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SULPHURIC ACID, OXYGEN PRESSURE LEACHING OF A BASE-METAL SULPHIDE ORE

THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

AT THE

SCHOOL OF ENGINEERING
UNIVERSITY OF AUCKLAND,
NEW ZEALAND

BY

G. J. TEGG

1975
To Grandad and Grandma Tegg
ABSTRACT

The investigation reported in this thesis was the initial phase of an experimental programme initiated in 1969 at Auckland University to study the application of hydrometallurgical techniques to the recovery of base-metals from New Zealand sulphide ores. The principal aim was to design and build a suitable autoclave for conducting pressure leaching experiments and with this to evaluate the sulphuric acid leaching kinetics of a bulk lead-zinc-copper-iron concentrate, under a range of experimental conditions that might have process potential.

The effects of temperature, oxygen partial pressure, initial acid concentration, excess or deficiency of acid, initial particulate surface area, agitation, catalyst additions (cupric and ferric sulphate) and time on the rate of leaching of sphalerite, galena, chalcopyrite and pyrite were investigated.

Galena was found to dissolve with the formation of hydrogen sulphide and lead sulphate. The hydrogen sulphide inhibited the dissolution of both sphalerite and chalcopyrite but not galena. The effect of experimental variables on the rate of oxidation of hydrogen sulphide to sulphur are reported. This reaction was found to take place on the surface of sulphide particles between adsorbed species and the rate determining step was the oxidation of adsorbed ferrous ions by dissolved oxygen. Scanning electron micrographs are presented which show that the lead sulphate forms as a non-coherent crystalline layer on the galena surface. Conversion reaction kinetics were consistent with rate control by liquid phase diffusion in the pores of this layer. The rate of conversion was independent of oxygen partial pressure, initial acid concentration and hydrodynamics but was directly proportional to the initial particulate surface area. A very low temperature dependence was exhibited.

Sphalerite was found to exhibit linear leaching kinetics up to extractions of eighty percent after reaction inhibiting hydrogen sulphide had been removed by oxidation. The rate of linear leaching was directly proportional to oxygen partial pressure and surface area but independent of acid concentration and hydrodynamics. The ultimate sulphide oxidation products were elemental sulphur and sulphate ions with the former usually accounting for over ninety percent of the reacted sulphide sulphur. The dissolution reaction producing sulphur was electrochemical in nature and the cathodic reaction involving the discharge of oxygen was found to be rate controlling. Soluble iron catalysed this reaction and a mechanism is proposed that involves the chemisorption of ferrous ions and dissolved oxygen at the mineral surface. Scanning electron micrographs are presented which show that certain crystal faces are preferentially attacked and that dissolution occurs by a pitting action. They also explain why sphalerite dissolution is severely curtailed at temperatures exceeding the melting point of sulphur. For extractions exceeding eighty percent the dissolution rate decreased rapidly due to a decrease in cathodic area and to the agglomeration of residues.

Chalcopyrite and pyrite dissolved much more slowly than sphalerite and were extensively coated by elemental sulphur because the oxidation of hydrogen sulphide was catalysed on their surfaces.

Some practical implications of the leaching results are discussed.
ACKNOWLEDGEMENTS

I would like to express my grateful thanks to the following:

The Consolidated Silver Mining Co. for providing finance for the design and construction of the autoclave and in particular Mr D. Alexander, a Director of the company for assistance in the autoclave design.

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<td>A</td>
<td>Particulate surface area/unit mass</td>
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<td>$A_0$, $A_1$</td>
<td>Initial particulate surface area/unit mass</td>
</tr>
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<td>a</td>
<td>Activity</td>
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<tr>
<td>C</td>
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<tr>
<td>D</td>
<td>Diffusivity</td>
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<td>$d_p$</td>
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<td>$E_a$</td>
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<td>H</td>
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<td>K</td>
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</tr>
<tr>
<td>k</td>
<td>Constant</td>
</tr>
<tr>
<td>$k_l$</td>
<td>Rate constant</td>
</tr>
<tr>
<td>$k_p$</td>
<td>Linear rate constant</td>
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<td>L</td>
<td>Parabolic rate constant</td>
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<td>M, Me</td>
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<td>M</td>
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<td>$M_i$</td>
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<td>$M_{\text{out}}$</td>
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<td>$M_{\text{tot}}$</td>
<td>Molecular weight</td>
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<tr>
<td>m</td>
<td>Mass</td>
</tr>
<tr>
<td>N</td>
<td>Number of molecules</td>
</tr>
<tr>
<td>n</td>
<td>An integer</td>
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<tr>
<td>P</td>
<td>Reaction product</td>
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<tr>
<td>$P_b$</td>
<td>Pressure</td>
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<td>$P_g$</td>
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\( P_g \)  \( p \)  \( P_{H_2O} \)  \( P_{H_2S} \)  \( P_{O_2} \)  \( R \)  \( r \)  \( r_0 \)  \( S_{OX} \)  \( T \)  \( t \)  \( V \)  \( V' \)  \( V_f \)  \( V_I \)  \( V_0 \)  \( v \)  \( W \)  \( W' \)  \( W_R \)  \( W_X \)  \( W_Y \)  \( W_Z \)  \( W_M \)  \( x \)  \( \alpha \)  \( \alpha_t \)  \( y \)  \( \rho \)  \( \delta \)  \( \Delta \)  \( \varepsilon \)  \( \theta \)  \( \omega \)  \( \phi \)
gauge pressure
Partial pressure
Partial pressure of water
Partial pressure of hydrogen sulphide
Partial pressure of oxygen
Universal gas constant
Reactant species
Particle radius
Initial particle radius
Surface oxidation, a kinetic parameter
Temperature
Time
Volume
Effective initial volume of leachant
Potential barrier
Initial reaction velocity
Initial particulate volume
Initial decrease in the volume of gas in the sample line
Weight of ore charged to the sample introducer
Weight of ore introduced to the leachant
Total weight of residue
Weight of residue suspended in the solution at the completion of leaching
Weight of residue adhering to the baffles at the completion of leaching
Weight of residue remaining in the sample introducer
Weight percent of metal M in the ore or residue
Thickness of a product layer on a mineral substrate
Electron affinity of an adatom
Fraction extracted after time \( t \)
Density
Thickness of the hydrodynamic boundary layer, defined by equation (18)
Difference
E.m. f.
Fraction of surface covered, defined by equation (53)
Agitator rotation velocity
Work function
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New Zealand has until recently been totally dependent on overseas markets for the supply of metals and it has always appeared that this condition would continue to prevail because of a lack of economic mineral deposits. However, with rapidly diminishing world reserves of easily extracted metals new methods are being found to economically treat more complex and lower grade deposits. The resultant technology is exemplified in the Glenbrook Steel Mill, constructed in 1968, which utilizes New Zealand's large deposits of titaniferous iron sand. In addition, about five years ago, there was a large upsurge in the amount of money and effort spent on mineral prospecting in New Zealand. This was mainly due to a buoyant economy and Government support for the recommendations of the Minerals Committee of the National Development Conference (1969). A variety of overseas and local companies have been involved and at least one new deposit of potentially exploitable iron ore has been discovered at Mt George in South Westland [1]. While reports indicate that it is unlikely that large deposits of base-metals remain undiscovered it has long been known that significant amounts of zinc, lead and copper sulphides are associated with the gold and silver bearing reefs of the old Hauraki goldfield. These lodes, which are scattered over an area of some 250 square kilometers, assay up to 20% base-metal but more generally have a grade of between 3 and 5%. Several unsuccessful attempts have been made over the years to smelt these ores - but for the silver and gold content rather than the base-metals. The geology and the working history of these deposits has been thoroughly described by Williams [2]. Two of the deposits were being worked when this study was begun in 1970 - the Tui mine at Te Aroha, which was producing zinc and lead-copper flotation concentrates and the Maratoto mine in the Maratoto valley, about 25 kilometers distant, which was producing a silver flotation concentrate. All three concentrates were shipped overseas for smelting but the mines have since ceased operations - the first when a favourable supply contract was not renewed and the latter because of a decline in ore grades.

Given New Zealand's dependence on overseas markets there is a strong economic incentive to smelt these lead-zinc-copper-silver ores in this country. However, several difficulties arise with conventional methods.

1. The deposits are not individually large enough to economically support a conventional smelter.
2. The close association of pyrite with sphalerite and galena makes differential flotation difficult.
3. The deposits (excluding the Tui ore) are generally low grade and disseminated.

Recent overseas developments in the field of hydrometallurgy hold promise of overcoming these difficulties and it was for this reason that research was begun in 1970 to examine the potential application of these new techniques to the extraction of New Zealand base-metal ores. The advantages of a hydrometallurgical process appeared to be the following:

1. Bulk concentrates can be handled, obviating the need for differential flotation.
2. In acid processes it is possible to recover most of the sulphide sulphur in the elemental form, thereby avoiding sulphur dioxide pollution and recovery problems and obviating the need for a sulphuric acid plant on the site.
3. Providing suitable controls are built in, the hydrometallurgical plant can accept a wider range of feed compositions providing flexibility in dealing with ores from different deposits.
(4) Costing studies of processes that have reached pilot-plant scale show that they compare more than favourably with existing technology, especially at the low tonnage end of the scale [3].

A hydrometallurgical process for sulphide ores can be broadly divided into three consecutive steps.

(1) Oxidative Leaching - Most of the metal values are taken into solution while the sulphide sulphur is oxidised to elemental sulphur or further to sulphate. Some preliminary separation of metal values can take place at this point if either a mineral (pyrite under some conditions) or an oxidation product (lead sulphate) is insoluble.

(2) Solution Purification - Minor impurities are removed by precipitation, solvent extraction, hydrolysis etc to provide solutions suitable for metal recovery.

(3) Metal Reduction - The metal is produced from the purified leach solution by electrolysis, hydrogen reduction etc. When two major metal values are soluble in the leach these may be recovered by successive reductions or, if selectivity is not adequate, by solvent extraction, precipitation and redisolution, or some other method.

The rate of the leaching step is of primary importance because it determines the commercial potential of a process. From the considerable volume of published work on the leaching of sulphide ores it is clear that the dissolution behaviour of ores from different sources can differ markedly and that many kinetic factors are not yet fully understood (§ 3.8). Furthermore, only two studies have been conducted on bulk lead-zinc concentrates (§ 3.6.3) and the results of one of these was published three years after the present project was initiated. It was therefore decided to examine the leaching behaviour of a bulk New Zealand concentrate and it remained to choose the potentially most effective leachant - oxidant system.

Forward and Warren [4] pointed out that most of the leachants proposed in the literature are unlikely to lead to full scale plant processes because of difficulties with chemistry, corrosion and the costs of sophisticated reagents. For example, of the acid systems that have been proposed, ferric sulphate leaves an equivalent amount of ferrous sulphate in solution and in addition starts to hydrolyse at higher pH's; chlorides and chlorine are expensive, produce extremely corrosive solutions and introduce an extra anion into solution; nitric acid and nitrates are expensive and reactions with sulphides are unpredictable producing various nitrogen oxides which makes regeneration of the leachant very difficult. Sulphuric acid in comparison is a cheap reagent and is simply regenerated in the metal reduction step. When used with oxygen or air as oxidant it has the further advantage of not introducing any extra anions to the solution.

Several basic systems have also been proposed. Caustic soda which causes caustic embrittlement in steels at elevated temperatures, is limited in use to those metals which form soluble complexes. Ammonia, which forms soluble amines with a number of important metals, combined with air under pressure as the oxidant has been successfully proven as a leachant by Sherritt Gordon Mines Ltd at Fort Saskatchewan, Alberta, for the production of nickel, cobalt and copper. Laboratory studies by this company indicate that zinc, copper and lead sulphides can be treated in the same way but the problem remains of dealing with the sulphide oxidised in the leach. Sherritt Gordon produce ammonium sulphate fertilizer, but unless a large market exists for this commodity, the economics of such a plant would be adversely affected. Ammonia is also an expensive reagent to produce although it can be regenerated.

The two most practical methods, and certainly the best researched, are sulphuric acid and ammonia, oxygen pressure leaching. The choice of sulphuric acid was based on the following considerations.

(1) Sulphuric acid is the cheaper reagent.

(2) Published studies indicate that the chemistry of sulphuric acid processes are comparatively simple.

(3) Regeneration of sulphuric acid is straightforward.
(4) In common with other acid systems, sulphur may be recovered in the elemental form with consequently lower oxygen consumption than basic systems where the oxidation product is sulphate.

(5) The handling of toxic gases is avoided. (c.f. ammonia, nitrogen oxides and chlorine.)

(6) Disposal of sulphate is circumvented.

The ore chosen for leaching tests was hand-picked from the stope of the Tui mine. Flotation concentrates were not used because contamination by flotation chemicals could introduce additional experimental variables. Base-metal assays of the ore were between 60 and 65% and the principal minerals were sphalerite, galena, pyrite and chalcopyrite in a quartz gangue. Other minerals were present in very small quantities (< 0.5%).

The literature review (Chapter 3) shows that published investigations of acid pressure leaching can be divided into two broad categories. The first category, containing the bulk of the literature output, includes work of a qualitative nature directed toward establishing an optimum balance between the various leaching parameters with process development in mind. The second category contains kinetic investigations undertaken to yield explicit rate and mechanistic data. Both approaches have deficiencies.

Kinetic investigations are usually conducted on pure or synthetic minerals under operating conditions well outside the practical range so that rate equations have strictly limited applicability. Data on the reaction mechanisms may have some use in understanding leaching behaviour but neither the dissolution reactions nor the mechanisms are necessarily the same in real concentrates. For example, kinetic investigations are traditionally conducted at very low pulp densities (= 1 g l⁻¹) compared with practical requirements of between 100 and 300 g l⁻¹. The oxygen demand in the latter case is so much greater that the rate of oxygen absorption or liquid phase transport may be rate determining, a fact which would not be discovered in a kinetic experiment.

Process oriented investigations make kinetic characterization extremely difficult because they introduce additional variables such as extra minerals. For this reason published investigations of this type have presented qualitative results only and few theories have been advanced to explain the observed leaching behaviour.

An attempt has been made in this research to incorporate the best features of the two categories delineated above. Specifically the research aims were as follows:

(i) To establish the stoichiometry of the leaching reactions by analysing the reaction products and employing material balances.

(ii) To investigate the effects of changes in temperature, oxygen partial pressure, initial acid concentration, acid/ore mol ratio, agitation, initial particle size (surface area), reactor material and catalyst additions on the rate and nature of the dissolution reactions.

(iii) To examine the partly leached minerals by scanning electron microscopy to investigate the form of attack on the minerals and the nature of insoluble product formation. No evidence of this kind has been presented before in support of theories of sphalerite and galena leaching.

In summary, the general aim of the research was to examine the sulphuric acid, oxygen pressure leaching of a bulk lead-zinc concentrate under a range of operating conditions that might have practical implications in process development. In particular it was desired to investigate and quantify where possible the leaching kinetics of the individual minerals present in the ore under conditions that would promote the production of elemental sulphur.
2. BASIC THEORY

2.1 INTRODUCTION

The theory of leaching reactions can be considered under the headings of thermodynamics, which gives an assessment of equilibrium conditions and the distance of the initial process conditions from equilibrium; and kinetics, which gives an assessment of the reaction rates and mechanisms by which the solids and solutions approach equilibrium. Thermodynamic considerations are generally of secondary importance because conditions are chosen so that dissolution of the metal values is accompanied by large negative free energy changes.

2.2 THERMODYNAMICS

The thermodynamics of leaching reactions can be summarised in the form of potential ($E_H$) - pH diagrams which describe solution composition or solid phase stability as a function of two variables - single electrode (reduction) potential and pH. The diagram is constructed by fixing all other variables at chosen values. However it is possible to depict solution composition in one variable, such as metal ion concentration, by contour lines on the diagram.

The condensation of thermodynamic data on such diagrams was first introduced by Pourbaix [5]. In a later book edited by him [6] $E_H$ - pH diagrams are presented for most metal-water systems at 25°C. The lines on the diagram are constructed from consideration of equilibria of the form

$$ bB + cC + mH^+ + ne^- \rightleftharpoons xX + yY $$

for which the free energy change is given by

$$ \Delta G_{T,P} = \Delta G^o + RT \ln K \quad \ldots (2) $$

where

$$ K = \frac{a_x^m a_y^n}{a_B^m a_C^n a_{H^+}^n} \quad \ldots (3) $$

The e.m.f. is calculated from the equation

$$ \Delta G_{T,P} = -nFc \quad \ldots (4) $$

so that

$$ e = e^o - \frac{RT}{nF} \ln K \quad \ldots (5) $$

i.e.

$$ e = e^o - \frac{2.3 \text{ RT}}{F} \left( \frac{m}{n} \right) \text{ pH} - \frac{2.3 \text{ RT}}{nF} \log \frac{a_x^m a_y^n}{a_B^m a_C^n} $$
By choosing values of the activities of the species B, C, X and Y this equation can be plotted as a straight line of slope $\frac{2.3 \text{RT}}{m}$. At 298°K the value of $\frac{2.3 \text{RT}}{m}$ is 0.0591 volt so that the slope is always 0.0591 $\frac{m}{n}$.

When $m = 0$ the line is horizontal (i.e. hydrogen ions do not take part in the reaction) and when $n = 0$ the line is vertical and there is no valency change in the reaction. In the latter case it is not possible to use equation (5) to locate the position of the line and this must be done by employing equation (2) in the following manner. At equilibrium,

$$\Delta G^o = - RT \ln \frac{a^x_B a^y_C}{a^m_H}$$

$$= - 2.3 \text{RT} (\text{mpH}) - 2.3 \text{RT} \log \frac{a^x_B a^y_C}{a^m_H}$$

$$\therefore \quad \text{pH} = - \frac{1}{m} \left( \frac{\Delta G^o}{2.3 \text{RT}} + \log \frac{a^x_B a^y_C}{a^m_H} \right)$$

which gives the position of the line for chosen values of the activities.

$E_h$ - pH diagrams constructed in this manner have become widely used in the study of metal corrosion, electrochemistry and geochemistry. Their application to the study of hydrometallurgical systems was first noted by Halpern [7] in 1957 but their use is limited by the paucity of data on the thermodynamic properties of ions in solution at temperatures above 25°C. The lines on an $E_h$ - pH diagram shift at higher temperatures due to the temperature dependence of $\Delta G^o$ and $e^o$, so that estimates must be made when constructing many of the diagrams of hydrometallurgical interest. The temperature dependence is explicitly related in the Gibbs-Helmholtz equation

$$d \left( \frac{\Delta G^o}{T} \right) = - \frac{\Delta H^o}{T^2}$$

or

$$d(\Delta G^o/T) \quad d(T/1) = - \Delta H^o$$

whence

$$d(e^o/T) \quad d(T/1) = - \frac{\Delta H^o}{nF}$$

These equations may be integrated if $\Delta H^o$ is known as a function of temperature. In the simplest case if it is assumed that $\Delta H \neq f(T)$ equation (9) may be integrated thus:

$$\Delta G^o = \Delta G^o_{298} \left( \frac{T}{298} \right) + \Delta H^o_{298} \left( 1 - \frac{T}{298} \right)$$

According to Peters [8] equation (11) has some usefulness up to 60°C. At higher temperatures special estimation techniques must be employed. One that has been used by various authors [9 - 14] for temperatures up to 300°C is the so called 'entropy correspondence principle' described by Criss and Cobble [15].

Three examples of $E_h$ - pH diagrams relevant to this study are shown in Figs. 1 to 3. Fig. 1 shows the simple S - H$_2$O system calculated at 25°C and unit activity of dissolved sulphur species. An important feature is the zone of elemental sulphur stability for pH < 7. This is relevant in the acid leaching of sulphide minerals because elemental sulphur is a desirable product. Firstly, it conveniently reports in the leach residue from which it may be relatively easily extracted and secondly oxidant requirements
Fig. 1  \(E_h\)-pH diagram of the S-H\(_2\)O system for standard conditions (after Peters [8]).

Fig. 2  \(E_h\)-pH diagram of Zn-S-H\(_2\)O system for standard and \(10^{-1}\) mol \(l^{-1}\) conditions (after Peters [8]).
are less than for the production of sulphate ions. The latter are the ultimate oxidation products at higher oxidation potentials in both acidic and basic solutions and they present removal and disposal problems.

The dotted lines in the diagrams represent the limits of stability of water. The upper limit is delineated by the reaction

\[ O_2 + 2H^+ + 2e^- = H_2O \]  

At unit fugacity of oxygen and 25°C the equation of the line is

\[ \epsilon = 1.229 - 0.0591 \text{pH} \]  

Similarly the lower limit is delineated by the reaction

\[ 2H^+ + 2e^- = H_2 \]  

and

\[ \epsilon = -0.0591 \text{pH} \]

for unit fugacity of hydrogen.

Fig. 2 shows the Zn-S-H₂O system and includes a region of stability of sphalerite (bounded by the shading). The diagram illustrates the way in which the lines are shifted by choosing different values of the activities in equation (5). In this case the diagram is plotted for unit activity of the dissolved sulphur species and for two activities of the zinc species (1M and 0.001M). The Cu-Fe-S-H₂O diagram (Fig. 3) serves to indicate the complexity of the mineral system used in this study (Pb-Zn-Cu-Fe-S-H₂O). In such systems the usefulness of \( E_h - \text{pH} \) diagrams in predicting possible products for a given set of process conditions is somewhat restricted by the equilibrium nature of the diagram. There is evidence [8] that some species that should form according to the diagram do so at such a slow rate that they are not found in the reaction products. This appears especially true where nucleation of a solid phase is indicated.

Fig. 3  \( E_h - \text{pH} \) diagram of the Cu-Fe-S-H₂O system. Conditions: 0.1 mol l⁻¹ Fe and S species; 0.01 mol l⁻¹ Cu species. (After Peters [8]).
2.3 KINETICS

The rate at which a thermodynamically predicted reaction occurs is determined by kinetic factors. In the case of leaching, the rate of dissolution of the mineral is of primary importance because in a continuous process it determines the volume and hence the cost of the reactor. This is a large unit cost and hence may materially affect the overall process viability. The rate of reaction may be limited by the rate of the chemical reaction itself or it may be controlled by transport processes. The three phase system employing dissolved gas as oxidant is complex and involves both heterogeneous reactions at the solid-liquid phase boundaries and homogeneous reactions in solution. In a three-phase leaching system the reaction process may be broken down into the following consecutive steps:

1. absorption of the gaseous reactant by the solution
2. transport of the dissolved reactants from the bulk of the solution to the mineral-solution interface
3. adsorption of the reactants by the mineral surface
4. heterogeneous chemical reaction at the surface
5. desorption of the soluble products of the reaction
6. transport of the desorbed soluble products into the bulk of the solution

Any one of these steps may be rate limiting depending on the process conditions. Steps (2) and (6) are controlled by the rate of diffusion of the solute species and in a stirred vessel by the hydrodynamics of the stirring system. Steps (3), (4) and (5) may be considered as chemically controlled while step (1) has mixed physical and chemical control. The steps are considered in more detail below where consideration is given to their possible contribution to an experimental rate law.

2.3.1 Absorption of Oxygen by the Solution

Two factors are important:

(i) The solubility of oxygen in the solution. (That is the equilibrium concentration of solute in the solvent for a given set of conditions.)
(ii) The rate of transfer of oxygen to the solution. (That is the rate of gas absorption.)

The equilibrium oxygen solubility is a thermodynamic consideration, dependent on the partial pressure of the gas above the solution, the nature of the solution and the temperature. If for a given solution composition and temperature Henry's Law applies then the equilibrium concentration of oxygen in solution is proportional to the partial pressure of the gas. The solubility is also determined by the temperature, independently of the partial pressure and exhibits a distinct minimum. Fig. 4 taken from Pawlek [16] shows that this occurs at about 100°C for oxygen in water. The presence of dissolved compounds such as acids, bases and soluble salts likewise have the effect of decreasing solubility (Fig. 5).

Analysis of the rate of gas absorption is usually based on the Whitman [17] two-film theory. Briefly this theory makes the following assumptions:

(a) Material is transferred in the bulk of the phases by convection currents and concentration differences are regarded as negligible except in the vicinity of the gas-liquid interface.
(b) On either side of the interface there exists a thin film of fluid through which transfer is effected by molecular diffusion.
(c) Fick's Law (see equation (17)) may be applied for transfer across the films. That is the rate of transfer by diffusion is proportional to the concentration gradient and to the area of the interface.
Fig. 4 Oxygen solubility in water as a function of temperature (after Pawlek [16]).

Fig. 5 The ratio of oxygen solubility in various aqueous solutions to the oxygen solubility in water as a function of solution concentration (after Pawlek [16]).
(d) The resistance to transfer lies solely in the two films and not at the interface where equilibrium conditions prevail.

The rate of oxygen transfer may be rate controlling when the rate of chemical reaction is rapid. An example of this is given by Forward and Mackiw [18]. Several ways of increasing rate of absorption can be deduced from the Whitman assumptions given above. These include increasing the gas partial pressure, increasing the gas-liquid interfacial area and decreasing the thickness of either or both of the resistance films. Efficient agitation increases the absorption rate by both decreasing the liquid film thickness and increasing the gas-liquid interfacial area. The latter effect can be especially marked when a self-sucking stirrer is used. This acts in the manner of a centrifugal pump, sucking gas from above the solution and distributing it in the form of bubbles. For a given suction rate the rate of absorption is dependent on bubble diameter since the interfacial area per unit volume increases as bubble diameter decreases.

Pawlek et al. [19] evaluated the performance of a variety of self-sucking stirrers by employing the reaction

\[ \text{SO}_3^{2-} + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_4^{2-} \]  

which proceeds so rapidly that the transfer of oxygen to the solution is rate controlling. They found that for all stirrers the bubble diameter decreased with increasing rotation speed until a certain limiting value was reached. Rotation speeds above this value did not affect the rate of absorption.

2.3.2 Transport Processes

Fig. 6 is a schematic model of the leaching process. It is assumed that in a system with reasonable agitation the concentration of a reactant R in the bulk of the solution [R]_b is uniform but that a concentration gradient is established close the mineral surface due to the rapid consumption of R in the surface reaction. M represents a metal ion produced in the reaction and P an auxiliary product.

The rate of diffusion of reactant molecules to the mineral surface from the bulk of solution is given by Fick's law.

\[ \frac{d[R]}{dt} = -DA \frac{d[R]}{dx} \]  

To solve this equation Nernst assumed that the concentration gradient was linear and defined \( \delta_R \) so that equation (18)
\[
\frac{dN_a}{dt} = -DA \left( \frac{[R_b]-[R_1]}{\delta R} \right) \tag{18}
\]

is identical to equation (17). This is shown diagrammatically in Fig 6 (b). Similar equations exist in terms of M and P with signs reversed.

δ is considered to be related to the thickness of the hydrodynamic boundary layer. Thus, increasing the rate of stirring in a well baffled tank will decrease δ resulting in increased diffusion rates. The mathematical relationship connecting diffusion rates with agitation can only be solved for the simplest systems because of the complexity of convective diffusion equations. One explicit solution that is available [20] is for a rotating disc of infinite diameter where the disc rotates about an axis perpendicular to the disc surface and through the centre of gravity. Several workers have made use of this to study leaching reactions (where transport processes are thought to be wholly or partly rate determining) by mounting mineral specimens in the form of discs. The solution is such that when reaction rate is plotted against \( w \) a linear graph indicates transport control. To determine the relative importance of the diffusion of the reactants to or products away from the mineral surface solution concentrations must be varied.

### 2.3.3 Heterogeneous Chemical Reaction at the Mineral - Solution Interface

It has been found that this step which is generally taken to include those of adsorption and desorption (steps (3) and (5) on pg 8), is rate controlling in many leaching reactions of interest. This is especially true when suitable agitation is provided. Unfortunately, the mechanisms involved in the sub-steps which taken together make up the overall mineral-solution phase boundary reaction, are at present little understood. The system is complex and a large number of rate influencing factors are possible. Some of these are discussed below.

#### 2.3.3.1 Mineralogy

The variation in leaching rates and behaviour of different ores and concentrates under similar leaching conditions has, on occasions, been ascribed to the difference in the fundamental properties of the minerals involved. There are a diversity of crystal structures exhibited by the sulphide minerals. For example, taking the minerals used in this study, galena has the rock salt structure, pyrite defines a class of its own and sphalerite and chalcopyrite have the zinc blende or diamond structure.

Another feature which may be important in leaching behaviour is the nature of the crystal bonding since bond breaking occurs during the course of the reaction. Bonds in sulphide crystals are classed as heterodemistic meaning that they are not of a single type but are usually a mixture of metallic and covalent bonding with ionics and van der Waals forces sometimes being important.

Sulphide minerals are conductors of electricity exhibiting electron conductivity and also ion and positive hole conductivity. They are normally classified as semiconductors having a conductivity in the range 10 to \( 10^{-5} \) ohm\(^{-1}\) cm\(^{-1}\) and assume definite electrode potentials in aqueous solutions. Noddack et al. [21] have tabulated an electrochemical series of the sulphides. Facts like this have led some workers to propose electrochemical theories for the oxidation reaction (see § 3.7).

Differences in the crystals of a particular mineral are due to the presence of various defects, such as lattice vacancies, interstitial ions and dislocations. These defects are common in naturally occurring minerals and their presence at the surface may account for leaching kinetics by initiating and propagating the reaction. Further as Woodcock [22] points out, the variation in defect structure from one specimen to another may correlate with variations in the degree of reactivity although quantitative evidence of this has yet to be published. Typical examples of nonstoichiometry in sulphide minerals are:
(i) subtractive solid solutions as in pyrrhotite which is deficient in iron exhibiting compositions in the range Fe$_{0.85}$S to Fe$_{1.00}$S

(ii) substitutional solid solutions as in sphalerite where iron can substitute for zinc to the extent of 17%.

Macroscopic defects in mineral structure such as textures due to growth zoning or deformation may also be important. As in the corrosion of metals, grain boundaries and lattice dislocations may provide sites for initial attack. Also, where several minerals are in close association in an ore and these are not unlocked by grinding, the possibility of galvanic interaction arises. Electron exchange can take place and galvanic corrosion may occur in a manner analogous to the corrosion of dissimilar contacting metals.

2.3.3.2 Surface Films

The presence of surface films on the mineral particles complicates the reaction mechanism, and if insoluble as in the formation of lead sulphate in the leaching of galena, transport across the film may be rate determining. The films can be divided into three categories:

(i) An oxidised surface layer which has formed on exposure of freshly ground particles to the atmosphere. Leaching of these particles is commonly characterised by an induction period corresponding to dissolution of the film after which the reaction proceeds as if fresh surface was exposed. Sometimes, however, the atmospheric oxidation layer is insoluble (e.g. lead sulphate), and is thickened by continued formation of the same compound under aqueous leaching conditions.

(ii) A reaction product is insoluble and forms a film on the particle surface. For reaction to continue transport must occur across this progressively thickening film. The mechanism may be solid-state diffusion for a non-porous film or liquid diffusion if the film is porous. Factors affecting the rate in the latter case are the pore volume and the tortuosity of the pores as well as the film thickness. Rate limiting steps may be either diffusion of a reactant into the mineral-film interface or diffusion of a product to the solution-film interface.

(iii) The film is a deposit on the surface produced by precipitation from solution.

A simple kinetic solution is possible for the case of transport control across a gradually thickening surface film if it is assumed that the increase in the thickness of the layer $x$ is a measure of the reaction rate. This rate $\left( \frac{dx}{dt} \right)$ will be inversely proportional to the film thickness assuming that Fick's Law applies (equation (18)). Thus

$$\frac{dx}{dt} = \frac{k}{x} \quad \ldots \ldots \quad (19)$$

where $k$ is proportional to the diffusion coefficient.

Integration yields

$$x^2 = 2kt \quad \ldots \ldots \quad (20)$$

assuming $x = 0$ when $t = 0$.

This equation (20) is commonly referred to as the parabolic law of diffusion. A graph of fraction dissolved (proportional to $x$) versus leaching time would show a parabolic decrease in leaching rate.

For complete dissolution of a spherical particle the film thickness $x$ must equal the initial radius of the particle ($r_0$). Therefore, the time ($t_f$) taken for this to occur is given by

$$t_f = \left( \frac{1}{2k} \right) r_0^2 \quad \ldots \ldots \quad (21)$$
which shows that fine grinding is a most effective way of decreasing dissolution times (compare with equation (27) for linear leaching) if the kinetic law is parabolic.

2.3.4 Surface Area Effects

According to the classical theory of the dissolution of a solid in a liquid, the rate of dissolution is directly proportional to the surface area of the solid. This prediction is based on the assumption that in a heterogeneous reaction, the chance of a collision between a solute and the solid surface is proportional to the solid surface area exposed. Thus

\[ \text{Rate} = kA \quad \ldots \ldots (22) \]

where \( k \) is a constant dependent on the other reaction variables and \( A \) is the surface area at any time \( t \). The rate will decrease with time because the rate per unit area remains constant while the total surface area decreases as the solid dissolves. It is possible to obtain an equation for the fraction dissolved as a function of time by assuming the particles to be spherical or by making geometric corrections for isometric shapes. The derivation for a spherical particle may be found in Appendix 1.

Equation (30) (Appendix 1) may be rearranged to make \( \alpha \) the subject which shows that the dissolution-time curve is a cubic. It is more convenient to graph \( 1 - (1 - \alpha)^{1/3} \) versus \( t \) which will give a straight line if equation (22) holds. In this way \( (1 - \alpha)^{1/3} \) may be regarded as a correction factor which takes into account the change in surface area with time. Hence, its application includes transport controlled as well as chemically controlled kinetics provided only that the rate per unit surface area is constant. This assumption does not hold when the surface reaction is impeded by reaction products, since the rate per unit surface area decreases with time in this case. Comparison of equations (27) and (21) show that the time taken for complete dissolution is proportional to the initial particle radius for linear leaching and to the square of the initial radius for parabolic leaching. As a consequence, fine grinding is more effective in reducing dissolution times in the latter case.

Surface area relationships other than equation (22) have been reported in the literature on sulphide leaching. These and the explanations made by the authors are discussed as special cases when they arise in the literature (see § 3.7).

2.3.5 Temperature Effects

The influence of temperature on the reaction rate of homogeneous reactions is commonly correlated by using the Arrhenius equation

\[ k = A \exp \left( - \frac{E_0}{RT} \right) \quad \ldots \ldots (31) \]

By applying this equation to heterogeneous reactions it is possible to calculate an apparent activation energy. This is more correctly called the critical increment of energy for the reaction, since it includes the heat of adsorption of the reactants and products and is clearly not the same as the activation energy of a homogeneous reaction.

The value of the critical increment of energy found for a particular leaching reaction is commonly used to support theories regarding the nature of the rate controlling step. This use is based on the fact that the activation energy for liquid diffusion usually lies in the range \( 8 \rightarrow 24 \) kJ mol\(^{-1} \) while the critical increment of energy for a surface reaction is usually much higher. Therefore, leaching reactions with a low temperature dependence are likely to be transport controlled. It is possible for an intermediate situation to exist, in which case the critical increment of energy will be determined by the extent to which each process controls the rate.
To find $E_a$, experiments are conducted keeping all variables constant except temperature. This presents a problem when one of the reactants is a dissolved gas because its solubility varies with temperature and this must be taken into account.

### 2.3.5 Other Factors

Under a given set of process conditions where two or more reactions are almost equally favoured thermodynamically kinetic factors determine which reaction predominates. Changes in the process variables, such as temperature, will alter the relative importance of the reactions to the overall dissolution process.

Homogeneous reactions between solute species may also affect the rate of dissolution, as for example, in the oxidation of ferrous ions in acid solutions by dissolved oxygen. In such cases however the reaction may be between reactants adsorbed on the mineral surface so that it is no longer homogeneous. Either way, the mechanism is different from any described above.
3. LITERATURE REVIEW

3.1 GENERAL

Hydrometallurgy as a distinct scientific discipline has grown from very small beginnings into an important and rapidly expanding field of endeavour in just twenty five years. The growth has largely resulted from efforts directed toward the development of processes to treat particular ore concentrates and smelter byproducts, especially in cases where traditional pyrometallurgical techniques proved impractical or uneconomic. As a consequence of this work the leaching behaviours of a large number of materials have been examined under a variety of experimental conditions. However, because of commercial pressures the results are largely qualitative and little attempt has been made to understand the complex underlying chemistry. The diverse and often contradictory nature of the results of such studies combined with a general lack of understanding of the reaction kinetics are probably the reason why few papers [25-26] and only one book [29] have attempted to review the whole field of hydrometallurgy. The rapid expansion of research and development has led, however, to a large number of papers dealing with specific topics within the general framework of hydrometallurgy. Examples are those reviewing recent developments [30-36], technological aspects of [37-40], physical chemistry of [7, 8, 41, 42], reactions under pressure [43-52] and the hydrometallurgy of sulphide ores [22, 4] and copper ores [4, 54-58]. Review papers make up a sizeable percentage of the total literature output - an outcome, perhaps, of the rapid growth in the field. A good guide to the range and scope of this growth can be found in two books [59, 60], which contain papers presented at two international conferences on hydrometallurgy convened by the Metallurgical Society of the A.I.M.E. in 1963 and 1973.

This chapter deals with the published work on the acid leaching of sphalerite, galena, pyrite and chalcopyrite as it pertains to the experimental work presented in this thesis and it is reviewed and discussed in the light of the basic theory presented in Chapter 2. The approach adopted has been to break the literature down into two broad categories which are distinguished by the emphasis placed by the various authors on (1) elucidating the kinetics and underlying mechanisms involved in leaching and (2) on providing empirical data for possible plant design and costing.

3.1.1 Kinetic Studies

There are a small number of reported studies in which carefully controlled kinetic experiments have been undertaken with the aim of gaining a better understanding of the fundamental nature of leaching reactions. The best of these studies have been successful in identifying the rate determining step and in writing strict kinetic equations. However, the latter are of limited use because they commonly cover a range well outside practical operating conditions. Synthetic or hand-picked high purity minerals are generally used - partly to exercise some control over the mineralogical variables (§ 2.3.3.1) but more particularly to reduce or eliminate catalytic effects caused by the presence of additional co-dissolving minerals. However Scott and Dyson [61] found that very small additions (< 0.1%) of some metals such as copper caused a very pronounced increase in the rate of dissolution of pure synthetic sphalerite. It is therefore apparent that the careful choice of high purity naturally occurring minerals is no guarantee that catalysis has been circumvented.

Kinetic studies can be further subdivided into three sections based on the form of the mineral being leached.
(i) Sintered discs - these have been used to provide a quantitative assessment of liquid phase diffusion control for reactions where this step is rate limiting (see § 2.3.3.2).

(ii) Single crystals - these have been used to show preferential attack on specific crystal faces. They are also useful in studying the possible influence of crystal defects (see § 2.3.3.3) and in identifying solid reaction products.

(iii) Finely ground pure crystals - these can be studied in the same manner as ores and concentrates. By the addition of impurity compounds, commonly associated with the latter, it is sometimes possible to assess their catalytic importance and their relationship to the leaching kinetics of real concentrates.

3.1.2 Process Oriented Studies

Most studies fall into this category. The leaching experiments are commonly conducted on specific sulphide flotation concentrates to evaluate the process possibilities of a particular combination of variables such as oxidant, acid, temperature, etc. The leaching reactions, their rate and products are studied as a function of changing experimental conditions. Results are usually qualitative and the only information supplied about the reactions are approximate stoichiometric relationships developed from mass and material balances. Some of the potentially variable experimental conditions are often not investigated because they are set by the requirements of the metal recovery system. For example, the minimum pulp density may be determined by the minimum concentration of the metal required in the pregnant liquor feed to an electrolysis circuit. Also, the experiments are invariably conducted on ground minerals which precludes a quantitative evaluation of liquid phase diffusion control (when this is important) because of the hydrodynamic complexity of the system.

3.1.3 Summary

Although kinetic studies remain rather academic they may sometimes indicate ways and means of increasing reaction rates under process conditions by pinpointing rate influencing factors not recognised in process oriented experiments. Because of the complex mineralogy of ores and concentrates it will never be possible to predict their leaching behaviour solely on the basis of fundamental considerations so that process oriented experiments will always be necessary. There is no doubt, however, that a fundamental understanding of leaching behaviour will eventually reduce the amount of work required to establish the optimum conditions for a given ore to a few well chosen experiments.

Published work in both categories will be reviewed, looking first at kinetic studies, so that when process oriented studies are discussed the behaviour of the composite whole may be compared to that of its component parts.

3.2 KINETIC STUDIES OF SPHALERITE LEACHING

A summary of these studies listing the range of experimental variables investigated and the important results can be found in Table 1. As far as possible data contained in the table is not repeated in the text but it is important to note that results and theories discussed below apply only to the particular range of experimental conditions listed in the table.

In 1958 Jackson and Strickland [62] studied the leaching kinetics of a variety of sulphide ores in dilute acid chlorine solutions. Reaction products of sphalerite were identified as elemental sulphur, sulphur monochloride and sulphate and zinc ions. Exact reaction stoichiometry was not established but it was shown that chlorine (5.5 - 31.6 mol l⁻¹) was effective in oxidising sulphide sulphur to elemental sulphur or further to sulphate. The surface reaction was so fast under most conditions that the rate of reaction, measured as chlorine consumption, was controlled by liquid phase diffusion of chlorine. It was
TABLE 1  KINETIC STUDIES OF ZINC SULPHIDE LEACHING

Notation:
Calc. - calculated from data given by the authors.
Acid - sulphuric unless otherwise stated.
V - varied. NV - not varied. A - area.
Blank - no information given by the authors.
Synthetic - high purity mineral prepared in the laboratory,
commonly a mixture of sphalerite and wurtzite.
MR - molar ratio of acid /ZnS

Particle Sizing - most minerals have been sized by sieving. \( d_p \) corresponds to
the sieve opening. Surface areas are listed in brackets when they have been
given by the authors.
Stirring - listed as V or NV to denote whether the authors made any attempt to
determine the importance of transport control. A single listing indicates an
experimental condition which was held constant during the study. Ranges
are given where applicable. Activation energies are for zinc dissolution
unless otherwise stated.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Year</th>
<th>Starting Material</th>
<th>Temperature (°C)</th>
<th>Oxygen Partial Pressure (MPa)</th>
<th>Initial Acid Concentration (mol 1^-1)</th>
<th>Stirring</th>
<th>Pulp Density (g 1^-1)</th>
<th>Acid/ZnS Molar Ratio</th>
<th>Particle Sizing ( d_p : \mu m )</th>
<th>Reaction Time (min.)</th>
<th>Observed Reactions</th>
<th>Apparent Activation Energy (kJ mol^-1)</th>
<th>Rate Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jackson &amp; Strickland [62]</td>
<td>1958</td>
<td>98% ZnS</td>
<td>25 &amp; 50</td>
<td>Chlorine used as oxidant</td>
<td>pH range 1.0 - 2.8</td>
<td>NV</td>
<td>not given but variable</td>
<td>841 - 1600</td>
<td>0 - 75</td>
<td></td>
<td></td>
<td>20.3</td>
<td>Rate = A_0, Liquid phase transport control</td>
</tr>
<tr>
<td>Heinglein &amp; Hirsch [63]</td>
<td>1961</td>
<td>Synthetic</td>
<td>100 - 190</td>
<td>Water</td>
<td>30</td>
<td>no acid</td>
<td>100</td>
<td>(34)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CuSO_4 had a marked catalytic effect</td>
</tr>
<tr>
<td>Romankiw &amp; de Bruyn [64]</td>
<td>1963</td>
<td>Synthetic</td>
<td>0.6 - 60</td>
<td>inert atmos.</td>
<td>V</td>
<td>60</td>
<td>not given but variable</td>
<td>0.18 (5.54)</td>
<td>0 - 60</td>
<td>(32)</td>
<td>f: 46.4</td>
<td>Rate = A_0, See below</td>
<td></td>
</tr>
<tr>
<td>Yaroslavstev et al. [65]</td>
<td>1964</td>
<td>97% ZnS, 0.6 Fe, 0.2 Cu</td>
<td>80 - 120</td>
<td>0.1 - 1.5</td>
<td>0.0 - 1.0</td>
<td>V</td>
<td>not given but variable</td>
<td>-250 - 160</td>
<td>-100 + 63</td>
<td>(33)</td>
<td>38.9</td>
<td>31.4 (sulphate)</td>
<td>Rate = A_0, ( P_{O_2}^{1/2} ) ( [H_2SO_4]^1 )</td>
</tr>
</tbody>
</table>

\[
\frac{d[Zn^{++}]}{dt} = A_0 \left( k_f[H^+] - k_p [Zn^{++}] \right) \frac{1}{p_{H_2S}}
\]  \( (32) \)

\[
\frac{d[Zn^{++}]}{dt} = 92.5 \left( 2.45 + 6.15 [H_2SO_4] \right) \frac{1}{p_{O_2}} \exp \left( -38,900/RT \right) g \text{ mol m}^{-2}\text{min}^{-1}
\]  \( (33) \)

\[
\frac{d[Zn^{++}]}{dt} = 8.88 \left( 0.5 + 28.2 [H_2SO_4] \right) \frac{1}{p_{O_2}} \exp \left( -31,400/RT \right) g \text{ mol m}^{-2}\text{min}^{-1}
\]  \( (34) \)
<table>
<thead>
<tr>
<th>Reference</th>
<th>Year</th>
<th>Starting Material</th>
<th>Temperature (°C)</th>
<th>Oxygen Partial Pressure (MPa)</th>
<th>Initial Acid Concentration (mol l⁻¹)</th>
<th>Stirring</th>
<th>Pulp Density (g l⁻¹)</th>
<th>Acid/ZnS Molar Ratio</th>
<th>Particle Sizing (d_p): μm (Å² m⁻²g⁻¹)</th>
<th>Reaction Time (min.)</th>
<th>Observed Reactions</th>
<th>Apparent Activation Energy (kJ mol⁻¹)</th>
<th>Rate Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Okamura [66]</td>
<td>1964</td>
<td>78% ZnS 7.3 Fe 2:2 Cu</td>
<td>70 → 126</td>
<td>0.3 → 1.0</td>
<td>1.0 → 4.0</td>
<td>V</td>
<td>0.8 → 3.0</td>
<td>75% &lt; 45</td>
<td>(0.25 → 0.5)</td>
<td>0 → 120 (33)</td>
<td>(34)</td>
<td>47.2</td>
<td>Rate ≠ (P_{O_2}) ≠ (f(H_2SO_4)) ≠ (f(A))</td>
</tr>
<tr>
<td>Dobrokhooev &amp; Onuchkina [67]</td>
<td>1964</td>
<td>75% ZnS 4.3 Fe 4.6 CaO</td>
<td>100 → 200</td>
<td>0.1 → 2.0</td>
<td>Water</td>
<td>V</td>
<td>12.5</td>
<td>acid as catalyst only</td>
<td>70 &amp; 80 [0.019 0.021]</td>
<td>60 (34)</td>
<td>(32) (33) (34)</td>
<td>72.5</td>
<td>Rate ≠ (H_2O) ≠ (A)</td>
</tr>
<tr>
<td>Scott &amp; Dyson [61]</td>
<td>1968</td>
<td>Synthetic</td>
<td>90 → 140</td>
<td>=1.7</td>
<td>0.05 → 0.8</td>
<td>V</td>
<td>40</td>
<td>0.75 → 1.5</td>
<td>(3.9 → 4.6)</td>
<td>60 (32)</td>
<td>(33) (34)</td>
<td>Cu &amp; Fe catalysis</td>
<td>Rate ≠ (f[H_2SO_4]) ≠ (f(MR))</td>
</tr>
<tr>
<td>Exner, Gerlach &amp; Pawlek [69] [70]</td>
<td>1969</td>
<td>99% ZnS 0.0 Fe 0.6 Cu</td>
<td>70 → 180</td>
<td>0 → 5.0</td>
<td>0.1 → 1.2</td>
<td>V</td>
<td>12.5</td>
<td>not given but variable</td>
<td>-120 → 0 +33</td>
<td>0 → 240 (32)</td>
<td>(33) (34)</td>
<td>52.0</td>
<td>Rate ≠ (f(P_{O_2})) Complex dependence on temperature.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>as above with active C added</td>
<td>70 → 130</td>
<td>0 → 2.0</td>
<td>0.1 → 0.6</td>
<td>V</td>
<td>12.5</td>
<td>not given but variable</td>
<td>-120 → 0 +33</td>
<td>0 → 240 (33)</td>
<td>(34)</td>
<td>30.1</td>
<td>See below** Equations apply for (P_{O_2} ≤ 0.5) MPa.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>seven concentrates variable Fe</td>
<td>70 → 130</td>
<td>1.0</td>
<td>0.5</td>
<td>V</td>
<td>50</td>
<td>1.0</td>
<td>-120 → 0 +33</td>
<td>0 → 240 (32)</td>
<td>(34)</td>
<td>38.7</td>
<td>Linear leaching, Fe catalysis via (H_2S) oxidation.</td>
</tr>
<tr>
<td>Locker &amp; de Bruyn [71]</td>
<td>1969</td>
<td>Synthetic</td>
<td>0.2 → 60</td>
<td>(H_2S) atmos.</td>
<td>0.5 → 5.0</td>
<td>V</td>
<td>60</td>
<td>not given but variable</td>
<td>(5.5 &amp; 28.8)</td>
<td>0 → 9 (32)</td>
<td>f: 40.5 r: 26.4</td>
<td>Rate control by proton adsorption. Rate equation (35).</td>
<td></td>
</tr>
</tbody>
</table>

\[ \frac{dz{^{Zn^{2+}}}}{dt} = 1.96 \times 10^5 \frac{P_{O_2}}{k} \exp(-72,500/RT) g \text{ mol m}^2\text{min}^{-1} \quad \ldots \quad (38) \]

\[ \frac{dz{^{Zn^{2+}}}}{dt} = 0.3 P_{O_2} A_0 [ZnS] \exp(-52,000/RT) g \text{ mol l}^{-1}\text{min}^{-1} \quad \ldots \quad (50) \]

\[ \frac{dz{^{Zn^{2+}}}}{dt} = 2.23 \times 10^{-5} P_{O_2} A_0 \exp(-30,100/RT) g \text{ mol l}^{-1}\text{min}^{-1} \quad \ldots \quad (51) \]
observed that the solid reaction products tended to coat the surface of the particles and under conditions of low chlorine concentration and low temperature the reaction kinetics followed the parabolic diffusion law (equation (20)).

