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SULPHURIC ACID, OXYGEN PRESSURE

LEACHING OF A BASE-METAL

SULPHIDE ORE

THESIS SUBMITTED FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

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BY

G. J. TEGG

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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.

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NOMENCLATURE

A	Particulate surface area/unit mass
	Prexponential factor in the Arrhenius equation
A_0, A_i	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
	Rate constant
k_l	Linear rate constant
k_p	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_7''	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.
MW	Molecular weight
m	Mass
N	Number of molecules
n	An integer
P	Reaction product
	Pressure
P_b	Barometric pressure

P_g	gauge pressure
P	Partial pressure
P_{H_2O}	Partial pressure of water
P_{H_2S}	Partial pressure of hydrogen sulphide
P_{O_2}	Partial pressure of oxygen
R	Universal gas constant
	Reactant species
r	Particle radius
r_0	Initial particle radius
S_{ox}	Surface oxidation, a kinetic parameter
T	Temperature
t	Time
V	Volume
V'	Effective initial volume of leachant
V_f	Potential barrier
V_I	Initial reaction velocity
V_0	Initial particulate volume
v	Initial decrease in the volume of gas in the sample line
W	Weight of ore charged to the sample introducer
W'	Weight of ore introduced to the leachant
W_R	Total weight of residue
W_X	Weight of residue suspended in the solution at the completion of leaching
W_Y	Weight of residue adhering to the baffles at the completion of leaching
W_Z	Weight of residue remaining in the sample introducer
W_M	Weight percent of metal M in the ore or residue
x	Thickness of a product layer on a mineral substrate
α	Electron affinity of an adatom
α_t	Fraction extracted after time t
γ, ρ	Density
δ	Thickness of the hydrodynamic boundary layer, defined by equation (18)
Δ	Difference
e	E.m. f.
θ	Fraction of surface covered, defined by equation (53)
ω	Agitator rotation velocity
ϕ	Work function

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