

THE ROLE OF SURFACTANTS IN THE LEACHING OF ZINC SULPHIDE
MINERALS AT TEMPERATURES ABOVE THE MELTING POINT OF SULPHUR

By

George Owusu

B.Sc.(Hons) Metallurgical Eng., University of Science & Tech., Kumasi, Ghana, 1985

M. A. Sc. Metallurgical Eng. University of British Columbia, Vancouver, Canada, 1989

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES

METALS AND MATERIALS ENGINEERING

We accept this thesis as conforming

to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

June 1993

© George Owusu, 1993

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.



Metals and Materials Engineering
The University of British Columbia
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date:

26/7/93

ABSTRACT

The role of the surfactants lignin sulfonic acid, cocoamido hydroxyl sulfobetaine (CAHSB), tallowamido hydroxyl sulfobetaine (TAHSB), cocoamido betaine (CAB), naphthalene sulfonic acid-formaldehyde condensates and orthophenylene diamine (OPD) in the liquid sulfur-aqueous zinc sulphate-zinc sulfide mineral system has been studied. The effect of the various surfactants on the liquid sulfur-aqueous system interfacial tensions and the liquid sulfur-mineral contact angle were measured in a high temperature-high pressure apparatus. In the absence of any surfactant, the liquid-liquid interfacial tension measured 54 ± 1 mN/m, and the liquid sulfur-mineral contact angle was $80 \pm 5^\circ$. In the presence of 0.3 g/L lignin sulfonic acid, the interfacial tension decreased to about 29 ± 1 mN/m; the interfacial tension was not sensitive to any further increase in the surfactant concentration. The contact angle measured $145 \pm 5^\circ$ in the presence of 0.07–0.3 g/L of the surfactant. The presence of OPD in the solution did not have any effect on the liquid sulfur-aqueous solution interfacial tension but increased the contact angle to about $130 \pm 5^\circ$. At a concentration of 0.1 g/L, naphthalene sulfonic acid-formaldehyde condensates decreased the interfacial tension to 21 ± 1 mN/m. Beyond this concentration, the liquid-liquid interface was not sensitive to any further increase. The contact angle increased to $155 \pm 5^\circ$ even at concentrations as low as 0.05 g/L. CAHSB exhibited just about the same efficiency as lignin sulfonic acid. TAHSB and CAB required higher concentrations in order to effect any substantial changes in the liquid sulfur-aqueous solution interfacial tension. They also effected a contact angle increase to $135 \pm 5^\circ$. With the exception of OPD, all the surfactants adsorbed at both the liquid-liquid and aqueous-solid interfaces. OPD, on the other hand adsorbed at only the aqueous-solid interface.

When introduced into leaching systems, the surfactants influenced the metal extraction to different extents. OPD and lignin sulfonic acid were the most efficient surfactants (or dispersants for liquid sulfur). The extent of zinc extraction was enhanced to about 94 % for lignin sulfonic acid and over 99 % for OPD under both low or high pulp density conditions. The other surfactants were unable to enhance zinc extraction even under low pulp density conditions. Application of metaphenylene diamine as dispersant for liquid sulfur under both low and high pulp density leaching conditions resulted in zinc extractions in excess of 98 %. A combination of the interfacial studies and the leaching experiments indicates that the most important characteristic for any effective surfactant under pressure leaching conditions is for the surfactant to adsorb at the aqueous phase–solid interface and increase the liquid sulfur–mineral contact angle.

Infrared spectral analysis of both sphalerite leach residue and pulped sphalerite indicates that the lignin sulfonate ions are adsorbed both physically and chemically by the mineral. The chemically adsorbed species form a Zn(II)–based complex that has an organic portion similar to the bulk surfactant structure. OPD, on the other hand, is adsorbed chemically through the interaction of the C–N functional group with the metal ions forming a metal–amine complex.

Table of Contents

ABSTRACT	ii
List of Tables	vii
List of Figures	xi
List of Symbols	xvi
ACKNOWLEDGEMENT	xx
1 INTRODUCTION	1
2 LITERATURE SURVEY	4
2.1 ELECTROCHEMICAL PROPERTIES OF METAL SULFIDES	5
2.2 LEACHING OF SULFIDE MINERALS	6
2.2.1 Leaching of Zinc Sulfide Minerals	9
2.2.2 The Behaviour of Sulfur in Oxidative Leaching of Sulfide Ores . .	22
2.2.3 Effect of Sulfur in Blocking Leaching Reactions	24
2.2.4 Interfacial Phenomena	25
2.3 PROPERTIES OF LIQUID SULFUR	26
2.4 SURFACTANTS AND INTERFACIAL PROPERTIES	27
2.4.1 Characteristic Features of Surfactants	27
2.4.2 Surfactants Identified for Study	30
2.4.3 Properties of Individual Surfactants	31

2.5	INFRARED SPECTROSCOPY	36
2.5.1	Theory of Infrared Spectroscopy	37
2.5.2	Molecular Force Constants	38
2.5.3	Absorption of Infrared Radiation	40
2.5.4	Infrared Techniques	42
3	OBJECTIVES AND EXPERIMENTAL APPROACH	51
3.1	OBJECTIVES	51
3.1.1	Scope of Study and Approach	52
4	EXPERIMENTAL TECHNIQUES	53
4.1	INTERFACIAL PHENOMENA	53
4.1.1	Interfacial Tension	56
4.1.2	Contact Angle Measurements	58
4.1.3	Work of Adhesion	64
4.2	PRESSURE LEACHING OF SPHALERITE, (ZnS)	65
4.2.1	Low Pulp Density Leaching	66
4.2.2	High Pulp Density Leaching	67
4.3	INFRARED STUDIES	70
4.3.1	KBr Technique	71
4.3.2	Attenuated Total Reflection Technique	71
5	RESULTS AND DISCUSSION	80
5.1	INTERFACIAL PHENOMENA	80
5.1.1	Results	80
5.1.2	Discussion	84
5.2	PRESSURE LEACHING OF SPHALERITE CONCENTRATE	101

5.2.1	Results	101
5.2.2	Discussion	109
5.3	INFRARED SPECTROSCOPY	132
5.3.1	Results	132
5.3.2	Adsorption Studies in the Presence of Orthophenylene Diamine .	156
6	CONCLUSIONS AND RECOMMENDATIONS	175
6.1	CONCLUSIONS	175
6.2	RECOMMENDATIONS	178
	Bibliography	180

List of Tables

2.1	Electronic properties of selected sulfide minerals	5
5.2	Surface activity of OPD at a concentration of 0.3g/L in the presence of [Fe ²⁺] = 0.05 M, [Fe ³⁺] = 0.12 M, [H ₂ SO ₄] = 0.2 M, and [ZnSO ₄] = 1.2 M, Temp.= 135±5°C	81
5.3	Effect of silicate ions (0.15g/L) on the surface activity of OPD (0.3 g/L) in the presence of [H ₂ SO ₄] = 0.2 M and [ZnSO ₄] = 1.2 M, Temp.= 135±5°C	81
5.4	Contact angle measurements in the presence of the various surfactants: conditions - [ZnSO ₄] = 1.2 M, Temp.= 135±5°C	82
5.5	Contact angle measurements in the presence of different surfactants and ionic species; conditions: [ZnSO ₄] = 1.2 M, [Fe ²⁺] = 0.05 M, [Fe ³⁺] = 0.12 M and [H ₂ SO ₄] = 0.2 M, Temperature = 135°C	83
5.6	Work of adhesion, W_a , in the presence of 0.3g/L of different surfactants; conditions: [ZnSO ₄] = 1.2 M, Temperature = 135°C; no other ionic species present in solution	84
5.7	Work of adhesion, W_a , in the presence of 0.3g/L surfactants; conditions: [ZnSO ₄] = 1.2 M, [H ₂ SO ₄] = 0.2 M, [Fe ²⁺] = 0.05 M and [Fe ³⁺] = 0.12 M, Temperature = 135°C.	84
5.8	Resultant work, W , for complete sulfur wetting (a hypothetical situation) in the presence of 0.3 g/L of surfactant and [ZnSO ₄] = 1.2 M	90
5.9	Variation of $\gamma_{MA} - \gamma_{MS}$ with respect to aqueous condition; [ZnSO ₄] = 1.2 M; other ionic species absent	91

5.10	Extent of zinc extraction using different surfactants under low pulp density conditions and nitrogen atmosphere; initial conditions: $[\text{ZnSO}_4] = 2 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$; $[\text{Fe}^{3+}]=[\text{Fe}^{2+}]=0.15 \text{ M}$; Temp.= $140\pm 1^\circ\text{C}$; $P_{N_2} = 1100 \text{ kPa}$; B–batch addition; C–continuous addition	102
5.11	Effect of naphthalene sulfonic acid on the extent of zinc extraction under low pulp density conditions; initial conditions: $[\text{ZnSO}_4] = 2 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$; $[\text{Fe}^{3+}]=[\text{Fe}^{2+}]=0.15 \text{ M}$; Temp.= $140\pm 1^\circ\text{C}$; $P_{N_2} = 1100 \text{ kPa}$; B–batch addition; C–continuous addition	102
5.12	Extent of zinc leaching using OPD as surfactant under low pulp density conditions; initial conditions: $[\text{ZnSO}_4] = 2 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$; $[\text{Fe}^{3+}]=[\text{Fe}^{2+}]=0.15 \text{ M}$; Temp.= $140\pm 1^\circ\text{C}$; $P_{N_2} = 1100 \text{ kPa}$; B–batch addition; C–continuous addition	103
5.13	Extent of zinc extraction using MPD and PPD as surfactants (batch additions) under low pulp density conditions; initial conditions: $[\text{ZnSO}_4] = 2 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$; $[\text{Fe}^{3+}]=[\text{Fe}^{2+}]=0.15 \text{ M}$; Temp.= $140\pm 1^\circ\text{C}$; $P_{N_2} = 1100 \text{ kPa}$	103
5.14	Extent of zinc extraction after 30 minutes of low pulp density leaching under oxygen pressure; concentrate sample size: 8-10 g; initial conditions: $[\text{ZnSO}_4] = 2 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$; $[\text{Fe}^{3+}]=[\text{Fe}^{2+}]=0.15 \text{ M}$; Temp.= $140\pm 1^\circ\text{C}$; $P_{O_2} = 1100 \text{ kPa}$; Batch addition of surfactants	105
5.15	Weight loss due to leaching in the absence and presence of different surfactants under high pulp density conditions; initial conditions: $[\text{ZnSO}_4] = 1.27 \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.12 \text{ M}$; $[\text{Fe}^{2+}]=0.14 \text{ M}$; Temp.= $140\pm 1^\circ\text{C}$; $P_{O_2} = 1100 \text{ kPa}$; Batch addition of surfactants	120

5.16	Extent of zinc extractions (computed from residue analysis) and the changes in Zn^{2+} (aq) concentration of the filtrate in the presence of different surfactants and under high pulp density conditions; initial conditions: $[\text{ZnSO}_4] = 1.27 \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.12 \text{ M}$; $[\text{Fe}^{2+}] = 0.14 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$; batch addition of surfactants. * Residue analysis	120
5.17	Iron extractions (based on residue analysis) in the presence of different surfactants and under high pulp leaching conditions; initial conditions: $[\text{ZnSO}_4] = 1.27 \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.12 \text{ M}$; $[\text{Fe}^{2+}] = 0.14 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$	121
5.18	Oxygen and acid (as H^+ ions) requirements per 100 gram sphalerite concentrate and 1.5 L leach solution <i>assuming</i> complete oxidation of concentrate after test period. "x" represents the fractional conversion of sulfur to sulfate	121
5.19	Experimental data for oxygen and acid (measured as H^+) consumptions in the presence of different surfactants; initial conditions: $[\text{ZnSO}_4] = 1.27 \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.12 \text{ M}$; $[\text{Fe}^{2+}] = 0.14 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$	122
5.20	Elemental sulfur analysis of leach residue and filtrate and the extent of total sulfide sulfur oxidation to sulfate (as %); initial conditions: $[\text{ZnSO}_4] = 1.27 \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.12 \text{ M}$; $[\text{Fe}^{2+}] = 0.14 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$	122
5.21	Calculated oxygen and acid (as H^+) requirements for the different experimental conditions, assuming NO elemental sulfur oxidation	123
5.22	Comparison between experimental and calculated oxygen requirements for the different experimental conditions; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$	123

5.23 Total leaching efficiencies and iron:zinc ratios; initial conditions: $[\text{ZnSO}_4]$ $= 1.27 \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.12 \text{ M}$; $[\text{Fe}^{2+}] = 0.14 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} =$ 1100 kPa	124
--	-----

List of Figures

2.1	Current density- potential diagram; after Wadsworth [1].	47
2.2	Viscosity of liquid sulfur; after Tuller [78].	47
2.3	Possible structure of lignin sulfonate; after Pearl [86].	48
2.4	Structure of OPD; after reference [92].	48
2.5	Structure of naphthalene sulfonic acid-formaldehyde condensates; after Rosen [83].	49
2.6	Atomic energy levels; after Hair [121].	49
2.7	Internal reflection effect; after references [121].	50
4.8	Profile of pendant drop.	75
4.9	Contact angle between a liquid and solid surface: a) in the absence of any surfactant; b) in the presence of a surfactant.	75
4.10	Cross-section of high temperature and pressure stainless-steel bomb. . .	76
4.11	Experimental set-up for monitoring oxygen flow rate.	77
4.12	Injection Unit.	78
4.13	KBr Transmission.	78
4.14	ATR Accessory.	79
5.15	Liquid sulfur-aqueous solution interfacial tensions in the presence of dif- ferent surfactants; $[\text{ZnSO}_4] = 1.2 \text{ M}$; Temperature = $135 \pm 5^\circ\text{C}$; $P_{\text{N}_2} = 620$ kPa.	96

5.16	Liquid sulfur–aqueous solution interfacial tensions in the presence $[\text{Fe}^{3+}] = 0.12 \text{ M}$, $[\text{Fe}^{2+}] = 0.05 \text{ M}$ and 0.3 g/L naphthalene sulfonic acid; $[\text{H}_2\text{SO}_4] = 0.2 \text{ M}$, Temperature = $135 \pm 5^\circ\text{C}$; $P_{N_2} = 620 \text{ kPa}$	96
5.17	Liquid sulfur–zinc sulfide mineral contact angle in surfactant-free system; $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = 135°C ; $P_{N_2} = 620 \text{ kPa}$	97
5.18	Liquid sulfur–zinc sulfide mineral contact angle in the presence of 0.3 g/L naphthalene sulfonic acid–formaldehyde condensates, $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = 135°C ; $P_{N_2} = 620 \text{ kPa}$	97
5.19	Liquid sulfur–zinc sulfide mineral contact angle in the presence of 0.15 g/L OPD; conditions: $[\text{Fe}^{2+}] = 0.05 \text{ M}$, $[\text{Fe}^{3+}] = 0.12 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.2 \text{ M}$, Temperature = 135°C ; $P_{N_2} = 620 \text{ kPa}$	98
5.20	Photograph of liquid sulfur suspended in surfactant-free zinc sulfate solution: conditions; $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = $135 \pm 5^\circ\text{C}$; $P_{N_2} = 620 \text{ kPa}$	98
5.21	Photograph of liquid sulfur suspended in aqueous solution in the presence of 0.3 g/L naphthalene sulfonic acid–formaldehyde condensates; conditions: $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = 135°C ; $P_{N_2} = 620 \text{ kPa}$	99
5.22	Different stages of wetting	99
5.23	Interfacial excess of naphthalene sulfonic acid–formaldehyde condensates at the liquid sulfur–aqueous solution interface; conditions: $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = $135 \pm 5^\circ\text{C}$; $P_{N_2} = 620 \text{ kPa}$	100
5.24	Interfacial excess of lignin sulfonic acid at the liquid sulfur–aqueous solution interface; conditions: $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = $135 \pm 5^\circ\text{C}$; $P_{N_2} = 620 \text{ kPa}$	100

5.25	Extent of zinc extraction in the presence of OPD, MPD, PPD and naphthalene sulfonic acid-formaldehyde condensates; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa; sample weight ~ 12 grams.	125
5.26	Extent of zinc extraction under high pulp density leaching conditions in the presence of OPD; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa.	125
5.27	Instantaneous oxygen flow rate in the absence of any surfactant; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa.	126
5.28	Instantaneous oxygen flow rate in the presence of lignin sulfonic acid; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa.	126
5.29	Instantaneous oxygen flow rate in the presence of OPD; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa.	127
5.30	Instantaneous oxygen flow rate in the presence of 0.1 g/L MPD; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa.	127
5.31	Cumulative oxygen consumed in the absence and presence of lignin sulfonic acid; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa.	128
5.32	Cumulative oxygen consumed in the presence of OPD; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa.	128
5.33	Cumulative oxygen consumed in the presence of MPD; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa.	129
5.34	Relative consumptions of oxygen in the presence of the different surfactants; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa.	129
5.35	A photograph of zinc sulfide leach residue in the absence of a surfactant after 60 minutes; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa.	130
5.36	A photograph of zinc sulfide leach residue in the presence of 0.1 g/L lignin sulfonic acid after 60 minutes; Temp.= $140\pm 1^{\circ}\text{C}$; P_{O_2} = 1100 kPa.	130

5.37	A photograph of zinc sulfide leach residue in the presence of 0.1 g/L OPD after 60 minutes; Temp.= $140\pm 1^{\circ}\text{C}$; $P_{O_2} = 1100$ kPa.	131
5.38	A photograph of zinc sulfide leach residue in the presence of 0.1 g/L MPD after 60 minutes; Temp.= $140\pm 1^{\circ}\text{C}$; $P_{O_2} = 1100$ kPa.	131
5.39	Infrared spectrum of sphalerite using KBr pellet technique.	146
5.40	ATR spectrum of wet sphalerite.	146
5.41	KBr disc spectrum of lignin sulfonic acid.	147
5.42	KBr disc spectrum of Zn-based lignin sulfonate complex.	148
5.43	KBr pellet spectrum of Na-based lignin sulfonate complex.	149
5.44	ATR spectrum of lignin sulfonic acid solution; solution condition: $[\text{Fe}^{3+}] = 0.025$ M, $[\text{H}_2\text{SO}_4] = 0.036$ M, Temperature = 25°C ; reference spectrum: solvent.	150
5.45	ATR spectrum of sphalerite conditioned in surfactant solution for 20 minutes; solution condition: $[\text{Fe}^{3+}] = 0.025$ M, $[\text{H}_2\text{SO}_4] = 0.036$ M, Temp. = 25°C : (a) reference: solvent spectrum (b) less solution spectrum.	151
5.46	ATR spectrum of washed sphalerite after conditioning in surfactant/ferric solution, reference spectrum: solvent.	152
5.47	ATR spectrum of sphalerite conditioned in ferric free-surfactant solution for 20 minutes; solution condition: $[\text{H}_2\text{SO}_4] = 0.036$ M, Temp.= 25°C . (a) reference: solvent spectrum (b) less the solution spectrum.	153
5.48	ATR spectrum of washed sphalerite after contact with ferric free-surfactant solution, reference spectrum: solvent.	154
5.49	KBr pellet spectrum of leached sphalerite (in the presence of surfactant) residue; leaching performed at $140\pm 1^{\circ}\text{C}$ for 15 minutes under $P_{N_2} = 1100\text{kPa}$; lignin sulfonate solution concentration: 5 g/L at flow rate = 2 mL/min.	155

5.50 KBr pellet spectrum of OPD.	168
5.51 ATR spectrum of 5 g/L solution of OPD; solution condition: $[\text{H}_2\text{SO}_4] = 0.036 \text{ M}$, Temperature = 25°C ; reference spectrum: solvent.	169
5.52 ATR spectrum of sphalerite conditioned in OPD solution (no ferric pre-treatment) for 20 minutes; solution condition: $[\text{H}_2\text{SO}_4] = 0.036 \text{ M}$, Temp. = 25°C (a) reference spectrum: solvent (b) less solution spectrum.	170
5.53 ATR spectrum of sphalerite washed after conditioning in 5 g/L OPD solution for 20 minutes, reference spectrum: solvent.	171
5.54 ATR spectrum of sphalerite conditioned in 5 g/L OPD solution (after ferric pre-treatment) for 20 minutes; solution condition: $[\text{H}_2\text{SO}_4] = 0.036 \text{ M}$, Temp. = 25°C (a) Reference spectrum: solvent (b) less the solution spectrum.	172
5.55 ATR spectrum of washed sphalerite after contact with ferric/OPD solution, reference spectrum: solvent.	173
5.56 Metal-OPD complex on interaction.	174

List of Symbols

- a_i – activity of species i
- a – surface area of solid substrate in contact with liquid, cm^2 or m^2
- A – integrated absorbance; cm^{-1}
- c_{RX_z}, c_2 – concentration of solute in bulk solution, mol/L
- $\bar{c}$ – concentration of absorbing species; moles
- c – speed of light; 3×10^{10} cm/sec
- d_e – equatorial diameter of drop, cm
- d_s – diameter of drop at a distance D_e from apex, cm
- d_e^m – magnified diameter of pendant drop, cm
- E_h – electrode potential; V
- e – electron
- E° – standard electrode potential; V
- E – energy; ergs, joules or eV
- E_{total} – resultant molecular energy; ergs, joules or eV
- E_{elec} – electronic energy contribution; ergs, joules or eV
- E_{vib} – vibrational energy contribution; ergs, joules or eV
- $E_{rotn.}$ – rotational energy contribution; ergs, joules or eV
- $E_{transl.}$ – translational energy contribution; ergs, joules, or eV
- f_i – activity coefficient of component i
- F – Faraday's constant
- g – acceleration due to gravity, 9.81 m/s^2 or 981 cm/s^2

$-\Delta G$	–	interfacial free energy change; joules or ergs
h	–	Planck's constant
H	–	dimensional parameter as a function of drop shape
I_a	–	anodic current density; A/m ²
I_c	–	cathodic current density; A/m ²
I	–	intensity of transmitted radiation
I_o	–	intensity of incident radiation
K_{eq}	–	equilibrium constant
k	–	absorption coefficient of sample; mol ⁻¹ liter cm ⁻¹
l	–	path length of radiation through absorbing sample, cm
m	–	ionic speciation parameter of surfactant
m_1, m_2	–	atomic masses
MS	–	metal sulfide
n	–	number of electrons
n_2, n_1	–	refractive indexes of sample material and reflector respectively
n_{21}	–	ratio of sample to IRE refractive indexes
p	–	differential pressure, atmospheres or kPa
R_1, R_2	–	radii of curvature, cm
R	–	universal gas constant
RX	–	ionic surfactant
S°	–	elemental sulfur
S	–	shape ratio of pendant drop
$\vec{T}$	–	transmittance
T	–	temperature; °C

- w_o – original diameter of drop forming tip, cm
- w_m – magnified diameter of drop forming tip, cm
- W_a – reversible work of adhesion per unit area; ergs/cm² or joules/cm²
- W_a^D – dispersion force component of work of adhesion
- W_a^P – polar force component of work of adhesion
- W_a^H – hydrogen bonding force component of W_a^P
- W_a^{DD} – dipole–dipole interactions component of W_a^P
- W_a^E – electrostatic interactions component of W_a^P
- W_a^π – π bonding component of W_a^P
- $\bar{x}$ – molar concentration ratio of inorganic to organic salts
- Y, X – dimensionless variables
- y – vertical height of liquid measured from apex of drop, cm or m
- z – valency of organic surface active ion

θ	–	mineral - liquid sulfur contact angle, degrees
γ_{MA}	–	mineral - aqueous solution interfacial tension, mN/m or dynes/cm
γ_{SA}	–	liquid sulfur - aqueous solution interfacial tension, mN/m or dynes/cm
γ_{MS}	–	mineral - liquid sulfur interfacial tension, mN/m or dynes/cm
Γ_2^1, Γ_i	–	relative surface/interface excess of solute at the interface per unit area, mol/m ²
μ_2	–	chemical potential of solute
ξ_i	–	activity coefficient parameter for component i
φ_o	–	surface/interface potential
σ	–	Boltzman's constant
η_a	–	anodic overpotential; V
η_c	–	cathodic overpotential; V
ν	–	frequency of vibration; sec ⁻¹
κ	–	force constant or strength
μ_m	–	reduced mass of atoms
ϑ	–	wavenumber; cm ⁻¹
λ	–	wavelength of incoming (incident) radiation; cm
ϵ	–	extinction coefficient; cm ⁻¹
θ_c	–	critical angle of IRE; degrees
γ	–	interfacial tension, mN/m or dynes/cm
ρ	–	difference in density between liquids under test, kg/m ³ or g/cm ³
β	–	dimensionless parameter

ACKNOWLEDGEMENT

I wish to express my sincere thanks to my research supervisors Drs. David Dreisinger and Ernest Peters for their patience and guidance during the course of my research.

I will like to express my gratitude to NSERC and the Department of Metals and Materials Engineering of this university for financial support during my professional studies. I also wish to extend my sincere thanks to any person who in any way contributed to making this work a success.

Lastly, I owe much gratitude to my uncle and mother for their moral and material support throughout my education.

Chapter 1

INTRODUCTION

Sulfide minerals are the main source of most non-ferrous base metals, and can be an important source for some precious metals as well. The most important source of zinc is the mineral sphalerite (ZnS). Chalcopyrite (CuFeS_2) is the predominant copper mineral, although copper may be extracted from other sulfide minerals such as bornite (Cu_5FeS_4), chalcocite (Cu_2S), and covellite (CuS). Until the last forty years or so, sulfide minerals were treated mainly by roast-leach-electrowin (for Zn) and roast smelt-convert or flash-smelt-convert (for Cu) technologies with the resultant production of large volumes of sulfur dioxide that must be collected to minimize environmental damage. In most cases, the collected sulfur dioxide is converted to sulfuric acid in acid plants located on site.

The cost of recovering SO_2 and converting it into acid, the SO_2 pollution problems associated with incomplete SO_2 recovery, and the increasing demand for metals, along with the progressive depletion of high grade ores require the development of new, clean and efficient metal extraction techniques for the treatment of sulfide minerals and low-grade ores. Much time and money have been spent to understand hydrometallurgical sulfide decomposition reactions in the last forty years and this work has had a great impact on the research and development of hydrometallurgical processes for sulfide ores and concentrates. The direct acid pressure leaching of sulfide minerals, notably ZnS and copper sulfides - Cu_2S , CuFeS_2 and FeS_2 has certain potential advantages over the roast-leach and roast-smelt technologies. For example, in the Sherritt Gordon acid pressure leach for zinc the process achieves high metal extraction (about 96–98 %) and good

recovery of elemental sulfur (more than 85 %) without any sulfur dioxide production. Pyrite, when present as an impurity can vary in reactivity under leaching conditions. The oxidation of the impurity pyrite can influence the leaching kinetics as a source of iron catalyst. Furthermore, pressure leaching of pyrite during zinc pressure leaching yields only 10-50 % elemental sulfur (depending on leaching conditions) with the remainder of the mineral sulfur being oxidized to the sulfate form.

The physical state of the elemental sulfur depends on the operating conditions. At temperatures higher than 119°C, elemental sulfur exists as a liquid which tends to wet and occlude any unoxidized sulfide mineral particles, thus slowing down the reaction rate at higher extractions. At temperatures below 119°C, sulfur forms a porous solid product layer on the reacted mineral surface. Complete reaction can be achieved but the presence of the sulfur layer impedes the reaction and therefore lengthens the retention time for acceptable metal extractions. This sulfur issue was one of the main obstacles¹ to commercializing the zinc pressure leach process during the early days of its invention. It continued to hamper the development of the process for at least 20 years until finally, it was found that ligninsulphonic acid or its salts are effective surface active agents (surfactant) for dispersing liquid sulfur in the process, thus preventing it from coating the unreacted sulfide particles, and thereby enhancing the metal dissolution rate.

Surfactants are important reagents in the metal extraction industry. They are used as wetting agents, dispersants, flotation reagents, etc. in mineral beneficiation processes. However, the role of surfactants in leaching processes has not been widely studied. The goal of increasing metal sulfide recovery and the desire to minimize cost and pollution, and increase extraction efficiency require a thorough understanding of mineral-surfactant interactions during pressure leaching. It is therefore imperative that surfactants with

¹The problem of liquid sulfur prevented the early development of the commercial zinc pressure leach on a commercial scale until about 1977; the process as currently practiced takes place at temperatures between 135 and 155°C.

properties that can affect mineral decomposition in aqueous solutions should be studied, and a data base needs to be accumulated on such surfactants that improve (or impede) extractions, affect leaching kinetics, or play a role in separations between minerals and their residual or precipitated leach products.

Unlike flotation systems which have been well documented, there has been no extensive investigation of the nature of molecular interactions that take place between surfactants and sulfide minerals in leaching reactors. It is the objective of this research to study the effect of surfactants on mineral-solution-sulfur systems with a view to understanding their behaviour during zinc pressure leaching.

Chapter 2

LITERATURE SURVEY

Leaching is basically the act of selectively dissolving metals from an ore or concentrate. Generally, sulfide minerals are semi-conductors and thus, the oxidative or reductive leaching of metal sulfides may be an electrochemical process which involves the transfer of electrons across phase boundaries. Since most sulfide minerals occur as impure materials, the impurities may affect the electrochemical leaching kinetics of the process. The leaching of metal sulfides such as ZnS, FeS, CuFeS₂, FeS₂ under particular conditions results in the generation of elemental sulfur which, depending on the operating temperature, can be either liquid or solid.

The presence of liquid sulfur tends to slow or stop the metal dissolution process if there is complete wetting of reacting mineral particles by the sulfur. This slow down can be prevented by an interfacially active reagent that will create an unfavourable thermodynamic environment for wetting. The nature of the surfactant-mineral interactions under leaching conditions has not been extensively studied (unlike flotation systems), so this study seeks to focus on the basic mechanisms of the interactions in the leaching systems. One of the direct methods of surface analysis of solids (eg. for adsorption of surface active species) is by employing infrared spectral analysis and this approach is adopted in this study.

Table 2.1: Electronic properties of selected sulfide minerals

Mineral	Resistivity, Ohm-M	Conductor type
Cu_5FeS_4	$10^{-3} - 10^{-6}$	p
Cu_2S	$4(10^{-2}) - 8(10^{-5})$	p
CuFeS_2	$2(10^{-4}) - 9(10^{-3})$	n
CuS	$8(10^{-5}) - 7(10^{-7})$	metallic
FeS_2	$3(10^{-2}) - 1(10^{-3})$	n & p
ZnS	$1 - 1(10^4)$	n

2.1 ELECTROCHEMICAL PROPERTIES OF METAL SULFIDES

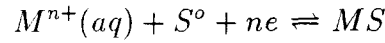
Metal sulfide minerals are good electronic conductors. Table 2.1 summarizes the electronic properties of some sulfide minerals [1, 2]. Generally, they are semi-conducting¹, and hence can be used as electrode materials in laboratory studies. The kinetics of their dissolution are often controlled by electrochemical processes. Oxidative leaching proceeds by the anodic dissolution of the sulfide mineral. The electronic conductivity of metal sulfide minerals can be attributed to the covalent character which results in non-localization² of charge. Semi-conducting minerals possess "rest" potentials³. The equilibrium potential of a mineral electrode depends on the solution composition as well as on the exact composition of the mineral. This observation holds true for the dissolution of metals too as has been indicated by Jun Li et al. [3]. The electronic properties of most metal sulfides and certain oxides readily lead to corrosion and galvanic couples

¹There is no reason for semi-conductors to behave differently from conductors *unless* the conductivity is so low that cathodic and anodic reactions are polarized by electron or electron-hole transport through the mineral grain.

²Motion of free-charge carriers which may be either electrons in the normally empty conduction band or holes in the normally full valence band; conductivity may be referred to as a n-type or p-type depending on whether electrons or holes dominate the conduction.

³"Rest" potential is the potential at which there is no net anodic or cathodic current and can be a mixed potential or an equilibrium potential.

in aqueous systems. As a result of their electronic character, the kinetics of the leaching of sulfides can be related to the potential of the solid in contact with an aqueous electrolyte. Thermodynamically, dissolution reactions are strongly favoured so that the effects of reverse reaction kinetics are usually ignored⁴. However, the build-up of products in the solution may markedly affect the kinetics by influencing the potential at the mineral-solution interface [1]. The reversible electrode potential, E_h , of a sulfide mineral in equilibrium with elemental sulfur can be written in a Nernst equation form, viz:



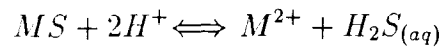
$$E_h = E^o + \frac{RT}{nF} \ln \frac{a_{M^{n+}} \cdot a_{S^o}}{a_{MS}}$$

a_i = activity of species i.

2.2 LEACHING OF SULFIDE MINERALS

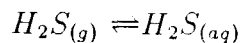
The leaching of metal sulfides is often considered electrochemical in nature and the extensive work done by different investigators [1]–[19] has led to the advancement and understanding of the theory. Under oxidative leaching conditions, a sulfide mineral is presumed to give up electrons to an oxidant e. g. Fe^{3+} , Cu^{2+} , dissolved oxygen, etc. The reactions occurring during sulfide mineral decomposition in an aqueous environment can be classified as follows [9]:

- molecular mechanism in which oxygen and sulfur transfer and where H_2S is considered as an intermediate product in the leaching process. H_2S is considered to be immediately oxidized to elemental sulfur by ferric ions and dissolved oxygen during the oxidation of sulfide minerals:

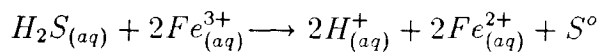


⁴This is not a general statement. Depending on the system under consideration, the reverse reaction may or may not be ignored.

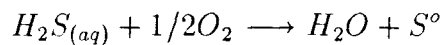
The hydrogen sulfide is distributed between the aqueous and gaseous phases as



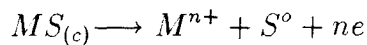
then



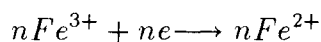
and/or



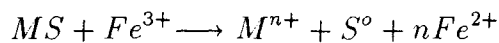
- electrochemical mechanisms promoted by high overvoltages as a result of high redox potentials (in acidic ferric ion solution); the decomposition reaction would be:



and

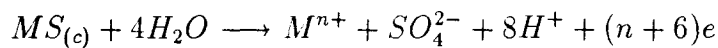


with

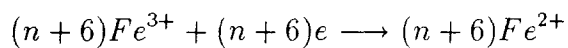


as the overall reaction

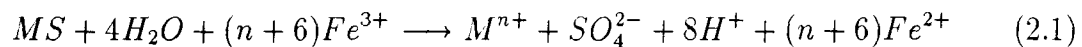
- and/or a mechanism that generates sulfate



and



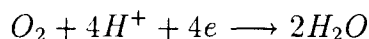
with



- a combination of the above

If the electrochemical process prevails during sulfide leaching, the leaching rate is determined entirely by the physical and structural nature of the mineral surface and by the electrochemical potential of the surface. The mineral surface may be clean (i.e. a freshly fractured surface) or it may be coated with elemental sulfur and/or metal oxide or hydroxide solids. These coatings may have varying degrees of porosity and electrical conductivity. The electrode (mineral) potential would be determined in most cases by a steady-state process involving the anodic and cathodic reactions.

The cathodic reaction of an oxidant operating on a sulfide mineral surface is governed by the mass transfer rate of the species⁵ and/or the activation polarization of the electrode reaction (which can vary with the identity of the cathode surface). The most important oxidants in hydrometallurgy are O_2 , Fe^{3+} ions, Cl_2 (or ClO^-) and HNO_3 acid and these have very different reduction kinetics. Oxygen reacts cathodically as:



but this process is very irreversible and slow unless overvoltages are large. Ferric ions are very reactive on a conducting surface and so react almost reversibly. The consequence is that in ferric ion leaching the limiting rate is either mass transfer of ferric ion to the mineral surface (concentration polarization) or slow anodic dissolution of the mineral. Aqueous chlorine is also a powerful oxidant which exhibits high E_h values, negligible activation polarization, and high leaching rates. The disadvantage of using chlorine for the leaching of metal sulfides is that chlorine will oxidize sulfur to sulfate⁶.

Thus, the potential of the mineral may be governed by the electrochemical kinetics of both anodic and cathodic processes. Mixed potentials⁷ are determined by balancing

⁵This can lead to concentration polarization.

⁶Not if Cl_2 oxidizes another species that in turn exerts a lower E_h .

⁷At the mixed potential the sum of the anodic current is counterbalanced by the sum of cathodic current i. e. $\Sigma I_a = -\Sigma I_c$; different minerals have different mixed potentials unless in galvanic contact

the current between separated anodic and cathodic processes. Potentials more positive than the mineral rest potential drive the half-cell reaction in the net anodic direction and potentials more negative than the rest potential drive the reaction in the net cathodic direction⁸, Figure 2.1.

The anodic overvoltage is $\eta_a = E - E_{e1}$ and the cathodic overvoltage, $\eta_c = E - E_{e2}$.

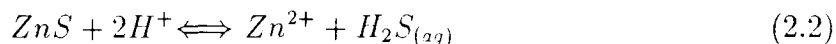
2.2.1 Leaching of Zinc Sulfide Minerals

Oxidative dissolution is an important part of the hydrometallurgical extraction of metals from sulfide ores/concentrates and a lot of energy and time has been spent in order to develop a process for the leaching of ZnS in Cl^- and SO_4^{2-} media using an oxidizing agent such as ferric ions or oxygen.

Ferric sulfate leaching of sphalerite

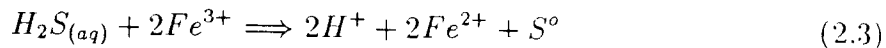
Ferric sulfate – sulfuric acid (0.3 M each) leaching of sphalerite was carried out by Perez and Dutrizac [34]. Their data display an increase in the metal dissolution rate with temperature (50–90°C). The kinetic data show that the rate determining factor in sphalerite leaching is the surface chemical reaction (i.e. the data fit the shrinking core model). The rate of leaching increases with increasing iron content of the sulfide mineral.

It has been suggested by Scott and Nicol [35] that during ferric sulfate leaching of sphalerite, the first step in the series of reactions is the non-oxidative reaction which produces H_2S as an intermediate product which is then oxidized to elemental sulfur by either dissolved oxygen or ferric ions in solution. The molecular mechanism may be represented by [35, 9]:



with each other.

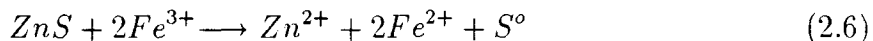
⁸Figure 2.1 depicts a hypothetical polarization curve for the dissolution of a metal sulfide in the presence of a cationic oxidant N^{n+} , eg. Fe^{3+} .



The H_2S has to be dissolved before it can be oxidized. From reaction 2.2, the extent of metal dissolution is sensitive to the acidity of the process but Peters and Doyle [9] have reported that in spite of the fact that this mechanism is easy to understand, it is inconsistent with practical oxidative acid leaching. In practice, there is no dependence of the rate on acid concentration. Secondly, according to reaction 2.2, an increase in the zinc ion concentration of the leach solution should lower the activity of H_2S at the mineral surface. This will put a constraint on reaction 2.3 particularly if it is the rate-determining step. Thus Peters and Doyle [9] have indicated that the oxidative acid leaching of sulfides is best described in terms of an electrochemical mechanism and this is consistent with observations made by others, [1, 6, 7, 11, 19]. The presence of Fe^{3+} and Fe^{2+} in the leach solution contributes to the kinetics through the ferric/ferrous redox couple [9, 19] and the electrochemical dissolution of the metal is thus written as:



The overall reaction is:



These reactions are equivalent to the molecular version, i.e. reactions 2.2, and 2.3 and the overall reaction are the same in both mechanisms. The presence of the ferric ions in the leach solution enhances the metal dissolution rate by oxidizing H_2S to elemental sulfur and ferrous ions⁹. Verbaan and Crundwell [19] observed a linear relationship between the initial metal dissolution rate and the redox couple's potential and an activation energy of 79 kJ/mol was obtained for their studies in the temperature range 25–85°C.

⁹This oxidation reaction is very fast even at room temperature.

In a report on the oxidative dissolution of sphalerite concentrate in ferric sulfate media, Crundwell [36] indicated that in the early part of the process, the rate-limiting step was the surface chemical reaction. The extent of leaching increased with increasing ferric ion concentration and decreased with increasing ferrous concentration and an activation energy of 46 kJ/mol was obtained for this rate control regime. As the sulfur product layer grows in thickness, diffusion through the product layer becomes the rate-controlling step. The initial metal dissolution (reaction) rate was insensitive to the presence of 0.05 and 0.01 M zinc sulfate in the leach solution. This is consistent with an earlier observation made by Dutrizac and MacDonald [37] and the comment made by Peters and Doyle [9] viz, that the electrochemical mechanism for the ferric ion leaching of sphalerite (involving an electron pair as the intermediate product) is more favoured over the molecular pathway which involves H_2S as the intermediate product¹⁰.

The refractory nature of two sphalerite concentrates leached in 0.5 M ferric sulfate–0.1 M sulfuric acid media resulted in not more than 45 % zinc extraction [38] after 5 hours of leaching at 78°C. This was assigned to the formation of insoluble lead sulfate and/or plumbojarosite on the particles' surface.

In an independent study into the influence of flocculants on the extent of metal extraction, Crundwell [39] reported that the addition of organic surfactants such as flocculants lowers the rate of sphalerite dissolution. The decline was attributed to a decrease in the surface area available for charge transfer processes (otherwise the chemical reaction) as a result of the surfactant adsorption.

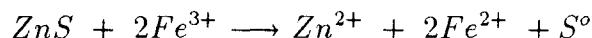
¹⁰The reason is that with an increase in zinc ion concentration in solution, equation 2.2 should shift the equilibrium state in such a way as to re-establish equilibrium according to:

$$K_{eq} = \frac{[Zn^{2+}] \cdot [H_2S_{aq}]}{[H^+]^2}$$

this will mean decreasing the rate of either metal dissolution or H_2S generation either of which will result in a decrease in the extent of metal extraction.

Ferric chloride leaching of sphalerite

Despite the success and the apparent advantages of sphalerite leaching in either sulfate or chloride media, most of the work has been in sulfate media, probably because of the established commercial technology for electrowinning zinc from purified sulfate solutions. Numerous similarities exist in the reactions occurring in the ferric chloride and ferric sulfate leaching of sphalerite [40] – identical free energies, enthalpies and entropies of leaching. The reaction is electrochemical in nature and controlled by charge transfer processes at the sphalerite surface (as has been reported by others [1, 7, 9, 11, 19]) with the potential of the sphalerite being dependent on the ferric/ferrous couple at the surface. The overall reaction for ferric chloride leaching of zinc sulfide is



In ferric chloride leaching of complex sulfide ores containing pyrite, sphalerite, minor amounts of chalcopyrite, galena, etc., the abundant pyrite is relatively inert to the lixiviant resulting in the preferential leaching of the sphalerite component. The most important reactions taking place during ferric ion (chloride) leaching of complex sulfide concentrates are the oxidation of CuFeS_2 , PbS , ZnS , FeS_2 , etc. generating elemental sulfur and/or sulfate and ferrous ions. The kinetic data obtained by Ngoc et al. [41] on the leaching of a complex sulfide ore suggested that the simultaneous dissolution of chalcopyrite, sphalerite and galena in ferric chloride occurred as if each individual mineral was leached separately. The mechanism of Cu and Zn dissolution was reported to be controlled by surface chemical reaction.