Because chlorine solutions are both corrosive and expensive most later studies concentrated on the dilute sulphuric acid - oxygen system, where the following reactions appear to be important.

\[ \text{ZnS(s)} + \text{H}_2\text{SO}_4(aq) \rightleftharpoons \text{ZnSO}_4(aq) + \text{H}_2\text{S}(g) \]  

\[ \text{ZnS(s)} + \text{H}_2\text{SO}_4(aq) + \text{O}_2(aq) + \text{ZnSO}_4(aq) + \text{H}_2\text{O}(aq) + \text{S}^8(s) \]  

\[ \text{ZnS(s)} + 2\text{O}_2(aq) + \text{ZnSO}_4(aq) \]  

Reaction (32) occurs when little or no oxidant is present. The kinetics of this reaction were studied by Romankiw and de Bruyn [64] who followed the increase in H$_2$S pressure in a constant volume reactor. Results showed that equilibrium was quickly established (2 to 20 mins) with zinc dissolution never exceeding 30%. Rate control by liquid phase diffusion was eliminated by vigorous agitation. High activation energies (Table 1) were taken as evidence of this (§ 2.3.5). The reaction was also studied using three samples of natural sphalerite containing varying amounts of iron as the major impurity. The rate of dissolution was found to increase with increasing iron and elemental sulphur appeared as a reaction product. The former effect was attributed to the increased ionic character of the lattice bonding caused by the presence of Fe-S bonds. The formation of sulphur was not explained.

Etching studies of single crystals showed that dislocation and strain effects led to faster attack. It was also observed that the (111) sulphur faces were more strongly attacked that the (111) zinc faces which led the authors to suggest that bond breaking occurred via attack on the sulphur atoms. In a later extension of this work Locker and de Bruyn [71] found evidence to suggest that the mechanism of dissolution is via adsorption of protons at the sulphur surface sites followed by a reaction producing HS$^-$ ions which then combine with a proton in solution to give H$_2$S. The discovery that the apparent activation energy was independent of the electrical properties of the material was attributed to rate control by proton adsorption. The presence of minor impurities of iron (0.1%), while not affecting the apparent activation energy, produced a ten fold increase in reaction rate. The authors rather hazily explain this in terms of an increased number of surface reaction sites. In both studies [64, 71] the initial reaction rate was found to be proportional to the surface area of the particles (see § 2.3.4) and to the initial acid concentration (equation (35) - Table 1).

Exner and co-workers [70] in experiments with a very pure natural zinc blende containing 0.6% Cu (but no iron or other heavy metals) were disappointed to find very low zinc extractions despite the use of relatively high oxygen pressures and temperatures. The effect of temperature was complex. Up to 150°C the dissolution versus time curves rapidly approached a limiting value, while at higher temperatures the curves were approximately linear. Oxygen partial pressures in excess of 0.5 MPa had no effect on the rate of zinc dissolution while increase in the initial acid concentration increased the rate for a short period after which the curves paralleled those for lower concentrations. Hydrogen sulphide was observed to form directly after the addition of sulphuric acid to the solid and continued, despite the introduction of oxygen, until the end of the experiment. No elemental sulphur was detected in the residue and only a small increase in sulphate concentration was recorded. Exner et al. presented convincing evidence that at temperatures below 150°C, reaction (32) rapidly reached equilibrium preventing further zinc dissolution except via slow oxidation of H$_2$S to sulphate. At higher temperatures the dissolution proceeded slowly with the formation of sulphate. They were unable to characterise the kinetics of the reaction in the temperature range investigated.

The oxidation of sphalerite according to reaction (34) was recorded by Heinglein and Hirsch [63] in aqueous solution in the absence of acid. A thorough kinetic evaluation of the reaction was not made but they reported a very marked increase in reaction rate for small additions of copper sulphate (up to 50 fold
for a 2% Cu addition). The rate increase was ascribed to the exchange reaction (36) whose driving force is the difference in solubility of CuS and ZnS. Copper sulphate was supposed to be regenerated according to the reaction (37)

$$
\text{ZnS} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{CuS} \quad \ldots \quad (36)
$$

$$
\text{CuS} + 2\text{O}_2 \rightarrow \text{CuSO}_4 \quad \ldots \quad (37)
$$

so that the nett reaction is that represented by equation (34). The authors concluded that the presence of CuS in a sphalerite concentrate could explain the rapid dissolution rate of the latter compared with that of the pure mineral. Experiments with two zinc concentrates were performed to illustrate this point.

Dobrokhotoov and Onuchkina [67] reported on the leaching kinetics of a sphalerite concentrate which reacted according to the stoichiometry of equation (34). In calculating the reaction rate (g mol m⁻² min⁻¹) allowance was made for the decrease in particulate surface area with leaching time. The analysis outlined in Appendix 1 was used for this purpose and results with two initial surface areas agreed with equation (22). The rate equation (38) in Table 1 shows a half power dependence on oxygen pressure. Copper sulphate, sulphuric acid, calcium oxide and magnesium sulphate were investigated as potential catalysts. Only the first two resulted in increased rates - a fourfold increase on the addition of 0.5 g l⁻¹ of CuSO₄ and a twofold increase for an addition of 2 g l⁻¹ of acid. The catalytic activity of CuSO₄ additions was attributed to the provision of the following reaction path.

$$
5\text{ZnS} + 8\text{CuSO}_4 + 4\text{H}_2\text{O} \rightarrow 5\text{ZnSO}_4 + 4\text{CuS} + 4\text{H}_2\text{SO}_4 \quad \ldots \quad (39)
$$

$$
4\text{CuS} + 100\text{O}_2 + 8\text{H}_2\text{O} \rightarrow 8\text{CuSO}_4 + 4\text{H}_2\text{SO}_4 \quad \ldots \quad (40)
$$

The overall nett reaction reduces to that of equation (34).

Both reactions (33) and (34) were reported by Yaroslavstev and co-workers [65] in an investigation of the initial stage leaching kinetics of sphalerite. They found that the initial rate was dependent on the initial acid concentration and could be represented by two straight lines of differing gradients intersecting at a value of 0.1 mol l⁻¹. These findings were interpreted as meaning that for [H₂SO₄] < 0.1 reaction (34) occurs and for 0.1 < [H₂SO₄] < 1.0 reaction (33) occurs. Both initial rates were found to be proportional to the initial particulate surface area and to the half power of the oxygen partial pressure (see equations (41) and (42) in Table 1). The rate of reaction (34) remained constant for 2.5 hours whereas in the same time the rate of reaction (33) declined rapidly from its initial value. An explicit relationship was not developed for the latter case. It is interesting to note that values of the initial rates of reaction (34) computed using equation (42) are at least ten times lower than those computed from equation (38). A probable explanation lies in the large iron impurity (4.3%) in the ore used by Dobrokhotoov and Onuchkina [67].

In contrast to the findings of Yaroslavstev et al., Okamura [66] reported a rate dependence on the first power of the oxygen partial pressure and a rate independence of acid concentration in the range 1.0 to 4.0 mol l⁻¹. He also reported a surface area dependence but no explicit relationship was developed. The maximum dissolution rate occurred at about 105°C. Above this value the author reported a rapid decrease in rate which he attributed to blocking of the particle surface by a film of liquid elemental sulphur.

The substantially unreactive nature of pure synthetic zinc sulphide reported by Heinglein and Hirsch [63] and Romankiw and de Bruyn [64] was confirmed by Scott and Dyson [61]. Under a wide variety of experimental conditions not more than 5% of the mineral dissolved. A large number of elements were examined as possible catalysts for both reactions (33) and (34). Copper, bismuth, ruthenium, molybdenum and iron (listed in decreasing order of effectiveness) were found to increase the rate of reaction (33). Additions of as little as 0.15% Cu resulted in a 30 fold increase in the amount of zinc dissolved in one
hour while much larger additions of iron (= 100 x) were required to produce the same effect. On the basis of this evidence the authors suggest that the common association of copper and iron sulphides with naturally occurring sphalerite could, at least partially, account for the greater reactivity of the native mineral. It was also noted that even in copper free ores a small amount of copper is likely to be present on the surface of the mineral because of the almost universal use of copper sulphate as an activator in sphalerite flotation.

The authors also qualitatively examined the effects of a number of other reaction variables and reported that both reactions (33) and (34) occurred under all conditions. The amount of zinc dissolved after one hour increased with temperature but was insensitive to the initial acid concentration in the range 0.2 to 0.8 mol l⁻¹. The extent to which reaction (34) occurred (about 30%) measured by sulphate analysis of the product solutions, was insensitive to acid concentration for copper catalysis but increased with decreasing acid concentration for iron catalysis. Acid additions ranging from a 50% excess to a 25% deficiency (based on the stoichiometry of equation (33)) resulted in less than a 9% variation in zinc dissolution.

The observation that all the catalysts except iron were precipitated as sulphides on the sphalerite surface during an experiment led the authors to suggest that the catalytic effect was due to activation of the sphalerite crystals by the incorporation of catalytic ions in place of zinc in the surface layers of the lattice. A galvanic mechanism was proposed as a possible explanation of their observations with the two half-cell reactions being:

\[
\begin{align*}
\text{anodic:} & \quad \text{ZnS} + \text{Zn}^{2+} + 2\text{S}^0 + 2\text{e}^- \\
\text{cathodic:} & \quad \frac{1}{2}\text{O}_2 + \text{Zn}^{2+} + 2\text{e}^- + \text{H}_2\text{O} \\
\text{O.C.R.:} & \quad \text{ZnS} + 2\text{H}^{+} + \frac{1}{2}\text{O}_2 = \text{Zn}^{2+} + 2\text{S}^0 + \text{H}_2\text{O}
\end{align*}
\]

(33) (34) (43) (44)

The overall cell reaction is represented by equation (33). Similar mechanisms have been proposed by other authors [69, 70, 72, 73] and will be considered more fully in § 3.7. Scott and Dyson suggested that the reduction of oxygen was rate controlling based on their observation that copper showed no catalytic effect when oxidants other than oxygen were used. X-ray diffraction studies of residues from copper experiments showed that copper precipitated in the form of covellite but the authors did not explain the reason for its occurrence. However copper ions are thermodynamically unstable in the presence of hydrogen sulphide, which they found in the autoclave at the end of most experiments. It would appear, therefore, that reaction (32) occurred to some extent as well as the reported (33) and (34). Reactions leading to the production of hexavalent sulphur were assumed to be chemical, rather than electrochemical in nature and hydrogen sulphide, despite its slow oxidation by dissolved oxygen, was suggested as a more likely intermediate than elemental sulphur.

Exner and co-workers [70] also extended their study of pure sphalerite (pg. 19) to look at possible catalysts. Leaching experiments were conducted with eight zinc concentrates having iron contents ranging from 0.7 to 11.0%. They found that the rates of dissolution of those containing higher iron concentrations were about five times that of the pure mineral. Linear leaching was exhibited and sulphur and sulphate appeared as the major oxidation products. Hydrogen sulphide evolution was only recorded for three low iron concentrates. Fig. 7 shows correlations between zinc extraction and iron content for two different leaching times. The results agree with the earlier observations of Scott and Dyson [61] and Vizsolyi et al. [77] that large iron concentrations (> 5%) are required to exert any catalytic influence. One exception to the general rule was found for a concentrate containing 10.25% iron (Fig. 7). X-ray diffraction analysis revealed that this slow leaching concentrate contained iron in solid solution (marmatite) whereas it was present in all the others as ferrous sulphate or pyrite. Exner et al. therefore concluded that effective catalysis is only provided by fast dissolving iron compounds.
The authors listed the following equations as possible oxidation reactions of hydrogen sulphide.

\[
\begin{align*}
H_2S + H_2SO_4 & \rightarrow H_2SO_3 + H_2O + S^0 \\
H_2S + 3O_2 & \rightarrow H_2O + S^0 \\
H_2S + 2O_2 & \rightarrow H_2SO_4 \\
H_2S + 2Fe^{+++} & \rightarrow 2Fe^{++} + 2H^+ + S^0 \\
H_2S + 8Fe^{+++} + 4H_2O & \rightarrow 8Fe^{++} + 10H^+ + SO_4^{2-} 
\end{align*}
\]

(45)  (46)  (47)  (48)  (49)

The ferric ions are formed by oxidation of ferrous sulphate according to the following reaction:

\[
2FeSO_4 + 3O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O
\]

(50)

To explain the non-appearance of H_2S as a product, the oxidation reaction for hydrogen sulphide must be at least as fast as the dissolution reaction (32). Of the five possibilities listed above, reaction (45) occurs in concentrated acid only while reactions (46) and (47) are extremely slow at temperatures below 150°C (see Exner’s results for pure sphalerite on pg. 19). However oxidation by ferric ions occurs at lower temperatures and judging from the high ratio of S^0/SO_4^{2-} (4/1) realised, reaction (48) is preferred. These observations were confirmed in a blank experiment without mineral addition which showed that sulphur and sulphate production became appreciable only after ferric ions had been added to the solution.

Exner et al. also showed that ferric ions added to the leachant were effective in accelerating the rate of dissolution of pure sphalerite. Results were analogous to those for zinc concentrates with a minimum addition of 5% by weight being required to produce any effect. Additions of other possible redox catalysts were tried (Cu^{++}, I_2, Ti^{+++}, Ce^{+++}) but all were destroyed or precipitated by hydrogen sulphide. The conclusion reached was that sphalerite dissolution is accelerated by the removal of hydrogen sulphide and this is facilitated by the provision of an alternative oxidation path (reaction 48).

Activated carbon was also found to catalyse the oxidation of hydrogen sulphide by providing additional oxygen adsorption sites. It was postulated that reactions (46) and (47) could then take place between dissolved hydrogen sulphide and adsorbed oxygen or between two adsorbed species. The kinetics of leaching under these conditions were extensively examined (Table 1). The influence of oxygen pressure
was explained in terms of the Langmuir adsorption isotherm.

\[ \theta = \frac{k_p}{1 + k_p} \]  

At low pressures \( \theta = k_p \) and the proportion of possible surface covered is proportional to the pressure. The authors observed that this occurred up to 0.5 MPa. Above this pressure all active adsorption sites are occupied and further increases do not increase the dissolution rate.

Exner et al. [70] brought all their observations together in a leaching theory based on an electrochemical model (equations (43) and (44)) involving the chemisorption of oxygen molecules (see § 3.7).

### 3.3 KINETIC STUDIES OF GALENA LEACHING

Oxidative leaching of galena differs from that of the other sulphides considered because the sulphate product is insoluble. This affords a primary separation of lead from the other metal values, but because the lead sulphate product is impure and unsuitable as smelter feed a second leach is necessary. Two leachants have been proposed for this purpose [74, 75] but both rely on lead being present in the residue as lead sulphate. Unfortunately, later studies (§ 3.6.3) indicate that lead jarosites are more common acid leach products at \( \text{pH} > 2 \) when iron is present in solution. Neither of the proposed leachants will dissolve jarosites and because of this and other difficulties the hydrometallurgical production of lead from galena appears less attractive than that of copper or zinc. This is reflected in the small number of published investigations. Only one, conducted by Exner and co-workers [76], makes a detailed study of the acid pressure leaching behaviour of pure galena.

The hand-picked ore in question contained iron (1.1%) and copper (1.4%) as the only impurities. Employing a pulp density of 60 g

\( \text{l}^{-1} (0.23 \text{ mol} \text{l}^{-1} \text{Pb}) \) the authors examined the effect of temperature (70 to 150°C), oxygen partial pressure (0 to 4 MPa) and initial acid concentration (0.6 to 1.0 mol l

\( ^{-1} \)) on the rate of lead dissolution over a period of four hours. Dissolution-time curves (Fig. 8) show that the reaction rate is initially fast but decreases until a constant value is attained after an elapsed time of about one hour. The subsequent linear leaching was attributed to rate control by diffusion of lead ions through a lead sulphate film which formed on the surface, the build-up of which caused the initial decrease in rate. In the temperature range 70 to 110°C, the apparent activation energy for the linear leaching stage was found to be 15.0 kJ mol

\( ^{-1} \) which provided further support for the proposed diffusion mechanism (see § 2.3.4). At temperatures of 130°C and 150°C the dissolution stopped after about 30 minutes due to occlusion of the mineral surface by a uniform layer of molten sulphur. Removal of this layer from the residue by carbon disulphide extraction resulted in dissolution behaviour consistent with unleached ore.

The effect of lead sulphate film formation on the leaching rate was demonstrated by leaching in two stages of 90 minutes. In between the two stages the residue was washed with ammonium tartrate solution to remove the sulphate film. Leaching behaviour in the second stage was identical to that in the first. Changes in initial acid concentration and oxygen pressure did not alter the leaching rate. In fact results showed that use of an inert autoclave atmosphere had no effect on the dissolution rate, but in this case the residue contained no elemental sulphur.

The following reactions were cited as important.

\[
PbS(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + H_2S(g) \quad \ldots \quad (54)
\]

\[
PbS(s) + H_2SO_4(aq) + \frac{1}{2}O_2(aq) \rightarrow PbSO_4(s) + S(s) + H_2O(aq) \quad \ldots \quad (55)
\]

\[
PbS(s) + 2O_2(aq) \rightarrow PbSO_4(s) \quad \ldots \quad (56)
\]
These are analogous to reactions (32), (33) and (34) for sphalerite leaching. Reaction (56) occurred only when acid was absent and under the conditions investigated Exner et al. considered reactions (54) and (55) to be occurring in parallel. Although reaction stoichiometry was not established (SO and H₂S not determined) reaction (54) was considered predominant as extensive hydrogen sulphide emission was noted immediately on addition of sulphuric acid to the ore. Addition of 10% by weight of ferric sulphate did not increase the rate - in contrast to the findings of Vizsoyli et al. [77] for lead concentrates (§ 3.6.2). The byproduct distribution may have been affected, via reaction (48) for example, but this possibility was not examined.

Fig. 8 The effect of temperature on the conversion to lead sulphide to sulphate at 1 MPa oxygen partial pressure (after Exner et al. [76]).

3.4 STUDIES OF PYRITE LEACHING

There has been little interest in the direct leaching of pyrite for the recovery of iron because it is the least valuable of the base-metals and the mineral is one of the most difficult to dissolve [82, 83]. Its leaching behaviour is important however, because pyrite is commonly found in association with other base-metal sulphides and hence is present to some degree in their concentrates. The few studies that have been conducted are reviewed here. A summary of the range of variables investigated is contained in Table 2.

In the earliest studies the dissolution of pyrite was investigated as a source of elemental sulphur [78] or sulphuric acid [79] and the production of iron bearing solutions (or ferric hydroxide on hydrolysis at high pH) was merely a side effect. Downes and Bruce [78], investigating the feasibility of sulphur recovery from pyrite and pyrrhotite, leached the ore in aqueous solutions at elevated temperatures under oxygen pressure. The pyrite was first thermally decomposed at 700°C to produce artificial pyrrhotite by removal of the labile sulphur. Both natural and artificial pyrrhotite gave good yields of elemental sulphur providing the pH of the solution was less than 1.5. The authors suggest that hydrogen sulphide generated according to the following equation

\[ \text{FeS} + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2\text{S} \]  

\[ \ldots \ldots (57) \]
**TABLE 2**

**STUDIES OF PYRITE LEACHING**

Notation: is the same as Table 1 with the exception that pyrite (FeS₂) should be substituted for sphalerite (ZnS) and Fe for Zn.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Year</th>
<th>Starting Material</th>
<th>Temperature (°C)</th>
<th>Oxygen Partial Pressure (MPa)</th>
<th>Initial Acid Concentration (mol l⁻¹)</th>
<th>Stirring</th>
<th>Pulp Density (g l⁻¹)</th>
<th>Acid/FeS₂ Molar Ratio</th>
<th>Particle Sizing d_p : µm (Å / m²g⁻¹)</th>
<th>Reaction Time (min.)</th>
<th>Observed Reactions</th>
<th>Apparent Activation Energy (kJ mol⁻¹)</th>
<th>Rate Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Downes &amp; Bruce</td>
<td>1951</td>
<td>Concentrate</td>
<td>0 → 150</td>
<td>0.3 → 2.1</td>
<td>Water</td>
<td>NV</td>
<td>250 + 500</td>
<td>0</td>
<td>65% -74</td>
<td>0 → 120</td>
<td>(57)</td>
<td>(59)</td>
<td>Qualitative only</td>
</tr>
<tr>
<td>Warren</td>
<td>1956</td>
<td>83-95% FeS₂</td>
<td>130 → 190</td>
<td>0.2 → 1.3</td>
<td>Water</td>
<td>V</td>
<td>31</td>
<td>0</td>
<td>99% -74</td>
<td>0 → 30</td>
<td>(59)</td>
<td>83.6 (sulphate formation)</td>
<td>Rate = P_j O₂</td>
</tr>
<tr>
<td>Sherman &amp; Strickland</td>
<td>1957</td>
<td>&gt; 97% FeS₂</td>
<td>10 → 40</td>
<td>Chlorine used as oxidant</td>
<td>pH &lt; 2 (HCl)</td>
<td>V</td>
<td>5</td>
<td>841 → 1600</td>
<td>0 → 120</td>
<td></td>
<td>20.0 (chlorine consumption)</td>
<td>Liquid phase transport control</td>
<td></td>
</tr>
<tr>
<td>McKay &amp; Halpern</td>
<td>1958</td>
<td>98% FeS₂</td>
<td>100 → 130</td>
<td>0.1 → 0.4</td>
<td>0 → 0.15</td>
<td>V</td>
<td>20 → 80</td>
<td>variable &lt; 0.5</td>
<td>-105 +74</td>
<td>0 → 480</td>
<td>(59)</td>
<td>(60)</td>
<td>Rate* = A_0 = P_j O₂ = P_j [H_2SO₄]</td>
</tr>
<tr>
<td>Gerlach, Hohnne &amp; Pawle</td>
<td>1966</td>
<td>92-95% FeS₂ 0.03% Cu</td>
<td>60 → 160</td>
<td>0 → 1.6 5 x 10⁻⁵→0.4</td>
<td>Variable</td>
<td>V</td>
<td>24 + 192</td>
<td>variable &lt; 0.5</td>
<td>36 → 548 (597 88 x 10⁻⁴)</td>
<td>0 → 300</td>
<td>(59)</td>
<td>(63)</td>
<td>49.8 (pyrite) 54.8 (sulphate)</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\frac{d[FeS_2]}{dt} &= 0.125 \ A_0 \ P_j O_2 \ exp\ (-55,700/RT) \quad (65a) \\
\frac{d[FeS_2]}{dt} &= 0.14 \ A_0 \ P_j O_2 \ exp\ (-54,800/RT) \quad (65b) \\
\frac{d[SO_4^{2-}]}{dt} &= 0.034 \ A_0 \ P_j O_2 \ exp\ (-49,800/RT) \quad (65c)
\end{align*}
\]
is a necessary intermediary in the production of elemental sulphur which is formed when H₂S is oxidised either directly by oxygen

\[ \text{H}_2\text{S} + \frac{3}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{S}^\circ \]  \hspace{2cm} (46)

or by ferric sulphate.

\[ \text{Fe}(\text{SO}_4)_3 + \text{H}_2\text{S} \rightarrow 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{S}^\circ \]  \hspace{2cm} (48)

The ferric sulphate is produced by oxidation of ferrous sulphate according to equation (50). When the pH rises towards the end of the reaction due to the consumption of acid, ferric hydroxide is formed.

\[ \text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + 3\text{H}_2\text{SO}_4 \]  \hspace{2cm} (58)

The authors suggest that this product may be suitable as smelter feed material once contaminants have been removed. Minor impurities of pyrite present in the artificial pyrrhotite feed were found to oxidise as follows

\[ 2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \]  \hspace{2cm} (59)

providing the acid necessary to keep the pH below 1.5. The most suitable operating temperature was 110°C. The recovery was reduced at temperatures above this value due to occlusion of unreacted sulphides by molten sulphur.

In 1967 Sherritt Gordon presented details of a process scheme [83] to recover pure iron and sulphur from pyritic ores by first leaching artificial pyrrhotite in a manner similar to that described above. The economics of the process [84] were made more attractive by the simultaneous recovery of the impurity base-metals and precious metals.

Warren [79] investigated the kinetics of sulphuric acid production from pyrite according to equation (59). The rate of sulphate formation was very sensitive to temperature change and was proportional to the half power of the oxygen pressure. Insufficient evidence was obtained to determine the reaction order but rate control by heterogeneous reaction on certain surface sites was suggested. In contrast to Warren’s results McKay and Halpern [81], investigating a lower temperature range, found a linear dependence of rate on oxygen pressure and a lower activation energy was established (see Table 2).

These authors also investigated the addition of sulphuric acid and found that elemental sulphur now appeared as a reaction product. The percentage of sulphide sulphur converted to the elemental form increased with acid concentration and up to 50% yields were obtained. The rate of dissolution was proportional to the initial surface area of the particles but did not decrease with leaching time as expected from equation (22). The primary leaching reactions were supposed to be those given by equations (59) and (60).

\[ \text{FeS}_2 + 2\text{O}_2 \rightarrow \text{FeSO}_4 + \text{S}^\circ \]  \hspace{2cm} (60)

It was suggested that the direct oxidation of sulphur might also lead to the production of acid.

\[ 2\text{S}^\circ + 3\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]  \hspace{2cm} (61)

The formation of H₂S according to the following reaction

\[ \text{FeS}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2\text{S} + \text{S}^\circ \]  \hspace{2cm} (62)

was noted in the absence of oxygen but it did not appear to be a necessary intermediate in the formation
of sulphur, via equation (46) or (48), as proposed by Downes and Bruce. However the reaction schemes put forward by the authors do not explain their observation that acid was essential for sulphur formation.

The dependence of rate on surface area and oxygen pressure and the lack of dependence on solution composition suggest that the rate determining step is a heterogeneous surface reaction involving the reduction of oxygen. By comparison, Shermer and Strickland [30] found that chlorine used as oxidant resulted in such rapid dissolution that the rate was entirely controlled by liquid phase diffusion. Ferric and sulphate ions were cited as the only products.

The most thorough study of the oxygen pressure leaching of pyrite has been made by Gerlach, Hähne and Pawlek [82]. Reactions (59), (60), (62), (63) and (64) were put forward as possible contributors to the observed leaching behaviour.

\[ \text{Fe}_2\text{S}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + 2\text{S}^0 + \text{H}_2\text{O} \]  
\[ \text{Fe}_2\text{S}_2 + \text{Fe}_2(\text{SO}_4)_3 \rightarrow 3\text{FeSO}_4 + 2\text{S}^0 \]  

Experiments showed that oxidation of pyrite by ferric ions via equation (64) did not occur to a measurable extent and that HgS was produced, in accordance with equation (62), only if the oxygen partial pressure was less than 0.1MPa. Both these observations concur with McKay and Halpern's findings but Gerlach et al. cite the two principal reactions as (59) and (63) rather than (59) and (60). Reaction (63) was dominant at temperatures below 50°C and (59) at temperatures above 120°C. At temperatures between these values the differing rates of the two reactions resulted in varying S^0/SO_4^2- ratios. At 100°C this ratio was found to be 1/3.

The initial acid concentration did not affect the rate of reaction or the distribution of products and its presence was necessary only to prevent the early hydrolysis of iron (equation (58)) which blocked the surface of the particles preventing further reaction. A linear dependence of dissolution rate on oxygen partial pressure and initial surface area was reported for leach times up to one hour. This corresponded to a pyrite dissolution of less than 30%. After longer times the rate decreased, due to a decrease in particulate surface area, but an explicit relationship was not developed. Apparent activation energies for pyrite dissolution and sulphate formation were similar and approximated McKay and Halpern's result (Table 2).

3.5 LEACHING OF CHALCOPYRITE

A worldwide shortage of copper smelting capacity, coupled with the difficulty of operating existing smelters to meet increasingly stringent air pollution standards, has provided a substantial incentive for the development of alternative smelting methods. Hydrometallurgical schemes have the potential of eliminating sulphur dioxide emissions and for this reason many leaching studies have been made of the copper minerals. Because chalcopyrite is a minor constituent (4.3%) of the ore used in this investigation the acid leaching studies of both type (1) and (2) (§ 3.1) will be reviewed together in this section.

3.5.1 Kinetic Leaching Studies

A summary of these studies containing much of the experimental information and the principal results is contained in Table 3.

The following reactions have been variously reported to account for the reaction stoichiometries observed in the acid leaching of chalcopyrite.

\[ \text{CuFe}_2\text{S}_2 + 4\text{H}^+ + 2\text{O}_2 \rightarrow \text{Cu}^{++} + \text{Fe}^{++} + 2\text{S}^0 + 2\text{H}_2\text{O} \]  

\[ \cdots \]  

\[ \cdots \]
TABLE 3  KINETIC STUDIES OF CHALCOPYRITE LEACHING

Notation: is the same as Table 1 with the exception that chalcopyrite (CuFeS_2) should be substituted for sphalerite (ZnS)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Year</th>
<th>Starting Material</th>
<th>Temperature (°C)</th>
<th>Oxygen Partial Pressure (MPa)</th>
<th>Initial Acid Concentration (mol 1⁻¹)</th>
<th>Stirring</th>
<th>Pulp Density (g 1⁻¹)</th>
<th>Acid CuFeS₂ Molar Ratio</th>
<th>Particle Sizing d₀ : μm (Å : m²g⁻¹)</th>
<th>Reaction Time (min.)</th>
<th>Observed Reactions</th>
<th>Apparent Activation Energy (kJ mol⁻¹)</th>
<th>Rate Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dobrokhov &amp; Malorova* [84]</td>
<td>1962</td>
<td></td>
<td>125 - 175</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>29 Rate = [H₂SO₄] / pO₂</td>
</tr>
<tr>
<td>Peters &amp; Loewen [85]</td>
<td>1968</td>
<td>99% CuFeS₂</td>
<td>70 - 140</td>
<td>0.2 - 0.7</td>
<td>0.25 - 4.0 (perchloric)</td>
<td>V</td>
<td>40</td>
<td>0.4 - 6.0 (calc.)</td>
<td>105 - 74 100% - 74</td>
<td>0 → 360</td>
<td></td>
<td></td>
<td>47 (sulphur) 63 (sulphate) Qualitative</td>
</tr>
<tr>
<td>Dutrizac et al. [86]</td>
<td>1969</td>
<td>Synthetic</td>
<td>50 - 94</td>
<td></td>
<td>0.001 g Fe₃⁺ as oxidant</td>
<td>rotating disc V</td>
<td>not applicable</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>71 Parabolic kinetics</td>
</tr>
<tr>
<td>Baur, Gibb &amp; Wadsworth [87]</td>
<td>1972</td>
<td>99.5% CuFeS₂</td>
<td>27 - 92</td>
<td>0.004 Fe⁺⁺ also Fe⁺⁺⁺</td>
<td>0.69 mol 1⁻¹ ph range 0.3 - 4.6</td>
<td>V</td>
<td>1 &amp; 2</td>
<td>5 - 10 (calc.)</td>
<td>40 - 60</td>
<td>0 - 60</td>
<td></td>
<td></td>
<td>43 A combination of linear and parabolic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>52 reaction 85 diffusion 87 parabolic</td>
</tr>
<tr>
<td>Yu, Hansen &amp; Wadsworth [88]</td>
<td>1973</td>
<td>88% CuFeS₂, 5% Fe₇S₄, 4% Fe₂O₄</td>
<td>125 - 175</td>
<td>0.5 - 2.8</td>
<td>0 - 0.05</td>
<td>V</td>
<td>5.7</td>
<td>0 - 17 (calc.)</td>
<td>-297 - 210 149 - 210</td>
<td>0 - 240</td>
<td></td>
<td></td>
<td>141 Rate = P₂O₅</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>37 (surface reaction)</td>
</tr>
</tbody>
</table>

* as reported by Wadsworth [36]
Peters and Loewan [85] in an investigation of the acid leaching behaviour of covellite, chalcocite, bornite and chalcopyrite used dilute perchloric acid to permit easy determination of sulphate. Reaction stoichiometry was not established since neither iron nor sulphur determinations were made. Oxygen consumption was used as a measure of the reaction progress but because elemental sulphur and sulphate ions were formed in two parallel reactions, each having a different oxygen demand, its relationship to the amount of copper dissolved was complex. Consequently the results obtained for changes in acid concentration were only qualitative.

Apparent activation energies were obtained for both the sulphur and sulphate forming reactions in the temperature range 105 to 120°C. Decreased reaction rates at temperatures above 120°C were attributed to stifling by a liquid layer of elemental sulphur. Based on the discovery that the activation energy of chalcopyrite was very close to that of covellite the authors tentatively proposed that the reaction mechanism in both cases involved the dissolution of covellite. This was assumed to form from chalcopyrite according to the reaction

\[
CuFeS_2 + 2H^+ + \frac{1}{2} O_2 \rightarrow CuS + Fe^{4+} + S^0 + H_2O
\]

but was not detected as a reaction intermediate. The difference in the rates of dissolution of chalcopyrite and covellite was attributed to the difference in the areas of covellite present in both cases. Micro-areas of covellite on the chalcopyrite surface were viewed as preferential sites for oxygen adsorption.

The percentage of sulphide sulphur oxidised to sulphate increased slightly with temperature, reaching a maximum of about 20% at 130°C. No sulphate was formed when ferric sulphate was used as oxidant [86] which suggests that the presence of oxygen is essential for this to occur. In this study [86] Dutrizac and co-workers used rotating discs of synthetic chalcopyrite and established that the leaching kinetics were parabolic in the range investigated. This was attributed to diffusion through a progressively thickening sulphur film (see equation (20)), although the activation energy (see Table 3) was somewhat higher than that normally associated with a diffusion mechanism. Changes in acid concentration had no affect on the dissolution rate and this, together with the fact that acid alone did not attack chalcopyrite, led the authors to conclude that the only function of the acid is to prevent hydrolysis of iron according to equation (58). Diffusion of ferric sulphate from the solution-sulphur interface to the mineral surface was found to be rate controlling for \([Fe^{4+}] < 0.01\). Above this concentration the outward diffusion of ferrous sulphate was rate controlling. Overall reaction stoichiometry was established as that of equation (69).

In a recent exhaustive study by Baur, Gibbs and Wadsworth [87], radiochemical techniques were used to follow the initial stage leaching kinetics of carefully sized and extremely pure samples of natural chalcopyrite. Two distinct dissolution periods were observed - an initial period of rapid dissolution lasting a few minutes followed by a second period of much slower rate. The initial period followed first order kinetics and was consistent with either the dissolution of surface oxidation products or the formation of an iron depleted surface layer. An apparent activation energy of 19.6 kJ mol\(^{-1}\) was found for this process and taken to imply solution diffusion control. The second stage process was linear at room temperature but became decreasingly so at elevated temperatures. The curves fitted an equation of the type

\[
\frac{\Delta n^2}{k_p} + \frac{\Delta n}{k_I} = t
\]
first applied by Wagner and Grünemwald [89] to the oxidation kinetics of copper. It suggests that the reaction is controlled jointly by diffusion through a thickening sulphur film and by a surface reaction. The activation energies for both processes are given in Table 3. As the temperature was increased the importance of the surface reaction decreased until at 90°C pure parabolic leaching was exhibited. The surface reaction was shown to be controlled by a non charge transfer step in the reduction of oxygen. Overall stoichiometry followed equation (66).

Additions of ferric sulphate increased the dissolution rate markedly with dissolution kinetics now following the parabolic diffusion law (equation (20)). Diffusion of ferric ions through the sulphur film appeared to be rate controlling but no satisfactory explanation could be found for the very high activation energy obtained. It was, however, comparable to that obtained by Dutrizac et al. [56] under similar conditions. The authors developed a generalised rate expression for sulphide leaching based on both film transfer and surface reaction kinetics. Two types of possible surface reactions were considered - one involving charge transfer (galvanic) and one not. The results for chalcopyrite were shown to fit this model.

In another study Wadsworth and co-workers [83] investigated the kinetics of reaction (68), which was found to occur at higher temperatures and oxygen pressures. The only deviations from reaction stoichiometry were the 20% iron which remained in the ferrous state and the production of up to 4% sulphur according to equation (67). Linear leaching kinetics were exhibited in all experiments providing surface area changes with time were taken into account by graphing equation (30). Changes in initial acid concentration had a complex effect on the dissolution rate. The rate increased up to 0.1 mol 1⁻¹ when a broad maximum value, which extended from 0.1 to 0.25 mol 1⁻¹, was reached. Above 0.25 mol 1⁻¹ the rate decreased. The authors attributed this jointly to the decrease in oxygen solubility with increasing solute concentration and to surface blocking by sulphate ions. Cupric, ferrous and ferric ions, at one sixth by weight of chalcopyrite, were added in separate experiments to investigate possible catalytic effects. Only ferric ions resulted in a rate increase (138).

The authors interpreted the dissolution process electrochemically - oxygen being reduced in cathodic areas and the sulphide dissolving, liberating electrons, to complete the couple. They suggest that the following reactions occur to make up the observed stoichiometry of equation (68).

\[
\begin{align*}
\text{cathodic:} & \quad O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad \cdots (72) \\
& \quad H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad \cdots (73) \\
\text{nett cathodic:} & \quad O_2 + 4H^+ + 2e^- \rightarrow 2H_2O \quad \cdots (44) \\
\text{anodic:} & \quad CuFeS_2 + 8H_2O + Cu^{++} + Fe^{++} + 2SO_4^{--} + 16H^+ + 16e^- \quad \cdots (74) \\
& \quad Fe^{++} \rightarrow Fe^{+++} + e^- \quad \cdots (75) \\
\text{nett anodic:} & \quad CuFeS_2 + 8H_2O \rightarrow Cu^{+++} + Fe^{+++} + 2SO_4^{--} + 16H^+ + 17e^- \quad \cdots (76) \\
\text{overall cell reaction:} & \quad 4CuFeS_2 + 17O_2 + 4H^+ \rightarrow 4Cu^{+++} + 4Fe^{+++} + 8SO_4^{--} + 2H_2O \quad \cdots (68)
\end{align*}
\]

The rate had a linear dependence on oxygen pressure over most of the pressure range but approached zero at high pressures. This dependence indicates that cathodic reactions are rate controlling. The observed kinetics were explained in terms of a two step mechanism involving steady state adsorption of oxygen followed by reaction. Application of the absolute rate theory [90] led to values of 141 kJ mol⁻¹ and 37.2 kJ mol⁻¹ for the activation enthalpy of the two steps. At very low oxygen pressures the adsorption step of high enthalpy was rate controlling, while at high pressures the surface reaction with relatively low enthalpy was controlling. The apparent activation energy lay somewhere between these two values being
dependent on both temperature and pressure. Wadsworth and co-workers advance this theory to explain the variety of activation energy values reported by other authors. Reaction rate did not exhibit a voltage dependence so that chemical reactions rather than charge transfer (galvanic) processes were rate controlling.

3.5.2 Process Oriented Studies (see Table 4)

Ever since their successful application of an ammonia pressure scheme for Ni-Co-Cu concentrates in 1953 [91], the research department of Sherritt Gordon Mines have been investigating the pressure leaching of sulphide ores, usually in collaboration with the University of British Columbia Metallurgy Department. In 1967 two papers were published on chalcopyrite leaching [93, 94]. The first - a report on the optimum autoclave conditions for leaching a copper concentrate - showed that chalcopyrite was more difficult to dissolve than sphalerite or galena. The aim of producing a pregnant solution containing 60 g l⁻¹ copper, the minimum concentration acceptable for subsequent copper recovery by electrowinning or hydrogen reduction, fixed both the initial pulp density and acid concentration.

Reaction stoichiometry was found to approximate equation (67) until the pH increased due to acid consumption. Iron then hydrolysed according to reaction (58), a desirable result because solutions suitable for electrowinning must contain < 5 g l⁻¹ iron. A 25% excess of concentrate over that required by the stoichiometry of equation (77) was used to ensure that the pH increased to the point of iron hydrolysis in a reasonable time (about 1 hr.).

\[
\text{CuFeS}_2 + \text{H}_2\text{SO}_4 + \frac{5}{2}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{CuSO}_4 + \text{Fe(OH)}_3 + 2\text{SO}_4^2^- \\
\text{..... (77)}
\]

The autoclave retention time for the attainment of copper and iron target concentrations was reduced from 12 to 2.5 hours at 110°C by increasing the oxygen partial pressure from 0.21 to 3.4 MPa. Above 120°C copper extraction ceased about halfway through the reaction. This phenomenon was attributed to surface blocking by a liquid film of sulphur (compare Peters and Loewan [65]). Fine grinding resulted in faster extraction rates but the authors point out that in practice an economic balance would have to be struck between the benefits of faster leaching and the costs of extra grinding.

Subsequent treatments of both the leach solution and the residue were investigated and a process flowsheet was presented. Several factors adversely affect the possibility of commercial application of this scheme.

(i) The high operating pressure (3.5 MPa) required to achieve rapid dissolution (2.5 hrs.).

(ii) The necessity for separation of unleached concentrate from the residue for recycling.

(iii) The buildup of sulphate in the leach circuit - up to 15% of the sulphide sulphur is oxidised to sulphate in a side reaction.

The second Sherritt Gordon paper [94] demonstrated that the reactivity of chalcopyrite was enhanced by a sulphidization treatment which involved heating the mineral for two hours at 475°C with 10% by weight of sulphur. After this treatment almost complete dissolution was achieved in one hour under less severe oxidising conditions than those required for untreated concentrate. Evidence presented showed that the increased dissolution rate was caused by the production of covellite during sulphidization according to the equation

\[
\text{CuFeS}_2 + \text{S}^0 \rightarrow \text{CuS} + \text{FeS}_2 \\
\text{..... (78)}
\]

Iron was not found in solution until after 95% of the copper had dissolved compared to the equal quantities produced in chalcopyrite leaching. Subramanian and Kanduth [69] attempted to utilize this result to obtain a clean separation of copper from iron by preferential dissolution. Their results, however, were not encouraging.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Year</th>
<th>Starting Material</th>
<th>Temperature (°C)</th>
<th>Oxygen Partial Pressure (MPa)</th>
<th>Initial Acid Concentration (mol l⁻¹)</th>
<th>Stirring</th>
<th>Pulp Density (g l⁻¹)</th>
<th>Acid CuFe₅₂ Molar Ratio</th>
<th>Particle Sizing (d_p: \mu m) (A : m²g⁻¹)</th>
<th>Reaction Time (min.)</th>
<th>Observed Reactions</th>
<th>Apparent Activation Energy (kJ mol⁻¹)</th>
<th>Rate Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Warren [92]</td>
<td>1958</td>
<td>80% CuFe₅₂ 20 Fe₂</td>
<td>120 → 180</td>
<td>0.17 → 2.4</td>
<td>0.04 → 0.2</td>
<td>V</td>
<td>31</td>
<td>0.25 → 1.25</td>
<td>-149 → 74</td>
<td>-53 → 44</td>
<td>0 → 150</td>
<td>96</td>
<td>Rate = A HgS produced for (P,O₂ &lt; 0.7 ) MPa</td>
</tr>
<tr>
<td>Warren, Vizsoyi &amp; Forward [94]</td>
<td>1967</td>
<td>heat treated CuFe₅₂</td>
<td>90</td>
<td>0.5</td>
<td>1.0</td>
<td>V</td>
<td>200</td>
<td>1.0</td>
<td>95% → 44</td>
<td>0 → 600</td>
<td>Qualitative only.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vizsoyi et al. [93]</td>
<td>1967</td>
<td>91% CuFe₅₂ 4.5 Fe₅</td>
<td>100 → 150</td>
<td>0.2 → 3.5</td>
<td>1.0</td>
<td>V</td>
<td>200 → 400</td>
<td>0.5 → 1.0</td>
<td>52 → 100%</td>
<td>-44</td>
<td>0 → 480</td>
<td>(67) (77)</td>
<td></td>
</tr>
<tr>
<td>Emilov et al. [95]</td>
<td>1969</td>
<td>FeCl₃ as oxidant</td>
<td></td>
<td></td>
<td></td>
<td>V</td>
<td>300</td>
<td>not given but variable</td>
<td>2.4 → 17.0</td>
<td>0 → 120</td>
<td>(79)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haver &amp; Wong [96]</td>
<td>1971</td>
<td>85% CuFe₅₂ 4 SiO₂ 6 Al₂O₃</td>
<td>30 → 106</td>
<td></td>
<td>FeCl₃ as oxidant (Hydrochloric)</td>
<td></td>
<td>V</td>
<td>300</td>
<td>not given but variable</td>
<td>2.4 → 17.0</td>
<td>0 → 120</td>
<td>Rate more rapid than the (O₂ - acid) system.</td>
<td></td>
</tr>
<tr>
<td>Prater et al. [97]</td>
<td>1972</td>
<td>60% CuFe₅₂ 10 Cu₃Fe₅₂ 10 Fe₂</td>
<td>75 → 95</td>
<td>HNO₃ as oxidant</td>
<td>2 → 14</td>
<td>NV</td>
<td>150 → 330</td>
<td>not given but variable</td>
<td>NV</td>
<td>0 → 240</td>
<td>(80)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gerlach et al. [68]</td>
<td>1973</td>
<td>90% CuFe₅₂ 4.5 Insol 0.2 Ni</td>
<td>50 → 110</td>
<td>0.2 → 2.0</td>
<td>0.19 → 0.53</td>
<td>NV</td>
<td>50 → 300</td>
<td>0.4 → 2.4</td>
<td>different grinding times</td>
<td>0 → 120</td>
<td>(67) (77)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* as reported by Haver and Wong [96]
Ferric chloride leaching of chalcopyrite has been reported by Ermilov et al. [95] and Haver and Wong [96]. The former found that the overall reaction stoichiometry could be represented by equation (63). Leaching kinetics were parabolic which was attributed to diffusion through a sulphur film. Haver and Wong showed that by adjusting the FeCl₃/CuFeS₂ weight ratio to 2.7 the following reaction stoichiometry was achieved.

\[
\text{CuFeS}_2 + 3\text{Fe}^{+++} \rightarrow \text{Cu}^+ + 4\text{Fe}^{++} + 2\text{S}^0
\]  

(79)

This reduced the amount of oxygen required to regenerate the ferric chloride and also the amount of reductant to produce copper metal. Dissolution rates were increased by finer grinding and higher temperatures - a maximum of 106°C was dictated by the natural boiling point of the solution. Under optimum conditions near complete dissolution was effected in two hours. A process scheme employing these conditions was elaborated.

Prater, Queneau and Hudson [97] investigated a nitric acid leach scheme. They used four responses - metal extraction, elemental sulphur yield, iron rejection and reagent consumption - to optimise a process in which nitric acid concentration, sulphuric acid concentration, temperature, time and percent solids were all varied. Mineral type, particle size and agitation were held constant. The idealized reaction (80) was never achieved in practice and a small amount of copper nitrate, acid and ferric salts remained in the leach solution. The formation of sulphate ions and nitrogen dioxide gas was also noted under some conditions.

\[
6\text{CuFeS}_2 + 10\text{HNO}_3 + 10\text{H}_2\text{SO}_4 + 6\text{CuSO}_4 + 10\text{NO} + 12\text{S} + 6\text{H}_2\text{O} + 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}
\]

(80)

In 1973 Gerlach and co-workers [68] reported that impact milling of chalcopyrite resulted in dissolution rates superior to ball mill ground chalcopyrite. The improvement was attributed to the nature of the grinding process. Impact milling resulted in a strong "... stressing, distortion or defect formation in the crystalline particles ...". The extent of the distortion was measured qualitatively by the reduction in intensity of X-ray diffraction peaks and showed that ½ hour in an impact mill produced the same lattice distortion as 5 hours in a ball mill. Unfortunately the authors did not report the screen analyses or particulate surface areas resulting from grinding in the two mills making quantitative interpretation of the data impossible.

An examination of the equations reported for chalcopyrite leaching reveals that none of the major studies have noted the presence of hydrogen sulphide as a product. Only Warren [92] mentioned hydrogen sulphide evolution. This occurred at oxygen pressures of less than 0.7 MPa.

3.6 PROCESS ORIENTED LEACHING STUDIES OF ZINC, LEAD AND LEAD-ZINC CONCENTRATES.

3.6.1 Zinc Concentrates

The most desirable reaction on which to base a hydrometallurgical extraction process for sphalerite is that given by equation (33).

\[
\text{ZnS} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow \text{Zn}^{++} + \text{S}^0 + \text{H}_2\text{O}
\]  

(33)

Such a process would possess several advantages over other schemes.

1. Zinc is solubilized in a single step with potentially greater recovery than in the conventional roast-leach scheme.

2. Sulphide sulphur reports as solid elemental sulphur in the leach residue so avoiding the toxic
gas formation of other processes - \( \text{SO}_2 \) from conventional roasting operations and \( \text{H}_2\text{S} \) from a non-oxidising leach (equation (32)).

3. It is unnecessary to have a sulphuric acid plant on site.

4. The reaction consumes a minimum of oxidant. A leach scheme based on equation (34), for example, would use four times as much oxygen and result in an undesirable build up of sulphate ions in the recycled leach solution.

For the above reasons considerable effort has been directed toward empirical derivation of optimum leach parameters, using sulphur production and reaction rate as principal responses. Experimental details and results of the major studies are summarised in Table 5A.

