer model cannot explain the dissolution behaviour of either the iron oxides or the iron sulphides as functions of potential. A similar conclusion was reached by Valverde[17] in a study of the effects of various oxidizing and reducing agents on the dissolution of various metal oxides in acidic solution. In the discussion that follows, the application of the two theories to the kinetic data for the dissolution of iron sulphides is compared.

Ionic Charge Transfer

In terms of this theory, the non-oxidative dissolution of iron sulphides in acid solutions would be governed by the rate of transfer of ferrous cations and sulphide or protonated sulphide anions across the electrochemical potential barrier at the solid–solution phase boundary. Both Engell and Vermilyea used the ionic charge transfer equations to predict how changes in the surface potential would affect the dissolution rate. Both postulated that a change in surface potential would cause a change in the surface concentrations of the ions, since the rate of the dissolution of one ion would be retarded whereas that of the other would be enhanced. Engell's rate expressions are used here in the modelling of the rate of dissolution of an exactly stoichiometric FeS compound.

The quantitative application of the high-field approximation of the theory requires that the dissolution process should be far from equilibrium. Thermodynamic data[18] for the various species involved in the dissolution reaction can be used in conjunction with the well-known equations[19] for mass transport to or from a rotating disc to show that, under the conditions of the above experiments, this condition is valid. Details of these calculations are given elsewhere[20]. The rate equations for ionic charge transfer can be written, in terms of the high-field form of the familiar Butler–Volmer equation, as

$$V_+=k_+C_+\exp\left\{\frac{a_+Z_+F}{RT}\right\}E,\text{ and}$$

$$V_-=k_-C_-C_H^m\exp\left\{\frac{a_-Z_-F}{RT}\right\},$$

where V_+ and V_- are the rates of dissolution of cations and anions respectively, at a potential E; k_+ and k_- are the corresponding rate constants; C_+ and C_- are the corresponding concentrations at the solid–solution interface, i.e., on the surface of the solid; C_H, the concentration of protons; a_+ and a_1 are the transfer coefficients (generally 0,5) for the ions of charge Z_+ and Z_- respectively; and the other symbols have their usual significance.

These two equations are combined in Engell's treatment by the assumption that the sum of the chemical potentials (μ_{FeS}) of the surface ions is constant and independent of potential. Under these conditions, the above equations can be combined to give an overall expression for the rate:

$$V=\left(k_+k_-C_H^m\right)^{\frac{1}{2}}\exp\left\{\frac{\mu_{FeS}}{2RT}\right\}\exp\left\{\frac{Fe}{RT}(a_+Z_++a_-Z_-)\right\}.$$

For $m=1$ in this expression, the dissolution rate should increase with the square root of the proton concentration. The observed reaction orders of 0,5 to 0,7 (Fig. 1) in the potential range, in which the ionic charge transfer is the rate-limiting process, are in fair agreement with the theory.

According to the above equation, the rate of dissolution by ionic charge transfer can, depending on the relative magnitudes of a_+ and a_-, decrease, increase, or remain constant with change in potential. For FeS and Fe_9S_{10}, the rate of dissolution at potentials less than about $-0,4$ V decreases slowly with decreasing solution, implying that a_+ is slightly greater than a_- (a_+-a_- is 0,08 for FeS and 0,06 for Fe_9S_{10}).

Electron Charge Transfer

It has been proposed that only an FeS compound that is exactly stoichiometric can dissolve non-oxidatively in acids, so that FeS and Fe_9S_{10} must be reduced to FeS that is exactly stoichiometric before dissolution can occur, whereas the Fe in Fe–FeS generates FeS that is exactly stoichiometric. An attempt will be made to justify this premise with thermodynamic calculations, and with the results of cyclic voltammetry and steady-state dissolution rates obtained for the iron sulphides.

A Pourbaix diagram (Fig. 6) was constructed for the iron sulphide compounds from thermodynamic data[21, 22]. Reliable thermodynamic data for Fe_9S_{10} are not available, and two metastable lines were therefore drawn for the reduction of Fe_9S_{10} based on data from two sources.

The cyclic-voltammetric behaviour of the various iron sulphides is complex, and the reactions can be unequivocally assigned to only a few of the processes. Nevertheless, an attempt is made to interpret the various features because of their possible relevance to the mechanism of non-oxidative dissolution.

Comparison of the anodic behaviour of iron with that of Fe–FeS (Fig. 3) suggests that dissolution of the excess iron is responsible for the anodic currents. Similarly, the cathodic currents can be attributed to the evolution of hydrogen, although reduction of FeS to iron metal cannot be ruled out since it is thermodynamically possible (Fig. 6).

