

AN ELECTROCHEMICAL MODEL FOR THE LEACHING OF A SPHALERITE CONCENTRATE

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ABSTRACT

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The leaching of a sphaleritic flotation concentrate in an acidic ferric sulphate solution is described by an electrochemical charge-transfer model in which the mineral surface potential is approximated by the solution redox potential for the ferrous–ferric redox couple. The oxidation of ferrous ions by dissolved oxygen is described by a model consistent with previously reported models, and the leaching of the sphalerite in the presence of dissolved iron and oxygen is described by the simultaneous integration of the two individual rate expressions.

INTRODUCTION

The use of ferric ion as an intermediate oxidant in the oxygen pressure leaching of sphalerite has distinct advantages over the conventional roast-leach zinc process. Doyle et al. [1] compared these processes, and estimated that the capital requirements were up to 30% less for the pressure leaching process. A fundamental understanding of the dissolution behaviour of sphalerite would aid in the choice and design of such processes. The important phenomena occurring during the pressure leaching of sphalerite are the leaching mechanism, in which ferric ions are reduced to their ferrous state, and the kinetics associated with the oxidation of ferrous ions to their ferric state. The literature associated with these phenomena is now reviewed.

Review of the literature

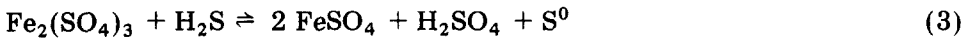
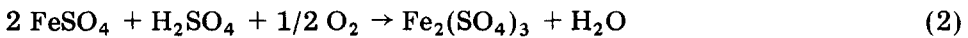
Leaching of sphalerite

Both Wadsworth [2] and Dutrizac and MacDonald [3] published papers in which the available literature was reviewed. Although much work on the dissolution of sphalerite was reported, most of it was to show that sphalerite could be readily dissolved under certain specific conditions, and fundamental

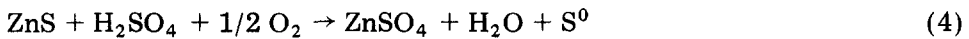
kinetic studies were rare. Wadsworth [2] commented that little attempt had been made to correlate the leaching behaviour with the ferric ion species in solution.

Dutrizac and MacDonald [3] reported that the leaching of sphalerite is controlled by the diffusion of ferric ion in solution, with an activation energy of about 24 kJ/mol, which is consistent with film-layer diffusion control. They also reported that the rate is proportional to the ferric ion concentration, and is not impeded by the formation of elemental sulphur.

Jan et al. [4] concluded that the rate-determining step was the reaction at the mineral surface, even though they observed an apparent activation energy of about 24 kJ/mol and a dependence on agitation. In the presence of ferric ion they proposed that the role of oxygen was to re-oxidise the ferrous ion reduced during the oxidation of hydrogen sulphide. This scheme was represented as:



The overall reaction was given as:



with reaction (3) as the rate-determining step.

Verbaan [5] leached a number of different types of sphalerites in the presence and absence of ferric ion in acid sulphate media. He attempted to explain the mechanism of dissolution in terms of Langmuir-Hinschelwood adsorption isotherms, and was relatively successful in the absence of ferric ion. He showed that the concentration of H_2S formed during reaction was dramatically reduced by the addition of ferric ion. He obtained conflicting evidence as to whether or not the elemental sulphur resulted in product-layer diffusion control.

Scott and Nicol [6] leached various different sphalerites and reported inconsistencies between the experimental observations and the predictions based on the assumption that the dissolution occurs by means of a non-oxidative attack. They suggested that the mechanism of dissolution in acidic ferric sulphate media could have been the result of direct oxidation. They concluded that the mechanism of dissolution was dependent on the type of sphalerite. Using a sphalerite-graphite electrode they indicated that the process responsible for the rate of dissolution occurred on the surface of the electrode, and that if direct oxidation had occurred, one would expect the potential at the zinc sulphide surface to lie in the region of +0.4 V with reference to the standard calomel electrode. They experienced difficulties performing this type of experiment due to the high resistivity of sphalerite.

It appears that more recent studies of the leaching of sphalerite, and other sulphide minerals (as reviewed by Dry [7]) favour the proposition that the leach dissolution reaction is electrochemical in nature. However, every general category of rate-controlling mechanism has been proposed, and the controlling step appears to be dependent on the composition of the sphalerite and the solution conditions chosen.

Although electrochemical mechanisms have been proposed [2,8], an electrochemical model describing the kinetics has not been tested. The object of this study is to apply an electrochemical leaching model to the dissolution of a sphaleritic concentrate.