It should be pointed out that oxidants other than dissolved oxygen can be effective in producing elemental sulphur. Examples have already been quoted in which chlorine [62], ferric sulphate (equation (69)) and nitric acid (equation (80)) have been successfully used. However dissolved oxygen has been chosen by most investigators (for reasons discussed in Chapter 1) and there is considerable evidence to suggest that such a process will ultimately proceed to full plant scale. In 1967 Mackiw [33] reported that processes based on leaching reaction (33) had been successfully piloted by Cominco and by Dowa Mining in Japan and a later report [110] in 1970 details Hudson Bay Smelting and Mining Co.'s commitment to piloting Sherritt Gordon's accelerated zinc leach scheme [102] at Flin Flon Manitoba.

3.6.1.1 Sherritt Gordon Studies

Sherritt Gordon researchers have published a number of papers dealing with the acid pressure leaching behaviour of sphalerite concentrates. The first [98] appeared in 1959 and reported rapid dissolution at temperatures below 110°C with overall stoichiometry approaching the ideal of equation (33). This result appeared to conflict with earlier observations of Björling [53] who found that reaction was extremely slow unless catalysed by additions of nitric acid, ferric or cupric salts. The conflict has been resolved by subsequent research. Many workers have substantiated the slow reaction rate of pure sphalerite [63, 64, 61, 71] and the presence of 10% by weight of iron in Forward and Veltman's [98] concentrate (as substitutional solid solution, marmatite) was later isolated [77] as the catalytic agent.

Investigating the effect of temperature on dissolution rate, Forward and Veltman found an expected initial rate increase with temperature rise. However above 110°C the reaction ceased after about ten minutes with less than 70% of the zinc dissolved. This phenomenon was attributed to occlusion of unreacted mineral by molten sulphur. The rate increased with oxygen pressure but was not influenced by the presence of copper (1%) or lead (up to 66%) in the concentrate. It was found that acid had to be added in accordance with that required by the stoichiometry of equation (54) as well as equation (33) since galena dissolved substantially faster than sphalerite. Elemental sulphur production paralleled sphalerite dissolution but some sulphate formation was reported. Hydrolysis of iron dissolved in the leach occurred when the acid concentration dropped below 10 gl⁻¹.

With process possibilities in mind some experiments were conducted using a synthetic return electrolyte for leaching instead of pure sulphuric acid. Electrolyte composition was based on that leaving a zinc electrowinning plant for recycling and contained about 50 gl⁻¹ zinc and 150 gl⁻¹ sulphuric acid. Results showed that the reaction rate was unaffected by the zinc concentration in the leach solution (no back reaction effect). The authors therefore proposed a hydrometallurgical process for zinc recovery involving the pressure leaching of sphalerite in return electrolyte. Subsequent purification of the pregnant liquor would produce a solution suitable for conventional electrowinning where sulphuric acid consumed in the leach would be regenerated. Elemental sulphur, lead and precious metals would be recoverable from the leach residue.

A follow-up paper [101] published in 1965 records the results of subsequent extensive laboratory studies aimed at establishing the technical viability and optimum operating conditions of the process. Optimum conditions for leaching were: oxygen partial pressure 0.25 MPa, grind 99% minus 44 \( \mu \)m, temperature 110°C.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Year</th>
<th>Concentrate Analysis (weight %)</th>
<th>Temperature (°C)</th>
<th>Oxygen Partial Pressure (MPa)</th>
<th>Initial Acid Concentration (mol l⁻¹)</th>
<th>Pulp Density (g l⁻¹)</th>
<th>Acid/ZnS Molar Ratio</th>
<th>Particle Sizing d₀ (µm)</th>
<th>Reaction Time (min.)</th>
<th>Observed Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forward &amp; Veltman</td>
<td>1959</td>
<td>42 8 10 25</td>
<td>90 - 140</td>
<td>0.07 - 0.4</td>
<td>0.45 - 1.0</td>
<td>140</td>
<td>three grinding times</td>
<td>0 - 240</td>
<td>(33)</td>
<td>Occlusion of ZnS above 110°C. PbS more reactive than ZnS. Return electrolyte was suitable leachant</td>
</tr>
<tr>
<td>Umetsu et al. [99]</td>
<td>1960</td>
<td>21 4 11 35</td>
<td>160 - 190</td>
<td>2 - 4</td>
<td>Water</td>
<td>100 - 250</td>
<td>100% - 74</td>
<td>0 - 300</td>
<td>(34)</td>
<td>Increased oxygen pressure has a greater effect on Cu dissolution than on Zn.</td>
</tr>
<tr>
<td>Heinglein &amp; Hirsch</td>
<td>1961</td>
<td>69 1 2 33</td>
<td>100 - 190</td>
<td>2.5</td>
<td>Water</td>
<td>33.3</td>
<td>sieve analysis given</td>
<td>100</td>
<td>(34)</td>
<td>The increased reactivity of zinc concentrate attributed to the presence of Cu.</td>
</tr>
<tr>
<td>Yaroslavstev &amp; Smirnov</td>
<td>1964</td>
<td>46 7 11 235</td>
<td>100 - 115</td>
<td>0.4 - 1.2</td>
<td>1.5</td>
<td>200</td>
<td>1.0 (calc.)</td>
<td>100% - 63</td>
<td>165</td>
<td>(33) Two stage countercurrent leach with return electrolyte. Sulphate and Fe buildup in the circuit.</td>
</tr>
<tr>
<td>Kunda et al. [101]</td>
<td>1965</td>
<td>7 concentrates 48 0.6 31.31 64 6 10.34</td>
<td>100 - 130</td>
<td>0.07 - 0.28</td>
<td>1.5</td>
<td>0.9 - 1.4</td>
<td>80 - 99% - 44</td>
<td>0 - 360</td>
<td>(34)</td>
<td>Occlusion by S above 110°C. Low Fe concentrates catalysed by Fe additions.</td>
</tr>
<tr>
<td>Veltman &amp; O’Kane</td>
<td>1968</td>
<td>47 6 11 124</td>
<td>110 - 150</td>
<td>0.14 - 0.35</td>
<td>1.5</td>
<td>320</td>
<td>0.66 - 1.1</td>
<td>60% - 44</td>
<td>0 - 360</td>
<td>(33) No occlusion by S above 110°C if excess ore/acid used - hence increased reaction rates.</td>
</tr>
<tr>
<td>Yaroslavstev et al.</td>
<td>1968</td>
<td>17 11 18 3 24</td>
<td>110</td>
<td>0.6</td>
<td>1.2</td>
<td>100% - 63</td>
<td>0 - 300</td>
<td>(33)</td>
<td>Single stage leach - results similar to [101]</td>
<td></td>
</tr>
<tr>
<td>Nabotchenko et al.</td>
<td>1969</td>
<td>22 0 28 240</td>
<td>70 - 115</td>
<td>0.2 - 1.0</td>
<td>0.4 - 1.6</td>
<td>110 - 250</td>
<td>1.1 - 2.2</td>
<td>0 - 480</td>
<td>(33)</td>
<td>Occlusion of all minerals above 110°C</td>
</tr>
</tbody>
</table>

Notes:
- Znₙ = f [H₂SO₄]ₙ
- Cuₙ + f Fe f [H₂SO₄]ₙ
- Reaction rates and mechanisms vary significantly between studies.
(omission above this), acid/sphalerite mol ratio, slightly greater than 1.0 (to allow for acid consumption by impurities) and a reaction time of six hours. Seven concentrates from various sources were leached under these conditions and extractions after six hours were similar in all cases. However it was noted that a four fold increase in initial dissolution rate was achieved for a concentrate containing 0.6% iron by the addition of 20 g l\(^{-1}\) of soluble iron from an external source. The catalytic role of iron was attributed to its ability to act as an 'oxygen carrier' and the following sequence of reactions was postulated (see also references [77] and [70]).

\[
\begin{align*}
\text{ZnS} + \text{H}_2\text{SO}_4 & \rightleftharpoons \text{ZnSO}_4 + \text{H}_2\text{S} \\
\text{Fe}_2\text{(SO}_4)_3 + \text{H}_2\text{S} & \rightarrow 2\text{FeSO}_4 + \text{S} + \text{H}_2\text{SO}_4 \\
2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} & \rightarrow \text{Fe}_2\text{(SO}_4)_3 + \text{H}_2\text{O}
\end{align*}
\]

The overall reaction reduces to that of equation (33). When the sulphuric acid concentration dropped below 10 g l\(^{-1}\) iron was found to hydrolyse according to the reactions:

\[
\begin{align*}
4\text{FeSO}_4 + \text{O}_2 + (4 + 2x)\text{H}_2\text{O} & \rightarrow 2\text{Fe}_2\text{O}_3 \cdot \text{xH}_2\text{O} + 4\text{H}_2\text{SO}_4 \\
\text{Fe}_2\text{(SO}_4)_3 + (2 + 2x)\text{H}_2\text{O} & \rightarrow 2\text{Fe(OH)}\text{SO}_4 \cdot \text{xH}_2\text{O} + \text{H}_2\text{SO}_4 \\
2\text{Fe(OH)}\text{SO}_4 \cdot \text{xH}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{Fe}_2\text{O}_3 \cdot \text{xH}_2\text{O} + 2\text{H}_2\text{SO}_4 + \text{xH}_2\text{O}
\end{align*}
\]

Equilibrium iron concentrations in solution eventually dropped below 1 g l\(^{-1}\) but this required long reaction times. Hydrolysis was therefore hastened by neutralizing the solution with zinc calcine. The additions were calculated to give a final solution pH slightly lower than 5.2. Above this value zinc itself begins to hydrolyse. Conversion of sulphide sulphur to elemental sulphur varied from 72 to 89% with up to 10% oxidising further to sulphate.

In a third Sherritt Gordon paper [102], Voltman and O’Kane showed that the retention time considered optimum in reference [101] could be reduced four fold by changing two experimental variables.

(i) temperature from 110 to 150°C
(ii) acid/sphalerite mol ratio from 1.1 to 0.66

For some unexplained reason occlusion of unreacted sphalerite by molten sulphur did not occur at temperatures above 110°C when a stoichiometric excess of concentrate was leached. This permitted the use of higher temperatures with consequent increases in reaction rates. Upper temperature limitations were imposed by the rapid rise in the water partial pressure which substantially increases capital and operating costs. Two other advantages of using excess concentrate are immediately apparent.

(a) a larger surface area is presented for leaching resulting in more rapid realisation of the target concentration
(b) almost complete iron hydrolysis is achieved without external additions because of the initial stoichiometric deficiency of acid.

A major disadvantage of the scheme, however, is the necessity of separating unreacted sulphides from the residue for recycling. Voltman and O’Kane demonstrated the technical feasibility of this step but recognised an additional problem of pyrite build-up in the recycled concentrate because of its relative inertness under the prescribed leach conditions. The overall reaction stoichiometry of equation (33) was closely approached, with 80 to 85% elemental sulphur production. The remainder formed sulphate which, like pyrite, tended to build up in the circuit. Cost data presented in this paper show that both leach schemes [101] and [102] compare favourably with existing roast-leach smelters.
3.6.1.2 Russian Studies

Since 1964 Yaroslavstev and co-workers have published a number of papers on sphalerite leaching [65, 100, 103, 112]. In one paper [100] they examined a two stage countercurrent leach using similar operating conditions to those established as optimum by Forward and Veltman [98] and Kunda et al. [101]. An exception was the higher oxygen partial pressure (0.6 MPa) employed. Experiments with return electrolyte (40 g l⁻¹ Zn and 150 g l⁻¹ H₂SO₄) resulted in overall extractions of 97% Zn, 51% Cu, 24% Fe and 75% S. An optimum retention time of 150 minutes in the first autoclave resulted in exit concentrations of 33 g l⁻¹ acid, 113 g l⁻¹ Zn, 5.4 g l⁻¹ Fe and 1.6 g l⁻¹ Cu. After 15 minutes in the second stage, the acid concentration fell to 3 - 4 g l⁻¹, Zn increased to 140 g l⁻¹ and Fe to 6.4 g l⁻¹. Some sulphate production was realised and this was attributed to the combined effects of reactions (59) and (61). No information was presented on subsequent purification of the exit leach liquor and buildup of iron in the leach circuit was not discussed. This occurs when iron hydrolysed in the low acid stage redissolves on transference to the high acid stage.

In a later paper [103] these workers describe a laboratory investigation of the leaching behaviour of two sphalerite-chalcopyrite-pyrite concentrates and one intermediate product. Optimum conditions were similar to those obtained above but a 300 minute retention time was required to extract 93% zinc and between 70 and 98% of the copper in a single stage leach.

Naboichenko et al. [104] studied the leaching behaviour of a zinc-copper intermediate product from the flotation of copper-zinc ores. They found that while zinc extraction increased with acid concentration, copper and iron extractions were largely independent. Overall extractions for all minerals decreased at temperatures greater than 110°C. Increases in oxygen pressure resulted in faster dissolution but the effect was most marked for copper. Results presented on the effect of acid concentration were conflicting. The authors confirmed that return electrolyte was a suitable leachant.

3.6.1.3 Other Studies

Oxygen pressure leaching of zinc concentrates in water was investigated by Heinglein and Hirsch [63] and Umetsu et al. [99]. The former workers postulated that the marked increase in reactivity of zinc concentrate over pure sphalerite was due to the presence of copper in the ore which was dissolved by the free acid formed from iron hydrolysis (equation (58)) and pyrite dissolution (equation (59)). Addition of copper sulphate to the leachant further increased the rate of extraction. Umetsu et al. investigating the behaviour of a zinc-iron-copper concentrate found that 99% zinc, 95% copper and less than 20% iron were extracted after 60 minutes at a total pressure of 4 MPa and a temperature of 185°C. In all experiments copper dissolved more slowly than zinc but the rate of copper dissolution increased more rapidly than zinc with rise in oxygen pressure.

3.6.2 Lead Concentrates

There has been little interest in the leaching of galena (§ 3.3) and only one investigation [77] of the acid pressure leaching of lead concentrates has been published (Table 58). These workers found that concentrates dissolved more rapidly than pure galena and produced almost quantitative yields of elemental sulphur instead of hydrogen sulphide. Iron, present in the concentrates as pyrrhotite (about 10% by weight), was singled out as the catalytic agent. The following reaction sequence was proposed to explain the role of iron.

\[
PbS + H_2SO_4 \rightarrow PbSO_4 + H_2S \quad \text{..... (58)}
\]

\[
Fe_2(SO_4)_3 + H_2S + 2FeSO_4 + S_0 + H_2O \quad \text{..... (48)}
\]

\[
2FeSO_4 + H_2SO_4 + 1O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \quad \text{..... (50)}
\]
### TABLE 58  PROCESS ORIENTED STUDIES OF LEAD AND LEAD-ZINC CONCENTRATES

**Notation:** The same as Table 1 with the exception that galena (PbS) should be substituted for sphalerite (ZnS)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Year</th>
<th>Concentrate Analysis (Weight %)</th>
<th>Temperature (°C)</th>
<th>Oxygen Partial Pressure (MPa)</th>
<th>Initial Acid Concentration (mol l⁻¹)</th>
<th>Pulp Density (g l⁻¹)</th>
<th>Acid (H₂SO₄)+ZnS Molar Ratio</th>
<th>Particle Size (µm)</th>
<th>Reaction Time (min.)</th>
<th>Observed Reactions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vizsoyli et al. 77</td>
<td>1963</td>
<td>4.63 13 8 0 18 24</td>
<td>70 - 200</td>
<td>0.04 - 0.4</td>
<td>0.4 (calc.)</td>
<td>V</td>
<td>1.1 - 2.0</td>
<td>97% - 44</td>
<td>0 - 360</td>
<td>(55) (56)</td>
<td>Occlusion of PbS and ZnS above 110°C At pH &gt; 2 PbSO₄ 'reconverts' Fe has an important catalytic role</td>
</tr>
<tr>
<td>Mackiw &amp; Veltman 107</td>
<td>1967</td>
<td>29 11 18 4 34 1.43</td>
<td>93 &amp; 110</td>
<td>0.04 &amp; 0.14</td>
<td>1.5</td>
<td>300</td>
<td>1.0 - 1.1</td>
<td>93% - 44</td>
<td>0 - 480</td>
<td>(33) (55) (34) (56)</td>
<td>Pyrite and chalcopyrite unattacked. Galena attacked more rapidly than ZnS. No mention of 'reconversion'.</td>
</tr>
<tr>
<td>Scott 108,109</td>
<td>1973</td>
<td>25 10 13.5 29</td>
<td>95 - 120</td>
<td>0.2 - 0.7</td>
<td>1.0</td>
<td>280</td>
<td>0.8 - 1.3</td>
<td>35 - 85 per stage. 3 stages (33) (55) (34) (56)</td>
<td>No occlusion by S at 120°C. PbSO₄ 'reconverts' to jarosites. Recycle electrolyte was a suitable leachant. Difficulties with the recovery of S and Pb from the leach residue.</td>
<td></td>
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It is completely analogous to the sequence presented \([101, 102]\) for sphalerite leaching. The increased dissolution rate of pure galena when pyrite and ferric oxide were added to the leachant in separate experiments was taken as supportive evidence for this sequence of reactions. In contrast, Exner et al. \([76]\) (§ 3.3) found that iron additions had no effect on the rate. The limiting step was diffusion through a thickening layer of lead sulphate. However both studies reported that sulphur occlusion occurred above \(110^\circ\text{C}\). At temperatures below this Vizsolyi et al. \([77]\) found that the rate was so fast (97% in 1 hr. at \(90^\circ\text{C}\)) that increases in oxygen pressure above 0.14 MPa had little influence. Sphalerite dissolution was considerably slower than lead but Peters and Majima \([111]\) suggest that the reason for this may have been overgrinding of galena, resulting in a smaller mean particle size than the other minerals in the concentrate.

An important observation made by Vizsolyi et al. was that lead sulphate, formed in the rapid initial reaction, 'reconverted' to a basic iron-lead sulphate in the presence of ferric ions. The 'reconversion' reaction was accelerated by the presence of zinc and copper ions and the product formed was insoluble in ammonium acetate and amine solutions. Extraction of lead from the leach residue by solvent extraction methods proposed earlier \([74, 75]\) was clearly impossible. It was found that the compound, identified later by Scott \([109, 113]\) as plumbojarosite, could be rendered soluble by heating at \(560^\circ\text{C}\).

Also investigated was the rate of the water reaction (equation \((55)\)). It was considerably slower than reaction \((54)\) and more profoundly affected by the temperature (Fig. 9).

![Fig. 9](image)

**Fig. 9** The effect of temperature on the conversion of lead sulphide at 0.14 MPa oxygen pressure with and without acid additions (after Vizsolyi et al. \([77]\)).

3.6.3 Lead-Zinc Concentrates (Table 58)

In a report of a further investigation by Sherritt Gordon \([107]\), Mackiw and Veltman discuss the process possibilities for the recovery of zinc and lead by oxygen pressure leaching of a complex low grade concentrate produced by the bulk flotation of a New Brunswick disseminated pyrite ore. Experimental results indicated that both galena and sphalerite can be dissolved in less than eight hours at \(110^\circ\text{C}\) with almost quantitative yields of sulphur according to equations \((33)\) and \((54)\). The role of iron was again reiterated, with reaction sequences \((53)\), \((48)\), \((50)\) and \((33)\), \((48)\), \((50)\) being cited for lead and zinc respectively. The rate of galena dissolution was somewhat faster than sphalerite but the discrepancy was not as marked as in study \([77]\).
Return electrolyte was shown to be an effective leachant and sulphur recovery from the residue by pelletization and by flotation was demonstrated. Pyrite and chalcopyrite were largely unattacked in the leach providing a simple separation of these minerals from galena and sphalerite. Dissolved iron started to hydrolyse after 60 minutes and the concentration dropped below 2 gl\(^{-1}\) after eight hours. Surprisingly, no mention was made of the 'reconversion' of lead sulphate.

The leaching behaviour of a similar bulk concentrate from McArthur River in Australia was very thoroughly investigated by the C.S.I.R.O. in Melbourne [108] and Scott [109] describes the results of the pilot plant study. The aims of this work were "... to recover the maximum amount of zinc in the minimum time and to produce pregnant liquors suitable for subsequent purification preferably containing < 1 gl\(^{-1}\) iron and < 2 gl\(^{-1}\) free sulphuric acid. Simultaneously it was desired to produce residues with lead predominantly in the form of lead sulphate so that the ammoniacal ammonium sulphate procedure [74] could be used for lead recovery ..." Several possible leach schemes were investigated.

(a) Two stage countercurrent leaching - gave excellent results but the elimination of soluble iron from the circuit presented a major problem.

(b) Leaching with excess concentrate [102] - gave unsatisfactory results because sulphur in the residue could not be pelletized.

(c) Low-acid leaches [98, 101] adding an amount of acid just sufficient to react with all the lead and zinc. Results were satisfactory, finishing with a low free acidity due to incompleterecoaction. The liquors produced were suitable for further processing but the residues contained much lead jarosite and releaching was necessary to convert this to lead sulphate.

(d) High-acid leaches using 20 to 30\% excess acid - eliminated jarosite formation and achieved faster and more complete leaching but produced liquors high in iron and free acid. Despite good leaching results no acceptable way of purifying leach liquors could be found.

Leach scheme (c) was adopted for pilot plant study. Leaching was carried out in three stages with co-current flow of leachant (recycled electrolyte) and concentrate. The dissolution rates of all minerals increased with temperature and contrary to most reported findings [66, 98, 100, 101, 104, 107] no restriction of dissolution was noted above 110\(^\circ\)C. Higher temperatures were not considered desirable, however, because of the rapid increase in the dissolution of pyrite. Increased oxygen pressures also increased the rate but again enhanced pyrite dissolution especially when coupled with high temperatures. A moderate value (0.4 MPa) was considered a reasonable compromise. Good yields of elemental sulphur were obtained but about 15\% of the sulphide sulphur was oxidised further to sulphate (reactions (34), (55) and their analogues for other sulphides). As the free acidity decreased during the leach the following hydrolysis reactions were observed to occur in addition to (81) and (82).

\[
3\text{Fe}_2(\text{SO}_4)_3 + 14\text{H}_2\text{O} \rightarrow 3\text{Fe}_2\text{O}_3.4\text{SO}_3.9\text{H}_2\text{O} + 5\text{H}_2\text{O} \quad \ldots \quad (84)
\]

\[
\text{PbSO}_4 + \text{CuSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} \rightarrow \text{PbO}\cdot\text{CuO}\cdot\text{Fe}_2\text{O}_3.2\text{SO}_3 + 3\text{H}_2\text{O} + 3\text{H}_2\text{SO}_4
\]

(beaverite) \quad \ldots \quad (85)

\[
\text{PbSO}_4 + 3\text{Fe}_2(\text{SO}_4)_3 + 12\text{H}_2\text{O} \rightarrow \text{PbO}\cdot3\text{Fe}_2\text{O}_3.4\text{SO}_3.6\text{H}_2\text{O}
\]

(plumbojarosite) \quad \ldots \quad (86)

The conversion of lead sulphate to jarosites (favoured by high ferric ion concentrations and low free acidity) rendered it insoluble in ammoniacal ammonium sulphate. Several successful methods of regenerating lead sulphate were cited.

(i) using acid solutions via the reverse of reactions (85) and (86).
(ii) using ammonia solutions to produce ferric hydroxide and ammonium sulphate.
(iii) pugging with concentrated sulphuric acid.
(iv) roasting at 600 → 700°C.

Additions of potassium sulphate were successful in limiting the formation of plumbojarosite because of preferential deposition of potassium jarosite but the rate of zinc dissolution was substantially reduced. Upgrading of the leach residues presented several problems.

(i) flotation of pyrite was unsuccessful. Reasons cited included the presence of composite grains, the extreme fineness of the residues and surface coatings of sulphur.
(ii) removal of sulphur by pelletization was unsuccessful because of the high pyrite content.
(iii) cyanidation for silver (5 oz/ton) was unsuccessful even after sulphur removal and roasting.

For these reasons, combined with difficulties of lead recovery after jarosite formation, the process has not proceeded to full scale plant.

Two further papers [105, 106] review the process possibilities of acid leaching pressure oxidation schemes for lead-zinc-copper concentrates.

3.7 ELECTROCHEMICAL THEORIES OF SULPHIDE DISSOLUTION

Examination of the literature reviewed so far reveals that our knowledge of the fundamental processes which govern the rate of sulphide dissolution is very sketchy and incomplete. This is particularly true of the processes which occur on or about the mineral/solution interface. It has only been in the last decade that the importance of the minerals electronic structure has been fully recognized. This recognition was originally due to an analogy drawn between sulphide dissolution and metallic corrosion and it has been stimulated by important advances in the understanding of semiconductors. Most electrochemical studies of the sulphide minerals have been concerned with direct electrolyses, oxidation mechanisms in nature and semiconductive properties. Very few electrochemical interpretations have been made of the kinetics of pressure leaching but there is sufficient evidence of the importance of charge transfer reactions to include a brief review here.

Cornelius and Woodcock [114] first drew attention to electrochemical leaching mechanisms in 1958. In a microscopic study of partly leached pyrite they found that dissolution had started at certain preferred sites, forming pits, while the remaining surface was virtually unattacked. It was supposed that the pits were anodic sites for the dissolution of pyrite and the unattacked area was cathodic for the reduction of oxygen. In this model rate control is via oxygen reduction and because the cathode area is essentially unaltered during leaching, it predicts a rate independence of the fraction leached (compare to equation (22)). This was confirmed by experiment. Dislocations, point defects and impurity atoms were regarded as having possible significance in determining initial sites for attack. In addition it was pointed out that oxygen poor regions at the bottom of pits and cracks would be favoured as anodic zones. Studies by Warren [79] and Peters and Majima [115] confirmed that pitting occurs in pyrite leaching. The latter authors discovered that the anodic dissolution of pyrite yielded only sulphate ions. They concluded that the sulphur producing reaction, which can account for up to 50% of the sulphide sulphur [81], is not electrochemical.

Hisamatsu and Masuko [73] were the first workers to propose an electrochemical mechanism for the dissolution of zinc sulphide. In their investigation reactions (32), (33) and (34) were all observed but only (33) was interpreted electrochemically. When dilute acid solutions were added to pure synthetic zinc sulphide hydrogen sulphide was evolved and it persisted despite the presence of oxygen (compare with the results of Exner et al. p.19). Addition of cupric ions to the solution, however, resulted in reaction (33) occurring. Two mechanisms for this catalytic effect were considered.
(i) Homogeneous oxidation of hydrogen sulphide in solution.

(ii) Activation of the sphalerite by formation of covellite on the surface. It was proposed that covellite acted as an active cathode for the reduction of oxygen according to reaction (44) allowing zinc to dissolve anodically via reaction (43). This mechanism is illustrated schematically in Fig. 10.

![Electrochemical model of the oxidation of copper activated sphalerite (after Hisamatsu and Masuko [73]).](image)

A mechanism similar to (ii) above was ventured independently by Scott and Dyson [61]. They assert that activation occurs by incorporation of catalyst ions in the surface layers of the pure mineral, thereby increasing its conductivity and allowing galvanic dissolution. The fact that the reactivity was not increased by other ions which also displace zinc from the sphalerite lattice led the authors to suggest that, to exert a catalytic effect, the foreign ion must also participate in one of the chemical reactions which take place. The most likely reaction was the reduction of oxygen (44) since the catalysts had no influence on dissolution rate when oxidants other than oxygen were employed. The presence of covellite on the surface of partially reacted sphalerite was confirmed by X-ray diffraction. However, additions of copper ions in excess of those which could be incorporated in the zinc sulphide lattice were found to further increase the dissolution rate. Scott and Dyson could not explain this phenomenon but one possible explanation is provided by Hisamatsu and Masuko's mechanism (i) above.

A somewhat more extensive but still qualitative electrochemical model of leaching has been described by Exner, Hähne and Pawlek [70] to partially explain their leaching results with sphalerite (pg. 21). Only reactions (32) and (33) were found to be of an electrochemical nature and the half cell reactions (43) and (44) were supposed to occur. The authors' model is based on the boundary layer theory of chemisorption proposed by Hauffe and Engell [116] which is illustrated schematically in Fig. 11 for anion (oxygen) chemisorption on an n-type semiconductor (pure sphalerite). In this model oxygen is chemisorbed at the semiconductor/electrolyte interface. Electrons from donor levels near the surface of the semiconductor transfer to the adsorbate. Each transfer increases the space charge in the boundary layer, thereby creating a growing potential barrier for further electron transport. A state of equilibrium is reached when the potential energy of the electrons in the semiconductor (i.e. the Fermi level) equals that of the electrons in the adsorbate (viz: \( V_F + \phi = \omega \) in Fig. 11).
Exner et al. obtained a value of $6 \times 10^9$ Ω cm for the resistivity of pure sphalerite (about an order of magnitude greater than most other sulphides) and suggested that the slow dissolution of this material may be due to the very slow cathodic discharge of oxygen. Increased conductivity can be brought about in several ways.

(i) Irradiation, which can raise electrons from the valence to the conduction band.

(ii) By increasing the number of lattice defects - in particular by the presence of foreign atoms (electron donors) in the lattice.

(iii) By the addition of chemical additives (redox systems) which change the Fermi level.

Experiments with ultraviolet radiation on doped zinc sulphide gave the expected increase in dissolution rate. It was associated with a decrease in resistivity from $2 \times 10^{13}$ to $6.5 \times 10^7$ Ω cm providing direct evidence of an electrochemical mechanism. Reaction (33) became predominant when iron concentrates were leached and the increased leaching rates were attributed to the presence of foreign atoms in the lattice of naturally occurring sphalerite. This interpretation is odd in the light of contradictory evidence presented in the same paper. Specifically they found that in the fast dissolving concentrates iron was present as pyrite and ferrous sulphate whereas slow dissolving concentrates contained iron in solid solution as marmatite. This suggests that iron is not effective as a donor in the zinc blende lattice.

Further experiments showed that iron in solution was effective in accelerating the dissolution rate of pure sphalerite by rapidly oxidising and preventing the build up of hydrogen sulphide. This mechanism appears to be a more likely interpretation of Exner's results with concentrates, being analogous to Hisamatsu and Masuko's proposed mechanism (i) for copper catalysis. The sulphate producing reaction, which occurred concurrently with reaction (32) for pure sphalerite leaching, was described as purely chemical because the rapid rate increase with temperature was not paralleled by a corresponding increase in conductivity.

In recent papers [85, 87, 88, 117, 118] electrochemical models have also been proposed for the leaching of chalcopyrite. The creation of pits and the enlargement of cracks on polished surfaces were observed by Peters and Loewan [85]. Wadsworth and co-workers [87, 88] proposed a mechanism in which chalcopyrite dissolved anodically and the cathodic reduction of oxygen was rate controlling. The dissolution rate was found to be potential independent, indicating that a non charge transfer step (probably bond breaking in the oxygen molecule) was rate determining.
Electrochemical studies of sulphides in related fields may have some bearing on pressure leach studies. For example, compilation of single electrode potentials shows that pyrite is the most noble of the sulphide minerals. One might therefore expect a galvanic contact effect when pyrite is in intimate contact with another sulphide, with the anodic dissolution of the latter being accelerated while that of pyrite is depressed. This effect has been demonstrated [115, 119] and may explain the observations of several authors that pyrite begins to react only after most of the sphalerite and galena have dissolved. Similar enhancement of reaction rate was found by Wadsworth and co-workers [88, 117] for galvanic contact between chalcopyrite and either copper or iron metal. The cathodic dissolution of chalcopyrite was extremely rapid and the reaction rate was determined by the subsequent anodic dissolution of the covellite formed, which in turn was more rapid than direct anodic dissolution of chalcopyrite.

In summary, evidence has been presented that indicates the importance of electrochemical reactions in sulphide leaching, particularly the anodic dissolution reaction producing sulphur. It appears that in the future fundamental studies of semiconductor/electrolyte phase boundaries will contribute significantly to an understanding of the kinetics of leaching.

3.8 SUMMARY AND CONCLUSIONS

1. The following generalized dissolution reactions have been reported for most sulphide minerals under pressure leaching conditions in acidic and neutral solutions.

\[ \text{MeS} + 2\text{H}^+ = \text{Me}^{++} + \text{H}_2\text{S} \quad \ldots \quad (87) \]

\[ \text{MeS} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Me}^{++} + \text{H}_2\text{O} + \text{S}^0 \quad \ldots \quad (88) \]

\[ \text{MeS} + 2\text{O}_2 \rightarrow \text{MeSO}_4 \quad \ldots \quad (89) \]

where Me represents any divalent metal.

There are two exceptions. Reactions of pyrite are slightly different because of the labile sulphur atom and reaction (87) has not been reported for the copper sulphides.

2. Reaction (87) is favoured by low oxygen pressures and high acidity. Reaction (89) is favoured by high oxygen pressures, low acidity and high temperatures (>110°C). Reaction (88) fits somewhere between these extremes but is not observed for pure synthetic ZnS [61, 73].

3. Pure ZnS has a high resistivity and the catalytic effect of small additions of impurity ions on the rate of reaction (88) suggests an electrochemical mechanism for this reaction.

4. All three reactions occur to some extent in the acid leaching of concentrates but there is disagreement on their relative importance and whether they occur concurrently or consecutively.

5. A consensus of results places the order of reactivity as PbS > ZnS > CuFeS₂ > FeS₂. This can only be treated tentatively because few comparative experiments have been based on equal initial particulate areas.

6. For well agitated systems below 110°C the dissolution rate is most often governed by the rate of the phase boundary reaction when oxygen is used as the oxidant. However diffusion mechanisms are important in galena leaching because of insoluble lead sulphate formation.

7. Stiffling of the dissolution reaction has been reported for all four minerals at temperatures exceeding 110°C. This is attributed to the wetting and subsequent occlusion of the unreacted mineral by molten sulphur. However, a small number of studies [61, 70, 102, 109] have not observed this effect and the matter needs clarification.
8. Naturally occurring minerals dissolve more rapidly than pure synthetic minerals because of the presence of foreign atoms. Although no consensus is available on the mode of this catalysis, two possible mechanisms have been proposed. One suggests that increased conductivity aids the cathodic discharge of oxygen and the other that impurities which dissolve in the solution catalyse the oxidation of hydrogen sulphide which blocks the reaction.

9. Iron and copper have been identified as the most important catalysts for reaction (88) regardless of whether they are present in the ore or added with the leachant. Two mechanisms proposed in explanation are identical to those in paragraph (8) above. In this case increased conductivity is visualized to occur by precipitation of the catalyst, as a sulphide, on the mineral surface. At least 5% of soluble iron by weight of the ore is considered the minimum requirement for catalysis.

10. It is impossible to compare dissolution rates of process oriented studies because of differences in initial particulate surface areas.

11. The most desirable stoichiometry on which to base an extraction process would be equation (88) (see § 3.6.1). Close approximations to this have been achieved in practice, especially for sphalerite and galena and solutions suitable for subsequent metal recovery have been produced.

12. Return electrolyte is a suitable leachant. This is a distinct advantage of the sulphuric acid system because acid consumed in the leach (except by lead) is regenerated in the metal reduction stage and may be recycled.

13. The physicochemical system of leaching is extremely complex, especially when three phases are involved.

14. Empirical results suggest that leaching rates are sufficiently rapid to attract commercial interest but understanding of the rate processes involved is still an infant science.

15. Very few studies have microscopically examined partly leached minerals and no such studies have been reported for galena and sphalerite after oxygen pressure treatment.

16. Few studies have been made of lead and lead-zinc concentrates. Those that have indicate difficulties with lead recovery because of the formation of jarosites at low acidities. Soluble copper may be precipitated as beaverite under such conditions [109].

17. A diversity of apparatus and experimental techniques have been used to study leaching behaviour and this makes comparison of published data very difficult. It also means that most reported results are not reproducible.

18. Mineralogical factors make it necessary to conduct separate kinetic studies for ores from different sources.
4. EQUIPMENT DESIGN AND OPERATION

4.1 INTRODUCTION

Although the results of a large number of pressure leaching investigations have been published, few papers [120-124] deal in depth with laboratory reactor (autoclave) design. It is apparent that when programmes of research in this field were first initiated specialist equipment had to be constructed because no suitable commercial product was available. However in the last fifteen years considerable use has been made of pressure hydrogenation autoclaves (designed for studying the catalytic hydrogenation of organics at elevated temperatures) which can be modified for pressure hydrometallurgical work. The design of Dresher et al. [121], for example, employs a standard Parr Instrument Co. autoclave as the basic unit.

On beginning the project reported in this thesis the problem of obtaining a suitable autoclave was resolved into two possibilities - purchase a pressure hydrogenation unit from U.S.A. and modify, or design and build a suitable reactor in Auckland. The latter course was chosen because of difficulties and delays in obtaining a unit from overseas and because some local assistance was forthcoming (see Acknowledgements). The resultant reactor (Figs. 12 and 13) combines some of the best features of other designs but is simpler in operation, method of construction and ease of assembly.

The autoclave design requirements and the manner in which they were met are now described.

4.2 GENERAL REQUIREMENTS

The leaching unit must be capable of furnishing accurate kinetic data for a three phase (solid-liquid-gas) reaction system. Agitation is necessary to keep the solid particles suspended and to disperse the gas phase. Some form of heating is required and accurate temperature control in the range (20 to 150°C) must be incorporated. The autoclave should operate safely in the pressure range (0 to 3.5 MPa) and the oxygen supply system should be capable of maintaining a constant pressure. It is desirable to provide for ore charging when the apparatus is equilibrated at operating conditions and for some form of liquid sampling while the reaction is taking place. The material of the vessel in contact with the solution should be inert, since corrosive products may catalyse the reactions involved and obscure the results.

Also the autoclave must be designed for ease of assembly, disassembly and cleaning because it is used for batch operations of a few hours duration. Finally, the overall cost of the leaching unit must be kept within reasonable bounds.

4.3 BASIC AUTOCLAVE UNIT

A reduced working drawing of the autoclave unit designed for a maximum operating pressure of 7 MPa is shown in Fig. 12. The vessel was constructed from a length of 6 in. I.D., ½ in. wall, stainless steel tube threaded externally at one end and internally at the other. A 1 in. flange screwed and welded into the internally threaded end formed the base. The lid was constructed in two sections which were later welded together - a 1 in. flange turned out and threaded to take the vessel and a larger diameter 1 in. flange which supports the stuffing box and agitator assembly.
4.3.1 Agitator

The impeller shaft is belt driven by an underworked ½ H.P., 1425 r.p.m., A.C. motor. A range of pulleys and belts is provided to enable operation at 500 and 1000 r.p.m. The ½ in. diameter agitator shaft is supported between two bearings to allow accurate alignment and to give adequate rigidity. Several types of gland packing were tried but the most successful in terms of sealage and operating life proved to be 'Fluolion' teflon impregnated acid resistant packing. The top gland was designed so that the gland nut could be tightened while the agitator was operating. The lower gland, which is accessible only when the vessel is unscrewed, served more as a bearing (in maintaining shaft alignment) than as a pressure seal. Two difficulties with this agitator design are apparent.

(i) It is impossible to effect a perfect gas seal with a stuffing box of this kind. Two designs which overcome this problem have been cited in the literature. The first uses a magnetically driven stirrer which allows the drive shaft and bearings to be sealed in the pressure vessel. The second [121] incorporates a compartment above the autoclave which is pressurized to within a few inches of Hg of the autoclave operating pressure with an inert gas. The driving force for leakage through the agitator glands is thereby drastically reduced. Unfortunately a suitable magnetic drive was not available when the unit was designed. The construction of a second pressure compartment with associated control equipment was ruled out on a cost-benefit basis.

(ii) To avoid corrosive attack of the bearings they must be placed above the glands which results in a long section of unsupported shaft. To maintain adequate rigidity in the shaft, especially when driving a powerful impeller at high speeds, a large diameter must be employed. This increases gland leakage problems because of the large surface area which must be sealed.

4.3.2 Attachments (Fig. 14)

Access to the reaction zone of the autoclave is gained through seven bushes in the lid. They are threaded ½ in. B.S.P. and 'Keelaring' tube couplings which screw into the bushes are used to make the following connections: thermocouple well, pressure gauge, safety valve, oxygen inlet, vent outlet, ore charger, liquid sample line and baffles.

4.3.3 Assembly (Fig. 15)

The lid and agitator unit are secured on a mild steel table by four bolts (Fig. 14). The vessel is located on a counterbalanced rotating table by four pins. To assemble the autoclave this table is raised by hand and the vessel screwed into the lid. Final tightening is effected by a large spanner provided with two pins that fit into holes in the rotating table. Sealing is provided by a 5/16 in. neoprene 'O-ring' which has given good service at temperatures up to 150°C. The heaters are plugged in after the vessel has been locked in place.

This method of assembly overcomes the following two difficulties which occur in most of the published designs.

(i) No bolts need be undone to remove the lid.

(ii) No services need be uncoupled to lift the lid from the vessel because the vessel is removed from the lid.

The counterbalanced table reduces physical effort and the consequent likelihood of accidental spillage to a minimum.
Fig. 12  Working drawings of the autoclave (continued overleaf).
Fig. 12 continued...
Fig. 13  A general view of the autoclave cabinet showing the control panel, oxygen reservoir, temperature and pressure recorders and the sampling window.

Fig. 14  A view of the autoclave lid showing the agitator drive and bearings, upper gland cooling jacket, tube couplings, safety valve and pressure gauge diaphragm.
Fig. 15 A general view of the autoclave showing the lid and agitator unit, the teflon internals - agitator shaft, impeller, sample tube, thermocouple well, blank baffle - and the autoclave body with wrap-round insulated elements.
Fig. 16 overleaf Two views of the self-sucking impeller agitating and aerating one litre of water in a three litre pyrex liner.
(a) in operation
(b) almost stationary

Fig. 17 Sample Introducer
Fig. 18 Schematic diagram of the autoclave and services
4.4 MATERIALS OF CONSTRUCTION

4.4.1 Autoclave

A suitable construction material must meet the strength requirements imposed by the design pressure and that part in contact with the solution must be resistant to attack by boiling 5% sulphuric acid under both oxidising and reducing conditions. The degree of corrosion resistance desired is set by the following considerations.

(i) The corrosion rate must not unduly shorten the life of the equipment nor should it lead to the possibility of catastrophic failure due to weld attack.

(ii) Corrosion products in solution may take part in the leaching reactions (c.f. the catalytic role of iron § 3.8).

(iii) When corrosion occurs strict material balances are impossible - acid is consumed and in some cases the same cation may be produced concurrently by dissolution of the ore and attack of the leaching vessel.

Ideally the construction material should be totally inert under pressure leaching conditions, otherwise it must be considered as a possible kinetic factor and studied accordingly.

The present autoclave was fabricated from 316 stainless steel and it was initially anticipated that the leaching experiments would be conducted in this vessel. Blank trials with no ore, however, resulted in severe intergranular corrosion which was somewhat unexpected in view of the fact that most autoclaves prior to 1965 had employed this material without reporting corrosion as a serious problem. Based on considerations (ii) and (iii) above a suitable material was sought with which to fabricate a lining for the vessel. Unfortunately there is little documentation of the behaviour of materials under boiling 5% sulphuric acid conditions. Of the sophisticated metals and alloys which might have offered good resistance, only titanium could be located in New Zealand in sheet form. This metal has been reported as inert providing oxidising conditions prevail [125]. Accordingly a liner was fabricated and tested but, although it performed well in blank trials, quite marked corrosion was found to take place under leaching conditions. This was attributed to reducing conditions prevailing at the beginning of a leaching experiment caused by the rapid evolution of hydrogen sulphide. Recently it has been reported that a titanium-palladium alloy gives much better service than pure titanium [126] but the incentive to procure some of this material was reduced when a suitable glass liner was developed. The glass liner was simply a 3 litre pyrex beaker modified by removing the pouring lip and by shortening it slightly so that when the vessel is screwed up the flared opening of the beaker fits lightly against the taper of the lid (Fig.12). An 'O-ring' placed loosely on top of the beaker prevents splashes from entering the small gap between the rim of the beaker and the vessel wall.

The only drawback of the liner is the combination of the high thermal resistance of the glass and the air gap created which makes temperature control difficult when external heating is used. However this problem was satisfactorily resolved (§ 4.6) and the inertness of glass makes it an otherwise ideal material.

4.4.2 Autoclave Internals (Figs. 12 and 15)

Autoclave internals consist of agitator shaft and impeller, thermocouple well, sample tube, baffle and sample introducer. Glass is not a suitable construction material and titanium-palladium tube was unavailable. Teflon was selected as the best alternative but because of its tendency to soften at the higher temperatures used, teflon sheathed stainless steel was used for the agitator shaft and the sample introducer. The impeller, sample tube and baffle were machined from solid lengths of teflon rod. The thermocouple well was constructed from a length of ½ in. O.D. stainless steel tube by welding a plate over one end. This well was shrouded by a teflon cylinder with a very thin end face to minimise the effects of the high thermal resistance of this material.
4.4.3 **External Piping and Fittings**

All the external pipework was constructed from either ¼ in. or 5/16 in. 0.0. thickwall stainless steel tubing (Fig. 18). To prevent the possibility of stainless steel corrosion products appearing in the solution sample, the sample tube was lined with polythene. This was contrived by drawing through a stretched length of polythene tube. When this had expanded against the sides of the outer tube it was sealed in place by an epoxy glue ('araldite'). Excellent protection was provided in service so long as the temperature in the sample tube did not exceed 100°C. Cooling was provided, by encasing the tube in a larger diameter polythene pipe to form a concentric tube heat exchanger, but was unnecessary for most experiments.

The 'Keelaring' tube couplings and all the valves servicing the autoclave were also constructed from 316 stainless steel. Some corrosion occurred, and the tubes and valves were periodically cleaned by flushing with water followed by compressed air. In particular the valve springs in the non-return valve and the safety valve required replacement after approximately 100 operating hours.

4.5 **HEATING** (Fig. 15)

Four methods of heating the vessel were considered.

(i) internal electrical resistance element
(ii) internal steam coil
(iii) external wrap round electrical resistance element
(iv) external gas flame

Methods (i) and (ii) have the important advantage of providing rapid corrective response to temperature deviations from the controller set point but this is offset by some severe disadvantages.

(a) They require additional holes in the endcap of the autoclave which inherently weaken it.
(b) They clutter the inside of the vessel.
(c) They are subject to rather severe corrosive and erosive conditions during leaching. A material which combined good heat transfer properties with high corrosion resistance under both oxidising and reducing conditions could not be found (see §4.4).

These are strong reasons for using external heating. Of methods (iii) and (iv), the former is cleaner, simpler and offers more controlled heating. The only limitation is the power that can be supplied through unit area of element. Accordingly, method (iii) was adopted and two one kilowatt elements were installed. They were sheathed in stainless steel as protection from acid spillage. Power is supplied to the elements via normal two-pin plug fittings. The use of two elements with separate switching arrangements offers better temperature control because the top one can be switched off when the reaction temperature is attained and heat losses balanced by the other. Heat losses from the outer surface of the elements were minimised by covering this surface with a layer of asbestos lagging.

4.6 **TEMPERATURE CONTROL**

The temperature of the solution within the autoclave must be rigidly controlled to enable reproducibility when studying reactions with a high rate dependence on temperature and to maintain constant water and oxygen partial pressures over the solution. Two methods of control were investigated with the emphasis on simplicity and low cost. In both cases the sensing element was a Ni/Cr, Ni/Al thermocouple placed inside
a well extending into the reaction zone of the autoclave. A similar thermocouple immersed in an ice bath was used as a reference junction.

(i) Separate on-off switching was provided for both heating elements. The top element (Fig. 15) was either on or off and was used only during the heat-up period. A Brown Pyr-o-vane indicating millivoltmeter two position controller was used to make or break the circuit to the bottom element. The voltage to this element was manually adjusted using a Variac variable voltage transformer to minimise cycling about the set point. The method did not give adequate control for two reasons.

(a) Normal operating temperatures were only a quarter of full scale and therefore the set point accuracy was not good enough.

(b) The large heat capacity of the stainless steel vessel plus the thermal resistance of the air gap between liner and vessel resulted in lag times of up to 10 mins. between switching and response measured by the thermocouple. This resulted in unacceptable temperature overshoot and cycling.

(ii) This method was essentially the same as (i) above but substituted manual for automatic control of the lower element. A 'Neeco Simmerstat' was used to control the voltage to the element instead of the 'Variac' used above. The procedure adopted was to use both elements during the heat-up period and by a process of experience, establish a suitable thermostat setting for the lower element to just balance heat losses under operating conditions. The sample was introduced only after the desired temperature had been attained and a suitable setting established. This method exploits the large heat capacity of the apparatus because the heats of reaction and minor changes in ambient temperature have little effect on the solution temperature. Experiment showed that the operating temperature could be maintained within close limits (± 2°C) with only very minor manual adjustments required over a period of eight hours operation. The mV output of the thermocouple was recorded continuously on a Honeywell Lab/Test recorder which was standardised and regularly checked with a potentiometer.

Method (ii) was adopted for all leaching experiments and gave a satisfactory performance without recourse to the sophisticated automatic control action that would be necessary to cope with such large lag times.

4.7 AGITATION

The requirements of a suitable agitator are that it provides:

(i) efficient oxygen dispersion so that dissolution occurs over as great an area as possible

(ii) suspension of the solid so that the entire surface can take part in the reaction

(iii) uniformity of mixing

(iv) a large shear force between the fluid and the suspended particles

The reasons for the importance of agitation to the gas absorption and transport steps of mineral dissolution have been outlined in sections 2.3.1 and 2.3.2. In summary, it is the sole purpose when designing an agitator to make these steps fast enough so that they are not rate limiting. Design of impellers to achieve this goal has received little attention in the literature of pressure leaching with the notable exception of an excellent study by Pawleki and co-workers[16, 19]. Most researchers have simply increased the stirring speed until a point is reached where further increase does not affect the mineral dissolution rate. It is assumed that dissolution is not transport controlled for rotation speeds above this value.
The validity of this assumption is challenged by the results of Pawlek et al., who found that the rate of dissolution may remain constant or even decrease above a certain critical stirring speed because of surface blocking by gas bubbles. These same authors [16, 19] tested the oxygen dispersion abilities of a wide range of impellers by measuring the rate of oxidation of sulphite ions in water (equation (16)). In this way an optimum design and range of rotational speeds was determined. Accordingly, the impeller design selected for use in this autoclave was similar to the modified self-sucking turbine Rm designed by Pawlek et al. [19]. It combines high suction capabilities with good solid suspension characteristics and at a normal operating speed of 1000 r.p.m. achieves minimum bubble diameter [16].