Majima et al. [15] have studied the non-oxidative leaching of sphalerite in aqueous hydrochloric acid solutions at 75°C and reported activation energy values of about 83.4 kJ/mol, indicative of surface chemical reaction control kinetics. De Bruyn and his colleagues [42, 43] reached similar conclusions in their investigations into the non-oxidative

sulfuric acid dissolution of zinc sulfide minerals. A similar study by Crundwell and Verbaan [44] in sulfuric acid media at 25–65°C had a similar conclusion. On the addition of ferric ions to the leach solution, Crundwell and Verbaan observed an enhanced metal dissolution rate as the ferric ions oxidized H_2S to elemental sulfur and ferrous ions.

The addition of NaCl to the chloride leaching media has been observed to enhance the leaching rate of sphalerite [15, 41] probably due to the formation of chlorocomplex species on the sulfide mineral surface as a result of the increased chloride ion concentration or activity. The non-oxidative acidic leaching of sphalerite is represented by reaction 2.2.

Evidence presented by Dutrizac and MacDonald [45] who carried out test work on the leaching of sphalerite in 0.1 M FeCl_3 – 0.3 M HCl solution at 85°C for a period of 0–500 hours indicate that most of the sulfide sulfur reported as porous elemental sulfur in the leach residue. Both elemental sulfur and sulfate were produced. The elemental sulfur was the predominant product – (85–95 % conversion of sulfide sulfur to elemental sulfur). A similar study by Jin et al.[46] resulted in less than 5 % sulfide sulfur oxidation to the sulfate. The rate-determining step for the process was found to be the chemical reaction at the solid surface; this observation is consistent with that made by Ngoc [41] and others [15, 34, 42, 43, 46]. Dutrizac and MacDonald indicated that: (a) the leaching rate is enhanced by the presence of CuCl_2 in the system, the rate increasing with increasing Cu concentration; (b) the build-up of FeCl_2 tends to slow the reaction rate – Su [47] had made a similar observation¹¹; (c) higher HCl concentrations increased the rate of reaction because of increased direct acid attack of the sphalerite¹²; at HCl concentrations in excess of 1 M, H_2S was generated, part of which was, however, oxidized to elemental sulfur by the ferric ion.

¹¹This implies that in commercial practice, the continuous build-up of ferrous chloride in the system will have an adverse effect on the process efficiency unless a way is sought to continuously eliminate/reduce the ferrous chloride build-up.

¹²This observation should not be confused with comments by Peters and Doyle [9] who were referring to industrial practice.

Perez and Dutrizac [34] observed a shrinking core leaching behaviour (i.e. surface chemical reaction being the rate-determining factor) and linear leaching kinetics in the ferric chloride leaching of sphalerite. This observation is in agreement with that of others. The rate of sphalerite dissolution was found to be related to the iron content of the sulfide solid solution. They indicated that the magnitude of the increase in the metal extraction rate was approximately the same as in the analogous ferric sulfate system.

The ferric chloride leaching of zinc sulfide (size range -100+150 mesh size) has been investigated by Bobeck and Su [47]. These workers observed a change in the kinetic behaviour of the system with time – in the early stages of the process the rate-determining regime was surface chemical reaction whilst in the latter stages when substantial surface elemental sulfur had been formed, there was a shift in the rate-controlling mechanism to product layer (elemental sulfur) diffusion control.

Venkataswamy and Khangaonkar [48] studied the kinetic behaviour of sphalerite leaching in ferric chloride media in the presence of tetrachloroethylene as a solvent for elemental sulfur. In the presence of about 100 mL solvent, approximately 95 % Zn extraction was achieved in 3 M FeCl_3 at 104–106°C after six hours of leaching as compared to 68 % achieved under similar conditions but in the absence of the organic solvent. The use of the solvent also permitted almost complete recovery of sulfide sulfur. The solvent dissolves the sulfur from the mineral surface. A mixed rate-control regime (i.e. combination of diffusion and chemical reaction) is proposed, i.e. their data fit both surface chemical reaction and diffusion control models over the entire test time. This observation is in contrast to that made by others.

In contrast to the surface chemical reaction control regime proposed by most investigators, Rath et al. [49] proposed a diffusion control kinetic regime (of either Fe^{3+} , Fe^{2+} or Zn^{2+} through the product layer). However, the activation energy value of 90 kJ/mol obtained by them is inconsistent with diffusion control kinetics.

In their studies on the kinetics of ferric chloride leaching of iron-activated bulk sulfide (Cu-Zn) concentrate (size range $-104 + 53$ microns) at 95°C , Neou-Singouna and Fourlaris [50] made some observations which are in contrast to those reported by others. These authors reported an increase in the Cu dissolution rate with increasing ferric ion concentration between 0.5 and 2.5 M in a 0.6 M HCl solution. With regards to sphalerite dissolution, there are some contradictions. They mentioned an increase in percent Zn dissolution in 0.5 to 1 M ferric chloride, beyond which the rate decreases. This is in sharp contrast to the observations made by Dutrizac [45] and others [41, 46, 48] who observed increasing zinc dissolution for ferric ion concentrations¹³ as high as 4 M. The metal extractions versus HCl concentration plots presented by the authors also indicate an increasing rate with increasing HCl up to about 1 M concentration beyond which the extent of extraction begins to decrease. This effect is more pronounced in the zinc dissolution curve. Again this observation does not agree with the work of Dutrizac et al. [45] and others [15] who indicated that a HCl concentration of unity or more increases the sphalerite dissolution rate due to increased direct acid attack of the mineral. On the rate-determining mechanism for the sphalerite dissolution, Neou-Singouna et al. again disagreed with others with the exception of Rath et al. [49] – that the rate is dependent on product layer diffusion. An activation energy of 32 kJ/mol computed for the sphalerite dissolution over a period of one hour is too high to be consistent with a diffusion-controlled mechanism¹⁴.

¹³Moreover, Majima et al. [15] and Ngoc et al. [41] have pointed out that increasing the Cl^- ion concentration or activity increases the rate of metal dissolution probably through the formation of chlorocomplex species on the mineral surface. Since an increase in ferric ion concentration of the system is accompanied by a simultaneous increase in the chloride ion concentration, a decrease in metal dissolution rate is not expected.

¹⁴One of the effects of temperature may be on the sulfur morphology. If at higher temperatures the sulfur layer has larger pores, the diffusion rate will increase through this layer more than the effect of temperature alone, yielding an apparently high activation energy when porosity is not adjusted for temperature. 32 kJ is too high for diffusion, but only a bit too high (20 kJ is usually an upper limit). When the diffusion is through a porous layer, the effect of temperature on porosity needs to be added to the effect of temperature on the diffusion constant in aqueous media. Due to these effects, the reaction

One consistent observation made by all authors is the formation of a surface layer of elemental sulfur on leaching zinc sulfide particles. At temperatures below the melting point of sulfur, the sulfur product layer is reported to be porous. At these temperatures, Jin et al. [46] report that the elemental sulfur layer is porous enough that it provides no resistance to the diffusion of reacting ionic species across the layer.

Oxygen pressure leaching of sphalerite

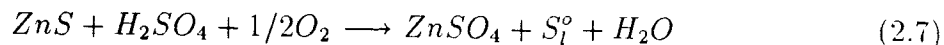
The pressure leaching of zinc has been reported as far back as 1954 by Bjorling [51]. Further work by later investigators [52] led to more understanding of the chemistry involved in the zinc pressure leaching. Forward and Veltman [52] found that at a reaction temperature of 140°C and above, the leaching process ceased almost completely in about ten minutes giving 65–72 % zinc dissolution. Further leaching of concentrate for up to six hours at 140°C resulted in only a minor increase in dissolved zinc. Jan et al. [53] also observed an increase in the zinc extraction rate up to 120°C beyond which the rate decreased and the leach residue appeared as several lumps. These were the result of molten sulfur occluding unoxidized zinc sulfide particles. However, with the introduction of lignin sulfonic acid or its salt¹⁵ into the system (after 20 years of sporadic research) this problem no longer exists in the zinc pressure leach. There have been many investigations and publications [54]–[65] on the successful use of this surfactant as a dispersant for liquid sulfur in the oxidative pressure leaching of zinc sulfide minerals. The agent dispersed the liquid sulfur that previously inhibited high zinc extraction and so made it possible to commercialize the process¹⁶. The process as currently practiced takes place at temperatures between 135 and 155°C at a total pressure of about 14

mechanism is obscured by the activation energy values computed.

¹⁵This reagent is marketed with the trade name lignosol.

¹⁶Quebracho can also be added as a supplement to boost the effectiveness of the lignin sulfonate.

atmospheres, with a chemical stoichiometry close to



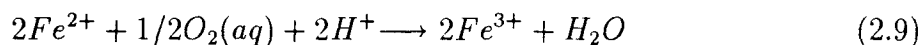
as the overall reaction. The overall reaction as given by equation 2.7 is impractically slow in the absence of dissolved iron, which acts as a catalyst. Bernal [65] tried to use other metals such as Ni^{2+} , Co^{2+} , and Cu^{2+} as catalysts only to find out that dissolved iron (ferric/ferrous) was the most effective catalyst of all the dissolved metals investigated. Jan et al. also observed that the presence of ferric ions in the leach solution increased the leaching rate dramatically and that the rate-determining step was the chemical reaction occurring on the mineral surface.

The sequence of reactions including iron catalysis can be represented as [64]:

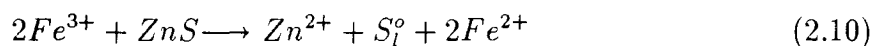
a) gas-liquid mass transfer of oxygen



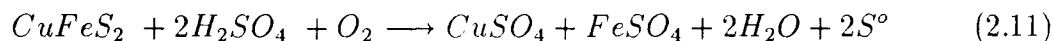
b) homogeneous oxidation of ferrous ions

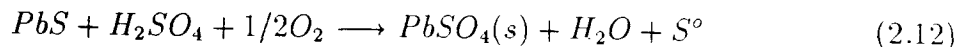


c) ferric ion leaching of zinc sulfide

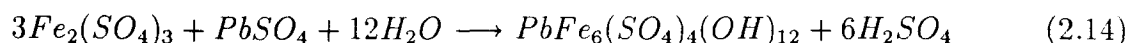
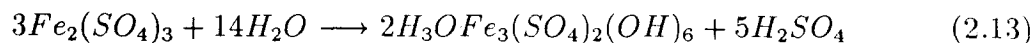


with cyclic regeneration of Fe^{3+} by reaction 2.9. Normally, there is sufficient acid-soluble iron in the concentrate (in the form of marmatite($ZnFe$)S, pyrite(FeS_2), or pyrrhotite(FeS)) to satisfy the iron requirements for the catalysis. If copper and lead are present in the concentrate (often in the form of chalcopyrite and galena), they may also dissolve according to:

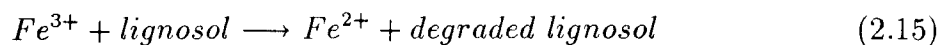




Hydrolysis of iron may occur as the leaching reaction progresses (at low acidity), through the formation of hydronium jarosite and plumbojarosite:



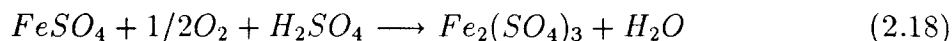
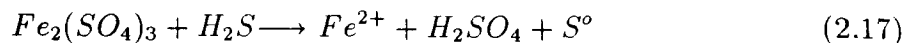
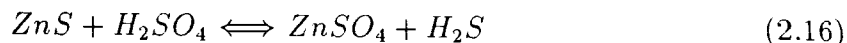
It has been reported by Dreisinger et al. [54] that under zinc pressure leaching conditions, lignin sulfonic acid or its salt is degraded by ferric ions according to the reaction:



Bernal [65] has also reported that in the presence of cupric ions as catalyst (instead of dissolved iron), zinc extraction in their study almost ceased after 40 % dissolution (in the presence of lignin sulfonate). However, they did not assign any reason to this behaviour. It is possible that the decreased metal dissolution rate was due to enhanced degradation of lignin sulfonate by the cupric ions in solution. It is unclear at what point in the degradation process the sulfur again occludes the mineral surface.

Scott and Dyson [66] investigated the catalytic role of different metal ions on the pressure leaching of zinc sulfide in 0.1 N sulfuric acid, at 250 psi oxygen partial pressure and 113°C (in the absence of a surfactant). After one hour of leaching in the presence of 0.6 mg Cu (as the catalyst) per gram of ZnS, 92 % zinc extraction was achieved whilst 14 mg Fe per gram of ZnS yielded only 51 % extraction under the same leach conditions as compared to only 6 % (this value seems very low) in the absence of any catalyst. Jan et al. [53] proposed a chemical reaction which involves H_2S as an intermediate product which is further oxidized indirectly by oxygen through the help of the metal catalyst such as ferric ions to elemental sulfur with H_2S oxidation by the catalyst as the rate-controlling

step. The proposed mechanism is:



But, as has been pointed out by Peters and Doyle [9], the electrochemical mechanism is more favoured as the above molecular mechanism is inconsistent with practical experience.

Previous work by Owusu [55, 56] has shown that lignosol acts on both the solution–mineral and solution–liquid sulfur interfaces, to lower the work of adhesion between liquid sulfur and zinc sulfide minerals.

De Nys and Terwinghe [67] have also reported that the oxidative pressure leaching of zinc sulfide concentrate was successfully done at a temperature of about 150°C in the presence of orthophenylene diamine (OPD) as surfactant. The authors report that the reagent was used to enhance the transfer of reactants to the mineral surface. However, they did not elaborate on the mechanisms involved.

Effect of solid solution iron content on sphalerite leaching behaviour

Investigations carried out by different workers [15, 18, 34, 68, 69], on different sphalerite concentrates and ores indicate that the leaching rate of sphalerite increases with an increase in the solid-solution content of iron. The metallic impurity is believed to increase the ionic character or the electrical conductivity of the mineral. This results in an increase in charge transfer across the mineral–solution interface (i.e. electron transfer from mineral to solution) and hence an increasing rate of dissolution. Iron increases the mineral conductivity through the creation of holes in the crystal lattice [18].

Majima et al. [15] reported the leaching of four different zinc sulfide concentrates in 2 M HCl media at 55°C in the absence of ferric ions and observed a linear leaching rate increase with increasing iron content of the solid; there was approximately a six fold increase in the rate with the iron content varying from 0.28–2.15 %. There was no noticeable effect of the iron content on the system's activation energy.

A similar linear relationship between the metal (Zn) extraction rate and the iron content of the mineral in 0.2 M FeCl_3 – 0.3 M HCl – 2 M NaCl at 45, 65, and 85°C has been reported by Crundwell [68] in a study of five sphalerite minerals of different iron contents ranging from 0.55 to 8.6 %. There was approximately a twenty-fold increase in the rate over this iron content range. Activation energies obtained indicated a slight decline with increasing iron content of the mineral.

Piao and Tozawa [69] studied the leaching of sphalerite samples of different iron contents in oxygen-sulfuric acid media at a temperature of 150°C. They reported a seven-fold linear increase in the leaching rate as the solid solution iron content increased from 1.87–8.9 %.

A linear correlation between the sphalerite leaching rate and the solid solution iron content had been reported by Kametani et al. [70] from the work done on the leaching of six sphalerite concentrates of different iron contents. The study was conducted in 10 g/L ferric sulfate–100 g/L sulfuric acid media at 90°C. There was a seventeen-fold increase in the dissolution rate in moving from 0.79 to 13.4 % iron content. The rate of leaching depended on the ferric ion concentration for $[\text{Fe}^{3+}] < 10$ g/L. No dependence on the ferric ion concentration was found at $[\text{Fe}^{3+}] > 10$ g/L.

Perez and Dutrizac [34] studied the leaching of fifteen sphalerite mineral samples at temperatures of 20–90°C in ferric chloride and sulfate media. The increasing leaching rate – increasing Fe content showed a linear correlation. A decrease in the apparent activation energy for leaching with increasing iron content of the sulfide was noted. Bobeck and Su

[47] also reported a decreasing activation energy with increasing iron content of sphalerite mineral. Perez and Dutrizac observed similarities in the kinetics in both media, the rate-determining factor being the transfer of charge at the sphalerite surface. A similar mechanism has been mentioned by Crundwell [68] who postulated that "the sphalerite dissolution rate is directly dependent on the number of occupied sites in the d orbital conduction band i.e. to the iron content in the absence of other impurities".

Xia Guang-xiang et al. [62] have also reported that under the conditions of their study on oxidative zinc pressure leaching, the rate of oxygen consumption is linearly related to the iron content (percentage Fe) of the concentrate as:

$$R_{oxy.} = 30 * [Fe] \text{ mol/m}^2 \text{ minute}$$

The increased rate of oxygen consumption (with increasing iron content) is a direct reflection of the increase in the rate of zinc dissolution.

In contrast to the linear correlations reported by most authors (as mentioned above), Kammel et al. [71] reported that in the absence of Cu^{2+} , there is a logarithmic relationship between the extent of zinc extraction (from sphalerite) and the iron content in the range tested (0.11 to 10.3 %). The test was done in 5 g/L ferric sulfate – 50 g/L sulfuric acid at 70°C. The logarithmic correlation reported is

$$\%Zn \text{ extraction} = A + B * \log[\%Fe]$$

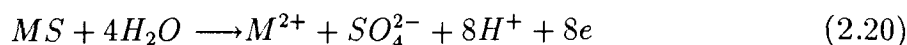
. where A and B are constants.

2.2.2 The Behaviour of Sulfur in Oxidative Leaching of Sulfide Ores

The behaviour of sulfur in the oxidative leaching of sulphidic minerals is not clearly understood. The overall oxidation¹⁷ reaction is usually given by:



The formation of sulfate occurs to a lesser extent:



Peters [7] has reported that under acidic conditions e.g. at 1 M sulfuric, perchloric or hydrochloric acid, under oxygen pressure, minerals such as PbS, ZnS, CuS and CuFeS₂ can yield nearly 100 % elemental sulfur. Under the same conditions, FeS₂ yields 30–50 % elemental sulfur and MoS₂ leaching results in the complete conversion of sulfide sulfur to the sulfate. The leaching of pyrite and molybdenite by ferric ions at temperatures below 120°C is extremely slow.

In their study on the oxidative pressure leaching of pyrite, McKay and Halpern [12] reported that in the absence of initial sulfuric acid in the reactor, all sulfide sulfur was oxidized to sulfate (with half appearing as sulfuric acid and the other half as ferric and ferrous sulfates) with no elemental sulfur being present. However, when 0.15 M sulfuric acid was initially added to the system, 50 % elemental sulfur was realized from the oxidation of the pyrite, the rest occurring as ferric and ferrous sulfates. Thus, the yield of elemental sulfur in pyrite leaching is influenced by the acidity of the leach liquor and increases as the pH drops¹⁸ to below unity.

In a series of investigations carried out by Lotens and Wesker [20] on ZnS, PbS, and FeS₂ in chloride media, at pH=2 (i.e. roughly 0.01 M H⁺ concentration) and at 30–60°C

¹⁷The mechanisms involved in the sulfide sulfur oxidation process during the oxidative leaching process are detailed in ref. [20].

¹⁸In virtually all reports of the oxidative acidic pressure leaching of ZnS and copper sulfides, the acidity is very high i. e. pH < 1.0

temperature, using chlorine as the primary oxidant, they reported that pyrite was the only exception where virtually all sulfide sulfur was converted to sulfate. The sulfur yield from ZnS leaching under similar conditions was 50 %. Lotens and Wesker [20] have reported that in addition to elemental sulfur and sulfate, other intermediate sulfur compounds are present in the leach liquors, eg. thiosulphates and sulphites during the leaching of sulfide minerals. This has been confirmed by other investigators [22]–[25].

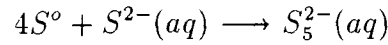
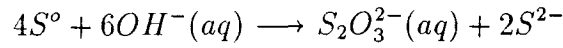
In a study on the ferric ion leaching of chalcopyrite (in 0.5 M sulfuric acid) Dutrizac [26] reported that at temperatures below its melting point, elemental sulfur is hardly oxidized, if at all. Similar sulfur behaviour was observed when the leaching was repeated in acidic ferric chloride (0–2 M) media [27] where at temperatures less than 100°C, elemental sulfur conversion in excess of 95 % (5 % sulfate) was consistently realized. This is consistent with an earlier study done by Paynter [28] on the ferric chloride leaching of chalcopyrite. Corriou and Kikindai [31] arrived at similar conclusions (for temperatures below the melting point) when they tried to oxidize elemental sulfur in ferric ion–sulfuric acid medium over a wide temperature range up to 230°C.

At temperatures greater than 159°C, polymeric S₈ rings break down to polymeric chains which are believed to exhibit higher oxidation rates than the S₈ rings (in a given aqueous environment). This statement is consistent with the activation energy numbers reported by Corriou and Kikindai [31]: between 125 and 160°C, the activation energy reported is 119.2 kJ/mol and between 175 and 230°C the number reported is 64.8 kJ/mol. The authors also reported that an increase in the sulfuric acid concentration of the aqueous phase slows down the rate of sulfur oxidation. These observations imply that once the elemental sulfur is formed in the leaching process¹⁹ (below 160°C) it hardly oxidizes. On the basis of this argument, the oxidation of sulfide sulfur to sulfates in the oxidative leaching of pyrite and MoS₂ (at below 159°C) does not necessarily involve

¹⁹This is true for pyrite, sphalerite, or any other sulfide mineral.

elemental sulfur as an intermediate product.

In ammoniacal systems (i.e. at high pH's), mineral or elemental sulfur is oxidized to oxy-sulfur products such as $S_2O_3^{2-}$, SO_4^{2-} , $S_nO_6^{2-}$ or $NH_2SO_3^-$ [9]. However, as has been observed by Reilly [32], an elemental sulfur by-product in oxidative ammonia leaching can be recovered as such in the presence of C_2Cl_6 , a non-aqueous solvent for sulfur. Valensi [33] describes the most probable dissolution path for sulfur in this aqueous medium as:



equilibrium being attained at a pH of about 9. These species are oxidized slowly by molecular oxygen in the absence of copper ions or at low temperatures [9].

2.2.3 Effect of Sulfur in Blocking Leaching Reactions

At temperatures less than 119°C, the morphology of the sulfur product formed during acid leaching of sulfide minerals can have a marked influence on the extent of reaction. Peters [7] reports that if the formation of sulfur is accompanied by a positive molar volume change (eg. as with pyrite), the sulfur layer is protective at extremely small thickness whereas those with negative molar volume changes (e. g. sphalerite, galena, chalcopyrite, etc.) develop cracks and pores and the sulfur is not protective but only acts to slow the transport processes through the sulfur layer. At temperatures greater than the melting point of sulfur, liquid sulfur spreads over the unreacted mineral surface and inhibits further reaction. Since sulfur is a non-conductor, both anodic and cathodic processes in sulfide leaching should take place underneath any sulfur layer that is formed, and its presence is bound to slow down both anodic and cathodic processes by limiting mass transfer and possibly by decreasing the available solution-mineral interface area.

2.2.4 Interfacial Phenomena

A recent study by Owusu et al. [54, 55, 56] shows that when lignin sulfonic acid or its salt is introduced into a leaching reactor as a surfactant (or dispersant) during zinc pressure leaching, it tends to adsorb at the liquid sulfur - aqueous solution and on the solid mineral - aqueous solution interfaces. By so doing, the liquid sulfur - aqueous solution interfacial tension decreases from 54–55 mN/m in the absence of the surfactant to 28–30 mN/m in the presence of 0.3 g/L lignin sulfonate concentration, beyond which no further increase in the surfactant dosage effects any change. The liquid sulfur - zinc sulfide mineral contact angle also increases from about $80 \pm 5^\circ$ in the absence of the surfactant to $145 \pm 5^\circ$ in the presence of the surfactant. These phenomena resulted in the reduction of the work of adhesion²⁰ from about 64 mJ/m² in the absence of any surfactant to about 5 mJ/m² in the presence of 0.3 g/L lignin sulfonic acid. When 0.3 g/L quebracho was added as a supplement to the lignosol, the work of adhesion as computed was about 2 mJ/m². The quebracho by itself effected only minor changes in the interfacial tension—it dropped from 54–55 mN/m to about 45 mN/m in the presence of 0.3 g/L quebracho; but the change in the contact angle was quite significant under similar aqueous conditions. There was an increase in the contact angle from about 80° in the absence of a surfactant to about 126° in the presence of surfactant. In the presence of equal amounts (0.3 g/L each) of quebracho and lignosol, the contact angle increased to about 156° whereas the liquid sulfur–aqueous solution interfacial tension obtained was no different from that obtained in the presence of 0.3 g/L lignosol. The presence of ionic species such as ferric, ferrous and hydrogen ions in solution did not influence either the contact angle nor the computed work of adhesion in the presence of the surfactants.

²⁰The work of adhesion is defined as the reversible work required to separate a unit area of liquid from the solid substrate.

The effect of tergitol²¹ was also reported. The presence of 0.5–1.0 g/L tergitol lowered the interfacial tensions to about 42–43 mN/m and increased the contact angle to about 105°. However, the presence of 0.5 g/L each of tergitol and lignosol decreased the interfacial tensions to about 27–28 mN/m but could not effect any further change in the contact angle measured, the measured value being about 107°. This observation implies a higher affinity of lignosol for the liquid sulfur–aqueous phase interface and a higher affinity of tergitol for the aqueous phase–solid mineral interface when these two surfactants compete for adsorption sites in a system. In the presence of these two surfactants, the reported work of adhesion was about 19 mJ/m².

2.3 PROPERTIES OF LIQUID SULFUR

The melting point of sulfur could be either 113 or 119°C depending on the crystalline allotrope. Below 94°C, sulfur exhibits a rhombic structure and above 94°C, a monoclinic structure is stable. However, the transition from rhombic to monoclinic is slow and if the rhombic form is heated rapidly, it can easily reach its melting point of 113°C and spread over any surface before recrystallizing to the monoclinic form (melting point 119°C). Thus, it is easy for the sulfur produced in the pressure leaching process to be molten, wetting the mineral and impeding the leaching reaction.

At the melting point, sulfur forms a light yellow, low viscosity liquid. On heating, the liquid darkens, and becomes deep orange. Nickless [77] reports that viscosity increases with temperature and passes through a maximum at 159°C, beyond which there is discontinuity in all physical properties²². This observation is in contradiction to that made by Tuller and others [78]–[81] who have reported that the viscosity drops with increasing

²¹Tergitol is a non-ionic surfactant which has been reported to slow down the Zn extraction rate in the zinc pressure leach [57].

²²The viscosity behaviour reported by Nickless is undoubtedly a mistake.

temperature up to about 159°C above which any further increase in temperature makes the liquid more viscous up to about 200°C beyond which it begins to fall again with increasing temperature up to its boiling point, (Figure 2.2). The increase in viscosity at temperatures above 159°C is the result of the rupturing of the puckered sulfur rings (S_8) to form chains of varying lengths. Above 200°C, the long chains begin to break up resulting in decrease in viscosity with temperature.

The measurement of surface tension on highly purified sulfur (i.e. sulfur-air interface) was carried out by Fanelli [82]. He concluded that the surface tension decreases linearly with temperature, but that there is a sharp discontinuity at about 159°C, the rate of fall being smaller above this temperature. Based on Fanelli's results, Tuller [78] derived a relationship between the surface tension of sulfur and temperature as: below 159°C

$$\gamma = 73.4 - 0.105t \quad (2.21)$$

above 159°C

$$\gamma = 65.7 - 0.0566t \quad (2.22)$$

where t is the temperature in degrees Celsius, and γ is the surface tension in mN/m.

The density of liquid sulfur is reported [78] as decreasing with increasing temperature.

2.4 SURFACTANTS AND INTERFACIAL PROPERTIES

2.4.1 Characteristic Features of Surfactants

A surface-active agent (or a surfactant) is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system resulting in a lowering of one or more of the surface or interfacial free energies. Surfactants always act to reduce interfacial free energy rather than to increase it

although there are occasions when they are *apparently* used to increase it [83].²³ Surfactants become significant (or applicable) when the interfacial phenomena occurring at phase boundaries within a system are so unusual relative to the expected bulk phase interactions that the entire system behaviour becomes dependent on the interfacial process (eg. corrosion, detergency or flotation).

Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a lyophobic group, together with a group that has strong attraction for the solvent, called a lyophilic group. This is known as an *amphipatic* structure. In solution, the presence of the lyophobic group in the interior of the solvent causes a distortion of the solvent-liquid structure, increasing the free energy of the system. In an aqueous solution of a surfactant, this distortion of the water by the lyophobic (hydrophobic) group of the surfactant and the resulting increase in the free energy of the system when it is dissolved means that less work is needed to bring a surfactant molecule than a water molecule to the surface. The surfactant therefore concentrates at the surface. This decreases the surface/interfacial tension. On the other hand, the presence of the lyophilic (hydrophilic) group prevents the surfactant from being expelled completely from the aqueous phase. Thus, the amphipatic structure causes the reduction of the surface or interfacial tension of the solvent as well as orientation of the molecules at the surface or interface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

The chemical structure of groupings suitable as the lyophobic and lyophilic portions of the surfactant molecule vary with the nature of the solvent and the conditions of use. As the temperature and use conditions (eg. presence of electrolyte or organic additives)

²³Because surface tension is a free energy, a 'surfactant' that raises the surface/interfacial tension must necessarily interact with, and reduce the adsorption of a previously present (though not necessarily detectable) surfactant. A surfactant that can displace another (by substitution) will always lower the surface tension. Only when a surfactant is destroyed (precipitated or oxidized) by a second reagent can the surface tension rise.

vary, modifications in the structure of the surface-active agent become necessary. Thus, for surface activity in a particular system *the surfactant molecule must have a chemical structure that is amphipatic in that solvent under conditions of use.*

The hydrophobic group is usually a long chain hydrocarbon residue, less often a halogenated. The hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are grouped as:

1. anionic - the surface-active portion of the molecule has a negative charge e. g. ligninsulphonates, xanthates, and carboxylates.
2. cationic - the surface-active portion bears a positive charge e. g. $RN(CH_3)_3^+Cl^-$ (quaternary ammonium chloride).
3. zwitterionic - both positive and negative charges may be present in the active portion e. g. sulfobetaines.
4. nonionic - the active portion bears no apparent ionic charge e. g. tergitol (a derivative of ethylene oxide) but is polar enough to bind to aqueous solution.

The choice of a particular surfactant depends on availability, cost and efficiency. This requires knowledge of : a) characteristic features of available surfactants (physical and chemical properties and uses), b) interfacial phenomena involved in the job to be done and the role of the surfactant and c) the surface chemical properties of various structural types of surfactants and the relationship of the structure of a surfactant to its behaviour in various interfacial phenomena [83, 84, 85].

In comparing the performance of different surfactants, it is necessary to distinguish between the *amount* of surfactant required to produce a given amount of change in the phenomenon under investigation and the *maximum change* in the phenomenon that the

surfactant can produce, regardless of the amount used. The former parameter is known as the efficiency of the surfactant and the latter its effectiveness.

2.4.2 Surfactants Identified for Study

In this study the chemicals were chosen based on their chemical and physical properties coupled with the conditions prevailing during the pressure leaching of zinc sulfide minerals and concentrates. In the zinc pressure leach process, any surfactant introduced in the leaching stage should be neutralized by the time the slurry reaches the solution purification, sulfur recovery, and zinc electrowining stages. Thus, the degradation property of the reagents selected is an advantage provided these reagents are effective during the leaching. Their ability to degrade under oxidizing conditions implies that there will be no residual surfactant to interfere with the subsequent extraction steps. This is one of the factors considered in the selection of the reagents. The chemicals identified include:

1. Lignin sulfonate/lignin sulfonic acid
2. Orthophenylene diamine (OPD)
3. Water-soluble product of naphthalene sulfonic acid-formaldehyde condensates
4. Cocoamido hydroxyl sulfobetaine (CAHSB)
5. Tallowamido hydroxyl sulfobetaine (TAHSB)
6. Cocoamido betaine (CAB)

The only commercially important surfactant among these is lignin sulfonic acid, which is currently being used in the pressure leaching of zinc sulfide minerals.

2.4.3 Properties of Individual Surfactants

Lignin Sulfonates/Lignin Sulfonic Acids

Organic Chemistry

Lignin sulfonates are derivatives of lignin whose exact definition and structure still remains a matter of debate. They are complicated condensation polymers, fig. 2.3, whose exact structure is not completely known.

The most common lignin sulfonic acids have a molecular weight of about 4000. However, molecular weights can vary from 200 to 100,000. Sulfonate groups are attached to the carbon chains but not to the benzene ring. The sulphonatable carbon atoms are in alpha-positions to the benzene ring. Secondary and tertiary OH⁻ groups are present in the side chains and these augment the hydrophilic properties of the lignin sulfonates provided by the sulfonic group.

Lignin sulfonic acids are *only soluble in water or in a solvent where hydrogen bonding is very strong*. They undergo hydrolysis or oxidation. Lignin sulfonates are anionic polyelectrolytes [88].

Adsorption Characteristics

The surface activity of lignin sulfonates is affected by the number of hydrogen bonding groups present in the molecule, such as side chain hydroxyl, phenolic and carboxyl groups. The adsorption of lignin sulfonates is known to be determined by the nature of the hydrogen bonding. Lignin sulfonates do not form micelles. *Lignin sulfonates are not capable of forming any oriented layer* when adsorbed upon a liquid or solid surface [88].

Uses and Applications of Lignin Sulfonates

The major quantity of purified lignin sulfonates is used in oil-well drilling mud formulations. The lignin sulfonates are effective in controlling the fluidity of the drilling mud, keeping mineral salt contaminants encountered in drilling suspended and preventing them from flocculating the mud while, at the same time, performing a sequestering function [88].

Lignin sulfonates play very important roles in the mining industry, functioning as ore-flotation agents for a number of minerals. They are used as depressants. They are also very good dispersing agents for slimes and are used for this purpose in both the flotation and tabling of slimy ores. In tabling operations, lignin sulfonates disperse the slime and prevent occlusion of ore particles. In flotation operations the dispersing action on slime increases the degree of separation, which results in an increased recovery and better grade of concentrate. Lignin sulfonates are used in the zinc industry as dispersants for dispersing liquid sulfur from the surface of the unreacted mineral particles, thus enhancing the extent of zinc extraction at temperatures above the melting point of elemental sulfur. The surfactant degrades in the presence of oxidizing agents. It has been reported [54] that at zinc pressure leaching temperatures (and aqueous conditions), lignin sulfonic acid has a half life of ten minutes. A study of the flocculating properties of lignin sulfonates shows that low-molecular weight lignin sulfonates act as dispersants at all concentrations. High-molecular weight lignin sulfonates, (as any other polyelectrolyte), in contrast, act as flocculating agents at low concentrations and as dispersants at high concentrations. The flocculating effect increases with the molecular weight of the lignin sulfonate [88]. Reducing the pH enhances the dispersing action of the low molecular weight lignin sulfonates. Other uses of lignin sulfonates as effective dispersants are in the blending of carbon black into rubber, the distribution of vat dyes in the textile industry,

the preparation of wettable agricultural powders and sprays, and the manufacture of portland cement.

Lignin sulfonates are good sequestrants for heavy metal ions such as ferric, cupric, and stannous, and (less effectively) for cobalt, manganese, nickel, silver, stannic, uranium, and zinc.

Orthophenylene Diamine

Orthophenylene diamine is sometimes called orthamine or 1,2 benzenediamine. It has the chemical formula $C_6H_4(NH_2)_2$ and the structure shown in Figure 2.4 and belongs to the aromatic amine family. It is colourless, forms monoclinic crystals, and darkens in air. It has a molecular weight of 108.1. The melting point is 102-104°C and the boiling point is 252-258°C. It is soluble in alcohol, ether, chloroform and water. The solubility in water is reported to be about 3g/100g of water [91] but Dupont Chemicals [92] reports a solubility of 17 % at 60°C. It is stable at normal temperatures and conditions of storage. Moist air and excess heat cause product quality to degrade. It is incompatible with oxidizing agents and decomposes at high temperatures. It can be used as an oxidation inhibitor. Morrison and Boyd [93] report that any functional group attached to the aniline structure²⁴ in the *ortho* position imparts more acidic characteristics to the molecule irrespective of whether it is electron donating e.g NH_2 or withdrawing, e.g NO_2 ; however, the effect is more intense if it is an electron withdrawing group.

Cocoamido Betaine (CAB)

CAB is a member of the surface-active betaines and is derived from coco-fatty acids. Betaines are pH-sensitive zwitterionics (or amphoterics) which show the properties of anionics at high pHs and those of cationics at low pHs. CAB has a chemical formula

²⁴The aniline structure consists of an aromatic ring with one amino group.

$R-CONH-(CH_2)_3-N^+(CH_3)_2CH_2-COO^-$. It is a clear yellow liquid with a faint odour. The specific gravity is 1.05 and the boiling point $> 100^\circ\text{C}$. It is highly soluble in water. Slightly better wetting and foaming properties are reported at acidic pH's. It is stable under normal conditions but incompatible with strong oxidizing and reducing agents [83, 94, 95] and degrades if overheated. Betaines are used in the textile industry as assistants in vat dyeing and printing. They are also used as detergents, foaming and wetting agents.

Cocoamido- & Tallowamido-Hydroxyl Sulfobetaines (CAHSB & TAHSB)

CAHSB and TAHSB belong to the amphoteric group of surface active agents called *sulfobetaines*, with the general chemical formula²⁵ $RN^+(CH_3)_2(CH)(OH)(CH_2)_xSO_3^-$, where R is either a coco-fatty or tallow-fatty derived alkyl group. They are also referred to as pH-insensitive zwitterionics, i.e. at no pH do they possess only cationic or anionic characters. They are therefore "ionic neutral", stable and substantially non-reactive in acid, neutral, and alkaline solutions and have strong surface activity. They adsorb onto charged surfaces at all pH's without forming a hydrophobic film [96]. Sulfobetaines are very soluble in water and strong electrolyte solutions and are not sensitive to hard water. They are compatible with all other types of surfactants, but are insoluble in most organic solvents. The effect of pH and added electrolytes on the surface active properties of sulfobetaines is generally minimal. Sulfobetaines are partially degraded in the presence of oxygen producing carbon dioxide. This leads to a loss of surface activity [97].

Sulfobetaines form good wetting, foaming, flotation, dispersing, dyeing agents or as emulsifiers, detergents and as a component of laundry and cleaning agents. They exhibit

²⁵Structurally, a sulfobetaine molecule has two different hydrophilic parts - one positive and the other negative situated at different parts within the molecule.

good complexing properties with respect to divalent ions. Sulphobetaines are gradually replacing petroleum sulfonate²⁶ in the petroleum industry for enhanced oil recovery²⁷. Sulphobetaines, present in only very small concentrations, lower the interfacial tension between mineral oil and water, especially salt-containing water. They are compatible with anionics, cationics or nonionic surfactants as well as with organic thickening agents. Hydroxylated sulfobetaines have improved solubility [96]–[102].

Naphthalene Sulfonic Acid - Formaldehyde Condensates

Naphthalene sulfonic acid-formaldehyde condensates have the chemical structure shown in Figure 2.5 and the formula $[C_{10}H_6SO_3NaCH_2]_n$. The average molecular weight is approximately 2000. These products are used as wetting agents for powders (agricultural wettables, powdered pesticides) and paint formulation. Their uses are similar to those of ligninsulphonates [96]. They are completely soluble in water. They are suited for applications in highly concentrated aqueous solutions and dispersions and retain their dispersing ability over a wide pH and temperature range. They can be used in combination with anionic or nonionic surfactants when lower surface or interfacial tensions are required. They degrade in the presence of oxidizing agents and undergo thermal degradation under extremely high temperatures greater than 230°C. These reagents when used will stabilize and reduce the viscosity of thick pastes and produce smooth, uniformly wet paste without separation of the solid particles. They are used in the leather industry as dyeing and levelling assistants. These surfactants can be used to produce very high strength concrete by reducing the water-to-cement ratio and reducing the concrete's water requirement by about 20-30 %.

²⁶This replacement is due to the high sensitivity of the petroleum sulfonates to divalent cations producing precipitates during the progress of the surfactant solution in the reservoir.

²⁷Lignin sulfonate is also used in the petroleum industry for the same purpose.

2.5 INFRARED SPECTROSCOPY

One of the most direct approaches to the study of adsorbed molecules on solid surfaces is by infrared spectral analysis of the surface. The spectrum provides information about the adsorbed molecules and the nature of surface bonding or interactions. As far as leaching systems are concerned, no infrared investigations have been reported that characterize the possible mechanisms of interactions between any commercially important surfactant²⁸ and the mineral (or adsorbent) on a molecular level. However, there have been many infrared studies [103]–[120] to investigate reagent–mineral molecular interactions in flotation systems. Several in-situ mineral–aqueous solution studies have been reported in the last 10–15 years in the literature [107]–[120] and they have contributed to explaining the mechanisms and the nature of interactions on a molecular scale between flotation reagents and their mineral substrates. Some ex-situ work has been performed by others [103]–[106]. Sulfide minerals are among the few which have been thoroughly investigated under flotation conditions. With the exception of sphalerite (or ZnS), all other sulfide minerals reported in the literature were readily rendered floatable on reagent adsorption; on the other hand, sphalerite must be activated first with heavy metal ions eg. Cu^{2+} , and Fe^{3+} , before the mineral adsorbs the flotation reagent and is rendered hydrophobic and floatable. The metal ions, eg. Cu^{2+} , transform the surface of the ZnS mineral into a chalcocite-like surface before it can adsorb the reagent [105, 113, 118, 119, 120].

Termes and Richardson [113] have reported that natural sphalerite absorbs at 4800–2500 cm^{-1} and below 800 cm^{-1} in the infrared region. This observation makes it easier to characterise the mineral–surfactant interface since most of the characteristic absorptions due to the surfactant occurs in the transparent region. Any infrared absorption band

²⁸So far the only commercially important surfactants in the zinc pressure leaching systems are lignin-sulphonic acid or its salt and quebracho.

in the 2500–800 cm^{-1} region would be either due to impurities in the mineral²⁹ or to molecules adsorbed on the surface of the mineral.

A significant portion of the present research was concerned with the study of the adsorption mechanism of leaching reagents (surfactants, notably ligninsulphonic acid, and OPD) on the surface of sphalerite. This objective was achieved by employing in-situ attenuated total reflection³⁰ (ATR) - Fourier transform infrared (FTIR) spectroscopy technique.

The conventional transmission technique³¹ was used in this work primarily to record the reference spectra of sphalerite and the surfactants studied.

2.5.1 Theory of Infrared Spectroscopy

All spectra are the result of absorption or emission of electromagnetic radiation (by atoms or molecules) that occurs between definitely quantized energy levels. The transfer of energy between the molecule and the electromagnetic field is given by [121]:

$$\Delta E = h\nu$$

where h is known as Planck's constant and ν is the frequency of incident radiation. A positive ΔE implies absorption of radiation by a molecule resulting in an absorption spectrum. A negative ΔE implies that a molecule emits radiation and hence represents an emission spectrum. This results in a spectrum being unique to the molecule under investigation, and the spectrum is represented on a light intensity - frequency plot, with peaks occurring wherever the above conditions are satisfied.

Both atoms and molecules give rise to spectra. The atomic spectrum consists of a series of sharp lines, whereas a molecular spectrum consists of a series of bands. The

²⁹Naturally occurring minerals will always contain some amount of impurities.

³⁰This is sometimes referred to as internal reflection spectroscopy (IRS).