A model for the oxidation of ferrous ion by oxygen

The role of oxygen in the ferric-ion leaching of sphalerite is to re-oxidise the ferrous ion in solution [4]. A review of the literature [9–11] suggested that the overall rate of the ferrous-ion oxidation reaction, eqn. (2), can be described by an equation of the form:

$$\frac{d[\text{Fe(III)}]}{dt} = k_0 [\text{Fe(III)}]^2 [\text{O}_2] / [\text{H}^+]^b \exp(-E_a/RT) \quad (5)$$

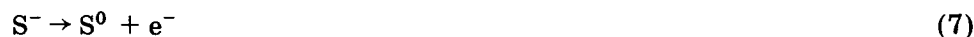
where k_0 is the overall (apparent) reaction rate constant in units such that the left hand side is measured in mol/l s, b is a constant, and E_a is the activation energy. The square brackets indicate concentration, and the other symbols have their usual significance.

Much discrepancy exists as to the actual reaction mechanism [11]. Despite this, the overall dependence presented above is used in this study to describe this reaction.

PROPOSED ELECTROCHEMICAL LEACHING MODEL

The dissolution of a particle by electrochemical attack is described in a way that is analogous to the electrochemical corrosion mechanism. The Butler–Volmer equation is used to describe electrochemical kinetics in terms of the current density and the surface potential [12]. A distinction can be made between an oxidative reaction, in which one or more of the solute species exist in different oxidation states in the solid and the solution phases, and a non-oxidative dissolution, in which the oxidation states in the solution and solid phases are identical.

Assuming that the kinetics proposed by Paul et al. [13] for the oxidative leaching of galena apply to sphalerite, then:



where S^- is some sulphur intermediate which allows two single electron-transfer steps to take place. In the high anodic surface-potential region the anodic dissolution current, i_A , is given by:

$$i_A = 2k_{6A} F \exp[(1 - \beta_{6A})F\Delta\phi/RT] \quad (8)$$

where $\Delta\phi$ is the mineral surface potential, β_{6A} is the symmetry factor or transfer coefficient from the Butler—Volmer equation for reaction (6), F is Faraday's constant, and k_{6A} is a rate constant. The other symbols have their usual significance.

There is evidence to suggest that in some cases the non-oxidative reaction is the first step in the reaction with ferric ions [6]. An equation of similar form to that of eqn. (8) is obtained by proposing non-oxidative kinetics with hydrogen sulphide as an intermediate. An electrochemical scheme involving a non-oxidative reaction step may be represented by:



with reaction (10) as the rate-controlling step. This would be consistent with the results of Jan et al. [4] and the fact that dissolution can be completely inhibited by an over-pressure of 2 atm of H_2S [2]. The anodic current is described by:

$$i_A = k_{10A} F [\text{H}_2\text{S}] \exp[(1 - \beta_{10A})F\Delta\phi/RT] \quad (11)$$

If reaction (10) is rate-controlling, then the concentration of the intermediate, H_2S , will remain constant, and eqn. (11) then has the same form as eqn. (8). Since the forms of the oxidative and non-oxidative expressions are analogous, these electrochemical mechanisms can not be distinguished from one another (in the high-potential region) on the basis of parameter fitting.

The presence of dissolved iron in solution contributes to the kinetics by the redox couple:



for which the net anodic current density is given by:

$$i_{\text{Fe}} = Fk_{12A} [\text{Fe}^{2+}] \exp[(1 - \beta_{12A})\Delta\phi F/RT] - Fk_{12C} [\text{Fe}^{3+}] \exp(-\beta_{12C} \Delta\phi F/RT) \quad (13)$$

where β_{12A} and β_{12C} refer to the anodic and cathodic transfer coefficients for reaction (12). Since no net current flows during leaching, the following expression is obtained:

$$0 = 2k_{6A} \exp[(1 - \beta_{6A})\Delta\phi F/RT] + k_{12A} [\text{Fe}^{2+}] \exp[(1 - \beta_{12A}) \Delta\phi F/RT] - k_{12C} [\text{Fe}^{3+}] \exp(-\beta_{12C} \Delta\phi F/RT) \quad (14)$$

This leads to three different reaction regimes, depending on the relative importance of the partial anodic currents for reactions (6), (7) and (10) [14].

Dry [7] leached low-grade base metal sulphide mattes in acidic ferric sulphate media, and observed that the redox potential of the solution, E_h , measured using a platinum electrode, followed the extent of reaction. When used as an approximation for the mineral surface potential, the E_h successfully predicted his results. He was also able to calculate the ferric-ferrous redox potential successfully by accounting for the following species in solution: FeHSO_4^{2+} , FeSO_4^+ , FeSO_4 , FeHSO_4^+ , and HSO_4^- , and by using the Debye-Huckel equation to determine the activity coefficients of the ferrous and ferric ions which form the redox couple.