The impeller (Figs. 12 and 15) was machined from solid teflon and screwed onto the agitator shaft. Originally the shaft was also constructed in solid teflon with an air passage down the centre. It was keyed onto the stainless steel shaft just below the bottom gland. This arrangement proved unsatisfactory because softening of the teflon at the maximum operating temperature of 150°C resulted in a lack of rigidity. The teflon shaft was therefore strengthened by extending the stainless steel rod right through the centre. Gas passages were provided by machining 1 mm square channels at 2 mm intervals around the inside circumference of the teflon sheath. Corrosion of the exposed stainless steel was found to be minimal because contact with the solution occurs only when the impeller is stationary - before heat-up begins and at the end of the reaction when most of the acid has been consumed (§ 4.3.4).

Baffling, which facilitates requirements (ii), (iii) and (iv) above, was provided by three 5/8 in. diameter teflon rods. Two of these have a dual role. One is a sheath for the thermocouple well and the other with a fine hole bored through it and a sintered glass filter fastened in the end doubles as the sampling tube. Fig. 15 shows the baffle arrangement. They were lengthened after this photograph was taken and before experimentation began so that they were as long as the combined agitator shaft - impeller assembly (Fig. 18). Photographs of the agitator in operation (Fig. 16a) and just coming to rest (Fig. 16b), taken using the glass liner filled with the normal operating volume of 1000 ml. give some idea of bubble formation and flow patterns. No attempt was made to measure the oxygen dispersion or solid suspension capabilities as leaching results suggested that these were adequate (see § 7).

4.8 OXYGEN SUPPLY

Oxygen is stored in a New Zealand Industrial Gases (N.Z.I.G.) 240 S.C.F. pressure cylinder which is used to charge a N.Z.I.G. 24 S.C.F. pressure cylinder to a desired pressure before each experimental run. An N.Z.I.G. diaphragm regulating valve connected between this second cylinder or 'oxygen reservoir' and the autoclave maintains a constant pressure in the latter during an experiment. The fall in pressure of the reservoir is constantly monitored by a Foxboro Recording Pneumatic Consitrol Receiver and is translated into an oxygen consumption versus time curve by prior calibration of the reservoir (Appendix 2). This curve can then be compared with the results of chemical analysis of reaction products.

Pressure in the autoclave is monitored visually from a 4 in. dia. British Teltherm oil filled Bourdon gauge which is separated from the reaction zone by a stainless steel diaphragm to prevent distillation of corrosive fluids to the Bourdon tube. Since the partial pressure of water is accurately known at the operating temperature the oxygen partial pressure is the difference between this value and the gauge plus barometric pressure.

The oxygen supply line is formed from 5/16 in. O.D. thick wall tube and a Keelaring non return valve prevents distillation to the oxygen reservoir in the event of gaseous reaction products causing a pressure rise in the reactor. A Keelaring metering needle valve situated between the regulating and non-return valves can be used to isolate the reservoir from the autoclave. Under operating conditions this valve is normally fully open.
4.9 ORE CHARGING

The most common technique of ore charging described in the literature is simply addition of the ore and acid at the beginning of the experiment. The autoclave is then sealed, purged and pressurised with oxygen and heated. This method suffers from two serious disadvantages.

(i) Satisfactory kinetic results are not achieved if the reaction rate is fast or the heat-up time is slow.

(ii) The autoclave is purged after the reaction has started (assuming it starts when the acid and ore are mixed) which results in the removal of gaseous reaction products.

The only way to avoid these problems is to charge the ore once the autoclave is stabilized at the desired operating temperature and pressure. Very few researchers have employed this technique and the designs available [121, 124] are limited to ore charges of a few grams.

Accordingly, a method of introducing up to 150 grams of ore was developed and this gave satisfactory service over a period of many experiments at autoclave pressures up to 0.7 MPa. Essentially the device (Fig. 17) consists of a cylinder open at one end and two pistons held a fixed distance apart by a connecting rod. Welded on to the closed end of the cylinder is a ¼ in. B.S.P. fitting which allows the device to be screwed into one of the holes in the autoclave lid. A ¼ in. hole bored through this fitting and the cylinder end allows a ¼ in. stainless steel rod to pass through and screw into the top piston. When the 'sample introducer' is in place the stainless steel rod passes through the autoclave lid and is sealed against the internal pressure by a standard ¼ in. 'Keelaring' tube coupling.

The device is charged by removing it from the autoclave at the end of an experiment, inverting it, and unscrewing the bottom piston from the connecting rod. When the space between the two pistons has been filled with the desired amount of ore the bottom piston is screwed on again, the device set the right way up and relocated in the autoclave lid. The ore is introduced to the solution, after the vessel has been purged, heated and pressurised, by unscrewing the 'Keelaring' fitting half a turn and forcing the rod through the lid by hand. The dimensions of the sample introducer are such that when the rod is fully down the top piston just leaves the cylinder and the bottom piston is located just below the solution surface. After holding in this position for several seconds the pistons are drawn back into the cylinder by pulling the rod back up through the autoclave lid. The 'Keelaring' seal is then retightened. Gas escape during sample introduction is negligible because an 'O-ring' seal is maintained on the shaft throughout the whole operation.

The bottom piston was machined from solid teflon and the outside surface of the cylinder was shrouded with teflon. All other components were made from 316 stainless steel and were teflon sprayed to reduce corrosion.

4.10 SAMPLE WITHDRAWAL

A method of sample withdrawal allows liquid reaction products to be analysed at discrete time intervals during an experiment to furnish kinetic data. This experimental device which has been used in only about one half of the published studies allows economical use of charge material and time, because it reduces to one the number of experiments that need to be conducted to furnish a kinetic curve.

In this design the sample tube extending into the reaction zone of the autoclave was constructed from a solid section of 5/8 in. diam. teflon rod (Fig. 12). When a ball valve is opened the sample is forced out of the autoclave by the internal pressure. A sintered glass disc covering the sample tube opening (autoclave end) prevents the collection of solid particles. Sampling procedure involves running off 9 mls of solution to clear the sample line (volume 8 mls) followed by collection of a 5 ml sample for subsequent analysis. The collection time is dependent on the operating temperature and pressure but averages about 3 minutes.
One worker [109], at least, has taken solid samples for analysis in the same way. However it was decided that under these conditions collection of a representative sample would be extremely unlikely which is unfortunate because one of the important reaction products, lead sulphate, is a solid. The disadvantage of sample withdrawal is that the concentration of the remaining reactants is changed. To minimise errors due to this factor the sample size was kept as small as possible (15 mls per sample for 5 samples) compared to the volume charged of 1000 mls. Also, once the sample has been analysed the results were corrected to allow for the amount withdrawn (Appendix 5).
5. EXPERIMENTAL METHOD

5.1 LEACHING

5.1.1 Ore Preparation

The ore was received in the form of two massive hand-picked samples (≈ 40 kg) from the Tui mine at Te Aroha. These were broken down with a sledgehammer into sizes suitable for feeding to a laboratory jaw crusher (< 5 cm). Some upgrading of the ore was achieved during this process by separating and discarding low grade fragments. A hammer mill with a 250 μm screen installed across the outlet was used for secondary grinding. The output from this mill was predominantly minus 100 mesh (149 μm) so that tertiary grinding was unnecessary. This material was dry screened in laboratory sieves for one hour and the sized fractions were stored in labelled glass jars until required for analysis or leaching experiments.

Sufficient ore for all the planned experiments was ground at the one time so that one head analysis could be applied to the whole batch. Otherwise analyses would have been required each time fresh material was ground. Unfortunately preparation of all the ore before embarking on the leaching programme has one serious disadvantage - the fresh surface created on grinding is exposed to the atmosphere for varying lengths of time, with the result that surface oxidation may affect the leaching results (§ 2.3.3.2). This problem was minimized by conducting comparative experiments (e.g. the influence of temperature) on consecutive days. Also, replicate experiments were conducted after various storage periods to estimate the effect of surface exposure.

The method of ore analysis is described briefly in § 5.2.1 and fully in Appendix 4. Analyses of different size fractions varied considerably as expected from the differences in grindability of the component minerals. The procedure adopted, therefore, was to obtain an analysis of each size range by sampling from the total amount of ore in that size range. A laboratory splitter was used to prepare a suitable quantity of representative material.

5.1.2 Chemicals

Leach solutions were prepared by diluting 98% sulphuric acid with distilled water and were standardised by titration with 1 mol l⁻¹ sodium hydroxide. A large quantity (= 20 l) of 0.8 mol l⁻¹ acid was prepared in this way and stored in a polyethylene flask. One litre quantities were drawn off for leaching experiments as required. The concentration of this stock solution was checked periodically and in one instance sulphate was determined gravimetrically and it agreed well with the results of acid-base titrations. The catalytic effects of copper and iron were assessed by adding anhydrous cupric sulphate and ferric sulphate decahydrate to the leachant. A complete catalogue of the chemicals used, and their grades, is contained in Appendix A4.5.

5.1.3 Equipment Calibrations

(i) Oxygen Reservoir

The volume of oxygen in the reservoir was recorded as a function of pressure in the range 3.5 to 0 MPa by discharging it slowly through a wet gas meter. The results are given in Appendix 2.
(ii) Thermocouple

The mV output of the thermocouple was correlated with the temperature registered by high accuracy Hg thermometers in the range 0 to 150°C. The ice and steam points were carefully established and intermediate points in the 0 to 100°C range were found using a constant temperature water bath. Above 100°C an oil bath was employed. Deviation of the readings from the standard output for a Ni/Cr, Ni/Al thermocouple was less than 0.5°C and in practice little error would have been sustained by using published calibrations.

(iii) Autoclave Pressure Gauge (0 to 0.7 MPa)

An oil filled Bourdon gauge was used to measure the autoclave operating pressure in the range 0 to 0.48 MPa. The gauge was calibrated by the suppliers, British Teltherm, on purchase and subsequent checking in the range 0 to 0.14 MPa with a Hg manometer revealed excellent agreement.

(iv) Temperature Recorder

A Honeywell Leb/Test Recorder was preset to give a full scale deflection of 25 cm for a 5 mV input. The recorder was calibrated with a Tinsley potentiometer and zeroed with the same instrument before each experiment. The potentiometer was also used to check the recorded temperature at 15 min intervals throughout an experiment because the recorder output was found to drift slightly.

5.1.4 Equipment Operating Procedure

A complete set of operating instructions have been included in Appendix 3. The following procedure is a brief summary.

Sized and weighed samples of assayed ore were loaded into the sample introducer which was assembled and locked into position in the autoclave lid. One litre of acid and any catalyst chemicals were charged to the autoclave liner which was then fitted into the autoclave vessel. The vessel was screwed into the lid, the gland cooling water started and the agitator motor switched on. The autoclave was then purged of air by slowly discharging the contents of the oxygen reservoir through the vessel. When the reservoir had been recharged from a large storage cylinder, the autoclave pressure was set at a small positive value (0.01 MPa), the temperature recorder was activated and both heaters were switched on. When the operating temperature was attained the oxygen partial pressure was set to the desired value (§ A5.1) and the system was allowed time to equilibrate. After the autoclave temperature and pressure had stabilized, the ore sample was introduced to the leachant. This was recorded as time zero.

Solution samples were collected after 1, 2, 3, 5 and 7 hours leaching by opening the sampling valve and allowing liquid to be forced out under pressure. A 9 ml clearance volume was discarded before collection of a 6 ml sample for analysis.

After the 7 hour sample had been collected the heaters and agitator motor were switched off and the autoclave was slowly vented back to atmospheric pressure. When this was attained, the vessel was unscrewed from the lid, the liner removed and the solution filtered immediately. Residue held up on the baffles above the waterline was collected separately for analysis as was any ore remaining in the sample introducer. Filtered residues were thoroughly washed with distilled water and the filtrate and wash water were then evaporated back to the starting volume of one litre. Residues were dried and weighed preparatory to analysis.

5.2 ANALYTICAL

A complete description of the analytical techniques and procedures used is given in Appendix 4.
5.2.1 Ore Analysis

The ore was prepared in the manner described in § 5.1.1 and six samples were split from bulk stores of each screen size fraction for analysis. After drying overnight at 100°C and cooling in a dessicator, 0.5000 g of each sample was weighed out and transferred to a zirconium crucible. A weighed mixture of sodium peroxide and sodium carbonate was added and the contents fused over a bunsen flame. When cooled the crucible was placed in a beaker and distilled water added. The vigorous reaction with sodium peroxide caused the melt to break away from the crucible which was then removed from solution and rinsed. Subsequent acidification with a 100% excess of concentrated hydrochloric acid produced a clear solution, dissolving everything including silica. This solution was made up to one litre and was used directly for the determination of iron, copper and lead by atomic absorption spectroscopy and, after dilution, for zinc by the same method. A Techtron A.A.S machine was used for all determinations. Standards were corrected for matrix and viscosity effects by adding sodium and chloride ions equivalent to those generated in the fusion and acidification operations. Stock solution of NaCl/HCl was prepared so that standards or samples could be diluted without altering the matrix.

The peroxide fusion technique was developed after conventional acid digestions resulted in incomplete decomposition and gave consistently low values for lead. Similar difficulties with various types of acid digestions of zinc and lead sulphides were reported by Gambrell [130] and the technique which he finally found to be successful is extremely tedious. Another wet digestion technique suggested by Thomas [132] is equally complex and both methods appear to rely on extensive operator experience for their accuracy. In contrast, the fusion is complete in 5 mins. and room for error is substantially reduced. A peroxide fusion method is used to decompose silicate rocks [132] but was not documented for sulphide ore analysis until 1974, when Scott [109] independently developed such a method for this purpose.

A useful property of the fusion technique is that all the sulphur in the ore is quantitatively oxidised to sulphate by the peroxide. The total sulphur can therefore be determined gravimetrically using barium chloride to precipitate sulphate from the 0.5 g l⁻¹ solution. Unfortunately silica was rendered soluble and had to be determined by evaporating the solution to dryness and redissolving all but the silica in dilute hydrochloric. This solution was filtered and the residue weighed directly as silica or, if impure, fumed with hydrofluoric acid in a platinum crucible and weighed by difference.

Two non-destructive techniques were used to check the geologists assessment of the ore’s mineralogy.

(i) X-ray diffraction
(ii) Scanning electron microscopy and EDAX.

5.2.2 Residue Analysis

The washed residues X, Y and Z (Appendix 4) were left to dry on their filter papers overnight. After subsequent oven drying at 100°C for one hour they were scraped from the papers into labelled bottles. These were then re-heated at 100°C overnight to remove the last traces of moisture. After cooling in a dessicator half gram samples of X and Y were taken from the bulk residues using a laboratory splitter. These samples were decomposed by peroxide fusion and analysed for Zn, Cu, Fe, Pb, S total and SiO₂ in the manner described in § 5.2.1. Lead sulphate was extracted by boiling 1 g of the residues with 25% ammonium acetate solution for one hour. The solution prepared by cooling, filtering and making up to one litre was analysed for Pb by atomic absorption spectroscopy using matrix matched standards. Elemental sulphur was extracted from 10 g samples of the residues in a soxhlet apparatus using carbon disulphide as solvent. It was determined by evaporating CS₂ from the soxhlet flask and weighing the residue directly as sulphur. Checks on the accuracy of this technique were made by oxidising the sulphur residue with bromine and determining gravimetrically as sulphate. Close agreement was realised between the two techniques.

X-ray diffraction scans of the residues were used to identify new compounds and to qualitatively assess their relative amounts. Scanning electron microscopy coupled with an EDAX facility was also used
to gain valuable information on the nature of the solid leach products and the mode of leach attack (§ 5.3).

5.2.3 Solution Analysis

The 6 ml solution samples (§ 5.1.4) were cooled and then diluted ten times by pipetting 5 ml into a 50 ml volumetric flask and making up with distilled water. Pb, Cu and Fe determinations were made directly on this solution by atomic absorption spectroscopy using standards with the same sulphate concentration. The Zn resonance line is very sensitive and further dilution of up to 2000 times (1 ml made up to 2 l) was necessary before determination. Sulphate in the final leach liquor (prepared by evaporating the filtrates and wash water back to 1 l) was determined gravimetrically. Pb, Cu, Fe and Zn determinations were also made on this solution for comparison with the final solution sample analyses. Lastly, the pH of the final leach liquor was determined with a Radiometer pH meter.

Occasional checks of the Fe values obtained by atomic absorption were made by performing redox titrations of Fe$^{2+}$ with potassium dichromate using barium diphenyl aminosulphonate as internal indicator. Total iron was determined in the same way after first reducing any ferric ions present in a silver reductor. Allowance was made in this case for cupric ions which are also reduced in the reductor.

5.3 SCANNING ELECTRON MICROSCOPY

The recent purchase by the University of a JEOL JSM-U3 scanning electron microscope interfaced to an EDAX (energy dispersive analysis of X-rays) 505 system enabled extension of the investigation to the examination of leach residues at high magnifications. Scanning electron micrographs showing the nature of the leach attack on the major minerals and the distribution of solid reaction products were obtained in this way.

5.3.1 Sample Preparation

Ore samples required no special preparation. Small quantities representative of each screen fraction were obtained by splitting. Dried residue samples were treated in various ways to facilitate the identification of solid leach products which were expected to be elemental sulphur and lead sulphate.

(i) Sulphur was extracted in a soxhlet apparatus with carbon disulphide.

(ii) Lead sulphate was extracted by ammonium acetate leaching while ensuring that the temperature did not exceed the melting point of sulphur (112→119°C) because of its possible redistribution.

(iii) Lead sulphate extraction was followed by sulphur extraction.

(iv) Sulphur extraction was followed by lead sulphate extraction.

5.3.2 Sample Mounting

A special sample mounting was developed that enabled 8 different powder specimens (Fig. 19) to be mounted in the one (W.D. 32) specimen holder. This device was a vast improvement over the conventional mounting, which holds one sample per specimen holder, because it enables adjacent samples to be compared simply by rotation of the holder. This technique was particularly suited to identification of reaction products.

Sample mounting proceeded as follows:

(i) Double sided sticky tape was fastened to one end of each ¼ in. diameter rod (Fig. 19).

(ii) The sticky end was dipped into the powdered sample, removed and the excess blown off.
Experience in this process enabled some measure of control over particle spacing.

(iii) Each sample was numbered in marking ink on the blank end of the rod.

(iv) The samples were placed in the mounting block in the following order. The start of the sequence was marked by a scratch on the block.

1. Unleached ore - nominal 49 μm particle size.
2. Residue from experiment 1 (R1, 70°C) treated by sulphur removal followed by lead sulphate removal.
3. R1 with lead sulphate removed, then sulphur.
4. R1 with lead sulphate only removed.
5. R1 with sulphur only removed.
6. R1 untreated.
7. Unleached ore - nominal 137 μm particle size.
8. Residue from experiment 16 (137 μm) untreated.

(v) The following samples were placed in another mounting block.

9. Residue from experiment 14 (130°C) untreated
10. R14 with lead sulphate removed
11. R14 with sulphur removed
12. Residue from experiment 20 (iron catalysis)
13. Residue from an acid digestion at room temperature and atmospheric pressure.
14. Residue from experiment 2 (70°C)
15. R2 with lead sulphate removed.

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Fig. 19 An eight position sample mounting for the scanning electron microscope.
5.3.3 Operating Procedure

(i) Photomicrographs of ore specimens 1 and 7 were taken at a suitable magnification for subsequent particle sizing. The major minerals were identified by EDAX.

(ii) The images of successive specimens from 1 to 6 were compared and the reaction products identified. Supportive evidence for visual identification was provided by EDAX.

(iii) Photomicrographs of these specimens were taken showing the form of leach attack with the major minerals and reaction products identified.

(iv) The extent of leach attack on large and small ore particles was examined by comparing images of specimen 2 and specimen 8.

(v) Specimens 9, 10 and 11 were compared to determine the form of elemental sulphur after leaching at temperatures exceeding its melting point.

(vi) Specimens 12 and 13 were compared with specimens 6 and differences were recorded by photomicrographs.

(vii) Specimens 14 and 15 were examined and compared with specimens 6 and 4 to check whether the distribution of sulphur was different at 70°C from that at 110°C.
6. EXPERIMENTAL RESULTS

6.1 ORE

6.1.1 Sizing

Ground ore was sized by dry screening for 1 hour in a laboratory sieve shaker. As it was originally intended to investigate the effect of surface area on leaching kinetics using screened fractions of ore, -100 +120 mesh (-149 +125 μm), -170 +200 mesh (-88 +74 μm) and -270 +325 mesh (-53 +44 μm) fractions were prepared. The smallest size fraction, corresponding to an average mesh opening (d_p) of 49 μm, was used as standard in the leaching experiments. Some hold-up of ultra fine material was experienced with the two smallest fractions but the actual extent of this was not realised until a scanning electron microscope became available late in the project enabling a visual assessment to be made. Fig. 36 is a scanning electron micrograph (s.e. micrograph) of the nominally 49 μm fraction. It can be seen that most of the larger particles have at least one dimension corresponding to the mesh opening but there are a large percentage of fines. A calculation of specific surface area based on a uniform particle size is therefore impossible.

Oven drying and screening for long times (+5 hrs) at low screen loadings did not produce a significant decrease in fines retention. Evidence of the hold-up effect was provided in one experiment in which ore passing the 325 mesh screen after 5 hrs was recharged to the 100 mesh screen. Subsequent shaking for 1 hr provided no minus 325 mesh fraction. Similar difficulties have recently been reported by Exner et al. [70] for sphalerite and by Baur et al. [87] for chalcopyrite.

Although other methods of particle sizing such as wet screening, elutriation or Cyclosizing may have given better results these were not tried as most of the leaching experiments had already been conducted using the 49 μm fraction depicted in Fig. 36. The surface area of this and the other fractions could have been determined by inert gas adsorption but the easier route of investigating the effect of surface area by varying the initial pulp density was chosen. Because the desirable situation of uniform sizing of each of the sulphide minerals was not met, the absolute reaction rates of the four minerals could not be compared on a standard basis - nor could a strict rate equation be evaluated for any mineral.

Examination of Fig. 34(a) which is a s.e. micrograph of the -100 +120 mesh fraction (d_p = 137 μm) reveals that there are very few fines. This sample was therefore leached to obtain a rate comparison between the four minerals using surface areas reported by Brown [140]. For a mean diameter of 137 μm these are, in cm² g⁻¹, sphalerite, 210, galena, 100 and pyrite 170. The surface area of chalcopyrite, calculated from data reported by Baur et al. [87] is 290 cm² g⁻¹.

In view of the irreproducibility of screening results it was fortuitous that sufficient ore for most of the comparative experiments was prepared at one time (§ 5.1.1).

6.1.2 Analyses

The analyses of the 49 μm and 137 μm fractions are contained in Table 6. Although sufficient 49 μm ore was prepared for all the intended experiments, equipment failures and other problems necessitated the preparation of a second batch. The analysis of this material is shown in column 3 of Table 6 and the numbers of the experiments for which these batches were used are also included. Table 9 relates experiment numbers to leaching conditions.
Theoretical sulphur (S. theoret.) is calculated assuming the ideal stoichiometry of sphalerite, chalcopyrite, pyrite and galena. An interesting result is the markedly higher Pb values in the smaller size fractions indicating the relative ease of grinding galena. A similar but less pronounced effect is exhibited by chalcopyrite.

6.1.3 Mineralogy

The importance of mineralogy to the kinetics of leaching was outlined in § 2.3.3.1. As much data as possible has therefore been collected on this parameter.

The geology and mineralogy of the Tui mine have been extensively examined and reported by Weissburg and Wodzicki [141, 142] and Cochrane [143]. The mineralogy has also been discussed by Whittle [144] who reports that the ore is "... essentially a coarse grained aggregate of sphalerite, chalcopyrite, galena and pyrite with subordinate finer grained marcasite, tennantite and chalcocite in a quartz gangue ... Tennantite is intergrown with the chalcopyrite ... The chalcopyrite - tennantite combination partly replaces the sphalerite around its edges and traverses it in thin veinlets. Galena is not intergrown with sphalerite in the normal manner found in most lead-zinc ores and may be considered the last phase of mineralization. Minor secondary sulphide enrichment exists by virtue of chalcocite replacing the edges of chalcopyrite and sphalerite." Cochrane could not positively identify tennantite and stated that the secondary sulphide minerals, covellite, chalcocite and cerussite were present as surface coatings only in the more oxidised regions of the veins. He states that "... Anglesite and cerussite have formed where oxidising solutions have had direct access to the mineralization and are especially prevalent in old workings."

Cochrane also determined the crystal cell size of sphalerite by X-ray diffraction, using the method of Williams [145], to assess the iron content in the lattice. The value he obtained, 5.4090 ± 0.0010 Å corresponded well with the value of 5.4093 ± 0.0007 Å found by Williams for iron-free sphalerite, falling in the 0 to 3% range for mol percent FeS in ZnS.

The ore used in this study was collected as massive (40 kg), highly mineralized samples from the stope of a relatively unoxidised part of the mine. An X-ray powder diffraction scan of the ore was made to check its mineralogy. Only peaks of the primary minerals could be identified in the resultant diffractogram (Fig. 20) indicating that secondary minerals, if present, are unlikely to exceed one percent. The ore was also examined by scanning electron microscopy and elemental analyses of individual particles made by EDAX (Fig. 35). The resulting micrographs with major minerals identified are presented in Figs.
Fig. 20 X-ray powder diffraction scan of nominal 49 μm ore showing peaks of quartz, galena, sphalerite, chalcopyrite and pyrite.

Fig. 21 X-ray powder diffraction scan of residue from experiment 1 showing reaction products anglesite and rhombic sulphur.
(For standard X-ray settings see 5 A4.4)
EDX (Energy Dispersive X-ray) analysis of the sphalerite particles showed that a small percentage of iron was present in the lattice (Fig. 35a). This was observed to vary slightly from crystal to crystal.

Assuming that the primary minerals conform to their formula stoichiometry the approximate mineralogy of the ore can be deduced. The results are shown in Table 7. The close agreement between determined sulphur and calculated sulphur (S. theoret.) in Table 6 supports this assumption.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>49 µm</th>
<th></th>
<th>137 µm</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>44.3</td>
<td>43.2</td>
<td>49.9</td>
</tr>
<tr>
<td>PbS</td>
<td>32.5</td>
<td>33.4</td>
<td>15.7</td>
</tr>
<tr>
<td>FeS₂</td>
<td>5.3</td>
<td>4.5</td>
<td>7.7</td>
</tr>
<tr>
<td>CuFeS₂</td>
<td>4.2</td>
<td>4.2</td>
<td>3.8</td>
</tr>
<tr>
<td>SiO₂</td>
<td>13.5</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>TOTAL</td>
<td>99.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7 Mineralogy

6.2 LEACHING RESULTS

6.2.1 General

The effects of changes in the following experimental parameters on the kinetics of the dissolution of sphalerite, galena, chalcopyrite and pyrite were investigated: temperature (T), oxygen partial pressure \( (P_{O_2}) \), initial acid concentration \( ([H_2SO_4]_i) \), molar ratio of acid to ore \( (MR) \), initial particulate surface area \( (A_i) \), agitation \( (\omega) \), catalysts \( (C) \) and time \( (t) \). The autoclave operating procedure \( (Op) \), vessel lining material \( (L) \), ore mineralogy \( (M) \) and mineral surface oxidation \( (S_{ox}) \) were kept constant.

Standard operating conditions, the number of levels and the ranges of each investigated are listed in Table 8. The initial surface area \( (A_i) \) is a function of the particle diameter \( (d_p) \) taken as the average mesh opening of two adjacent screens - see § 6.2.1. The variables \( MR, [H_2SO_4]_i \) and \( p_p \) (pulp density) are related by the expression

\[
MR \propto \frac{[H_2SO_4]_i}{p_p}
\]

so that changes in \( MR \) at constant acid concentration result in a change in pulp density which in turn is equivalent to a change in initial surface area.

Leaching results are shown in Table 9 with values of the non-standard experimental conditions listed. The calculations and assumptions used to derive the figures used in this table are described fully in Appendix 5 together with a complete sample calculation for experiment 18. Some additional results are recorded in Appendix 6.

Extraction \( (a) \) values for sphalerite and chalcopyrite refer to the fraction of the mineral dissolved calculated from the concentration of zinc and copper ions in the solution samples. Extraction values for pyrite were calculated from the iron concentrations in solution by subtracting the contributions from chalcopyrite and stainless steel corrosion (where significant). They include, however, an approximately
constant contribution from elemental iron which derived from severe wear of the hammers in the hammer mill. This iron was detected by passing an electromagnet over the ground ore but unfortunately a magnetic separator suitable for removal of this material was not available. Chemical removal was tried but resulted in attack of the ore minerals. For this reason the iron was left in the ore with the expectation that it would rapidly dissolve under leaching conditions. Results (Table 9) confirm this, showing that it was completely dissolved after one hour in all experiments.

<table>
<thead>
<tr>
<th>Experimental Parameter</th>
<th>Standard Value</th>
<th>Levels</th>
<th>Range</th>
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<tbody>
<tr>
<td>T</td>
<td>110°C</td>
<td>4</td>
<td>70 + 130</td>
</tr>
<tr>
<td>P0₂</td>
<td>0.138 MPa (20 psi)</td>
<td>4</td>
<td>0.069 + 0.414</td>
</tr>
<tr>
<td>MR</td>
<td>1.10</td>
<td>3</td>
<td>0.83 + 1.56</td>
</tr>
<tr>
<td>[H₂SO₄]ᵢ</td>
<td>0.8 mol l⁻¹</td>
<td>4</td>
<td>0.2 + 1.2</td>
</tr>
<tr>
<td>oₚ</td>
<td>115 g l⁻¹</td>
<td>6</td>
<td>29 + 170</td>
</tr>
<tr>
<td>oₚ</td>
<td>49 μm (nominal)</td>
<td>3</td>
<td>49 + 137</td>
</tr>
<tr>
<td>oₚ</td>
<td>1000 rpm</td>
<td>2</td>
<td>500 + 1000</td>
</tr>
<tr>
<td>C</td>
<td>none</td>
<td>2</td>
<td>CuSO₄ and Fe₂(SO₄)₃</td>
</tr>
<tr>
<td>S₀ₓ</td>
<td>constant</td>
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<td></td>
</tr>
<tr>
<td>L</td>
<td>Pyrex glass</td>
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<td></td>
</tr>
<tr>
<td>Oₚ</td>
<td>as per § 5.1.4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>as received</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>1, 2, 3, 5, 7 hrs</td>
<td>5 per exp.</td>
<td>1 + 7</td>
</tr>
</tbody>
</table>

Table 8 Leaching Conditions

Lead conversion (\(\alpha_{PbS}\)) values refer to the fraction of galena converted to lead sulphate measured by extraction of lead sulphate from the residue by ammonium acetate. Additional confirmation of the conversion of galena to anglesite (lead sulphate) is provided by Fig. 21 which is an X-ray diffractogram of a typical residue (R). Fig. 21 also identifies rhombic sulphur as the other major reaction product. Comparison of the peaks heights in Fig. 21 with those in Fig. 20, a diffractogram of the unleached ore, allow an estimation of the extent of reaction. The distribution of sulphide reaction products among the species, \(H₂S\), \(S²⁻\) and \(SO₄²⁻\) is very important because it gives an indication of the relative importance of reactions (87), (88) and (89) to the overall dissolution rate. Because four different minerals contribute to the total weight of each product formed it is impossible to quantify their respective reaction stoichiometries. \(H₂S\) was detected at the beginning of all experiments but had generally been removed by oxidation within the seven hour leaching period. No provision was made for determining this gas so that in the two cases where it persisted for seven hours (experiments 15 and 16) sulphur mass balances could not be completed. Based on a maximum partial pressure of \(H₂S\) of 15 kPa (§ 6.2.3. - (iv)) and a gas volume of 4 litres the maximum weight of sulphur in the gas at the end of an experiment would be 0.3 g. The presence of \(H₂S\) in the solution samples is indicated by an X in Table 9 against the corresponding chalcopyrite extraction which was invariably so small as to be undetectable by A.A.S.

The maximum theoretical elemental sulphur production was calculated assuming that the minerals reacted quantitatively according to the stoichiometry of reactions (33), (55), (63) and (66) (§ A5.6). The actual yield (measured by CS₂ extraction from the residue) as a fraction of this figure is recorded in Table 9 as the fraction theoretical sulphur yield. Computation of the weight of sulphate formed was possible by determining the total sulphur in the ore residue and/or the final leach liquor (§ A5.7). Mass balances, for example Table A8, § A5.9, showed that, within the limits of experimental error, sulhide sulphur not converted to elemental sulphur reported as sulphate. The maximum theoretical sulphate production is shown in § A5.7 to be equal to the maximum theoretical sulphur production so that
| Experiment | Values of the Non-standard Parameters | Spalerite Extractions \( \frac{260}{265} \) | Chalcopyrite Extractions \( \frac{250}{265} \) | Pyrite Extractions* \( \frac{260}{265} \) | Loss % (wt%) | Theoretical 
Conversion | Theoretical 
Mineral Yield | Experimental 
Mineral Yield | Min. |
<table>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>70°C</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>90°C</td>
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<tr>
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<tr>
<td>10</td>
<td>.2 mol 1°- 29.0 g ( \ell )^{-1}</td>
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<tr>
<td>11</td>
<td>.4 mol 1°- 57.5 g ( \ell )^{-1}</td>
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<tr>
<td>12</td>
<td>1.2 mol 1°- 170.0 g ( \ell )^{-1}</td>
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<td></td>
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<td>14</td>
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<tr>
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</tr>
<tr>
<td>16</td>
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<tr>
<td>17</td>
<td>.069 MPa</td>
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</tbody>
</table>

\( X \) denotes the presence of FeS in the solution sample

* The \( \frac{260}{265} \) figures include an approximately constant fraction attributable to elemental iron in the ground ore. All of this dissolves in the first hour.

** The \( \frac{260}{265} \) figures in this experiment include a variable fraction due to corrosion. This fraction was higher than normal which precluded an adequate estimate.

N.D. not determined.
fraction theoretical sulphur plus fraction theoretical sulphate equal 1.

6.2.2 The Effect of Changing Experimental Conditions on the Rate of Mineral Dissolution

Graphs of the results contained in Table 9 for the dissolution of sphalerite, chalcopyrite and pyrite are presented in Figs. 22 to 31. Where possible the three curves pertaining to changes in one experimental parameter were drawn one under the other on the same page to facilitate comparison. Several rather general observations can be drawn regarding the nature of the leaching curves.

(i) Chalcopyrite curves exhibit an induction period during which no copper dissolves. The length of this period correlates strongly with the presence of \( \text{H}_2\text{S} \) in the solution samples (Table 9). The curves after induction can be divided into two sections - a short period of fairly rapid dissolution followed by a longer period of approximately linear leaching at a somewhat lower rate.

(ii) Sphalerite curves exhibit up to three sections - a period of fairly slow dissolution (e.g. Fig. 28) followed by a period of linear leaching at a much higher rate and finally by a section of much reduced rate as extractions approach 100%. The end of the first section corresponds approximately to the end of the chalcopyrite induction period.

(iii) Pyrite curves cannot be completed for the first hour because of the lack of experimental information. However it is apparent from the curves that all of the elemental iron has dissolved in this time.

The measurement of the rate of appearance or disappearance of a solid reactant or product requires the halting of an experiment after each selected time interval to take a solid sample. The fraction of galena converted to lead sulphate and the quantity of elemental sulphur produced were measured at the completion of seven hours leaching only, to avoid a fourfold increase in the number of experiments involved. Graphs of percent theoretical sulphur yield and \( (\Sigma \text{pDS})_7 \) versus \( T, \text{P}_{\text{O}_2}, [\text{H}_2\text{SO}_4]_1 \) and MR are shown in Figs. 32 and 33 respectively. Solution sulphate concentrations were also determined at the completion of leaching only, to minimise the amount of solution required during sampling. Sulphate formation curves, Fig. 32, mirror sulphur production as mass balances established the relationship:

\[
S (S^{2-} \text{reacted}) = S (SO_4^{2-} \text{formed}) + S (S^0 \text{formed})
\]  

An interesting feature of the galena conversion curves is the narrow range of conversion values indicating a general independence of leaching conditions.

6.2.3 Experimental Observations

(i) Gland sealing difficulties (§ 4.3.1) resulted in slight leakage of the autoclave gas. This negated the use of the oxygen reservoir as a measure of oxygen consumption and allowed some \( \text{H}_2\text{S} \), formed at the beginning of most experiments, to escape. Estimates of this loss are available from the pressure drop in the reservoir after allowing for oxygen consumption and from sulphur mass balances. Both estimates show that this loss is negligible.

(ii) \( \text{H}_2\text{S} \) was detected in some solution samples by smell (Table 9), a method which has a limit of detection of better than 0.1 ppm. It was also occasionally smelt while introducing the ore sample to the hot solution since the procedure of pushing down the valve stem (Fig. 17) allowed a small amount of gas to escape past the O-ring seal, especially at high autoclave pressures. This observation implies that \( \text{H}_2\text{S} \) production was virtually instantaneous.
The effect of temperature on the dissolution of sphalerite, chalcopyrite and pyrite with other leaching parameters standard ($P_{O_2} = 0.138$ MPa, $MR = 1.1$, $[acid]_i = 0.8$ mol l$^{-1}$, $P_d = 115$ g l$^{-1}$, $\omega = 1000$ rpm, $d_p = 49$ $\mu$m). The $\alpha_{FeS_2}$ values include the dissolution of tramp iron.
Fig. 23(a) The effect of oxygen partial pressure on the dissolution of sphalerite and chalcopyrite with other leaching parameters standard. (T = 110°C, [acid] = 0.8 mol l⁻¹, \( \rho_p = 115 \text{ g l}^{-1} \), \( \omega = 1000 \text{ rpm} \), \( \text{MR} = 1.1 \), \( d_p = 49 \mu\text{m} \).)
Fig. 23(b) The effect of oxygen partial pressure on the dissolution of pyrite with other leaching parameters standard. \( (T = 110^\circ\text{C}, \text{MR} = 1.1, [\text{acid}]_1 = 0.8 \text{ mol l}^{-1}, \rho_p = 115 \text{ g l}^{-1}, \omega = 1000 \text{ rpm}, d_p = 49 \text{ \mu m}) \). \( \alpha_{\text{FeS}_2} \) includes the dissolution of some tramp iron all of which occurs in the first hour.
Fig. 24 The effect of oxygen partial pressure on the dissolution of sphalerite, chalcopyrite and pyrite with other leaching parameters standard except for particle size. (T = 110°C, [acid]₀ = 0.8 mol l⁻¹, \( \rho_p = 115 \text{ g l}^{-1} \), \( \omega = 1000 \text{ rpm} \), MR = 1.1, dp < 40 \text{ μm} - ore batch 2.) The \( \alpha_{\text{FeS}_2} \) figure includes the dissolution of tramp iron.
Fig. 25 The effect of acid/ore mol ratio (and pulp density) on the dissolution of sphalerite, chalcopyrite and pyrite with other leaching conditions standard. (T = 110°C, \( P_{O_2} \) = 0.138 MPa, [acid]_i = 0.8 mol l\(^{-1}\), \( \omega \) = 1000 rpm, \( d_p \) = 49 \( \mu \)m.) The \( \alpha_{FeS_2} \) figure includes the dissolution of tramp iron.
Fig. 26 The effect of acid/ore mol ratio (and pulp density) on the dissolution of sphalerite, chalcopyrite and pyrite ($T = 110^\circ C$, $P_d = 0.138$ MPa, $[acid]_t = 0.2$ mol l$^{-1}$, $\omega = 1000$ rpm, $d_p = 49$ $\mu m$). The $\alpha_{FeS_2}$ figure includes the dissolution of tramp iron.
Fig. 27 The effect of initial particle size (surface area) on the dissolution of sphalerite, chalcopyrite and pyrite with all other leaching parameters standard (T = 110°C, P_{O_2} = 0.138 MPa, \( \omega = 1000 \) rpm, [acid] = 0.8 mol l\(^{-1}\), \( \rho_p = 115 \) g l\(^{-1}\), MR = 1.1). The \( \alpha_{FeS_2} \) figure includes the dissolution of tramp iron.
Fig. 28 The effect of initial acid concentration on the dissolution of sphalerite, chalcopyrite and pyrite. (T = 110°C, \( p_{O_2} \) = 0.138 MPa, \( \omega = 1000 \) rpm, \( MR = 1.1, d_p = 49 \) μm.) The \( a_{FeS_2} \) figure includes the dissolution of tramp iron.
Fig. 29(a) The effect of cupric sulphate and ferric sulphate additions on the dissolution of sphalerite and chalcopyrite. \( T = 110^\circ \text{C}, [\text{acid}]_1 = 0.8 \text{ mol} \, 1^{-1}, p_{O_2} = 0.138 \text{ MPa}, n_p = 115 \text{ g} \, 1^{-1}, \) \( MR = 1.1, \omega = 1000 \text{ rpm}, d_p < 49 \mu \text{m} \, \text{batch 2.} \)
Fig. 29(b) The effect of cupric sulphate and ferric sulphate additions on the dissolution of pyrite. (T = 110°C, [acid]_1 = 0.8 mol l⁻¹, pO₂ = 0.139 MPa, c_p = 115 g l⁻¹, MR = 1.1, ω = 1000 rpm, d_p < 49 μm - batch 2). The c_{FeS2} figure includes the dissolution of tramp iron all of which occurs in the first hour.
Fig. 30 The effect of agitation on the dissolution of sphalerite, chalcopyrite and pyrite. 
(T = 110°C, \( pO_2 = 0.069 \) MPa, [acid]) = 0.8 mol l\(^{-1}\), \( \rho_p = 115 \) g l\(^{-1}\), MR = 1.1, 
\( d_p = 49 \) \( \mu \)m.) The \( \alpha_{FeS_2} \) figure includes the dissolution of some tramp iron.
Fig. 31 Dissolution curves for sphalerite, chalcopyrite and pyrite from replicate leaching experiments. Values of the experimental parameters are given in Table 9. The $\alpha_{FeS_2}$ figure includes the dissolution of tramp iron.
The effect of temperature, oxygen partial pressure, initial acid concentration and molar ratio on the percent theoretical sulphur and sulphate yields after seven hours leaching. Values of the experimental parameters are given in Table 9.
Fig. 33 The effect of temperature, oxygen partial pressure, initial acid concentration and molar ratio of acid/ore on the fraction of galena converted to lead sulphate after seven hours leaching. Values of the experimental parameters are given in Table 9.
(iii) Temperature charts were used as a control measure to facilitate the manual adjustments of simmerstat settings but also provided a permanent record of the maximum and minimum temperature attained. If for some reason, such as operator error, the temperature deviated more than ±2°C from the desired value the experiment was repeated. Usually performance was better than ±1°C.

(iv) Autoclave pressure, although not continuously recorded was regularly observed. Some minor fluctuations occurred as a result of slight changes in temperature but because of the oxygen regulating valve it never dropped below the preset value. Maximum deviation was about +15 kPa. Small increases in pressure of about this magnitude were also observed occasionally immediately after sample introduction, presumably due to H2S evolution. In one experiment using 100% minus 325 mesh ore at 200 g 1⁻¹ H2S evolution was so rapid that the pressure rose to a value in excess of 1.0 MPa before the autoclave was vented and the experiment discontinued. This result was attributed to the very high specific surface coupled with a low oxygen partial pressure (0.069 MPa).

(v) Collection of solution samples was uneventful providing allowance was made for the longer collection times (up to 5 mins) at low temperatures and pressures.

(vi) Appearance of the autoclave interior after an experiment.

(a) Commonly there was a small amount of ore (< 1 g) left behind in the sample introducer and a larger amount adhering to the baffles and agitator shaft above the average waterline. This latter amount appeared to be a function of the extent of reaction, increasing with increased reaction.

(b) Highly reacted residues contained a fairly large proportion of white fines which were not present in the ground ore. They were identified as lead sulphate. These residues also tended to adhere to the impeller blades and to bind tightly during filtration decreasing the voidage and prolonging this operation.

(c) Very fine flakes of crystalline sulphur were found on the underside of the autoclave lid after most experiments and less often on the upper walls of the autoclave body and the pyrex liner. This could not be satisfactorily collected but it never exceeded about 50 mg.

(vii) Separation of the residue from the solution was effected as rapidly as possible after autoclave shut-down by filtration on Whatman No. 1 filter circles. However, an appreciable quantity of white fines passed through before the bed had built up. These were collected by refiltering after first decanting most of the filtrate.

(viii) Analyses of the residue held-up on the baffles at the conclusion of leaching (residue Y) led to the following general observations:

- \( W_X < W_Y \)
- \( W_X < W_Y \)
- \( W_X < W_Y \)
- \( W_X < W_Y \)
- \( W_X < W_Y \)

and also:

\[
\frac{W_{Pb\text{(sulphate)}}}{W_{Pb\text{(total)}}} = \frac{W_{Pb\text{(sulphate)}}}{W_{Pb\text{(total)}}}
\]
\[(a_{\text{PbS}})^\gamma = (a_{\text{PbS}})^\chi\]

and

\[Y \text{ increases as } (\alpha_{\text{ZnS}} + a_{\text{PbS}}) \text{ increases.}\]

\[Y \text{ increases as } \rho \text{ increases.}\]

6.3 SCANNING ELECTRON MICROSCOPY

6.3.1 Ore Mineralogy and Sizing

Ore mineralogy and sizing have been considered in § 6.1.1 and § 6.1.3. The relevant micrographs are shown in Figs. 34(a) and 36 and EDX elemental analyses of the major ore minerals, performed on the 137 \(\mu\text{m}\) size fraction, are shown in Fig. 35. The following points are of interest.

(i) Cubic galena crystals are readily identifiable.

(ii) Submicron fines, generated during comminution, adhere to the surface of the larger particles.

(iii) Screening of the 49 \(\mu\text{m}\) size fraction was unsatisfactory as evidenced by the large volume of fines (Fig. 36).

(iv) Apart from the submicron fines ((ii) above) the 137 \(\mu\text{m}\) screen fraction shows satisfactory uniformity of particle sizes.

(v) The EDX analysis of sphalerite (Fig. 35(a)) shows the presence of iron in the lattice.

As the ratio of peak heights (sulphur/metal) are characteristic of a particular mineral these are recorded to aid in identifying reaction products in the residue. The ratios are for the sulphur 2.3 keV peak/the principal metal peak.

\[S/\text{Zn} = 1.60, S/\text{Pb} = 8.75, S/\text{Fe (pyrite)} = 1.62, S/\text{Fe (chalcopyrite)} = 1.73, S/\text{Cu} = 2.53.\]

6.3.2 Visual and EDAX Identification of the Leach Products

To facilitate the visual identification of the leach products in the residue a systematic sequence of micrographs were prepared of ore that had been leached for seven hours at 110\(^\circ\text{C}\) (R1). The sequence is outlined in § 5.3.3 and the results displayed in Figs. 37 to 40. By viewing in sequence it is also possible to assess the distribution of the products.

6.3.2.1 R1 Treated by Sulphur Removal followed by Lead Sulphate Removal (Fig. 37)

(i) Lead sulphate and sulphur were removed in the reverse order but no differences could be detected in the micrographs which indicates that lead sulphate does not have a sulphur coating.

(ii) Sphalerite particles have retained their initial overall dimensions and attack has been via extensive pitting on certain preferred crystal faces.

(iii) Galena particles show reduced dimensions, based on viewing a larger area of residue than that shown in this micrograph.
6.3.2.2 RI Treated by Lead Sulphate Removal (Fig. 38)

(i) Elemental sulphur is present in the form of agglomerate particles of approximately the same dimensions as the original particles (50 µm). An EDX elemental analysis of the surface of a sulphur agglomerate (Fig. 38(b)) shows that some iron is also present.

(ii) Galena, although extensively pitted, retains its cubic form.

6.3.2.3 RI Treated by Sulphur Removal (Fig. 39)

(i) The appearance of the cubic galena crystals is distinctly different from those in Figs. 37 and 38. The large number of small crystals covering the surface of the cube are evidently lead sulphate. An EDX elemental analysis of the surface of the cube is shown in Fig. 39(c) showing it to contain lead and sulphur in the same ratio as galena (Fig. 35(b)). As EDAX cannot distinguish between PbS and PbSO₄ the difference must be ascertained visually.

(ii) There are a large number of small, smooth, regular particles which were not present in Figs. 36, 37 or 38. An EDAX analysis (Fig. 35(a)) reveals that they contain lead and sulphur. Evidently these particles are also lead sulphate.

(iii) Of the two sphalerite particles identified, one is severely pitted while the other is virtually unattacked.

6.3.2.4 RI untreated (Fig. 40)

(i) Galena particles can be distinguished by their approximately cubic shape and the granular appearance of the lead sulphate coating.

(ii) Sulphur appears to be coat partially reacted sulphide minerals but not lead sulphate or silica.

(iii) Fine lead sulphate particles can be seen as in Fig. 39(a).

6.3.3 Nature of the Leach Attack and the Form of the Products

Figs. 41 to 47 present micrographs of individual mineral particles after leaching to show the nature of the leach attack and the form of the products.

6.3.3.1 A Sulphur Particle (R16) (Fig. 41)

(i) This is a magnified view of the sulphur particle identified in Fig. 34(h). Residue 16 has a sulphur content of only 1% by weight.

(ii) The particles appear to be composed of numerous small crystals.