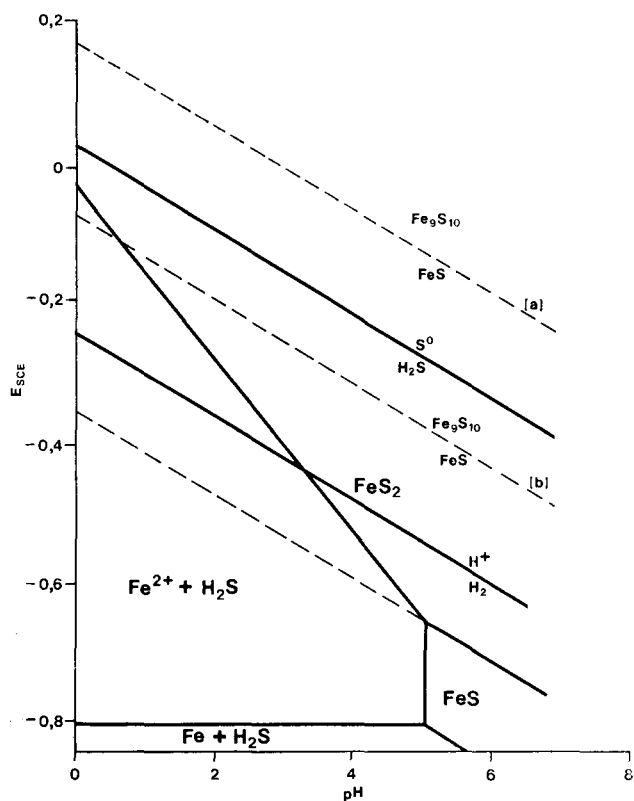At low currents, the cathodic behaviour of both FeS and Fe_9S_{10} is similar in all respects. Both sulphides give

cathodic peaks, although that of FeS is considerably the smaller (by at least an order of magnitude). The reduction of Fe_9S_{10} to FeS by the reaction

$$Fe_9S_{10}+2H^++2e \rightarrow 9FeS+H_2S \qquad \ldots \ldots \quad (5)$$

is consistent with the thermodynamic potential (Fig. 6) required for this reaction, and the observed cathodic shift is consistent with increasing pH. It is suggested that, by analogy, the reduction of FeS that is slightly deficient in iron (i.e., $Fe_{1-x}S$ with $x<0,02$) to stoichiometric FeS is responsible for the cathodic peak on FeS. The value of x would be less than 0,02 because the cathodic currents that flowed during the steady-state dissolution of FeS were so low that x could not exceed 0,02. Since the free energies of formation (per gram-atom of iron) of the various iron-deficient sulphides are approximately the same[22], the potential for the reaction

$$Fe_{1-x}S+2xH^++2xe \rightarrow (1-x)FeS+xH_2S \quad \ldots \quad (6)$$
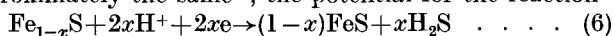
can be approximated to that for the reaction

$$S+2H^++2e \rightarrow H_2S. \qquad \ldots \ldots \ldots \ldots \ldots \ldots \quad (7)$$

Examination of Fig. 6 shows that this is thermodynamically possible at potentials below about 0 V at a pH value of 1 (i.e., in the region where FeS shows cathodic currents).

The reduction of FeS and Fe_9S_{10} at steady-state potentials cathodic to $-0,1$ V in 0,1 M hydrochloric acid should be described by the Butler–Volmer expression
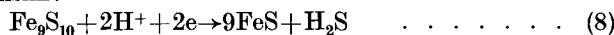
$$i=k \; C_H^m \exp\left[\frac{-\alpha nF}{RT}E\right].$$

The observed potential dependences of the dissolution rates of FeS and Fe_9S_{10} (between $-0,1$ and $-0,2$ V in 0,1 M hydrochloric acid) can be predicted by this equation if $n=1$ and $\alpha=0,4$, and the hydrogen ion dependences (Fig. 1) are fairly closely predicted if $m=1$.

The claim that the excess iron in Fe–FeS produces stoichiometric FeS is substantiated by an experiment in which an Fe_9S_{10} electrode was short-cricuited to a piece of iron wire placed in the same solution (0,5 M sulphuric acid). Before contact with the iron, the Fe_9S_{10} disc assumed a potential of $+0,05$ V and, as expected, did not dissolve at a measurable rate. After being connected to the iron wire, the potential decreased to $-0,3$ V and appreciable dissolution occurred. In this cell, anodic dissolution of the iron is coupled to cathodic reduction of Fe_9S_{10} to stoichiometric FeS, which dissolves non-oxidatively.