Use of the solution redox potential as an estimation of the particle surface potential essentially assumes that the partial anodic current due to sphalerite leaching is negligible in comparison to that of the ferrous-ion oxidation, and that the kinetics of the ferrous-ion oxidation and the ferrous-ion reduction are symmetrical in this potential region.

Accounting for the formation of the ZnSO_4 complex in solution, as well as the previously mentioned complexes, and using a computational procedure similar to that used by Dry, the redox potential was calculated. This approximation was substituted directly in the leaching rate equation. The rate of reaction is expressed in terms of Faraday's law:

$$r = -\frac{1}{A} \frac{dM}{dt} = \frac{i_A}{2F} = -k_{1A} \exp[(1 - \beta_{6A})E_h F/RT] \quad (15)$$

where M is the amount of leachable material remaining in the particle cores (mol), and A is the available surface area (m^2). Applying the shrinking-core model [15], the leaching rate can be described by:

$$-\frac{dM}{dt} = KA_0(M/M_0)^{2/3} \exp(kE_h) \quad (16)$$

where A_0 is the total initial area available for reaction, M_0 is the initial value of M , $k = (1 - \beta_{10A})F/RT$, and K is a rate constant which includes the activation energy.

Leaching of sphalerite in the presence of both ferric ion and oxygen can be modelled as a dissolution reaction involving ferric ion, which reduces to form ferrous ion, and the oxidation of ferrous ion in solution by dissolved oxygen. Wadsworth [2] reports that in the absence of any iron species the oxygen reacts at the mineral surface to form intermediates, such as H_2O_2 and HO_2 in a series of single-electron charge-transfer steps. This results in a relatively slow discharge of oxygen due to the strength of the oxygen-oxygen double bond. Even though the presence of oxygen may act as a sphalerite oxidant, the partial current due to this reaction is likely to be small. Assuming that the oxygen does not itself contribute significantly to

the leach-reaction rate, the combined process could then be described by the simultaneous integration of the two individual rate equations, eqns. (5) and (16).

EXPERIMENTAL

Reagents

The sample was a sphaleritic flotation concentrate from the Gamsberg ore deposit in the Northern Cape of South Africa. The BET surface area was measured as $1471.0 \text{ m}^2/\text{kg}$, and the chemical composition is given in Table 1. A layer of zinc oxide, consisting of 8.3% of the total zinc, was present on the particle surface. Analytical-grade sulphuric acid, ferrous sulphate and ferric sulphate, and distilled water were used.

TABLE 1

Chemical composition of sphalerite sample

Element	Mass %	Element	Mass %
Zn	50.9	F	0.04
S	30.8	Cl	0.016
Fe	9.1	Al	0.4
Mn	2.5	Na	0.14
Pb	0.47	K	0.19
Cu	0.14	Mg	0.08
Cd	0.08	Ca	0.2
Co	0.014	Ni	0.015
SiO ₂	2.2		

Apparatus

The reactor used to leach the sphalerite in the absence of oxygen consisted of a 10-l glass vessel, with an impeller driven by a variable-speed motor. Probes permitted sampling, E_h measurement, gas supply, and a gas vent. The solution redox potential was measured with a platinum electrode, using an Ag/AgCl reference electrode. Ferrous-ion oxidation experiments, as well as leaching experiments in the presence of oxygen, were conducted in a stainless steel, stirred pressure reactor. Constant temperature and pressure were maintained throughout each experiment.

Procedure

For leaching without oxygen present, a solution of the desired composition was brought to temperature, and the sphalerite solids were added at the start ($t = 0$). Samples were taken at discrete time intervals and filtered,

and the zinc concentration determined by atomic absorption spectrometry.

For ferrous-ion oxidation experiments, the solution was heated to the correct temperature under a pressure of nitrogen, and at the start ($t = 0$) the nitrogen was purged and flushed by oxygen. The required pressure was then allowed to build up. Samples were taken at discrete time intervals, the ferric ion and total iron concentrations were determined by titration and atomic absorption spectrometry respectively.

RESULTS

Leaching of sphalerite by ferric ion without oxygen present

The rate of leaching in an inert nitrogen atmosphere was found to be independent of the degree of turbulence for both an increase in stirrer speed and the presence of baffles, indicating that liquid-film diffusion was not rate limiting under the leaching conditions selected. The rate was found to be proportional to the BET surface area for sphalerite samples ground to various degrees of fineness, and having surface areas of 702, 1471, and 1910 m²/kg respectively.

A quadratic polynomial was fitted to the concentration–time data, from which the initial rate of reaction is given by the coefficient of the first-order term in time.

Leaching tests were conducted to determine the effects of redox potential and temperature.