6.3.3.2 Reacted Sphalerite Surface (R2) (Figs. 42, 43 and 44)

(i) Pitting is evident in the dark coloured surface of Fig. 42.

(ii) The light coloured patches are identified as elemental sulphur by the EDX analyses shown in Figs. 42(b) and 42(c). The former is a point analysis of a light coloured patch and the latter a general analysis of the whole surface shown in Fig. 42(a). The change in S/Zn peak height ratios from 2.1 to 1.5 suggests that the patches are sulphur.

(iii) Fig. 43(a) shows a more highly reacted sphalerite surface. Pitting is more pronounced and sulphur covers most of the unpitted surface.

(iv) The top face of the crystal appears to be virtually unattacked.

(v) The white crystalline mass at mid-bottom of the micrograph is lead sulphate resting on the sphalerite surface. It may have caught there during sample mounting.
6.3.3.3 Pyrite Surface (R2) (Fig. 44)

(i) Sulphur covers a large percentage of the pyrite surface. It is indicated by the EDX analyses shown in Figs. 44(b) and (c) in a manner analogous to described in § 6.3.3.2 for sphalerite.

(ii) The uncovered surface appears unblemished suggesting that little or no attack has occurred.

6.3.3.4 Chalcopyrite Surface (R2) (Fig. 45)

(i) Sulphur covers approximately 30% of the surface and, as with pyrite above, the uncovered surface shows no signs of leach attack.

(ii) Sulphur is indicated by EDX analyses shown in Figs. 45(b) and (c).

6.3.3.5 Reacted Galena Surface (R1) (Figs. 46(a) and 46(b))

(i) This is a close-up view of one of the cubic particles shown in Fig. 39(a) and shows distinctly the small (~1 μm) crystals of anglesite (identified by XRD - Fig. 21) that have formed on the galena surface. Despite the fact that the specific volume of anglesite is higher than that of galena the coating is not coherent.

(ii) Direct evidence that the small crystals are lead sulphide is provided by Fig. 46(b) which shows a similar surface after lead sulphate removal. The crystals have disappeared and the underlying surface is extensively pitted.

6.3.3.6 Reacted Galena Surface (R2) (Figs. 47(a) and 47(b))

(i) Figs. 47(a) and (b) are a similar pairing to 46(a) and (b) but for a lower temperature (70°C) experiment (R2). The lead sulphate crystals are not as regular but are generally much larger (~5X).

(ii) Small crystals of lead sulphate of a rather different form can be identified on the left hand side of Fig. 47(a). These are similar to those identified in Fig. 39(a).

6.3.4 High Temperature Residues (R4 - 130°C) (Figs. 48 and 49)

(i) Fig. 48(a) is a micrograph of the residue with lead sulphate removed. The appearance of the residue is strikingly different from those in previous micrographs in that the individual sulphide particles are bound together to form agglomerate particles. These agglomerates include all the fines present in the 49 μm fraction (Fig. 36) and attain overall dimensions exceeding 49 μm. There is no obvious evidence of elemental sulphur. It constitutes 3.6 weight % of the residue compared with 1.02% for R16, 6.1% for R2 and 18.1% for R1. In the latter cases it was clearly detectable (Figs. 34(b), 43 and 38(a) respectively).

(ii) Fig. 48(b) is a micrograph of the residue with sulphur removed. Fine crystals of lead sulphate are present in abundance and some of the agglomerates appear to have broken down. EDX analyses of the general surfaces of the agglomerates reveals peaks for S, Fe, Cu and Zn (e.g. Fig. 49(b)) indicating that only sulphides are present. Galena evidently forms a coating of lead sulphate before agglomeration occurs.

(iii) Fig. 49(a) is closeup of one of the agglomerates and EDX analyses of points on the surface of several component particles are shown in Figs. 49(c), (d) and (e).
6.3.5 Residues from Iron Catalysed Leaching (R20) (Figs. 50 and 51)

(i) Table 9 shows that in this experiment the ore had almost completely reacted. The residue analysis is, 0.6% Zn, 2.1% Fe, 0.8% Cu, 28.7% Pb and 20.5% S with 80% of the sulphur being in elemental form.

(ii) Fig. 50(a) shows the presence of large agglomerate particles of sulphur having dimensions exceeding that of the individual ore particles (49 μm). An EDX elemental analysis of one such agglomerate (Fig. 50(b)) shows that while it is composed principally of elemental sulphur it also contains some iron and silica and traces of copper, lead and zinc. The only particles in Fig. 50(a) that can be identified separately from the agglomerates are lead sulphate covered galena and silica.

(iii) Fig. 51(a) is a magnified view of the particle indicated by an X in Fig. 50. The EDX analysis of the surface, Fig. 51(b), shows principal peaks for copper and sulphur with a minor peak for iron indicating either chalcocite or covellite. The gold peaks result from the coating applied during preparation of the samples (§ 5.3.1). The particle has been extensively attacked and small blobs of sulphur can be seen on the surface.

6.3.6 Ore Leached at Room Temperature (Figs. 52(a) and 52(b))

The residue depicted in Fig. 52(a) was the result of leaching nominally 49 μm ore for three weeks at room temperature in an uncovered, unstirred pyrex beaker. Hydrogen sulphide was evolved on adding the ore to the acid and was smelted for some days afterward. Examination of Fig. 52(a) reveals the following:

(i) Galena is highly reacted judging from the advanced development of the coating of anglesite crystals.

(ii) Some faces of the sphalerite particles show pitting attack.

(iii) No elemental sulphur is detectable.

Fig. 52(b) is a magnified view of the sphalerite surface marked by an X in Fig. 52(a). It reveals that the surface is rough and extensively pitted.

6.3.7 Anglesite Formation

It was noted in § 6.3.3.6 that the anglesite crystals formed on the surface of galena were larger for the 70°C experiment than for 110°C. Table 10 presents approximate transverse dimensions of crystals formed under various leaching conditions as measured from micrographs.

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Experimental Parameter</th>
<th>Figure</th>
<th>Transverse Dimension (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>d_p (μm)</td>
<td>C</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>49</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>70</td>
<td>49</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>49</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>110</td>
<td>137</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>110</td>
<td>49</td>
<td>Fe''''</td>
</tr>
</tbody>
</table>

Table 10 The Size of Anglesite Crystals Formed as a Function of Experimental Conditions.
Fig. 34(a) Scanning electron micrograph of unreacted ore screened -149 + 125 µm. (nominal 137 µm). x 120 Mag.

Fig. 34(b) Scanning electron micrograph of leached 137 µm ore (residue from experiment # 16) x 100 Mag.
Fig. 35  EDX elemental analyses of mineral surfaces (a) sphalerite (b) galena (c) pyrite (d) chalcopyrite.
Fig. 36  Scanning electron micrograph of unreacted ore screened -53 + 44 μm (nominal 49 μm). x 400 Mag.

Fig. 37  Scanning electron micrograph of residue from experiment 1 (R1) treated by sulphur removal followed by lead sulphate removal. x 500 Mag.
Fig. 38(a) Scanning electron micrograph of R1 after lead sulphate removal. x 400 Mag.

Fig. 38(b) EDX elemental analysis of the surface of a sulphur amendment (R1).
Fig. 39(a) Scanning electron micrograph of R1 after sulphur removal. x 500 Mag.

Fig. 39(b) EDX elemental analysis of a point on the surface of one of the fine particles showing them to be lead sulphate.

Fig. 39(c) EDX elemental analysis of the surface of the cubic particle.
Fig. 40  Scanning electron micrograph of R1, x 400 Mag.

Fig. 41  Scanning electron micrograph of a sulphur particle (R16), x 1000 Mag.
Fig. 42(a) Scanning electron micrograph of reacted sphalerite surface (R2) showing patches of elemental sulphur. x 3000 Mag.

Fig. 42(b) EDX elemental analysis of a point on the surface of one of the sulphur patches.

Fig. 42(c) EDX elemental analysis of the general surface.
Fig. 43(a) Scanning electron micrograph of reacted sphalerite surface (R2) showing patches of elemental sulphur and the pitting form of attack. x 2000 Mag.

Fig. 43(b) Scanning electron micrograph of a similar surface with sulphur removed. x 3000 Mag.
Fig. 44(a) Scanning electron micrograph of pyrite (R2) showing an extensive coating of sulphur. x 3000 Mag.

Fig. 44(b) EDX elemental analysis of a point on the surface of the sulphur layer.

Fig. 44(c) EDX elemental analysis of the general surface.
Fig. 45(a) Scanning electron micrograph of chalcopyrite (R2) showing a partial sulphur coating. \( \times 3000 \) Map.

Fig. 45(b) EDX elemental analysis of a point on the surface of a sulphur patch.

Fig. 45(c) EDX elemental analysis of the general surface.
Fig. 46(a) Scanning electron micrograph of reacted galena surface (R1, 110°C) showing small crystals of anglesite. x 7000 Mag.

Fig. 46(b) Scanning electron micrograph of a similar surface (R1) after the removal of anglesite by ammonium acetate leaching. x 3000 Mag.
Fig. 47(a)  Scanning electron micrograph of reacted galena surface (R2, 70°C) showing the larger crystals of anglesite formed at the lower temperature. x 2000 Mag.

Fig. 47(b)  Scanning electron micrograph of a similar surface (R2) after the removal of anglesite by ammonium acetate leaching. x 2000 Mag.
Fig. 48(a) Scanning electron micrograph of ore leached at 130°C, R4, showing agglomerate particles comprised of sphalerite, pyrite and chalcopyrite and including most of the fines. x 400 Mag.

Fig. 48(b) Scanning electron micrograph of R4 with sulphur removed showing that some of the agglomerates have broken down. x 400 Mag.
Fig. 49(a) Scanning electron micrograph of an agglomerate particle from Fig. 48(a). x 1600 Mag.

(b) the general agglomerate surface.

(c) points 1, 2 and 3 on the agglomerate surface

(d) points 4 and 5 on the agglomerate surface showing sulphur deficient sphalerite.

(e) point 6 on the agglomerate surface showing sulphur deficient pyrite.

Fig. 49(b) (c) (d) and (e) EDX analyses of the general surface and points 1, 2, 3, 4, 5 and 6 on the surface.
Fig. 50(a) Scanning electron micrograph of ore leached using ferric sulphate as a catalyst (R20). It shows almost complete dissolution of the sulphide minerals and the large sulphur agglomerates resulting. x 300 Mag.

Fig. 50(b) EDX elemental analysis of a sulphur agglomerate (R20) showing traces of pyrite, silica, chalcopyrite, sphalerite and lead (sulphide or sulphate).
Fig. 51(a)  Scanning electron micrograph of sulphur agglomerate (R20) consisting principally of covellite. x 1200 Maq.

Fig. 51(b)  EDX elemental analysis of the general surface of the agglomerate.
Fig. 52[a] Scanning electron micrograph of 49 μm ore leached for three weeks in 0.8 mol l⁻¹ sulphuric acid at room temperature, showing the extensive conversion of galena to anglesite. x 300 Mag.

Fig. 52(b) Scanning electron micrograph of reacted sphalerite surface showing pitting attack. x 2000 Mag.
6.4 ERRORS

6.4.1 Sources of Error

(i) Ore Analyses (§ A4.1)

(a) splitting of a homogeneous sample
(b) analytical errors including fusion, dilution and instrumental.

The ore assays were taken as the mean of six individual determinations.

(ii) Residue Analyses (§ A4.2)

(a) loss or ore on collection leading to a low value for the total weight out.
(b) as per (a) and (b), paragraph (i).

(iii) Solution Analyses (§ A4.3)

(a) solution holdup on surfaces above the waterline, in particular holdup with the ore residue adhering to the baffles.
(b) solution loss from the liner by evaporation and recondensation on the lid and upper walls of the autoclave.
(c) solution loss as vapour through the gland.
(d) analytical errors.

Errors (a), (b) and (c) lead to an overestimate of extractions.

(iv) Final Solution Analysis (§ A4.3)

(a) incomplete washing of the residue.
(b) incomplete rinsing of the autoclave internals.
(c) analytical errors.

(v) Calculation of Extractions

A number of assumptions were required to calculate the "true" extractions of sphalerite, chalcopyrite and pyrite from the weight of metal in the solution samples. The primary assumptions predicted:

(a) the rate of solution loss from the autoclave (errors (a), (b) and (c) in paragraph (iii)) above.
(b) the rate of buildup of ore residue above the waterline (residue Y - § A5).

Assumptions (a) and (b) minimise the errors in the solution analyses due to solution losses and to a gradual reduction in the surface area available for leaching. While these assumptions produce better estimates of the extractions than the raw solution analyses they become inaccurate when solution losses and ore holdup are large. The assumptions are thoroughly discussed and quantified in Appendix 5.

6.4.2 Magnitude of Errors

(i) Mass Balance

The errors in the mass balances, [i.e. the difference between the weight of a metal introduced in the ore and the weight of metal out (solution plus residue)] expressed as a percentage
of total weight introduced, are given in Table A10, Appendix 7. This table shows that the mean error is less than 3 percent. The high values in experiment 20 can be ascribed to the unusually large dilutions necessary because of the high iron concentrations in solution. The difference between the weight of iron in the residue and solution at the completion of leaching and the weight of iron added in the ore was assumed to be due to corrosion. The Fe\text{corr} values in Table A10 correspond to this weight expressed as a percentage of the weight of iron added. A value of zero means that the weight of iron out was less than or equal to the weight of iron in. The Fe\text{corr} values also contain the mass balance error (§ A5.4). Because of this, only values over 5 percent can be considered significant.

(ii) Sphalerite and Chalcopyrite Extractions

A more useful estimate of the error in the final extraction values is the weight of a metal in minus the weight of the metal out expressed as a percentage of the weight of metal extracted rather than the total weight of metal out. Values of these errors (EM%) are also listed in Table A10. These results show that EM averages 4.4% for sphalerite and 6.4% for chalcopyrite. The larger value for chalcopyrite is attributable to the lower extractions of this mineral. These errors are generally overestimates of the actual error because they include the error in both the solution estimate and the residue estimate of the final extraction value. In practice for experiments with extractions in the range 30 to 70 percent the mean of these two estimates was used but for low extractions, the residue estimate and for high extractions, the solution estimates are more accurate (§ A5.3).

Calculation of extractions during the experiment necessitated the use of the assumptions outlined in § 6.4.1, paragraph (v). Solution losses usually resulted in extractions calculated from the final solution sample being larger than the extractions calculated from the final leach solution (Mac > M𝑎𝑐′ - see Table A9 for zinc results). However the differences were generally small so that application of assumption (a) above introduced little error. The values of the weight of residue held up on the baffles above the waterline (Wy) are listed in Table A9, Appendix 6. In eight of the twenty-six experiments this weight was greater than 10% of the total residue weight. The assumption that the holdup residue accumulated at a linear rate (§ A5.3) would lead to a lack of precision in calculating extractions in these cases.

(iii) Iron Extractions

Iron extractions include iron contributions from the dissolution of tramp iron, sphalerite, chalcopyrite, pyrite and stainless steel corrosion. Extractions were normally low and this together with the variable contribution from corrosion is reflected in the large average error in the final iron extractions shown in Table A10.

(iv) Galena Conversions

Galena conversions are not subject to mass balance errors because both reactant and product were determined in the residue. Values for final conversions are therefore of higher precision than corresponding sphalerite, chalcopyrite and pyrite extractions.

(v) Replicate Experiments

Two replicates of four experiments were conducted and the results of three of these are displayed in Fig. 31. In actuality the pairs of experiments are not true replicates because a different method of sample introduction was used in the (a) series prior to the development of the piston and valve model (Fig. 17). This method resulted in inconsistent delivery of ore into the solution, hence its replacement. In view of this fact the agreement between the sphalerite results is good, especially when only the linear section of the curves are considered. These sections are compared in Fig. 63. The chalcopyrite and "pyrite" curves are less consistent and reflect the larger error in calculating their extractions (Table A10).
7. DISCUSSION OF RESULTS

7.1 THE FORM OF THE LEACHING CURVES

Before discussing the effects of various experimental parameters on the rate of mineral dissolution it is informative to examine the leaching curves (Figs. 22 to 31) as a whole. In this way it is possible to draw some conclusions regarding their general form (§ 6.2.2). Fig. 53 illustrates the resultant generalized curves for sphalerite, chalcopyrite and pyrite.

SPHALERITE

The sphalerite curve (Fig. 53a) can be divided into three sections:

(I) A short period of rapid dissolution followed by an incubation period during which little or no zinc dissolves. This section is well developed in some experiments (e.g. the low acid concentration curves in Fig. 28) but virtually disappears under conditions that are conducive to rapid leaching (e.g. 0.414 MPa curve, Fig. 23(a)).

(II) An approximately linear section of variable length covering the extraction range from approximately $\alpha = 0.1$ to 0.8.

(III) A section of rapidly decreasing rate as extraction approaches 100%.

CHALCOPYRITE

The chalcopyrite curve (Fig. 53b) can similarly be divided into three sections:

(I) An induction period of length $t_E$ during which no copper ions appear in solution.

(II) A short period of fairly rapid dissolution which generally terminates at an $\alpha$ value of approximately 0.7. There are insufficient data points to characterise this section of the curve.

(III) An approximately linear leaching period of reduced rate.

PYRITE

The "pyrite" curve (Fig. 53c) can be divided into two sections:

(I) A short period of rapid reaction corresponding to the dissolution of the elemental iron in the ore. This occurs during the first hour of leaching in all experiments.

(II) A section of much lower rate corresponding to the dissolution of iron from pyrite and sphalerite.

GALENA

As the conversion of galena was determined only at the conclusion of an experiment, the true form of the galena conversion curves is not known. However several items of additional experimental evidence allow the general form to be deduced. Firstly, the (α₁₈PbS₃) value determined for experiment 4 was approximately 75% of the α₁ value. Secondly, scanning electron micrographs of reacted lead residues show that a lead sulphate coating builds up on the galena surface (Figs 39a, 46a and 47a). This suggests
Fig. 53 Generalised leaching curves for sphalerite, chalcopyrite and pyrite.
a film diffusion kinetic model. The narrow range of final lead conversions (Table 9), indicating a
general independence of operating conditions, supports a diffusion control model in which the leaching
rate declines as the film thickness increases. The simplest model (equation (20)) predicts a parabolic
decline in rate with time.

Hydrogen sulphide was produced on sample introduction in all experiments and its absence in the
solution samples was found to correspond approximately to $t_E$, the beginning of chalcopyrite dissolution
(Table 9). Hydrogen sulphide was also evolved when samples of nominally 49 µm ore were added to acid
at room temperature. A scanning electron micrograph of ore leached for three weeks under these
conditions (Fig. 52a) shows that the most highly reacted mineral is galena. This observation was
supported by XRD evidence. The implication is that, upon introduction of the ore to the acid, galena
reacts rapidly evolving hydrogen sulphide. The rapid initial rate is no doubt partly due to a high
percentage of galena in the fines shown in Fig. 36 leading to a higher surface area per unit mass than
the other minerals. The high percentage of galena fines is caused by the ease of grinding this mineral
and is exemplified by the analyses of two size fractions in Table 6 (pg. 68). Additional support for
the production of H$_2$S from galena is provided by the scanning electron microscope results (§6.3.2)
which show that elemental sulphur is not formed at the galena/anglesite interface or at the anglesite/
solution interface.

Two possible leaching sequences satisfy the above observations of actual behaviour.

(1) Galena initially dissolves rapidly evolving primarily H$_2$S according to reaction (54).

\[ \text{PbS(s)} + \text{H}_2\text{SO}_4(aq) \rightarrow \text{PbSO}_4(s) + \text{H}_2\text{S(g)} \]  (54)

H$_2$S is removed by oxidation, but the rate of this process is initially slower than the rate of
evolution, leading to a buildup in the H$_2$S concentration in solution. Chalcopyrite ceases dissolving
almost immediately, as the concentration of copper ions that can exist in solution with H$_2$S is very
low (§ 4.8.3). This leads to the induction period for chalcopyrite dissolution. As the H$_2$S buildup
continues the rate of sphalerite dissolution decreases as the equilibrium product concentrations
of equation (32) are approached.

\[ \text{ZnS(s)} + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2\text{S(g)} \]  (32)

A qualitative illustration of this proposed sequence of events is presented in Fig. 54.
Fig. 54a shows the H$_2$S formation and oxidation curves. The former is identical to the hypothetical
galena conversion curve. The latter is discussed further in § 7.2. Fig. 54b is plotted by sub-
tracting the H$_2$S oxidation curve from the H$_2$S formation curve and it represents the concentration
of H$_2$S in the autoclave as a function of time. (The ordinate scale in Fig. 54b has been expanded
three times for clarity.) According to Fig. 54b the H$_2$S concentration reaches the equilibrium of
equation 32 after time $t_A$ causing sphalerite dissolution to cease. Then, as the rate of galena
conversion decreases, a point is reached where the H$_2$S oxidation rate exceeds its rate of formation
and the concentration declines until, at time $t_B$, the equilibrium concentration is again reached
and sphalerite dissolution restarts. Time $t_B$ corresponds to the end of section I, Fig. 53a.
The H$_2$S concentration continues to decline until after time $t_E$ copper begins to dissolve (Fig. 53b).

The zinc concentration in solution appears to increase slightly in the period $t_A$ to $t_B$
(e.g. Fig. 26), rather than decrease, as would be expected if the H$_2$S concentration exceeded the
equilibrium value set by equation (32). Therefore the times $t_A$ and $t_B$ probably do not denote
the actual attainment of the equilibrium value, but a close approach to it.
moles H\textsubscript{2}S formed = moles PbS converted via reaction (54)

moles H\textsubscript{2}S oxidised

(a)

moles of H\textsubscript{2}S in
the autoclave
t\textsubscript{A} t\textsubscript{B} t\textsubscript{E}

H\textsubscript{2}S formation - H\textsubscript{2}S oxidation

(b)

Fig. 54 Graphs of H\textsubscript{2}S concentration versus time per proposal (i).
(a) The formation and oxidation curves.
(b) The resultant concentration curve.

moles H\textsubscript{2}S formed from

I PbS and ZnS
II PbS only
III PbS and ZnS

moles H\textsubscript{2}S oxidised

(a)

moles of H\textsubscript{2}S in
the autoclave
t\textsubscript{A} t\textsubscript{B} t\textsubscript{E}

H\textsubscript{2}S formation - H\textsubscript{2}S oxidation

(b)

Fig. 55 Graphs of H\textsubscript{2}S concentration versus time per proposal (ii).
(a) The formation and oxidation curves.
(b) The resultant concentration curve.
(11) Both galena and sphalerite evolve $\text{H}_2\text{S}$ on dissolution. This proposal, which would shorten $t_\alpha$ and lengthen $t_\varepsilon-t_\eta$ (Fig. 55), satisfies the experimental observations equally as well as proposal (1). The period $t_\eta-t_\varepsilon$ would not be altered because during this time only galena reacts.

While both proposals provide logical explanations of the observed incubation period for zinc and induction period for copper, it remains to examine their thermodynamic feasibility. The analysis which is presented in Appendix 8 is not exact because it makes the simplifying assumptions that the solutions are ideal and that the reactions occur at 25°C. In view of the complexity of the system under examination and the dearth of thermodynamic data available at elevated temperatures it is the best approximation possible and serves as a qualitative check rather than a quantitative characterization.

Calculation of free energy and equilibrium data in Appendix 8 shows that only galena is favoured thermodynamically to produce hydrogen sulphide. An illustrative calculation for the period $t_\varepsilon$ of experiment 11 shows that the observed concentration of zinc in solution at the end of this time ($t_\eta$) can be predicted from the weight of galena reacted. It further shows that detectable quantities of copper dissolve only when $[\text{H}_2\text{S}]_{\text{aq}} < 2 \times 10^{-19}$. The maximum $\text{H}_2\text{S}$ pressure generated in experiment 11 was calculated to be 2 kPa. This would have been undetectable by visual observation of the autoclave pressure gauge.

The calculations presented in Appendix 8 support proposal (1) above for the initial leaching behaviour of sphalerite, chalcopyrite and galena. The subsequent behaviour of sphalerite ($> t_\eta$) and chalcopyrite ($> t_\varepsilon$) are discussed in more detail in sections 7.4 and 7.5.

7.2 FACTORS AFFECTING THE LENGTH OF THE CHALCOPYRITE INDUCTION PERIOD ($t_\varepsilon$)

The length of the chalcopyrite induction period ($t_\varepsilon$) is a measure of the persistence of $\text{H}_2\text{S}$ in the autoclave. Accurate determination of $t_\varepsilon$ from graphs of $a_{\text{CuFeS}_2}$ versus $t$ is impossible because of the large time intervals between data points. It is possible, however, to make several qualitative observations regarding the effect of the experimental conditions on the length of the induction period.

7.2.1 Ferric Sulphate Addition

Reference to Fig. 29a shows that $t_\varepsilon$ is reduced substantially by the introduction of 8.35 g l$^{-1}$ ferric sulphate to the leachant at the beginning of the experiment. This dependency on the ferric ion concentration is important because variable concentrations of iron are present in all experiments, largely as a result of trap iron dissolution. Interpretation of data on the dependence of $t_\varepsilon$ on experimental conditions must take account of this additional uncontrolled variable, ferric ion concentration. It would be ideal if a quantitative relationship between $t_\varepsilon$ and iron concentration could be established but the data from experiment # 20 is insufficient for this purpose.

The $a_{\text{FeS}_2}$ values plotted in Figs. 22 to 31 are not adequate for comparing the effects of iron concentration between experiments because they do not include the variable iron contributions from corrosion, chalcopyrite and sphalerite. (The contribution from chalcopyrite should be zero during the induction period.) More useful in this respect are the figures for total iron concentration per unit weight of iron added ($a_{\text{Fe total}}$) listed in Table A9.

7.2.2 Galena Leakage

The reservoir pressure drops and the corresponding volume of oxygen delivered to the autoclave in the time $t_\eta$ ($- t_\varepsilon$) are included in Table A9. The actual volume of gas lost through the gland is less than this amount by the volume of oxygen consumed minus the volume of $\text{H}_2\text{S}$ evolved. The actual loss of $\text{H}_2\text{S}$ is not estimable because it depends on the partial pressure of $\text{H}_2\text{S}$ which was not determined. However estimates of $P_{\text{H}_2\text{S}}$ in Appendix 8 suggest that it is very small (< 10 kPa). Assuming a value of 15 kPa, the maximum observed pressure rise (§ 6.2.3), and a gas leakage of 4 litres, the weight of
H₂S lost would be 0.3 g. While this is insignificant when computing total sulphur mass balances it may produce a significant decrease in tₑ. Consequently both gland leakage and iron concentrations must be considered as additional variables when comparing tₑ values of different experiments.

7.2.3 Temperature

Examination of Fig. 22 shows that tₑ apparently increases slightly with temperature below 110°C. However in addition to temperature both iron concentration and H₂S leakage, which both influence tₑ, vary during the experiment. Table A9 shows that there is only one iron data point in the tₑ range. The αᵦ Fe total values increase slightly with decreasing temperature. Pressure drop data shows a decrease with increasing temperature. That is, iron concentrations imply an increase in tₑ with temperature (observed) while gland leakage suggests a decrease in tₑ with temperature. Evidently no conclusions can be drawn regarding the actual effect of temperature on tₑ except that this effect is slight.

7.2.4 Oxygen Partial Pressure

Examination of Fig. 23a shows that tₑ apparently decreases with increasing oxygen pressure. Iron concentrations in Table A9 are similar for experiments 5 and 1 and increase slightly for 6 and 7. Pressure drop data puts experiment 1 - 5 > 6 - 7 which suggests a shorter tₑ for the two lower oxygen pressures. Taking the data as a whole it may be concluded that although the increased iron concentrations in 6 and 7 may be partially responsible for the decreased tₑ's in these experiments there in conclusive evidence of a tₑ dependency on Pₒ₂.

7.2.5 Surface Area

Changes in mol ratio at constant acid concentration are equivalent to changes in pulp density or initial particulate surface area. The fact that the α Vs t curves in Fig. 25 are identical (within the limits of experimental error) for three different initial surface areas means that the fractions leached/unit surface area are identical. That is, the rate of reaction is proportional to the surface area.

Examination of Fig. 25 shows that the tₑ values are similar although that for experiment 1 is a little longer than those of 13 and 14. Fig. 33 and Table 9 reveal that the final lead conversions are proportional to surface area indicating that twice as much H₂S was evolved in experiment 13 as in experiment 14 in the same time period. However, because a constant analysis ore was used, twice as much iron was added in experiment 13. Based on a direct rate dependence of H₂S oxidation on iron concentration one might therefore predict identical tₑ values for 13 and 14. Table A9 reveals that the actual ratios of iron in solution/iron added are not exactly equal. The order of magnitudes is 14 > 13 > 1 suggesting the reverse order for tₑ, viz: 1 > 13 > 14 so that the H₂S lost through gland leakage will be greater in the latter case due to the lower oxygen consumption. The pressure drop for experiment 1 is larger than 13 or 14 so that this data predicts a tₑ order of 1 < 14 < 13.

In addition to the difference in iron concentrations and gas leakage between these experiments there is also a difference in surface area. It seems possible that the twofold increase in surface area in experiment 13 over experiment 14 may account for the twofold increase in the rate of H₂S oxidation equally as well as the similar increase in iron concentration. Direct evidence of a surface area dependence is provided by experiment 16, Fig. 27. In this experiment the 137 μm fraction was leached under otherwise standard conditions. The ratio of iron in solution during the incubation period to lead added in experiment 16 was 0.029 compared to 0.015 for experiment 1 so that twice as much iron was available per mole of H₂S evolved in the former case. Despite this, H₂S persisted for the full seven hours of leaching (tₑ > 7 hrs). The only other difference between the two experiments was in initial surface area. This was 172 cm² g⁻¹ for the 137 μm fraction (§ 6.1.1) but was not calculated for the 49 μm fraction because of the presence of fines. However a conservative estimate of the latter area makes it at least 8 times that of the 137 μm fraction. To account for the long induction period in experiment 16, despite the availability of twice as much iron in solution, one must presume an H₂S
oxidation dependence on surface area. This result does not clarify the \( t_E \) results for experiments 13 and 14.

7.2.6 Acid Concentration

Examination of Fig. 28 shows that \( t_E \) appears to increase with decreasing acid concentration except for an apparently anomalous result for the 1.2 mol l\(^{-1}\) curve. The average values of iron dissolved/iron added over the induction periods have the following order of magnitude (Table A9), experiment 10 - 11 > 12 > 11 - 10 which does not accord with the observed results. Therefore \( t_E \) must be influenced by acid concentration. The anomalous result for experiment 12 is presumably related to the high pulp density used, which resulted in an extremely high residue holdup (Y residue) at the completion of leaching (Table A9).

Having discovered a \( t_E \) dependence on acid concentration it is necessary to reassess the other observed dependencies in view of the fact that acid concentration decreases with time in all experiments. As only a little sphalerite dissolves during the induction period, the decline in acid concentration is due almost exclusively to the conversion reaction of galena. Assuming that 50\% of the galena in the ore has reacted in an experiment employing 0.8 mol l\(^{-1}\) acid this corresponds to 0.07 moles or a decline in acid concentration of about 9\%. This is unlikely to have a major effect on \( t_E \).

7.2.7 The Reactions

The reactions which determine the value of \( t_E \) are the H\(_2\)S producing reaction, which from proposal (i), § 7.1, is the conversion reaction of galena (54), and the H\(_2\)S oxidation reaction or reactions. Results for the conversion of galena to anglesite (Table 9 and Fig. 33) show that the fraction converted after seven hours leaching is largely independent of \( T \) (70-110°C), \( P_{O_2} \) (0.138-0.414 MPa) and \([\text{acid}]_1\) (0.2-1.2) which suggests a diffusion controlled reaction of low activation energy. The rate of H\(_2\)S production is therefore also independent of operating conditions except for surface area where a linear dependence was found (see MR curve, Fig. 33). The value of \( t_E \) is determined therefore, by the rate of H\(_2\)S oxidation (Fig. 54a). But \( t_E \) is a function of ferric ion concentration (§ 7.2.1), oxygen partial pressure (§ 7.2.4), surface area (§ 7.2.5) and acid concentration (§ 7.2.6) so that the oxidation reaction sequence must include these variables (except area) in or before the rate determining step.

The following equations represent the possible oxidation reactions of H\(_2\)S:

\[
\begin{align*}
\text{H}_2\text{S} + \text{H}_2\text{SO}_4 & \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{S} + \text{S}^0 \quad \text{..... (45)} \\
\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{S}^0 \quad \text{..... (46)} \\
\text{H}_2\text{S} + 2\text{O}_2 & \rightarrow \text{H}_2\text{SO}_4 \quad \text{..... (47)} \\
\text{H}_2\text{S} + 2\text{Fe}^{+++} & \rightarrow 2\text{Fe}^{++} + \text{Zn}^2+ + \text{S}^0 \quad \text{..... (48)} \\
\text{H}_2\text{S} + 8\text{Fe}^{+++} + 4\text{H}_2\text{O} & \rightarrow 8\text{Fe}^{++} + 10\text{H}^+ + \text{SO}_4^{2-} \quad \text{..... (49)}
\end{align*}
\]

The observed dependency on ferric sulphate concentration coupled with the fact that dissolved iron was present during the induction period of all experiments suggests that reaction (48) and/or (49) is at least partially responsible for H\(_2\)S removal. Ferric ions (other than in experiment 20 in which they were added) are produced by the oxidation of ferrous ions according to reaction (50).

\[
2\text{Fe}^{++} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{+++} + \text{H}_2\text{O} \quad \text{..... (50)}
\]

As the ratio of \( S/\text{SO}_4^{2-} \) (Table 9) usually exceeds 9/1 reaction (48) must be predominant so that a likely oxidation sequence is (50), (48), (50) ... In this sequence two different rate expressions are
predicted depending on whether reaction (50) or reaction (48) is the slower step.

Slow step reaction (50):

\[
\text{Rate} = f ([\text{Fe}^{++}], P_0, [\text{H}^+])
\]  

(90)

Slow step reaction (48):

\[
\text{Rate} = f ([\text{Fe}^{++}], P_0, [\text{H}^+], [\text{H}_2\text{S}])
\]  

(91)

Rate expression (91) is not supported experimentally because it predicts that \( \text{H}_2\text{S} \) would only be completely removed at \( t = \infty \). It follows then, that reaction (50) is the rate limiting step. Rate expression (90) predicts the observed rate dependencies exactly, thereby lending strong support to the proposed reaction sequence.

The experimental results are inadequate to quantify equation (90) as the changes in iron concentration, acid concentration and surface area with time are not accurately known. However, the rate expression does have three important corollaries:

(i) The initial observation of \( \text{H}_2\text{S} \) in the autoclave in all experiments (except \# 20) is predicted. \( \text{H}_2\text{S} \) evolution was observed immediately upon introduction of ore to the solution (§ 6.2.3). However, the \( \text{H}_2\text{S} \) oxidation reaction is dependent on the presence of iron in solution. There is therefore a short time, during which the elemental iron in the ore is dissolving, when the rate of \( \text{H}_2\text{S} \) evolution exceeds the rate of removal in all experiments. This situation was depicted in Figs. 54a and 55a by a short section of rate build up at the beginning of the \( \text{H}_2\text{S} \) oxidation curve. The induction period for chalcopryte and the incubation period for sphalerite appear to have been eliminated by the addition of ferric sulphate (experiment 20 - Fig. 29a). Sulphur flakes were, however, observed on the autoclave lid at the conclusion of leaching showing that some \( \text{H}_2\text{S} \) was formed. This implies that a short time lag exists between \( \text{H}_2\text{S} \) production and \( \text{H}_2\text{S} \) oxidation even when excess ferric ions are present.

(ii) The rate of \( \text{H}_2\text{S} \) oxidation is approximately linear (after the short buildup period) as depicted in Figs. 54a and 55a.

The rate of oxidation is dependent on \( P_0, [\text{acid}], [\text{surface area}] \) and [Fe\(^{++}\)]. In any particular experiment \( P_0 \) is constant. The acid concentration and surface area decline but in the period \( t_E \) this is almost solely due to the reaction of galena. Calculation shows that the decline in acid concentration under these conditions is small (§ 7.2.6). Furthermore, the scanning electron micrographs depicted in § 6.3 conclusively show that sulphur is not formed on the reacted galena surface presumably because of the sulphate coating. This suggests that only sulphide surfaces are active in \( \text{H}_2\text{S} \) oxidation so that the effective surface is reduced only by sphalerite dissolution which is small during the incubation period. The iron concentration in solution after the dissolution of the elemental iron in the ore is approximately constant during the induction period in most experiments (Table A9). Therefore the rate determining factors are approximately constant.

(iii) The observed dependence of \( t_E \) on surface area implies that the oxidation of ferrous ions via equation (50) is heterogeneous and takes place between adsorbed species.

Of the other possible oxidation reactions for \( \text{H}_2\text{S} \), reaction (45) occurs only at high acid concentrations [70] and the two equations representing direct oxidation by oxygen, (46) and (47), do not explain the observed rate dependency on ferric ion concentration and acid concentration. Furthermore, Exner et al [70] found the rate of these reactions to be negligible below 150°C even at 10 atm. oxygen pressure. However, some sulphur was found on the roof and walls of the autoclave at the conclusion of
many experiments. This could only have been formed via reaction (46) suggesting that the stainless steel surfaces have a catalytic effect.

7.3 REACTION STOICHIOMETRIES

At times exceeding $t_e$ the only sulphur oxidation products are $S^0$ and $SO_4^{2-}$ and the overall leaching stoichiometry can be represented by a combination of reactions (88) and (89).

\[
\text{MeS} + \frac{1}{2}O_2 + H_2SO_4 \rightarrow \text{MeSO}_4 + S^0 + H_2O \quad \ldots \ldots (88)
\]

\[
\text{MeS} + 2O_2 \rightarrow \text{MeSO}_4 \quad \ldots \ldots (89)
\]

Because pyrite and chalcopyrite constitute a small proportion of the weight of sulphide sulphur in the ore, the major determinants of the final distribution of $S^0$ and $SO_4^{2-}$ are sphalerite and galena. Fig. 32 depicts the effect of the four major experimental variables on this distribution. It shows that the production of sulphur is predominant, with the ratio of $S(S^0)/S(SO_4^{2-})$ usually exceeding 9:1. Analysis of the effect of the experimental variables is complicated by presence of two major contributors to the final weight of the sulphur oxidation products. For example, while Fig. 32 indicates that sulphate production is favoured by low acid concentrations, Table 9 shows that the fraction of lead converted to lead sulphide is higher than the final fraction of sphalerite reacted under the same conditions. If it is assumed that sulphate production is primarily due to the conversion of lead via reaction (56), then this may account for the higher yield of sulphate in experiments 10 and 11 rather than the low acid concentration. The same reasoning can be applied for the results at 70°C and 130°C. In an attempt to clarify the respective contributions of galena and sphalerite the ratios of $S(\text{PbS reacted})/S(\text{ZnS reacted})$ have been listed next to the fraction theoretical sulphate production in Table 11. This data shows that there is a strong correlation between the ratio of $S(\text{PbS reacted})/S(\text{ZnS reacted})$ and the fraction of sulphate produced. Increases in the ratio correlate with increased sulphate fractions. However this result is misleading because it is impossible to assess whether the change in an experimental variable leads directly to increased sulphate production by favouring the sulphate forming reaction/s of both sphalerite and galena, or indirectly by changing the ratio of $S(\text{PbS reacted})/S(\text{ZnS reacted})$ without altering the rates, or whether it is a mixture of both effects.

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>1</th>
<th>1a</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<th>7</th>
<th>8</th>
<th>9</th>
<th>9a</th>
</tr>
</thead>
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<tr>
<td>Fraction Theoretical Sulphate Yield</td>
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<td>.066</td>
<td>.160</td>
<td>.091</td>
<td>.386</td>
<td>.093</td>
<td>.090</td>
<td>.074</td>
<td>.149</td>
<td>.126</td>
<td>.088</td>
</tr>
<tr>
<td>$S(\text{PbS reacted})/S(\text{ZnS reacted})$</td>
<td>.204</td>
<td>.230</td>
<td>.860</td>
<td>.267</td>
<td>1.40</td>
<td>.310</td>
<td>.182</td>
<td>.160</td>
<td>.562</td>
<td>.578</td>
<td>.292</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>10</th>
<th>11</th>
<th>11a</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
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</table>

Table 11 The ratio of moles of galena reacted/moles of sphalerite reacted, for each experiment.
While it is impossible to assess the relative contributions of galena and sphalerite to the production of sulphur and sulphate, without conducting experiments with varying ratios of these two minerals, several important conclusions can be made regarding the effect of experimental conditions when the \( \frac{S(\text{PbS reacted})}{S(\text{ZnS reacted})} \) is similar:

(i) Both the sulphur and sulphate producing reactions are proportional to the particulate surface area.

Table 11 shows that within the limits of experimental error the fractions theoretical sulphate produced are identical for experiments 1, 13 and 14 in which the initial surface area was varied. As the ratios of \( \frac{S(\text{PbS reacted})}{S(\text{ZnS reacted})} \) are also similar it may be concluded that the ratio of \( \frac{S(S^0)}{S(SO_4^2-)} \) is independent of surface area, implying that both the sulphate and sulphur producing reactions exhibit the same dependency. This observation is further supported by the results of experiments 6 and 21 (Table 9) which show identical sulphur/sulphate ratios for different initial surface areas.

(ii) The sulphur and sulphate reactions exhibit the same dependency on oxygen pressure.

Reference to Table 11 shows, in a manner similar to (i) above, that both the ratios of \( \frac{S(\text{PbS reacted})}{S(\text{ZnS reacted})} \) and the fractions theoretical sulphate produced are identical for experiments 1, 6, 7, 18 and 21 indicating an independence of \( \frac{S(S^0)}{S(SO_4^2-)} \) on oxygen pressure. Experiment 5 (0.069 MPa) is interesting because the ratio of \( \frac{S(S^0)}{S(SO_4^2-)} \) is identical to that of experiments 1, 6 and 7 but the \( \frac{S(\text{PbS reacted})}{S(\text{ZnS reacted})} \) is higher by 50 percent (Table 11).

(iii) Ferric and cupric sulphate additions in experiments 19 and 20 did not effect the ratio of \( \frac{S(S^0)}{S(SO_4^2-)} \), cupric sulphate because it did not catalyse either reaction and ferric sulphate because it increased the rate of both reactions equally.

As cupric sulphate addition did not catalyse sphalerite (Fig. 29a) or galena dissolution (Table 9) the result for copper is expected. However as ferric sulphate did catalyse sphalerite dissolution (but not galena) it must be concluded that it produced a similar rate increase for both the sulphate and sulphur forming reactions.

Yaroslavstev et al. [65] investigating the leaching kinetics of sphalerite found that both the sulphur and sulphate forming reactions exhibited the same dependency on oxygen pressure in the range 0.1 to 1.5 MPa (equations (41) and (42), Table 1). Exner et al. [70] observed the same result in the range 0 to 0.5 MPa (equations (50) and (51), Table 1). Based on this evidence and the result for experiment 5 in (ii) above one can make the rather tenuous conclusion that the \( \frac{S(\text{PbS reacted})}{S(\text{ZnS reacted})} \) does not exert a very pronounced influence on the distribution of sulphur and sulphate. That is, the fractions of sulphur and sulphate produced from galena and sphalerite are similar.

If this assumption is valid it allows assessment of the effects of experimental variables when the ratios of \( \frac{S(\text{PbS reacted})}{S(\text{ZnS reacted})} \) are different. For example, Fig. 32 shows that sulphate production is favoured relative to sulphur production by low acid concentrations. This result has been reported by a number of researchers (§3.8) for most sulphide minerals. It is predicted by the equation (89), which suggests a rate independence of acid concentration for the sulphate forming reaction, and reaction (50) (the rate determining step for HgS oxidation to sulphur, §7.2) which was shown to exhibit a rate dependence. An important corollary of the acid concentration independence of the sulphate forming reaction is that it precludes sulphate formation via ferric ion oxidation of HgS (equation (49)) because the first step is ferrous ion oxidation (equation (50)) and thus exhibits acid concentration dependence.

Assuming once again that the effect of the \( \frac{S(\text{PbS reacted})}{S(\text{ZnS reacted})} \) on the final distribution is slight, it is possible to examine the influence of temperature. Fig. 32 shows an increase in the \( \frac{S(S^0)}{S(SO_4^2-)} \) ratio with temperature in the range 70 to 110°C which suggests that the activation
energy is higher for the sulphur forming reaction. This result agrees with those of Yaroslavtsev et al. [65] and Exner et al. [70] for sphalerite (Table 1). The sudden increase in the sulphate/sulphur ratio at 130°C is indicative of a large increase in sulphate production or a decrease in sulphur production. It may in part be due to the oxidation of sulphur to sulphate via reaction (61) which Habashi and Bauer [141] reported occurred at significant rates at temperatures above 120°C.

\[ \text{S}^0(1) + \frac{3}{2}\text{O}_2(aq) + \text{H}_2\text{O}(aq) \rightarrow 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) \]  

..... (61)

To summarise:

(i) No information regarding the stoichiometry of chalcopyrite and pyrite dissolution can be gained from the leaching results.

(ii) At times exceeding t_E, the only sulphide oxidation products are \( \text{S}^0 \) and \( \text{SO}_4^{2-} \) and the ratio generally exceeds 9/1. Therefore equation (88) closely represents the overall leaching stoichiometry of sphalerite and galena under most conditions.

\[ \text{MeS} + \frac{3}{2}\text{O}_2 + 2\text{H}^+ \rightarrow \text{Me}^{2+} + \text{S}^0 + \text{H}_2\text{O} \]  

..... (88)

However it has been established in § 7.1 that galena, at least, dissolves with the evolution of \( \text{H}_2\text{S} \). This is subsequently oxidised to elemental sulphur by ferric ions.

(iii) Both the sulphate and sulphur forming reactions exhibit the same dependence on surface area, oxygen partial pressure and ferric ion concentration at temperatures below the melting point of sulphur.

7.4 POST INCUBATION LEACHING OF SPHALERITE

7.4.1 General

The post incubation leaching curves of sphalerite were rather arbitrarily divided into two sections in § 7.1. In actuality, the data was tested for fit with several possible curve forms, including equation (30), which allows for surface area reduction with time, and equation (30a) for film diffusion. Neither of these equations fit the data as well as the proposed linear (section II) plus rapid decrease (section III) model. The linear fit is very good in a number of experiments, especially those that do not exhibit a section III (e.g. experiment 3, Fig. 22). In addition it is shown in the sequel that experimental rate dependencies, derived under a variety of leaching conditions, support this simple zero order kinetic model. The termination of linear leaching and the beginning of section III, after extractions of approximately 80 percent, is also supported by experimental observations (§ 7.4.9).

Two important observations can now be made with respect to post incubation leaching.

(i) The concentration of \( \text{H}_2\text{S} \) in solution, \( [\text{H}_2\text{S}]_{\text{aq}} \), is less than \( [\text{H}_2\text{S}]_E \) (Fig. 54), because chalcopyrite also dissolves during this period. This means that the rate of \( \text{H}_2\text{S} \) oxidation equals its rate of production at times exceeding \( t_E \). There is no direct evidence from the leaching experiments for the evolution of \( \text{H}_2\text{S} \) from sphalerite, but if it is an intermediate in the production of sulphur, in the same manner as in galena dissolution, its rapid oxidation rate prevents it from accumulating.

(ii) The linearity of the curves implies a rate independence of acid concentration, which declines during leaching, and iron concentration, which increases in the range 0.5 to 1.5 g l\(^{-1}\). It also implies that the rate is either independent of particulate surface or that the effective surface area does not decrease with the extent of dissolution.
The linear sections of the curves were compared by finding the coordinates of the point characterising the start of linear dissolution \((a_0, t_0)\) - Fig. 53) and making these points the origin of a new graph. The resultant plots are therefore of \(a-a_0\) versus \(t-t_0\). In practice this point was located by extrapolating sections I and II as shown by the dotted lines in Fig. 53. Because of the large time interval between data points the result is not accurate, but this is unimportant as it does not affect the subsequent analysis. The time \(t_0\) was commonly found to be slightly longer than \(t_e (\approx 30\) mins). The straight lines of best fit were calculated by the method of least squares, omitting those points which obviously fitted into Section III. No allowance was made for the change in oxygen solubility with time, due to the decrease in acid concentration, as this was at least partially offset by the increase in cation concentration (Fig. 5).

In the sequel the effects of changing experimental parameters on the rate of leaching, measured as the slope of the best fit \(a-a_0\) versus \(t-t_0\) lines, are discussed. Ferric sulphate addition is examined first because of its possible implications for all other experiments due to the varying concentration of soluble iron in each.

7.4.2 Ferric Sulphate Addition

Reference to Fig. 27 shows that the addition of 8.4 g \(l^{-1}\) Fe (10% by weight of the sulphide minerals) as ferric sulphate had two effects. The first was to decrease the length of the incubation period (see § 7.2) and the second was to increase the rate of linear leaching. This latter effect is particularly interesting because it implies that ferric ions exert a catalytic influence on sphalerite dissolution other than via the oxidation of \(H_2S\).

The influence of iron has received much attention in the literature of sphalerite leaching (§ 3.2 and § 3.6.1), because of its proven catalytic effect. However its role remains unresolved. Sherritt Gordon workers, in a series of process oriented studies [77, 98, 101, 102], attributed this effect solely to the increased oxidation rate of \(H_2S\) via the reaction sequence (50), (48) ... but they did not report the presence of \(H_2S\) in their autoclaves in any experiments. Exner et al. [70], in contrast, observed extensive evolution of \(H_2S\) in experiments with pure sphalerite. Increased rates of extraction were achieved by adding ferric ions and parallel results were observed with iron concentrates (Fig. 7). The rate increase was jointly attributed to the oxidation of \(H_2S\) via reaction (48) and to the increase in conductivity of sphalerite due to the presence of iron atoms in the crystal lattice. Their results were ambiguous however, as pointed out in § 3.2, because they found no rate increase for a marmatite concentrate. The importance of their results is twofold. Firstly, in agreement with Sherritt Gordon researchers, a minimum of 10% of Fe by weight of ZnS was required to produce significant rate increases, and secondly, they only detected \(H_2S\) in their autoclave for iron concentrates containing 2.5% Fe, or less, but observed rate increases for iron concentrations up to 14% (Fig. 7). Although this latter point was not recognised by the authors, it is significant because it is in agreement with the results portrayed in Fig. 27. Both indicate that iron acts catalytically other than via \(H_2S\) oxidation.