³¹This technique is the KBr pellet/wafer method.

difference between atomic and molecular spectra depends on the different energy levels involved in the transitions. Atomic spectra are the results of *transitions between the different allowed energy levels for the orbital electrons*, whereas for molecular spectra, the atoms within the molecule vibrate and *the molecule as a whole rotates*, and thus the resultant energy contributions are given by [121]:

$$E_{total} = E_{elec} + E_{vib.} + E_{rotn.} + E_{transl.}$$

The translational energy, $E_{transl.}$ is usually extremely small, and hence can be ignored. The isolation of the electronic, vibrational and rotational energies is possible because the separation between electronic energy bands is much greater than separation between vibrational levels which in turn is larger than the separation between rotational levels, see Figure 2.6.

Thus, a series of vibrational levels is associated with each electronic level and a series of rotational levels is associated with each vibrational level. Electronic level transitions result in electronic spectra which are observable in the visible or UV regions of the spectrum; vibrational level transitions in the same electronic state give absorption in the infrared region of the spectrum. These vibrational transitions are usually accompanied by rotational transitions. At low frequencies, in the far infrared (below 500 cm^{-1}), pure rotational spectra are observed.

2.5.2 Molecular Force Constants

The vibration of atoms within a molecule can be equated to a simple harmonic oscillator. whose frequency of vibration is given by classical mechanics as [121, 122, 123]:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu_m}}$$

or

$$\frac{1}{\lambda} = \frac{1}{2\pi c} \sqrt{\frac{\kappa}{\mu_m}} = \vartheta$$

where

κ = force constant or strength

μ_m = reduced mass of atoms

ϑ = wavenumber

ν = frequency of vibration

λ = wavelength

c = speed of light

The reduced mass is given by:

$$\frac{1}{\mu_m} = \frac{1}{m_1} + \frac{1}{m_2}$$

where m_1 and m_2 are the masses of the two atoms involved in the particular bonding in the molecule. The force constant of the harmonic oscillator is considered to be analogous to the strength of the chemical bond, and hence κ is a measure of the strength of a chemical bond. It is easy to conclude that larger force constants are indications of stronger chemical bonds. Changes in the positions of the vibrational frequency upon adsorption of a molecule on a surface can be directly attributed to changes in the strength of the bond that gives rise to the particular vibration. Shifts to lower wavenumbers indicate weakening of the bond (a lower force constant) and shifts to higher wavenumbers indicate strengthening of the bond under consideration. Frequency is also dependent upon the mass of atoms that constitute the molecule. Chemical bonds involving atoms of low mass will have higher vibrational frequencies than those involving atoms of high mass for equal force constants.

Spectral Units ν = frequency, sec⁻¹ λ = wavelength (cm) $\lambda\nu = c$, the velocity of light = 3*10¹⁰ cm/sec $1\mu = 10^{-4}$ cm = 10⁴ Å ϑ = wavenumber, cm⁻¹

$$\vartheta(\text{cm}^{-1}) = \frac{1}{\lambda(\text{cm})} = \frac{10^4}{\lambda(\mu)}$$

Hence,

$$E = h\nu = \frac{hc}{\lambda} = hc\vartheta$$

 E = ergs, joules or eV h = Planck's constant = 6.63*(10⁻³⁴) J s.**2.5.3 Absorption of Infrared Radiation**

Electrodynamically, a molecule can absorb radiation if: i) *it possesses a vibrational or rotational frequency the same as that of the incoming electromagnetic radiation; and ii) a change in the magnitude and/or direction of the dipole moment occurs.* [121]-[124].

When the electrical field of the molecule rotates or vibrates at the same frequency as the incident electromagnetic radiation, transfer of energy takes place³². The dipole moment acts as a coupler, coupling the energy from the incident radiation to the molecule.

Absorption band intensities are related to the concentration of the absorbing species. The intensity of light (I) transmitted through an absorbing medium at a wavenumber ϑ is given by Beer's law:

$$I = I_0 e^{-k\bar{c}l}$$

where

³²This transfer of energy is usually absorption of radiation by the molecule.

I_o = intensity of incident radiation

$\bar{c}$ = concentration of absorbing species in the sample

l = path length of radiation in the sample

k = absorption coefficient, which is characteristic of the absorbing species

The definitions of transmittance and absorbance are given as:

- transmittance, $\vec{T} = I/I_o$ or percent transmittance, $\% \vec{T} = 100I/I_o$

- absorbance, $A = \ln 1/\vec{T} = \epsilon l$

where $\epsilon = k\bar{c}$, an "extinction coefficient" which has units of cm^{-1} [121].

Adsorption Processes

There are two distinct types of adsorption processes: a) physical adsorption (or physisorption) - a process in which the bond between adsorbent and adsorbate is considered to be due to Van der Waals or electrical forces and permanent dipoles; b) chemisorption in which the adsorbate goes through chemical interaction with the adsorbent; it may be dissociative, non-dissociative or reactive in nature [121].

A physically adsorbed species is usually considered to be an adsorbed material that can be completely removed from the surface without decomposition.

The infrared spectrum of a molecule is the result of vibrations of the atoms within the molecule; the number and frequency of vibrations being determined by the symmetry and bond strength of the molecule as a whole. The infrared spectrum of physically adsorbed species is only slightly altered and small frequency shifts are observed. In chemisorption, a completely new infrared spectrum *may* be observed and band shifts and intensities are far removed from those of the independent bulk species [121]. Both physical and chemical adsorption processes can take place simultaneously on a surface, especially at lower temperatures.

The Fingerprint Region of an IR Spectra.

At frequencies greater than 1500 cm^{-1} , assignment of absorption bands to functional groups is easy. Below 1500 cm^{-1} , band assignment is possible (but not easy) and this region is usually known as the "fingerprint region" of the spectrum [121]-[126]. The vibrations of the molecule as a whole give rise to a series of absorption bands at low energy, below 1500 cm^{-1} , the positions of which are characteristic of the molecule under study.

Vibrational Changes on Adsorption

The spectrum of any given molecule is unique and depends on the vibrations of the atoms within the molecule and the rotation of the molecule as a whole. On adsorption of the molecule on a surface, the rotational movement is severely restricted and if the process of adsorption is chemisorption, the vibrational modes will be severely affected as well. If the process of adsorption is physical adsorption, much of its rotational movement will be lost but the vibrational movements will be little affected by the process. Thus, the adsorption bands before and after adsorption should be similar.

2.5.4 Infrared Techniques

KBr Pellet/Wafer Transmission Technique

Before the advent of the attenuated total reflection - FTIR technique³³, the KBr window transmission method was the standard infrared practice. In the transmission measurement or spectral recording, the radiation of wavelength λ passes through a sample (e.g. KBr pellet) and the absorption of the radiation by the sample causes its intensity to drop from I_0 to I . The KBr window per se is transparent to infrared radiation. This method

³³This technique is described in the next section.

is applicable to solids and involves the use of KBr salt³⁴ to prepare sample pellets or discs³⁵. The sample disc can then be scanned for infrared absorbance or transmittance. The technique is based on the assumptions that the KBr does not interact with the sample. The KBr technique is a useful means of studying adsorbed reagents on minerals but remains an "ex-situ" technique, so that any details about the adsorbate in an in-situ situation are lost [116].

Attenuated Total Reflection (ATR) Technique

The ATR technique otherwise referred to as the Internal Reflection Spectroscopy (IRS), presents an opportunity for an in-situ study of the mineral-aqueous solution interface³⁶. It is a technique for recording the optical spectrum of a sample material that is in contact with an optically denser but transparent medium [116, 127]–[130]. The ATR technique, has been successfully employed in in-situ studies of flotation systems. The principle of this method is that an infrared beam should be internally reflected through a trapezoid of an internal reflecting element (IRE)³⁷. For total internal reflection to take place, the incident beam should have an incident angle greater than the critical angle, θ_c , of the crystal, so that (coupled with the high refractive index of the reflecting crystal), it can be reflected by the flat faces of the IRE. The critical angle is given by:

$$\theta_c = \sin^{-1} \frac{n_2}{n_1}$$

where n_1 and n_2 are the refractive indexes of reflector and sample respectively.

³⁴The salt should be of infrared grade.

³⁵Adequate precautions should be taken to avoid contamination of the pellet.

³⁶It is important to note that all techniques (eg. KBr) which deal with the adsorbent being transferred from an aqueous (or liquid) medium to a gaseous environment are liable either to pick up species adsorbed at the liquid-gas interface, or to shed some of the adsorbate onto the liquid-gas interface. This means that the interpretation of adsorption at the solid-liquid interface cannot be ascertained unless done by an in-situ method and only the ATR method is capable of handling that situation [116].

³⁷This can be any crystal that is transparent to infrared rays and has a higher refractive index than the sample under investigation.

Theoretically, during the course of the beam being reflected by the IRE, it appears to penetrate slightly beyond the reflecting surface and into the rarer medium³⁸, Figure 2.7.

A material (or sample) placed in contact with the IRE will selectively absorb radiation corresponding to its vibrational frequencies owing to interactions with the beam. The outgoing beam will have an absorption spectrum characteristic of whatever is next to the crystal face e.g. surface coating. As a result, only the layer situated very close to the surface may be examined spectroscopically. The thickness of the layer may be a fraction of wavelength or several wavelengths. Increasing the number of reflections (i.e. multiple reflections) is equivalent to increasing the path length in transmission studies³⁹. This increases the amount of the beam absorbed by the sample. The depth of beam penetration is a function of a) beam wavelength, b) refractive index of both sample and reflector (IRE), and c) angle of incidence.

The advent of Fourier Transform Infrared (FTIR) spectrometers coupled with computers has made the application of the ATR technique in surface chemistry easier. FTIR spectroscopy can give an average infrared spectrum of the compounds present on the surface of minerals, even in very low concentrations. FTIR spectrometers have high energy throughput, high signal-to-noise ratio, high sensitivity, high data acquisition speeds and flexibility to manipulate the data.

Internal reflection spectroscopy can take three different approaches: in one method the mineral (or sample) is deposited by vacuum evaporation as a thin layer on the reflecting element and then used as the adsorbent. The second approach uses finely ground sample/mineral particles conditioned externally and introduced into the ATR cell. The third

³⁸The rarer medium mentioned here represents the working sample material or any other surface coating on the IRE.

³⁹The ATR technique as practiced nowadays makes use of multiple internal reflections and this results in better sensitivity.

approach involves direct adsorption of surfactants from solution onto reactive mineral-reflecting element substrate. The use of vacuum evaporation/deposition of mineral sample has its own problems. The vapour deposited mineral will certainly be different from a natural mineral. The second approach permits spectral measurement of a natural mineral surface in the presence of an aqueous solution. Direct adsorption onto a reactive mineral IRE provides more quantitative information regarding the nature, structure and orientation of adsorbed species than the other two methods.

SUMMARY

It can be seen from the literature that much work has been done in the area of sphalerite leaching in ferric sulfate and ferric chloride media and in the presence of oxygen. All of these studies are related to the kinetics of the leaching process and the role of liquid sulfur in the process both at temperatures lower and greater than the melting point of elemental sulfur (i.e. 119°C). The leaching mechanism is usually electrochemical in nature. It is noted that the presence of ferric ions in the leach solution and the solid solution iron content tend to speed up the metal dissolution rate. The leaching of ZnS in an acidic medium at temperatures less than 159°C converts almost all of the sulfide sulfur to the elemental state with minor oxidation to the sulfate form. Depending on the temperature, the elemental sulfur can slow down the reaction rate or have a negligible effect. At temperatures greater than 119°C , liquid sulfur slows the rate down by complete wetting of the particles and the only way to avoid this wetting is by the introduction of a surface active agent (e.g. lignin sulfonic acid) which plays a very important interfacial role by creating unfavourable thermodynamic conditions for the wetting by liquid sulfur to continue.

The mechanisms of the surfactant adsorption process on a molecular scale in the leaching system are not well understood. Unlike flotation systems which have been well

studied spectroscopically, infrared studies of surfactant adsorption in leaching systems are not reported in the literature.

Thus, it is the objective of this study to further our knowledge of mineral-surfactant interactions in zinc pressure leaching systems. High temperature surface tension and contact angle measurements in the liquid sulfur-mineral-aqueous system will be employed to determine the macro effects of a range of surfactants. Laboratory scale zinc pressure leach experiments will be performed to measure surfactant performance in relation to measured interfacial activity. On a molecular scale, ATR-FTIR methods will be employed to further our understanding of mineral-surfactant interactions in an aqueous environment.

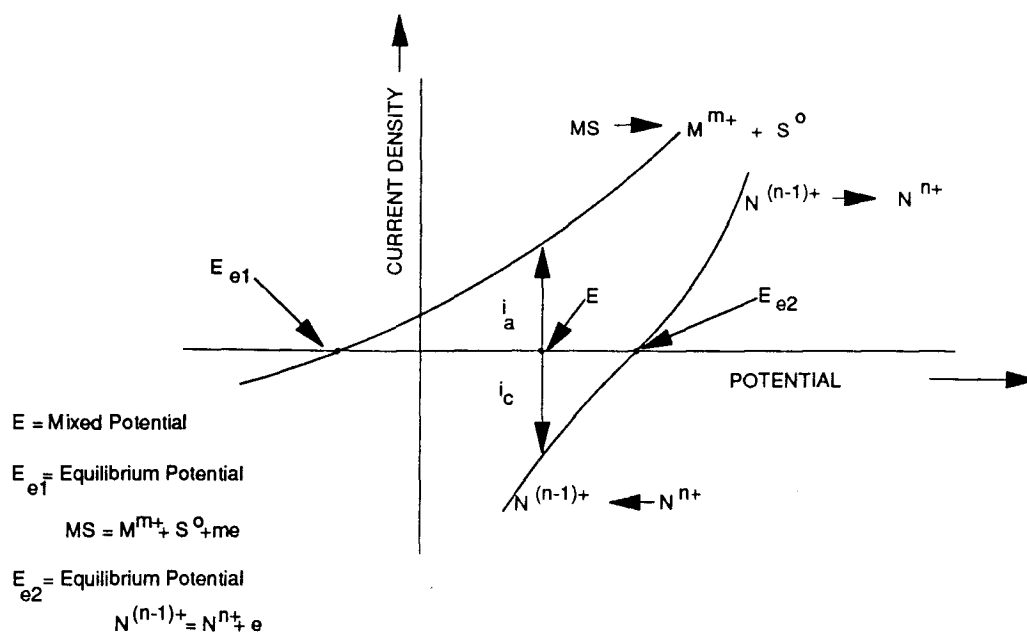


Figure 2.1: Current density- potential diagram; after Wadsworth [1].

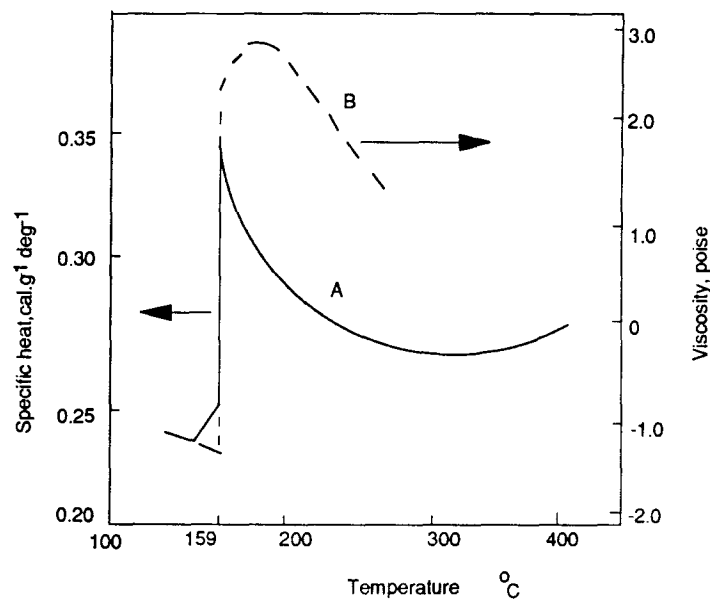


Figure 2.2: Viscosity of liquid sulfur; after Tuller [78].

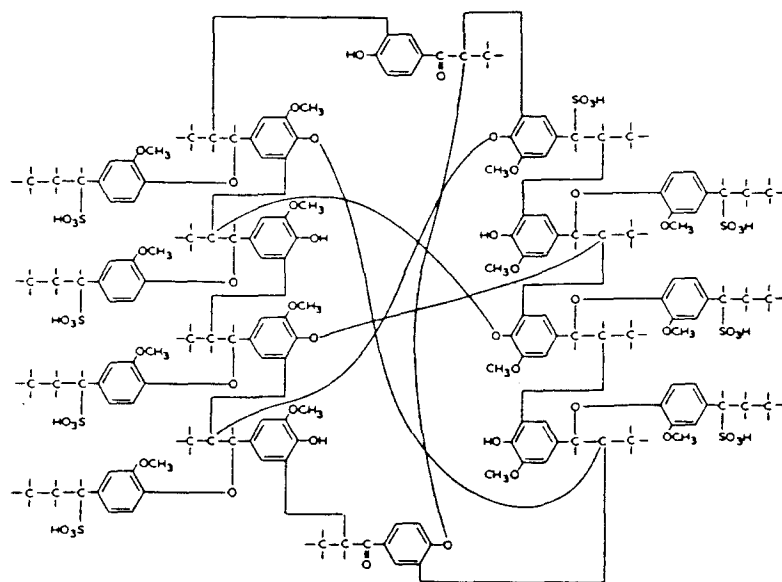


Figure 2.3: Possible structure of lignin sulfonate; after Pearl [86].

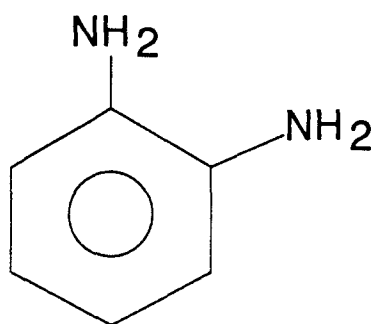


Figure 2.4: Structure of OPD; after reference [92].

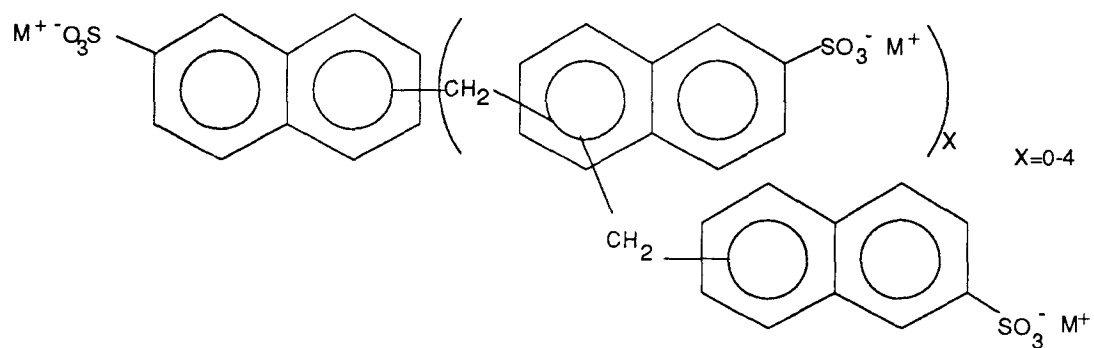


Figure 2.5: Structure of naphthalene sulfonic acid-formaldehyde condensates; after Rosen [83].

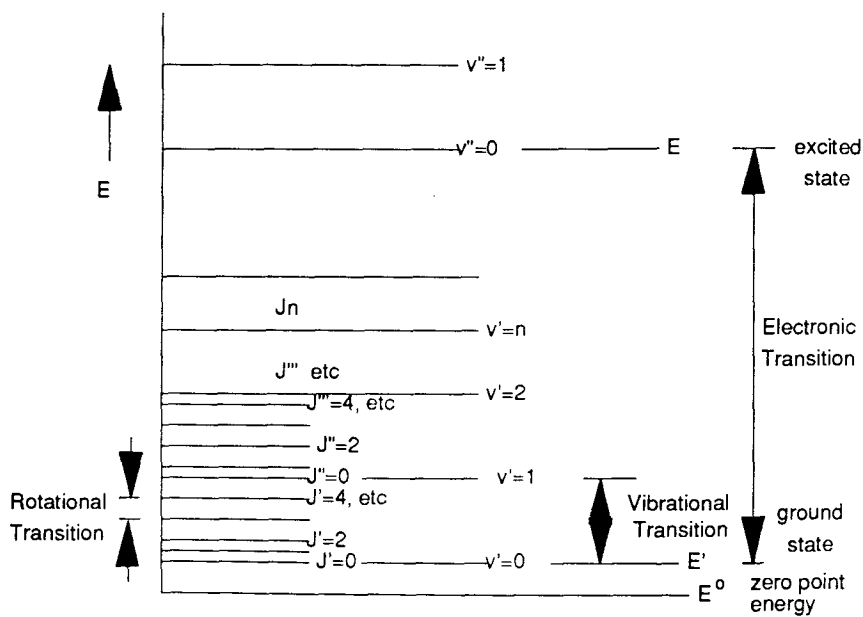


Figure 2.6: Atomic energy levels; after Hair [121].

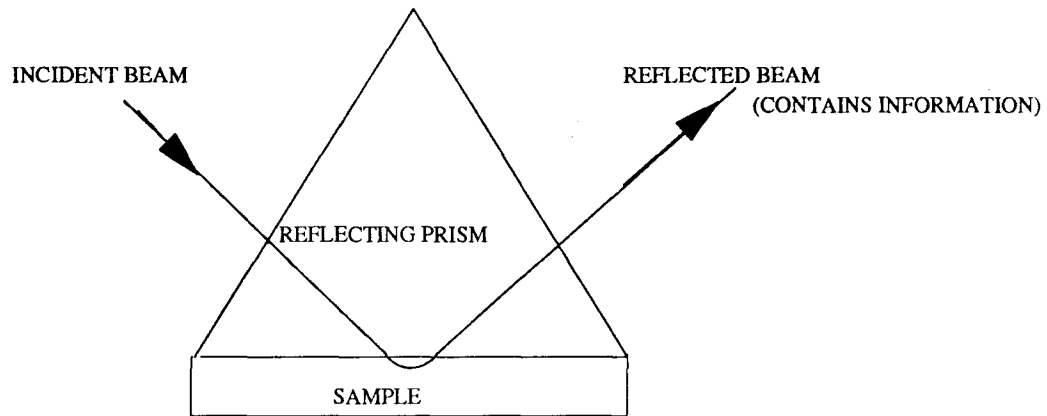


Figure 2.7: Internal reflection effect; after references [121].

Chapter 3

OBJECTIVES AND EXPERIMENTAL APPROACH

3.1 OBJECTIVES

In-situ investigations of solid–aqueous solution interactions are becoming very important in the development of novel technological and scientific applications. Until recently, not very much was known about the nature and structure of adsorbed species formed on the surfaces of solids fully immersed in liquids. Recent studies on in-situ solid-solution interactions have contributed tremendously to the understanding of the mechanisms and the nature of interactions occurring between flotation reagents and their substrates. It is evident from the literature that, unlike flotation systems, not much is known about mineral–surfactant solution interactions in leaching systems on a molecular level. A critical review of the literature has shown that very little work has been done on the leaching behaviour of sulfide minerals (particularly ZnS) with commercially important surfactants or dispersants, in spite of the fact that many studies have been carried out in terms of process kinetics and chemistry in the different leaching media. It is time that the fundamental mechanisms governing surfactant–mineral interactions in leaching systems be looked into as has been done in the past decade or more for flotation systems. Practical leaching processes are complex phenomena in which numerous variables come into play, and where possible, these variables need to be studied. The growing importance of pressure leach processes at temperatures greater than the melting point of elemental sulfur creates opportunities for research and development of other surfactants as substitutes for

lignin sulfonic acid. This objective can be achieved only when the fundamental chemistry involving surfactant–mineral interactions is well understood.

The present study builds on an earlier investigation of mineral–surfactant interactions [54, 56].

It is the objective of this study to investigate the molecular interactions that occur between zinc sulfide (or sphalerite) minerals and surface active agents during oxidative pressure leaching and to understand the basic principles governing the adsorption and effectiveness of surfactants or dispersants in the zinc pressure leach process.

3.1.1 Scope of Study and Approach

The scope of the study involved identifying some selected surfactants¹ and applying them in the following areas of study:

- interfacial tension and contact angle measurements: the measurements made include liquid sulfur–aqueous solution interfacial tensions and liquid sulfur–solid mineral contact angles both in the absence and presence of surfactants employing the pendant drop and sessile drop techniques respectively.
- leaching studies: these involve the use of the selected surface active agents as dispersants for the oxidative pressure leaching of the ores or concentrates.
- infrared studies: these involve the study of the nature of bonding or interactions between the surface of the mineral and any added surfactant in the solution. The in-situ ATR–FTIR technique was employed in this study.

¹These were selected based on their physical and chemical properties.

Chapter 4

EXPERIMENTAL TECHNIQUES

The experimental study was divided into three distinct phases:

1. Interfacial phenomena investigations in the aqueous - mineral - liquid sulfur - surfactant system.
2. Pressure leaching experiments designed to evaluate surfactant performance.
3. Infrared spectroscopy of mineral - surfactant systems.

4.1 INTERFACIAL PHENOMENA

The purpose of this study was to investigate the interfacial behaviour exhibited by the liquid sulfur - aqueous zinc sulfate - zinc sulfide mineral system under simulated zinc pressure leaching conditions in the absence and the presence of different surfactants. This requires the measurement of the liquid sulfur - aqueous solution interfacial tensions and liquid sulfur - zinc sulfide - aqueous solution contact angles in the absence and presence of the different surfactants mentioned. There are numerous techniques for determining these quantities; however, each of these has its own limitations. A thorough review of the literature [132]-[151] shows that for the purpose of this study, the pendant drop technique has a number of outstanding advantages over other methods for measuring the interfacial tension. Advancing contact angles were measured using the sessile drop approach. The pendant drop technique involves taking a photograph of liquid sulfur suspended in an aqueous solution of zinc sulfate while in the sessile drop method, a photograph is taken

of a drop of liquid sulfur droplet resting on a flat mineral surface fully immersed in a zinc sulfate solution. The interfacial tension and the advancing contact angle can be determined by measuring the shape and position of the sulfur droplet. The aqueous solution may contain other solutes which are typical of zinc pressure leach solutions. Such measurements require the use of a pressurized apparatus capable of raising the boiling point of the solution to temperatures above the melting point of elemental sulfur. These methods are static: once the surface of the drop is formed, equilibrated, and photographed, the data for surface tension measurement are complete and not affected by any outside influence prior to or during the measurement.

The pendant drop technique is suitable for measuring the interfacial tensions between two liquids. In brief, the pendant drop method consists of suspending a small drop of one liquid (the denser liquid) from the end of a vertical cylindrical tube in a second liquid (the lighter liquid). The shape and size of the drop can be determined by measurements made on a photograph. The drop formed is influenced by two opposing forces, namely surface/interfacial tension and gravitational forces. The effect of the presence of the force of gravity is to elongate the drop so that its length exceeds its width. Without the presence of a gravitational force, the drop assumes a shape of minimum surface area or energy (i.e. a sphere). Figure 4.8 shows the profile of a pendant drop.

Advancing contact angles were measured using the same experimental setup as that for the interfacial tension determinations. However, instead of a suspended drop as in the interfacial tension determinations, the liquid sulfur drop was made to rest on the flat surface of a zinc sulfide mineral specimen that was fully immersed in an aqueous solution and a picture taken of the drop. Once in contact with the sulfide mineral, the sulfur droplet begins to spread and the pictures were taken when this lateral movement ceased. Figure 4.9 shows the profile of the drop shape under different aqueous environmental conditions.

Apparatus

Figure 4.10 shows the details of the equipment used for the interfacial tension and contact angle measurements. The bomb was heated externally by wrapping it with a heating tape followed by an insulating blanket. The inner chamber of the bomb was totally enclosed to prevent loss of liquid by evaporation. The tip was made from tubing having a circular cross-section. The end was cut off perpendicular to the vertical axis. Microscopic perfection was not essential since the liquid tends to bridge over any minor irregularities.

Chemicals

The chemicals used were: reagent grade zinc sulfate, sulfuric acid, sulfur flowers, ferric sulfate, ferrous sulfate, sodium silicate, zinc sulfide mineral (marmatite) specimens (obtained from Cominco Ltd). The surfactants and the sources of supply were:

- Calcium-based lignin sulfonic acid obtained through the courtesy of Cominco Metals Ltd, Trail, British Columbia (supplied by Reed Inc., Quebec).
- Orthophenylene diamine (often referred to as OPD in this work) obtained through the courtesy of Dupont Chemicals, Wilmington, Delaware, U.S.
- Sodium salt of naphthalene sulfonic acid - formaldehyde condensates supplied by Handy Chemicals Ltd., Laprairie, Quebec
- Cocoamido hydroxyl sulfobetaine (CAHSB)
- Tallowamido hydroxyl sulfobetaine (TAHSB)
- Cocoamido betaine (CAB)

The last three surfactants were obtained through the courtesy of Alkaril Chemicals Ltd., Mississauga, Ontario.

EXPERIMENTAL METHODS

The bomb and its accompanying accessories were carefully cleaned¹ and dried to get rid of any unwanted material or dirt. A thermocouple was constructed from type E (chromel-constantan) wire and calibrated. After the cleaning process, the equipment was assembled and calibrated by measuring the interfacial tension of water and benzene at room temperature². After this test, the equipment was thoroughly cleaned again and dried to make sure there was no residual benzene in the system to affect the subsequent determinations. The focus of the study was on the interfacial role of different surfactants in the liquid sulfur - aqueous zinc sulfate - zinc sulfide system under conditions similar to those prevailing in the zinc pressure leaching process. This involves the measurement of liquid sulfur - aqueous solution interfacial tensions and liquid sulfur - zinc sulfide mineral - aqueous solution contact angles.

4.1.1 Interfacial Tension

All experiments were carried out at a pressure of 620 kPa and a temperature of $130 \pm 5^\circ\text{C}$ using 1.2 mol/L zinc sulfate solution³. The conditions of the aqueous solution environment (due to the presence of added solutes) were varied in accordance with the experimental objectives. These included:

- the effect of different surfactants and dosages
- the presence of ferric and ferrous ions

¹The cleaning was performed using acetone and distilled water.

²The purpose of this test was to determine how the measurement deviates from the theoretically listed interfacial tension for water-benzene systems.

³The choice of these conditions was based on results obtained from earlier work [55, 56] in which it was observed that above a zinc sulfate solution concentration of 1.0 mol/L, there was no change in the liquid sulfur-aqueous solution interfacial tensions (in the absence of any surfactant) and within a pressure range of 276–620 kPa the effect of pressure on the interfacial tensions was negligible.

- the presence of acid

In each test, the syringe was partially filled with sulfur. The rectangular optical cell was carefully mounted on the adjustable seat, K, in the bomb such that the sapphire windows of the pressure vessel were parallel to the optical sides of the cell. The cell was then carefully filled with the aqueous solution. The syringe was then mounted and the thermocouple inserted into the thermowell to record the temperatures as the bomb was being heated. The heating rate was controlled using a powerstat. The chamber was closed and sealed and then subjected to nitrogen pressure at 620 kPa. Since the operating temperature was higher than the melting point of elemental sulfur ($\sim 119^{\circ}\text{C}$), the sulfur melted in the syringe. At the operating temperature, the drive-screw of the syringe was moved in a downward direction until the sulfur formed pendant drops at the tip immersed in the aqueous solution. The design and construction of the syringe was such that it allowed the position (i. e. height) of the tip to be adjusted. This enabled the drop to be positioned appropriately to be photographed. Several drops were formed and photographed for each experimental condition after which one of the controlling variables was changed and the sequence of operations was repeated. All experiments were done in duplicate and some in triplicate to ensure that any data obtained were reproducible. The results of repeated experiments were within $\pm 2\%$. The measurements were made from the photographs of drop profiles and interfacial tensions were calculated using these profile measurements. The measurements were made at points on the drop which were remote from the end of the tip and where the influence of imperfections in the shape of the tip was normally negligible. Adequate precautions were taken to ensure attainment of interfacial equilibrium. The required dimensions were measured with a rule graduated to 0.5mm. These dimensions were estimated to the nearest 0.1mm. Repeated measurements of the same drop were reproducible to within $\pm 0.1\text{mm}$. Some of the

dimensions were remeasured using a computer scan to determine the accuracy of the manual measurements. The variation was within ± 2 %.

The magnification of the pendant drop was determined from a knowledge of the enlarged diameter of the capillary tip (actual diameter was known to within ± 0.002 mm).

4.1.2 Contact Angle Measurements

After the surface tensions experiments, a series of experiments was carried out to determine the zinc sulfide mineral - liquid sulfur - aqueous solution advancing contact angles in the absence and presence of the different surfactants. Determinations were carried out in the following environments:

- zinc sulfate (1.2 M) solution
- 1.2 M zinc sulfate, 0.05 M Fe^{2+} , and 0.12 M Fe^{3+} in 0.2 M sulfuric acid solution

The technique used was similar to that employed in the previous work. The difference was that a picture was taken of liquid sulfur resting on a solid mineral surface (instead of being suspended) in an aqueous environment.

The marmatite mineral specimen was carefully cut into a rectangular shape. The surface was carefully polished using a 600 grit sand paper. The specimen was then rinsed several times with distilled water. The mineral was carefully mounted horizontally in the optical cell. The cell was filled with the aqueous solution and the set up completed as described above. The drops were carefully controlled in order to determine the advancing contact angles by gradually increasing the droplet size. Once in contact with the sulfide mineral, the sulfur droplet begins to spread and the pictures were taken when this lateral movement ceased. As has been pointed out by Good and Oss [152], the system does not need to attain thermodynamic equilibrium before taking the pictures for the necessary measurements. After each run, the mineral was carefully cleaned (as described above)

to remove any residue that might have been deposited on the surface during the course of the experiment and the series of measurements repeated. The contact angles were measured directly from the photographs.

Quantifying Interfacial Parameters

Interfacial Tensions

Unlike contact angles which can be measured directly from the photographs, the interfacial tensions have to be computed [133]–[150]. There are three techniques for the mathematical treatment of the pendant drop profile: a) the method of the plane of inflection b) the equation of state approach [153] c) the method of a selected plane. However, the method of the plane of inflection has two severe limitations which make its application very tedious and inaccurate. These are i) the true plane of inflection of the drop must be accurately located (which is graphically difficult) since a slight deviation from the true plane might introduce a large error and ii) the volume of the drop must be computed from its profile. These difficulties limit the precision of the method [134, 137]. The second method involves rigorous mathematical formulation but this is simplified by being incorporated into a computer software. It involves direct digitizing of the profile of the liquid droplet resting on a solid surface. This method measures the interfacial tension and the contact angle simultaneously. The drop is considered to be at equilibrium with its surroundings. It results in a precise solution. The third treatment is an indirect approach and also leads to a more rapid and precise solution. In this method, the drop profile, (Fig. 4.8), is considered to be at equilibrium with its surroundings, symmetrical and to possess two radii of curvature, R_1 and R_2 (as with any curved surface). At the apex (or bottom of the drop), O , the two are the same. The mathematical treatment is based on the assumption that the pressure difference developed at any curved surface due to the surface or interfacial tensions is proportional to the sum of the principal curvatures

of the surface, i. e.

$$p \propto \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (4.23)$$

or

$$p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (4.24)$$

where γ is the interfacial tension in mN/m. This equation is known as the Laplace equation.

If y is the vertical height of the liquid measured from the apex of the drop profile where the two radii of curvatures are equal to each other i. e. $R_1 = R_2 = h$, then the hydrostatic pressure due to the curvature of the hanging drop at any point is given by:

$$p = \frac{2\gamma}{h} - \rho g y \quad (4.25)$$

Combining equations (4.24) and (4.25)

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\gamma}{h} - \rho g y \quad (4.26)$$

where ρ is the density difference between the liquids in question. From geometry⁴ [133, 160, 161]

$$R_1 = \frac{(1 + (\frac{dy}{dx})^2)^{3/2}}{\frac{d^2y}{dx^2}} \quad (4.27)$$

and

$$R_2 = \frac{x}{\sin \phi} = \frac{x(1 + (\frac{dy}{dx})^2)^{1/2}}{\frac{dy}{dx}} \quad (4.28)$$

Therefore

⁴The geometrical derivation is described in appendix A

$$\frac{\frac{d^2y}{dx^2}}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{3/2}} + \frac{\frac{dy}{dx}}{x \left[1 + \left(\frac{dy}{dx}\right)^2\right]^{1/2}} = \frac{2}{h} - \frac{\rho g y}{\gamma} \quad (4.29)$$

hence,

$$\frac{d^2y}{dx^2} + \frac{dy}{dx} \left[1 + \left(\frac{dy}{dx}\right)^2\right] = \left[\frac{2}{h} - \frac{\rho g y}{\gamma}\right] \left[1 + \left(\frac{dy}{dx}\right)^2\right]^{3/2} \quad (4.30)$$

This second-order, second-degree differential equation cannot be easily integrated; however it can be simplified by transforming it into a non-dimensional form such that:

$$Y'' + \frac{Y'}{X} [1 + (Y')^2] = [2 - \beta Y] [1 + Y^2]^{3/2} \quad (4.31)$$

where

$$\beta = \frac{g \rho h^2}{\gamma} \quad (4.32)$$

and

$$X = x/h, Y = y/h, Y' = dY/dX, \text{ and } Y'' = d^2Y/dX^2$$

From equation (4.32),

$$\gamma = \frac{g h^2 \rho}{\beta} \quad (4.33)$$

The dimensionless parameter β and the radius of curvature h cannot be precisely determined for a pendant drop from a picture of the drop.

In order to solve for the interfacial tension, values must be assigned to β and h in equation 4.32): consider the drop profile in figure 4.8 - the size is dependent on its equatorial diameter, d_e , and the shape is also dependent on the ratio of the diameters measured at two different horizontal planes [134]. The line CD is at a distance d_e from

the apex of the drop, where d_e is the equatorial (or maximum) diameter of the drop⁵. From the measured values of d_e and d_s , the shape ratio,

$$S = d_s/d_e \quad (4.34)$$

is computed for each drop profile. The value of the shape ratio is dependent on the drop.

Another parameter, H , can also be defined as a function of the drop shape such that:

$$H = \beta \left(\frac{d_e^2}{h} \right) \quad (4.35)$$

$$= \rho g \frac{d_e^2}{\gamma} \quad (4.36)$$

H is considered to be a function of S . Tables of values of H as a function of S are available [132, 133] from which γ can be quantified from the photograph. Rewriting equation (4.36)

$$\gamma = \frac{\rho g (d_e)^2}{H} \quad (4.37)$$

where

ρ = density difference between the two liquids in question;

g = acceleration due to gravity;

d_e = equatorial diameter of the drop and is obtained from:

$$d_e = \left(\frac{w_o}{w_m} \right) d_e^m \quad (4.38)$$

w_o = original diameter of the tip

w_m is the magnified diameter of the tip as measured from the photograph

d_e^m is the magnified diameter of drop as measured from the picture.

The density of the liquid sulfur with temperature was obtained from the literature[78].

⁵The diameter d_e is first measured, then by constructing the base line AOB, a parallel line CD, (d_s), is drawn at a distance d_e from AOB.

The density of the aqueous solutions were determined at room temperature and corrected for high temperatures (i. e. at the operating temperature) on the assumption that the solutions have about the same coefficient of expansion as water (though this might introduce a slight error).

Contact Angle

Contact angles were measured directly from the photographs with a fair degree of accuracy. The contact angle between a liquid and any other phase(s) in contact with it at equilibrium⁶ is related to the interfacial tension or free energy per unit area of those phases. In the case of sulfur in contact with a marmatite mineral surface and the aqueous phase these can be related as:

$$\gamma_{MA} = \gamma_{MS} + \gamma_{SA} \cos \theta \quad (4.39)$$

and

$$\gamma_{MA} - \gamma_{MS} = \gamma_{SA} \cos \theta \quad (4.40)$$

where γ_{MA} is the mineral - aqueous solution interfacial tension, γ_{MS} is the mineral - liquid sulfur interfacial tension, γ_{SA} is the liquid sulfur - aqueous solution interfacial tension, and θ is the contact angle measured in the liquid. The above equation is known as Young's equation [134]–[150], [162].

$\gamma_{MA} - \gamma_{MS}$ can be computed for the different systems. This will help in identifying the interface(s) at which surfactant adsorption takes place in the system. For no adsorption at the mineral surface, $\gamma_{MA} - \gamma_{MS}$ has to be constant for all systems irrespective of the aqueous environment.

⁶The contact angles measured in this study are not really thermodynamic equilibrium values. They are pseudo equilibrium or steady state values. However, for the purpose of computation, the contact angles will be assumed to be equilibrium values

4.1.3 Work of Adhesion

In the initial stages of a batch zinc pressure leach, liquid sulfur is non-existent. However, it immediately begins to form in the system due to the reaction. In a continuous process, there is a steady state of liquid sulfur present at all times. The sulfur tends to displace the aqueous phase from the solid surface by adhesional wetting (i. e. liquid sulfur forms on the surface, or makes contact and adheres to the surface). The surface free energy change associated with this wetting by liquid sulfur is:

$$-\Delta G_w = a(\gamma_{MA} + \gamma_{SA} - \gamma_{MS}) \quad (4.41)$$

where a is the surface area of the solid substrate (i. e. mineral) in contact with an equal surface of the liquid (sulfur) after adhesion. The driving force of this phenomenon is $\gamma_{MA} + \gamma_{SA} - \gamma_{MS}$.

The work of adhesion, W_a , is the reversible work required to separate a unit area of liquid from the solid substrate:

$$W_a = \gamma_{MA} + \gamma_{SA} - \gamma_{MS} = -\Delta G_w/a \quad (4.42)$$

This is known as Dupre's equation [83, 133, 149, 151]. In this process, any reduction of the mineral - sulfur interfacial tension results in an increased tendency for adhesion to occur, but reduction of either the liquid-liquid or mineral-aqueous interfacial tensions decreases the adhesive tendencies.

Substituting for $\gamma_{MA} - \gamma_{MS}$ from equation 4.40 into equation 4.42,

$$W_a = \gamma_{SA} \cos \theta + \gamma_{SA} \quad (4.43)$$

$$= \gamma_{SA}(1 + \cos \theta) \quad (4.44)$$

W_a can be computed from a knowledge of γ_{SA} and $\cos \theta$. The driving force in adhesional wetting can never be negative and is equal to zero only when the contact angle is 180° , which is never attainable in practice.

4.2 PRESSURE LEACHING OF SPHALERITE, (ZnS)

A series of leaching experiments was performed in the absence and presence of the different surfactants as dispersants for liquid sulfur. The objective of this study was to investigate the performance of each of these surfactants in leaching systems in relation to their interfacial activities and compare the findings to those obtained with lignin sulfonic acid.

Chemical Reagents and Surfactants used

The following chemicals were used in the preparation of the leaching solution: reagent grade zinc oxide, sulfuric acid, ferrous sulfate and hydrogen peroxide. The concentrate used for these studies was obtained through the courtesy of Snow Lake Mines - a subsidiary of Hudson Bay Mining and Smelting Co., Manitoba, Canada. The surfactants used were the same as mentioned earlier.