Effect of solution redox potential

Figure 1 represents a log–linear plot of the initial rate of reaction against the measured redox potential (Ag/AgCl reference electrode) and indicates a strong dependence on redox potential. The straight line indicates that eqn. (16) is valid at least during the initial stages of leaching.

The parameters K and k in eqn. (16) were estimated using an ordinary least-squares criterion, in which the sum of squared differences between the measured concentration data and the model fit was minimised. The numerical solution of eqn. (16) incorporated the calculation of the redox potential.

A contour diagram of the sum-of-squares surface illustrated a valley of almost equal depth in a banana shape, and a choice of any set of parameters along the bottom of the valley would have yielded a fit that is almost as good as any other. However, there was a shallow minimum along the bottom of the valley, which indicated a unique minimum, and a slight linear dependence of the sensitivity coefficients (the partial derivatives of the model equation with respect to the model parameters). This indicated that either the model was not very good at describing the experimental data, or that the data had not been selected over a wide enough redox-potential range. A more common example of this type of parameter-fitting problem is experienced when a poor estimate of the activation energy is obtained from rate

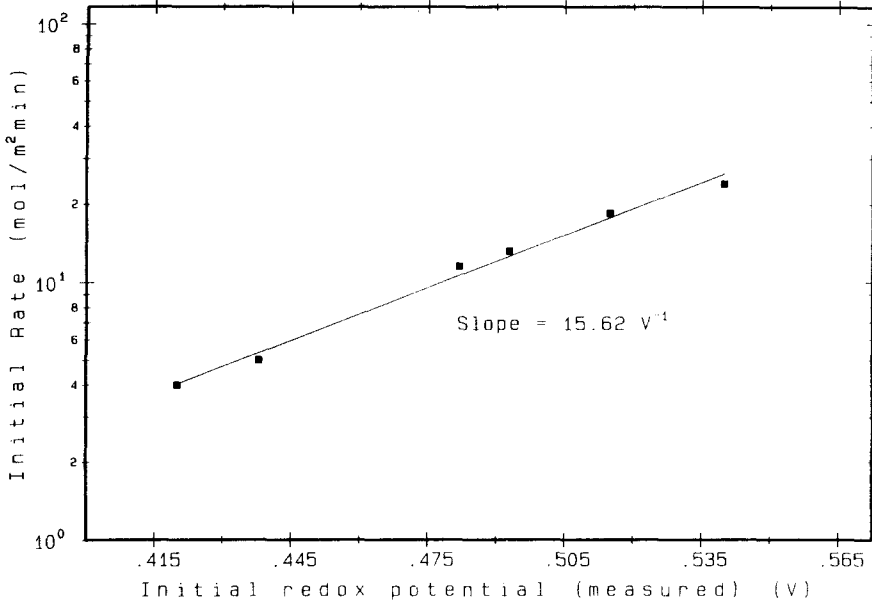


Fig. 1. Initial rate of leaching against the measured redox potential (Ag/AgCl reference) for Gamsberg sphalerite. Conditions: 65°C, 0.038 M Fe(II), 0.1 M H₂SO₄, 1 kg/m³ solids, 1471 m²/kg.

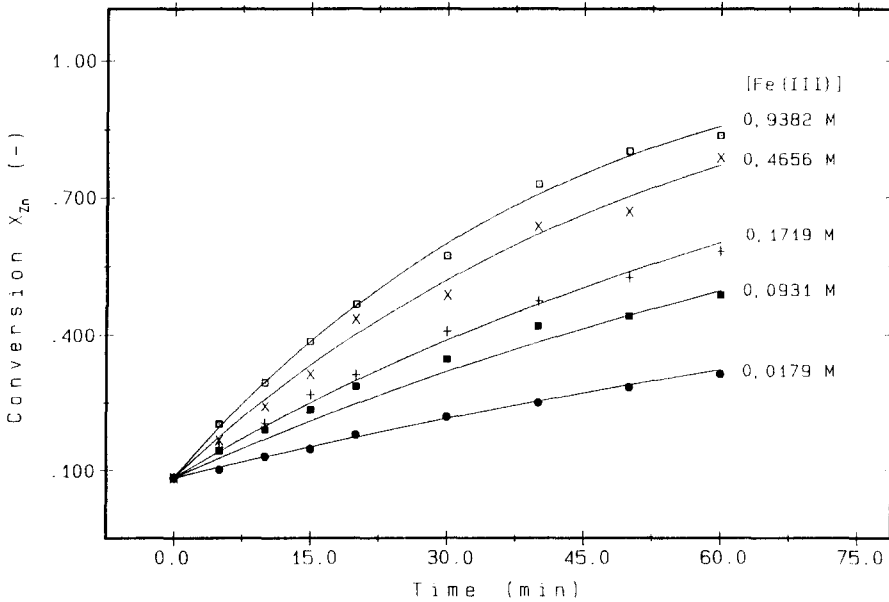


Fig. 2. Equation (15) fitted to Gamsberg leaching data for parameters at the minimum sum of squares, for increasing ferric ion concentrations. Conditions: 65°C, 0.038 M Fe(II), 0.1 M H₂SO₄, 1 kg/m³ solids, 1471 m²/kg.

data representing too small a temperature range. The more likely event for this model is that the range of initial redox potentials is not large enough, although the measured redox potential ranged between 420 mV and 540 mV Ag/AgCl.