Scott and Dyson [61] also examined the catalytic effect of iron. Concentrations of 1.5% produced a fourfold, and 15%, a ninefold increase in the fraction of pure zinc sulphide dissolved. These results were interpreted solely on the assumption that a small fraction of iron atoms were incorporated in the surface layers of the zinc sulphide lattice thereby causing activation. The results were ambiguous because the authors reported that \(H_2S\) persisted in the autoclave for the duration of their experiments. Hence, the observed rate increases may have been attributable to \(H_2S\) oxidation and removal.

The catalytic effect of iron during post incubation leaching, and its significance to the mechanism of sphalerite dissolution, is discussed further in § 7.8.2. Its implications for practical plant design are discussed in Chapter 9.

At this point, however, it is necessary to evaluate the significance of iron concentration to the leaching experiments 1 to 22 as it increases with time in most cases.
The following observations are pertinent to this evaluation:

(i) Iron concentrations varied from approximately 0.5 to a maximum of 1.5 g l⁻¹ (between 1 and 3% of the ZnS in the ore) during the experiments. Therefore the maximum increase in iron concentration during an experiment was threefold (experiment 18 - Table 11). Only half of this increase actually occurred during the linear leaching period (Fig. 29a). For less highly reacted experiments the increase was much less than this.

(ii) The iron concentrations were similar at the beginning of most experiments because the elemental iron, which constituted an approximately constant fraction of the ore, accounted for the bulk of the iron dissolved in the first hour.

(iii) The addition of 8.4 g l⁻¹ Fe⁺⁺ in experiment 20 (26% by weight of ZnS) resulted in only a twofold increase in the rate of sphalerite dissolution, as measured from the linear slopes of the curves for experiments 18 and 20 in Fig. 29a.

The linearity of the zinc curves implies that the small increase in iron concentration during an experiment did not affect the leaching rate. This is supported by observation (iii) above, which in turn receives additional support from the observation of Exner et al. [70] that iron concentrations of less than 5% produced a minimal increase in rate.

On the basis of these observations the effects of the other experimental parameters have been examined assuming that the small differences in iron concentration between comparative experiments do not influence the reaction rates.

7.4.3 Temperature

The effect of temperature on the dissolution of sphalerite is illustrated in Fig. 22. It is apparent that the curves do not resemble the generalised curve (Fig. 53) very closely. However there is only one data point in the incubation period for each of the curves so that it is impossible to estimate the true shape in this region. It can also be seen that section III had not developed after seven hours leaching at 70, 90 and 130°C. The 130°C curve obviously represents a major change in leaching behaviour.

The 1-10 versus t₁₀ curves are shown in Fig. 56. The least square gradients of these curves were used to calculate the apparent activation energy for sphalerite dissolution by employing the Arrhenius equation (31). The graph of log rate versus 1/T is shown in Fig. 57. It gives a value of 41.3 kJ mol⁻¹ (9.9 kcal mol⁻¹) for the apparent activation energy. A range of values have been reported in the literature (Table 1) but this agrees reasonably well with those of Yaroslavstev et al. [65], 38.9 kJ mol⁻¹, Okamura [66], 47.2 kJ mol⁻¹ and Exner et al. [70], 38.7 kJ mol⁻¹. As the apparent activation energy is higher than that normally associated with a diffusion process, it suggests that the phase boundary reaction is rate controlling.

No allowance was made for the change in oxygen solubility with temperature, when calculating the above results, because Fig. 4 shows that this change is small in the temperature range examined.

The results for leaching at 130°C, which show a rapid rate for the first hour, followed by a period of very slow dissolution resulting in a maximum extraction of 16.7% (Fig. 22), agree with the observations of most authors for leaching above the melting point of sulphur. These authors contend that the reduced dissolution is caused by the buildup of a coherent layer of liquid sulphur on the sphalerite surface. An attempt was made to check the validity of this contention by examining the residue from the 130°C experiment (R4) by scanning electron microscopy. Two resultant micrographs are shown in Figs. 48 and 49. These micrographs show that the residue is strikingly different from the sub 130°C experiments. The notable features are:
Fig. 56  The effect of temperature on the linear leaching of sphalerite, chalcopyrite and pyrite.

Fig. 57  Arrhenius plot for sphalerite dissolution.
(i) The large agglomerate particles composed of a whole range of particle shapes and sizes.

(ii) The agglomerates contain a mixture of sphalerite, chalcopyrite and pyrite but no galena or 
silica (Fig. 40b).

(iii) The absence of detectable elemental sulphur in Fig. 48a.

(iv) The absence of pitting on the sphalerite surfaces exposed in the agglomerate.

The absence of visible sulphur is unlikely to be due to the small percentage present in the residue 
because R4 contains half the percentage contained in R2 and 4 times the percentage contained in R16. 
In both the latter cases it was clearly detectable (§ 6.3.4). Furthermore, an XRD scan of R4 showed 
that the sulphur was in the same (rhombic) crystalline form as in the other residues. Based on the 
weight of sulphur in R4 (3 g) and a surface area of 0.054 m g⁻¹ for the 49 µm ore fraction one can 
calculate that a coherent layer of sulphur would have a thickness of 0.3 μm. Because only approximately 
half this area is attributable to sphalerite, chalcopyrite and pyrite, which are the only minerals that 
exhibit sulphur coatings (§ 6.3), the layer would be double this thickness. Clearly if a 0.6 μm 
layer existed, it would be visible on the mineral surfaces in Fig. 48a (c.f. R2 – Fig. 43) and 
detectable by EDAX. The elemental EDX analyses of several points on an agglomerate surface, Figs. 49c, 
d and e, show that the peak ratios exhibit ratios consistent with either unleached or sulphur deficient 
minerals. This leads to the conclusion that the sulphur has not formed a coherent layer but instead 
has formed on specific crystal surfaces (c.f. Fig. 43a) which, because they are not visible, are inward 
facing in the agglomerate particles. Liquid sulphur is the binding agent which holds the agglomerates 
together. Evidence of this is provided by Fig. 48b which shows that after leaching the residue for 
twelve hours with CS₂ some of the agglomerates had broken down into component particles. The incomplete 
breakdown is presumably due to the lack of penetration of the solvent between closely bound surfaces. An 
XRD scan of CS₂ leached residue confirmed that a trace of sulphur remained.

A sequence of events which explain the above observations can now be proposed.

(i) On introduction of ore to the acid the rate of reaction is initially more rapid than at 
100°C as expected.

(ii) Sulphur forms on the crystal faces of sphalerite which show preferential dissolution (see 
 further discussion in § 7.8.2).

(iii) Due to the repeated jostling of particles as a result of agitation those with a liquid 
sulphur coated surface contact and bind together. This reduces the effective surface area 
for leaching and more importantly removes the preferred dissolution faces from further 
reaction. This explains the unattacked nature of the exposed agglomerate surfaces and why the 
reaction rate almost stops (Fig. 22).

(iv) Galena dissolves rapidly forming predominantly HgS and is unhindered because the coating 
of anglesite which builds up prevents wetting by liquid sulphur. Galena particles are 
therefore not incorporated in the agglomerates. HgS oxidation proceeds by the mechanism 
proposed in § 7.2.7 but the rate of removal is decreased by the decrease in effective surface 
area leading to longer HgS persistence in the autoclave compared to the lower temperature 
experiments (Table 9).

(v) Chalcopyrite and pyrite are wetted by sulphur and incorporated in the agglomerate. This 
sulphur does not come from the minerals themselves because they do not dissolve (Fig. 22). 
Coating without dissolution was noted in sub-melting point experiments (Figs. 44 and 45) and 
can be attributed to these surfaces catalysing the ferric ion oxidation of HgS (see § 7.8.3 
and § 7.8.4). Once the particles are incorporated in agglomerates reaction is further 
hindered.
Romankiw and de Bruyn [64] found that <111> sulphur faces were more rapidly attacked than <111> zinc faces in sphalerite and similar results have been reported for other crystals having the sphalerite structure [142]. While this supports the preferred dissolution behaviour observed in this investigation, it also may explain the results illustrated in Figs. 49d and e, which show two examples of sulphur deficient surfaces facing outermost in an agglomerate particle.

7.4.4 Oxygen Partial Pressure

The effects of oxygen partial pressure in the range 0.069 to 0.414 MPa (10 to 60 psia) on sphalerite dissolution are shown in Figs. 23a and 24. The curves more closely resemble the proposed model in Fig. 53a than those of Fig. 22. Exceptions are experiment 7 (0.414 MPa) which exhibits a very short incubation and experiment 5 (0.069 MPa) which does not exhibit a section III. The 0.276 MPa curve appears slightly anomalous having lower oc and oD values than expected. While no adequate explanation can be offered for this phenomenon it does not appear to affect the linear leaching rate. The section II portions of the curves are replotted in Fig. 58 and the least squares gradients of these lines were plotted against P02 in Fig. 59. This figure shows that the linear leaching rate is directly proportional to oxygen pressure in the range investigated. The rates for experiments 18 and 21, Fig. 24, are also plotted in Fig. 59 and, within the limits of experimental error, they exhibit the same rate dependence. The increased rate is attributable to the larger particulate specific surface of the second batch of nominally 49 μm ore.

The observed rate dependency on the first power of the oxygen pressure accords with the reported findings of Exner et al. [70] and Okamura [66] but disagrees with those of Dobroktvoov and Onuchkina [67] and Yaroslavstev et al. [65] who observed a half power dependence. The results indicate that oxygen is involved in the rate determining step for post incubation leaching.

7.4.5 Surface Area

It was pointed out in § 7.4.1 that the linearity of the leaching curves implies that the rate is either independent of surface area or that, assuming a dependency, the effective surface area does not change with extraction. The results of leaching with different initial specific surface areas are shown in Fig. 25. The close agreement between the three curves means that the weight of sphalerite dissolved is proportional to the initial surface area (weight added) because the fractions dissolved at any time are identical. This dependency on initial surface area, combined with the observed zero order reaction, implies that the effective surface area for leaching does not change in the linear region. The scanning electron micrographs of sphalerite leaching (§ 6.3) support this result. They clearly show that attack is via pit formation on specific crystal faces (e.g. Figs. 42, 43 and 44) and that this pitting action persists until only a skeleton of the original particle remains. One may therefore propose that the area of the bottom of the pits and the unattacked surface remain approximately unaltered over a wide range of extraction values. The implications of pit formation to the reaction mechanism are discussed further in § 7.8.2.

In Fig. 26 the leaching results of two experiments at an acid concentration of 0.2 mol l−1 are portrayed. The results show that rates of pre-incubation leaching are similar, indicating an initial rate dependence on surface area. The incubation period for experiment 15, however, lasts for the full term of the experiment, so that the linear rates cannot be compared.

In experiment 16 an attempt was made to evaluate the quantitative relationship between rate and surface area by employing a larger screen fraction of ore (137 μm), of known initial surface area. However H2S persisted for the full seven hours in this experiment (Fig. 27) so that post-incubation leaching was not exhibited. As pointed out in § 7.2.5, the long incubation period could only be accounted for by a dependence of H2S oxidation on surface area.
Fig. 58 The effect of oxygen partial pressure on the linear leaching of sphalerite and chalcopyrite.

Fig. 59 The linear leaching rate as a function of oxygen partial pressure for sphalerite.
7.4.6 Acid Concentration

There are two ways of examining the effect of acid concentration. The first is to keep the pulp density constant and increase the acid concentration and the second to change both the pulp density and acid concentration to maintain a constant mol ratio. The first results in a changed mol ratio and leads to stoichiometric excesses or deficiencies of acid. The second approach, which was adopted in this investigation, leads to changes in initial surface area. In view of the direct rate dependence on area established in the previous section, the gradients of $\alpha$ versus $t$ curves for changing acid concentrations may be compared directly. Such curves of the acid concentration range 0.2 to 1.2 mol $l^{-1}$ are shown in Fig. 28. These curves closely resemble the model proposed in Fig. 53a especially at low acid concentration. The difference in length of the incubation periods has been dealt with in § 7.2. A comparison of the linear slopes is possible from Fig. 60, which shows a rate increase with acid concentration. A graph of the linear slopes of these lines versus acid concentration (Fig. 61) (after adjustments to take account of the change in solubility of oxygen with concentration (Fig. 5)) suggests that this increase is linear. However the result must be regarded with some suspicion in view of the following observations.

(i) The linear sections of the curves for 0.4 mol $l^{-1}$ and 0.2 mol $l^{-1}$ (Fig. 28) are not fully developed. This leads to considerable uncertainty regarding their true slopes.

(ii) The 1.2 mol $l^{-1}$ curve cannot be treated as a quantitative result because of the very high holdup (Y) residue at the completion of leaching (42% of the total residue - Table A9). This was due to the high pulp density employed in this experiment. The simplistic assumption that the buildup of these residues was linear (§ A5.3) no doubt leads to considerable error in calculating the extraction values in this case.

(iii) The observed linearity of most leaching curves over a wide $\alpha$ range (section II) implies a lack of dependency on acid concentration which declines during the associated time period. Further evidence of a lack of dependency is provided by the mol ratio curves, Fig. 25, which demonstrate that the rate is unaffected by large excesses of acid which lead to variations in concentration between experiments 1, 12 and 14 during leaching.

Based on observation (iii), the results displayed in Figs. 28, 60 and 61 are somewhat unexpected, even taking account of the possible errors ((i) and (ii) above) and no adequate explanation of this behaviour can be offered.

7.4.7 Agitation

Reference to Fig. 30 and the resultant $\alpha$-$\omega$ plot, Fig. 62, shows that at 0.069 MPa $p_{O_2}$ and 115 g $l^{-1}$ the rate of sphalerite dissolution is independent of impeller rotation speed in the range 500 to 1000 rpm. This indicates that the transfer of dissolved oxygen to the mineral/solution interface is not rate controlling under these conditions, in agreement with the deduction from the apparent activation energy for sphalerite dissolution (§ 7.4.3). It was intended to carry out a replicate of a higher oxygen pressure, higher pulp density experiment to test the agitation dependence under higher oxygen demand conditions. This would have necessitated preparing a new batch of 49 $\mu$m ore because batches 1 and 2 had been exhausted. In view of the activation energy implication and the observed linear dependence on oxygen pressure, which indicates a direct dependence on $O_2$ dissolved, (one would expect a decrease in rate dependence with increasing pressure if there was a change to transport control) this appeared unnecessary.

It may be concluded that the high performance impeller design of Pawlek et al. [19], used in this investigation, provided adequate solid suspension and transfer under the conditions experienced. The only qualification is that at 170 g $l^{-1}$, experiment 12, the autoclave design was unsuitable for quantitative determinations because of the high holdup.
Fig. 60 The effect of acid concentration on the linear leaching of sphalerite, chalcopyrite and pyrite.

Fig. 61 The linear leaching rate of sphalerite as a function of initial acid concentration.
7.4.8 Replicate Experiments

The extraction curves for three pairs of replicate leaching experiments are shown in Fig. 31 and the linear gradients are compared by omitting the incubation sections in Fig. 63. The implications of these results to the reproducibility of experimental data are discussed in § 6.4.
7.4.9 Section III Leaching

It was noted in § 7.1 that the end of the linear leaching sections ($q_c$) fell within the extraction range of 0.7 to 0.8. There are at least two reasons why linear leaching could not continue to 100% extraction.

(i) The constancy of effective surface area for leaching must break down at high extractions (§ 7.4.5).

(ii) It was observed in § 6.2.3 - (vi) that highly reacted residues adhered to the impeller blades. This would have the effect of reducing the surface area and may even cause a change to transport control at high extractions.

7.5 POST INDUCTION LEACHING OF CHALCOPYRITE

7.5.1 General

The generalized chalcopyrite post induction dissolution curve is illustrated in Fig. 53b. It shows a short section (II) of rapid dissolution followed by a longer linear section (III) of considerably slower rate. Interpretation of the results is complicated by the shortage of data points in section II (usually only one), which makes quantitative characterisation of this section impossible, and the long incubation periods in some experiments, most notably 10 and 11 (Fig. 28).

The short section of rapid dissolution which commonly terminates at an extraction value of approximately 0.1 ($q_f$ - Fig. 53b) suggests the presence of a small percentage of a fast dissolving copper mineral in the ore. This could be chalcocite or covellite, both of which have been shown by several independent researchers [85, 143, 144] to dissolve more rapidly than chalcopyrite. The proposal is supported by the following points:

(i) Traces of chalcocite and covellite were found in Tuí ore by several geologists (§ 6.1.3).

(ii) Although neither mineral was detected by XRD (Fig. 20), only 0.2 weight percent CuS in the ore is required to account for an $q_f$ value of 0.1. This may well be below the limits of detection.

(iii) The presence of an approximately constant percentage of covellite/chalcocite in the ore satisfactorily explains the observed changes in $q_f$ with changes in experimental parameter with the exception of experiment 3 (90°C).

The $q_f$ value, which can only be rather crudely estimated, should be composed of a constant fraction due to covellite/chalcocite dissolution and a variable fraction due to chalcopyrite dissolution. Consideration of Figs. 22 and 23 shows that the slope of section III is very low in experiments 2 (70°C) and 5 (0.069 MPa). That is, the rate of chalcopyrite dissolution is low. Therefore the $q_f$ values should correspond solely to the dissolution of covellite/chalcocite. In these experiments $q_f$ is approximately 0.8 in both cases. In experiments 1 and 7 the $q_f$ values are higher by a fraction which can be attributed to the dissolution of chalcocite in the period $t_f$-$t_E$. Similar analyses can be applied to other leaching curves (e.g. Fig. 25). Two results appear anomalous, experiment 6 which has been discussed in § 7.4.4 and experiment 3 which has a very low $q_f$ value (Fig. 22). This latter result can only be ascribed to a low value of the weight percent of chalcocite/covellite in the ore batch used in this experiment. As the weight added at 0.2% would have been only 0.23 g such a variation is not unlikely, despite careful splitting of samples.

(iv) A particle of highly leached chalcocite/covellite was fortuitously (considering its low percentage) identified by EDAX during scanning electron microscope observations of leach residues (Fig. 51).
It is therefore concluded that section II of the "chalcopyrite" extraction curves is due to the dissolution of chalocite or covellite. The subsequent linear section of reduced rate then corresponds to the dissolution of chalcopyrite. The curves are therefore not strictly graphs of chalcopyrite extraction.

In the following discussion of the effects of changing experimental parameters on chalcopyrite it should be remembered that copper constituted only 1.5% of the ore and that extractions were often small. The results are therefore less accurate than those for sphalerite (§ 6.4). A comparison of the section III linear slopes was made from $\alpha$-$\eta$ versus $t$-$\eta$ graphs (Figs. 58, 60, 62) by omitting section II points when calculating the least squares line. Another important point is that nothing can be deduced from the leaching results concerning the stoichiometry of chalcopyrite dissolution (§ 7.3).

7.5.2 Ferric Sulphate Addition

The effect of adding 8.4 g l$^{-1}$ of ferric ions is depicted in Fig. 29a. Aside from a reduction in the length of the induction period which has been fully discussed in § 7.2.1 there does not appear to be any nett increase in the rate of dissolution. However this observation rests rather heavily on the validity of the $\alpha$$_{2}$ value for experiment 18 (no addition). If this point was neglected the dissolution curve would be approximately linear, as in the bulk of the other experiments, and the ferric ion addition curve (experiment 20) would then represent a twofold increase in rate. Because an analytical error was suspected, the diluted sample was reanalysed but gave the same result. The curve for experiment 18 is also depicted in Fig. 24 where it is compared to an experiment conducted at a higher oxygen partial pressure. The $\alpha$$_{5}$ and $\alpha$$_{7}$ values again appear anomalous and no logical explanation can be offered.

It may be concluded therefore that while large ferric ion additions may have a small effect on the rate of chalcopyrite dissolution, the changes in iron concentration during the experiments are small, and the resultant influence on dissolution rate is likely to be negligible. This conclusion is similar to that made for the effect of soluble iron on sphalerite leaching (§ 7.4.3).

7.5.3 Temperature

The Arrhenius plot for chalcopyrite dissolution, with linear rates taken from the $\alpha$-$\eta$ versus $t$-$\eta$ graphs, Fig. 56, is depicted in Fig. 64. It gives an activation energy of 40.0 kJ mol$^{-1}$ (9.6 kcal mol$^{-1}$) which agrees tolerably well with the values reported by Peters and Loewan [85] of 47 kJ mol$^{-1}$ and Bauer et al. [87] of 43 kJ mol$^{-1}$. While this result may be taken to indicate surface reaction control, two authors [86, 87] have reported apparent activation energies larger than this for sulphur film diffusion control (Table 3) of chalcopyrite dissolution.

![Fig. 64 Arrenhius plot for chalcopyrite dissolution.](image-url)
Consideration of Fig. 22 shows that no chalcopyrite was dissolved in the experiment at 130°C. This was attributed, in § 7.4.3, to the incorporation of chalcopyrite particles in large agglomerates as a result of surface wetting by liquid sulphur from an external source. This phenomenon is examined further in § 7.8.3 in the light of scanning electron microscope observations.

7.5.4 Oxygen Partial Pressure

The effect of oxygen partial pressure on leaching rate is illustrated in Figs. 23a and 24. This effect appears to be complex, as illustrated in Fig. 65, which shows an increase in rate in the range 0.069 MPa to 0.138 MPa, followed by a section of rate independence up to a pressure of 0.276 MPa. The rate then increases again with pressure. The similar rate of leaching for pressures of 0.138 and 0.276 MPa is rather unexpected, in view of reported dependencies (Tables 3 and 4), but is supported by the results of identical experiments performed on ore batch 2 (Fig. 24). While the results might indicate mixed rate control, for example, the mixed diffusion, surface reaction dependency reported by Yu et al. [87], there is insufficient data to begin to explore this possibility.

![Fig. 65: The linear leaching rate of chalcopyrite as a function of oxygen partial pressure.](chart)

7.5.5 Surface Area

The concordance of the extraction curves for three different initial pulp densities, illustrated in Fig. 25, implies a direct rate dependence on surface area for both chalcocite/covellite and chalcopyrite. Results for an acid deficiency of 75%, Fig. 26 and 137 µm ore, Fig. 27 show that the induction period lasted for the full leaching time in these experiments, precluding additional evidence of surface area dependence.

7.5.6 Acid Concentration

It is impossible to assess the effect of acid concentration from Fig. 28 for several reasons:
(i) There are only two data points for experiments 10 and 11 so that no section III gradient can be obtained.

(ii) The initial acid concentration has little bearing on the concentration at the beginning of chalcopyrite dissolution because the latter is dependent on the extent of sphalerite and galena dissolution.

However it may be inferred from the approximate linearity of the chalcopyrite curves for experiments exhibiting high extractions of sphalerite, galena and chalcopyrite (e.g. 0.414 MPa curve, Fig. 23a) that the rate is largely independent of acid concentration.

7.5.7 Copper Additions

The addition of 0.63 g l⁻¹ (0.01 mol l⁻¹) of cupric ions to the leachant had no effect on sphalerite dissolution (Fig. 29a). The α_Cu total curve (where Cu total includes the weight added) shows that all of the added copper was initially precipitated by HgS. This agrees with thermodynamic predictions (Appendix 8) and with the reported observations of Scott and Dyson [61], Exner et al. [70] and Hisamatsu and Masuko [73]. However, in contrast to Scott and Dyson and Hisamatsu and Masuko and in agreement with Exner et al., the precipitated copper did not exert a catalytic effect on sphalerite dissolution except by way of removing some of the reaction inhibiting HgS. The HgS removal should be reflected by a shortened incubation period for experiment 19 relative to experiment 18. That this was not exhibited (Fig. 29a) can be attributed to the greater loss of HgS through the gland in the latter case (Table 11).

After incubation the α_Cu total curve has the same form as the generalised curve in Fig. 53b. In comparison with experiment 18, however, the α value is approximately twice as large (0.28/0.14). The value of 0.28 corresponds exactly to the fraction of the total copper added as cupric sulphate. As it is expected that the same percentage of fast dissolving copper (chalcopyrite or covellite) was present in the ore added in experiments 18 and 19 this observation implies that the added copper was precipitated in approximately equal proportions as covellite/chalcopyrite and chalcopyrite.

7.6 PYRITE LEACHING

7.6.1 General

An evaluation of the effect of leaching variables on the dissolution of pyrite is complicated by the presence of five possible sources of soluble iron, three in the ore, [pyrite, chalcopyrite and sphalerite (a small iron content identified by EDAX, Fig. 35a)], one resulting from comminution [elemental iron] and one in the autoclave itself [stainless steel]. Although it is possible to estimate the contributions of chalcopyrite and corrosion to the total iron concentration in solution (§ A5.4), a curve of α_{FeS²⁻} versus time contains contributions from elemental tramp iron and sphalerite, in addition to that of pyrite.

From the general form of the "pyrite" curves it is evident that the elemental iron is completely dissolved after one hour in all experiments. The curves after one hour therefore represent contributions from pyrite and sphalerite only. The percentage of iron in the zinc lattice could not be determined. However, assuming that it is constant in each batch of ore that was leached, and taking note of the form of the sphalerite dissolution curve for each experiment, some general conclusions can be made regarding pyrite dissolution.

7.6.2 The Effect of Changing Experimental Conditions

Ferric and Cupric Ion Addition

The addition of ferric ions to the leachant resulted in the complete dissolution of pyrite within 5 hours (Fig. 29b). The subsequent decrease in the fraction dissolved was due to the precipitation of
plumbojarosite (PbO · 3Fe₂O₃ · 4SO₃ · 6H₂O). This was identified in the residue from an X-ray diffraclogram using the data of Mumm and Scott [113]. The large rate increase compared to the no catalyst addition curve suggests that pyrite dissolution may be autocatalytic providing, of course, that the rate of oxidation of ferrous ions to ferric via equation (50) is rapid. The general form of the "pyrite" curves after one hour may be interpreted as supporting this contention because the majority show a gradual non-linear increase in rate with leaching time (Fig. 53c). For example, close examination of the data points for experiment 18, in Fig. 29b reveals this trend, even though a linear curve has been drawn. The increase in rate with time cannot be ascribed to an increase in the rate of sphalerite dissolution because it often occurs during section III leaching of sphalerite.

The addition of cupric ions also resulted in an increased dissolution rate (Fig. 29b). This can be attributed to pyrite because the sphalerite curves are identical for both cupric sulphate addition and no addition (Fig. 29a).

Temperature

It is apparent from Fig. 22 that the increase in "pyrite" extraction in all experiments is very small and may be due solely to the sphalerite contribution. The rate of iron dissolution from sphalerite might be expected to be a constant fraction of the zinc dissolution rate with the fraction determined by the ratio of iron to zinc in the sphalerite lattice. If this were so the activation energy for iron dissolution should approximate the value obtained from the $a_{ZnS}$ curves of Fig. 22. Calculation of the least squares gradients of the section II portion of the curves from Fig. 56 and the use of these in an Arrhenius plot (Fig. 66) gives an apparent activation of 13.8 kJ mol⁻¹ (3.3 kcal mol⁻¹) which is only 30% of the value derived for sphalerite. This result means that the rate of iron dissolution from sphalerite does not obey the constant fraction relationship and implies that rate control may be via a diffusion mechanism. In the light of scanning electron microscope evidence this mechanism is discussed further in § 7.8.3

![Arrhenius plot for "pyrite" dissolution.](image)

Oxygen Partial Pressure

The curve shapes in Fig. 23b closely resemble the generalised model in Fig. 53c. The high value of $q_1$ for the 0.414 MPa curve is presumably partly attributable to the corresponding high value of $q_1$ for sphalerite dissolution (Fig. 23a). It is interesting to note the very low rate dependency of "pyrite"
dissolution on oxygen pressure in the range 0.069 to 0.276 MPa shown in Figs. 23b and 24. As in the
temperature curves considered above, the total dissolution in the final six hours may be attributable
solely to sphalerite dissolution for this pressure range. However, it is apparent that at 0.414 MPa
P\text{O}_2, a large fraction of pyrite has also dissolved. The sudden change in extraction rate from 0.276 to
0.414 MPa (Fig. 67) suggests that, under a given set of experimental conditions, pyrite is inert until
a given oxidation potential is exceeded. This would be expected to be higher than the other sulphides
since pyrite has been shown to be the most noble [21].

![Graph showing the linear leaching rate of pyrite as a function of oxygen partial pressure.]

**Surface Area (Figs. 25, 26, 27)**

Reference to Fig. 25 shows that in experiment 13 (0.83 MR) the pH of the leach solution increased
sufficiently for iron hydrolysis to occur after 5 hours. The similarity of curve shapes for the other
two experiments (1, 14) suggests a direct rate dependence on surface area. The difference in \( \eta \) values
only can be ascribed to a difference in the elemental iron content in the batches of added ore. Fig. 26
shows similar results, while Fig. 27 shows that for the 137 \( \mu \)m ore fraction, no iron extraction occurs
after tramp iron dissolution. As the fractions extracted in the period \( t_2-t_6 \) are not large, it is
possible that no pyrite dissolves in any of these experiments, so that the surface area dependence may be
for iron dissolution from sphalerite.

**Acid Concentration (Fig. 28)**

The 0.2 mol \( l^{-1} \) was not plotted because low extraction combined with a higher than normal corrosion
contribution introduced high errors because of the high holdup in this experiment (§ 7.4.6). The
similarity of the curves for 0.4 and 0.8 mol \( l^{-1} \) lead to the tentative conclusion that the rate is
independent of acid concentration in this range.

7.7 **Galena Leaching**

The general independence of galena conversions on experimental conditions was used in § 7.1 as
support for rate control by diffusion through a lead sulphate film on the surface. This lack of dependence
is now discussed in more detail. The relevant data is contained in Table 9 and the most important
results are displayed pictorially in Fig. 33.

**Oxygen Partial Pressure**

Reference to Fig. 33 shows that, within the limits of experimental error (see replicate results,
Table 9), the final extraction is independent of \( P_{O_2} \). This is expected from the observed (§ 7.1)
dissolution reaction (54).

\[ \text{PbS(s)} + \text{H}_2\text{SO}_4(aq) \rightarrow \text{PbSO}_4(s) + \text{H}_2\text{S(g)} \]  

...... (54)

The increase in \( \text{H}_2\text{S} \) pressure does not hinder the conversion of galena because its concentration never rises high enough to exert a back reaction effect (§ A8.3.1).

**Acid Concentration**

The observed independence of galena conversion on acid concentration (Fig. 33) suggests that the diffusion of protons is not the rate controlling step. Further evidence of rate independence is provided by the results of experiment 15 which show that despite a 75% stoichiometric deficiency of acid the conversion was identical to that of experiment 10 (no deficiency).

**Surface Area**

The independence of galena conversions on mol ratio of acid/ore means that the rate is directly proportional to surface area. This observation is supported by the results of experiments 18 and 21 in which ore batch 2 was used. The conversions are higher for experiments 18 and 21 than for the corresponding experiments 1 and 6, which employed ore batch 1. Ore batch 2 had a lower specific surface than 1. Experiment 16 also shows a lower final conversion for a lower initial surface area.

**Catalyst**

The results show that lead conversions are independent of ferric and cupric ion additions. The removal of \( \text{H}_2\text{S} \) from solution by ferric ions, while having a major effect on sphalerite dissolution, does not affect galena conversions.

**Temperature**

It was anticipated that the influence of temperature on the lead conversion rate would lead to a low apparent activation energy consistent with a diffusion mechanism. For example Exner et al. [77] reported a value of 15 kJ mol\(^{-1}\). The approximately constant conversions in the range 70-110°C were therefore unexpected. The results of experiments 8, 8a and 9, 9a can be compared directly with experiments 2 and 3 respectively because of the observed rate independence of oxygen partial pressure. This comparison supports the approximate temperature independence. The \( \alpha_7 \) conversion values cannot strictly be used for comparing reaction rates because of the parabolic nature of the leaching curves. The differences in final extractions would be less for two parabolic curves than two linear curves having the same initial slope. One must therefore conclude that the approximate constancy of conversions is indicative of a very low activation energy which supports the proposed diffusion mechanism.

At 130°C there is a marked increase in the galena converted, which suggests a change in reaction mechanism. This is discussed further in § 7.8.1. However it is pertinent to note that this result disagrees with the two previous studies of galena leaching [76, 77] both of which reported decreased extractions due to sulphur occlusion (Figs. 8 and 9).

7.8 THE MECHANISMS OF LEACHING

Although it is not possible to give a quantitative discussion of the mechanisms by which dissolution is effected for any of the minerals studied, a few qualitative comments may be made.

7.8.1 Galena

The analysis of the available experimental data (§ 7.7) suggests that the reaction of galena to form lead sulphate may be regarded as controlled by diffusion of either reacting species, or reaction
products, through a film of lead sulphate (anglesite) that forms on the surface of the galena crystals. Scanning electron micrographs of leach residues (Fig. 39a, 40, 46a, 47a) show the lead sulphate layer quite clearly, especially when compared with Figs. 46b and 47b which show similar galena particles after ammonium acetate leaching. The layer was shown to be crystalline by XRD (Fig. 21). The peaks accord with those of anglesite - X-ray diffraction card file number 5-0577.

The most notable feature of the anglesite layer is that it is not coherent, despite the fact that the molar volume of anglesite is larger than that of the substrate, galena. This observation is contrary to the rule of Pilling and Bedworth [145] which states that compact layers are expected if the ratio of molar volumes of the surface layer and the substrate is greater than one. The presence of a non-coherent, porous film suggests that diffusion takes place in the liquid phase occupying the pores. This is consistent with the low activation energy observed in this investigation, since solid phase diffusional processes commonly exhibit larger values.

The observed evolution of H₂S from galena on contact with acid and the independence of conversion rate on oxygen partial pressure (§ 7.7) suggest that reaction (54) occurs.

\[
PbS(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + H_2S(g) \quad \quad \quad \quad (54)
\]

It has been established that the H₂S so formed is subsequently oxidised to elemental sulphur but this does not occur at the anglesite/galena or the anglesite/solution boundaries (§ 6.3.2.1, § 6.3.3.5). Consequently, H₂S oxidation is not involved in the reaction sequence controlling the conversion rate. Furthermore, it was pointed out in § 7.7 that the independence of rate of acid concentration implies that neither the diffusion of protons or sulphate ions through the layer are rate controlling.

It may therefore be tentatively proposed that one or other of the following diffusion steps is controlling:

(i) The outward diffusion of HS⁻ ions formed from the reaction of a proton with a sulphur atom at the galena surface. The HS⁻ ions then react with another proton to form H₂S.

(ii) The outward diffusion of Pb²⁺ ions from the galena surface to a point where the concentration of sulphate ions is sufficient to exceed the solubility of lead sulphate, causing precipitation.

As noted above, sulphur formed from the oxidation of H₂S was not observed on the anglesite surface. This result is consistent with the observation of Sherritt Gordon workers [107] that lead sulphate did not float with the sulphur-sulphide fraction of their leach residues.

At temperatures above the melting point of sulphur the galena conversion was found to increase. This result disagrees with the observations of Exner et al. [70] and Vizsoyli et al. [77] who found decreased galena conversions which they attributed to surface occlusion by liquid sulphur. Sulphur wetting of the anglesite coating was not observed in the 130°C experiment in this investigation. However, the result is not necessarily inconsistent with those of Exner and Vizsoyli because a large fraction of sulphide minerals was present, in addition to galena. It is possible that although sulphur adheres preferentially to sulphides, it occludes lead sulphate when these are absent.

The diffusion model proposed above requires experimental quantification and it must be noted that a parabolic rate equation predicts infinite reaction rates at time zero. That is, before the film builds up. Obviously, another process is rate controlling under these conditions.

7.8.2 Sphalerite

The scanning electron micrograph depicted in Fig. 52b shows that sphalerite is attacked by cold sulphuric acid under non-oxidising conditions. The non appearance of elemental sulphur in the residue (XRD, S.E.M.) suggests that H₂S is evolved on dissolution. This is supported by the work of a number of researchers [61, 64, 70, 71]. Reference to Fig. 52b further shows that the attack takes the form of
pitting which indicates an electro-chemical mechanism, similar to the corrosion of metals, for reaction (32).

\[ \text{ZnS(s)} + 2\text{H}^+ (\text{aq}) \rightarrow \text{Zn}^{++} (\text{aq}) + \text{H}_2\text{S(g)} \]  

Although no oxidation occurs in this reaction there must be a rupture of what is essentially a covalent bond (ZnS) accompanied by the transfer of electrons to yield zinc and sulphide ions. Hence the rate may be dependent on the conductivity of the solid.

Experimental results did not definitely establish whether H_2S was an intermediate in the production of elemental sulphur during the linear leaching of sphalerite. However, if it was formed, it must have been equally rapidly oxidised, because it did not build up in solution. It was noted in § 7.2 that the presence of iron in solution was required to remove H_2S formed from the reaction of galena. This is supported by the work of Exner et al. [70] who found that pure sphalerite evolved H_2S even at high oxygen pressures. Sulphur was formed only when soluble iron was present in the autoclave. While iron catalyses the dissolution of sphalerite by removing H_2S via reaction sequence (50), (48) ..., as demonstrated in this investigation, it does not explain the increase in linear leaching rate for ferric ion addition. A similar effect of an increase in dissolution rate with iron addition, in excess of that required to oxidise H_2S, can be deduced from the results of Exner et al. (§ 7.4.2). These observations suggest that iron has a catalytic role, other than that of H_2S oxidation, during linear leaching of sphalerite. In the following discussion a tentative explanation of this role is proposed.

Consideration of the scanning electron micrographs of sphalerite particles after leaching (e.g. Fig. 37, 42a, 43a, 43b) shows that the attack takes the form of pitting on preferred crystal faces. These observations provide the first visual support for the electrochemical mechanisms of leaching proposed by Hisamatsu and Masuko [73], Habashi [72], Scott and Dyson [61] and Exner et al. [70]. These authors have suggested that the overall reaction (33) is comprised of two half cell reactions (43) and (44)

anode: \[ \text{ZnS} \rightarrow \text{Zn}^{++} + \text{S} + 2\text{e}^- \]  
cathode: \[ \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \]  
O.C.R.: \[ \text{ZnS} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow \text{Zn}^{++} + \text{S} + \text{H}_2\text{O} \]

While these reactions approximate observed stoichiometries they obviously represent an oversimplification of the actual reaction mechanism in view of the fact that sulphur is only formed when soluble iron is present in the leachant.

The marked increase in dissolution rate on the addition of ferric ions to the leachant in experiment 20 may be at least partially ascribed to the additional cathodic reaction (92) which provides another source of electrons.

\[ \text{Fe}^{+++} + \text{e}^- \rightarrow \text{Fe}^{++} \]  

The large concentration of ferric ions required to produce a twofold increase in rate suggests that this results in only a small increase in the number of adsorbed ferric ions. However, for iron to exert a catalytic role when added as ferrous sulphate, iron etc., as observed by Sherritt Gordon researchers [77, 98, 101, 102, 107] and Exner et al. [70] (Fig. 7), it must first be oxidised.

It seems reasonable that the theory of boundary layer chemisorption may be applied to the reactions of the semiconductor, sphalerite, in aqueous solutions as proposed by Exner et al. (§ 3.7, pp. 42, 43). However, in view of the fact that no sulphur was formed, when oxygen alone was used, it appears that adsorbed oxygen is not effective in accepting electrons from the semiconductor (Fig. 11b) due, perhaps, to the slow rate of bond breaking in the oxygen molecule. To explain the catalytic role of iron, Exner et al. suggested that the number of lattice defects in the sphalerite crystals were somehow increased by
the addition of iron to the solution. A similar argument had earlier been advanced by Scott and Dyson [61] but the proposal seems unlikely, since Exner et al. found no increase in rate for a marmatite concentrate. This fact is supported by the observations of Sherritt Gordon researchers that to act catalytically the iron must be soluble.

A tentative alternative mechanism which explains the catalytic role of soluble iron is now described:

Consider the chemisorption of ferrous ions on the semiconductor (sphalerite) surface in addition to oxygen molecules. The schematic representation of Fig. 11b was only described for anion chemisorption by Hauffe and Engell [116], but the effect of ferrous ion (cation) adsorption is the same, as the only requirement is that the ion (ferric) exhibits an electron affinity. The adsorption of ferrous ions can therefore be represented by equation (93), where the electron comes from the donor level of the semiconductor (Fig. 11b).

\[ \text{ZnS} + \text{Fe}^{+++} + e^- \rightarrow \text{ZnS} - \text{Fe}^{++} \quad \ldots \quad (93) \]

It is envisaged that the adsorbed ferrous ions participate in the reduction of adsorbed oxygen by donating an electron, thus being reoxidised to ferric. The process is therefore repeatable and it is for this reason that ferrous ions catalyse the rate of zinc sulphide dissolution. A schematic diagram of the mechanism is depicted in Fig. 68.

It is implicit in this mechanism that ferric ions are better electron acceptors than oxygen. Thus, both ferrous ions and oxygen are adsorbed at cathodic sites. Oxygen accepts an electron from Fe\(^{+++}\) to form Fe\(^{+++}\) which then accepts an electron from the mineral to reform Fe\(^{+++}\). The nett cathodic reaction is therefore represented by equation (44).

\[ \text{cathode} \quad \text{solution} \quad \text{cathode} \quad \text{solution} \quad \text{cathode} \quad \text{solution} \]

\[ \begin{align*}
\text{Fe}^{++} + e^- & \rightarrow \text{Fe}^{+++} \\
\text{O}_2 & \rightarrow \text{Zn}^+ \\
\text{Fe}^{++} + e^- & \rightarrow \text{Fe}^{+++} \\
\text{H}_2\text{O} & \rightarrow \text{Fe}^{++}
\end{align*} \]

(a) \quad \quad \quad \quad (h) \quad \quad \quad \quad (c)

Fig. 68: Schematic representation of the catalytic role of soluble iron in promoting the cathodic discharge of oxygen.

The observed dependence of the linear leaching rate of sphalerite on the oxygen partial pressure implies that the cathodic reaction is rate controlling. The rate also depends on iron concentration (> 5%, § 7.4.2) but is independent of acid concentration. This suggests that step (a) (Fig. 68) of the cathodic reaction is rate controlling.

The proposed mechanism has two corollaries:

(i) The decrease in sphalerite extraction for iron additions exceeding 14% observed by Exner et al. (Fig. 7) may be interpreted as the concentration at which the total number of Fe\(^{+++}\) adsorption sites are filled. However, another equally reasonable hypothesis is that the rate of dissolution had become so rapid that rate control switched from the surface reaction to oxygen transport or absorption. (All experiments depicted in Fig. 7 were conducted at the same oxygen partial pressure.)

(ii) The presence of H\(_2\)S is not required to support the catalytic role of iron as proposed by Sherritt Gordon researchers [77, 98, 101, 102, 107]. However, the observation of several
authors that a minimum of 5% iron is required for catalysis appears to be linked to the production of H$_2$S. Exner et al. [70] observed that H$_2$S appeared in their autoclave for iron concentrates containing up to this amount of iron. The implication is that a certain minimum iron concentration is required, at a given oxygen pressure, before reaction can proceed by the mechanism proposed above. At concentrations below this minimum H$_2$S is formed according to reaction (32). The results of this investigation showed that soluble iron concentrations of the order of 1% by weight of sphalerite (0.5 g l$^{-1}$) or 5% by weight of sphalerite plus galena were sufficient to oxidise the H$_2$S formed. However, in some experiments this resulted in a lengthy incubation period for sphalerite dissolution. Hence these results are not necessarily inconsistent with those of Exner et al. as their measured extractions after 1 and 2 hours leaching for ore containing 2.5% iron (Fig. 7) were still in the incubation period (H$_2$S observed).

The preferential attack on certain crystal faces of sphalerite observed in Fig. 37, for example, is supported by the experimental results of several workers [64, 71, 146] and can be predicted from atomic models of crystal faces [147, 142]. The work of Romankiw and de Bruyn [64] has already been quoted (§ 7.4.3). Their observation of the preferential leaching of sulphur bearing faces is supported by the work of McGlashan et al. [147] who have predicted this from theoretical considerations for chalcopyrite. Gatos [142] has shown from atomic models that differences in surface reactivity of III-V semiconductor compounds (e.g. InSb) can be attributed to the presence of A or B atoms at the surface, combined with their associated bond types which vary with the orientation of the face. III-V compounds have the zinc blende structure so a similar analysis can be applied to sphalerite. Gatos also graphically demonstrated the effect of crystallographic polarity by using oxidising etchants on A and B type $\langle 111 \rangle$ planes. He found that B atoms were more reactive under oxidising conditions.

The sites for initial leach attack (i.e. pit nucleation) undoubtedly occur at surface heterogeneities such as dislocations that extend into the bulk of the crystal, vacancy clusters, cleavage steps etc. An excellent discussion of etching semiconductors, dealing with pit nucleation and morphology, has been given by Faust [148].

The elemental sulphur produced during the linear leaching of sphalerite should form at the anode (equation (43)). Reference to Fig. 43a, a micrograph of a partly leached sphalerite surface, shows that sulphur appears to be concentrated on horizontal surfaces adjacent to pits. Mishra and Wadsworth [118] used scanning electron microscopy to study the residues from low temperature leaching experiments with chalcopyrite. They observed extensive sulphur coatings and concluded that the rifts in the coating were cathodic sites for the discharge of oxygen. It seems unlikely, however, that the bottom of pits should be cathodic because they represent oxygen starved regions. There is insufficient information in the scanning electron micrographs to locate the anodic and cathodic regions or to explain the location of sulphur deposits. Two important factors emerge, however:

(i) Sulphur does not form a coherent layer, so that the rate does not become transport limited.

(ii) The leaching results indicate that the effective surface area for leaching remains approximately constant for extractions up to about 80% (§ 7.4.5). As the rate controlling process is the cathodic reaction this implies that the cathode area is unaltered. Calculations, based on the boundary layer theory of chemisorption on semiconductors, show that the total number of absorption sites is limited to less than 1 percent of the total surface area [149]. It therefore seems quite possible that this condition is met.

The production of sulphate from sphalerite dissolution is not readily explained in terms of the electrochemical mechanism proposed above. It has been shown in § 7.2.7 that its production from H$_2$S is unlikely. Also Habashi and Bauer [141] have shown that the rate of production of sulphate from sulphur via reaction (61) is negligible below 120°C. This suggests that sulphate is formed directly from sphalerite according to reaction (34), in parallel with the sulphur producing reactions.
The reduced extractions of sphalerite at temperatures exceeding the melting point of sulphur (112-119°C) have been thoroughly discussed in § 7.4.3 and an explanatory sequence of events proposed.

### 7.8.3 Oxidation of Hydrogen Sulphide

The rate determining step in the oxidation of H₂S was shown in § 7.2.7 to be the oxidation of ferrous ions via reaction (50). This reaction exhibited rate dependence on P0₂, [Fe²⁺], pH and surface area. The surface area dependence implies that at least one reactant is adsorbed on a sulphide surface. The proposed mechanism for sphalerite dissolution, Fig. 68, suggests that both oxygen and ferrous ions are adsorbed and includes a ferrous oxidation step. In view of this, one can envisage the oxidation of H₂S proceeding as follows. Step (a), Fig. 68 occurs followed by step (b). However, instead of the electrons being supplied from the mineral due to the anodic oxidation of sulphide at the anode, they came from H₂S, which is thereby oxidised to sulphur. This is deposited on the surface.

Reference to Fig. 43a, which depicts a very slightly attacked sphalerite surface, shows that the volume of sulphur on the surface is considerably greater than the pit volume. It therefore appears likely that the bulk of this sulphur was deposited by iron catalysed H₂S oxidation on the surface. Similar conclusions can be made regarding the sulphur coatings on pyrite and chalcopyrite, shown in Figs. 44a and 45a respectively, as in both cases attack of the exposed surface appears to be minimal. In this regard, it is interesting to note that EDX elemental analyses of sulphur agglomerates, contained in leach residues, commonly contained traces of iron and occasionally copper (e.g. Fig. 38b). It is conceivable that sulphur formation from H₂S was seeded by fine particles of pyrite and/or chalcopyrite or that contact between a sulphur agglomerate, growing on dissolving sphalerite for example, and such fines resulted in their adhesion and occlusion.

Another important point is that sulphur was never observed to be deposited on lead sulphate coated galena or quartz particles.

### 7.8.4 Chalcopyrite and Pyrite

Scanning electron micrograph observations added no evidence to the leaching results for chalcopyrite and pyrite because the low concentrations of these minerals in the leach residues resulted in no highly reacted particles being located. It is interesting to note, however, that the apparent activation of 40.0 kJ mol⁻¹ derived from chalcopyrite, § 7.5.3, is consistent with either a diffusion or surface controlled mechanism based on the results of Bauer et al. (Table 1). In view of the observed sulphur coating (Fig. 45a) that built up largely from H₂S oxidation and the unusual oxygen dependency (§ 7.5.5), mixed rate control appears likely. The apparent activation energy for pyrite dissolution (§ 7.6) of 13.8 kJ mol⁻¹, although subject to considerable error (§ 6.4), strongly supports a sulphur film diffusion model at 0.138 MPa oxygen pressure. An interesting possibility that arises from the formation of H₂S on galena dissolution and its subsequent oxidation on chalcopyrite and pyrite surfaces is that if these minerals are present in low concentrations, they may be completely occluded by sulphur during the copper induction period.
8. SUMMARY AND CONCLUSIONS

8.1 GALENA

Sulphuric acid, oxygen pressure leaching of galena resulted in the formation of lead sulphate and hydrogen sulphide via equation (54) (§ 7.8.1). H₂S was ultimately oxidised to sulphur under suitable conditions but the concentration of H₂S in solution did not affect the galena conversion rate. The lead sulphate formed as a non-coherent crystalline (anglesite) layer on the galena surface.