Chemical analysis of the concentrate gave the following elemental composition:

- 49.2 % zinc
- 11.4 % iron
- 0.6 % copper
- 0.6 % lead and
- 31.6 % sulfur

X-ray diffraction analysis of the concentrate indicated that the bulk of the concentrate was present as ZnS, the rest being mainly pyrite and copper sulfide minerals.

Two sets of leaching experiments were performed - low pulp density tests in which the amount of concentrate used was between 1–12 grams and high pulp density leaching tests in which the amount of concentrate used was 100 ± 5 grams for each test. The leaching tests were performed in a 2-L Parr titanium autoclave. The operating temperature for each test was $140 \pm 1^\circ\text{C}$.

4.2.1 Low Pulp Density Leaching

The size range of the concentrate used for these tests was -270+325 mesh. The variables which were investigated were: type and concentration of surfactant in question, time of leaching, and the mode of introduction of surfactant (either batch or continuous) into the system. For those surfactants available in only the liquid state, the tests were done with continuous addition of the surfactant. All batch additions were injected into the autoclave together with the concentrate sample. Prior to the introduction of the concentrate into the autoclave, about 1 or 1.5 L of the pre-prepared leaching solution (or lixiviant) was heated to the operating temperature of about $140 \pm 1^\circ\text{C}$ in the autoclave. The leaching solution was made up of:

- ~ 2 mol/L zinc ions (or zinc sulfate)
- ~ 0.15 mol/L ferric ions
- ~ 0.15 mol/L ferrous ions
- ~ 0.5 mol/L sulfuric acid

Once the operating temperature was reached, the concentrate was injected into the solution under oxygen or nitrogen pressure of about 1100 kPa using a specially designed

injection unit attached to the autoclave. The experiments lasted for a predetermined time of up to 30 minutes after which the autoclave was quickly quenched in an ice water bath until cooled to 75–80°C after which it was de-pressurised. The pulp was quickly filtered using a pressure filtration unit. Samples of the filtrate were collected for chemical analysis. After each run, care was taken to ensure that all of the leach residue was recovered for subsequent chemical analysis. The residue was dried in a vacuum drier for about 3–4 days, chemically digested⁷, and analysed for metal content. The extent of zinc extraction was determined from the residue analysis. The change in zinc concentration in solution was too small to determine the zinc extraction values accurately enough. The other forms of phenylene diamine: meta- and para- phenylene diamines were also tested under low pulp density conditions.

4.2.2 High Pulp Density Leaching

High pulp density leaching was carried out in the presence and absence of a surfactant. The principal surfactants used as dispersants were lignin sulfonic acid and orthophenylene diamine, although some experiments were performed using metaphenylene diamine (MPD) as the surfactant. The decision to use these surfactants was based on the results of the low pulp density tests⁸. The leaching time was 35–60 minutes. The particle size distribution of the concentrate sample used was:

- 3.4 % +170 mesh
- 43 % -170+230 mesh
- 23.8 % -230+325 mesh and

⁷The digestion was performed with concentrated sulfuric acid and dropwise nitric acid additions to a beaker on a hot plate.

⁸In the low pulp density leaching experiments only lignin sulfonic acid, OPD and MPD gave favourable results.

- 29.8 % -325 mesh

Equipment

The details of the equipment and the setup used for the high pulp density pressure leaching are shown in Figure 4.11.

Experimental Approach

Chemical analysis of the stock (or leach) solution for the oxidative pressure leaching was:

- 0.14 mole/L Fe^{2+}
- 1.27 moles/L Zn^{2+} (in the form of sulfate)
- 1.12 moles/L (or 109 g/l) sulfuric acid which dissociated incompletely to give
- 1.95 moles/L total acidity⁹ (H^+).

The recipe was designed so that enough sulfuric acid would be left in the system at the end of the process even if all of the soluble zinc and iron in the concentrate were dissolved in order to prevent or minimize the oxidation of elemental sulfur to sulfate, and also to prevent the hydrolysis of ferric ions.

A standard leaching procedure was followed throughout the course of the study. About 100 ± 5 grams of concentrate was weighed into an autoclave and 1.5 L of leach solution was added. The autoclave was sealed air-tight and flushed with nitrogen gas¹⁰. The autoclave was connected to the computer and the gas mass flow meter (as shown

⁹The method of determination of total acidity is described in the appendix B.

¹⁰This was to make sure there was no residual oxygen present in the space above the solution in the autoclave before the introduction of commercial grade oxygen. This was to ensure that at least within the limits of the experimental technique there was no reaction taking place during the heating period.

in Fig. 4.11) via the gas tubing to measure the oxygen flow rate at 1 second time intervals. Since any leakages in the system were registered on the computer, adequate steps were taken to eliminate leaks. The autoclave was heated to the working temperature of $140 \pm 1^\circ\text{C}$. In the runs with surfactants, a predetermined amount of the surfactant¹¹ under study was weighed into the injection unit. A brief sketch of the injection unit and its operation is shown in Fig. 4.12. At the working temperature, the agitator was started and oxygen was admitted into the autoclave via valve A and through the injection unit to pressurize it initially (valve C should be closed when performing this operation, B was opened all the time). Immediately after this operation, valve A was closed and C opened to allow oxygen to flow through the flow meter and into the autoclave as it is being consumed in the leaching reaction. The computer then began to register the oxygen flow rate. All these operations were completed within a time window of less than 8 seconds and it was assumed that the errors introduced into the data as a result of some reactions occurring in this time frame were very minimal as compared to the total extent of reaction in the predetermined time of 60 minutes or 35 minutes for the process (from the data obtained, it was in fact, estimated to be within $\pm 0.4\%$). The oxygen was delivered at a pressure of 1100 kPa. The use of the injection device ensured that the surfactant was introduced into the autoclave at the same time as the oxygen (when the reaction was assumed to begin).

At the end of the pre-determined time (for leaching), the oxygen flow was stopped and the autoclave was quickly quenched in an ice water bath to about $75\text{--}80^\circ\text{C}$ and filtered. The filtrate was analysed chemically for metal, sulfur and total acid content. The leach residue was washed and dried in a vacuum oven for about 4 days and samples were taken for chemical analysis.

¹¹Surfactants were added in batch form for all the tests carried out under high pulp density conditions.

4.3 INFRARED STUDIES

Infrared studies were performed using the attenuated total reflection–Fourier transform infrared technique (ATR–FTIR). The application of this technique permitted the study of the surfactant adsorption "in-situ". The transmission KBr disc/wafer technique was also employed to record the infrared spectra of the concentrate and the surfactants used before they were introduced into the solution.

Chemicals

The chemicals used were potassium bromide of infrared quality, sphalerite concentrate¹², lignin sulfonic acid and OPD. All other chemicals were of reagent grade.

Equipment

The ATR accessory had a germanium crystal internal reflection element (of 45° angle of incidence). The FTIR equipment used was a Bomem MB 100 series spectrophotometer with a frequency range of 6000–200 cm⁻¹.

The accessory was a model 11086 Specac clamp ATR. It had a micrometer controlled clamp-down facility. The sample material in the form of a paste/film or fine powder was evenly spread on the reflecting crystal and then sandwiched between the crystal and a top pressure plate to which an even pressure was applied via a micrometer thumb screw and a leaf spring. The applied pressure could be set with the micrometer.

¹²The concentrate was subjected to 35–40 minutes of fine (dry) grinding to expose fresh mineral surface.

4.3.1 KBr Technique

The FTIR equipment was first calibrated using polystyrene disc¹³ prior to any sample analysis. Regular calibration of the equipment was adopted since any change in atmospheric conditions could influence the spectra.

The absorption spectra of the organic surfactant and the sphalerite concentrate were recorded by both KBr transmission and ATR-FTIR technique.

About 3 mg of the reference material¹⁴ and 300 mg of KBr were thoroughly mixed and ground in an agate mortar and pressed into a disc at a pressure of about 28000–34000 kPa. Two pellets/discs were made for each material to ensure reproducibility.

Infrared spectra were recorded from the discs with the spectrophotometer, the samples being mounted in a holder in the path of the radiation beam, (figure 4.13). The inability of the KBr to absorb any infrared radiation between 4000–400 cm^{-1} wavenumber means that any absorption band within this region was due to the sample. Prior to the recording of any sample spectrum, the reference spectrum (of the sample chamber) was taken. The sample spectrum obtained was then plotted using a plotter connected to the FTIR computer.

4.3.2 Attenuated Total Reflection Technique

The ATR-FTIR technique was employed to investigate the nature of the surfactant adsorption at the solid-liquid interface in-situ. It permitted the recording of the spectra of the sphalerite conditioned in different aqueous phases. This technique was used for the spectral recording of both surfactant solutions and the conditioned (wet) sphalerite mineral. Figure 4.14 shows the set-up of the ATR accessory used.

¹³This disc was supplied, together with its spectrum by the manufacturers of the equipment

¹⁴The reference materials referred to here are the lignin sulfonic acid, OPD and the dry sphalerite concentrate.

A spectral record was first taken of the solvent (distilled water containing 0.036 mol/L acid) by spreading a thin film of the solvent on the germanium reflecting crystal and mounting the accessory in the infrared beam path.

A 3–4 gram sample of the concentrate was conditioned¹⁵ in the solvent (acidified distilled water) for about 20 minutes. This time window was selected based on the effect of time on the extent of zinc extraction from the leaching studies. A paste of the wet sample was then uniformly spread on the germanium crystal¹⁶ and mounted in the beam path to record the spectrum of the wet sample. These spectra served as the blank or reference spectra of the solvent and natural sphalerite when wet.

The scanning was done at a resolution of 4 cm^{-1} and 100 scans were done for each sample. After each test, the reflecting crystal was thoroughly cleaned using warm chromic acid followed by cold dilute nitric acid and distilled water in order to remove any residual chromate ions.

Lignin sulfonic acid tests

Two solutions, each containing 5.0 g/L of lignin sulfonic acid, and 0.036 mol/L sulfuric acid were prepared. One solution contained 0.025 mol/L ferric ions (added in the form of sulfate). The other solution did not contain ferric ions. The spectra for the surfactant solutions were recorded¹⁷ by spreading a thin film of the solutions on the internal reflection element. Spectra of 3–4 grams of concentrate conditioned in the appropriate surfactant solution for about 20 minutes were then recorded. After each conditioning in the surfactant solution, the sample was cold washed 3–4 times with the solvent (distilled water) and then subjected to a more drastic washing with boiling distilled water followed by cold washing again with the solvent. The infrared spectra of the washed samples were

¹⁵The concentrate was suspended for about 15 minutes and then allowed to settle.

¹⁶Sample is sandwiched between the reflecting crystal and the pressure plate.

¹⁷These were used for the appropriate spectral subtraction.

also recorded. Prior to each scanning, the background spectrum of the solvent had to be recorded.

Below is the list of the different conditions studied:

- KBr analysis of lignin sulfonic acid
- ATR analysis of 5.0 g/L surfactant and ferric solution
- ATR analysis of sphalerite conditioned in surfactant/ferric solution
- ATR analysis of washed sphalerite after conditioning in surfactant/ferric solution
- ATR analysis of sphalerite conditioned in surfactant solution in the absence of ferric ions
- ATR analysis of washed sphalerite after contact with surfactant solution in the absence of ferric ions
- KBr analysis of leached sphalerite residue

Orthophenylene diamine tests

A surfactant solution containing 5.0 g/L of OPD, and 0.036 mol/L sulfuric acid was prepared. A 0.025 mol/L ferric solution (in the form of sulfate) was also prepared. The spectrum for the surfactant solution was recorded¹⁸ by spreading a thin film of the solution on the internal reflection element as described earlier. About 3–4 grams of concentrate was conditioned in the surfactant solution (with and without ferric ion pre-treatment¹⁹) for about 20 minutes. The spectra for the conditioned samples were

¹⁸These were used for the appropriate spectral subtraction.

¹⁹In some of the tests carried out, the mineral concentrate was first preconditioned in a solution containing 0.025 mol/L ferric ions and 0.036 mol/L acid for 15–20 minutes, washed 3 times with the solvent before being introduced into the surfactant solution.

then recorded. After contact with the surfactant solution, the sample was subjected to the washing procedure described above and scanned as well. The background spectrum (of the solvent) had to be taken prior to each test.

Listed below are the different conditions studied:

- KBr analysis of orthophenylene diamine. This was compared with available spectra in the literature.
- ATR analysis of 5.0 g/L surfactant.
- ATR analysis of sphalerite conditioned in surfactant solution (no ferric pre-treatment).
- ATR analysis of washed sphalerite after conditioning in surfactant.
- ATR analysis of sphalerite conditioned in surfactant solution after pre-treatment with ferric ions.
- ATR analysis of washed sphalerite after contact with ferric/surfactant solution.

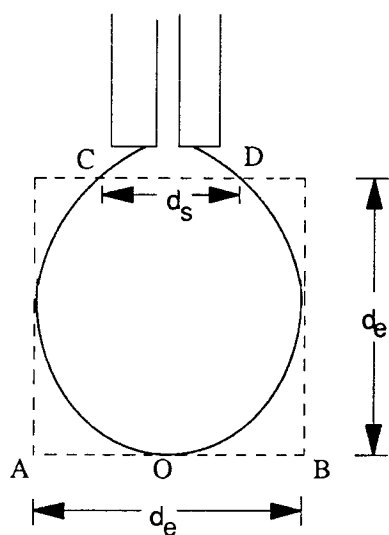


Figure 4.8: Profile of pendant drop.

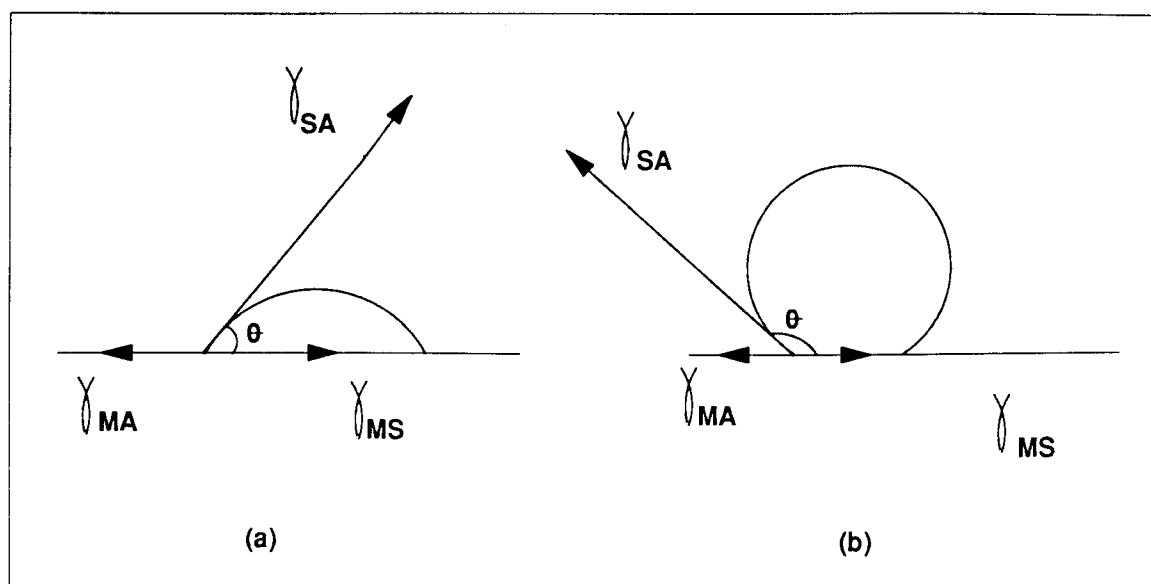
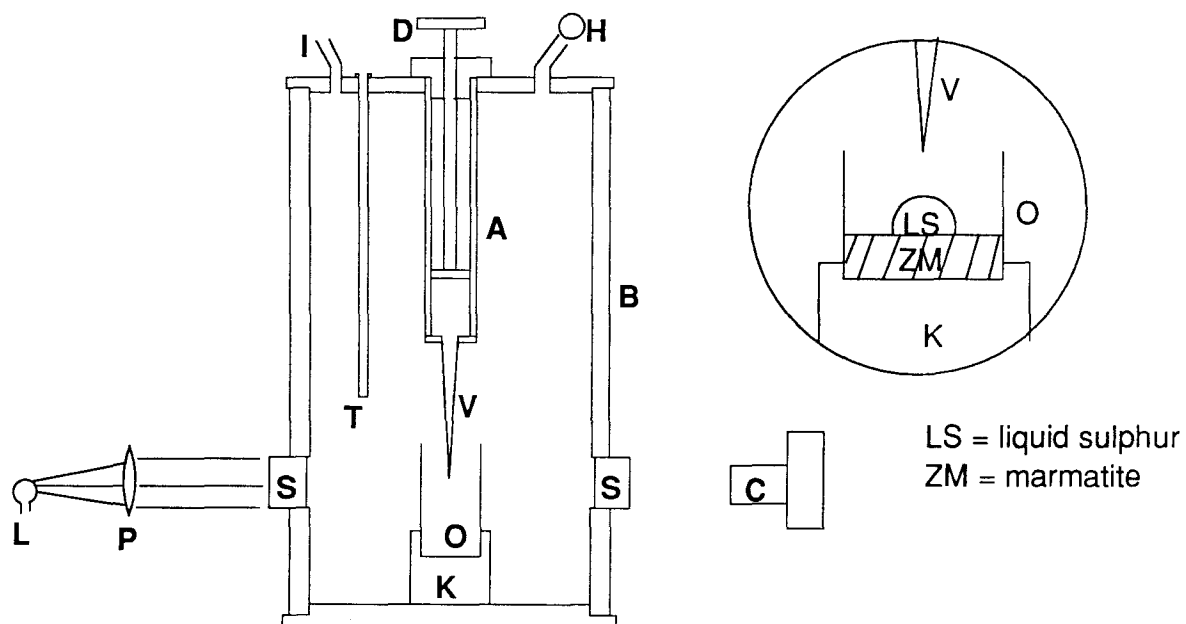


Figure 4.9: Contact angle between a liquid and solid surface: a) in the absence of any surfactant; b) in the presence of a surfactant.

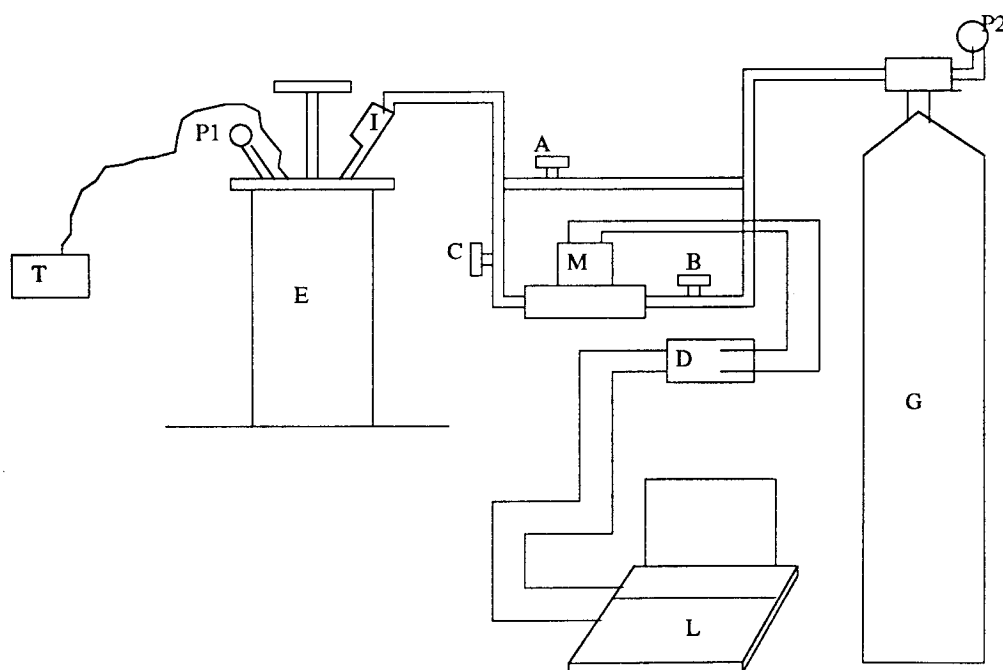


P: converging lens ;
 L: light source for backlighting
 B: stainless-steel bomb, (7.6 x 20.3 cm)
 T: thermowell (for thermocouple)
 C: camera for taking pictures
 O: rectangular optical glass cell

I: gas inlet
 A: drive-screw syringe with plunger D
 V: replaceable pyrex glass tubing tip
 (for creating liquid sulphur drops)
 S: sapphire windows (1.3 cm diameter)
 K: adjustable height seat
 H: pressure gauge

LS = liquid sulphur
 ZM = marmatite

Figure 4.10: Cross-section of high temperature and pressure stainless-steel bomb.



A,B,C - VALVES
L - PORTABLE COMPUTER
D - DATA ACQUISITION BOARD
M - GAS MASS FLOW METER
T - THERMOCOUPLE
I - INJECTION UNIT
P1,P2 - PRESSURE GAUGES
E - AUTOCLAVE
G - OXYGEN TANK

Figure 4.11: Experimental set-up for monitoring oxygen flow rate.

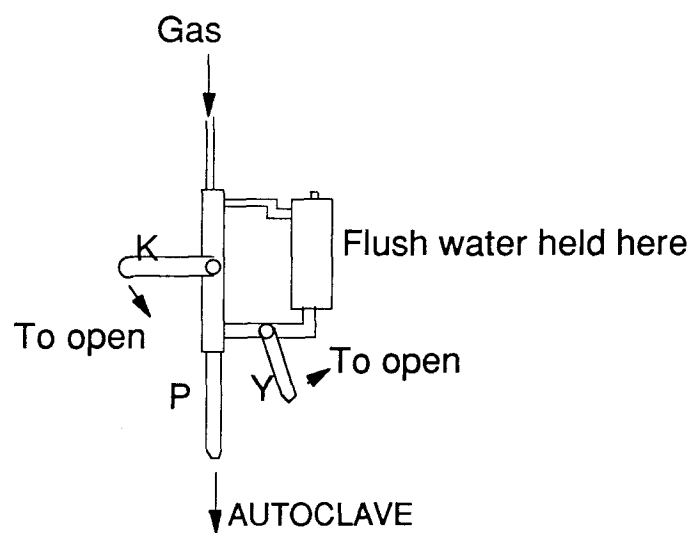


Figure 4.12: Injection Unit.

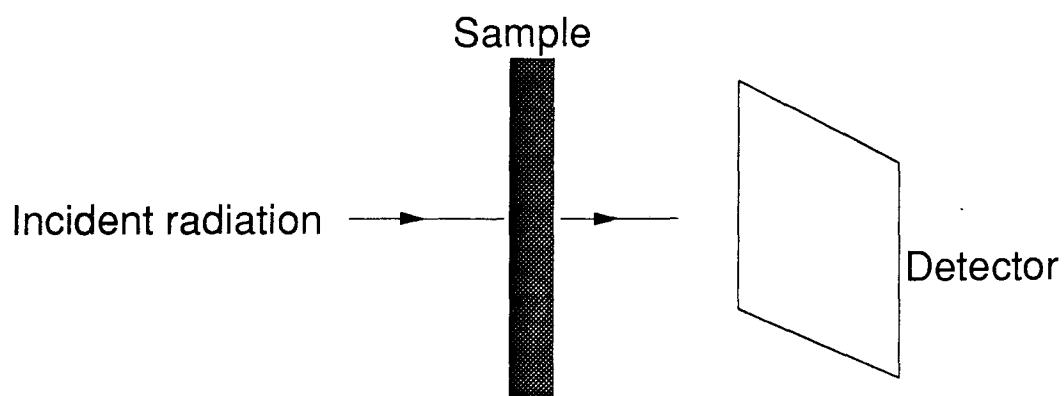


Figure 4.13: KBr Transmission.

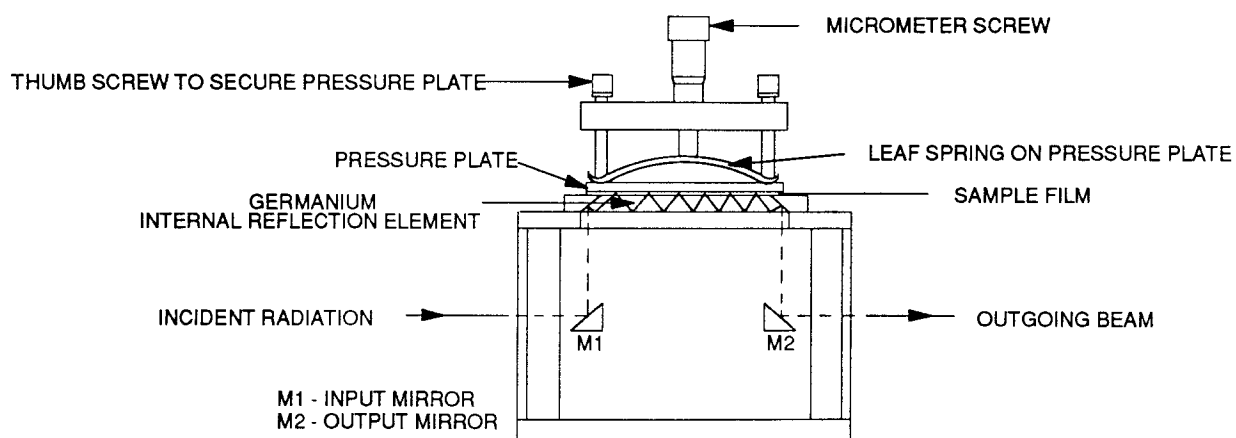


Figure 4.14: ATR Accessory.

Chapter 5

RESULTS AND DISCUSSION

The results and complete discussion of each area of study are presented here and attempts are made to correlate the results.

5.1 INTERFACIAL PHENOMENA

5.1.1 Results

Interfacial Tension

Figure 5.15 shows the results obtained using the different additives as surfactants in the interfacial tension measurements. Included in the figure are the data obtained (from an earlier work) using lignin sulfonic acid [54, 55].

In the absence of any surfactant, the liquid sulfur–aqueous solution interfacial tension measured 54–55 mN/m. It can be observed that irrespective of how much OPD is added to the solution, there was no significant change in the interfacial tension. However, the other surfactants influenced the interfacial tension to different degrees, depending on the surfactant. The most efficient surfactant in terms of interfacial tension reduction was naphthalene sulfonic acid–formaldehyde condensate. It reduced the interfacial tensions to values lower than those achieved with equal concentrations of lignin sulfonic acid (about 20–22 mN/m as compared to 28–30 mN/m for lignosol). It required only a minimum dosage of about 0.1 g/L to effect the maximum influence whereas lignin sulfonic acid required a concentration of 0.3 g/L to effect its maximum influence. Cocoamido

Table 5.2: Surface activity of OPD at a concentration of 0.3g/L in the presence of $[\text{Fe}^{2+}] = 0.05 \text{ M}$, $[\text{Fe}^{3+}] = 0.12 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.2 \text{ M}$, and $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temp. = $135 \pm 5^\circ\text{C}$

Expt.	1	2	3	4	5	6	Mean value	Std. Deviation
γ , mN/m	52.7	54.4	54.2	54.9	55.5	54.7	54.4	0.86

Table 5.3: Effect of silicate ions (0.15g/L) on the surface activity of OPD (0.3 g/L) in the presence of $[\text{H}_2\text{SO}_4] = 0.2 \text{ M}$ and $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temp. = $135 \pm 5^\circ\text{C}$

Expt.	1	2	3	Mean value	Std. Deviation
γ , mN/m	53.6	52.4	52.5	52.8	0.54

hydroxyl sulfobetaine (CAHSB) has about the same effect as lignin sulfonic acid up to a concentration of about 0.3 g/L beyond which it further reduces¹ the interfacial tension until it attains a maximum effect at about 0.5 g/L.

Table 5.2 shows the surface activity of OPD in the presence of acid, ferrous and ferric ions. The data show that the presence of these ionic species did not change the behaviour of OPD at the liquid sulfur - aqueous solution interface. Table 5.3 shows the effect of silicate ions on the surface activity of OPD². Again, it was observed that under the conditions of the experiment, these species do not have any effect on the liquid-liquid interfacial tensions. In the absence of a surfactant but in the presence of ferric, ferrous and hydrogen ions (i.e. an acid), the liquid-liquid interfacial tension measured 53–54 mN/m.

The effect of ferric/ferrous ions on the efficiency of naphthalene sulfonic acid-formaldehyde condensates as a surfactant was significant. Figure 5.16 shows how the surfactant degrades with time (in terms of an increase in the liquid-liquid interfacial tensions) in the

¹At surfactant concentrations greater than 0.3 g/L, lignin sulfonic acid does not exert any noticeable influence on the liquid sulfur-aqueous solution interfacial tension.

²These tests were performed in order to find out if the enhanced leaching rate observed with OPD was due to the presence of these species (or not) which are typical of zinc pressure leaching conditions.

Table 5.4: Contact angle measurements in the presence of the various surfactants: conditions - $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temp. = $135 \pm 5^\circ\text{C}$

Surfactant type	Surfactant concentration, g/L					
	0.05	0.07	0.15	0.3	0.33	0.6
Naphth.	154 $\pm$ 5	148 $\pm$ 5	150 $\pm$ 4	155 $\pm$ 5	-	-
CAHSB	-	-	143 $\pm$ 4	148 $\pm$ 5	152 $\pm$ 4	148 $\pm$ 5
OPD	-	124 $\pm$ 5	125 $\pm$ 6	127 $\pm$ 5	125 $\pm$ 4	-
TAHSB	-	-	133 $\pm$ 5	138 $\pm$ 5	135 $\pm$ 4	-
CAB	-	-	-	135 $\pm$ 5	136 $\pm$ 6	134 $\pm$ 6
Lignin.	-	144 $\pm$ 5	146 $\pm$ 5	143 $\pm$ 5	-	-

presence of ferric and ferrous ions in the solution in one of the measurements made, where the time in minutes includes the time taken to heat the system from room temperature to the working temperature³ of $130 \pm 5^\circ\text{C}$, and the period over which the photographs were taken of the pendant drops. The data indicate that this surfactant has a fairly high rate of degradation. The degradation could be due to the surfactant reacting with either the ferrous or the ferric ions in solution⁴. As one of its chemical properties, this surfactant is known to degrade rapidly in the presence of an oxidizing agent [83, 163]. This property *probably* indicates a ferric reaction degradation mechanism.

Contact Angle Measurement

Advancing contact angles have been measured in the liquid sulfur - aqueous zinc sulfate - marmatite system both in the absence and presence of the various additives or surfactants. Tables 5.4 and 5.5 show the negligible changes effected in the liquid sulfur - aqueous zinc sulfate - marmatite mineral contact angle in the presence of a given surfactant (at varying concentrations) and ionic species. All measurements made had a spread of

³It takes roughly 13–15 minutes of heating to reach this temperature.

⁴No attempt was made to determine which of the iron species was involved in the degradation process.

Table 5.5: Contact angle measurements in the presence of different surfactants and ionic species; conditions: $[\text{ZnSO}_4] = 1.2 \text{ M}$, $[\text{Fe}^{2+}] = 0.05 \text{ M}$, $[\text{Fe}^{3+}] = 0.12 \text{ M}$ and $[\text{H}_2\text{SO}_4] = 0.2 \text{ M}$, Temperature = 135°C

Surfactant type	Surfactant concentration, g/L	
	0.15	0.3
Naphth.	149 ± 5	148 ± 5
CAHSB	145 ± 4	147 ± 5
OPD	136 ± 5	135 ± 3
TAHSB	116 ± 5	113 ± 6
CAB	119 ± 5	122 ± 5
Lignin.	146 ± 5	148 ± 5

within $\pm 6^\circ$. In the absence of any of the surfactants, the contact angles measured were about $80 \pm 5^\circ$ and $98 \pm 5^\circ$ respectively in the absence and presence of ionic species such as H^+ , ferric and ferrous, Figure 5.17. Again, it was observed that the largest increase in contact angle was achieved with naphthalene sulfonic acid-formaldehyde condensates and CAHSB with orthophenylene diamine effecting the least increase (Table 5.4). In the presence of other ionic species (Table 5.5), the contact angles remained almost the same for the naphthalene sulfonic acid-formaldehyde condensates, lignin sulfonic acid and CAHSB. However, there was a small increase with respect to OPD while there was a decrease in the case of TAHSB. Considering these increases in the contact angle coupled with the interfacial tension reductions it is very easy to conclude that naphthalene sulfonic acid and CAHSB should be more efficient as surfactants in the zinc pressure leach process than lignin sulfonic acid and OPD should be the least efficient surfactant. Tables 5.6 and 5.7 summarize the work of adhesion values for the liquid sulfur-aqueous solution-marmatite system in the presence of the different surfactants and ionic species⁵.

These tables show that under pressure leaching conditions⁶, it is much easier to displace

⁵The mineral is considered as a two-dimensional plane. The figures shown in the tables will be different if the mineral is treated as a three-dimensional object.

Table 5.6: Work of adhesion, W_a , in the presence of 0.3g/L of different surfactants; conditions: $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = 135°C ; no other ionic species present in solution

Surfactant	None	Lignin.	Naphth.	OPD	CAHSB	TAHSB	CAB
$W_a(\text{mJ/m}^2)$	64.0	5.3	2.3	25.4	4.0	9.0	10.7

Table 5.7: Work of adhesion, W_a , in the presence of 0.3g/L surfactants; conditions: $[\text{ZnSO}_4] = 1.2 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.2 \text{ M}$, $[\text{Fe}^{2+}] = 0.05 \text{ M}$ and $[\text{Fe}^{3+}] = 0.12 \text{ M}$, Temperature = 135°C .

Surfactant	None	Lignin.	Naphth.	OPD	CAHSB	TAHSB	CAB
$W_a(\text{mJ/m}^2)$	46.2	4.6	3.6	16.0	4.5	25.0	18.8

liquid sulfur from the particle surface in the presence of naphthalene sulfonic acid, lignin sulfonic acid, CAHSB, TAHSB than it is with OPD and CAB and thus effect high zinc dissolution rates. Figures 5.17–5.19 show photographs of liquid sulfur resting on the marmatite mineral surface in different aqueous environments.

5.1.2 Discussion

Surface tension is the boundary tension between a liquid and a gas or vapour, and interfacial tension is the boundary tension at a phase boundary between two immiscible condensed phases. Surface/interfacial tension is a measure of the free energy of the fluid interface and at equilibrium it is the same at every point in all directions along the surface/interface. It is defined as *the work required to increase the area of a surface isothermally and reversibly by a unit amount*. For solid systems, it is defined as the restoring force necessary to bring freshly exposed surface molecules to equilibrium position. It has units of *dynes/cm* (cgs units) or *milli-Newton/m* (SI units). Any substance which

⁶i.e. if these data are projected into the zinc pressure leaching conditions.

lowers the surface/interfacial tension of a system tends to accumulate at the interface such that its concentration at the interface is higher than the bulk concentration.

The measurements reported here indicate the roles of the individual surfactants at the interfaces present in the liquid sulfur–aqueous solution–sulfide mineral system (which can be projected into the industrial zinc pressure leach process). With the exception of orthophenylene diamine, all surfactants used here reduced the liquid sulfur–aqueous solution interfacial tension from a maximum⁷ of 54–55 mN/m in the absence of any surfactant and at a zinc sulfate concentration of 1.2 mol/L to their respective minimum values: lignin sulfonic acid effects a maximum decrease to 28–30 mN/m in the presence of 0.3 g/L of surfactant; naphthalene sulfonic acid–formaldehyde condensates effected a maximum drop to 20–22 mN/m at a concentration of 0.1 g/L. Beyond these surfactant dosages, the interfacial tensions were insensitive to any further increase. Among the amphoteric surfactants, cocoamido hydroxyl sulfobetaine (CAHSB) was the most effective. It has about the same effect as lignin sulfonic acid up to a concentration of about 0.3 g/L beyond which it further decreases the interfacial tension to about 19–21 mN/m at about 0.5 g/L; additional increase of concentration beyond this point did not introduce any further change in the liquid sulfur–aqueous solution interfacial tension. In spite of the fact that cocoamido betaine (CAB) and tallowamido hydroxyl sulfobetaine (TAHSB) were effective in reducing the interfacial tension, their working efficiencies are lower than either lignin sulfonic acid or CAHSB or naphthalene sulfonic acid, Figure 5.15.

With an increase in the surfactant concentration, the amount of the additive adsorbed at the liquid–liquid interface increases (accompanied by a corresponding decrease in the interfacial tension) until a state is reached (i.e. the limiting state) when the interface is virtually completely covered with a layer (or layers) of the surfactant molecules. It

⁷Fanelli [82] has reported that liquid sulfur has a surface tension of 57–61 mN/m in the temperature range 120–150°C, decreasing with increasing temperature. Interfacial tension values usually lie between the individual surface tension values for the individual condensed phases.

is at this point that increasing the surfactant concentration further does not effect any additional influence on the interface. This limiting point corresponds to about 0.3 g/L for lignosol, 0.5 g/L for CAHSB, 0.1 g/L for naphthalene sulfonic acid-formaldehyde condensates, etc.

The interfacial activity of OPD (at the liquid-liquid interface) is insensitive to the presence and absence of solutes such as ferric, ferrous, hydrogen and silicate ions.

The adsorption of a surfactant at the solid-liquid interface is probably the most versatile phenomenon involved in surfactant applications. The adsorption of a surfactant by a solid can transform the solid surface from a hydrophobic to a hydrophilic one and vice versa. Adsorption can cause finely divided solids to be readily dispersible in a liquid or make the solid particles flocculate. Surfactant adsorption is important in the flotation separation of mineral particles.. It can also cause the solid to be easily wetted by a given liquid or very difficult to wet by sulfur. It is the last of these properties that allows for the development of an efficient leaching process for metal sulphides in the presence of liquid elemental sulfur.

Ideally, the ability of these surfactants to reduce the liquid sulfur-aqueous solution interfacial tension (with the exception of OPD) to the lowest value possible coupled with the ease of increasing the liquid sulfur-mineral contact angle (all surfactants increased the contact angle from about $80 \pm 5^\circ$ in the absence of any additive), Figures 5.17-5.19, creates a favourable environment for the liquid sulfur to be dispersed from the mineral surface. This phenomenon 'rolls' the liquid sulfur film (on the surface of the sulfide mineral) into droplets which are easily removed from the solid surface by vigorous agitation and dispersed in the liquid. This is the basic theoretical principle underlying the removal of a liquid from the surface of a solid substrate. The process of wetting of the mineral particles by the liquid sulfur is the result of the relatively high degree of attraction between the solid and the liquid molecules. A high contact angle value indicates that the liquid sulfur

has a low affinity for the mineral surface whereas a low value for the contact angle is an indication of the liquid sulfur's ability to spread over the mineral surface and hence make the mineral less accessible to the leaching solution. Complete wetting of the solid by the liquid sulfur implies a contact angle of 0° and absolutely no wetting corresponds to an angle of 180° .

When this phenomenon is projected into the zinc pressure leach process, a surfactant that increases the contact angles tends to lower the work of adhesion⁸ which is the reversible work required to separate a unit area of the liquid from the solid substrate. Tables 5.6 and 5.7 show the work of adhesion calculated for the different aqueous environmental conditions. The work of adhesion, W_a , between the two dissimilar phases can also be expressed as the sum of the different intermolecular forces acting between the liquid and the solid mineral [149, 152] such that

$$W_a = W_a^D + W_a^P \quad (5.45)$$

where W_a^D is due to the dispersion force component of the intermolecular forces which is always present in all systems and W_a^P is due to the polar component of the interacting forces depending on the polar nature of the phases and occurs to different degrees depending on the system and is given by

$$W_a^P = W_a^H + W_a^{DD} + W_a^E + W_a^\pi + \dots + \dots \quad (5.46)$$

W_a^H = hydrogen bonding force component

W_a^{DD} = bonding force component due to dipole-dipole interactions

W_a^E = bonding force component due to electrostatic interactions

W_a^π = π bonding component of the adhesional work, etc.

For non-polar systems, only dispersive forces are present and hence such a phase interacts

⁸The contact angles give us an idea about how much energy is necessary to remove a drop of liquid sulfur of unit area from the surface of the mineral substrate.

with polar systems only through W_a^D , e. g. zinc sulfide mineral (polar) and liquid sulfur (non-polar).

If the zinc sulfide particles are treated as hypothetical three-dimensional objects, e.g. as cubes of unit volume or dimensions [154], a similar pattern in the work of adhesion values are obtained. Consider Figures 4.9 and 5.22. From equation 4.40

$$\gamma_{MA} - \gamma_{MS} = \gamma_{SA} \cos \theta \quad (5.47)$$

neglecting the vertical force component⁹ of γ_{SA} . Assume the particle in Figure 5.22 is completely wetted by the aqueous solution (stage I) and that stages II, III, and IV are the different stages that each particle goes through in order to completely spread liquid sulfur all over the surface. By moving from I to II, adhesional wetting of the particle by liquid sulfur takes place such that the work of adhesion W_1 is given by:

$$W_I = (5\gamma_{MA} + \gamma_{MS}) - (6\gamma_{MA} + \gamma_{SA}) \quad (5.48)$$

$$= \gamma_{MS} - \gamma_{MA} - \gamma_{SA} \quad (5.49)$$

which coupled with equation 5.47 gives

$$W_I = -\gamma_{SA}(1 + \cos \theta) \quad (5.50)$$

This implies that in order to prevent wetting of the surface (stage II) by the liquid sulfur, an amount of work (positive work) equal to or greater than $\gamma_{SA}(1 + \cos \theta)$ must be done¹⁰. The expression in equation 5.48 indicates that there is a change in the net surface energy when the system consisting of mineral-aqueous solution and liquid sulfur-aqueous solution interface changes to one consisting of a liquid sulfur-mineral interface (stage II). If

$$\gamma_{MA} + \gamma_{SA} > \gamma_{MS} \quad (5.51)$$

⁹Chattoraj and Birdi [149] have reported that on a rigid solid surface, the vertical component is negligible but on soft surfaces is not negligible.

¹⁰This work had been compiled in Table 5.6.

adhesional wetting of the solid will occur. Thus, in order to prevent adhesional wetting from taking place (in physical terms), an applied surfactant must be able to increase γ_{MS} and/or decrease either γ_{MA} or γ_{SA} or both.

During stage II, the process is said to be immersion wetting where the particle is wetted on all sides but one by liquid sulfur. The accompanying work of immersion is:

$$W_{II} = (5\gamma_{MS} + \gamma_{MA}) - (5\gamma_{MA} + \gamma_{MS}) \quad (5.52)$$

which is equivalent to

$$W_{II} = 4(\gamma_{MS} - \gamma_{MA}) \quad (5.53)$$

or

$$W_{II} = -4\gamma_{SA} \cos \theta \quad (5.54)$$

from equation 5.47 above. This implies that if γ_{MS} is less than γ_{MA} , the second stage sulfur wetting will occur. To prevent this immersional wetting from taking place, an equivalent amount of work must be done on the system.