The values of the parameters at the best fit at 65°C are:

$$K = 3.27 \times 10^{-12} \text{ mol/m}^2 \text{ s}$$

$$k = 17.3 \text{ V}^{-1}$$

The slope of the straight line from Fig. 1 has a value of 15.6 V^{-1} , which corresponds well to the best-fit value of k of 17.3 V^{-1} .

The parameter fit for the runs plotted on Fig. 1 is illustrated in Fig. 2. The points represent the measured data and the lines were calculated by the model using the best-fit parameters. The positive initial conversion represents the amount of zinc-oxide layer leached rapidly before sphalerite leaching occurs. This diagram illustrates that the model, despite the problems mentioned above, does fit the experimental results well.

Effect of temperature

To model the effect of temperature, the value of β_{10A} in the parameter k was assumed to be constant within the temperature range studied, 25 to 85°C, and using the definition of k , the value of k at temperatures other than 65°C was calculated. The rate constant, K , was then fitted to each of the leach runs at 25, 45 and 85°C respectively, to obtain the dependence of the rate on temperature. The fitted and experimental curves are shown in Fig. 3. The data for the reaction at 85°C appear to be inhibited at higher conversions. This is probably due to sulphur blocking the pores [2], and thus slowing the reaction.

Figure 4 represents the Arrhenius diagram for these rate constants, from which an activation energy of 79.4 kJ/mol and a pre-exponential constant of 6.505 mol/m²s was obtained.

The leaching of the Gamsberg sphalerite is therefore described by the following expression:

$$-\frac{dM}{dt} = 6.505 \exp(-79.4/RT) A_0 (M/M_0)^{2/3} \exp(17.3E_h) \quad (17)$$

Ferrous-ion oxidation by dissolved oxygen

The ferrous-ion oxidation reaction was monitored under different conditions of temperature, acid concentration, total iron concentration, and oxygen partial pressure. At constant $[O_2]$, $[H^+]$ and temperature, eqn. (5) is a second-order differential equation in $[Fe(II)]$. A plot of $1/[Fe(II)]$ against time should be a straight line if this is a second-order reaction. Typical experimental results are presented in Fig. 5, which illustrates that the reac-

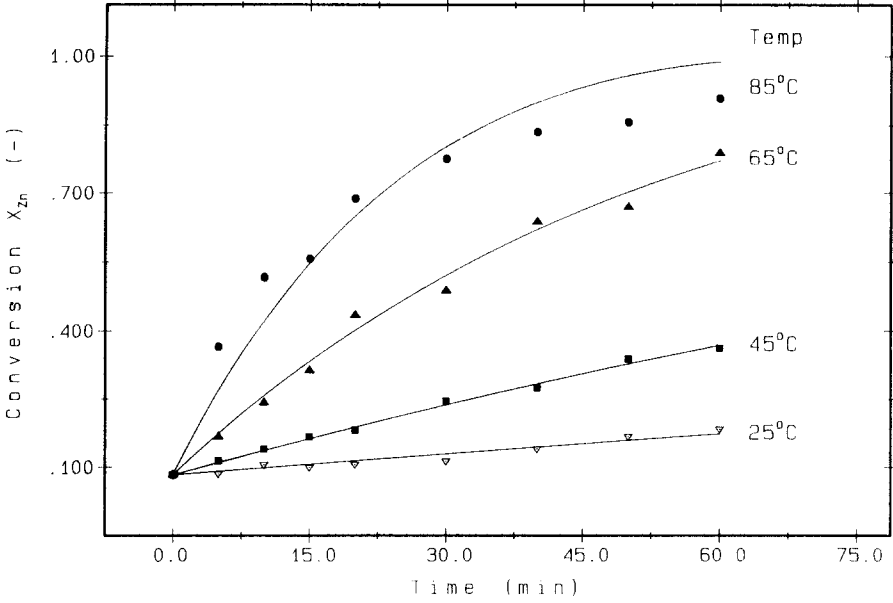


Fig. 3. Rate constant K fitted to sphalerite leaching results at different temperatures. Conditions: 0.45 M Fe(III) , 0.04 M Fe(II) , $0.1\text{ M H}_2\text{SO}_4$, 1 kg/m^3 solids, $1471\text{ m}^2/\text{kg}$.