It seems reasonable to argue that the anodic peaks observed for both FeS and Fe_9S_{10} can be assigned to the reverse of reactions (6) or (7). The results of the experiments on the Fe_9S_{10} electrode with the hydrogen sulphide bubble showed that the oxidation of hydrogen sulphide is at least partially responsible for the anodic currents. If it is true that the formation of stoichiometric FeS is a prerequisite for dissolution, then such FeS will be observed under open-circuit conditions only if a suitable reducing agent is present to force the potential into the region where reduction to FeS is possible (i.e., below about 0 V). Thus, in 0,1 M hydrochloric acid, Fe_9S_{10} shows little evidence of an anodic peak in this region (Fig. 5) and, as expected, does not dissolve under open-circuit conditions. At higher acid concentrations (above 1 M hydrochloric acid), it dissolves readily, and a pro-

nounced anodic peak is evident on the cyclic voltammo-grams. As this peak has been shown to be due to the oxidation of hydrogen sulphide, the open-circuit dissolution can be considered to proceed by the following mechansim:

$$Fe_9S_{10}+2H^++2e \rightarrow 9FeS+H_2S \quad \ldots \ldots \ldots (8)$$
$$H_2S \rightarrow S^\circ+2H^++2e \quad \ldots \ldots \ldots \ldots (9)$$
$$9FeS+18H^+ \rightarrow 9Fe^{2+}+9H_2S. \quad \ldots \ldots \ldots (10)$$

FeS dissolves at open circuit in 0,1 M hydrochloric acid, and the anodic peak at $-0,05$ V is probably partly attributable to the oxidation of hydrogen sulphide to elemental sulphur. This can be inferred from the observation that sulphur was detected after the open-circuit dissolution of FeS (about 0,2 per cent by mass).

The above mechanism is similar to that implicit in the work of Henry, Lecuir, and Bessiere[8], who assumed, in their measurement of the deviation from stoichiometry of several synthetic iron sulphides, that reduction to the stoichiometric iron sulphide is a prerequisite to dissolution. It should be pointed out that the results of this work are similar to those obtained by Tewari and Campbell[7] for the dissolution of commercial FeS powder in dilute sulphuric acid solutions. Thus, they found a first-order dependence of the rate on the acid concentration, and their extrapolated rate in 1 M acid at 25 °C of $2,7 \times 10^{-7}$ mol.cm^{-2}.s^{-1} compares favourably with the value of 4×10^{-7} mol.cm.$^{-2}$.s^{-1} found by the present authors for FeS in 1 M perchloric acid at a potential of $-0,2$ V.

Finally, the formation of a sulphur-rich sulphide such as pyrite is thermodynamically possible (Fig. 6) at the potentials at which open-circuit dissolution of FeS and Fe_9S_{10} occurs. An alternative mechanism requiring reduction of a passivating FeS_2 layer prior to open-circuit dissolution could be envisaged. However, this is considered unlikely in view of the fact that preliminary experiments with a pyrite electrode showed that no noticeable dissolution occurs at potentials above $-0,5$ V in 1 M acid (i.e., reduction of pyrite, although thermodynamically possible, does not occur at the potentials at which FeS and Fe_9S_{10} dissolve).

Conclusions

This work has shown that the kinetics involved in the non-oxidative dissolution of iron oxides and sulphides in acids is similar. The kinetic data can be adequately explained in terms of a reduction process followed by ionic charge transfer from a stoichiometric material. Semi-quantitative agreement of the experimental results with those predicted by well-known electrochemical models has been achieved. Less extensive experiments have indicated that the effects of potential on the rates of non-oxidative dissolution of the iron sulphides is not unique, but that nickel[23], lead[23], and zinc[3] sulphides show similar characteristics during non-oxidative dissolution.

The mechanism of dissolution proposed explains the occurrence of the induction period observed during the dissolution of pyrrhotite in acids. A quantity of hydrogen sulphide must be produced sufficient to remove residual amounts of oxidants, such as oxygen, and to provide the source of electrons for an anodic process, which, as discussed above, is necessary to promote cathodic reduction of the pyrrhotite. Control of the potential

during non-oxidative dissolution by the use of appropriate oxidizing or reducing agents can be envisaged as a technique for the selective leaching of one metal from a complex sulphide concentrate. Work on a variety of nickel sulphides is in progress with this aim in mind.