During the third and final stage of the sulfur wetting process, the particle is completely covered by the sulfur and the process is referred to as spreading wetting. Under zinc pressure leaching conditions, this is the stage when the leaching of the sulfide particle by the leaching solution is almost stopped because the aqueous solution has negligible access to the mineral surface. The accompanying work of spreading is given by:

$$W_{III} = (6\gamma_{MS} + \gamma_{SA}) - (5\gamma_{MS} + \gamma_{MA}) \quad (5.55)$$

From equation 5.47, this simplifies to

$$W_{III} = -\gamma_{SA}(\cos \theta - 1) \quad (5.56)$$

Thus, for complete wetting of the particle by liquid sulfur, the resultant work is

$$W = W_I + W_{II} + W_{III} \quad (5.57)$$

Table 5.8: Resultant work, W , for complete sulfur wetting (a hypothetical situation) in the presence of 0.3 g/L of surfactant and $[\text{ZnSO}_4] = 1.2 \text{ M}$

Work (mJ/m ²)	Surfactant type						
	None	Lignin.	Naphth.	OPD	CAHSB	TAHSB	CAB
W_I	-64	-5.3	-2.3	-23.4	-4.0	-9.0	-10.7
W_{II}	-37.5	95	74.5	125.3	91.6	104	103.2
W_{III}	44.9	52.8	40.0	85.9	49.9	61.0	61.5
W	-56.6	142.5	112.2	187.8	137.5	156	154

This implies that in order to prevent complete wetting of the zinc sulfide particles in the zinc pressure leaching process (assuming the particles are hypothetically of cubic shape and unit dimensions), an amount of work equivalent to W must be performed on the system. The presence of stable and efficient surface active agents in the system drastically reduces the required work to a lower value, Table 5.8, due to the ability of the surfactant to reduce the liquid–liquid interfacial tension and/or increase the contact angle. A negative W value implies spontaneous wetting of particles by the sulfur. This is most likely the condition present in the pressure leaching system in the absence of a suitable surfactant where the particles become completely occluded with liquid sulfur (with time) after enough sulfur has been formed in the system. This leads to the formation of agglomerates and large lumps of unreacted sulfide particles, Figure 5.35.

When W is positive (Table 5.8), sulfur wetting can only take place after performing an equivalent amount of work on the system i.e. there is a spontaneous and voluntary dispersion of liquid sulfur from the surface of the particles. This is what actually takes place in the presence of a suitable (and stable) surfactant under leaching conditions.

Considering the results (interfacial tensions and contact angles) obtained in these studies, it is very easy to conclude from the adhesional work data that surfactants with high interfacial tension reductions and high contact angle increases, e.g. naphthalene

Table 5.9: Variation of $\gamma_{MA} - \gamma_{MS}$ with respect to aqueous condition; $[\text{ZnSO}_4] = 1.2 \text{ M}$; other ionic species absent

Aqueous Condition	No Surfactant	Surfactant (0.3 g/L)					
		Lignin.	Naphth.	OPD	CAHSB	TAHSB	CAB
$\gamma_{MA} - \gamma_{MS}, \text{ mN/m}$	16.8	-18.5	-16.0	-20.8	-19.2	-19.7	-19.3

sulfonic acid-formaldehyde condensates, will be the most effective dispersant for liquid sulfur. In contrast, a reagent such as OPD which increases the contact angle but has no effect on the interfacial tension should be the least effective dispersant in the pressure leach process. The reason is that (from the tables), less effort and energy should be required to displace liquid sulfur of unit surface area from a solid substrate of an equal area in the presence of surfactants such as lignin sulfonic acid, naphthalene sulfonic acid-formaldehyde condensates, CAHSB, CAB, and TAHSB than in the presence of OPD. This should translate to higher zinc extractions in the presence of these surfactants than in the presence of OPD in the zinc pressure leach process.

It is concluded from the interfacial tensions and contact angle measurements that with the exception of OPD, all other surfactants applied are adsorbed at both mineral-aqueous and aqueous-sulfur interfaces. OPD on the other hand adsorbs at only the solid-liquid interface thus increasing the contact angle from $80 \pm 5^\circ$ in the absence of the surfactant to $125-135 \pm 5^\circ$. From equation 5.47 above, it is realised that if the respective surfactants (with the exception of OPD) are adsorbed only at the liquid-liquid interface, then γ_{MA} and γ_{MS} must remain unchanged and $\gamma_{MA} - \gamma_{MS}$ should also be constant¹¹ irrespective of the aqueous conditions (for a given surfactant). It so happens that this is not the case, (Table 5.9). The interfacial tension is dependent on the solution composition, confirming that the respective surfactants are adsorbed at both solid-aqueous and liquid

¹¹i.e. the value of this parameter in the absence and presence of a surfactant should be the same.

sulfur–aqueous interfaces.

Generally, the adsorption of surfactants onto solids proceed through two steps:

- the adsorption of the surfactant species through interactions such as electrostatic and/or van der Waals etc., between surfactant species and solid surface
- the adsorption of a surfactant through interactions (polar, hydrophobic, hydrogen bonding etc.) between the already adsorbed surfactant and the approaching molecules.

In the first step, the surface active species are individually adsorbed (as ions or molecules) in the first adsorbed layer on the solid surface through electrostatic (present in only ionic surfactants where the surface active ions are adsorbed on the oppositely charged solid surface) and/or specific (i.e. van der Waals) attraction. In the second step, the adsorption increases dramatically as hemimicelles¹² form on the adsorbent through association or hydrophobic interaction between the hydrocarbon chains of the surface active species, and each of the ions or molecules adsorbed in the first steps provide a possible active center for aggregation.

Surface Excess at the Liquid Sulphur–Aqueous solution Interface

The Gibb's general thermodynamic expression for adsorption of a solute from dilute binary solutions at liquid–liquid interfaces at constant temperature and pressure is given by [149, 150]:

$$-d\gamma = \Gamma_2^1 d\mu_2 \quad (5.58)$$

or

$$\Gamma_2^1 = -\frac{c_2}{RT} \cdot \frac{d\gamma}{dc_2} = -\frac{1}{RT} \cdot \frac{d\gamma}{d\ln c_2} \quad (5.59)$$

¹²Hemimicelles refer to the formation of surfactant aggregates on the surface of the adsorbent.

where

c_2 = concentration of solute in the bulk solution

Γ_2^1 = relative surface/interface excess of solute at the interface per unit area of interface; it is an estimate of the concentration of the adsorbed species at the interface in excess of the bulk concentration of the solute; component 1 is considered to be the solvent whose interfacial concentration is assumed to be the same as in the bulk.

T = operating temperature and R = universal gas constant, 8.32 Joules/(mole-K).

For a multicomponent solution, e.g. solution containing an organic electrolyte (surfactant) and inorganic electrolyte (such as zinc sulfate)

$$-d\gamma = RT \sum_i \Gamma_i \xi_i \cdot d \ln c_i \quad (5.60)$$

where ξ_i is a parameter for the activity coefficient of component i and is given by

$$\xi_i = 1 + \frac{d \ln f_i}{d \ln c_i} \quad (5.61)$$

f_i = the activity coefficient of component i of concentration c_i . For the adsorption of an electrolyte (i.e. an ionic surfactant) at a liquid-liquid interface, equation 5.60 is modified to take into account the ionic speciation of the surfactant such that:

$$-d\gamma = mRT \Gamma_{RX_z} \cdot d \ln c_{RX_z} \quad (5.62)$$

where RX_z represents the ionic surfactant. The details of the derivation of equation 5.62 are available in appendix C. For dilute solutions of surfactants, the value of m is estimated from either Helmholtz or Gouy's model of the electrical double layer in relation to Gibb's adsorption equations [149]. Gouy estimates that

$$m = 1 + \frac{z^2}{z + \bar{x}(1 + e^{\epsilon \varphi_o / 2\sigma T})} \quad (5.63)$$

where

$\bar{x}$ is the ratio of molar concentrations of the inorganic to organic salts (surfactant) present

in the medium

z is the valency of the organic surface active anion

φ_o = surface/interfacial potential

σ = Boltzman's constant.

In the absence of any inorganic electrolyte e.g. zinc sulfate in our situation, $\bar{x} = 0$ and $m = 1 + z$. When the concentration of the organic surfactant (electrolyte) is very small as opposed to the inorganic component e.g. 0.3 g/L surfactant versus 345 g/L zinc sulfate salt, $\bar{x}$ tends to infinity and m is equal to unity, resulting in

$$\Gamma_{RX_z} = -\frac{c_{RX_z}}{RT} \cdot \frac{d\gamma}{dc_{RX_z}} \quad (5.64)$$

or

$$\Gamma_{RX_z} = -\frac{1}{2.303RT} \cdot \frac{d\gamma}{d\log c_{RX_z}} \quad (5.65)$$

at constant temperature. The valency of the organic electrolyte disappears since m is equal to unity under the conditions of this study. Thus, the interfacial surfactant excess, Γ_{RX_z} , can be computed for each concentration of surfactant provided the molecular weight of the surfactant is known.

To compute interfacial excess for lignin sulfonic acid used in this study, a molecular weight of 4,000 was assigned¹³. The interfacial excess was computed for the naphthalene sulfonic acid-formaldehyde condensates adsorption as well; it has a molecular weight of about 2000. The interfacial excess plots are shown in Figures 5.23 and 5.24. These data show the concentration of the surfactant at the liquid sulfur-aqueous solution interface in excess of the bulk concentrations. Similar computations could be made for the amphoteric surfactants if information on their molecular weights was available¹⁴.

¹³Lignin sulfonic acid has no definite molecular weight: it varies from 4000 for the lower series to as high as 100,000 for the high molecular weight groups; however, the most common species are reported to have molecular weights of about 4,000.

¹⁴The R component of the structure can have between 12 and 24 or more carbon atoms.

The critical micelle concentrations for the lignosol and the naphthalene sulfonic acid-formaldehyde condensates are shown on the plots¹⁵. The critical micelle concentration (cmc) is the limiting concentration point at which the interfacial concentration of the surfactant reaches saturation. The cmc is about: 0.5–0.6 g/L for CAHSB; 0.1 g/L for naphthalene sulfonic acid-formaldehyde condensates, and 0.3 g/L for lignin sulfonic acid.

Summary

The results of the interfacial studies have shown that of all the surfactants used, OPD was the least effective in terms of interfacial tension reduction and contact angle effects, both in the presence and absence of other ionic species which are typical of zinc pressure leaching conditions. Both naphthalene sulfonic acid formaldehyde condensates and co-amido hydroxyl sulfobetaine were quite effective in terms of interfacial activity. Their interfacial activities compete very well with that of lignin sulfonic acid. These observations can easily lead one to conclude that they can be effective as dispersants for liquid sulfur in the zinc pressure leach process. Again, OPD could be expected to be least effective of all the reagents studied. However, as has been observed with naphthalene sulfonic acid formaldehyde condensates, the efficiency of a given surfactant is related to the stability of the surfactant under the operating conditions, (Figure 5.16).

¹⁵These points occur in Figure 5.15 at the points where maximum effect is attained irrespective of surfactant concentration.

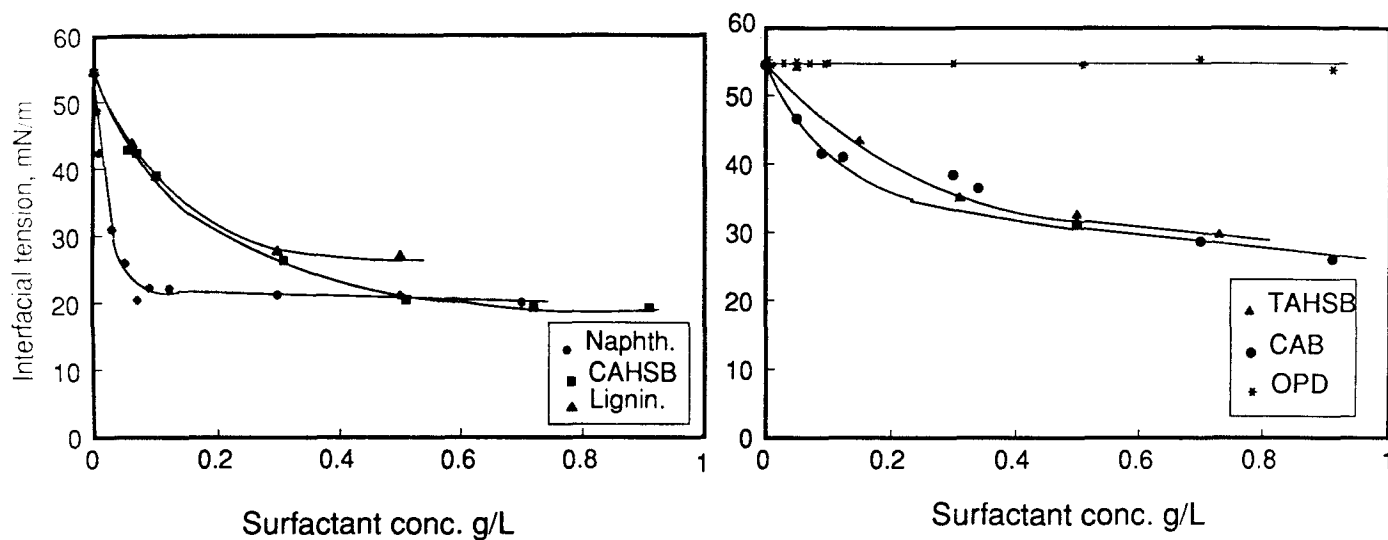


Figure 5.15: Liquid sulfur–aqueous solution interfacial tensions in the presence of different surfactants; $[\text{ZnSO}_4] = 1.2 \text{ M}$; Temperature = $135 \pm 5^\circ\text{C}$; $P_{\text{N}_2} = 620 \text{ kPa}$.

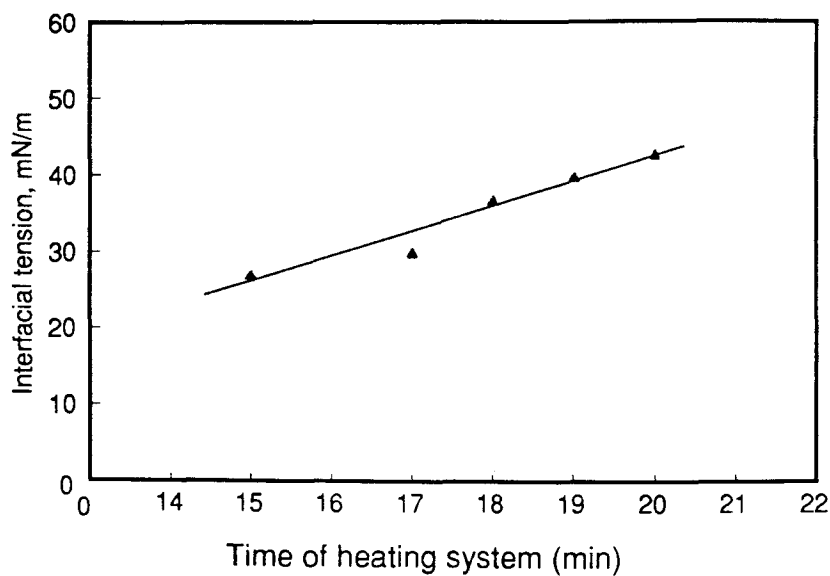


Figure 5.16: Liquid sulfur–aqueous solution interfacial tensions in the presence $[\text{Fe}^{3+}] = 0.12 \text{ M}$, $[\text{Fe}^{2+}] = 0.05 \text{ M}$ and 0.3 g/L naphthalene sulfonic acid; $[\text{H}_2\text{SO}_4] = 0.2 \text{ M}$, Temperature = $135 \pm 5^\circ\text{C}$; $P_{\text{N}_2} = 620 \text{ kPa}$.

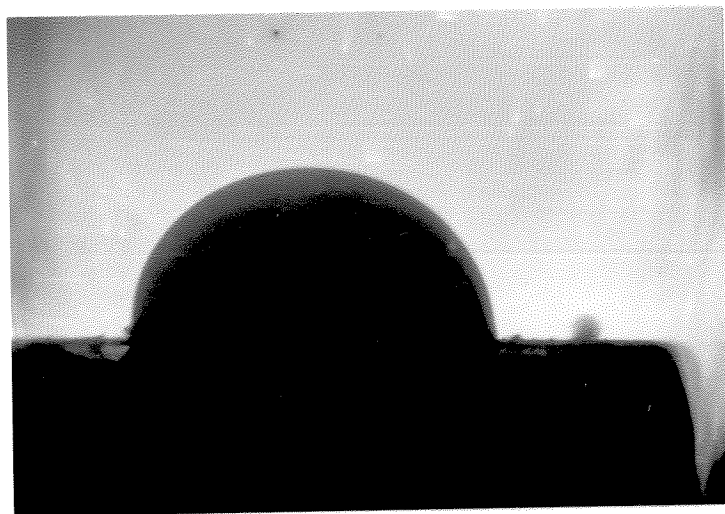


Figure 5.17: Liquid sulfur-zinc sulfide mineral contact angle in surfactant-free system; $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = 135°C ; $P_{\text{N}_2} = 620 \text{ kPa}$.

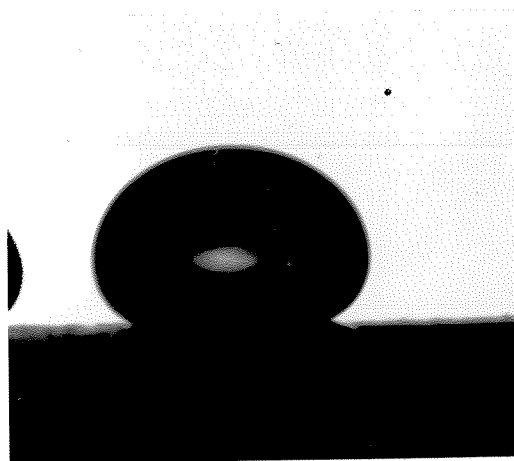


Figure 5.18: Liquid sulfur-zinc sulfide mineral contact angle in the presence of 0.3g/L naphthalene sulfonic acid-formaldehyde condensates, $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = 135°C ; $P_{\text{N}_2} = 620 \text{ kPa}$.

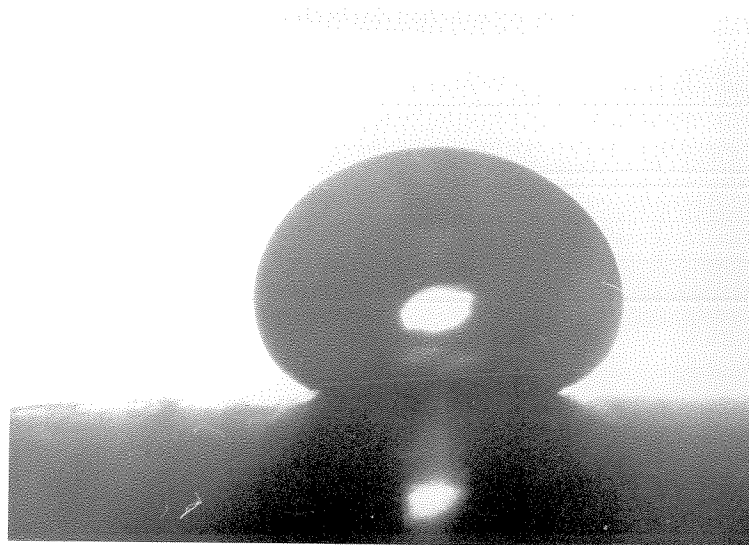


Figure 5.19: Liquid sulfur-zinc sulfide mineral contact angle in the presence of 0.15g/L OPD; conditions: $[\text{Fe}^{2+}] = 0.05 \text{ M}$, $[\text{Fe}^{3+}] = 0.12 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.2 \text{ M}$, Temperature = 135°C ; $P_{\text{N}_2} = 620 \text{ kPa}$.

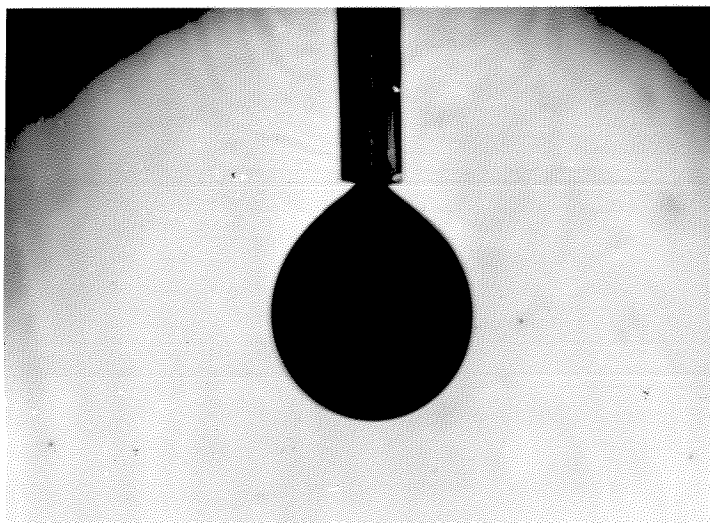


Figure 5.20: Photograph of liquid sulfur suspended in surfactant-free zinc sulfate solution: conditions; $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = $135 \pm 5^\circ\text{C}$; $P_{\text{N}_2} = 620 \text{ kPa}$.

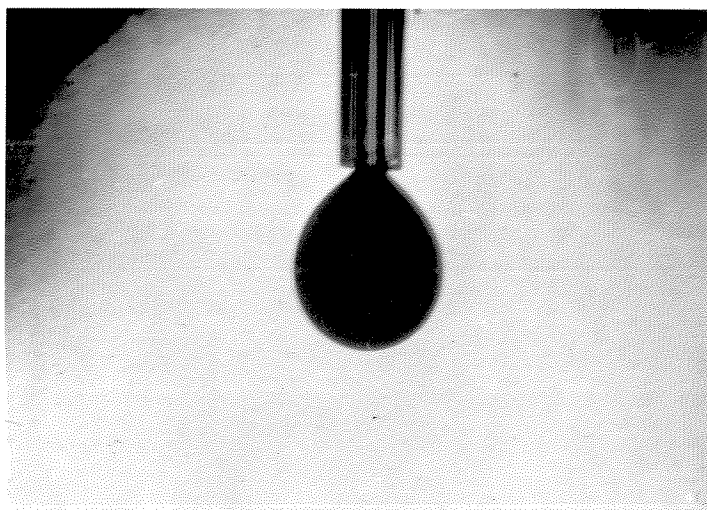


Figure 5.21: Photograph of liquid sulfur suspended in aqueous solution in the presence of 0.3g/L naphthalene sulfonic acid-formaldehyde condensates; conditions: $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = 135°C ; $P_{\text{N}_2} = 620 \text{ kPa}$.

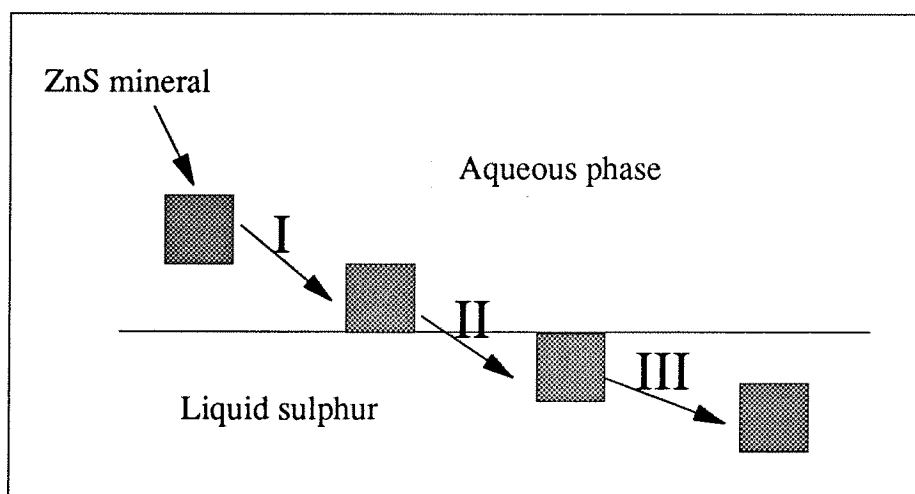


Figure 5.22: Different stages of wetting

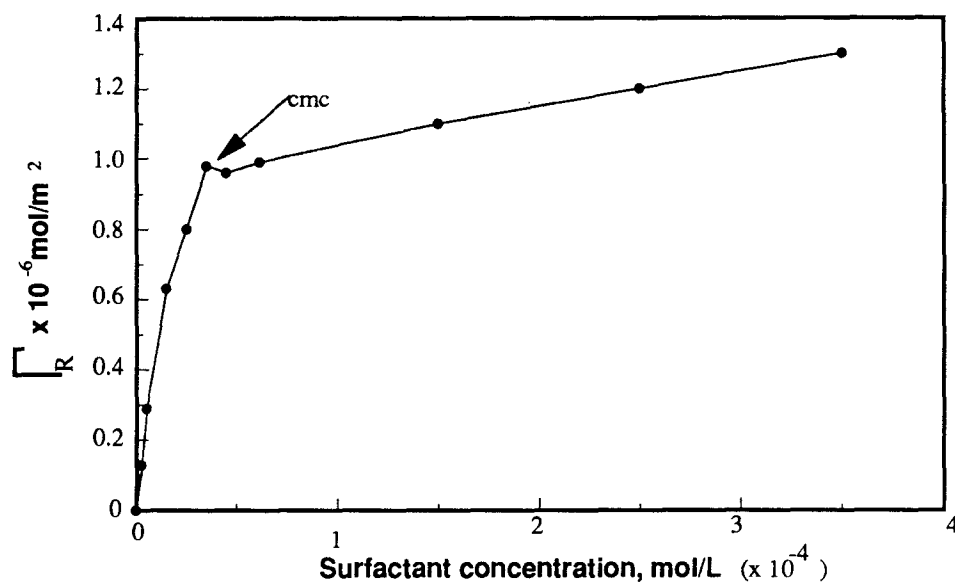


Figure 5.23: Interfacial excess of naphthalene sulfonic acid-formaldehyde condensates at the liquid sulfur-aqueous solution interface; conditions: $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = $135 \pm 5^\circ\text{C}$; $P_{\text{N}_2} = 620 \text{ kPa}$.

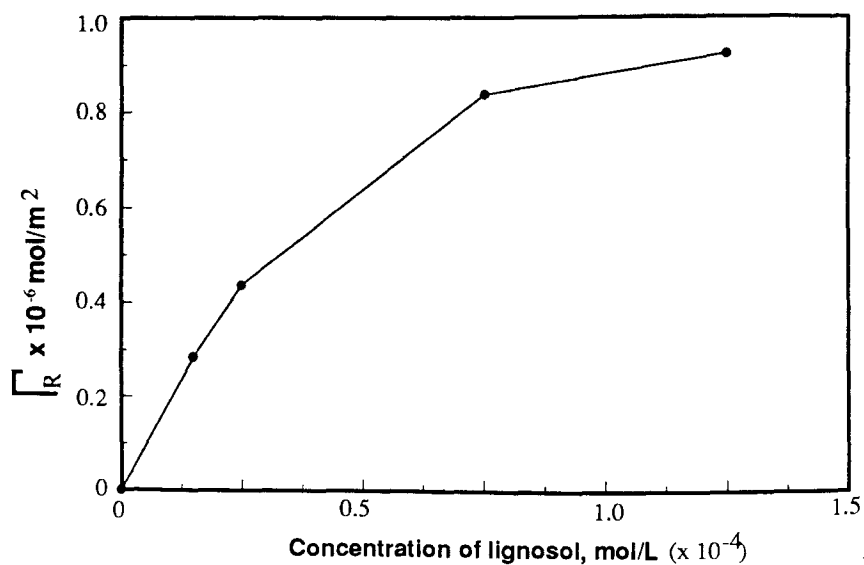


Figure 5.24: Interfacial excess of lignin sulfonic acid at the liquid sulfur-aqueous solution interface; conditions: $[\text{ZnSO}_4] = 1.2 \text{ M}$, Temperature = $135 \pm 5^\circ\text{C}$; $P_{\text{N}_2} = 620 \text{ kPa}$.

5.2 PRESSURE LEACHING OF SPHALERITE CONCENTRATE

5.2.1 Results

Three sets of leaching tests were performed.

- Low pulp density leaching under a nitrogen atmosphere
- Low pulp density leaching using oxygen overpressure
- High pulp density leaching in the presence of oxygen overpressure

Low Pulp Density Leaching Under Nitrogen Pressure

The primary aim of the low pulp density tests was to investigate the extent of zinc extraction in the presence of the different surfactants, relate the extraction data to the interfacial behaviour of the surfactants and then compare the results with the data obtained using lignin sulfonic acid under similar conditions. The amount of concentrate used for these tests was 1–3 grams in 1 L of leach solution. The variables investigated were: time of leaching, type and concentration of surfactant and the mode of introduction of the surfactant into the system, either batch (B) or continuous (C). The average surfactant solution flow rate was 1.5 ml/minute.

Results for the experiments using the different additives are shown in Tables 5.10–5.12.

The reason for the high leaching rates in the absence of any surfactant is that the liquid sulfur generated as a result of the zinc dissolution reaction is being dispersed from the mineral surface by the continuous agitation as a result of the low solid percentage in the system. The low zinc extraction values obtained in the presence of the other surfactants (apart from lignin sulfonic acid and the phenylene diamine) suggest that these surfactants may be chemically unstable under the leaching conditions, as shown

Table 5.10: Extent of zinc extraction using different surfactants under low pulp density conditions and nitrogen atmosphere; initial conditions: $[\text{ZnSO}_4] = 2 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$; $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 0.15 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{N}_2} = 1100 \text{ kPa}$; B–batch addition; C–continuous addition

Surf.	Surf.conc. (g/L)	Addition method	Time (min)	Zn extraction (%)
None	-	-	20	70 ± 0.4
None	-	-	30	72 ± 1.0
CAHSB	10.0	C	30	75 ± 0.5
Lignin.	5.0	C	30	94 ± 1.0
Lignin.	0.05	B	20	86 ± 0.8
Lignin.	0.1	B	30	90 ± 0.5
Queb.	0.05	B	20	90 ± 0.4
Queb.	0.05	B	30	96 ± 0.5
CAB	10.0	C	30	51 ± 0.6
CAB	6.0	C	20	45 ± 0.3
TAHSB	10.0	C	20	40 ± 0.3

Table 5.11: Effect of naphthalene sulfonic acid on the extent of zinc extraction under low pulp density conditions; initial conditions: $[\text{ZnSO}_4] = 2 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$; $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 0.15 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{N}_2} = 1100 \text{ kPa}$; B–batch addition; C–continuous addition

Surfactant conc.(g/L)	Addition method	Time (min.)	Zn extraction (%)
1.0	C	30	70 ± 0.3
2.0	C	30	72 ± 0.5
5.0	C	30	67 ± 0.8
0.05	B	30	64 ± 0.3
0.1	B	20	53 ± 0.3
0.1	B	30	64 ± 0.4
0.3	B	20	51 ± 1.0
0.3	B	30	65 ± 0.5
0.5	B	20	48 ± 0.4
0.5	B	30	63 ± 0.3
0.7	B	20	48 ± 0.3
0.7	B	30	61 ± 0.2

Table 5.12: Extent of zinc leaching using OPD as surfactant under low pulp density conditions; initial conditions: $[\text{ZnSO}_4] = 2 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$; $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 0.15 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{N_2} = 1100 \text{ kPa}$; B–batch addition; C–continuous addition

Surfactant conc.(g/L)	Addition method	Time (min)	Zn extraction (%)
0.05	B	30	95 ± 0.2
0.1	B	20	75 ± 0.4
0.1	B	30	94 ± 0.3
5.0	C	20	78 ± 0.3
5.0	C	30	87 ± 0.4

Table 5.13: Extent of zinc extraction using MPD and PPD as surfactants (batch additions) under low pulp density conditions; initial conditions: $[\text{ZnSO}_4] = 2 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$; $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 0.15 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{N_2} = 1100 \text{ kPa}$.

Surfactant	Conc. (g/L)	Time (min.)	Zn extraction (%)
MPD	0.1	30	95 ± 0.5
MPD	0.3	30	97 ± 0.2
PPD	0.1	30	96 ± 0.2
PPD	0.3	30	97 ± 0.6

in Figure 5.16. This could be due to these surfactants reacting with or sequestering the ferric ion oxidizing agent thus depriving the mineral of the oxidant.

Based on the results obtained from leaching in the presence of OPD, the other forms of phenylene diamine i.e. the meta- and para-phenylene diamines (MPD & PPD) were applied as surfactants in some low pulp density leaching tests, (they were not part of the primary list). The purpose of these experiments was to determine if the position of the amine functional group on the aromatic ring influences the extent of zinc extraction. Under the low pulp density conditions, the data obtained in the presence of these additives were quite comparable to those of lignin sulfonic acid and orthophenylene diamine. Table 5.13 shows the results obtained in the tests where these reagents were used as the

surfactants.

Low Pulp Density Leaching under Oxygen Pressure

Based on the results obtained from leaching under a nitrogen pressure, some of the surfactants were not used under oxygen pressure. The reason was that they did not give rise to zinc extractions greater than those obtained in the absence of any surfactant. These surfactants were CAHSB, CAB, and TAHSB. It was presumed that these degrade in the presence of oxidizing agents such as ferric ions and that the presence of oxygen will also catalyse the degradation process rendering the surfactants ineffective. These surfactants are reported to decompose in the presence of oxidizing agents. All surfactants used in oxygen pressure leaching were batch additions. The amount of concentrate used for each of these tests was 6–12 grams in 1.5 L leach solution. Table 5.14 shows the results of some of the experiments. The leaching data presented in this table were obtained after 30 minutes of leaching. As Table 5.14 shows, pressure leaching with oxygen resulted in higher zinc extractions than leaching with ferric ions under a nitrogen atmosphere, though the differences are not large. The differences may be due to either one or both of the following reasons:

- the continuous oxidation of ferrous to ferric ions in the system (due to the presence of oxygen) ensures that ferric ions are available throughout the leaching period and are never depleted
- the presence of oxygen in the system enhances the surface/interfacial activity of the surfactants in the system¹⁶.

The extent of zinc extraction achieved in the presence of the phenylene diamines compares very well with that of lignin sulfonic acid which have been well documented. Figure 5.25

¹⁶This is only a speculation which has not been confirmed in any of our studies.

Table 5.14: Extent of zinc extraction after 30 minutes of low pulp density leaching under oxygen pressure; concentrate sample size: 8-10 g; initial conditions: $[\text{ZnSO}_4] = 2 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$; $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 0.15 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$; Batch addition of surfactants

Surfactant	Conc. (g/L)	Zn extraction (%)
None	-	83 ± 0.7
Lignin.	0.1	98 ± 0.4
Naphth.	0.1	80 ± 0.3
OPD	0.05	97 ± 0.5
	0.1	97 ± 0.3
	0.3	98 ± 0.2
MPD	0.05	99 ± 0.2
	0.1	99 ± 0.2
	0.3	99 ± 0.4
PPD	0.05	91 ± 0.3
	0.1	98 ± 0.3
	0.3	99 ± 0.2

shows that 99 % zinc extraction can be achieved within 20 minutes of leaching in the presence of the amine additives (under low pulp density conditions¹⁷). The plot shows also the extent of zinc extraction at different leaching times in the presence of naphthalene sulfonic acid-formaldehyde condensates.

It should be noted that, at low pulp densities, the oxygen mass transfer rate in the process (and subsequent oxidation of ferrous ions to ferric ions by oxygen) is almost never rate determining, while at high enough pulp density, oxygen transfer may be sufficiently limited to result in a substantial lowering of the ferric:ferrous ratio.

¹⁷Until MPD and PPD have been extensively studied, much cannot be said about their performance under high pulp density conditions.

High Pulp Density Leaching under Oxygen Pressure

The results obtained from the chemical analysis of both the filtrate and the leach residues¹⁸ for the different conditions of leaching are shown in Tables 5.15–5.20. The extent of zinc extraction in the presence of OPD was not sensitive to the OPD concentrations used or the time of leaching (i.e. 35 and 60 minutes). However, the same cannot be said of lignin sulfonic acid. MPD was also quite effective as a surfactant under the leaching conditions adopted in this work. In contrast, the extent of iron extraction was dependent on surfactant concentration and time of leaching. The extent of iron extraction from the concentrate during leaching is shown in Table 5.17. It can be seen from the tables that leaching in the presence of OPD effects higher metal extractions than in the presence of the other surfactants used in these tests.

Shown in Figure 5.26 is the extent of zinc leaching with respect to time in the presence of OPD. The figure shows that within about 35 minutes, over 99 % zinc extraction was achieved in presence of either 0.06 or 0.1 g/L surfactant.

During the high pulp density tests, the instantaneous oxygen consumptions rates were monitored during the course of the leaching period. Figures 5.27–5.30 show the instantaneous oxygen flow rate for the leaching of sphalerite in the absence and presence of lignin sulfonic acid, OPD and MPD¹⁹. These figures show that in the absence of any surfactant, the flow of oxygen into the system comes to almost a complete stop after about 30–35 minutes of leaching whereas in the presence of a surfactant oxygen is still flowing at a low rate after the 35-minute mark. This indicates that in the absence of any surfactant, all reactions requiring oxygen cease almost completely after about 35 minutes of leaching.

Figures 5.31–5.34 show the cumulative oxygen consumed (in moles) under the different

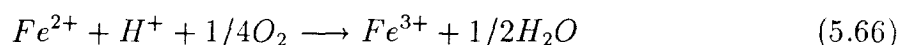
¹⁸The details of the chemical analysis procedure are given in appendix B.

¹⁹These were the only surfactants used in the high pulp density leaching tests

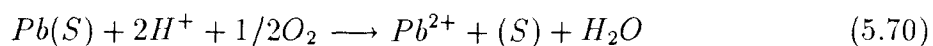
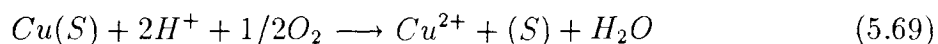
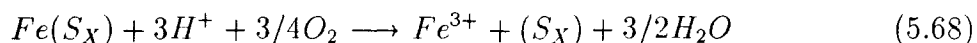
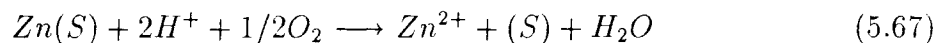
test conditions. These figures show that the gas mass flow rate is independent of OPD concentration (between 0.06 and 0.1 g/L) used while the rate is influenced to some extent by the lignin sulfonic acid concentration (also between 0.06 and 0.1 g/L).

It can be assumed that the reactions taking place during the leaching period are the following:

1) the homogeneous oxidation of ferrous ions present in the stock solution²⁰ to the ferric state:

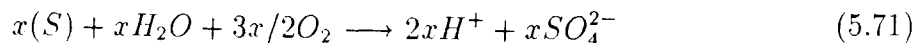


2) the oxidative dissolution of the metal sulphides such as:



and

(3) the oxidation of elemental sulfur to sulfate



where x is the number of moles of elemental sulfur oxidized to sulfate. Based on these reactions, equations can be written for the theoretical acid and oxygen consumptions for a sample size of 100 grams, Table 5.18. Ideally, the theoretical acid to oxygen (consumed) ratio should be equal to the experimentally measured values. Thus, from Table 5.18

$$\frac{H^+_{(expt.)}}{O_{2(expt.)}} = \frac{2.351 - 2x}{0.5876 + 1.5x} \quad (5.72)$$

²⁰In the 1.5 L solution used for each leaching test, the total ferrous concentration was 0.21 mole.

Thus, using this relationship, the extent of elemental sulfur oxidation through reaction 5.71 can be computed for each experiment.

Table 5.19 shows the experimental results for oxygen and acid consumption. Table 5.20 shows the experimental results for the elemental sulfur analysis of the leach residue, and a comparison between the experimental (using the barium sulfate method for the analysis of the filtrate²¹) and calculated extent of elemental sulfur oxidation to the sulfate through reaction 5.71 for the measured extent of metal extractions. The calculated data were computed using the following approach: for each experiment, assuming complete metal dissolution (for a 100-gram sample), equation 5.72 can be used to calculate the extent of sulfur oxidation, x , under the prevailing conditions (given the H^+/O_2 ratio). Using this value of x and the elemental sulfur content from the residue analysis, the extent of elemental sulfur oxidation, y , can be obtained for each experiment using the following equation²²:

$$\frac{0.986 - x}{0.986} = \frac{B}{B + y} \quad (5.73)$$

where B (moles) is the quantity of elemental sulfur in the residue for a given experiment and is shown in table 5.20 as S° . The experimental data are almost equal to or differ slightly from the computed values. The differences between the calculated (through reaction 5.71 and equation 5.73) and the experimental values can be attributed to indeterminate analytical errors.

Also shown in the same table is the extent of total sulfide sulfur (in the concentrate) oxidation to sulfate ($\% S_{oxidation}^{total}$) based on the barium sulfate figures. The extent of sulfur oxidation in the presence of OPD is about one and half to two times that observed with lignin sulfonic acid. The extent of elemental sulfur formation due to the metal extractions

²¹The purpose of this filtrate analysis was to determine the total change in the sulfur content of the solution after the experiment.

²²The total $\%$ sulfur oxidation in terms of x and y should be equal for each set of conditions.

is also shown²³. It can be seen that the presence of OPD speeds up the formation of sulfate due to the formation of sulfur particles of very fine sizes²⁴, (Figures 5.35–5.38). These finely-sized sulfur particles have a high specific surface area.

5.2.2 Discussion

Low Pulp Density Leaching

It has been observed that of all of the surfactants studied, the phenylene diamines and lignin sulfonic acid seem to be the most efficient surfactants (or dispersants) under the conditions of leaching. The amphoterics and naphthalene sulfonic acid-formaldehyde condensates were very poor dispersants.

A close look at the interfacial activities of the different surfactants suggests that naphthalene sulfonic acid and CAHSB should be very efficient in the leach and OPD the least efficient. However, this was not the case. The data collected show that the diamines and lignin sulfonic acid were the most efficient. This observation could lead to the conclusion that there may be other mechanisms operating during the zinc pressure leaching process (involving surfactants) that influence the interfacial phenomena either directly or indirectly. Thus, the interfacial property of the surfactant may deviate from the ideal situation, e.g., a surfactant may be very effective in reducing the liquid sulfur–aqueous solution interfacial tension and increasing the contact angle (a process which, theoretically favours high leaching rates), but the chemical may not be very efficient in enhancing the leaching process. One explanation is that the surfactant in question may not be stable under the oxidative pressure leaching conditions. From Table 5.11, it

²³Ideally, the extent of total sulfide sulfur oxidation to sulfate and the extent of elemental sulfur formation should add up to 100 %; however, due to analytical discrepancies, they differ by 1–2 %.

²⁴This is quite unexpected since it is believed that the inability of OPD to reduce the interfacial tension should result in the coalescence of sulfur and hence large particle sizes.

appears that even with an increase in naphthalene sulfonic acid formaldehyde condensates concentration, relatively low zinc extractions were still achieved. This suggests that the surfactant probably depletes ferric ions that directly attack the zinc sulfide mineral. This phenomenon is displayed graphically in Figure 5.16 for naphthalene sulfonic acid-formaldehyde condensates under simulated zinc pressure leach conditions. It can be seen from the plot that as the residence time increases, the interfacial tension also increases. This suggests that the naphthalene sulfonic acid is going through some form of degradation process in the presence of ferrous and ferric ions. Within a residence time of 15 minutes²⁵, in the presence of 0.05 M Fe^{2+} , 0.12 M Fe^{3+} , 0.2 M sulfuric acid and 0.3 g/L naphthalene sulfonic acid-formaldehyde condensates, the liquid sulfur-aqueous solution interfacial tension rises to about 27–28 mN/m from the 20–22 mN/m value recorded in the absence of the ferric and ferrous ionic ions. This implies that the surface activity of 0.3 g/L surfactant had been reduced to the equivalent of 0.05 g/L in a matter of 15 minutes by heating the solution from 25°C to 130°C in the presence of ferrous and ferric ions. A series of similar experiments was performed to confirm the above observation. In these tests, once the operating temperatures had been reached (after 13–15 minutes of heating), the system was heated for an additional 2–5 minutes at the same temperature before the pendant drop pictures were taken for the interfacial tension measurements. Additional increments of 4 and 5 minutes of maintaining the temperature resulted in interfacial tensions of 36–38 and 40–42 mN/m respectively. In the absence of ferric and ferrous ions, a surfactant concentration of 0.01 g/L gave an interfacial tension of 42.5 mN/m. This implies that the surfactant (of starting concentration 0.3 g/L) had been reduced to the equivalent of 0.05 g/L in about 15 minutes and shortly after, (about 4–5

²⁵It takes roughly 13–15 minutes to heat the pressure vessel from room temperature to the operating temperature of about 130°C.

minutes later), further degraded to the equivalent of 0.01 g/L. At the leaching temperature of 140°C, the degradation rate in the presence of Fe^{3+} and/or Fe^{2+} would probably be faster and hence render the naphthalene sulfonic acid ineffective as a sulfur dispersant within a short period of time. The tendency for a surfactant to degrade under leaching conditions could explain why this surfactant is such a poor dispersant (for liquid sulfur) for the leaching process. Similar observations have been made on lignin sulfonic acid degradation [55].