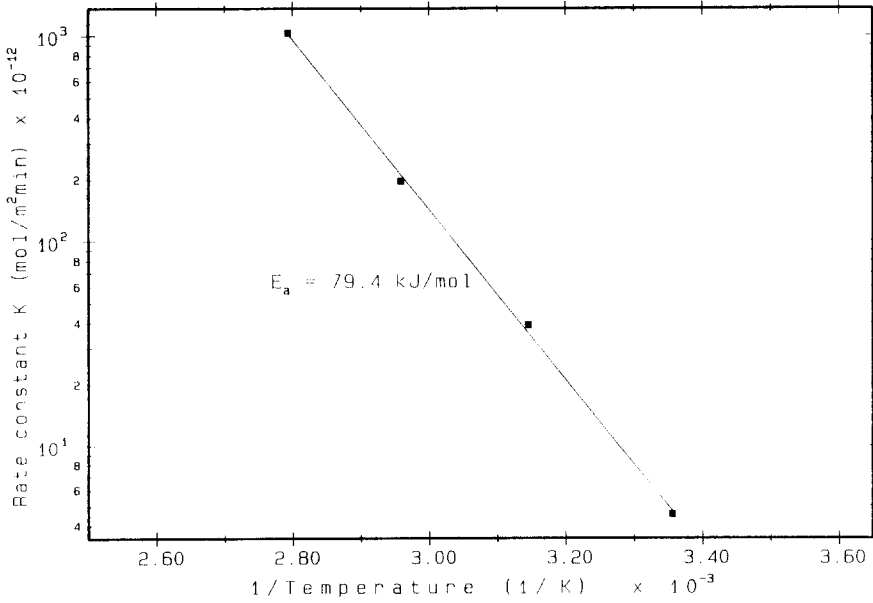


Fig. 4. Arrhenius diagram for Gamsberg sphalerite. Conditions: 0.45 M Fe(III) , $0.1\text{ M H}_2\text{SO}_4$, 1 kg/m^3 solids, $1471\text{ m}^2/\text{kg}$.

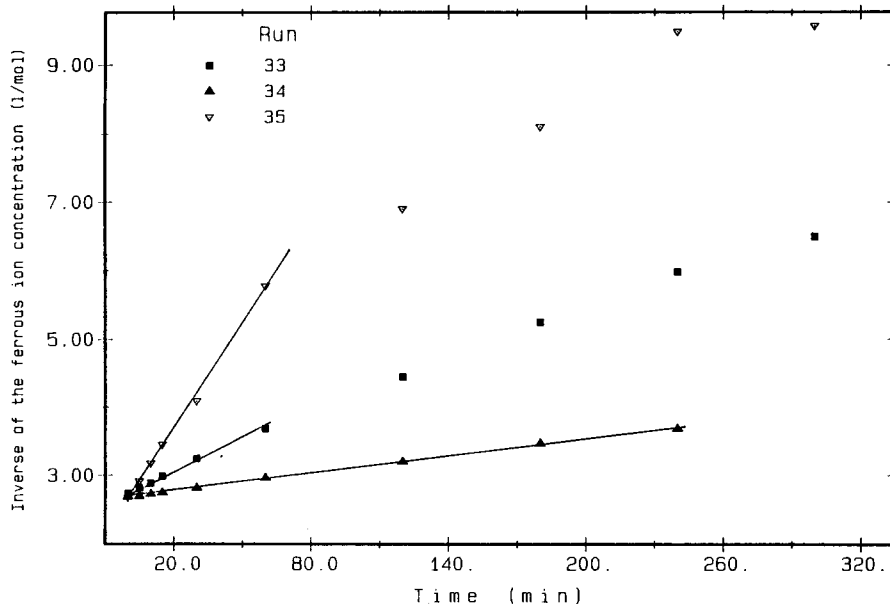


Fig. 5. Second-order plot for ferrous-ion oxidation indicating the deviance from second-order reaction. Conditions: 21.75 kg/m³ total iron, 0.25 M H₂SO₄, 450 min⁻¹. Run 33: 343 K, 4.5 bar O₂; Run 34: 333 K, 1 bar O₂; Run 35: 353 K, 3 bar O₂.

tion deviates from the expected second-order dependence at higher levels of conversion. This deviation from second-order kinetics has been reported previously [10,11].