Acknowledgement

References

1. SUBRAMIAN, K. N., STRATIGAKOS, E. S., and JENNINGS, P. H. Hydrometallurgical processing of pyrrhotite. *Can. Metall. Q.*, vol. 11. 1972. pp. 425-434.
2. DUTRIZAC, J. E., and MACDONALD, R. J. C. Ferric ion as a leaching medium. *Minerals Sci. Engng*, vol. 6, no. 2. 1975. pp. 59-100.
3. SCOTT, P. D., and NICOL, M. J. The kinetics of the leaching of zinc sulphide concentrates in acidic solutions containing ferric sulphate. Johannesburg, National Institute for Metallurgy, *Report no.* 1949. Mar. 1978.
4. PARSONS, H. W., and INGRAHAM, T. R. The hydrogen sulphide route to sulphur recovery from base metal sulphides. Ottawa, Dept. of Energy, Mines and Resources, *Inf. Cir.* 1C242. Jun. 1970.
5. INGRAHAM, T. R., PARSONS, H. W., and CABRI, L. J. Leaching of pyrrhotite with hydrochloric acid. *Can. Metall. Q.*, vol. 11. 1972. pp. 407-411.
6. VAN WEERT, G., MAH, K., and PIRET, N. L. Hydrometallurgy. *Can. Min. Metall. Bull.*, 1974. pp. 97-103.
7. TEWARI, P. H., and CAMPBELL, A. B. Dissolution of iron sulphide (troilite) in aqueous sulphuric acid. *J. Phys. Chem., Ithaca*, vol. 80. 1976. pp. 1844-1848.
8. HENRY, B., LECUIRE, J., and BESSIERE, J. Electrochemical reduction of sulphides. Application to measurements of non-stoichiometry. *J. Electroanalyt. Chem.*, vol. 83. 1977. pp. 111-115.
9. JIBICKI, K. Acid decomposition reactions on compounds and minerals in the Fe–Ni–sulphide system. Thesis, University of British Columbia, May 1974.
10. SCOTT, S. D. Experimental methods in sulfide synthesis. *SULFIDE MINERALOGY*, vol. 1. Ribbe, P. H. (ed.) Washington, D.C., Mineralogical Society of America, 1974. pp. S-1 to S-38.
11. VETTER, K. J. Electrochemical kinetics – the theoretical and experimental aspects. New York, Academic Press, 1967.
12. DIGGLE, J. W. (ed). Oxides and oxide films. New York, Marcel Dekker, 1972.
13. PREWITT, C. T., and RAJAMANI, V. Electron interactions and chemical bonding in sulfides. *SULFIDE MINERALOGY*, vol. 1. Ribbe, P. H. (ed.). Washington, D.C., Mineralogical Society of America, 1974. pp. PR-1 to PR-41.
14. IOFA, Z. A., and PHAN LUONG CAM. Effect of hydrogen sulfide inhibitor and pH of the medium on the rate of electrochemical reactions and ion corrosion. *Zasch. Metal.*, vol. 10, no. 3. 1974. pp. 300-303.
15. ENGELL, H. J. Solution of oxides in dilute acid. The electrochemistry of ion crystals. *Z. Phys. Chem. (Frankfurt)*, vol. 8. 1956. pp. 158-181.
16. VERMILYEA, D. A. The dissolution of some compounds in aqueous media. *J. Electrochem. Soc.*, vol. 113. 1966. pp. 1067-1070.
17. VALVERDE, N. Investigations on the rate of dissolution of metal oxides in acidic solutions with additions or redox couples and complexing agents. *Ber. Bunsen-Gesell.*, Bb 80. 1976. pp. 333-340.
18. SILLEN, L. G. Stability constants of metal-ion complexes. London, Chemical Society, 1965. *Special Publication no.* 17.
19. LEVICH, V. G. Physicochemical hydrodynamics. 2nd edition. Englewood Cliffs, N.J., Prentice-Hall, 1962.
20. SCOTT, P. D., and NICOL, M. J. The kinetics and mechanism of the non-oxidative dissolution of some iron sulphides in aqueous acidic solutions. Johannesburg. National Institute for Metallurgy, *Report no.* 1858. Nov. 1976.
21. YOUNG, P. A. The stability of copper–iron sulphides. *Amdel Bull.*, no. 3. 1967. pp. 1-19.
22. MILLS, K. C. Thermodynamic data for inorganic sulphides, selenides, and tellurides. London, Butterworths, 1974.
23. SCOTT, P. D., and NICOL, M. J. The kinetics and mechanisms of the non-oxidative dissolution of metal sulphides. *TRENDS IN ELECTROCHEMISTRY. J. O'M. Bockris, D. A. J. Rand, and B. J. Welch (eds).* New York, Plenum Press, 1976.