Dreisinger et al. [54] have reported that lignin sulfonic acid has a half-life of ten minutes under oxidative pressure leaching conditions. This means that after every ten minutes, the capability of the surfactant is degraded to a level equivalent to half its previous strength. Unlike naphthalene sulfonic acid-formaldehyde condensate which seems to degrade within a short time at high enough temperatures, it seems to take a relatively longer time for lignin sulfonic acid to be entirely degraded, and so it can still enhance the leaching rate.

All the amphoteric or zwitterionic surfactants performed very poorly in the leaching tests. Though they are all used as dispersants, detergents and wetting agents (like lignin sulphonates) in the laundry detergent industry, these reagents did not fare well in the leaching studies. It is believed that these surfactants undergo similar degradation process under oxidative leaching conditions, hence their inability to enhance the leaching rates. These three examples indicate that amphoteric surfactants *might* not do well in leaching unless the chemical stability of these materials can be enhanced.

A brief study was made to investigate the stability of OPD during use. In this study, the leach (or pregnant) solution from a previous experiment (12 grams concentrate in low pulp density conditions) was recycled. The solution already contained 0.1 g/L OPD from the previous experiment, and no surfactant was injected with the concentrate. After 30 minutes of leaching (amount of concentrate used was about 12 grams), about 98.4 %

zinc extraction was achieved. This indicates that OPD seems to survive a batch leaching experiment and so might survive in the full zinc circuit that includes electrowinning. Normally, it is desirable for the surfactants to be degraded before the leach solutions are passed to the very sensitive zinc electrowinning process. If OPD is to be introduced commercially, it is important to study further the degradation kinetics of OPD as well as the impact (if any) of OPD on zinc electrowinning.

Orthophenylene diamine was the only surfactant which had no effect on the liquid-liquid interfacial tension, yet managed to enhance the leaching rate to levels comparable to those obtained with lignin sulfonic acid. However, it increased the contact angle from 80 to 125–135°. These observations suggest that the most important criteria for a surfactant to be able to disperse liquid sulfur from the mineral surface are:

1. its ability to increase the sulfur-mineral contact angle and
2. remain kinetically stable under the conditions of zinc leaching

with the liquid sulfur-aqueous interfacial tension reductions being of secondary importance. The relative stability of the surfactant should be such that it does not interfere with the subsequent metal extraction stage. The interfacial tension reduction disperses the liquid sulfur into small droplets and the increase in contact angle 'rolls' the liquid into a spherical shape, which when combined with the continuous agitation of the pulp detaches the liquid from the solid surface. There remains another explanation for the high rates of zinc leaching in the presence of OPD: that the surfactant may form an intermediate product during the leaching process and this intermediate product has the ability to decrease the liquid sulfur-aqueous solution interfacial tension and disperse the liquid sulfur as well as to increase the contact angle resulting in an enhanced leaching rate²⁶.

²⁶This is only a speculation since there is no experimental proof.

High Pulp Density Leaching

From Table 5.16, OPD was the most efficient surfactant in the tests carried out under high pulp density conditions. About 99 % zinc extraction was achieved at a surfactant concentration of 0.06 g/L within 35 minutes, whereas, with lignin sulfonic acid (which is the commercially accepted surfactant for the process), a concentration of 0.1 g/L gave about 91 and 94 % zinc extractions after 35 and 60 minutes respectively. With MPD as a surfactant, 95 and 98 % zinc extractions were achieved at 35 and 60 minutes respectively at a surfactant concentration of 0.1 g/L.

Figure 5.26 shows that with OPD as a dispersant for liquid sulfur, it is possible to achieve about 95–96 % zinc extraction in about 25 minutes in the high pulp density leaching, which is higher than the extent of extraction achieved with lignin sulfonic acid even after 60 minutes of leaching. This is comparable to the 20 minutes the process takes to achieve 99 % zinc dissolution under the low pulp density conditions, Figures 5.25.

From Table 5.17 OPD may be expected to be more effective as a surfactant in the leaching of iron sulfide minerals, though the effectiveness may not be the same as that for zinc sulfide minerals. Tests conducted with OPD resulted in about 79–80 % iron extraction after 60 minutes as compared to 70 % iron extraction with 0.1 g/L lignin sulfonic acid for the same time period. The results obtained as to the extent of iron leaching are not strictly comparable with those that may be obtained with regard to the dissolution of individual iron sulfide minerals²⁷. This argument may be supported by the observation made by Ngoc et al. [41] in the leaching of complex sulfide concentrate containing CuFeS_2 , ZnS , PbS , and FeS_2 in which they observed that the leaching of CuFeS_2 , ZnS and PbS out of the complex ore was as if each individual mineral was being leached separately. FeS_2 , however, did not follow that pattern.

²⁷Galvanic effects between minerals may be important.

With OPD the extent of metal extraction was not sensitive to the surfactant concentration used. However, the same cannot be said for lignin sulfonic acid. The literature indicates that lignin sulfonic acid concentrations in excess of 0.3 g/L have no further influence on the zinc dissolution rate.

The extent of zinc and iron extraction (and hence the rate of reaction) for the different conditions are accurately correlated to the cumulative oxygen plots, Figure 5.34 and Table 5.19; the higher the extent of metal extraction, the higher the cumulative amount of oxygen consumed.

The instantaneous oxygen consumption plots show that in the absence of any surfactant (Figure 5.27), the oxygen flow into the reactor comes to almost a complete halt after about 35 minutes of leaching. This is believed to be due to liquid sulfur stability and to the encapsulation of the sulfide mineral particles. This implies that no further reaction (that requires oxygen) occurs beyond 35 minutes. On this basis the total sulfur oxidized to sulfate (Table 5.20) is partly due to pyrite oxidation and/or sulfur oxidation by molecular oxygen, (reaction 5.71). It is well accepted that under equal oxidative acidic conditions of leaching, pyrite is more likely to generate sulfate than sphalerite or pyrrhotite.

Figure 5.28 shows the typical behaviour of the system (in terms of instantaneous oxygen consumption) for the tests conducted with lignin sulfonic acid as the surfactant for dispersing liquid sulfur. The continuing flow of oxygen after 35 minutes shows that the zinc and iron dissolution reactions (and any other side reaction) were still in progress and hence the need for the continuous supply of oxygen. Data shown in Tables 5.16, 5.17, 5.19 and 5.20 are self-explanatory. The extent of zinc and iron extraction increases from 86 to 93 and 59 to 70 % respectively between 35 and 60 minutes of leaching. There is an increase in the acid consumption as well as the sulfur oxidation.

The continuing flow of oxygen for OPD and MPD leaching (Figures 5.29 and 5.30)

even after achieving 99 % zinc extraction (after 35 minutes) is due to the oxidation of impurity minerals such as pyrite taking over from the main zinc dissolution reaction. Table 5.17 shows that the percent iron dissolution increased from about 71 (after 35 minutes of leaching) to 81 % (after 60 minutes of leaching with OPD) and 63 to 70 % (for MPD leaching). It is also possible that there is some elemental sulfur oxidation occurring which usually takes place in a low acid medium and at high temperature. Thus, besides the main zinc dissolution reaction taking place in the system, other minor side reactions due to the presence of other minerals or sulphides contribute to the consumption of the reactants.

The cumulative oxygen consumptions for the different leaching conditions are shown in Figures 5.31–5.34. The plots shown are in agreement with the data in Tables 5.16 and 5.17. As mentioned earlier, approximately 0.0525 mole of these cumulative oxygen consumptions is used up in the oxidation of 0.21 mole ferrous ions present in the 1.5 L starting solution to the ferric state. From Figure 5.34, it can be observed that for leach times under ten minutes, the cumulative oxygen consumption is about the same for the different conditions. After the ten minute mark, the curves begin to diverge. It is proper to assume that at this point, enough liquid sulfur has been formed in the system such that, in the absence of surfactant in the system, the liquid sulfur has taken over the control of the reacting particles surfaces resulting in a slowing down of the reaction.

The acid:oxygen ratio shows that the lower the ratio, generally, the higher the sulfur oxidation to sulfuric acid to supplement the acid concentration in the starting solution.

If it is assumed that there is no elemental sulfur oxidation taking place during the leaching of the concentrate, the acid:oxygen ratio for the extent of metal (iron and zinc) dissolutions is equivalent to 4. Table 5.21 shows the theoretical oxygen and acid requirements as well as the acid to oxygen ratios for the extent of metal dissolution observed in

the absence of any sulfur oxidation. A comparison of the ratios in Table 5.21 to those experimentally measured, (Table 5.19), suggests about 10–20 % elemental sulfur oxidation. However, due to factors such as analytical discrepancies and the effect of side reactions (which have been ignored) the extent of the determined sulfur oxidation is less.

Physical examination of the leach residues (after the filtration) showed that the elemental sulfur by-product from the leaching experiment with OPD addition formed a filter cake with very fine particle sizes, whereas the residue produced with lignin sulfonic acid addition was of a coarse texture, (Figures 5.35–5.38); the residue produced in the MPD leaching experiment had an intermediate particle size. Fine particles sizes have large specific surface areas and high specific rates of reaction, hence the elemental sulfur produced in the OPD experiment will be more prone to oxidation. This explains the higher sulfur oxidation observed in the OPD leachings, Table 5.20.

Ideally, the inability of OPD to reduce the interfacial tension should enhance coalescence of sulfur and produce larger final drop sizes. On the other hand, if the OPD removes the sulfur from the solid surface faster than does the lignin sulfonic acid, this should result in the finer particles. However, then the sulfur particles should coalesce to form larger globules since they cannot be dispersed in the aqueous phase by the surfactant. The production of fine particles indicates the presence of other interfacial effects. There is a possibility that because OPD fails to degrade substantially during leaching, this could cause the decrease in the final drop sizes. For example, the lignin sulfonate degradation products may affect the coalescence of sulfur drops favourably (though we do not have any physical evidence of this). It is also possible that the interaction between surfactants and precipitated solids (or materials) such as jarosite, silica, lead sulfate, etc. during leaching could influence the coalescence of liquid sulfur in the system²⁸.

²⁸Unfortunately, this effect had not been considered in our interfacial studies and this is one area that needs to be studied.

Table 5.22 shows the comparison between the theoretical (calculated based on the extent of metal extraction and sulfur oxidation, y_{calc} and experimental oxygen requirements. The theoretically calculated oxygen consumptions and the experimentally measured data are within ± 2 % of each other. This is a very good agreement. The theoretical oxygen consumptions were calculated based on reactions 5.66, 5.67, and 5.68 and 5.71, neglecting reactions 5.69 and 5.70 which might occur to a very minor extent. Without considering any sulfur oxidation in the process (in the runs without any surfactant) the calculated oxygen requirements for the extent of metal extractions is about 0.288 mole, Table 5.21. When the calculated oxidized sulfur is taken into consideration through reaction 5.71, the total theoretical oxygen requirements for the reactions is about 0.308 mole. This value compares quite well with 0.306 mole, the experimental value, 5.22. Again, a close look at Tables 5.19 and 5.21 shows that the theoretical acid (as H^+ ions) requirements for the extent of reaction (based on reactions 5.66, 5.67, 5.68) are slightly higher than the experimentally measured data. The shortfall is caused by the oxidation of sulfur.

Shown in Table 5.23 is the total leaching efficiency as well as the Fe:Zn ratios in the presence of the different surfactants. The total leaching efficiency is given by:

$$Total\ leaching\ efficiency,\ \% = \frac{(Zn + Fe)_{leached}}{(Zn + Fe)_{concentrate}} \times 100 \quad (5.74)$$

As expected, the highest efficiencies were obtained in the presence of orthophenylene diamine and the lowest occurred in the absence of any surfactant. The Fe:Zn ratios show the extent of iron extraction for each mole of zinc dissolved in the process. In the concentrate, the Fe:Zn ratio is 0.272. If these two metals dissolve at the same rate, the ratio should be constant throughout. The lower numbers shown in Table 5.23 suggest the zinc dissolves faster than the iron. This is not unexpected since pyrite (the impurity mineral and the major source of iron in the concentrate) is known to dissolve at a slower rate than sphalerite under the same conditions. It is also possible that dissolved iron

may be precipitated in the form of jarosite and this will also result in low Fe:Zn ratios.

The information gathered from the above study makes OPD a potential supplement or substitute for lignin sulfonic and quebracho in the zinc pressure leaching systems.

Summary

The information gathered so far indicates that in spite of the fact that OPD was not very effective in terms of interfacial tension reduction as compared to the other surfactants, (though it increased the liquid sulfur–mineral contact angle from about $80\pm5^\circ$ to $135\pm5^\circ$ in the presence of ionic species), OPD proved to be a very effective surface active agent (dispersant for liquid sulfur) in the pressure leaching experiments. Naphthalene sulfonic acid–formaldehyde condensates and CAHSB which were very efficient in terms of interfacial tension reductions and contact angle increases, did not perform well in the leaching experiments, even in the low pulp density runs, due to high degradation rates under the leaching conditions. The metal dissolution rates obtained in the presence of OPD are very comparable to those obtained with lignin sulfonic acid. Thus, it is proper to conclude that the most important criterion for a surfactant to be a good dispersant is its ability to increase the solid–liquid sulfur contact angle, provided the said surfactant is stable under the operating conditions. This is achieved by adsorption of the surfactant onto the mineral. The increase in contact angle does not necessarily need to be very high provided the increase is enough to exceed a critical contact angle which is the angle above which sulfur dispersion can be achieved and below which the liquid sulfur is not dispersed from the mineral surface. Beyond that critical contact angle, the tendency for liquid sulfur to adhere to the solid surface will be very low and thus a high zinc extraction can be achieved. Metaphenylene diamine was also quite effective in the high pulp density

experiments and needs to be studied further²⁹. Despite the fact that both OPD and MPD proved to be very efficient in the pressure leaching experiments, nothing is known about their effects on the electrowinning of zinc from the leach solution. This is one area that needs to be investigated before any commercial application of these surfactants can be made. Lignin sulfonic acid is known to go through a degradation process by the time the zinc sulfate leach solution gets to the tank house and hence does not interfere with the electrowinning process. Thus, there is a need to investigate the effect of residual OPD on the electrowinning process. Nothing can be said about the effectiveness of paraphenylene diamine under the high pulp density conditions since this aspect was not investigated. However, it did prove to be very efficient on a low pulp density scale, with very reproducible results.

²⁹No studies were performed to determine MPD's interfacial activity at the liquid sulfur-aqueous phase-mineral interfaces, but it is believed it might fall into the same category as OPD since the $-NH_2$ groups attached are activating groups and hence tend to activate the benzene ring, though the activation effect is more pronounced in the ortho positions.

Table 5.15: Weight loss due to leaching in the absence and presence of different surfactants under high pulp density conditions; initial conditions: $[\text{ZnSO}_4] = 1.27 \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.12 \text{ M}$; $[\text{Fe}^{2+}] = 0.14 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$; Batch addition of surfactants

Surfactant	Conc. wt.(g/L)	Time(min)	Weight loss (%)
None	–	60	31 ± 0.3
Lignin.	0.06	35	53 ± 0.2
		60	58 ± 0.4
	0.10	35	57 ± 0.4
		60	59 ± 0.3
OPD	0.06	35	61 ± 0.5
		60	63 ± 0.6
	0.10	35	61 ± 0.5
		60	63 ± 0.3
MPD	0.10	35	58 ± 0.3
		60	61 ± 0.5

Table 5.16: Extent of zinc extractions (computed from residue analysis) and the changes in Zn^{2+} (aq) concentration of the filtrate in the presence of different surfactants and under high pulp density conditions; initial conditions: $[\text{ZnSO}_4] = 1.27 \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.12 \text{ M}$; $[\text{Fe}^{2+}] = 0.14 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$; batch addition of surfactants. * Residue analysis

Surfactant	Conc. (g/L)	Time (min)	Zn leached* (moles)	ΔZn filtrate (moles)	% Zn extraction
None	-	60	0.353	0.335	49 ± 0.5
Lignin.	0.06	35	0.616	0.599	86 ± 0.5
		60	0.675	0.654	92 ± 0.3
	0.10	35	0.653	0.637	91 ± 0.6
		60	0.688	0.672	93 ± 0.2
OPD	0.06	35	0.733	0.730	99 ± 0.5
		60	0.741	0.735	99 ± 0.2
	0.10	35	0.740	0.703	99 ± 0.2
		60	0.743	0.740	99 ± 0.4
MPD	0.10	35	0.707	0.679	95 ± 0.3
		60	0.731	0.732	98 ± 0.4

Table 5.17: Iron extractions (based on residue analysis) in the presence of different surfactants and under high pulp leaching conditions; initial conditions: $[\text{ZnSO}_4] = 1.27$ M; $[\text{H}_2\text{SO}_4] = 1.12$ M; $[\text{Fe}^{2+}] = 0.14$ M; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100$ kPa.

Surf.	Conc.(g/L)	Time(min)	Fe extraction (%)
None	–	60	40 ± 0.2
Lignin.	0.06	35	59 ± 0.3
		60	64 ± 0.3
	0.10	35	59 ± 0.2
		60	69 ± 0.3
OPD	0.06	35	70 ± 0.7
		60	78 ± 0.4
	0.10	35	72 ± 0.5
		60	79 ± 0.5
MPD	0.10	35	62 ± 0.5
		60	69 ± 0.5

Table 5.18: Oxygen and acid (as H^+ ions) requirements per 100 gram sphalerite concentrate and 1.5 L leach solution *assuming* complete oxidation of concentrate after test period. "x" represents the fractional conversion of sulfur to sulfate

Element	Source	Conc'n. (moles)	O_2 (moles)	H^+ (moles)
Fe (as Fe^{2+})	1.5 L sol'n.	0.21	0.0525	0.21
Zn	concentrate	0.751	0.3755	1.503
Fe	"	0.204	0.153	0.612
Cu	"	0.01	0.005	0.020
Pb	"	0.003	0.0015	0.006
S	"	0.986	$1.5x$	$-2x$
Total	–	2.164	$0.5876 + 1.5x$	$2.351 - 2x$

Table 5.19: Experimental data for oxygen and acid (measured as H^+) consumptions in the presence of different surfactants; initial conditions: $[ZnSO_4] = 1.27 \text{ M}$; $[H_2SO_4] = 1.12 \text{ M}$; $[Fe^{2+}] = 0.14 \text{ M}$; Temp. = $140 \pm 1^\circ C$; $P_{O_2} = 1100 \text{ kPa}$.

Surf.	Conc.(g/L)	Time(min)	O_2 (Moles)	H^+ (Moles)	H^+/O_2
None	–	60	0.306 ± 0.003	1.10 ± 0.01	3.61
Lignin.	0.06	35	0.480 ± 0.005	1.708 ± 0.03	3.56
		60	0.517 ± 0.003	1.867 ± 0.01	3.62
	0.10	35	0.503 ± 0.003	1.832 ± 0.02	3.64
		60	0.557 ± 0.005	1.898 ± 0.03	3.41
OPD	0.06	35	0.571 ± 0.004	2.000 ± 0.03	3.50
		60	0.620 ± 0.007	2.020 ± 0.02	3.26
	0.10	35	0.574 ± 0.006	2.030 ± 0.03	3.54
		60	0.619 ± 0.003	2.040 ± 0.02	3.30
MPD	0.10	35	0.538 ± 0.005	1.960 ± 0.02	3.64
		60	0.577 ± 0.005	2.030 ± 0.01	3.52

Table 5.20: Elemental sulfur analysis of leach residue and filtrate and the extent of total sulfide sulfur oxidation to sulfate (as %); initial conditions: $[ZnSO_4] = 1.27 \text{ M}$; $[H_2SO_4] = 1.12 \text{ M}$; $[Fe^{2+}] = 0.14 \text{ M}$; Temp. = $140 \pm 1^\circ C$; $P_{O_2} = 1100 \text{ kPa}$.

Surf. Conc.(g/L)	Time (min)	$S_{residue}^o$ (Moles)	y_{calc} (Moles)	$\Delta S_{filtrate}$ (Moles)	% $S_{oxidation}^{total}$	$\frac{S_{residue}^o}{S_{residue}^o + \Delta S_{filtrate}}$ %
None	60	0.381 ± 0.008	0.013	0.013 ± 0.001	1.4	97.0
Lignin. 0.06	35	0.563 ± 0.01	0.021	0.022 ± 0.001	2.3	96.0
	60	0.722 ± 0.008	0.024	0.034 ± 0.001	3.6	96.0
Lignin 0.10	35	0.658 ± 0.01	0.020	0.025 ± 0.002	2.3	97.0
	60	0.755 ± 0.01	0.041	0.037 ± 0.001	3.8	95.0
OPD 0.06	35	0.736 ± 0.01	0.032	0.056 ± 0.002	5.7	93.0
	60	0.786 ± 0.02	0.054	0.064 ± 0.002	6.6	93.0
OPD 0.10	35	0.769 ± 0.01	0.030	0.051 ± 0.001	5.2	94.0
	60	0.807 ± 0.01	0.052	0.064 ± 0.002	6.5	93.0
MPD 0.10	35	0.690 ± 0.008	0.020	0.034 ± 0.001	3.5	95.0
	60	0.735 ± 0.006	0.030	0.047 ± 0.001	4.8	94.0

Table 5.21: Calculated oxygen and acid (as H^+) requirements for the different experimental conditions, assuming NO elemental sulfur oxidation

Surfactant	Conc.(g/L)	Time(min)	O ₂ (Moles)	H ⁺ (Moles)	H ⁺ /O ₂
None	–	60	0.288	1.153	4.00
Lignin.	0.06	35	0.447	1.788	4.00
		60	0.486	1.944	4.00
	0.10	35	0.475	1.900	4.00
		60	0.501	2.002	4.00
OPD	0.06	35	0.526	2.102	4.00
		60	0.541	2.164	4.00
	0.10	35	0.532	2.130	4.00
		60	0.544	2.176	4.00
MPD	0.10	35	0.501	2.004	4.00
		60	0.523	2.092	4.00

Table 5.22: Comparison between experimental and calculated oxygen requirements for the different experimental conditions; Temp.= 140±1°C; P_{O₂} = 1100kPa

Surfactant	Conc.(g/L)	Time(min)	O ₂ ^{calc.} (Moles)	O ₂ ^{expt.} (Moles)
None	–	60	0.308	0.306
Lignin.	0.06	35	0.478	0.480
		60	0.522	0.517
	0.10	35	0.498	0.503
		60	0.562	0.557
OPD	0.06	35	0.574	0.571
		60	0.622	0.620
	0.10	35	0.572	0.574
		60	0.622	0.619
MPD	0.10	35	0.531	0.538
		60	0.568	0.577

Table 5.23: Total leaching efficiencies and iron:zinc ratios; initial conditions: $[\text{ZnSO}_4] = 1.27 \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.12 \text{ M}$; $[\text{Fe}^{2+}] = 0.14 \text{ M}$; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$.

Surfactant	Conc. (g/L)	Time (min)	Fe (Moles)	Zn (Moles)	Fe:Zn	% Total leaching efficiency
None	–	60	0.079	0.353	0.224	47.7
Lignin.	0.06	35	0.115	0.616	0.187	80.4
		60	0.128	0.675	0.189	86.5
	0.10	35	0.122	0.667	0.182	85.4
		60	0.139	0.688	0.202	88.5
OPD	0.06	35	0.142	0.733	0.194	92.8
		60	0.157	0.741	0.212	95.3
	0.10	35	0.147	0.740	0.198	93.4
		60	0.160	0.743	0.215	95.6
MPD	0.10	35	0.127	0.707	0.179	88.3
		60	0.140	0.731	0.191	92.2

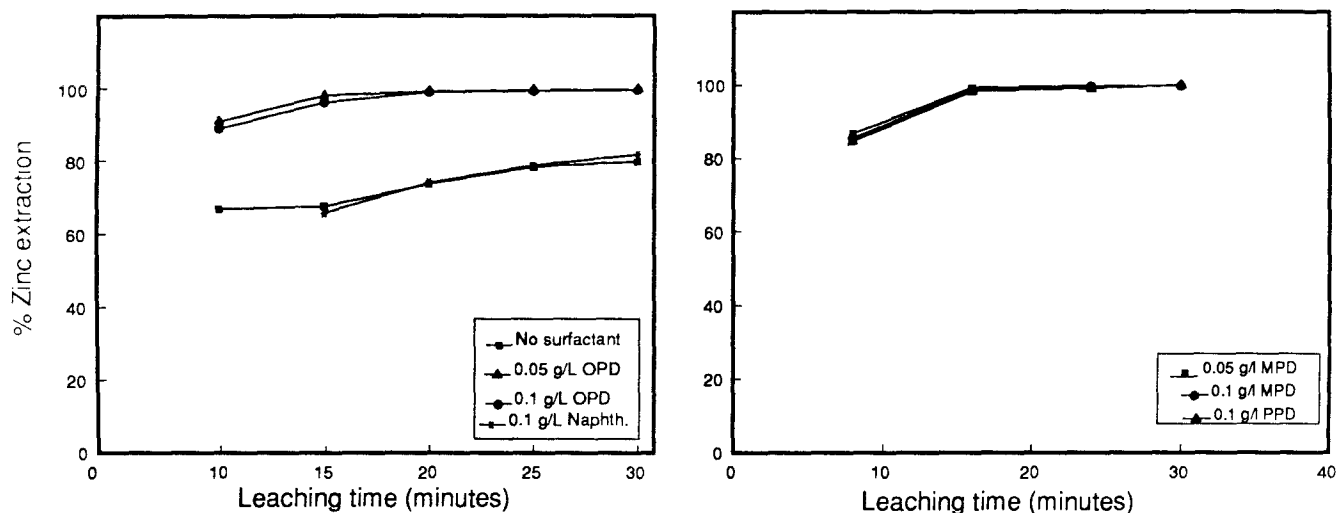


Figure 5.25: Extent of zinc extraction in the presence of OPD, MPD, PPD and naphthalene sulfonic acid-formaldehyde condensates; Temp. = $140 \pm 1^\circ\text{C}$; $P_{O_2} = 1100 \text{ kPa}$; sample weight $\sim 12 \text{ grams}$.

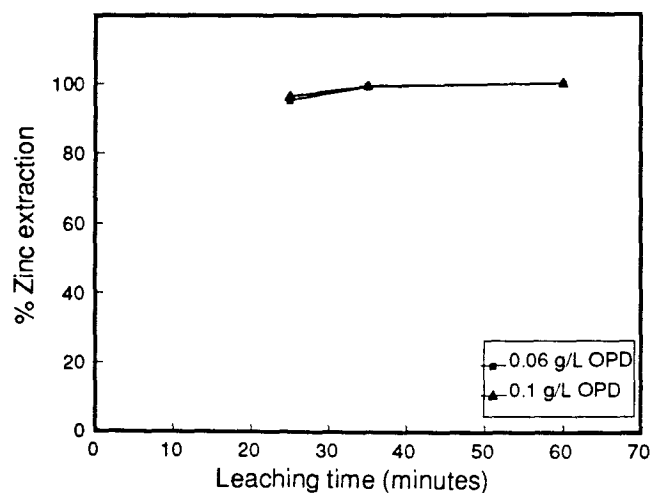


Figure 5.26: Extent of zinc extraction under high pulp density leaching conditions in the presence of OPD; Temp. = $140 \pm 1^\circ\text{C}$; $P_{O_2} = 1100 \text{ kPa}$.

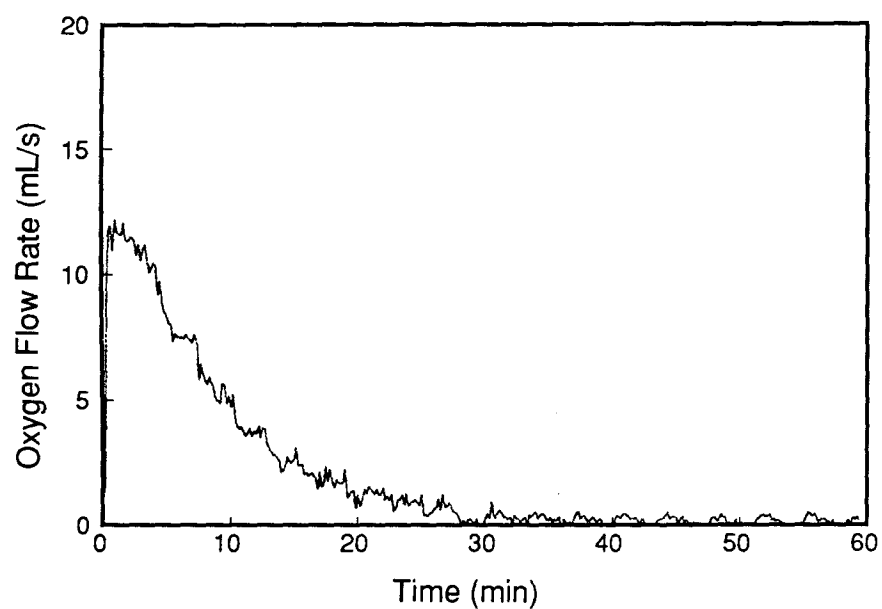


Figure 5.27: Instantaneous oxygen flow rate in the absence of any surfactant; Temp.= $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$.

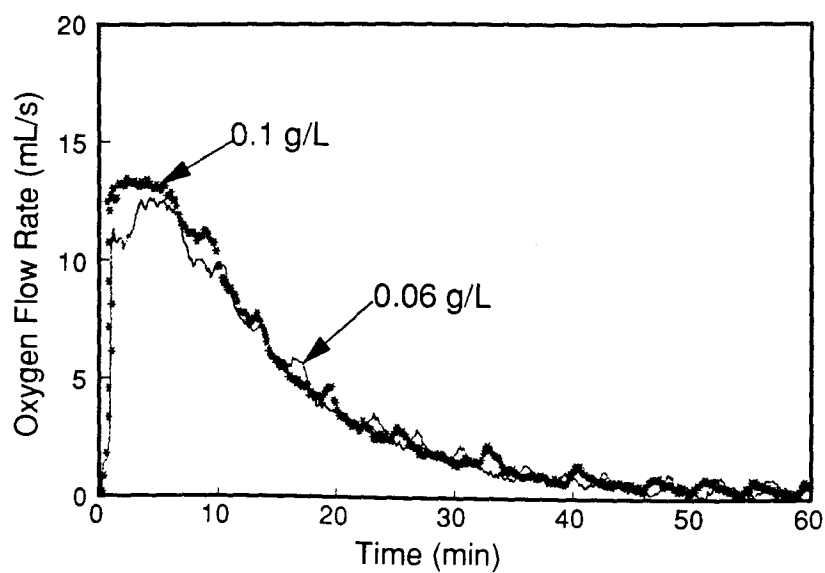


Figure 5.28: Instantaneous oxygen flow rate in the presence of lignin sulfonic acid; Temp.= $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$.

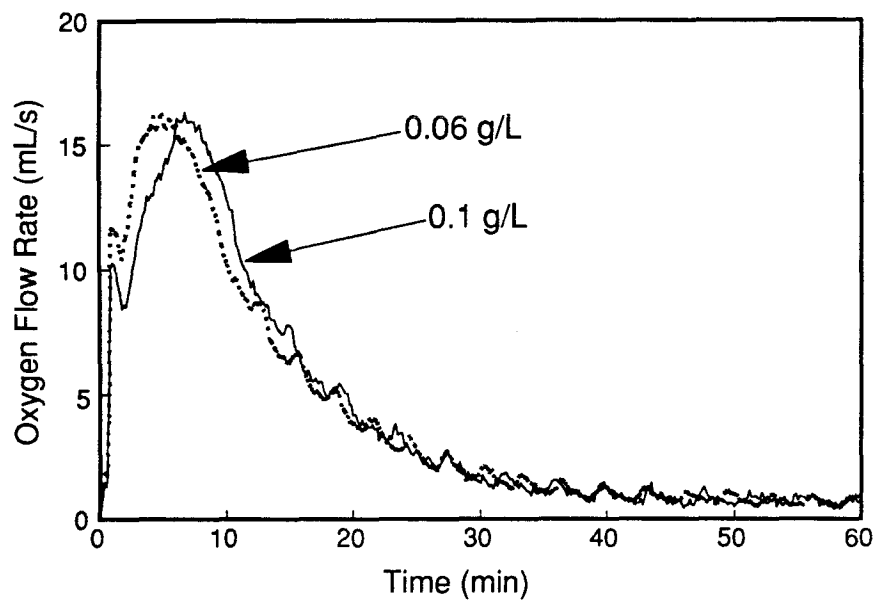


Figure 5.29: Instantaneous oxygen flow rate in the presence of OPD; Temp. = $140 \pm 1^\circ\text{C}$; $P_{O_2} = 1100 \text{ kPa}$.

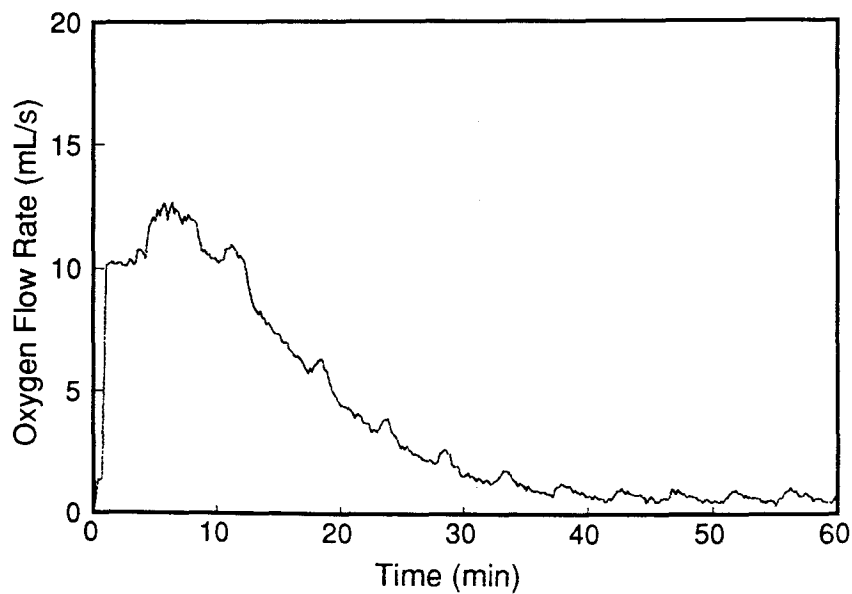


Figure 5.30: Instantaneous oxygen flow rate in the presence of 0.1 g/L MPD; Temp. = $140 \pm 1^\circ\text{C}$; $P_{O_2} = 1100 \text{ kPa}$.

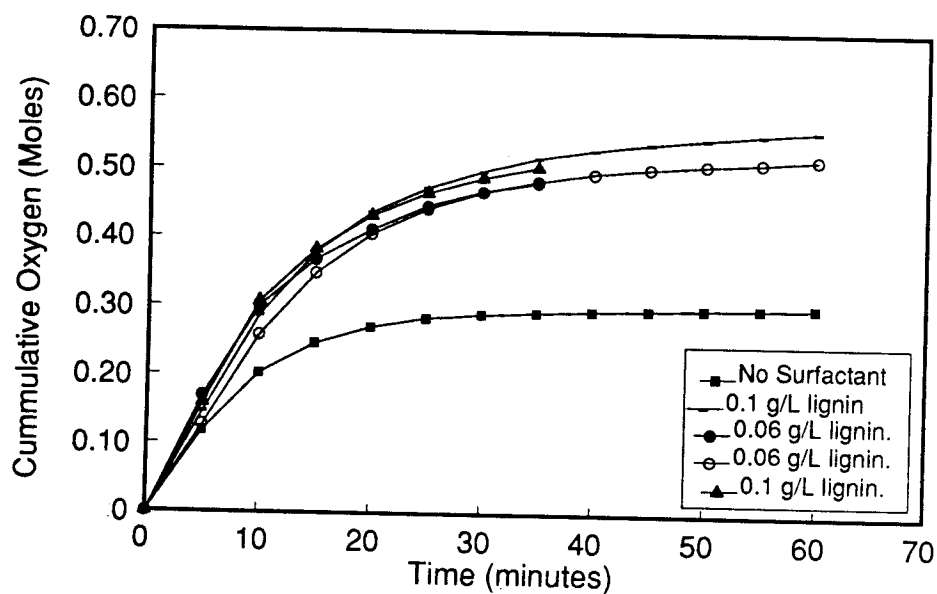


Figure 5.31: Cumulative oxygen consumed in the absence and presence of lignin sulfonic acid; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$.

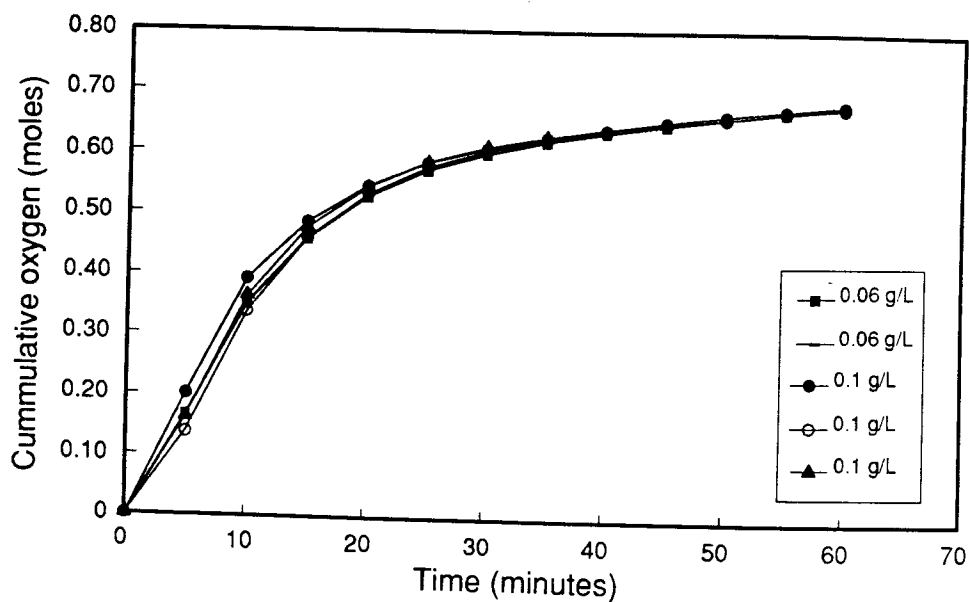


Figure 5.32: Cumulative oxygen consumed in the presence of OPD; Temp. = $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$.

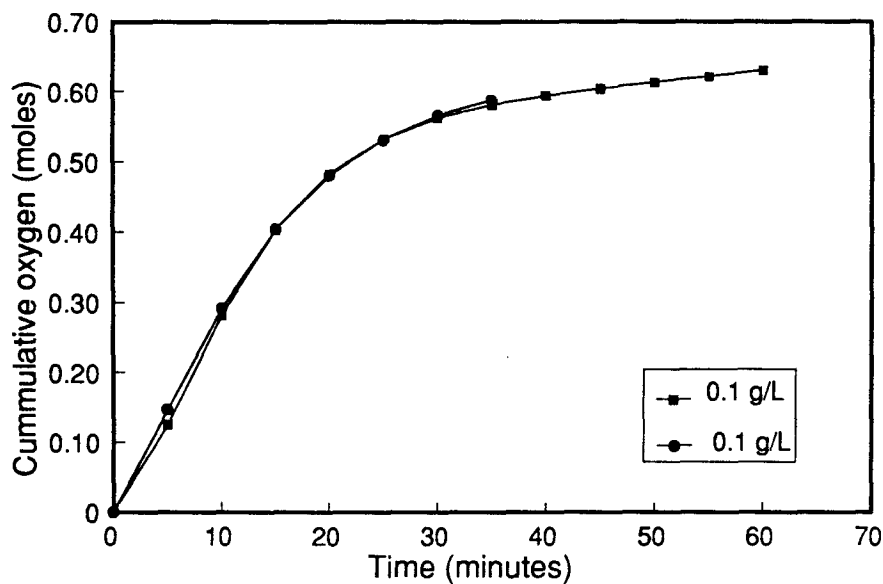


Figure 5.33: Cumulative oxygen consumed in the presence of MPD; Temp.= $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$.

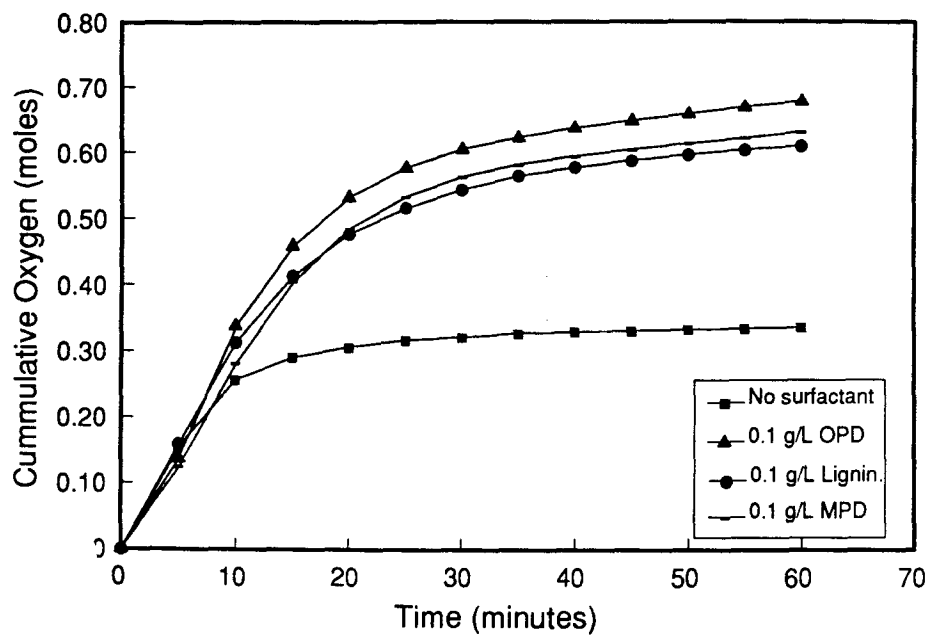


Figure 5.34: Relative consumptions of oxygen in the presence of the different surfactants; Temp.= $140 \pm 1^\circ\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$.



Figure 5.35: A photograph of zinc sulfide leach residue in the absence of a surfactant after 60 minutes; Temp.= $140\pm 1^{\circ}\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$.