Effect of hydrogen ion

The concentration of the hydrogen ion, for the determination of the dependence of the rate on hydrogen ion, was calculated by the same procedure used to calculate the redox potential described previously. Figure 6 illustrates that the rate is inversely proportional to the hydrogen ion concentration to the power 0.36. Keenan [16] reported a similar figure of 0.35, and Mathews and Robins [9] reported a value of 0.25. This discrepancy may be due to the way in which Mathews and Robins defined [H⁺], that is, as calculated from the pH measured at ambient temperature and not the temperature of reaction.

Effect of temperature

An Arrhenius plot showing the effect of temperature for this reaction is presented in Fig. 7, which gives a value of 68.6 kJ/mol for the activation energy. Therefore, the rate of ferrous-ion oxidation in the range 0–11 kg/m³ Fe(III), where the rate is second order in Fe(II), is described by:

$$\frac{d[\text{Fe(III)}]}{dt} = 2.08 \times 10^9 [\text{Fe(II)}]^2 [\text{O}_2] / [\text{H}^+]^{0.35} \exp(-68.6/RT) \quad (18)$$

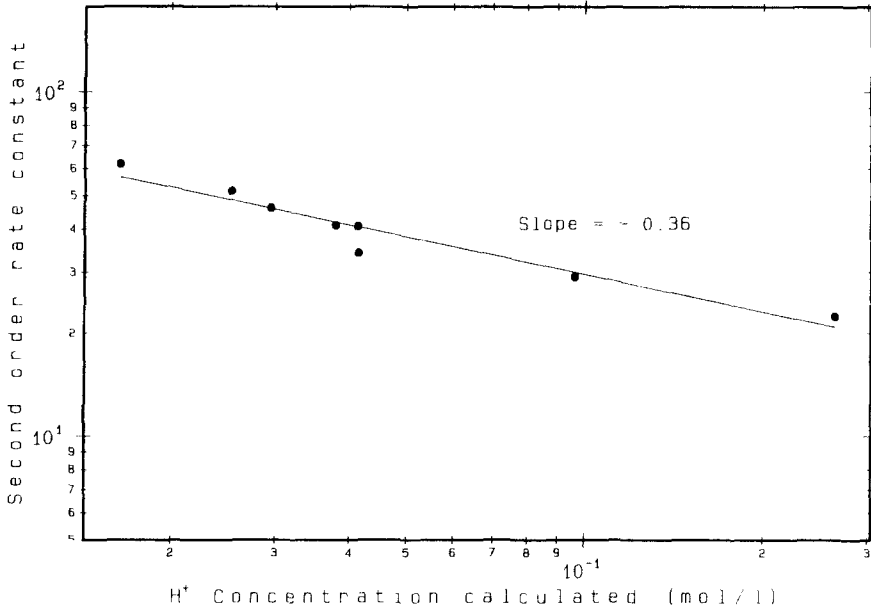


Fig. 6. Dependence of the Fe(II) oxidation rate on $[H^+]$ for different oxidation runs. Units of the rate constant are such that the rate of reaction is measured in $\text{mol l}^{-1} \text{min}^{-1}$.

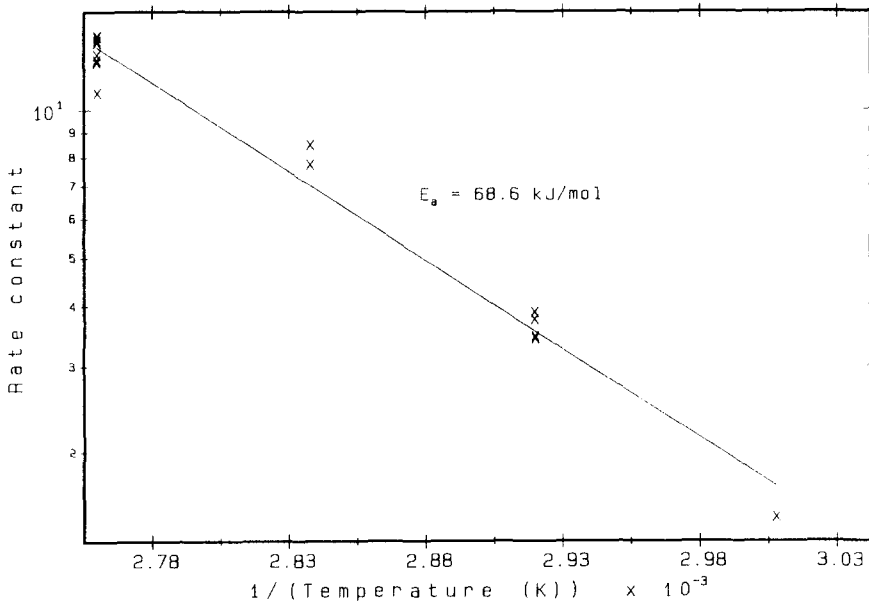


Fig. 7. Arrhenius plot of Fe(II) oxidation rate for different oxidation runs. Units of the rate constant are such that the rate of reaction is measured in $\text{mol l}^{-1} \text{min}^{-1}$.

