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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:

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NOMENCLATURE

A
Particulate surface area/unit mass

Preexponential factor in the Arrhenius equation

$A_0, A_1$
Initial particulate surface area/unit mass

a
Activity

C
Concentration, catalyst

D
Diffusivity

$D_p$
Particle diameter

E
Error defined by equation (A15)

$E_a$
Activation energy

e
Electron

F
Faraday constant

G
Gibbs free energy

H
Enthalpy

K
Equilibrium constant

k
Constant

$k_l$
Rate constant

$k_p$
Linear rate constant

Parabolic rate constant

L
Autoclave liner, a kinetic parameter

M, Me
Metal

M
Mineralogy of the ore, a kinetic parameter

$M_i$
Weight of metal M charged in the sample introducer

$M_i'$
Weight of metal M introduced to the leachant

$M_{out}$
Total weight of metal M present at the completion of leaching (solution + residue)

$M_t$
Weight of metal M extracted after time t, calculated from the sample analyses

$M_t'$
Weight of metal M extracted after time t, calculated from the final leach solution analysis

$M_t''$
Weight of metal M extracted after seven hours calculated from the residue and ore analyses

MR
Mol ratio of acid/ore based on the supposed requirement of one mol of acid for each mol of Zn, Pb, Fe and Cu in the ore.

M$
$
Molecular weight

m
Mass

N
Number of molecules

n
An integer

P
Reaction product

Pressure

$P_b$
Barometric pressure
\( p \)  
\( p \)  
\( P_{H_2O} \)  
\( P_{H_2S} \)  
\( P_{O_2} \)  
\( R \)  
\( r \)  
\( r_0 \)  
\( S_{OX} \)  
\( T \)  
\( t \)  
\( V \)  
\( V' \)  
\( V_f \)  
\( V_i \)  
\( V_o \)  
\( v \)  
\( W \)  
\( W' \)  
\( W_R \)  
\( W_X \)  
\( W_Y \)  
\( W_Z \)  
\( W_M \)  
\( x \)  
\( a \)  
\( a_t \)  
\( y_t \)  
\( \rho \)  
\( \delta \)  
\( \Delta \)  
\( \epsilon \)  
\( \theta \)  
\( \omega \)  
\( \phi \)  
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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