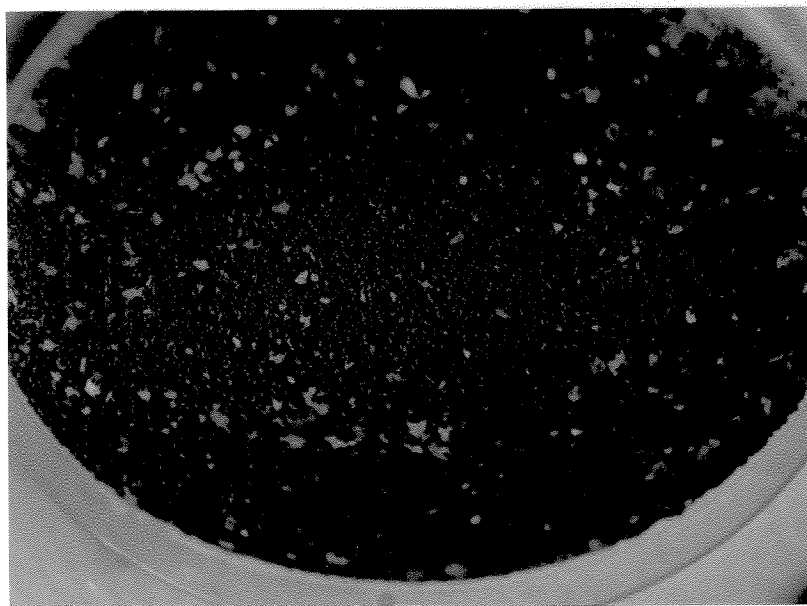


Figure 5.36: A photograph of zinc sulfide leach residue in the presence of 0.1 g/L lignin sulfonic acid after 60 minutes; Temp.= $140\pm 1^{\circ}\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$.



Figure 5.37: A photograph of zinc sulfide leach residue in the presence of 0.1 g/L OPD after 60 minutes; Temp.= $140\pm 1^{\circ}\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$.



Figure 5.38: A photograph of zinc sulfide leach residue in the presence of 0.1 g/L MPD after 60 minutes; Temp.= $140\pm 1^{\circ}\text{C}$; $P_{\text{O}_2} = 1100 \text{ kPa}$.

5.3 INFRARED SPECTROSCOPY

5.3.1 Results

Characterization of Sphalerite

Prior to any adsorption studies, the infrared spectral data of the sphalerite concentrate was recorded using:

- KBr pellet transmission technique (on dry sphalerite)
- ATR analysis (of wet concentrate)

Theoretically, natural sphalerite is transparent in the region $2500\text{--}800\text{ cm}^{-1}$ of an infrared spectrum [113]. This implies that any absorption in this region must be due to either impurities in the concentrate or to surface oxidation products such as Zn(II) oxy-sulfur products.

All of the accompanying spectral records are reported in absorbance³⁰.

Figure 5.39 shows the FTIR spectrum of natural sphalerite using the conventional KBr pellet transmission technique. The band at $1619\text{--}1617\text{ cm}^{-1}$ is most likely due to the bending vibrations of water absorbed by the KBr and/or water of crystallization of the concentrate. The absorption bands at 1381 to 1024 cm^{-1} may be due to oxy sulfur oxidation products formed on the surface of the mineral particles due to contact with the atmosphere. The broad peak frequency at $3500\text{--}3300\text{ cm}^{-1}$ is associated with the symmetric and asymmetric stretching vibrations of physically adsorbed water by the concentrate and possibly going through intermolecular hydrogen bonding.

Figure 5.40 shows the ATR-FTIR spectrum of natural sphalerite conditioned in distilled water for 20 minutes with the solvent serving as the background spectrum. This

³⁰It should also be noted that the absorption of infrared radiation by the solvent is not quantitatively compensated so spectral subtraction may be over compensated in some cases.

means that any absorbance due to the solvent in the suspension is cancelled out. The pH of the water was adjusted to that of the working solution ($\text{pH} = 1.37$) to ensure similar aqueous pH conditions throughout the study. The sharp absorption band at $1103\text{--}1102\text{ cm}^{-1}$ and the weak shoulder at 1024 cm^{-1} are due to the surface oxidation products which appeared at 1118 cm^{-1} (Figure 5.39). The shift from 1118 to 1103 cm^{-1} may be attributed to the solvent-concentrate interactions. The broad and weak intensity band at $1658\text{--}1620\text{ cm}^{-1}$ is due to the bending vibrations of water of hydration. The broad and weak absorption bands at $3490\text{--}2860\text{ cm}^{-1}$ may be designated to the asymmetric and symmetric stretching vibrations of the OH group of the water of crystallization and/or hydration.

Adsorption Studies in the Presence of Lignin Sulfonic Acid

Listed below are the different conditions employed in the infrared spectroscopic studies

- KBr wafer spectral analysis of lignin sulfonic acid
- ATR spectral recording of 5 g/L surfactant (lignin sulfonic acid) and ferric solution
- ATR spectral recording of sphalerite concentrate conditioned in surfactant/ferric solution
- ATR spectral analysis of washed sphalerite concentrate after conditioning in surfactant/ferric solution
- ATR infrared analysis of sphalerite concentrate conditioned in surfactant solution in the absence of ferric ions
- ATR recording of washed sphalerite concentrate after contact with surfactant solution in the absence of ferric ions

- KBr disc infrared recording of leached sphalerite concentrate residue

KBr Pellet Transmission Spectrum of Lignin Sulfonic Acid

The structure of lignin and hence lignin sulfonate/lignin sulfonic acid has not been well defined by wood chemists. Different chemists have put forward different structures for lignin sulfonate/lignin sulfonic acid. Figure 2.3 is one such structure [86].

Figure 5.41 shows the KBr pellet transmission spectrum of lignin sulfonic acid. The broad and strong peak frequency at $3402\text{--}3388\text{ cm}^{-1}$ is designated to the asymmetric and symmetric stretching vibrations of the OH functional group which are going through intermolecular hydrogen bonding. Water absorbed by the KBr window may also contribute to this band. The asymmetric stretching vibrations of the $\text{--CH}_2\text{--}$ group are represented by the absorption band at 2937 cm^{-1} whilst the shoulder band at 2842 cm^{-1} indicates the stretching vibrations of the --OCH_3 group in the molecular structure [123, 124, 170, 171]. The most important absorption bands or diagnostic peak frequencies occur in the region $1773\text{--}1039\text{ cm}^{-1}$. The bands at $1773\text{--}1716\text{ cm}^{-1}$ are representative of the stretching vibrations of the carbonyl (C=O) group. The band progression between 1653 and 1423 cm^{-1} are assigned to the skeletal vibrations of the molecule – the stretching C=C vibrations of the aromatic ring being responsible for the $1653\text{--}1463\text{ cm}^{-1}$ whilst C-H deformations account for the $1424\text{--}1423\text{ cm}^{-1}$ vibrational band. The absorption bands at $1370\text{--}1369$ and $1266\text{--}1265\text{ cm}^{-1}$ are assignable to the phenolic OH deformation (or bending) vibrations (of the structure). The peak frequencies at $1211\text{--}1160\text{ cm}^{-1}$ are the result of the asymmetric stretching vibrations of the sulfonate ($\text{--SO}_3\text{H}/\text{SO}_3^-$) group; the same group is responsible for the symmetric stretching vibrations at $1040\text{--}1039\text{ cm}^{-1}$, and the peak frequency at $650\text{--}649\text{ cm}^{-1}$ [123, 124], [165]–[171]. The absorption band at $527\text{--}526\text{ cm}^{-1}$ is characteristic of the type of lignin sulfonate [165]–[169] – in this case a hardwood type, and it is of no diagnostic importance. The absorption bands at $864\text{--}724\text{ cm}^{-1}$ are due

to the aromatic ring substitution pattern; though they are not of diagnostic importance their presence in a spectrum will help to confirm the presence of the reagent.

The KBr disc transmission spectrum for a zinc-chelated (or complexed) lignin sulfonic acid obtained through the courtesy of Georgia Pacific, Bellingham, WA. is shown in Figure 5.42. Basically, this spectrum has a lot in common with that for the lignin sulfonic acid. In spite of the similarities, there are some differences. There is the disappearance of the absorption bands due to the carbonyl group, and there are shifts in some of the bands compared to the spectrum for the lignin sulfonic acid.

The KBr infrared spectrum of sodium-based lignin sulfonate complex is shown in Figure 5.43.

ATR Technique for Surfactant Solutions

Figure 5.44 shows the ATR-FTIR absorption spectrum of 5 g/L lignin sulfonic acid solution³¹. The aqueous solution contained 0.036 mol/L sulfuric acid (pH=1.37), and 0.025 mol/L ferric ions (added as ferric sulfate). Compared to the KBr wafer spectrum, it is observed that some of the absorption bands have shifted in positions to either lower or higher frequencies. Others have disappeared from the solution spectrum as the result of solvent-surfactant molecular interactions³². The absorption bands at 1644, 1543, 1514–1513 (not shown on plot due to crowding) and 1464–1463 cm^{-1} are the result of stretching vibrations of the aromatic rings. These bands are well-defined with the 1514–1463 cm^{-1} bands appearing in the same wavenumber region as in the KBr spectrum. The band shift from 1653/1605 to 1644 is most likely due to the solvent-surfactant interactions; however, the bending vibrations of water molecules could contribute to this band. The weak intensity shoulder band at 1739–1738 cm^{-1} may represent the stretching vibrations of the

³¹Preliminary tests proved that lower surfactant concentrations of 1–1.5 g/L were not sufficient to achieve sensitivity in the recorded range.

³²The background spectrum is taken to be that of the solvent which is distilled water and acid.

carbonyl, C=O, group which is capable of hydrogen bonding. The shoulder at 1372–1371 cm^{-1} represents the OH bending vibrations. The asymmetric stretching vibrations of the sulfonate group are designated by the absorption band at 1194–1193 cm^{-1} (a significant shift from 1211 cm^{-1} in the solid) while the symmetric stretching vibrational modes are represented by the weak shoulder at 1050–1049 cm^{-1} . The broad absorption band at wavenumbers 3500–3100 cm^{-1} is the result of the asymmetric and symmetric stretching vibrations of the OH groups involved in hydrogen bonding. The strong absorption peak at 1106 cm^{-1} is due to the presence of a sulfate radical or ions in the solution which originate from the ferric sulfate.

Characterization of Surfactant Adsorption

Due to strong infrared absorption by natural sphalerite at wavenumbers lower than 800 cm^{-1} , the spectral analysis of surfactants or organic reagents in this region (in the presence of the concentrate) is less useful. Shown in Figure 5.45(a) are the spectral data of natural sphalerite conditioned in the ferric/lignin sulfonate solution for 20 minutes where the background spectrum (sometimes referred to as reference) is the solvent. The spectrum shown in Figure 5.45(b) is the result of the spectral subtraction of the ferric/surfactant solution spectrum from the sphalerite–surfactant (solution) spectrum. Both spectra display most of the characteristic peak frequencies of the surfactant solution spectrum. The spectrum of the adsorbate on the adsorbent agrees very well with that of the adsorbate solution from the high frequency end of the spectrum to about 1371 cm^{-1} (in both Figures (a) and (b)), beyond which there are some new developments, indicating the presence of new surface products due to the solid–liquid interactions. These spectra are very useful especially in the fingerprint region, where most of the diagnostic absorptions bands are located.

Figure 5.45(b): Region 3600 – 1265 cm⁻¹

The absorption bands at 3500–3100 cm⁻¹ correspond to the asymmetric and symmetric stretching vibrations of the OH groups and the band progression from 1372–1265 cm⁻¹ are also designated to the OH bending vibrations. There are changes in the relative intensities of the peaks as well. The vibrational bands at 1647–1265 cm⁻¹ are enough to confirm the presence of the surfactant (an aromatic compound) on the mineral surface [123, 170, 171].

Region 1265 – 650 cm⁻¹

There is the appearance of a sharp absorption band at 1098–1097 cm⁻¹. This may be due to the formation of a soluble zinc sulfate product on the mineral surface. This was not confirmed experimentally. The asymmetric stretching vibrations of the sulfonate group at 1193–1192 cm⁻¹ in the bulk solution spectrum has disappeared, and there is a significant shift in peak frequency of the symmetric vibrational band at 1050 (in the bulk solution) to 1013 cm⁻¹. These observations are indications of a chemical adsorption mechanism and the formation of a new surface compound. The bands between 870 – 750 cm⁻¹ (in the bulk solution spectrum, Fig.5.44) which are due to the substitution pattern on the aromatic rings (though diagnostically are less useful) have all changed their frequency positions following adsorption of the surfactant. These changes indicate that the lignin sulfonic acid is chemisorbed to some extent. Physical adsorption may co-exist with chemisorption.

Figure 5.46 is the ATR-FTIR absorption spectrum of the natural sphalerite conditioned in the ferric/surfactant solution and then washed 3–4 times with the solvent followed by more drastic washing in boiling distilled water for 25–30 minutes and cold washed again 3–4 times. The absorption bands from the high frequency end to 1266 cm⁻¹ still persisted after washing, though there were some minor shifts in some of the

band positions. The bands at 835 to 734 cm^{-1} disappeared with new ones appearing at 826 and 774 cm^{-1} . There was the formation of new bands at 1148–1147, 1035–1034, and 988 cm^{-1} as well. These new developments are indicative of the fact that the layer of adsorbate on the surface is a chemisorbed product and that it could not be removed by the washing procedure. The shoulder at 1148–1147 cm^{-1} is indicative of the presence of Zn-complexed compound on the surface of the mineral particles (as can be seen in the spectrum for the zinc-complexed lignin sulfonate). The weak bands at 2921 cm^{-1} which represent the stretching vibrations of $-\text{CH}_2-$ also indicate the presence of the surfactant. The band at 1640–1639 may be a contribution from both co-adsorbed water and the surfactant molecule.

Adsorption Tests in Ferric-free Surfactant Solution

Figure 5.47(a) shows the spectral record of a natural sphalerite conditioned in the ferric-free 5 g/L surfactant solution for 20 minutes (background spectrum being the solvent). The spectrum in Figure 5.47(b) is the result of the appropriate spectral subtraction (i.e. adsorbent–adsorbate spectrum minus adsorbate spectra). Like the ferric solution, the sulfonate absorption bands have disappeared from both spectra.

In Figure 5.47(a) the vibrational modes indicative of the presence of the aromatic compound [170, 171] form the series of weak bands at 3056–2930 cm^{-1} and 1550–1460 cm^{-1} in the fingerprint region. In Figure 5.47(b) the diagnostic bands present in the region 1741–1100 cm^{-1} coupled with the band at 2928 cm^{-1} (which is due to asymmetric $-\text{CH}_2-$ stretching vibrations) are indicative of the presence of the adsorbate molecules on the surface of the mineral particles. The band positions in the fingerprint region of the spectrum are very much the same as those obtained in the ferric–surfactant system, though there are some differences between the two in other regions of the spectra.

Figure 5.48 shows the spectral profile of a natural sphalerite conditioned in the ferric-free surfactant solution, washed several times with acidified distilled water followed by further washing in boiling water for 25–30 minutes and cold washed again. With the exception of the vibrations at $1608\text{--}1607\text{ cm}^{-1}$, the absorption bands in the fingerprint region $1608\text{--}1032\text{ cm}^{-1}$ and $776\text{--}775\text{ cm}^{-1}$ are in just about the same positions as those shown in Figure 5.46 (within the limits of instrument sensitivity) with minor frequency shifts. The vibrations at $1608\text{--}1509\text{ cm}^{-1}$ are due to the skeletal C=C stretching vibrations of the aromatic rings. The weak shoulder band at $1267\text{--}1266\text{ cm}^{-1}$ is due to the phenolic OH group. The absorption bands at 1143 and 1031 cm^{-1} may be attributed to the formation of a zinc-complexed surface compound. These observations together with those in the ferric system imply that the lignin sulfonate molecule is adsorbed both in the presence and absence of ferric ions in the leaching systems.

The decreases in the adsorption intensities or heights after the washing process stages indicate the removal of a physically adsorbed surfactant layer³³. Once this layer is removed by the washing, the chemisorbed layer is exposed and this is hard to remove. This observation implies that both physical and chemical adsorption processes take place during the adsorption, with physical adsorption probably occurring after the first chemisorbed monolayer is formed.

Discussion

Ideally, shifts in frequency or changes in relative intensities of absorption indicate chemisorption. Physically adsorbed species and pure reagent species are not expected to display any spectral differences. However, there are occasions when chemically adsorbed species do not show much spectral difference. The intensity of an absorption band is very much dependent on the magnitude of the dipole change during the vibrations, the larger the

³³The physically adsorbed layer can be multilayers.

change, the stronger the band.

Certain functional groups may not always give rise to absorption bands, even though they may be present in the sample.

Washing of the mineral particles/adsorbed species did not bring about significant changes in the positions of the absorption frequencies but showed a decrease in the intensities or height of the peaks (Figures 5.45(b) and 5.46). However, in the ferric-free system (Figures 5.47(b) and 5.48) some bands in the fingerprint region disappeared after the washing. This may be due to:

- the signals at those vibrational frequencies are so weak that the instrument could not respond to them³⁴
- and/or the absence of ferric ions in the system affected the adsorption pattern to some extent.

This behaviour persisted for different samples and repeated washings of some of them. Because of the drastic washing process adopted, it appears therefore that the species that remain on the surface after the washing/boiling can be attributed to chemical adsorption. It is reasonable to argue that the surface adsorbed species/layer after the washing process is due to chemical interaction, since any physically adsorbed layer is supposed to be dissolved or removed during the washing/boiling. The absorption bands at 1148–1147 and 1143–1142, 1034–1031, and 776–773 cm^{-1} can therefore be assigned to the presence of a zinc complexed lignin sulfonate, (Figures 5.42, 5.46 and 5.48).

Some of the peak frequencies obtained in the unwashed and washed samples occur in almost the same positions. However, the bands at 1148–1143, 1034–1031, 988, and 776–773 cm^{-1} are new (in the washed spectra). The appearance of these new bands indicates that underneath the top physically adsorbed layer lies a surface product(s) which give(s)

³⁴Some signals will not show up in the spectrum if they are very weak.

rise to these new vibrations. The unwashed spectra consist of chemically and physically adsorbed species but the fraction due to physical adsorption is removed by the washing process. It can thus be concluded that the peaks in the region $1741\text{--}1265\text{ cm}^{-1}$ (Figures 5.45(a) and 5.47(a)) represent both lignin sulfonate adsorbed in bulk form (i.e. physical adsorption) and chemisorbed zinc-complexed form which may differ in structure from the bulk compound. The disappearance of the strong sharp vibrational band at $1101\text{--}1097\text{ cm}^{-1}$ indicates the removal of soluble surface compounds such as oxysulphur products from the solid surface by the washing process.

A final confirmation of this spectral interpretation is obtained from the KBr disc transmission spectrum of sphalerite leached for 15 minutes in the presence of lignin sulfonic acid. The lignosol concentration was 5 g/L in solution and was added continuously at a rate of 2.0 mL/min. The amount of concentrate used was 2 grams. The leaching solution contained approximately 2 mol/L zinc ions, 0.4 mol/L sulfuric acid, 0.1 mol/L each of ferric and ferrous ions. The leaching was done under a nitrogen atmosphere. The leached residue was thoroughly washed several times with about 8 litres of distilled water, vacuum dried and a KBr disc made from the dried sample. No organic solvent could be used for further washing of the residue because lignin sulfonic acid is insoluble in organic liquids³⁵. The residue disc was then mounted in the path of the IR beam to record the spectral profile (Figure 5.49). Compared to Figure 5.46, it exhibits most of the characteristic peak frequencies of the ATR-FTIR spectrum. The appearance of bands at $1460\text{--}1459$, $1509\text{--}1508$, $1265\text{--}1264$, $1149\text{--}1148$ and $1032\text{--}1031\text{ cm}^{-1}$ agrees very well with the ATR spectra, indicating the presence of (a) similar compound(s) in both spectra (as well as Figure 5.48). The absorption band at $1149\text{--}1148\text{ cm}^{-1}$ present in both spectra is characteristic of a zinc-complexed compound. The differences which are shown

³⁵This was confirmed in the lab as attempts to dissolve 0.25 grams lignin sulfonate in 100 ml acetone failed.

may be attributed to the different sample preparation procedures and the environmental conditions (i.e KBr - dry and ATR - wet); otherwise the two are very similar. The vibrational modes due to the skeletal rings of the surfactant molecule are well-defined and occur in the same frequency range in the two spectra, the only exceptions being the bands at 1603–1602 cm^{-1} (Figure 5.49), and 1641–1640 and 988 cm^{-1} (in Figure 5.46). There exist, however, significant shifts from 1716 to 1687 cm^{-1} . The appearance of an absorption band at 1418–1417 cm^{-1} (Figure 5.49) compared to 1424–1423 cm^{-1} (figure 5.41) further confirms the presence of the adsorbate molecules on the solid surface. This observation further confirms the chemisorption argument.

The large size of the lignin sulfonate structure could create the condition for each reactive site on the solid surface to be occupied by only one lignin sulfonate ion. By interacting with the aqueous phase, electrical neutrality is maintained on the surface. The adsorbent–solvent interactions will result in an adsorbate structure which will be different from the bulk material and hence can be expected to show some differences in the spectral profile. This explains the minor differences between Figures 5.46 and 5.49 on one hand and Figure 5.42 on the other hand, e.g. the bands at 1033 and 1043 cm^{-1} respectively. The physically adsorbed lignin sulfonate will not be affected by the sulfide mineral surface and hence will exhibit the same spectrum as the bulk.

It is likely that the adsorbate is adsorbed on the ZnS mineral as a bulk-like Zn(II)–surfactant compound. The surface compound chemically formed has an organic portion which is very similar to the bulk adsorbate.

The shifts in the absorption bands of the OH stretching vibrations (in the upper frequency region) and the asymmetric and symmetric stretching vibrations of the sulfonate groups from 1161–1160 to 1148 and 1143, and 1040–1039 to 1034 and 1031 cm^{-1} (figures 5.41, 5.46, 5.48 and 5.49) indicate chemical interactions of the OH and SO_3^- groups with the solid surface.

It is believed that under the washing conditions adopted, no lignin sulfonate (or physically adsorbed species) could survive and hence the spectrum observed must therefore be due to chemisorbed species.

Although the absorption bands at 1603–1602, 1220–19 and 1509–1508 cm^{-1} (Figure 5.49) occur in the same frequency range as those of the bulk lignin sulfonic acid, the relative intensities of these bands have changed from more intense 1211 cm^{-1} in the bulk spectrum to almost equally intense bands in the leach residue.

The assignment of the peak frequencies between 1640–1264 cm^{-1} (in Figures 5.45(b) and 5.47(b)) to both forms of adsorbed species is due to:

- after the washing/boiling process, which is presumed to remove any physically adsorbed species, most pre-washing peak frequencies remained in almost the same positions (with the exception of the 1103 cm^{-1} which disappeared) although their relative intensities changed
- Zn-, Na-based lignin sulfonate have peaks in this region (just like the bulk lignin sulfonic acid) suggesting that metal-lignin sulphonates complexes also have absorption bands in that region and therefore that a surface metal-lignin sulfonate complex could have an absorption band in that region
- under the conditions of the washing process, physically adsorbed species could not be present and hence the layer is due to chemisorption.

In the KBr spectrum of the leach residue (Figure 5.49), there are some absorption bands present in the 3500–3100 cm^{-1} range. However, these bands have intensities similar to the noise background in that spectral region. Therefore, they cannot be regarded as true peak frequencies in spite of the fact that they occur in the appropriate wavenumber region.

It is possible that mineral–surfactant reaction products can co-exist with mineral surface oxidation product on the mineral surface where the mineral–surfactant product may exist as small islands on the oxidized mineral surface. However, hydrophilicity is enhanced on dissolution of any soluble surface oxidation product of sphalerite followed by adsorption of the surfactant.

The elemental sulfur present in the zinc leaching system is hydrophobic. This hydrophobic character makes it possible to interact with the hydrocarbon portion of the surfactant molecule, with the hydrophilic groups projecting into the aqueous phase. Thus, much as lignin sulfonic acid interacts with the mineral surface, it also interacts with the liquid sulfur through the hydrocarbon end of the molecular structure. This behaviour tends to lower the liquid sulfur – aqueous phase interfacial tensions or free energies as had been reported earlier [55].

Summary

The presence of multiple functional groups, OH^- , SO_3^- , and C=O , (all hydrophilic groups and capable of hydrogen bonding) and the three-dimensional nature of the lignin sulfonate structure suggests that during the process of surfactant-mineral interactions, one or more hydrophilic groups interact with the mineral surface whilst the other group(s) interact(s) with the aqueous phase through hydrogen bonding. Thus, the surfactant acts as a bridge between the solid and liquid phases. The disappearance of the sulfonate absorption bands and the shifts in the hydroxyl group frequencies (in the upper frequency region) implies that the surfactant molecule interacts with the solid surface most likely through them. This role played by the surfactant continuously renders the sphalerite surface hydrophilic and prevents it from becoming sulphophilic. Since lignin sulfonic acid or its salt does not form any oriented layer on adsorption, it is most likely that the molecule sits on the mineral surface as a "net" or a "sponge" when adsorbed. Formation

islands of metal-surfactant species on the oxidized mineral surface is probably enough to make the mineral particles sufficiently hydrophilic.

The complexities involved in the satisfactory analysis of more than one component or functional group from a given absorption band remain a problem even with the best resolution. In view of this difficulty it is not easy for one to predict with certainty the nature of the adsorbed species.

In conclusion, the above observations indicate the presence of physically and chemically adsorbed species on the mineral surface in an acidic medium. However, it is very difficult to discriminate between physically and chemically adsorbed molecules from the spectrum both qualitatively and quantitatively.

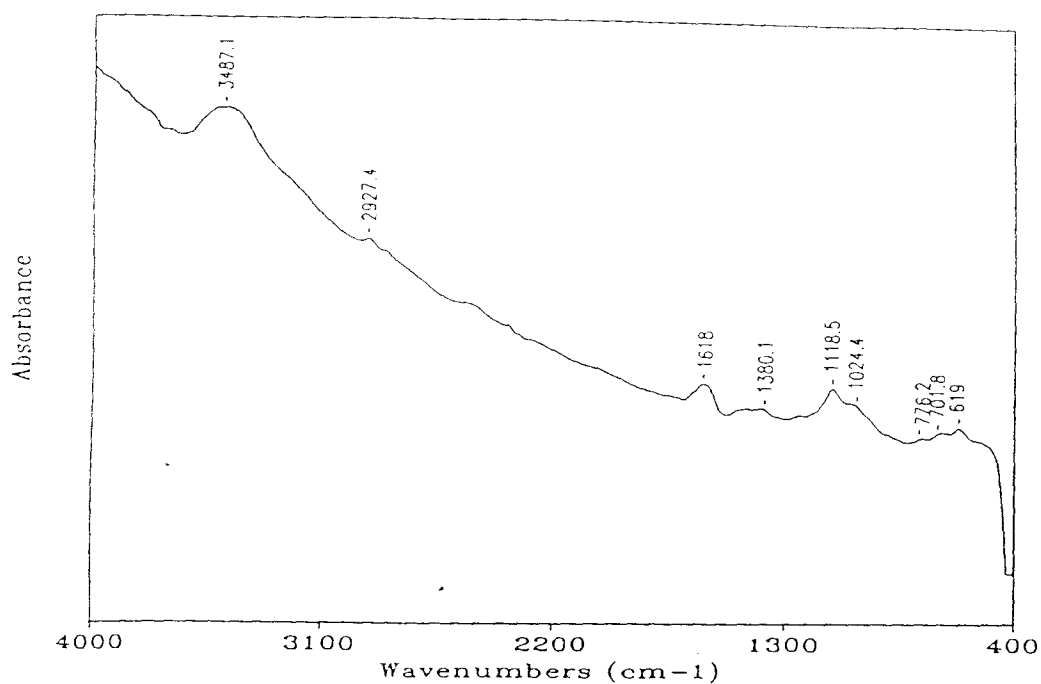


Figure 5.39: Infrared spectrum of sphalerite using KBr pellet technique.

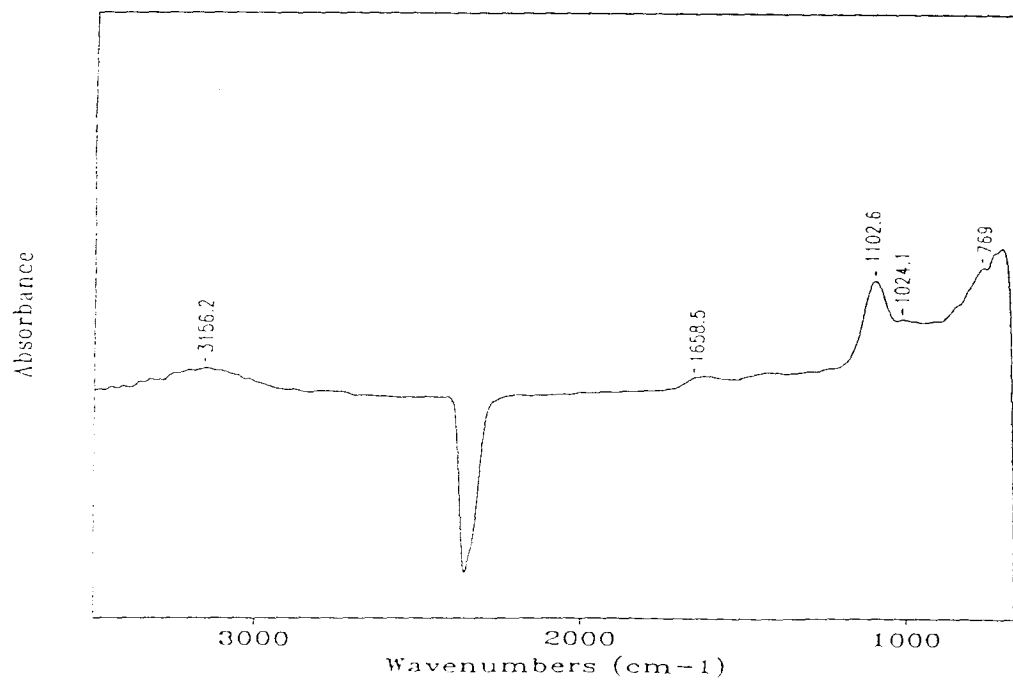


Figure 5.40: ATR spectrum of wet sphalerite.

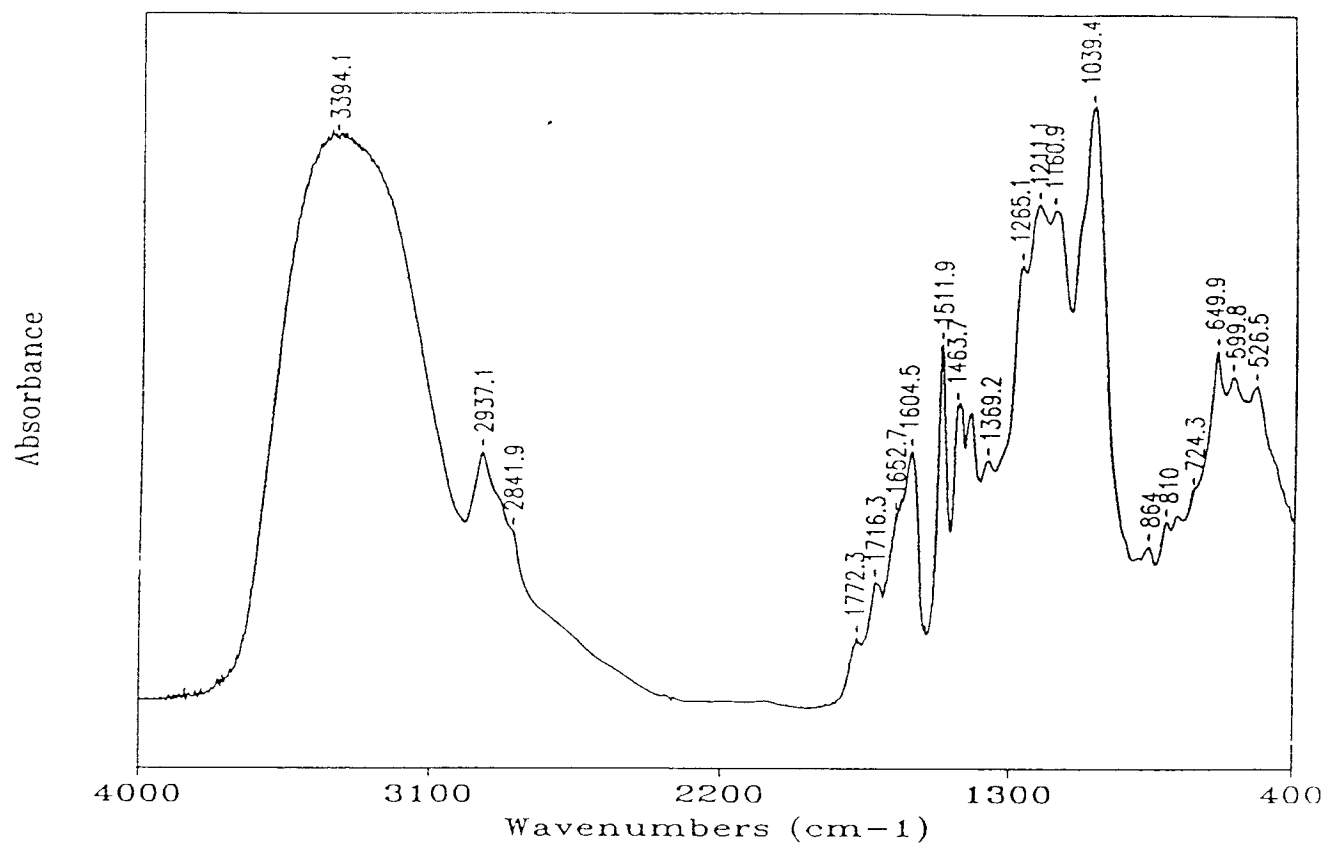


Figure 5.41: KBr disc spectrum of lignin sulfonic acid.

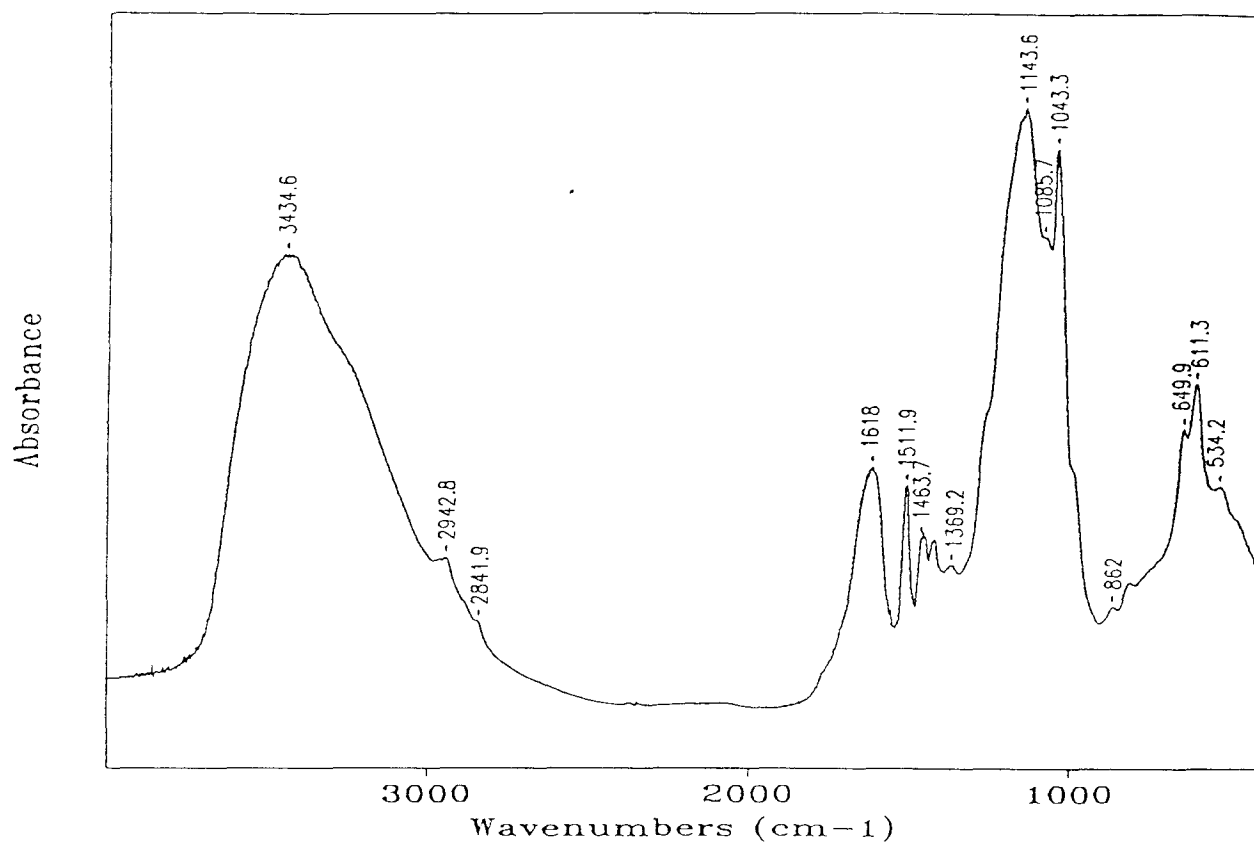


Figure 5.42: KBr disc spectrum of Zn-based lignin sulfonate complex.

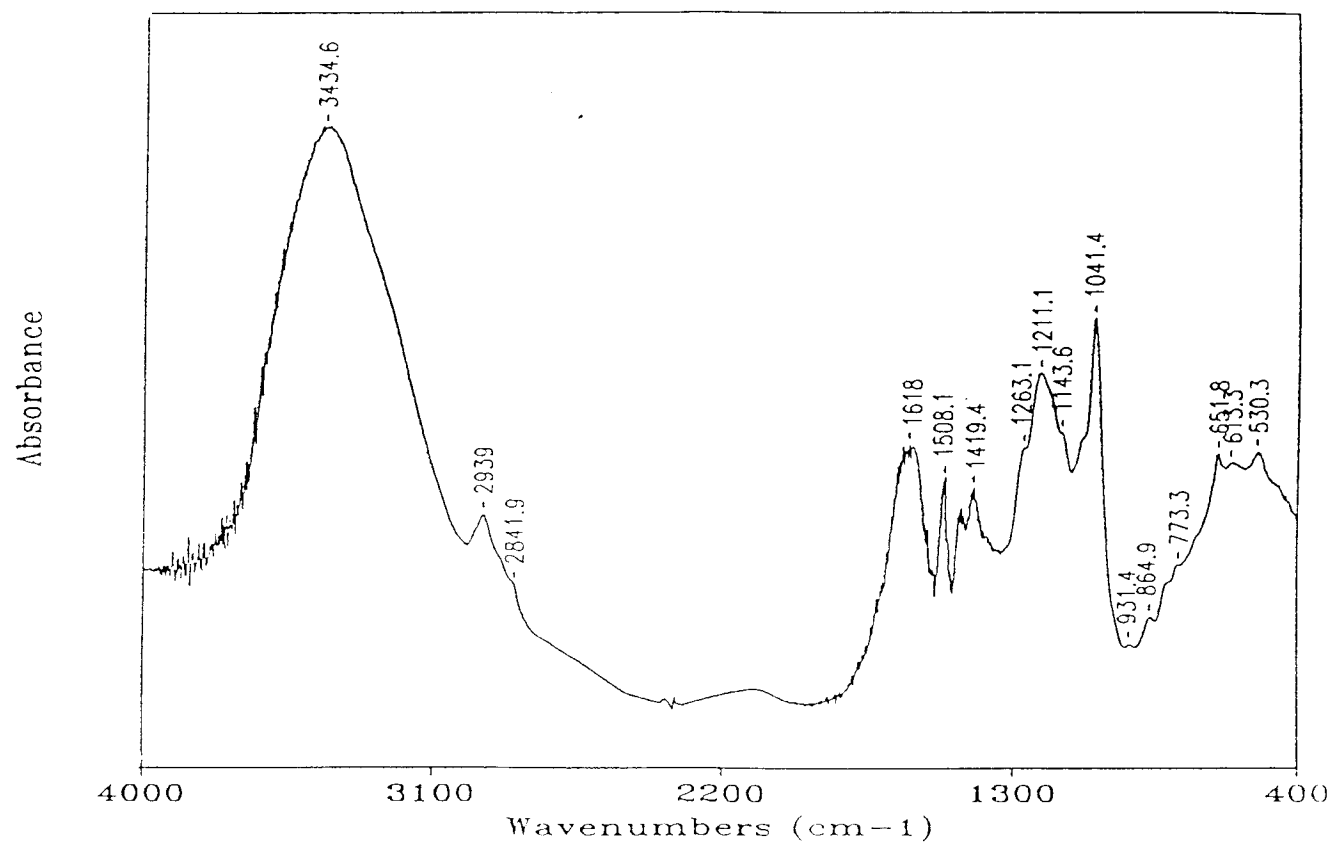


Figure 5.43: KBr pellet spectrum of Na-based lignin sulphonate complex.