TABLE 2

Comparison of ferrous ion oxidation kinetic expressions

Authors	Kinetic equation for $d[\text{Fe(III)}]dt$	E_a (kJ/mol)
Huffman & Davidson [17]	$k_8[\text{Fe(II)}]p(\text{O}_2) + k_7[\text{Fe(II)}]^2 p(\text{O}_2)$	67.9
Keenan [16]	$k[\text{Fe(II)}]^2 [\text{O}_2]^{1.04} [\text{H}^+]^{-0.35}$	94.1
Mathews & Robins [9]	$k[\text{Fe(II)}]^{1.84} [\text{O}_2]^{1.07} [\text{H}^+]^{-0.25}$	73.7
Chmielewski & Charewicz [10]	$k[\text{Fe(II)}]^2 p(\text{O}_2)$	56.9
Iwai, Majima & Awakura [11]	$k[\text{Fe}^{2+}]^2 p(\text{O}_2) + [\text{SO}_4^{2-}][\text{Fe}^{2+}]^2 p(\text{O}_2)$	51.6
This study	$k[\text{Fe(II)}]^2 [\text{O}_2][\text{H}^+]^{-0.36}$	68.6

This rate expression is compared in Table 2 with those reported previously.

Leaching of sphalerite in the presence of ferric ion and oxygen

Simultaneous integration of eqns. (17) and (18) was used directly to predict the data presented by Verbaan [8] for sphalerite from the same ore deposit leached in the presence of oxygen and ferric ion. These results are presented in Fig. 8, which indicates a good fit over the entire curve, in which the ferric ion concentration and associated redox potential change

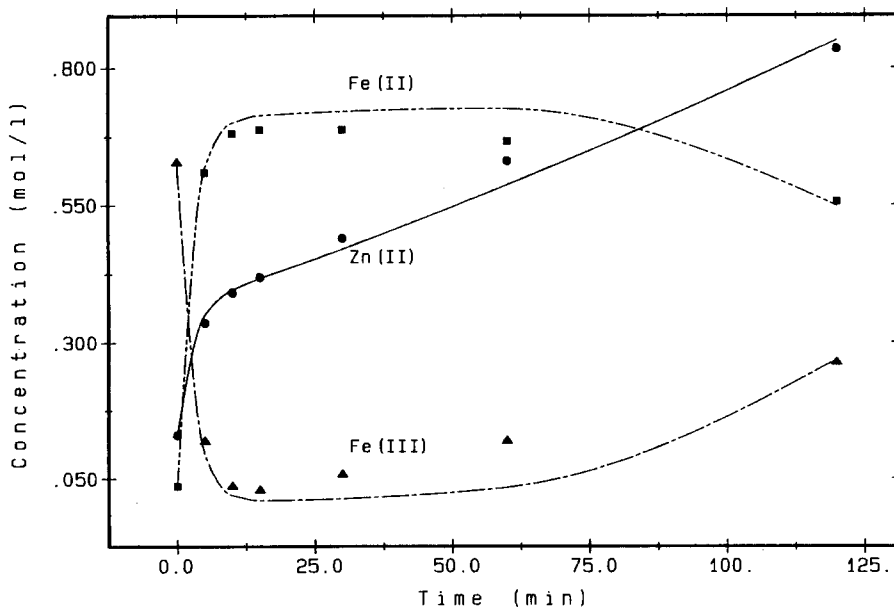


Fig. 8. Prediction of the leaching of Gamsberg sphalerite in the presence of oxygen, for Zn(II), Fe(II), and Fe(III). Conditions: 90°C, 116 kPa $p(\text{O}_2)$, 35 kg/m³ Fe, 200 kg/m³ solids, 1471 m²/kg. Points are measured, and lines calculated by eqns. (17) and (18).

dramatically. Despite the availability of data for only one experimental run, this is a satisfactory result, confirming the electrochemical proposition, and the ferrous-ion oxidation role played by the oxygen.

CONCLUSIONS

The leaching characteristics of a sphaleritic flotation concentrate have been described by an electrochemical reaction occurring at the surface of the particle, in which the mineral surface potential is dominated by the ferrous-ferrous redox couple. The oxidation of ferrous ion by oxygen was found to be second order in ferrous ion concentration, first order in oxygen concentration, and inversely proportional to the hydrogen ion concentration to the power 0.36. The simultaneous integration of the ferrous-ion oxidation rate equation and the sphalerite leach rate equation described the leaching results in the presence of oxygen.

ACKNOWLEDGEMENTS

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