The rate of reaction was independent of oxygen pressure (0.069 - 0.414 MPa), acid concentration (0.2 - 1.2 mol l⁻¹) and hydrodynamics but was directly proportional to the initial particulate surface area. A low temperature dependence was exhibited.

Leaching results and scanning electron micrographs indicated rate control by diffusion of reacting species or reaction products in the liquid filled pores of the anglesite layer. The most probable rate controlling diffusing species are Pb²⁺ or HS⁻ ions.

The form of the galena leaching curves was not evaluated, but the available data was consistent with a parabolic decrease in rate with time, probably including a correction factor for the decrease in surface area (equation 30a).

Although the rate of leaching was initially rapid, complete conversion was not attained in seven hours in any experiments. In view of the dependence of leaching time for complete conversion on the square of the initial particle radius in parabolic leaching (equation (21)), a most effective way of increasing conversions would be fine grinding.

Galena conversion was not restricted above the melting point of sulphur in contrast to the results of Exner et al. [76] and Vizsolyi et al. [77]. This was attributable to the oxidation of H₂S on the sulphide surfaces present, rather than on the lead sulphate layer.

The oxidation of H₂S took place in two steps:

\[ \text{Fe}^{2+} + \frac{1}{2} \text{O}_2 + 2 \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O} \quad \text{(slow)} \]  

\[ 2\text{Fe}^{3+} + \text{H}_2\text{S} \rightarrow 2\text{Fe}^{2+} + \text{H}_2 + \text{S}^0 \quad \text{(fast)} \]  

The slow step was the oxidation of ferrous ions (equation (20)). The rate of oxidation was dependent on [Fe²⁺], [O₂], [H⁺] and surface area. Only sulphide surfaces were active in catalysing reaction (50) which was envisaged to occur between adsorbed ferrous ions and oxygen molecules. Reaction (48), the final step, also occurred at the surface. It resulted in the deposition of sulphur on otherwise unreacted sulphide particles, especially pyrite and chalcopyrite.

The build up of H₂S in solution can be reduced by increasing the oxygen pressure or the ferrous ion concentration. However, H₂S was always formed on initial contact of the ore with acid because the evolution reaction was instantaneous, whereas the oxidation reaction takes a short time to get started. This is presumably due to the time required to establish equilibrium concentrations of adsorbed ferrous and oxygen ions on the sulphide surface.

Although H₂S and subsequently sulphur were the predominant sulphur reaction products some sulphate was also formed. As H₂S and S were shown to be unlikely intermediates in the production of sulphate (§ 7.2.7, § 7.8.2), it was envisaged to occur via reaction (56), parallel to reaction (54), but at a slower rate.
PbS(s) + 2O2(aq) + PbSO₄(s)  

8.2 SPHALERITE

Sphalerite dissolution was curtailed by the production of H₂S leading to incubation periods of low extraction. Reaction proceeded unrestricted only after H₂S had been almost completely oxidised. The rate of dissolution was then consistent with a zero order reaction up to extractions of approximately 80 percent.

The linear dissolution rate was proportional to oxygen partial pressure and initial surface area but was independent of hydrodynamics and excess or deficiency of acid. The apparent activation energy for dissolution was 41.3 kJ mol⁻¹. Leaching results supported a rate dependency on the phase boundary reaction.

The zero order reaction indicated an independence of acid concentration but experiments at different initial acid concentrations suggested some dependence. This question remains unresolved.

The overall stoichiometry of the leaching reaction was consistent with equation (33).

\[ \text{ZnS(s)} + \frac{3}{2} \text{O}_2(aq) + 2\text{H}^+(aq) + \text{ZnS(s)} + 5\text{O}_2(s) + \text{H}_2\text{O} \]  

This reaction is electrochemical in nature and can be represented by two half cell reactions (43) and (44).

**anode:** \[ \text{ZnS} \rightarrow \text{Zn}^{4+} + \text{S}^0 + 2e^- \]  

**cathode:** \[ \frac{3}{2} \text{O}_2 + 2e^+ + 2\text{H}^+ \rightarrow \text{H}_2\text{O} \]

The cathodic reaction was rate controlling under the experimental conditions investigated and the cathodic area remained approximately constant during linear leaching. However, equation (44) is a simplification in view of the rate dependence on iron concentration. The catalytic role of iron can be attributed to the boundary layer chemisorption of both ferrous ions and oxygen on the semiconductor (sphalerite) surface (§ 7.8.2).

Certain crystal faces were attacked more readily than others. Attack resulted in extensive pit formation. Nucleation can be attributed to surface heterogeneities such as dislocations and vacancy clusters.

Some sulphate was also produced on sphalerite dissolution but this amounted to less than 10 percent of the reacted sulphide sulphur. As pointed out in § 8.1 this was unlikely to be produced via sulphur or H₂S as intermediates.

The small percentages of iron present in the sphalerite lattice, (< 3%) where it isomorphically replaces zinc atoms, is considered to be liberated only by the dissolution of zinc and is therefore ineffective in promoting sphalerite dissolution.

At temperatures above the melting point of sulphur (112 → 119°C) sphalerite dissolution was severely curtailed. This was due to the formation of liquid sulphur film on the reactive faces which caused the particles to adhere. Agglomerate particles resulted, with unreactive surfaces facing outermost. Thus, the surface area for leaching was reduced and the reactive surfaces occluded. The sulphur film was not coherent as proposed by previous researchers.

The sulphur produced at temperatures below its melting point took the form of loosely bound, porous agglomerates and did not restrict sphalerite dissolution.

For extractions over 80 percent the dissolution rate decreased rapidly, due to agglomeration of reaction residues and to decrease in the cathodic area.
8.3 CHALCOPYRITE

Chalcopyrite did not dissolve when H₂S was present in solution. This led to long induction periods in some experiments. The oxidation rate of chalcopyrite was considerably lower than that of sphalerite but it exhibited a similar activation energy (40.0 kJ mol⁻¹).

The dissolution rate showed a complex dependency on oxygen pressure in the range 0.069 ± 0.414 MPa, but was directly proportional to surface area.

The oxidation of H₂S by ferric ions was catalysed by the chalcopyrite surface and extensive coatings of sulphur built up during the induction period when no chalcopyrite dissolved.

Rate control was probably a mixture of surface reaction and diffusion through the sulphur layer, as proposed by Bauer et al. [87].

8.4 PYRITE

Pyrite was practically inert under most leaching conditions. Exceptions were two experiments in which a high oxidation potential was achieved, the first by employing an oxygen pressure of 0.414 MPa and the second, a high concentration of ferric ions. This result may be interpreted as indicating that a certain oxidation potential must be exceeded before pyrite dissolves appreciably.

Like chalcopyrite, pyrite also catalysed the oxidation of H₂S resulting in extensive sulphur coatings.

The leaching results indicated that the dissolution of pyrite may be autocatalytic.

The activation energy derived at 0.138 MPa pO₂ of 13.8 kJ mol⁻¹ is indicative of a diffusion controlled dissolution mechanism.

8.5 GENERAL CONCLUSIONS

This investigation succeeded in its aim of establishing a pressure leaching facility and in providing data for a specific ore. The effect of the major kinetic parameters on the leaching rate of sphalerite, galena, chalcopyrite and pyrite, in a bulk concentrate, have been established under operating conditions that have process implications. This may be compared to previous kinetic investigations which have almost exclusively used pure minerals well outside a practical operating range. In addition, the first visual evidence of the nature of leach attack on sphalerite and of lead sulphate formation on galena has been recorded. A contribution has also been made in elucidating the oxidation mechanisms of hydrogen sulphide and sphalerite and the leaching behaviour of sulphides above the melting point of sulphur. Several practical implications have been recorded in Chapter 9 and suggestions for further research in Chapter 10.
9. PRACTICAL IMPLICATIONS

The following are some implications which may be drawn from this investigation with regard to the possible process application of sulphuric acid, oxygen pressure leaching to bulk sulphide ores.

(i) Eighty percent sphalerite dissolution was effected in three hours at 110°C and 0.4 MPa oxygen partial pressure using nominally 49 μm (-270 +325 mesh) ore. Because of the parabolic nature of galena leaching however, similar dissolutions would take considerably longer for the same sized particles. Fortuitously, galena is a softer mineral than sphalerite and this fact combined with its high density results in galena having a higher specific surface area than sphalerite after normal closed circuit grinding. It is therefore probable that preparation of a minus 270 mesh screen fraction for ore flotation would result in the subsequent reaction of galena in a similar time period to sphalerite.

(ii) The decrease in sphalerite leaching rate after 80 percent extraction results in long times for complete dissolution. The use of excess ore as suggested by Sherritt Gordon [102] and recycling of the unreacted fraction after flotation would reduce the time required to reach process concentrations as complete extraction would no longer be necessary.

(iii) It was observed that the sphalerite dissolution rate was increased by high concentrations of iron in solution. This had the twofold effect of catalysing the H2S oxidation reaction and the sphalerite dissolution reaction. In practice it would be logical to take advantage of this catalytic effect by supporting a reasonably high iron concentration in the leachant. The increased rate of dissolution achieved by increasing the oxygen pressure would have to be balanced against the increased cost of autoclave construction and gas compression.

(iv) Operating temperatures above the melting point of sulphur are impractical because of the sulphur occlusion of reactive sphalerite faces and the incorporation of sulphide particles into large agglomerates. This general observation is supported by most other research (§ 3.8). The observation by Veltman and O’Kane [102] that use of excess ore circumvents this effect is not explained by the results of this investigation.

(v) In a practical operation ore would be added to warm acid or recycle electrolyte in a premix tank before pumping to the autoclave. Under these conditions difficulty may be anticipated with H2S evolution. This could be minimized by ensuring that soluble iron was available in the ore or recycle leachant and by oxygenating the tank. Scott [109] did not report difficulties in this respect but the ore he used contained only a small proportion of galena.

(vi) The precipitation of lead as jarosite was observed in this investigation at high pH's in accordance with the results of Scott [109] and Vizayli et al. [77]. The problem of requiring a reasonably low pH at the completion of leaching to avoid jarosite formation and a high pH to eliminate soluble iron from the circuit by hydrolysis and to avoid wastage of acid due to subsequent neutralisation was not solved by either of these authors. However the observation in this investigation that the conversion rate of galena was virtually independent of process conditions provides one possible method of overcoming this dilemma. It would seem practicable to preleach the galena in the bulk concentrate with excess acid (to avoid jarosite formation) at low temperatures and pressures. At the completion of galena conversion the residue could be separated into a sulphate and sulphide fraction by flotation. The sulphide fraction containing largely unreacted sphalerite, chalcopyrite and pyrite would be
charged to an autoclave operating at higher temperatures and pressures under acid deficient conditions (excess ore - see paragraph (ii)). The formation of jarosite in the preleach reactor and subsequent flotation step would be avoided by maintaining a low pH. Furthermore, if pyrite was the only source of soluble iron, its concentration at the completion of preleaching would be extremely low because of the unreactivity of pyrite under these conditions. H2S would undoubtedly be evolved during preleaching but elemental sulphur could be recovered from this gas by introducing it to the penultimate stage of the sphalerite autoclave where a combination of high soluble iron concentrations and dissolved oxygen would be effective in oxidising it.

(vii) The same effect of preferential galena reaction could be achieved by leaching at temperatures in excess of the melting point of sulphur because it is the only mineral not occluded under these conditions (§ 7.7). However, because of the low temperature dependence of galena conversion there would be little kinetic advantage over a low temperature operation. Furthermore, regrinding of the sulphide agglomerates would probably be necessary before subsequent sphalerite leaching at a lower temperature.

(viii) Pyrite and chalcopyrite dissolve at a much slower rate than sphalerite and considering their low concentration in the ore it would probably be uneconomic to operate the autoclave at higher oxygen pressures for the sole purpose of recovering copper. The recycling of excess unreacted concentrate (paragraph (ii)) would then result in the buildup of chalcopyrite and pyrite in the autoclave feed. However, use might be made of the results of research reported by Warren et al. [93] who found that chalcopyrite could be activated by heating with elemental sulphur at just above its boiling point. In view of the fact that the elemental sulphur produced in the autoclave would float with the unreacted sulphide fraction, the processes of separating sulphur from the minerals by distillation and chalcopyrite activation could be combined. After this treatment the sulphide fraction would be returned to the autoclave and rapid dissolution of copper should result. This process does not preclude the possibility of pyrite buildup in the circuit although high pyrite extractions were observed in one experiment when ferric sulphate was added. It might therefore be expected that as the soluble iron concentration in solution increases, the rate of dissolution of pyrite would increase. In the event of pyrite buildup it may be necessary to occasionally bleed-off a part of the unreacted recycle fraction with consequent small losses of zinc and copper.

(ix) In agreement with previously published leaching results, high yields of elemental sulphur are possible by suitable choice of operating conditions. The production of sulphate is favoured at temperatures exceeding the melting point of sulphur and by low acid concentrations.
10. SUGGESTIONS FOR FURTHER WORK

As pointed out in § 8.5 this investigation was successful in its primary aim of establishing a leaching facility and in providing a good deal of kinetic and mechanistic information. It has also pinpointed a number of areas that require further research. Some of these are listed below.

1. The leaching of galena needs further investigation to quantify the time dependence of galena conversion rate. In view of the established rate dependency on surface area and temperature only, the experiments can be limited to changes in these variables.

2. Leaching experiments with uniformly sized particles would permit an absolute rate expression, including the surface area dependency, to be established. This would also enable the rates of sphalerite, galena, chalcopyrite and pyrite dissolution to be compared on a standard basis.

3. Leaching experiments at various initial acid concentrations for extended time periods would unequivocally establish whether or not the leaching of sphalerite is affected by this variable.

4. Leaching experiments with varying additions of soluble iron would allow the evaluation of the quantitative effect of this parameter on the leaching rate.

5. In view of the low galena conversion rate dependence on temperature, an investigation of the low temperature, low pressure leaching of galena is required to establish the practicality of pre-leaching under these conditions (see § 9 - paragraph (vi)).

6. The use of scanning electron microscopy to assist in understanding leaching behaviour could be extended to the investigation of the leaching of single crystals of pure minerals. These could be examined after different treatments and after the same treatment for different lengths of time. This would allow the form of attack and the formation of products (e.g. anglesite) to be evaluated in some detail. Some of the questions which require answers are:

   (i) Which crystal faces are preferred in sphalerite dissolution?
   (ii) How and where does the elemental sulphur form? (Studied free from the interference of sulphur deposited from H₂S oxidation.)
   (iii) How does the anglesite layer buildup on galena? An investigation of various growth conditions may lead to differences in the structure of the layer and in particular to a larger pore area which may be expected to lead to more rapid leaching.
   (vi) What are the sites for initial attack and can the number of these be increased by ore pretreatment (e.g. grinding)?

7. The leaching of chalcopyrite and pyrite requires further investigation with an ore or concentrate containing a higher proportion of these minerals to enable their reaction stoichiometries to be established. In particular the activation of chalcopyrite during sulphur distillation from leach residues needs to be investigated to establish its practicality (see paragraph (viii), § 9).

8. The mechanism of sulphate formation from sulphide minerals is still unknown. Leaching experiments under conditions that promote sulphate formation, such as low acid concentration, may lead to the evaluation of the rate controlling parameters for this reaction.

9. A similar investigation could be conducted on other Hauraki sulphide ores.
APPENDICES
APPENDIX I  ADDITIONAL THEORY

A1.1 AN EQUATION RELATING $\alpha$ AND $t$ ASSUMING A DIRECT RATE DEPENDENCE ON SURFACE AREA (FOR A SPHERICAL PARTICLE)

The incremental decrease in mass associated with an incremental change in particle diameter is given by

$$ -dm = d \left( \frac{4}{3} \pi r^3 \gamma \right) $$

i.e.

$$ - dm = 4 \pi r^2 \gamma dr $$

but from equation (22)

$$ dm = k 4 \pi r^2 dt $$

combining equations (23) and (24) we have

$$ \frac{dr}{dt} = \frac{k}{\gamma} = \text{constant} $$

i.e. the interface is moving at a constant velocity.

Integrating equation (25) assuming the boundary condition $r = r_0$ when $t = 0$ we get

$$ r = r_0 - \left( \frac{k}{\gamma} \right) t $$

and the time taken for complete dissolution $t_0$ is given by $r = 0$

$$ \therefore \quad t_0 = \left( \frac{\gamma}{k} \right) r_0 $$

Let $\alpha$ be the fraction reacted at time $t$. Then,

$$ \alpha = \frac{V_0 - V}{V_0} = 1 - \frac{V}{V_0} = 1 - \frac{r^3}{r_0^3} $$

rearranging

$$ \frac{r^3}{r_0^3} = 1 - \alpha $$

$$ r = r_0 (1 - \alpha)^{\frac{1}{3}} $$

$$ \therefore \quad r_0 - r = r_0 - r_0 (1 - \alpha)^{\frac{1}{3}} $$

$$ = r_0 [1 - (1 - \alpha)^{\frac{1}{3}} ] $$

but from equation (26)

$$ r_0 - r = \left( \frac{k}{\gamma} \right) t $$
An analogous equation can be derived for the parabolic leaching case (equation (20)) to take account of the surface area decrease with time.

\[ 1 - (1 - \alpha)^{3/2} = \left( \frac{k}{\gamma r_0^2} \right) t \]  

...... (30)

viz:

\[ 1 - (1 - \alpha)^{3/2} = \left( \frac{2k}{\gamma r_0^2} \right)^{1/2} t^{1/2} \]  

...... (30a)

The time taken for total dissolution (\( \alpha = 1 \)) is given by equation (21a).

\[ t_f = \left( \frac{1}{2k} \right) r_0^2 \]  

...... (21a)

which is analogous to equation (21).
APPENDIX 2  EQUIPMENT CALIBRATIONS

A2.1 THE OXYGEN RESERVOIR

A N.Z.I.G. 24 S.C.F. oxygen cylinder was used as a supply reservoir for the autoclave. The volume of oxygen in the reservoir was recorded as a function of pressure by slowly discharging through an Alexander Wright & Co. wet gas meter. The results are contained in the following Table.

<table>
<thead>
<tr>
<th>Reservoir Pressure (psig)</th>
<th>Volume Discharged (l) S.T.P.</th>
<th>Increment</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>3.738</td>
<td>16.216</td>
</tr>
<tr>
<td>450</td>
<td>19.954</td>
<td>16.002</td>
</tr>
<tr>
<td>400</td>
<td>35.956</td>
<td>16.873</td>
</tr>
<tr>
<td>350</td>
<td>52.829</td>
<td>16.834</td>
</tr>
<tr>
<td>300</td>
<td>69.663</td>
<td>16.933</td>
</tr>
<tr>
<td>250</td>
<td>86.596</td>
<td>17.120</td>
</tr>
<tr>
<td>200</td>
<td>103.716</td>
<td>16.947</td>
</tr>
<tr>
<td>150</td>
<td>120.663</td>
<td>16.973</td>
</tr>
<tr>
<td>100</td>
<td>137.636</td>
<td>16.584</td>
</tr>
<tr>
<td>50</td>
<td>154.220</td>
<td>15.398</td>
</tr>
<tr>
<td>0</td>
<td>170.618</td>
<td></td>
</tr>
</tbody>
</table>

Table A1: Oxygen reservoir calibration

Volume stored at 500 psig = 166.880 l (S.T.P.)
Volume discharged/psi pressure drop = 0.3338 l (S.T.P.)
APPENDIX 3  AUTOCLAVE OPERATING INSTRUCTIONS

A3.1 START-UP

1. Select the value of the following variables before commencement of an experiment: ore particle size, pulp density, acid concentration and acid/ore molar ratio. Only two of the last three are independent.

2. Withdraw approximately the desired weight of charge from the bulk supply of sized and assayed ore using a laboratory splitter to obtain a representative sample.

3. Dry the ore for one hour at 100°C in an oven, allow to cool in a dessicator and then weigh out the desired amount. Load into the sample introducer.

4. Screw the sample introducer into the autoclave lid and lock the piston assembly in place by tightening the Keelring coupling on the ½ in. shaft.

5. Withdraw one litre of acid from the bulk supply and discharge this into the glass liner.

6. Place the liner in the autoclave body, place the loose fitting "O-ring" on top of the liner and place the vessel sealing "O-ring" on top of the autoclave body.

7. Check all valves (Fig. 18) and ensure that they are closed.

8. Seal the autoclave by screwing the vessel into the lid, plug in the heaters, open valve W (which supplies water to the gland heat exchanger) and start the agitator motor.

9. Fill the oxygen reservoir to a pressure of 3.5 MPa from the large oxygen cylinder by opening valves F, G and H. When filled, close valves F and H.

10. Purge the autoclave of air by opening valve A, setting the pressure regulator J to about 0.07 MPa and then opening valve E which is used to regulate the flow through the system. Discharge 80 litres (20 autoclave volumes) through the vessel at a rate of about 160 litres/hour.

11. When purging is complete, close valves A and E and recharge the reservoir to 3.5 MPa as under paragraph 9 above.

12. Reopen valve A and reset the pressure regulator J to a nominal positive value, say 0.01 MPa. Open valve E and close again when the autoclave gauge registers this pressure.

13. Activate the temperature recorder and calibrate with a Tinsley potentiometer. Start heating by switching both elements full on. Use a predetermined switching arrangement to reach the desired operating temperature without overshoot (the vessel is not provided with cooling facilities). Establish the correct thermostat setting for the lower element so that heat losses are just balanced.

14. Read the barometric pressure. Obtain the partial pressure of the dilute acid solution at the operating temperature (equivalent to that of water - § A5.1) from steam tables. Calculate the required autoclave gauge pressure by adding the desired oxygen partial pressure to the water partial pressure and subtracting the barometric pressure. Set the total autoclave pressure to this value by charging oxygen to the autoclave. Venting, which may be necessary to release the pressure buildup on heating, is minimised by starting with a nominal pressure in the autoclave when heating is begun (paragraph 12).

15. Adjust the pressure regulator J to the desired total pressure. Leave valve A fully open during the course of the experiment.

16. Check all couplings and the gland for leakage at the operating pressure. Tighten the gland nut if necessary.

17. When the autoclave is equilibrated at the operating conditions, introduce the ore sample (§ 4.9). This is time zero. Mark the recording charts to this effect.

18. Record the following values: the oxygen reservoir pressure, the solution temperature (check the recorded value with the Tinsley potentiometer) and the autoclave gauge pressure.
19. Record the same values at intervals during the seven hour experimental run. Make any minor adjustments to the thermostat setting to compensate for heat of reaction (rarely necessary) and changes in ambient temperature.

A3.2 LIQUID SAMPLING

1. Take solution samples after 1, 2, 3, 5 and 7 hours by opening valve D and collecting the liquid which is forced out by the internal pressure of the autoclave.

2. Collect the first 9 ml in a 10 ml measuring cylinder and discard as the sample line clearance volume. Collect a further 6 ml in a calibrated test tube and cork immediately to minimise concentration by evaporation of the still warm solution.

3. When the sample has cooled to room temperature begin analysis by smelling the solution to detect whether HgS is present. Prepare dilutions for atomic absorption determinations.

4. Record the volume of the samples and clearance solutions together with the barometric pressure, reservoir pressure, autoclave pressure and solution temperature at the time of sampling.

A3.3 SHUT-DOWN

1. After collecting the final solution sample switch the heaters and agitator motor off. By stopping the impeller the amount of reaction which occurs while the autoclave is opened is reduced.

2. Vent the autoclave slowly by opening valve E.

3. When atmospheric pressure is attained, unplug the heaters, unscrew the vessel from the lid, lower the rotating table, lift out the liner using asbestos gloves and filter directly on a Whatman No.1 24 cm filter circle in a fume cupboard.

4. Wash down the residue that is held up on the horizontal surfaces of the impeller with distilled water and filter on the same paper. Call this combined residue X.

5. Wash down the residue adhering to the baffles and agitator shaft above the solution level. Filter this separately and label this residue Y.

6. Unscrew and remove the sample introducer. Wash out any ore remaining in it, filter separately and label Z.

7. Wash the residues thoroughly by passing several litres of distilled water through the filter beds. Collect all the filtrates and wash water together and evaporate back to one litre by heating in 3 litre pyrex beakers on hot plates. When this has cooled make up to one litre in a volumetric flask.

8. Remove the teflon sample tube by unscrewing from the autoclave lid and flush the sampling line and tube with tap water, followed by distilled water. This procedure prevents acid from lying in the line between runs. Clean down the autoclave lid, internals and liner.

9. Make general observations on the final appearance of the ore and solution.
A4.1 ORE ANALYSIS

A4.1.1 Sample Preparation

Grind and size ore in the manner described in § 5.1.1. Withdraw representative $\frac{1}{4}$ g samples from the total amount of ore in each size range using a laboratory splitter. Transfer these samples to 100 ml pyrex beakers and heat for one hour at 100°C to remove any trace of moisture. Allow to cool in a dessicator. Accurately weigh out 0.5000 g of the dry ore.

A4.1.2 Sample Decomposition

Transfer the weighed sample to a clean zirconium crucible. Add 1 g of sodium peroxide and 1 g of sodium carbonate and mix intimately with the ore using a platinum rod. Brush any particles adhering to the rod back into the crucible and cover the charge with a 3 g layer of sodium peroxide. Place a zirconium lid on the crucible and heat over a bunsen for 5 mins or until the whole mass has fused. Allow to cool and then place the crucible on its side in a 400 ml polypropylene beaker (glass should be avoided when silica determinations are being made). Place the lid beside the crucible in the beaker, cover with a watchglass and then carefully pour down the side of the beaker just sufficient distilled water to cover the sinter. When the reaction has ceased remove the crucible and lid, washing carefully. Allow the solution to cool and add slowly about twice the amount of concentrated HCl required to just neutralize the solution (about 20 ml). Record this amount. When cooled, make up the now clear solution to 1 litre in a volumetric flask. Use this directly for determination of Fe, Cu and Pb by atomic absorption spectrometry (A.A.S.) and with dilution for the determination of zinc by the same method.

A4.1.3 Iron, Copper and Lead Determinations Using A.A.S.

The weight % iron in the ore lies in the range 2 to 6%. Therefore the solution obtained from the fusion contains 10 to 30 ppm Fe. Determine this using the iron resonance line at a wavelength of 248.3 nm which gives a full scale deflection of $\pm 25$ ppm on the Techtron AA5 instrument [150]. The weight % copper in the ore lies in the range 1 to 3% and the solution obtained from the fusion therefore contains 5 to 15 ppm Cu. Determine this using the copper resonance line at 324.8 nm which gives a full scale deflection of $\pm 15$ ppm. The weight % lead in the ore lies in the range 10 to 30% and the fusion solution therefore contains 50 to 150 ppm Pb. Determine this using the lead resonance line at 283.3 nm in conjunction with a short burner which gives a full scale deflection $\pm 150$ ppm.

A4.1.4 Zinc Determination Using A.A.S.

The weight % zinc in the ore lies in the range 20 to 40% and the fusion solution therefore contains 100 to 200 ppm Zn. Dilute this solution 100 times (i.e. make up a 10 ml aliquot of solution to 1000 mls in a volumetric flask) putting the zinc concentration in the range 1 to 2 ppm. Use the sensitive zinc resonance line at 213.8 nm, which has a full scale deflection of $\pm 2$ ppm, to determine zinc concentrations.

A4.1.5 Standard Solution Requirements for A.A.S. Determinations

Before determining the concentration of an unknown solution using A.A.S. it is first necessary to establish a calibration curve using solutions of known concentration that span the concentration range under investigation. Accordingly standard solutions containing the following cation concentrations are required:
Fe: 10, 20, 30 ppm
Cu: 5, 10, 15 ppm
Pb: 50, 100, 150 ppm
Zn: 1, 1.5, 2 ppm

Method: Use these standards to determine the approximate analysis of the ore and then prepare standards in a narrow concentration band spanning the approximate analysis just derived. For example, if the approximate iron analysis is 22.3 ppm prepare fresh standards containing 20 and 25 ppm. By closely hemming in the unknown value, a greater degree of accuracy is attained.

There are a number of interferences possible in A.A.S determinations especially when large concentrations of ions other than those being determined are present. To avoid errors due to such interference, the matrix of the standards should be matched to the matrix of the samples. For example, the solution obtained from the peroxide fusion containing 500 ppm ore also contains 7,500 ppm NaCl and 2,650 ppm HCl. Assuming the 500 ppm ore is made up of 150 ppm Zn, 150 ppm Pb, 10 ppm Cu and 20 ppm Fe, the Fe standards (10, 20, 30 ppm) should contain: 10 ppm Cu, 150 ppm Pb, 150 ppm Zn, 2650 ppm HCl and 7500 ppm NaCl. In practice interference from Fe, Cu, Pb, Zn is negligible so prepare matrix matched standards containing the desired concentration of cation plus NaCl and HCl only.

A4.1.6 Preparation of Standard Solutions

The concentrations of very dilute ionic solutions tend to change with time of storage, the magnitude of the change being dependent on the nature of the storage vessel, conditions of storage etc. To avoid having to remake standards at regular intervals, prepare concentrated standards and store these in 500 ml polyethylene bottles with narrow necks. Prepare fresh A.A.S. standards every month from these stock solutions by dilution with matrix corrected solutions.

(i) Zinc Standards. Prepare 200 and 150 ppm solutions by dissolving 0.2000 g and 0.1500 g of 99.95% Zn in dilute HCl and making up to 1 litre with distilled water. Store these solutions in polyethylene bottles. Prepare 2.0 and 1.5 ppm standards by pipetting 10 ml aliquots of the 200 and 150 ppm solutions into 1 litre flasks and making up with a stock solution containing 75 ppm NaCl and 26.5 ppm HCl. Prepare 1.0 ppm standard by taking a 5 ml aliquot of 200 ppm Zn solution and diluting to 1 litre with stock 75 ppm NaCl, 26.5 ppm HCl solution. Prepare 0.5 ppm standard by taking a 5 ml aliquot of 200 ppm Zn solution and diluting to 2 litres with stock 75 ppm NaCl, 26.5 ppm HCl solution. Store all standards in 100 ml polyethylene bottles.

(ii) Copper Standards. Prepare 1500 and 1000 ppm solutions of copper in the following manner. Dissolve 1.5000 and 1.0000 g of 99.999% Cu in concentrated nitric acid. Evaporate to dryness and take up with 10 mls of concentrated HCl. Make up to 1 litre with distilled water and store. Prepare 15 and 10 ppm matrix matched standards by taking 10 ml aliquots of each solution and diluting to 1 litre with a stock solution containing 7,500 ppm NaCl and 2,600 ppm HCl. Prepare 5 ppm standard by taking a 5 ml aliquot of 1,000 ppm solution and diluting to 1 litre with stock NaCl, HCl solution.

(iii) Iron Standards. Prepare 1000 and 600 ppm solutions of iron by dissolving 1.0000 and 0.6000 g of 99.999% iron in 10 mls of concentrated HCl. Prepare 30, 20 and 10 ppm solutions by dilution with the stock NaCl, HCl solution of paragraph (ii) above.

(iv) Lead Standards. Prepare 1500 and 1000 ppm Lead solutions by dissolving 1.5000 and 1.0000 g of 99.98% lead in 1:4 nitric acid. Evaporate to dryness and reheat with dilute HCl. Take to dryness again and dissolve in excess distilled water. Prepare 150, 100 and 50 ppm matrix matched standards by dilution with the stock NaCl, HCl solution of paragraph (iii) above.
A4.1.7 Total Sulphur Determination

Take a 200 ml aliquot of the \( \frac{1}{4} \) g 1⁻¹ solution prepared in § A4.1.2. Place in a 400 ml pyrex beaker, cover with a watch glass and bring to the boil on a hotplate. Take off the boil and add 3 mls of 10% barium chloride solution dropwise. Test the clear solution for further precipitation. If none, leave to settle overnight. Then decant the clear solution and filter the barium sulphate residue on a 12.5 cm Whatman 42 "ashless" filter paper. Wash the residue several times with water since crystals of sodium chloride may be left behind. Then decant and filtrate for further precipitation with barium chloride after heating the solutions. If there is, discard the determination and start again. If there is no precipitate, take the filter paper and residue and ignite to constant weight in a platinum crucible. Then,

\[
\text{Weight \% S in the ore} = \frac{\text{g BaSO}_4 \times 137.3}{100}
\]

A4.1.8 Silica Determination

Proceed as in § 4.1.2 to the point where water is added to the sinter. Add excess concentrated HCl. If silica is still soluble, (a large excess of HCl will precipitate PbCl\(_2\)) evaporate the solution to dryness on a water bath. Keep at 100°C for approximately two hours to dehydrate the silica completely. Take up the residue in 25 to 30 ml of 20% HCl and excess ammonium acetate solution by heating on a water bath. When the precipitate has dissolved add 50 mls of distilled water, allow the solution to cool and to filter the silica on a Whatman 42 paper. Ignite to constant weight in a platinum crucible. If the silica appears impure, fume off with hydrofluoric acid and weigh by difference.

A4.2 RESIDUE ANALYSIS

The residue is the solid product resulting from the sulphuric acid pressure leaching of the ground ore analysed in § A4.1 above. The residue therefore contains unreacted sulphides, elemental sulphur, lead sulphate and if the final acidity of the leach solution is low, hydrolysis products of iron, which may also contain lead and copper as jarosites. Analyse the residue for Zn, Pb, Cu, Fe and S totals, PbSO\(_4\), elemental S and SiO\(_2\). (Jarosites were found in one experiment only and quantitative determination was not attempted.)

A4.2.1 Sample Preparation

Prepare dried residues X and Y as detailed in Appendix 3. Take each residue in turn and mix thoroughly with a pestle and mortar being careful to break up any lumps. Prepare 0.5000, 1.000 and 10.000 g samples by using a laboratory splitter.

A4.2.2 Elemental Sulphur Determination

Transfer the 10 g sample to a soxhlet thimble. If the total residue weight does not allow such a large sample use the maximum weight available. Accurately weigh the dried soxhlet flask and charge with carbon disulphide in a fume cupboard. Assemble the apparatus and leach for twelve hours on a water bath. Determine the weight of elemental sulphur by evaporating the solvent at the end of this period and reweighing the flask. If the purity of the sulphur is suspect, oxidise it to sulphate with bromine and determine gravimetrically as barium sulphate (see § A4.1.7).

A4.2.3 Lead Sulphate Determination

Transfer the 1 g sample to a 200 ml beaker and add 40 mls of 25% ammonium acetate. Cover with a watch glass and simmer at boiling point for 30 mins on a hot plate. Allow to cool a little but filter warm on a Whatman No. 4 paper. Wash the residue with about 400 mls of hot distilled water adding about
20 mls at a time. Allow the filtrate to cool overnight and make up next day to 1 litre in a volumetric flask. Determine the lead directly in an aliquot of this solution by A.A.S. The solution contains 1 g l\(^{-1}\) of residue which in turn contains between 5 and 25\% soluble lead, i.e. 50 to 250 ppm. Determine using the 283.3 nm resonance line. Prepare A.A.S. standards in this concentration range by dissolving high purity (99.98\%) lead in nitric acid, evaporating to dryness on a water bath and taking up with 40 mls of 25\% ammonium acetate.

A4.2.4 **Zinc, Iron, Copper and Lead Determinations Using A.A.S.**

Prepare residue samples for analysis of Zn, Fe, Cu and Pb in the manner described in sections A4.1.1 to A4.1.6. However, the range of possible concentrations in the leach residues is larger than that in the ore. Typically Zn, Fe and Cu values will be lower than those of the ore because of partial leaching. Therefore determine Zn by making trial dilutions (<100 times) and Fe and Cu by preparing additional standard solutions at the lower end of the concentration scale. Prepare these by diluting concentrated stock solutions in the manner described in § A4.1.6. Lead concentration in the residue is higher than in the ore and in the \(\frac{1}{2}\) g l\(^{-1}\) solution so further dilute with NaCl, HCl solution before analysing.

A4.2.5 **Total Sulphur Determination**

Determine total sulphur in the manner described in § A4.1.7. The result includes the elemental sulphur determined in § A4.2.2.

A4.2.6 **Silica Determination**

Determine total silica in the manner described in § A4.1.8. (Determinations were made on only a few residues to check mass balances. It was found that, as expected, silica was insoluble under the leach conditions and therefore appeared quantitatively in the residue.)

A4.2.7 **X-ray Diffraction (X.R.D.)**

Perform X-ray diffraction scans of the residues to determine the nature of the crystalline reaction products. Make a qualitative assessment of the extent of leaching by comparing residue scans to those of the unreacted ore. Perform scans on residues before wet analysis, so that if unusual reaction products are identified (e.g. jarosites), the wet analysis methods can be modified to determine these.

A4.3 **LEACH SOLUTION ANALYSIS**

The collection of 6 ml solution samples and the preparation of the final autoclave leach liquor is described in § A3.2. The samples contain the following species: Zn\(^{2+}\), Cu\(^{2+}\), Fe\(^{3+}\), Pb\(^{2+}\), SO\(_4\)^{2-}, H\(^+\), OH\(^-\) and H\(_2\)O. The Pb\(^{2+}\) concentration in solution is limited by the solubility product of PbSO\(_4\) and is consequently very low. Lead determinations are therefore not needed for the construction of overall mass balances but make occasional checks to verify this. Determine zinc, copper and iron totals by A.A.S. after suitable dilution of the solution samples. Determine sulphate gravimetrically on the final leach liquor only. Record the pH of the final leach solution.

A4.3.1 **Iron Determinations Using A.A.S.**

Iron concentrations in solution lie in the range 0.3 to 2.0 g l\(^{-1}\). The following resonance lines are available for iron - 248.3 nm full scale deflection (F.S.D.), 12.5 to 20 ppm and 372.0 nm, F.S.D., 120 to 180 ppm. Dilute the solution samples 10 times (5 ml aliquot made up to 50 mls with distilled water) giving an unknown iron concentration in the range 30 to 200 ppm. Therefore use the 372.0 nm resonance
line for all determinations. Use a short burner for the high end of the concentration scale because it approximately doubles the concentration required to give F.S.D.

A4.3.2 Zinc Determinations Using A.A.S.

Zinc concentrations lie in the range 0.5 to 45 g l\(^{-1}\) so that use of the resonance line 213.9 nm (F.S.D. = 2 ppm) requires large dilutions. In practice make dilutions by taking aliquots of the 10 times diluted samples prepared for iron determination. These contain 50 to 4,500 ppm zinc and therefore require further dilution of between 25 and 2000 times before determinations can be made. Make very approximate trial dilutions using measuring cylinders to give a concentration estimate before preparing accurate dilutions with pipette and volumetric flask. Make dilutions in one step from the 10 times diluted samples, the largest of 2000 times, by pipetting a 1 ml aliquot of solution and making up to 2 litres in a volumetric flask with distilled water.

A4.3.3 Copper Determinations Using A.A.S.

Copper concentrations lie in the range 0 to 1,200 ppm. The following resonance lines are available for copper: 324.8 nm, F.S.D. 10 to 15 ppm and 218.2 nm, F.S.D., 80 to 120 ppm. Therefore use the 1 ml remaining from the autoclave samples to determine very low concentrations using the 324.8 nm line. For intermediate concentrations use the 10 times diluted samples (5 A4.3.1) at 324.8 nm and for high concentrations use the 10 times diluted samples at 218.2 nm.

A4.3.4 Preparation of Standard Solutions

Prepare concentrated standard solutions for storage and prepare fresh A.A. standards from these every month. Chemical interference from cations is negligible so match the matrix by adding sulphate only. The acid concentration used in most leaching experiments was 0.8 mol l\(^{-1}\) (76.8 g l\(^{-1}\)) and although acid is consumed the sulphate concentration remains virtually unchanged at the end of an experiment.

(i) Iron Standards. Ten times dilution of the autoclave solution samples results in a sulphate concentration of 0.08 mol l\(^{-1}\) (7.69 g l\(^{-1}\)) Prepare iron standards from 2000 ppm ferrous sulphate solution (prepared by dissolving 2.0000 g of 99.99% Fe in 1:4 sulphuric acid and diluting with distilled water) by dilution with 0.08 mol l\(^{-1}\) sulphuric acid.

(ii) Zinc Standards. Dilution of autoclave samples varies between 250 and 20,000 times resulting in sulphate concentrations of between 300 and 4 ppm. Most solutions, however, fall in the range 60 to 4 ppm. Interference is found to be negligible for concentrations in this range and zinc standards are therefore not matrix matched. Prepare bulk 200 ppm solution by dissolving 0.2000 g of 99.95% Zn in 20 mls of 5% sulphuric acid and making up to 1 litre with distilled water. Prepare A.A. standards from this solution by dilution with distilled water.

(iii) Copper Standards. Prepare 1000 ppm solution by dissolving 1.0000 g of 99.999% Cu in 1:4 nitric acid, evaporate to dryness and take up in 10 mls of 1:4 sulphuric acid. Dilute to 1 litre with distilled water. Prepare 5, 10 and 15 ppm A.A. standards by taking aliquots of the bulk solution and diluting with 0.8 mol l\(^{-1}\) acid. Prepare further 5, 10 and 15 ppm standards in the same manner but dilute with 0.08 mol l\(^{-1}\) acid. Prepare 25, 50, 75 and 100 ppm solution by diluting aliquots with 0.08 mol l\(^{-1}\) acid.

A4.3.5 Sulphate Determination

Analyse final leach liquors gravimetrically for sulphate in the manner described in §A4.1.7 for total sulphur. Use knowledge of the initial acid concentration employed in the leach to select a suitable
aliquot size of final leach liquor. For example, assume the initial acid concentration is 0.2 mol l$^{-1}$. The sulphate concentration at the end of leaching will be approximately unaltered,

$$[\text{SO}_4^{2-}] = 0.2 \text{ mol l}^{-1}$$

$$= 6.4 \text{ g of sulphur/litre.}$$

Select an aliquot size that contains about 0.1 g of sulphur

$$\text{aliquot size} = \frac{1000}{6.4} \times 0.1 \sim 16 \text{ ml.}$$

Therefore take a 15 ml aliquot and add 10 ml of 10% barium chloride which is equivalent to 0.312 g of sulphur.

A4.4 GENERAL

(i) A-grade volumetric glassware was used in all analyses.

(ii) All dilutions were made with distilled, deionised water.

(iii) When making A.A.S. determinations a sample of distilled water was taken from the same batch as that used for the dilution of the unknown samples and used as a blank when zeroing the instrument. This precaution eliminated any errors that might have been caused by low cation concentrations in the diluent and is most important for zinc because it is analysed at only 2 ppm.

(iv) All weighings were made on a Sartorius, 200 g maximum, chemical balance.

(v) A.A. determinations were made on a Techtron AAS machine using an oxy-acetylene flame.

(vi) A Phillips X-ray set and goniometer were used for powder diffraction scans. The following standard conditions applied for comparative work:

Radiation: CoK$_\alpha$

Divergence Slit: 1°

Receiving Slit: $\frac{1}{4}$°

Scatter Slit: 1°

Scan Speed: 1°/min

Chart Speed: 60 cm/hr


Tube Voltage: 36 kV

Tube Current: 16 mA
### A4.5 LIST OF CHEMICALS USED

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Manufacturer*</th>
<th>Manufacturer's Specification</th>
<th>Grade</th>
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<tr>
<td>ammonium acetate</td>
<td>NH₄OOC₂H₂</td>
<td>MB</td>
<td>R</td>
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<td>BDH</td>
<td>AnalR</td>
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<td>CuSO₄</td>
<td>BDH</td>
<td>AnalR</td>
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<td>NDA</td>
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<td>hydrochloric acid</td>
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<td>R 1.18</td>
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<tr>
<td>iron</td>
<td>Fe</td>
<td>NPL</td>
<td>-</td>
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<tr>
<td>lead</td>
<td>Pb</td>
<td>BDH</td>
<td>AnalR</td>
<td>**</td>
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<td>Zn</td>
<td>BDH</td>
<td>AnalR</td>
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* MB: May and Baker  
BDH: British Drug Houses  
NPL: National Physics Laboratory  
NDA: National Dairy Association  

** see manufacturers catalogue

** TABLE A.2: Chemicals Used**
APPENDIX 5  CALCULATIONS

A5.1 DETERMINATION OF AUTOCLAVE OPERATING PRESSURE

The temperature-composition diagram for the sulphuric acid-water system, Fig. A1, shows that for acid compositions in the range used in this investigation (< 10%) the equilibrium vapour can be taken as pure water. Steam tables may therefore be used to find the partial pressure of the vapour at the desired operating temperature.

Let \( P_g \) be the gauge pressure
and \( P_b \) be the barometric pressure
then
\[
P = P_{O_2} + P_{H_2O} = P_g + P_b
\]
\[
P_g = P_{O_2} + P_{H_2O} - P_b
\]

\[ \ldots \quad (A1) \]

Fig. A1  Temperature-composition diagram for liquid-vapour equilibrium of \( \text{H}_2\text{SO}_4 \) and water. Data is taken from Perry [127] pages 3-62 and 3-63.
A5.2 CORRECTION OF RAW METAL EXTRACTIONS FOR SAMPLING VOLUME

We have that Initial volume of leachant \( V \) = 1000ml
Volume of the sample line = 8 ml

When the autoclave pressure is increased a volume \( v \) of leachant is forced into the sampling line. If the whole sample line attains the operating temperature \( v \) can be calculated. For the standard operating conditions \((110^\circ\text{C}, P_{O_2} = 0.138 \text{ MPa});
\)

\[
P = P_{O_2} + P_{H_2O}
\]
\[
= 0.138 + 0.143
\]
\[
= 0.281 \text{ MPa}
\]

\[
\therefore v = 8 \left( \frac{383}{272} \times 0.101 \times 8 \right)
\]
\[
= 8 (1 - 0.504)
\]
i.e. \( v \approx 4 \text{ ml} \)

The initial volume of leachant is also reduced by the amount of water that is present in the vapour phase at \(110^\circ\text{C} \). From steam tables this volume is \( 6 \text{ ml} \) based on a gas volume of 4 l. The effective initial autoclave volume \( V' \) is then

\[
V' = 0.990 l
\]

Let \( C \) be the concentration of Zn, Cu or Fe determined by analysis of the solution samples \((g \text{ l}^{-1})\).
Let \( t \) be the sampling time (hours)
and \( M \) be the weight of metal extracted \((g) \) after time \( t \).

Then

\[
M_1 = 0.990 C_1
\]

At the end of one hour 6 ml of sample 1 was collected after first allowing 9 mls of solution to flow through and clear the sample line. This represents 4 ml \( v \) of starting solution plus 11 mls of \( C_1 \) (assuming that there is no intermixing between the stirred solution and that in the sample line).

At the end of two hours sample 2 was collected in the same manner. The 15 ml of solution collected comprises 8 ml of \( C_1 \) and 7 ml of \( C_2 \). The total volume of solution of composition \( C_1 \) that is collected = 19 ml. This also represents the decrease in the volume of leachant available in the period between sample 1 and sample 2.

\[
\therefore M_2 = (0.990 - 0.019) C_2 + 0.019 C_1
\]
i.e. \( M_2 = 0.971 C_2 + 0.019 C_1 \)

The second term of equation \((A4)\) represents the weight of metal collected in 19 ml of sampling and clearance solution of concentration \( C_1 \).

At the end of three hours sample 3 was collected in the same manner as sample 2. In this case the total volume of solution of composition \( C_2 \) that is collected is 15 ml.

\[
\therefore M_3 = (0.971 - 0.015) C_3 + 0.015 C_2 + 0.019 C_1
\]
i.e. \( M_3 = 0.956 C_3 + 0.015 C_2 + 0.019 C_1 \)
Similarly:

\[ M_5 = 0.941 C_5 + 0.015 (C_3 + C_2) + 0.019 C_1 \]  \hspace{1cm} \text{(A6)}

and

\[ M_7 = 0.926 C_7 + 0.015 (C_5 + C_3 + C_2) + 0.019 C_1 \]  \hspace{1cm} \text{(A7)}

Sample 7' is taken from the final leach solution, which is filtrate plus wash water evaporated back to 1 litre, so that:

\[ M_{7'} = C_7 + 0.007 C_7 + 0.015 (C_5 + C_3 + C_2) + 0.019 C_1 \]  \hspace{1cm} \text{(A8)}

A5.3 CALCULATION OF EXTRACTION (\( \alpha \)) VALUES FOR SPHALERITE AND CHALCOPYRITE

Let

- \( W_X \) = weight of residue removed from the solution at the end of the experiment
- \( W_Y \) = weight of residue removed from the baffles at the end of the experiment
- \( W_Z \) = weight of ore removed from the sample introducer at the end of the experiment
- \( W \) = total weight of ore placed in the sample introducer
- \( W_M \) = weight percent of a metal M in the ore or residue where M = Zn, Cu
- \( \alpha_t \) = fraction dissolved after time t.

From the solution analyses:

\[ \alpha_t = \frac{M_t}{M_t' - M_Z} = \frac{M_t'}{M_t' - M_Z} \]  \hspace{1cm} \text{(A9)}

where

\[ M_t' = M_t - M_Z \]

\[ = (w_{M_i})_1 W - (w_{M_i})_2 W_Z \]

but

\[ (w_{M_i})_1 = (w_{M_i})_2 \text{ since the ore left in the sample introducer was found experimentally to be unreacted.} \]

i.e.

\[ M_t' = (w_{M_i})_1 (W - W_Z) \]  \hspace{1cm} \text{(A10)}

Note: the subscript M is dropped in the following equations and \( W \) values are understood to apply to the metal M under consideration.

From the residue analyses:

\( W_X \) and \( W_Y \) are obtained for each metal

\[ \therefore M_X = w_X \frac{w_X}{W_X} \]  \hspace{1cm} \text{(A11a)}

and

\[ M_Y = w_Y \frac{w_Y}{W_Y} \]  \hspace{1cm} \text{(A11b)}

The total weight of a metal contained in the residue, \( M_R \), is therefore given by:

\[ M_R = M_X + M_Y = w_X \frac{w_X}{W_X} + w_Y \frac{w_Y}{W_Y} \]  \hspace{1cm} \text{(A12)}
A mass balance on each metal gives:

\[ \begin{align*}
M_i' &= M_R + M_7' + E \\
&= M_{\text{out}} + E
\end{align*} \] ...... (A13a)

Combining equation (A13a) with equations (A10) and (A12)

\[ w_i(N - W_z) = w_X X + w_Y Y + M_7 + E \] ...... (A14)

By rearranging equation (A13a) the error in the mass balance is given by

\[ E = M_i' - (M_R + M_7') \] ...... (A15)

and the error % by

\[ E(\%) = \frac{M_i' - (M_R + M_7')}{M_i} \] ...... (A16)

Let

\[ M_7'' = M_i' - M_R \] ...... (A17)

where \( M_7'' \) is another estimate of the final weight of \( M \) extracted (c.f. \( M_7 \) and \( M_7' \)). Then from equation (A13a)

\[ M_7'' = M_7' + E \] ...... (A18)

It is now necessary to make some assumptions to proceed with the calculations.

(i) \( M_7' \) is a better measure of the final extraction than \( M_7 \).

(ii) The best measure of the final extraction (\( \alpha_7 \)) is the average value of \( M_7' \) and \( M_7'' \).

(iii) Once ore residue has collected on the baffles above the waterline the sphalerite and chalcopryite contained in this residue do not dissolve further.

(iv) This residue builds up at a linear rate throughout the experiment.

The validity of these assumptions is discussed later.

Now

\[ \alpha_7 = \frac{1}{2}(M_7' + M_7'')/\text{weight of } M \text{ available for leaching (assumption (ii))} \]

and the weight of \( M \) available for leaching is decreased by the amount adhering to the baffles.

but

\[ (M_7)_{\text{t}} = \frac{5}{7} M_7 \] (assumption (iv)) ...... (A19a)

and

\[ (M_7)_{\text{t}} = \frac{5}{7} M_7 \] ...... (A19b)

Therefore the average value of \( M \) unavailable for leaching during the two hour period between samples 5 and 7 is given by

\[ (M_7)_6 = \frac{6}{7} M_7 \]

but

\[ \bar{\alpha}_7 = \frac{(M_7'' + M_7'')}{2} \]

\[ \therefore \bar{\alpha}_7 = \frac{R_7}{M_i' - \frac{5}{7} M_7} \] ...... (A20)
where \( \bar{R}_7 = \frac{(M'_7 + M''_7)}{2} \)

Calculation of extractions after 1, 2, 3 and 5 hours require one further assumption:

(v) The difference between \( M_7 \) and \( M'_7 \) or \( M''_7 \) and \( \bar{R}_7 \) is due to small solution losses from the autoclave during an experiment resulting in \( M_7 \) being an overestimate of the true weight extracted. These losses occur at an constant rate.

Then \[ M_5 - \bar{R}_5 = \frac{5}{7} (M_7 - \bar{R}_7) \]

rearranging \[ \bar{R}_5 = M_5 - \frac{5}{7} (M_7 - \bar{R}_7) \]

or \[ \bar{R}_5 = M_5 - \Delta_7 \]

where \[ \Delta_7 = \frac{5}{7} (M_7 - \bar{R}_7) \]

similarly \[ M_3 = M_3 - \Delta_5 \text{ etc.} \]

The extraction values can be calculated by replacing \( M_x \) with \( \bar{R}_x \)

\[ \bar{a}_5 = \frac{R_5}{M'_1 - (M'_4)_5} \]

i.e. \[ \bar{a}_5 = \frac{R_5}{M'_1 - \left( \frac{5}{7} \right) M_7} \]

and similarly for \( \bar{a}_3, \bar{a}_2 \) and \( \bar{a}_1 \).

ASSUMPTIONS AND JUSTIFICATIONS

(i) \( M'_7 \) is a better measure of the final extraction than \( M_7 \).

\( M'_7 \) is determined in the filtrate after evaporating the wash water back to the starting volume of one litre. Errors in \( M'_7 \) may arise from

(a) inadequate washing the residue

(b) loss of solution through inadequate rinsing of the autoclave internals

(c) the fact that contact between the residue and solution exceeds the time of 7 hours set down for the end of the experiment.

The first two errors will reduce the value of \( M'_7 \) while error (c) will increase it. In actual fact (c) is not an error when calculating mass balances because the residue analysed has been in contact with the solution for the added time period. Thus \( M'_7 \) is used in conjunction with \( M'_x \) and \( M_y \) in the mass balances.

\( M_7 \), determined from the final solution sample is subject to the following errors:

(i) solution hold-up on surfaces above the waterline, in particular hold-up with the ore residue adhering to the baffles

(ii) solution loss from the liner by evaporation and recondensation on the lid and upper walls of the autoclave

(iii) a small loss due to vapour escape through the gland.
All three errors lead to an overestimation of $M_7$. $M_7$ was chosen as the better result for the following reasons:

(1) Errors (a) and (b) were reduced by attention to experimental detail.

(2) Error (c) was minimised by the autoclave operating procedure. This involved stopping the agitator after 7 hours, venting, opening, cooling by dilution and then rapid filtration. The residue was in contact with the solution for an extra 1½ hour but the slurry was cooled by dilution after 5 mins and with no agitation the reaction rate would slow considerably. This error would be particularly small for highly reacted residues where the rate of reaction had already slowed considerably (see Figs. 22 to 30).

(3) Errors (a), (b) and (c) are at least partially compensating.

(4) Errors (i), (ii) and (iii) in $M_7$ are additive.

(5) Since the experimental results (Table A9- Appendix 6) show that $M_7$ generally exceeded $M_7'$ it follows that 

$$E[(i) + (ii) + (iii)] > E[(c) - (a) - (b)]$$

(ii) The best measure of the final extraction is the average value of $M_7'$ and $M_7''$.

$M_7'$ for reasons discussed in (i) above is the best solution estimate of the true extraction. The only residue estimate is $M_7''$, where

$$M_7'' = M_7' - M_R$$

i.e.

$$M_7'' = M_i' - M_X - M_Y$$

The best estimate of the true extraction is the average of the two estimates viz:

$$R_7 = (M_7' + M_7'')/2$$

However there are two cases when the reliability of one estimate is greater than the other. These occur when $M_R$ is either very small, i.e. $M_R < M_i$ and when $M_R < M_i'$. In the first case since $M_i'$ is known accurately and $M_R$ is small the reliability of $M_7''$ as an estimator will be higher than $M_7'$. In the second case errors in $M_R$ are likely to be higher (it is the sum of three assays) and $M_7'$ will be the better estimate. In practice where $M_7'$ and $M_7''$ were widely divergent at high $M_R$ values $M_7'$ was used as $R_7$.

(iii) Once ore residue has collected on the baffles above the waterline, the sphalerite and chalcopyrite contained in this residue do not dissolve further.

It was experimentally observed that the residue adhering to the baffles was tightly packed and came into irregular contact with the solution. A diffusion mechanism would probably control the rate of reaction in this case and although reaction would not cease completely the rate of dissolution would be much slower than that of the ore in solution. Evidence to support this contention comes from analyses of hold-up (Y) residues which show that zinc, copper and iron concentrations are higher than in X residues.

(iv) This residue builds up at a linear rate throughout the experiment.

There is scant evidence to support this but it is necessary to make some assumption regarding the build-up of residue Y in order to compute the reduction in the weight of ore available for leaching. Experimental results listed in Appendix 6 show that Y residues are extremely small unless the ore is at least 50% reacted. In other words a critical dissolution may be required before binding and subsequent build-up can occur. Unfortunately it is impossible to characterise this in mathematical terms because of the number of unknowns. The linear build-up assumption
introduces little error even if none occurs for several hours and it derives some support from the expectation that build-up may follow the extraction curve of Zn which is approximately linear after an incubation period. The longer the incubation period the greater is the error inherent in this assumption.

(v) The solution losses occur at a linear rate

Presumptions regarding the way in which solution is lost from the operating volume are listed under assumption (i). If assumption (iv) is accepted then it appears reasonable to assume that the volume of solution held-up with the ore residue on the baffles also increases linearly with time. Vapour escape varies according to the performance of the gland and the linear assumption is at best an approximation.

A5.4 CALCULATION OF PYRITE EXTRACTIONS

Iron concentrations in solution are determined by solution sample analyses but, whereas copper and zinc extractions are direct measures of the fraction of chalcopyrite and sphalerite reacted, soluble iron can come from up to five sources.

(i) pyrite
(ii) chalcopyrite
(iii) tramp iron in the ore
(iv) corrosion of stainless steel autoclave internals.
(v) sphalerite

Let

- \( Fe_C \) be the chalcopyrite contribution to the total weight of iron in solution
- \( Fe_{Corr} \) be the corrosion contribution
- \( Fe_T \) be the tramp iron contribution
- \( Fe_{py} \) be the pyrite contribution
- \( Fe_S \) be the sphalerite contribution

Then

\[
Fe_T = (Fe_{py})_t + (Fe_C)_t + (Fe_{Corr})_t + (Fe_T)_t + (Fe_S)_t \quad \ldots \quad (A25)
\]

\((Fe_C)_t\) can be calculated from the weight of copper in solution assuming equimolar dissolution of iron and copper from chalcopyrite. This assumption appears justified as all published investigations have reported this result (§ 3.5).

then

\[
(Fe_C)_t = \frac{55.85}{63.54} Cu_t = 0.88 \, Cu_t \quad \ldots \quad (A26)
\]

\((Fe_{Corr})_7\) can be estimated from the difference between the \( Fe_7 \) and \( Fe_7'' \). \( Fe_7 \) was used instead of \( Fe_7' \) (see assumption (i) § A5.3) because some iron was found to precipitate in the filtrate evaporation step leading to low values of \( Fe_7' \).

i.e.

\[
(Fe_{Corr})_7 = Fe_7 - Fe_7'' \quad \ldots \quad (A27)
\]

This same difference was used to calculate the analytical error in the mass balances for zinc and copper (equation (A18)) and this error is included in equation A27. Consequently its reliability is not good. In practice only \((Fe_{Corr})_7\) values > 0.1 \( Fe_7'' \) were considered significant. Fortunately corrosion contributions were negligible in most experiments being limited to a few cases early in the development of the equipment.
(Fe\textsubscript{7})\textsubscript{t} + (Fe\textsubscript{S})\textsubscript{t} cannot be estimated because iron dissolving from tramp iron and sphalerite is indistinguishable from that from pyrite. Consequently pyrite extractions were calculated including these contributions.

viz: \( (\text{Fe}_\text{S})\textsubscript{t} + (\text{Fe}_\text{Py})\textsubscript{t} + (\text{Fe}_\text{7})\textsubscript{t} = \text{Fe}_\text{7} - (\text{Fe}_{\text{corr}})_\text{t} - (\text{Fe}_\text{C})\textsubscript{t} \)

\[ \Rightarrow \text{Fe}_\text{Py} = \text{Fe}_\text{7} = \text{Fe}_\text{7} - (\text{Fe}_{\text{corr}})_\text{t} - (\text{Fe}_\text{C})\textsubscript{t} - 0.88 \text{Cu}_\text{7} \]

\[ \text{i.e.} \quad (\text{Fe}_\text{Py})\textsubscript{t} = \text{Fe}_\text{7} = \text{Fe}_\text{7} - (\text{Fe}_{\text{corr}})_\text{t} - (\text{Fe}_\text{C})\textsubscript{t} - 0.88 \text{Cu}_\text{7} \]

where \( (\text{Fe}_\text{Py})\textsubscript{7} = (\text{Fe}_\text{Py})\textsubscript{t} + (\text{Fe}_\text{7})\textsubscript{t} + (\text{Fe}_\text{S})\textsubscript{7} \)

Now \( (\text{Fe}_\text{Py})\textsubscript{t} = \text{Fe}_\text{7} - 0.88 \text{Cu}_\text{7} \)

and \( (\text{Fe}_\text{Py})\textsubscript{7} = \text{Fe}_\text{7} - 0.88 \text{Cu}_\text{7} \)

Therefore from equation (A20) replacing \( R_7 \) by \( (\text{Fe}_\text{Py})\textsubscript{7} \) we have

\[ (\alpha_{\text{Py}})_7 = \frac{(\text{Fe}_\text{Py})\textsubscript{7}}{(\text{Fe}_\text{Py})\textsubscript{t} - (\text{Fe}_\text{Py})\textsubscript{7}} \]

and combining with equations (A26), (A28) and (A29)

\[ (\alpha_{\text{Py}})_7 = \frac{\text{Fe}_\text{7} - 0.88 \text{Cu}_\text{7}}{(\text{Fe}_\text{7} - \text{Fe}_\text{7}^\text{c} - 0.88 (\text{Cu}_\text{7} - \text{Cu}_\text{7}^\text{c}))} \]

Since \( \text{Fe}_\text{7}^\text{c} \) is only known at \( t = 7 \text{ hrs} \) it is necessary to estimate the rate of corrosion to calculate the corrosion contribution for \( t < 7 \). The simplest relationship of constant rate was adopted. This is unlikely to be a true representation but with no other information available it is better than making no allowance for corrosion at all.

then

\[ (\text{Fe}_{\text{corr}})_\text{5} = \frac{5}{7} (\text{Fe}_{\text{corr}})_\text{7} = \frac{5}{7} (\text{Fe}_\text{7} - \text{Fe}_\text{7}^\text{c}) \text{ etc.} \]

A5.5 CALCULATION OF LEAD CONVERSIONS

Lead conversion can only be calculated for \( t = 7 \text{ hrs} \). Equation (A13a) represents the mass balance.

viz: \( M_\text{7}' = M_\text{7}^\text{c} + M_R + E \)

where \( M = \text{Pb} \)

However \( \text{Pb}_\text{7}' \) is negligible because of the low solubility of lead sulphate.

\[ \Rightarrow \text{Pb}_\text{7}' = \text{Pb}_R + E \]

\[ \text{i.e.} \quad \text{Pb}_\text{7}' = \text{Pb}_\text{X} + \text{Pb}_\text{Y} + E \]

Now \( \text{Pb}_\text{X} = [\text{(w}_\text{X})\text{sulphide} + (\text{w}_\text{X})\text{sulphate}] \text{w}_\text{X} = \text{(Pb}_\text{X})\text{sulphide} + \text{(Pb}_\text{X})\text{sulphate} \)

and \( \text{Pb}_\text{Y} = [\text{(w}_\text{Y})\text{sulphide} + (\text{w}_\text{Y})\text{sulphate}] \text{w}_\text{Y} = \text{(Pb}_\text{Y})\text{sulphide} + \text{(Pb}_\text{Y})\text{sulphate} \)

The galena unavailable for leaching is given by \( (\text{Pb}_\text{Y})\text{sulphide} \).
and 

\[ (\alpha_{\text{PbS}})_7 = \frac{(\text{Pb}_x)_{\text{sulphate}} + (\text{Pb}_y)_{\text{sulphate}}}{\text{Pb}_R - (\text{Pb}_y)_{\text{sulphide}}} \]  

E, equation (A33), is usually positive due to residue losses during collection so Pb\(_R\) is used in calculating \(a_7\) rather than Pb\(_1\).

A5.6 CALCULATION OF THE FRACTION THEORETICAL SULPHUR YIELD

The maximum theoretical sulphur yield is based on the assumption that sulphur was formed quantitatively according to the following reactions:

\[
\begin{align*}
\text{ZnS} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{SO}_4 & \rightarrow \text{ZnSO}_4 + \text{H}_2\text{O} + \text{S}^0 \quad \ldots \quad (33) \\
\text{PbS} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{SO}_4 & \rightarrow \text{PbSO}_4 + \text{H}_2\text{O} + \text{S}^0 \quad \ldots \quad (56) \\
\text{CuFeS}_2 + 2\text{H}_2\text{SO}_4 + \text{O}_2 & \rightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{O} + 2\text{S}^0 \quad \ldots \quad (66) \\
\text{Fe}_2\text{S}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{SO}_4 & \rightarrow \text{FeSO}_4 + \text{H}_2\text{O} + 2\text{S}^0 \quad \ldots \quad (63)
\end{align*}
\]

Weight S\(^0\)/weight Zn = 32.06/65.37 = 0.4904 g S\(^0\)/g Zn

Weight S\(^0\)/weight Pb = 32.06/207.1 g = 0.1547 g S\(^0\)/g Pb

Weight S\(^0\)/weight Cu + weight Fe (in chalcopyrite) = 64.12/63.54

\[ g\text{ S}^0 \quad = \quad 1.009 \frac{g\text{ S}^0}{g\text{ Cu} + 0.88 g\text{ Fe}} \]

Weight S\(^0\)/weight Fe (pyrite) = 64.12/55.85 = 1.148 g S\(^0\)/g Fe

The actual weight of sulphur in the residues was found by soxhlet extraction with C\(_5\)\(_2\). Then the fraction theoretical sulphur yield is given by

\[ (\alpha_7)_{S^0} = \frac{\text{actual } S^0 \text{ yield}}{\text{max. theoretical } S^0 \text{ yield}} \]  

A5.7 CALCULATION OF THE FRACTION THEORETICAL SULPHATE YIELD

Assumptions:

(i) Sulphur forming reactions are given by equations (33), (56), (63) and (66) (§A5.6) and sulphate forming reactions are given by equations (34), (56), (59) and (68).

\[
\begin{align*}
\text{ZnS(s)} + 2\text{O}_2(aq) & = \text{ZnSO}_4(aq) \quad \ldots \quad (34) \\
\text{PbS(s)} + 2\text{O}_2(aq) & = \text{PbSO}_4(s) \quad \ldots \quad (56) \\
2\text{CuFeS}_2(s) + 17/2 \text{O}_2(g) + 2\text{H}_2\text{O}(aq) & = 2\text{Cu}^{++}(aq) + 2\text{Fe}^{+++}(aq) + 4\text{SO}_4^{2-}(aq) + \text{H}_2\text{O}(aq) \quad \ldots \quad (68)
\end{align*}
\]
\[
\text{FeS}_2(s) + 7/2\text{O}_2(aq) + \text{H}_2\text{O} = \text{FeSO}_4(aq) + \text{H}_2\text{SO}_4(aq) \quad \cdots \quad (59)
\]

(ii) Hydrogen sulphide is not present at the completion of leaching.

(iii) Loss of sulphate ions from solution is due only to lead sulphate formation via reaction (55). That is, no basic iron sulphates or jarosites are formed.

Consider the final distribution of the sulphur added as sulphuric acid.

\[
\begin{align*}
\text{S(SO}_4^{\text{aq}} \text{ acid in)} &= \text{S(SO}_4^{\text{aq}} \text{ final leach solution} + \text{solution samples}) \\
&+ \text{S(SO}_4^{\text{aq}} \text{ precip. as PbSO}_4 \text{ via reaction (55))} \\
&- \text{S(SO}_4^{\text{aq}} \text{ formed from Zn, Fe and Cu sulphides via (34), (59) and (68))}
\end{align*}
\]

The final term does not include \text{S(SO}_4^{\text{aq}} \text{ formed from PbS via reaction (56))} because this ends up in the residue not the solution.

Rearranging:

\[
\begin{align*}
\text{S(SO}_4^{\text{aq}} \text{ formed from Zn), } \text{Cu and Fe sulphides} &\text{ solution} = \text{S(SO}_4^{\text{aq}} \text{ out}) \text{ solution} + \text{S(SO}_4^{\text{aq}} \text{ precip. as PbSO}_4 \text{ (55)}, \text{ residue}) - \text{S(SO}_4^{\text{aq}} \text{ acid}) \text{ solution} \\
\end{align*}
\]

...... (A36)

Consider now the final distribution of sulphur added as sulphide.

\[
\begin{align*}
\text{S(S}_\text{2 ore in)} &= \text{S(S}_\text{2} + \text{S}_\text{2} + \text{S}_\text{O}_4^{\text{aq}} \text{ formed from PbS via reaction (56)), residue} \\
&+ \text{S(S}_\text{O}_4^{\text{aq}} \text{ formed from Zn, Fe and Cu sulphides) solution} \\
\text{i.e. S(S}_\text{2 ore}) &= \text{S(S}_\text{2} + \text{S}_\text{2} + \text{S}_\text{O}_4^{\text{aq}} \text{ formed from PbS (55))} - \text{S(S}_\text{O}_4^{\text{aq}} \text{ precip. as PbSO}_4 \text{ (55))}, \text{ residue} \\
&+ \text{S(S}_\text{O}_4^{\text{aq}} \text{ formed from Zn), } \text{Cu and Fe sulphides} \text{ solution}
\end{align*}
\]

\[
\begin{align*}
\text{S(S}_\text{2 total) residue} &= \text{S(S}_\text{2} \text{ total) residue} - \text{S(S}_\text{O}_4^{\text{aq}} \text{ precip. as PbSO}_4 \text{ (55)) residue} + \text{S(S}_\text{O}_4^{\text{aq}} \text{ formed from Zn), } \text{Cu and Fe sulphides} \text{ solution} \\
\end{align*}
\]

Rearranging:

\[
\begin{align*}
\text{S(S}_\text{O}_4^{\text{aq}} \text{ formed from Zn), } \text{Cu and Fe sulphides} \text{ solution} = \text{S(S}_\text{2 ore}) \text{ in}) - \text{S(S}_\text{2 total) residue} + \text{S(S}_\text{O}_4^{\text{aq}} \text{ precip. as PbSO}_4 \text{ (55)) residue} \quad \cdots \quad (A37)
\end{align*}
\]

but from equations (55) and (56)

\[
\begin{align*}
\text{S(S}_\text{2 as PbS) reacted} &= \text{S(S}_\text{2} \text{ formed from PbS (55)) residue} + \text{S(S}_\text{O}_4^{\text{aq}} \text{ formed from PbS (56)) residue} \\
\end{align*}
\]

but from equation (55)

\[
\begin{align*}
\text{S(S}_\text{2 formed from PbS (55))} &= \text{S(S}_\text{O}_4^{\text{aq}} \text{ precip. as PbSO}_4 \text{ (55))}
\end{align*}
\]

substituting we have
Substituting equation (A38) in equation (A36) we have

\[
S(\text{as PbS reacted}) = S(\text{PbSO}_4 \text{precip. as (55)})_{\text{residue}} + S(\text{SO}_4^{\text{aq}} \text{formed from PbS (56)})_{\text{residue}} = \ldots \quad (A38)
\]

Substituting equation (A38) in equation (A36) we have

\[
S(\text{SO}_4^{\text{aq}} \text{formed from Zn, Fe and Cu sulphides})_{\text{solution}} = S(\text{SO}_4^{\text{aq}} \text{out})_{\text{solution}} + S(\text{as PbS})_{\text{ore}} - S(\text{SO}_4^{\text{aq}} \text{formed from PbS (56)})_{\text{residue}} - S(\text{SO}_4^{\text{aq}} \text{acid})_{\text{solution}} = \ldots \quad (A39)
\]

i.e.

\[
S(\text{SO}_4^{\text{aq}} \text{formed from Zn, Fe, Cu and Pb sulphides})_{\text{solution}} = S(\text{SO}_4^{\text{aq}} \text{out})_{\text{solution}} + S(\text{as PbS})_{\text{reacted}} - S(\text{SO}_4^{\text{aq}} \text{acid})_{\text{solution}} = \ldots \quad (A40)
\]

From equation (A38)

\[
S(\text{as PbS reacted}) = S(\text{PbSO}_4 \text{total in residue}) = \frac{(\text{PbR})_{\text{sulphate}}}{207.2} \times 32.06
\]

i.e.

\[
S(\text{as PbS reacted}) = 0.155 (\text{PbR})_{\text{sulphate}} \quad \ldots \quad (A41)
\]

Substituting equation (A41) into equations (A39) and (A40) gives two means of calculating the weight of sulphide sulphur converted to sulphate from terms that can be determined simply by chemical analysis. The fraction theoretical sulphate yield can then be calculated from equation (42).

\[
(q_f)_{\text{sulphate}} = \frac{\text{actual weight of sulphate formed}}{\text{max. theoretical sulphate yield}} = \ldots \quad (A42)
\]

The denominator is based on the assumption that sulphate is formed quantitatively according to equations (34), (56), (59) and (68). That is, one mol of sulphate is formed for each mol of sulphide sulphur in the ore. The maximum theoretical sulphate yield is then equal to the maximum theoretical sulphur yield (SA5.6).

Now consideration of the final distribution of sulphur added as sulphide gave the following equation:

\[
S(S^\text{ore}) = S(S^\text{o}) + S(S^\text{r}) + S(\text{SO}_4^{\text{aq}} \text{formed form Zn, Fe, Cu and Pb sulphides}) = \ldots
\]

i.e.

\[
S(S^\text{ore}) - S(S^\text{r}) = S(S^\text{o}) + S(\text{SO}_4^{\text{aq}} \text{formed total}) = \ldots
\]

but

\[
S(S^\text{ore}) - S(S^\text{r}) = S(S^\text{r})_{\text{reacted total}} = S(S^\text{o} \text{theoretical max.}) + S(E) = S(\text{SO}_4^{\text{aq}} \text{theoretical max.}) + S(E) = \ldots
\]

\[
S(S^\text{theor.}) = S(S^\text{o}) + S(\text{SO}_4^{\text{aq}} \text{formed total}) - S(E)
\]
or \[ S(\text{SO}_4^{2-} \text{formed}) = S(\text{S}^6 \text{theoretical}) - S(\text{S}^6) + S(E) \]

i.e. \[ S(\text{SO}_4^{2-} \text{formed}) = S(\text{S}^6 \text{theoretical}) - S(\text{S}^6 \text{actual}) + S(E) \] \hspace{1cm} \text{(A43)}

where \( S(E) \) is the error in grams of sulphur. It will include both the error made in assuming formula stoichiometry when calculating \( S(\text{S}^6 \text{theoretical}) \) and the analytical error in determining \( S(\text{S}^6) \).

In the experiments where \( \text{H}_2\text{S} \) was present at the completion of leaching equation (A43) must be modified thus:

\[ S(\text{S}^6 \text{theoretical}) = S(\text{S}^6 \text{actual}) + S(\text{SO}_4^{2-} \text{formed}) + S(\text{H}_2\text{S}) - S(E) \] \hspace{1cm} \text{(A44)}

Equation (A44) is a better estimator of \( S(\text{SO}_4^{2-} \text{formed}) \) than equation (A39) because the analytical precision is considerably higher in determining \( S(\text{residue total}) \) than in determining \( S(\text{SO}_4^{2-} \text{solution out}) \) for the following reasons:

(i) \( S(\text{SO}_4^{2-} \text{solution out}) \) requires an estimate of the weight of sulphur removed from the autoclave with the solution samples as none of the samples were analysed for sulphate. (As \( S(\text{SO}_4^{2-} \text{solution out}) \) does not differ greatly from \( S(\text{SO}_4^{2-} \text{acid in}) \) the solution samples were assumed to contain the same concentration of sulphate as the acid added at the beginning of the experiment.)

(ii) There are small losses of sulphate during the filtrate evaporation procedure (see Fig. A1).

(iii) The fusion method of determining \( S(\text{residue total}) \) has a higher precision than the gravimetric method of determining \( S(\text{SO}_4^{2-} \text{solution out}) \).

In practice equation (A44) was used to calculate \( S(\text{SO}_4^{2-} \text{formed}) \).

### A5.8 Calculation of the Initial Acid/Ore Mol Ratio (MR)

The initial acid/ore mol ratio is based on the same reactions as the \( S(\text{S}^6 \text{yield}) \). The acid requirement is then 1 mol for each mol of \( \text{Zn, Pb, Cu and Fe} \). The initial mol ratio is given by

\[ \text{MR} = \frac{0.990 [\text{H}_2\text{SO}_4]^i}{\Sigma \frac{\text{M}}{\text{M}}^i} \] \hspace{1cm} \text{(A45)}

where \( \text{M} = \text{Zn, Pb, Fe, Cu} \) and \( \Sigma \text{M}^i \) is the molecular weight of \( \text{M} \).

### A5.9 Sample Calculation (Experiment 18)

Experiment 18 has been used to demonstrate the methods of calculation. Table A3 lists the conditions at the beginning of the experiment, Table A4 a complete mass balance at the completion of seven hours leaching, Table A5 the calculation of sphalerite and chalcopyrite extractions, Table A6 the calculation of pyrite extractions, Table A7 calculation of the fraction theoretical sulphur yield and Table A8 the fraction theoretical sulphate yield.
### TABLE A3  Starting Conditions

<table>
<thead>
<tr>
<th>Element</th>
<th>( W' ) (g)</th>
<th>( w'_X ) (g)</th>
<th>( w'_Y ) (g)</th>
<th>( w'_Z ) (g)</th>
<th>( V' ) (ml)</th>
<th>( [H_2SO_4]_i ) (mmol l(^{-1}))</th>
<th>MR</th>
<th>( P_p ) (g 1(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>115.0</td>
<td>71.6</td>
<td>7.5</td>
<td>7.1</td>
<td>107.9</td>
<td>1000</td>
<td>990</td>
<td>0.800</td>
</tr>
</tbody>
</table>

**A major contributor to E may be corrosion (see § A5.4)**

**A mass balance on sulphur in the solid form is not applicable because of the interchange of this element between solution and solid.**

### TABLE A4  Mass Balance after Seven Hours Leaching

<table>
<thead>
<tr>
<th>Sample Time (hrs)</th>
<th>( C_t ) (g T(^{-1}))</th>
<th>( Fe_t ) (g)</th>
<th>( (FeC)_t ) (g)</th>
<th>( (FeS)_t ) (g)</th>
<th>( (FeS)_t ) (g)</th>
<th>( (FeS)_t ) (g)</th>
<th>( G_t ) (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.55</td>
<td>0.550</td>
<td>0.055</td>
<td>0.495</td>
<td>0.008</td>
<td>3.66</td>
<td>0.218</td>
</tr>
<tr>
<td>2</td>
<td>0.745</td>
<td>0.735</td>
<td>0.193</td>
<td>0.542</td>
<td>0.024</td>
<td>3.65</td>
<td>0.284</td>
</tr>
<tr>
<td>3</td>
<td>0.940</td>
<td>0.922</td>
<td>0.238</td>
<td>0.684</td>
<td>0.040</td>
<td>3.63</td>
<td>0.307</td>
</tr>
<tr>
<td>5</td>
<td>1.260</td>
<td>1.224</td>
<td>0.414</td>
<td>0.810</td>
<td>0.064</td>
<td>3.61</td>
<td>0.368</td>
</tr>
<tr>
<td>7</td>
<td>1.760</td>
<td>1.676</td>
<td>0.651</td>
<td>1.025</td>
<td>0.096</td>
<td>3.57</td>
<td>0.473</td>
</tr>
<tr>
<td>7'</td>
<td>1.660</td>
<td>1.727</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Calculations**

\[
Fe_{7} = 1.65 \text{ (Table A4)}
\]

\[
Fe_{7} = 1.73
\]

\[
Fe_{7} = 1.69 \text{ (equation A21)}
\]

\[
(Fe_{corr})_t = Fe_{7} - Fe_{7}^*
\]

\[
(Fe_{corr})_t = 0.03
\]

- negligible

### TABLE A6  Calculation of Pyrite Extractions
<table>
<thead>
<tr>
<th>Element</th>
<th>Sample Time (hr)</th>
<th>$C_t$ (g T$^{-1}$)</th>
<th>$M_t$ (g)</th>
<th>$R_t$ (g)</th>
<th>$\Delta$ (g)</th>
<th>$(M_Y)_t$ (g)</th>
<th>$M_t' - (M_Y)_t$ (g)</th>
<th>$\bar{a}_t$</th>
<th>Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1</td>
<td>4.27</td>
<td>4.23</td>
<td>3.88</td>
<td>0.35</td>
<td>0.02</td>
<td>31.3</td>
<td>0.124</td>
<td>$M_Y'' = 29.7$ (Table A4)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>12.60</td>
<td>12.33</td>
<td>11.63</td>
<td>0.70</td>
<td>0.04</td>
<td>31.3</td>
<td>0.372</td>
<td>$M_Y''$ is the best estimate since $M_R &lt;&lt; M_t'$ (see Appendix 5.3).</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>20.90</td>
<td>20.27</td>
<td>19.02</td>
<td>1.05</td>
<td>0.09</td>
<td>31.2</td>
<td>0.610</td>
<td>$(M_Y)_7 = 0.26$ (Table A4)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>29.80</td>
<td>28.61</td>
<td>26.86</td>
<td>1.75</td>
<td>0.15</td>
<td>31.1</td>
<td>0.865</td>
<td>$(M_Y)_6 = (6/7) \times 0.26 = 0.22$ etc.</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>33.00</td>
<td>32.13</td>
<td>29.7</td>
<td>2.43</td>
<td>0.22</td>
<td>31.1</td>
<td>0.956</td>
<td>(equation A19b)</td>
</tr>
<tr>
<td></td>
<td>7'</td>
<td>29.46</td>
<td>30.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1</td>
<td>0.056</td>
<td>0.056</td>
<td>0.063</td>
<td>0.007</td>
<td>0.01</td>
<td>1.57</td>
<td>0.040</td>
<td>$M_Y'' = 0.75$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.210</td>
<td>0.205</td>
<td>0.219</td>
<td>0.014</td>
<td>0.03</td>
<td>1.55</td>
<td>0.142</td>
<td>$M_Y' = 0.73$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.255</td>
<td>0.249</td>
<td>0.270</td>
<td>0.021</td>
<td>0.05</td>
<td>1.53</td>
<td>0.176</td>
<td>$\ddot{\bar{R}}_7 = 0.74$ (equation A21)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.450</td>
<td>0.432</td>
<td>0.470</td>
<td>0.038</td>
<td>0.08</td>
<td>1.50</td>
<td>0.311</td>
<td>$(M_Y)_7 = 0.14$</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.724</td>
<td>0.690</td>
<td>0.740</td>
<td>0.050</td>
<td>0.12</td>
<td>1.46</td>
<td>0.507</td>
<td>$\ddot{\bar{R}}_7 = \frac{6}{7} \times 0.14 = 0.12$ etc</td>
</tr>
<tr>
<td></td>
<td>7'</td>
<td>0.710</td>
<td>0.730</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Equation | (A3)→(A8) | (A22b) | (A23) | (A19b) | (A20),(A24), etc. |

**Table A5** Calculation of Sphalerite and Chalcopyrite Extractions
Calculation of Lead Conversions.

\[ (\alpha_7)_{\text{PbS}} = \frac{(\text{Pb}_Y)_{\text{Sulphate}} + (\text{Pb}_Y)_{\text{Sulphate}}}{\text{Pb}_R - (\text{Pb}_Y)_{\text{Sulphide}}} \]  

\[ = \frac{21.0}{30.7 - 1.4} \]

\[ (\alpha_7)_{\text{PbS}} = 0.717 \]

<table>
<thead>
<tr>
<th>Element</th>
<th>( R_f ) (g)</th>
<th>( S^0_{\text{theoretical}} ) (g)</th>
<th>Actual ( S^0 ) (g)</th>
<th>Fraction Theoretical Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>30.2</td>
<td>14.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>22.0</td>
<td>3.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.74</td>
<td>0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(py)</td>
<td>0.40</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>19.37</td>
<td>17.50</td>
<td>0.904</td>
</tr>
</tbody>
</table>

**TABLE A7** Calculation of the Fraction Theoretical Sulphur Yield

<table>
<thead>
<tr>
<th>In</th>
<th>( S(\text{solid}) )</th>
<th>( S(\text{SO}_4^{2-}) )</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(ore)</td>
<td>24.8 ( S(S^0 ) ore)</td>
<td>25.6 ( S(\text{acid}) )</td>
<td>50.4</td>
</tr>
<tr>
<td>Diff.</td>
<td>26.4 ( S(\text{residue total}) )</td>
<td>23.9 ( S(\text{solution out}) )</td>
<td>50.3</td>
</tr>
</tbody>
</table>

\( S(\text{SO}_4^{2-} \) precip) = 3.40 g (equation (A37) - see Table A7 also)
\( S(\text{SO}_4^{2-} \) formed) = 3.40 - 1.6 = 1.8 g (equation (A40))
\( = 3.40 - 1.7 = 1.7 \) g (equation (A39))
\( S^0_{\text{theoretical}} - S^0_{\text{actual}} = 1.87 \) g
\( S(E) = 1.8 - 1.87 \) (equation A(43))
\( = -0.07 \) g

\( (\alpha_7)_{\text{sulphate}} = \frac{1.8}{19.37} = 0.093 \) (equation (A42))

\( (\alpha_7)_{\text{sulphate}} + (\alpha_7)_{\text{sulphur}} = 0.904 + 0.093 = 0.997 \sim 1.00 \)

**TABLE A8** Calculation of the Fraction Theoretical Sulphate Yield

In Table A8 if the error in the overall mass balance, 0.1 g, is assigned to the \( S(\text{solution out}) \) value (see § 5.7 for reasons why this value is likely to be in error), estimates of \( S(\text{SO}_4^{2-} \) formed) from equations (A39) and (A40) concur.
### APPENDIX 6 ADDITIONAL RESULTS

<table>
<thead>
<tr>
<th>EXPERIMENT NUMBER</th>
<th>WEIGHT DEPON (W₄)</th>
<th>TOTAL RESIDUE WEIGHT (WR)</th>
<th>WEIGHT OF NODULE RESIDUE (W₉)</th>
<th>FINAL ZINC EXTRACTION (Zᵧ, Zᵧ₁, Zᵧ₂)</th>
<th>TOTAL IRON EXTRACTION (Fe total)</th>
<th>δD</th>
<th>tD</th>
<th>RESERVOIR PRESSURE DROP AFTER TIME tD</th>
<th>VOLUME PRESERVATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g</td>
<td>g</td>
<td>g</td>
<td>Time (hours)</td>
<td>min. psi</td>
<td>l(STP)</td>
<td>-</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>103.4</td>
<td>80.5</td>
<td>11.0</td>
<td>26.9</td>
<td>0.133</td>
<td>0.170</td>
<td>0.214</td>
<td>0.257</td>
<td>0.292</td>
</tr>
<tr>
<td>1a</td>
<td>117.4</td>
<td>88.0</td>
<td>7.2</td>
<td>30.1</td>
<td>0.161</td>
<td>0.197</td>
<td>0.236</td>
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<td>0.167</td>
<td>0.164</td>
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<td>0.192</td>
<td>0.240</td>
<td>0.313</td>
<td>0.373</td>
</tr>
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</table>

** EQUATION **

\[ W_r' = W_f - W_z \]

\[ W_R = W_X + W_Y + W_Z \]

\[ a_{Fe total} = \frac{Fe_i}{(Fe_i') (ore)} \]

** TABLE A9 ** ADDITIONAL RESULTS
### APPENDIX 7  ERRORS

<table>
<thead>
<tr>
<th>EXPERIMENT NUMBER</th>
<th>E(%) *</th>
<th>Fe corr (%) **</th>
<th>E_m (%) ***</th>
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<td>Pb</td>
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<td>22</td>
<td>1.4</td>
<td>-4.8</td>
<td>3.9</td>
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#### Mean Error

* Mean Error = \( \frac{\sum |E|}{n} \)  

** E(%) = \( \frac{M^1 - (M_2 + M^2)}{M^1} \) \times 100 

*** Fe corr (%) = \( \frac{Fe^1 - Fe^2}{Fe^1} \) \times 100 

**** E_m (%) = \( \frac{M^1 - M^2}{M^2} \) \times 100 

******** Mean Error = \( \frac{\sum |E|}{n} \) 

| TABLE A10  ERRORS |
APPENDIX 8  THERMODYNAMICS

A8.1 FREE ENERGY DATA

<table>
<thead>
<tr>
<th>Formula</th>
<th>State</th>
<th>( \Delta G^\circ_f (298^\circ K) ) (kcal mol(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
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<td>S</td>
<td>- 47.4</td>
<td>[139]</td>
</tr>
<tr>
<td>CuS</td>
<td>S</td>
<td>- 11.8</td>
<td>[140]</td>
</tr>
<tr>
<td>PbS</td>
<td>S</td>
<td>- 21.9</td>
<td>[140]</td>
</tr>
<tr>
<td>FeS(_2)</td>
<td>S</td>
<td>- 39.8</td>
<td>[139]</td>
</tr>
<tr>
<td>FeS</td>
<td>S</td>
<td>- 23.3</td>
<td>[139]</td>
</tr>
<tr>
<td>PbSO(_4)</td>
<td>S</td>
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<td>H(_2)SO(_4)</td>
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<td>[140]</td>
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<td>Cu(^{++})</td>
<td>g</td>
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<td>[140]</td>
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<td>aq</td>
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</tr>
<tr>
<td>Fe(^{++})</td>
<td>aq</td>
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<td>[140]</td>
</tr>
</tbody>
</table>

Table A11 Thermodynamic Data

A8.2 EQUILIBRIUM CONSTANTS

Consider the following equilibria:

\[ \text{ZnS(s) + 2H}^+(\text{aq}) \rightleftharpoons \text{Zn}^{++}(\text{aq}) + \text{H}_2\text{S(aq)} \]  
\( \Delta G^\circ 298 = 23.4 \text{ kJ mol}^{-1} \)  

and

\[ \text{CuS(s) + 2H}^+(\text{aq}) \rightleftharpoons \text{Cu}^{++}(\text{aq}) + \text{H}_2\text{S(aq)} \]  
\( \Delta G^\circ 298 = 87.8 \text{ kJ mol}^{-1} \) and \( K(\text{A49}) = 4 \times 10^{-16} \text{ mol}^{-1} \)

Covellite data has been used in this illustration because of a lack of information on chalcopyrite.

\[ \text{PbS(s) + 2H}^+(\text{aq}) \rightleftharpoons \text{PbSO}_4(\text{s}) + \text{H}_2\text{S(aq)} \]  
\( \Delta G^\circ 298 = -8.4 \text{ kJ mol}^{-1} \) and \( K(\text{54a}) = 29.4 \text{ mol}^{-1} \)

From the free energy data it can be seen that only galena is favoured thermodynamically to produce \( \text{H}_2\text{S} \) under standard conditions.
A8.3 THERMODYNAMIC CALCULATIONS FOR EXPERIMENT II

Experiment II has been chosen as an illustrative example because it exhibits a well developed incubation period (Fig. 28).

A8.3.1 Galena

The final weight of lead (PbS) converted to lead sulphate was 10.6 g. Assuming parabolic leaching of galena enables the calculation of the weight of lead dissolved after time, \( t_A \). It is impossible to estimate accurately \( t_A \) from Fig. 28 because of the lack of data points but for the purposes of this calculation it is assumed that \( t_A \) equals 1 hr.

Then:

\[
\text{weight of Pb reacted at } t_A = 10.6 \left( \frac{7}{7} \right) = 4.4 \text{ g}
\]

\[
\therefore \quad \text{no. moles reacted} = \frac{4.4}{207} = 2.1 \times 10^{-2} \text{ mol}
\]

\[
= \text{no. moles of } H_2S \text{ formed via equation (54)}
\]

This \( H_2S \) is distributed between the gas and liquid phases. To calculate the fraction in each, consider the equilibrium:

\[
H_2S(aq) \rightleftharpoons H_2S(g)
\]

\[
\Delta G^0 = -5.45 \text{ kJ mol}^{-1}
\]

\[
K(A50) = \frac{[H_2S]_g}{[H_2S]_{aq}} = 9.0
\]

Let

\( n_g \) be the number of moles of \( H_2S \) in the gas

\( n_s \) be the number of moles of \( H_2S \) in solution

\( V_g \) be the volume of the gas

\( V_s \) be the volume of solution

Then, assuming equilibrium is rapidly attained,

\[
\frac{n_g}{V_g} = \frac{n_s}{V_s} = 9.0
\]

and

\[
n_s + n_g = 2.1 \times 10^{-2}
\]

but

\[
V_s = 1 \text{ l}
\]

and

\[
V_g = 3 \text{ l (the autoclave volume minus the solution volume)}
\]

\[
\therefore \quad \frac{n_g}{3n_s} = 9
\]

\[
\therefore \quad n_g = 27 n_s
\]

\[
28 n_s = 2.1 \times 10^{-2}
\]
and

\[ n_S = 7.5 \times 10^{-4} \text{ mol} \]

\[ [\text{H}_2\text{S}]_{\text{aq}} = 7.5 \times 10^{-4} \]

A8.3.2 Sphalerite

Assume that proposal (i) represents the true leaching behaviour, that is, only galena produces H₂S on dissolution. The maximum concentration of Zn in equilibrium with the above H₂S concentration can then be calculated from \( K_{(32a)} \):

\[ [\text{Zn}^{2+}] = \frac{K_{(32a)} \times [\text{H}^+]^2}{[\text{H}_2\text{S}]_{\text{aq}}} = \frac{7.9 \times 10^{-5} \times 0.25}{7.5 \times 10^{-4}} \]

where \( [\text{H}^+] = [\text{H}_2\text{SO}_4]/0.8 \) ...... reference [64]

then

\[ [\text{Zn}^{2+}] = 2.64 \times 10^{-2} \]

\[ C_Z = 2.64 \times 10^{-2} \times 65.4 \]

i.e.

\[ C_Z = 1.7 \text{ g l}^{-1} \]

In practice the \([\text{H}_2\text{S}]_{\text{aq}}\) value calculated from the weight of lead dissolved is reduced by the amount of H₂S oxidised in the first hour. This would lead to a larger estimate of \( C_Z \). The experimental value of \( C_Z \) after one hour's leaching was 1.0 g l⁻¹ which is in reasonable agreement with the predicted value considering the assumptions necessary to make the calculations.

Assume that proposal (ii) represents the true leaching behaviour, that is, sphalerite dissolves via reaction (32) with the evolution of H₂S. Then,

\[ K_{(32a)} = \frac{[\text{Zn}^{2+}] \times [\text{H}_2\text{S}]_{\text{aq}}}{[\text{H}^+]^2} \]

but from equation (32) equimolar quantities of \( \text{Zn}^{2+} \) and \( \text{H}_2\text{S} \) are produced

\[ [\text{Zn}^{2+}]^2 = [\text{H}_2\text{S}]_{\text{aq}}^2 = K_{(32a)} \times [\text{H}^+]^2 \]

\[ = 7.9 \times 10^{-5} \times 0.25 \]

\[ = 2 \times 10^{-5} \]

\[ [\text{Zn}^{2+}] = [\text{H}_2\text{S}]_{\text{aq}} = 4.5 \times 10^{-5} \]

i.e.

\[ C_Z = 4.5 \times 10^{-5} \times 65.4 \]

\[ C_Z = 0.003 \text{ g} \]

But \( C_Z \) was experimentally determined to be 1.0 g. Therefore proposal (i), in which galena only evolves H₂S on dissolution, is the favoured explanation of the leaching behaviour.
A8.3.3 Chalcopyrite

The \( \text{H}_2\text{S} \) concentration in equilibrium with the minimum concentration of copper ion detectable by AAS, 0.04 \( \mu \text{g} \text{ ml}^{-1} \), is very small.

\[
[H_2S]_{\text{aq}} = \frac{K(AAS) \cdot [H^+]^2}{[\text{Cu}^{2+}]} = \frac{4 \times 10^{-16} \cdot 0.25}{4 \times 10^{-5}/63.5}
\]

i.e.

\[
[H_2S]_{\text{aq}} = 1.6 \times 10^{-10}
\]

From the distribution of \( \text{H}_2\text{S} \) between gas and liquid the total number of moles of \( \text{H}_2\text{S} \) formed to achieve this concentration in solution is given by:

\[
n_l = n_g + n_s
\]

\[
= 28 n_s
\]

\[
= 28 \cdot 1.6 \times 10^{-10}
\]

\[
n_l = 4.5 \times 10^{-9} \text{ moles}
\]

The weight of galena reacted to produce this concentration is given by:

\[
Pb(PbS) = 207 \cdot 4.5 \times 10^{-9}
\]

\[
= 9.3 \times 10^{-7}
\]

i.e.

\[
Pb(PbS) = 10^{-6} \text{ g}
\]

It is obvious that \( n_l \) moles of \( \text{H}_2\text{S} \) are evolved in a matter of seconds and no copper will be detected in solution samples until the concentration drops below this value at \( t_E \).

A8.3.4 Partial Pressure of \( \text{H}_2\text{S} \) at \( t_A \)

The partial pressure of \( \text{H}_2\text{S} \) can be calculated from Henry's Law.

viz:

\[
P_{\text{H}_2\text{S}} = H \cdot x_{\text{H}_2\text{S}}
\]

from Table 14-21, Perry [127], \( H = 14.8 \text{ atm (mol fraction)}^{-1} \) at \( 100^\circ \text{C} \) for \( \text{H}_2\text{S} \) in pure water.

\[
P_{\text{H}_2\text{S}} = 14.8 \times 10^2 \cdot \frac{7.5 \times 10^{-4}}{55.56}
\]

\[
= 2 \times 10^{-2} \text{ atm}
\]

i.e.

\[
P_{\text{H}_2\text{S}} = 2 \text{ kPa}
\]

The solubility in sulphuric acid is lower than in pure water and this would lead to a slightly higher value for \( p_{\text{H}_2\text{S}} \). However, the partial pressure would still be very much less than the autoclave operating pressure and the pressure rise due to \( \text{H}_2\text{S} \) evolution would have been undetectable by visual observation of the pressure gauge.
REFERENCES


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125. Schäde, G. Personal communication.

126. Wright, G. Personal communication.