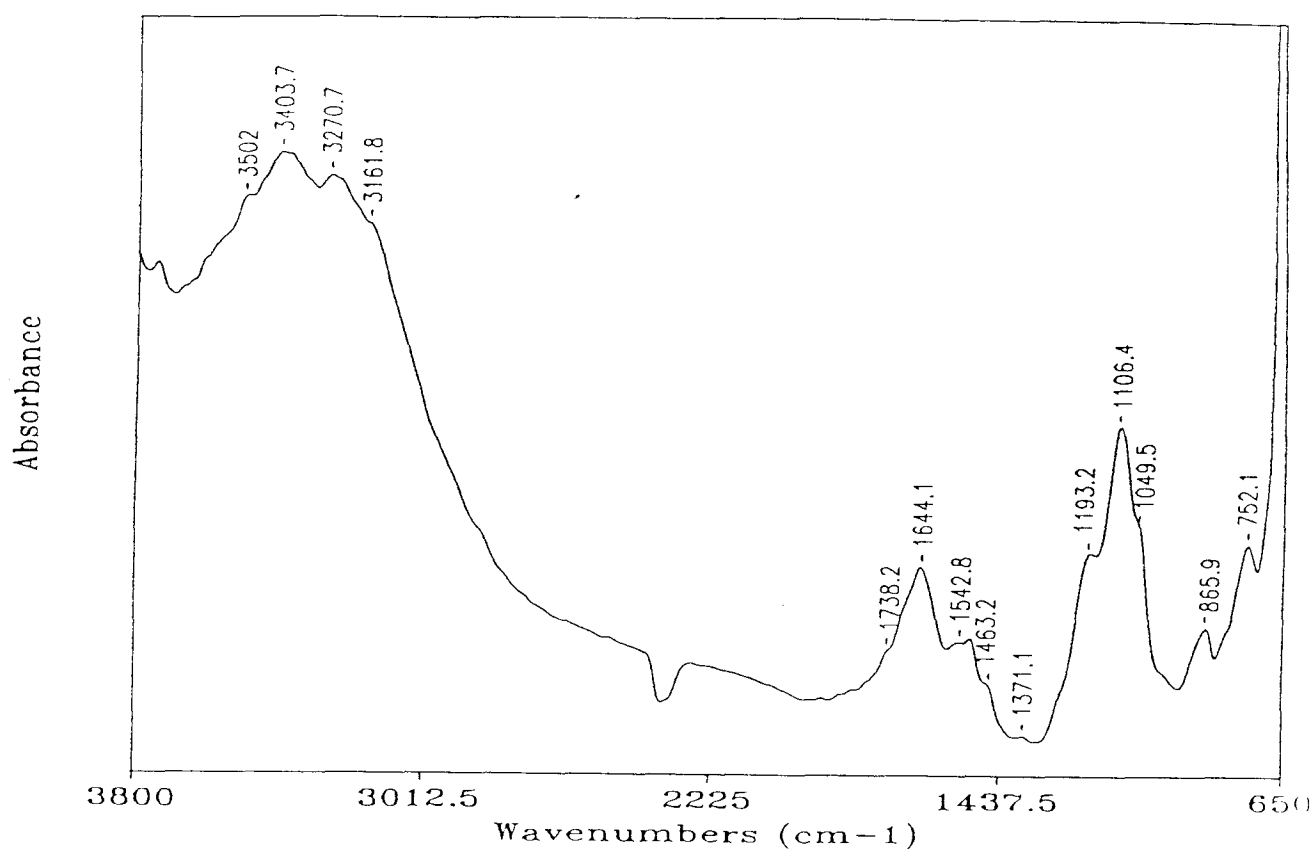
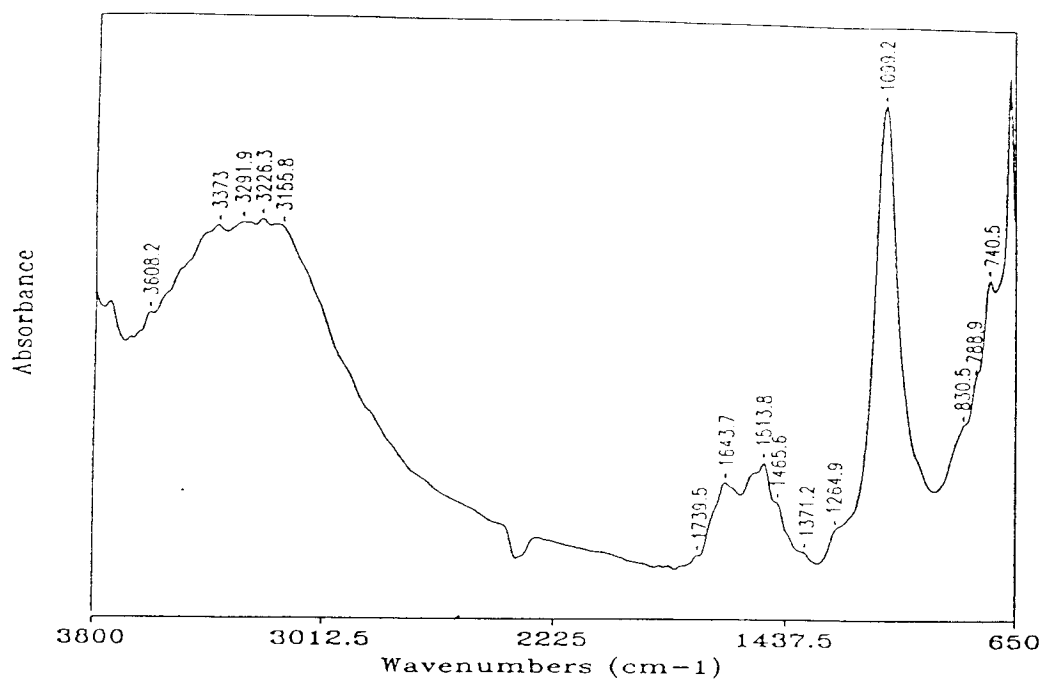
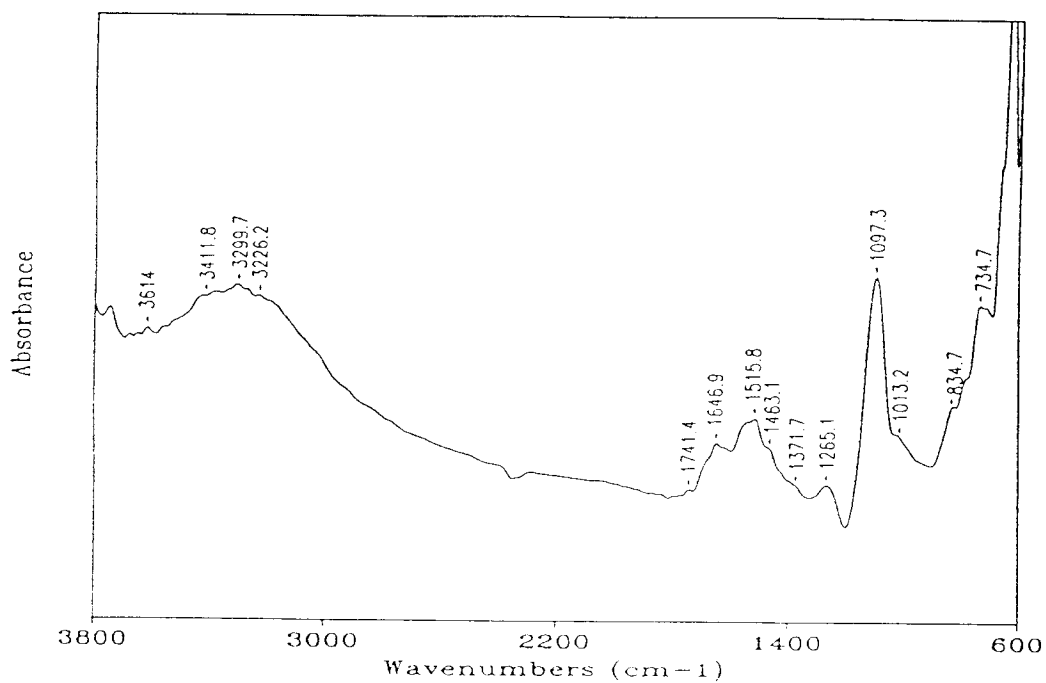


Figure 5.44: ATR spectrum of lignin sulfonic acid solution; solution condition: $[\text{Fe}^{3+}] = 0.025 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.036 \text{ M}$, Temperature = 25°C ; reference spectrum: solvent.



(a)



(b)

Figure 5.45: ATR spectrum of sphalerite conditioned in surfactant solution for 20 minutes; solution condition: $[\text{Fe}^{3+}] = 0.025 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.036 \text{ M}$, Temp. = 25°C: (a) reference: solvent spectrum (b) less solution spectrum.

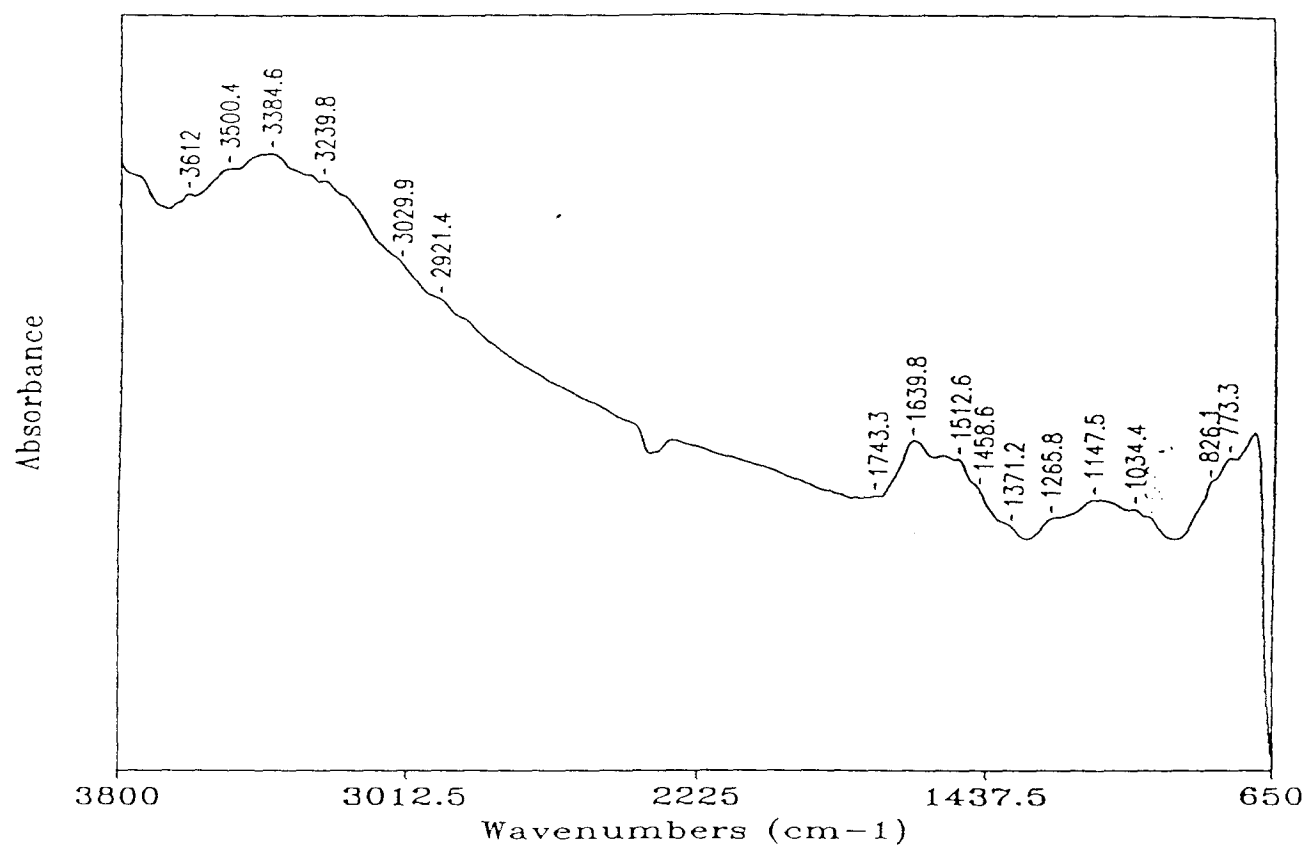
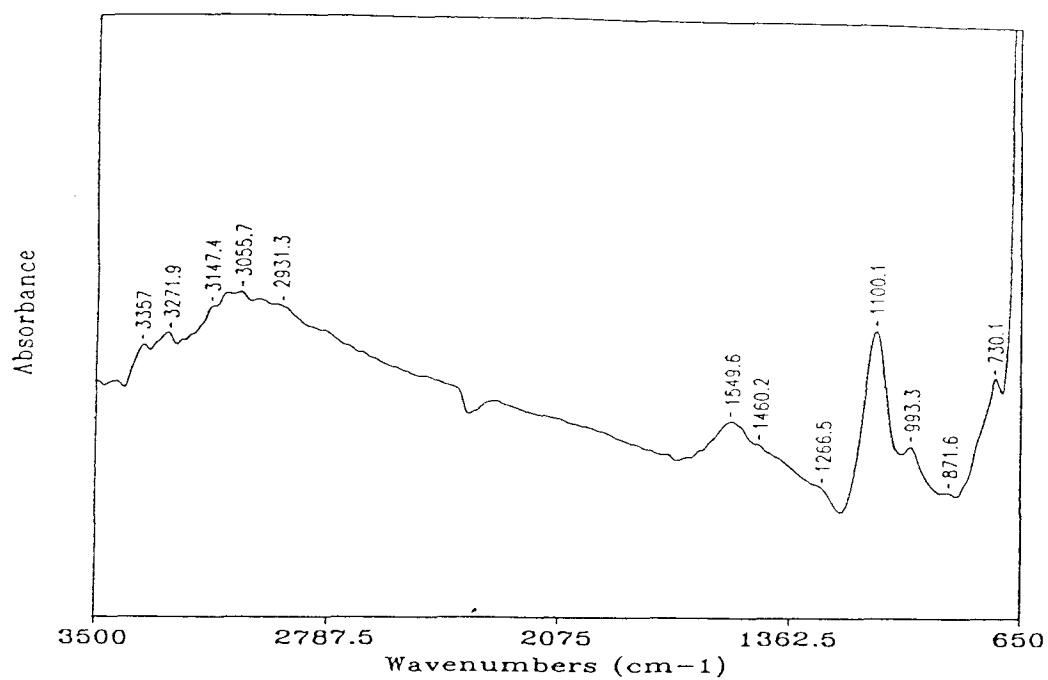
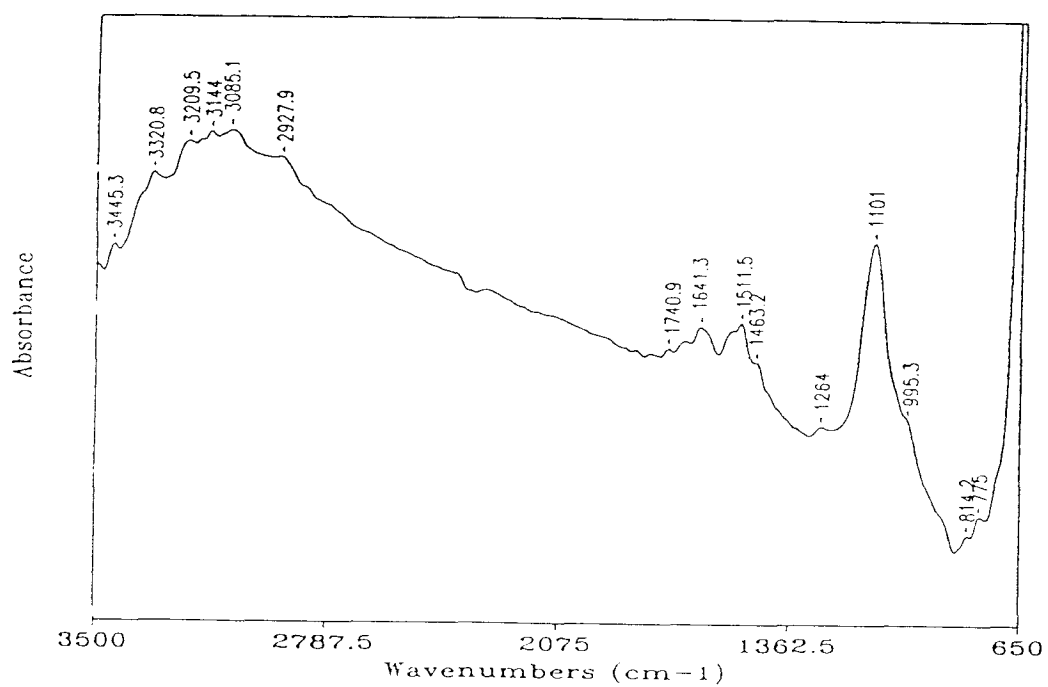


Figure 5.46: ATR spectrum of washed sphalerite after conditioned in surfactant/ferric solution, reference spectrum: solvent.



(a)



(b)

Figure 5.47: ATR spectrum of sphalerite conditioned in ferric free-surfactant solution for 20 minutes; solution condition: $[\text{H}_2\text{SO}_4] = 0.036 \text{ M}$, Temp. = 25°C . (a) reference: solvent spectrum (b) less the solution spectrum.

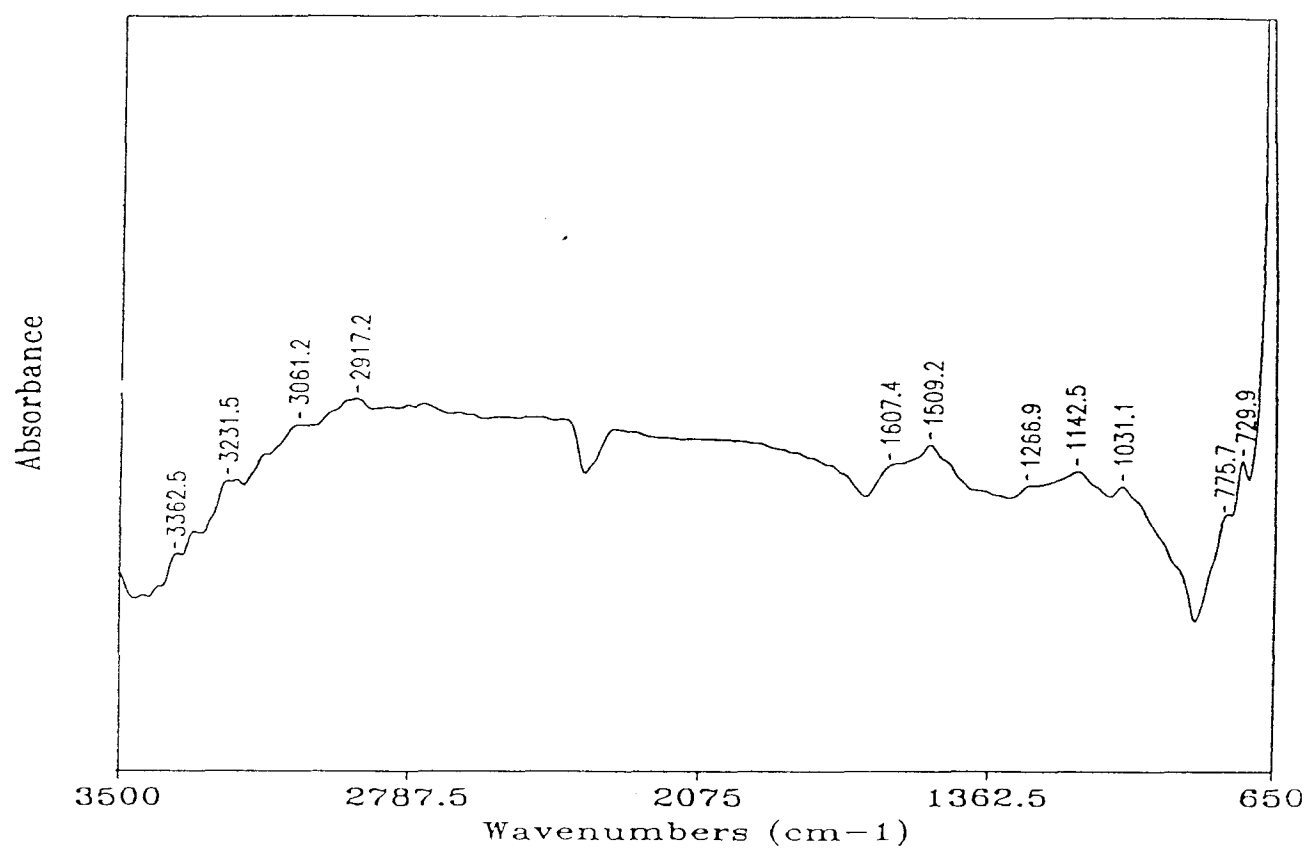


Figure 5.48: ATR spectrum of washed sphalerite after contact with ferric free-surfactant solution, reference spectrum: solvent.

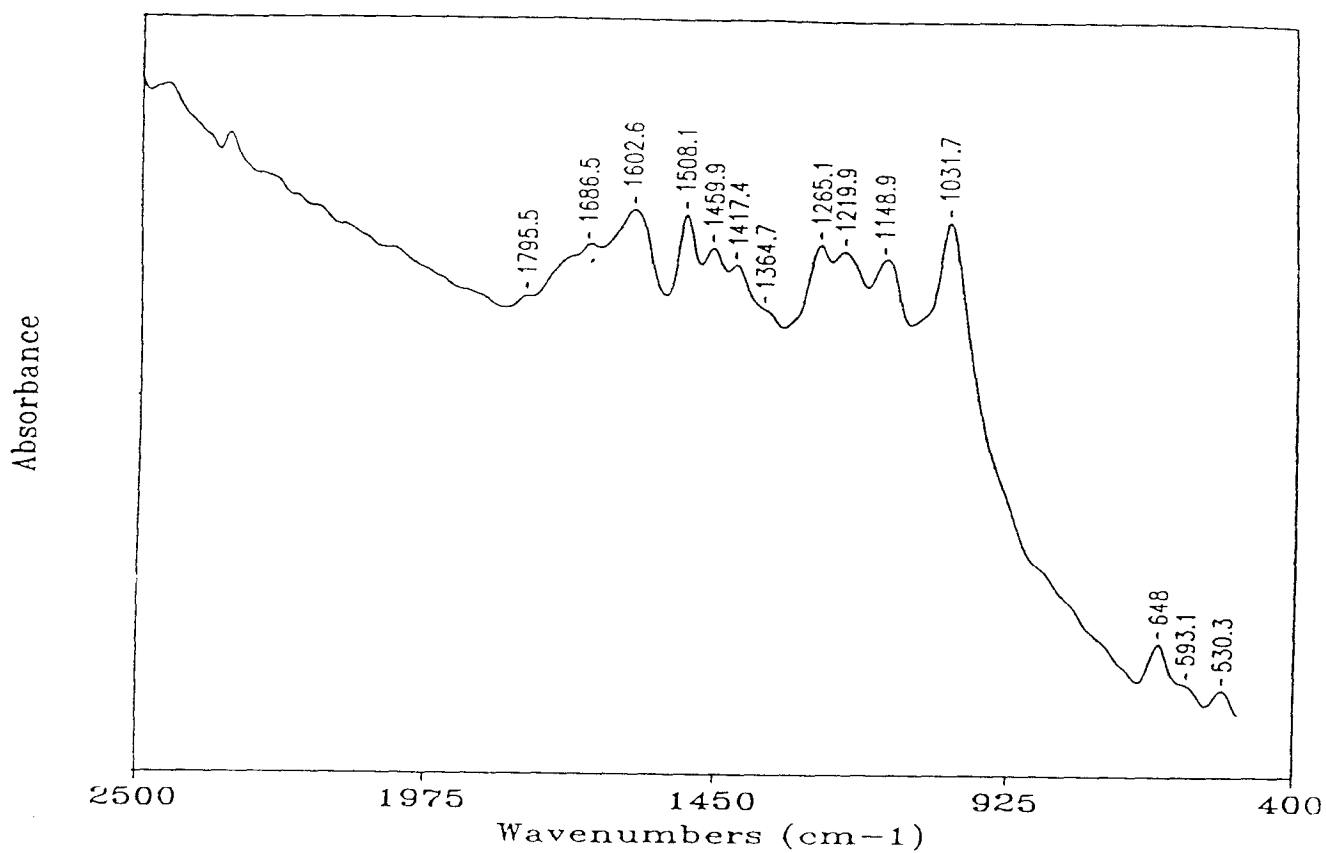


Figure 5.49: KBr pellet spectrum of leached sphalerite (in the presence of surfactant) residue; leaching performed at $140 \pm 1^\circ\text{C}$ for 15 minutes under $P_{N_2} = 1100\text{kPa}$; lignin sulfonate solution concentration: 5 g/L at flow rate = 2 mL/min.

5.3.2 Adsorption Studies in the Presence of Orthophenylene Diamine

Listed below are the different studies:

- KBr analysis of orthophenylene diamine
- ATR recording of 5 g/L surfactant solution
- ATR recording of sphalerite concentrate conditioned in surfactant solution (no ferric pre-treatment)
- ATR analysis of sphalerite concentrate washed after conditioning in surfactant
- ATR analysis of sphalerite concentrate conditioned in surfactant solution after pre-treatment with ferric ions
- ATR recording of sphalerite concentrate washed after contact with ferric/surfactant solution

KBr Pellet Absorption Spectrum of OPD

The KBr-FTIR spectrum of OPD powder is shown in Figure 5.50. The absorption bands above 3236 cm^{-1} represent the asymmetric and symmetric stretching vibrations of N-H bonds due to the -NH_2 functional group. The absorption band at $3036\text{--}3035\text{ cm}^{-1}$ represents the stretching vibrational modes of =C-H bonds of the aromatic ring. The shoulder band at $2922\text{--}2921\text{ cm}^{-1}$ is also attributed to -C-H asymmetric stretching vibrations [123, 124, 170, 171]. The characteristic (or diagnostic) bands of the molecule as a whole are found at 1632 cm^{-1} and below. The peak frequencies in the fingerprint region are assigned to the following functional groups [124, 170, 171]:

- 1632– 1589 cm^{-1} , due to the internal deformations (of -N-H bonds) of the -NH_2 functional group; stretching vibrations by the C=C bonds in the aromatic skeleton overlaps with the -NH_2 vibrations at 1590–1589 cm^{-1}
- 1497 – 1461 cm^{-1} , the result of stretching vibrations of the aromatic ring (or C=C bonds)
- 1333 – 1268 cm^{-1} are attributed to the C-N stretching vibrations
- 1152 – 1029 cm^{-1} are assigned to the C-H in-plane deformations of the ring
- the 926 – 925 cm^{-1} band is representative of the 1,2 substitution pattern on the ring
- bands between 828 – 711 cm^{-1} are assigned to either out-of-plane C-H ring deformations and/or -NH_2 out-of-plane bending vibrations i.e. there is an overlap of vibrational bands from these two functional groups in this region
- 544 – 439 cm^{-1} bands are designated to C-H out of plane deformations

The absorption bands at the wavenumbers 2780–1781 cm^{-1} are due to overtones and combinations [123, 124, 126].

Characterization of OPD solution

Figure 5.51 shows the ATR–FTIR spectrum of 5 g/L OPD in a solution containing 2 mL/L (about 0.036 mol/L) sulfuric acid. Compared to the spectrum obtained from the KBr disc, (Figure 5.50) some absorption bands observed in the solid spectrum have disappeared. Others have also shifted slightly in position. All these changes are due to surfactant–solvent interactions. However, a few bands occurred at almost the same positions in both spectra e.g. the stretching vibrational modes at 3036 – 3031 cm^{-1} . The

stretching absorption bands at $3084 - 3035 \text{ cm}^{-1}$ are designated to the $=\text{C}-\text{H}$ functional group of the aromatic ring. These bands, together with the stretching vibrations at $1593 - 1483 \text{ cm}^{-1}$ are representative of the aromatic molecular structure³⁶. The asymmetric and symmetric stretching peak frequencies at $3430 - 3247 \text{ cm}^{-1}$ are assigned to the $-\text{N}-\text{H}$ bonds (of the $-\text{NH}_2$ group) which normally go through hydrogen bonding in the aqueous phase. The absorption frequency at 1294 cm^{-1} and the shoulder band at 1194 cm^{-1} are indications of the $\text{C}-\text{N}$ bonds (or groups) while the absorption band at $885 - 827 \text{ cm}^{-1}$ may be assigned to the $-\text{NH}_2$ deformations. The $-\text{C}-\text{H}$ bonds in-plane deformations may be responsible for the vibrations at $975-974 \text{ cm}^{-1}$ [123, 124, 126, 170, 171]. The reference (or background) spectrum is that of the solvent³⁷.

Results of Adsorption tests

Figures 5.52(a) and 5.52(b) show the absorption spectra of sphalerite concentrate suspended in the 5 g/L OPD solution for 20 minutes in the absence of any ferric ions or ferric solution pre-treatment. In Figure 5.52(a), the reference/background spectrum is that of the solvent. The appropriate spectral subtraction³⁸ is shown in Figure 5.52(b). The band at $3231 - 3230 \text{ cm}^{-1}$ (Figure 5.52(b)) is a shift from $3247-46 \text{ cm}^{-1}$ (in Figure 5.51), whilst the stretching band at $3420 - 3419 \text{ cm}^{-1}$ (in Figure 5.52) occurs as a weak intensity band at $3429-3428 \text{ cm}^{-1}$ in the bulk solution spectrum. A detailed comparison of Figure 5.51 to 5.52(b) shows that there are shifts in some of the absorption frequencies, others have disappeared and there are some new developments as well. The appearance of the asymmetric stretching vibrational mode at $2928 - 2927 \text{ cm}^{-1}$ (Fig. 5.52(b)) indicates the presence of a $-\text{C}-\text{H}$ bond related compound on the solid surface. The appearance of stretching vibration absorption bands at $1601 - 1490 \text{ cm}^{-1}$, the shoulder band at 1444

³⁶The $\text{N}-\text{H}$ group also contributes to the absorption frequency at $1593-1592 \text{ cm}^{-1}$.

³⁷The solvent as often used in this text refers to distilled water containing 0.036 mol/L sulfuric acid.

³⁸The bulk solution spectrum is subtracted from that of the mineral conditioned in the solution.

cm^{-1} together with the weak absorption band near $3059\text{--}3058\text{ cm}^{-1}$ are attributed to the presence of an aromatic compound on the solid surface while the vibrational modes at $1274\text{--}1273\text{ cm}^{-1}$ represent the stretching vibrations of the C-N functional group of the compound. The -NH_2 in-plane deformations also contribute to the absorption band at $1601\text{--}1599\text{ cm}^{-1}$. The $3059\text{--}3058\text{ cm}^{-1}$ absorption band could be a shift from $3036\text{--}3035\text{ cm}^{-1}$ in the bulk solution spectrum due to perturbations upon solid – surfactant interactions.

Figure 5.53 shows the ATR – FTIR spectral record of the natural sphalerite conditioned in OPD solution (without ferric ions), cold-washed several times with the solvent, followed by further washing in boiling water for 20–25 minutes and then cold-washed again. The background spectrum is that of the solvent, implying that any absorption due to the solvent content of the sample paste is cancelled out by the background (or reference) spectrum.

The absorption bands at $1388\text{--}1386\text{ cm}^{-1}$ indicate the presence of -C-H bonds. The presence of the skeletal aromatic ring i.e. C=C bonding, on the solid surface even after the drastic washing process is indicated by the series of stretching vibrational modes at $1568\text{--}1566$ (a weak shoulder), $1539\text{--}1538$, and $1457\text{--}1456\text{ cm}^{-1}$ and the weak stretching vibrations near $3030\text{--}3029\text{ cm}^{-1}$ which is designated to the =C-H groups of the molecular structure. The skeletal ring vibrations at $1568\text{--}1456\text{ cm}^{-1}$ are absent in Figure 5.52(b) but surfaced after the washing.

The -NH_2 group deformation vibrational bands at $835\text{--}754\text{ cm}^{-1}$ in the pre-wash spectrum disappeared after the washing process, with the appearance of new ones at $870\text{--}869$, $816\text{--}815$ and 731 cm^{-1} .

The development of the stretching shoulder band at $1300\text{ -- }1299\text{ cm}^{-1}$ represents the formation of a C-N surface product. These observations point to the fact that the adsorbed layer is firmly held onto the solid surface such that even the boiling water could

not remove the species.

In the higher frequency range, the -N-H (of -NH_2) stretching vibrations occur in the same frequency range (within the limits of instrumental sensitivity) in Figures 5.50, 5.52, and 5.53, further suggesting the presence of an -NH_2 related compound on the solid surface. The same can be said for the band at 3238 cm^{-1} .

Figures 5.54(a) and (b) show the absorption spectra of ZnS concentrate conditioned in 0.025 mol/L ferric solution (containing 0.036 mol/L sulfuric acid) for 15 minutes prior to contact with the 5 g/L OPD solution. The surfactant solution conditioning time was 20 minutes. The conditioning was done at room temperature. The sample was cold-washed 3 times with the solvent in between the conditioning solutions. The spectral record of the washed concentrate after the surfactant conditioning period is shown in Figure 5.55.

With the exception of the vibrations near $1098\text{--}1095\text{ cm}^{-1}$, the rest of the absorption band positions (in the fingerprint regions) in Figures 5.54(a) and (b) are different from those of the bulk solution spectra, Figure 5.51. Between Figures 5.54 and 5.55, there are some new developments in the after-wash spectrum.

Discussion

No ferric ion pre-treatment

Figure 5.52(a) displays absorption bands at wavenumbers $3268\text{--}3267$, $3189\text{--}3188$, and $1503\text{--}1502\text{ cm}^{-1}$ which are absent from Figure 5.52(b). On the other hand, Figure 5.52(b) shows vibrations at such frequencies as $1491\text{--}1490$, and $1444\text{--}1443\text{ cm}^{-1}$ (in the fingerprint region) which are also absent from Figure 5.52(a). Between Figures 5.51 and 5.52, it can be observed that most of the absorption bands in the bulk solution spectrum shift to higher wavenumbers on surfactant adsorption e.g. 975 shifts to $996\text{--}991\text{ cm}^{-1}$, 1593 cm^{-1} shifts to $1601\text{--}1600\text{ cm}^{-1}$, 1483 cm^{-1} shifts to $1502\text{--}1491\text{ cm}^{-1}$, 1442 cm^{-1} shift

to 1445 cm^{-1} , 3036 cm^{-1} increases to $3060\text{--}3059\text{ cm}^{-1}$, and 3084 cm^{-1} shifts to $3096\text{--}3095$ (not shown on plot) cm^{-1} . These shifts in absorption frequencies to higher wavenumbers suggest the formation of strong chemical bonds between surfactant molecules and the mineral and hence chemically adsorbed species on the mineral surface.

The disappearance of the absorption bands at wavenumbers 1294 and 1194 cm^{-1} (in the bulk solution spectrum, Figure 5.51) due to C–N vibrations and the development of a new peak frequency at $1275\text{--}1273\text{ cm}^{-1}$ (on adsorbate adsorption) further support the chemisorption concept. This development indicates that the C–N group is involved in chemical interactions with the mineral. This is most likely due to the overlapping of the nitrogen lone pair of electron with the metal ion orbitals in the sulfide lattice. Figure 5.56 shows the possible molecular structure of the amine related complex that can be formed between the metal sulfide lattice and the surfactant molecule.

The appearance of an absorption band at $3364\text{--}3363\text{ cm}^{-1}$ (due to N–H asymmetric and symmetric stretching vibrations) further confirms the presence of the surfactant molecule on the mineral since this band is one of the prominent vibrations in the solid OPD spectrum (at $3368\text{--}3367\text{ cm}^{-1}$ in the KBr spectral record, Figure 5.50). The decrease in absorption frequency is expected (or normal) since a C–N group involved in a chemical interactions with a metal ion will tend to stretch the N–H bond and hence lower the wavenumber or frequency of vibration. Further evidence in support of this is obtained by making reference to the vibrational bands at $3429\text{--}3428$ and $3246\text{--}3245\text{ cm}^{-1}$ (Figure 5.51) and $3419\text{--}3416$ and $3240\text{--}3230\text{ cm}^{-1}$ (Figure 5.52). These bands are all due to the –N–H stretching vibrations. This development can be given a mathematical interpretation as well. Consider the equation [121, 122, 123]:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu_m}} \quad (5.75)$$

or

$$\frac{1}{\lambda} = \frac{1}{2\pi c} \sqrt{\frac{\kappa}{\mu_m}} = \vartheta \quad (5.76)$$

κ = force constant or bond strength

μ_m = reduced mass of atoms

ϑ = wavenumber

ν = frequency of vibration

and

$$\frac{1}{\mu_m} = \frac{1}{m_1} + \frac{1}{m_2} \quad (5.77)$$

m_1 and m_2 are the masses of the two atoms involved in the particular bonding in the molecule. As mentioned earlier, a strong chemical bonding between the nitrogen and metal ions, Figure 5.56, results in the increase in the –N–H bond length and a lower κ value for that bond. This will cause a decrease in the the frequency of vibration for that bond.

The C–N bond is also stretched or lengthened on bonding resulting in a low κ value for the C–N bonding leading to a lower ν value after the contact period. This explains the shift in frequency from 1294 cm^{-1} (in the bulk solution spectrum) to 1275–1273 cm^{-1} on adsorption.

Ideally, Zn^{2+} (or other metal) ions will be more reactive than hydrogen towards the nitrogen (with a lone pair of electrons). The formation of hydrogen bonding between the –N–H groups and the aqueous phase (i.e. water molecules) can also contribute to the lowering of the absorption band frequencies.

The appearance of the 3144–3143 cm^{-1} (Figure 5.52) absorption band may be attributed to the formation of a new amine related chemisorbed species.

The shift in the =C–H group wavenumbers from 3036 and 3084 (in Figures 5.50 and 5.51) to 3060–58 and 3096–3095 cm^{-1} (not shown on plot) respectively (in Figures

5.52 (a) and (b)) can also be explained on the basis of chemical interaction concepts. The weakening and hence the lengthening of the C-N bond results in this functional group having less influence on the adjacent =C-H group and hence results in higher C-H vibrations. Mathematically, the factor κ for the C-H bond increases leading to higher vibrational frequencies.

In the fingerprint region (Figures 5.52(a) and (b)), the absorption bands at 1667–1275 and 996–740 cm^{-1} are all new developments. In figure 5.51, the bands at 885–827 cm^{-1} were assigned to the bending vibrations of the $-\text{NH}_2$ group. These bands have disappeared with the formation of new ones at lower frequencies, 835 and 795 cm^{-1} , which is in agreement with the mathematical expression above and the chemisorption concept. These observations indicate that whatever surface layer or product is formed on the pre-wash mineral surface is a chemically adsorbed species and has molecular vibrational characteristics quite different from the bulk surfactant solution or material.

On washing the mineral, a whole new set of absorption bands is revealed, especially in the diagnostic region of the spectrum, (Figure 5.53). This suggests that two or more different layers of surface chemical species are formed, and that the top layer(s) is not as firmly held to the adsorbent surface as the bottom layer(s). The differences in the absorption band positions, particularly in the diagnostic region, indicate that the bottom layer may have a different molecular arrangement and/or vibrations from the top layer though both are chemisorbed species. The presence of stretching vibrational modes at 1540–1384 cm^{-1} (in the diagnostic region and assignable to molecular vibrations) and the weak shoulders near 3030 and 3095 cm^{-1} (assignable to =C-H bonds) are fingerprints of the adsorbate aromatic skeleton on the adsorbent surface. This is further supported by the presence of the stretching $-\text{N}-\text{H}$ bond vibrations at 3367 and 3238 cm^{-1} in the upper frequency region. The drastic shifts in absorption bands due to the aromatic structure to 1539, 1457, and 1385 cm^{-1} after the washing process also supports the chemisorption

mechanism.

There is the development of a new vibrational mode (weak shoulder) at 1300–1299 cm^{-1} which is different from the C–N vibrations at 1333 and 1270 cm^{-1} (Figure 5.50), 1294 cm^{-1} (Figure 5.51) and 1275–1274 cm^{-1} (Figures 5.52 (a) and (b)) and may be assigned to one of the characteristic molecular vibrations of the new surface product. This development further confirms the involvement of the C–N group in chemical interactions.

The appearance of new vibrational bands at 1149–1000 cm^{-1} is attributed to the perturbation of the C–H in-plane deformations as a result of the adsorption process.

The new absorption bands in the lower wavenumber region reinforce the proposed chemisorption route. Thus, in the absence of ferric ion conditioning, the OPD (surfactant) molecules are chemisorbed, resulting in the formation of two or more layers of chemisorbed species on the adsorbent with the top layer(s) being relatively loosely held on the surface compared to the lower layer(s).

Ferric ion pre-treatment

The spectral record shown in Figure 5.54(a) has the solvent as the background spectrum while that in Figure 5.54(b) is the spectral difference between the adsorbent-adsorbate (with prior conditioning of the concentrate in ferric solution) and bulk surfactant solution spectra. The two are very similar in shape and absorption band positions. However, there are a few differences e.g. the bands at 855 and 741 cm^{-1} (in Figure 5.54(a)). The absorption bands at 999–995, 1097–1095 and 3419–3363 cm^{-1} are present in all four spectra³⁹. However most of the absorption bands are different from those shown in Figure 5.52.

In the fingerprint region, the absorption frequencies are quite different compared to the same region in the bulk solution spectrum (Figure 5.51). This suggests that the

³⁹In comparison with those obtained in the absence of ferric conditioning.

region $1644\text{--}741\text{ cm}^{-1}$ (Figures 5.54(a) and (b)) represent chemically adsorbed species.

The disappearance of the absorption band at 1294 cm^{-1} and the shoulder at 1194 cm^{-1} (present in Figure 5.51) or $1333\text{--}1268\text{ cm}^{-1}$ (in Figure 5.50) assigned to the C–N functional group from Figures 5.54 (a) and (b) supports the existence of chemically adsorbed species on the adsorbent surface.

The vibrations occurring at $1643\text{--}1420\text{ cm}^{-1}$ are fingerprints from the aromatic skeleton of whatever surface product is formed. The --NH_2 group also has a strong absorption at $1643\text{--}1639\text{ cm}^{-1}$.

Figure 5.55 shows the absorption spectrum of the sample washed after the conditioning process. Between Figures 5.51 and 5.55, there are upward shifts in some of the absorption bands in the fingerprint region. These upward shifts in frequency positions further support the process of chemisorption.

Just as there is reappearance of some of the absorption bands (present in Fig. 5.54), e.g. $1644\text{--}1640\text{ cm}^{-1}$, others have disappeared with the emergence of new ones. This development of new vibrational modes suggests the formation of two (or more) layers of chemically adsorbed species with different vibrational characteristics (just like the previous condition) and that the top layer(s) is relatively loosely held to the mineral surface. The lower layer is, however, strongly bonded to the mineral surface such that even the drastic washing procedures adopted could not dislodge it from the adsorbent.

The band at $1775\text{--}1773\text{ cm}^{-1}$ may be due to overtones and/or combinations. The absorption band at 1641 cm^{-1} (Fig. 5.55) may be a contribution from the bending vibrations of --NH_2 (or --N--H) and co-adsorbed water molecules. The peak frequencies at $1641\text{--}1394\text{ cm}^{-1}$ are assigned to vibrational characteristics of the aromatic structural component of whatever surface product is being held on the surface after the washing process, though the characteristic aromatic absorption wavenumber positions are different from those of the KBr wafer and the bulk solution spectra.

The appearance of weak shoulders near 3040 and 3008 cm^{-1} coupled with the bands at 1641–1240 cm^{-1} confirms the presence of the adsorbate(aromatic)–related species on the washed mineral surface.

The disappearance of the stretching C–N vibrations (1294 in Figure 5.51 or 1333 and 1269 cm^{-1} Figure 5.50) and the appearance of new bands at the wavenumbers 1294 and 1240 cm^{-1} further confirm the involvement of this functional group in chemical interactions, most probably with the nitrogen trying to share its free electron pair with the metal ions of the sulfide lattice. In acidic media (e.g. under the zinc pressure leaching conditions), metal sulphides carry positive surface charges and the surfactant molecule will act as a base. The basic character of the amine group implies that it is willing to share the valence electrons with any electrophile, thus, it either picks up protons in solution and becomes protonated or interacts with the metal ions in the crystal lattice. With zinc ions being more reactive than hydrogen ions, the surfactant will be more willing to share its free electrons with the zinc than the hydrogen ions.

The disappearance of the band at 1098–1096 is due to the removal of soluble surface oxidation products from the sample material during the washing process.

A comparison between Figures 5.53 and 5.55 shows that the two have a lot of characteristic absorption bands in common (within the limits of instrument sensitivity) such as the bands at 1541–1538, 1300–1295, 1074–1073, and 998–994 cm^{-1} in the diagnostic region. This display of agreement in the fingerprint region indicates that whatever adsorbed species is formed on the adsorbent surface is common to both conditioning methods inspite of the differences in the upper frequency regions of the spectra. On the other hand, it may be speculated that this agreement is probably due to the chemical composition of the concentrate. The concentrate contains about 11 % iron mostly in the form of pyrite and probably this minor amount of iron in the sulfide matrix is just enough to affect any surface characteristics and hence the adsorption mechanism such that the

presence of externally introduced ions on the surface is not reflected⁴⁰.

Summary

The mechanism of adsorption of the surfactant orthophenylene diamine onto zinc sulfide mineral (i.e. sphalerite) is through chemical interactions of the adsorbate with the adsorbent and this is independent of the pre-adsorption surface characteristics of the concentrate. The study indicates the formation of two (or more) different layers of chemisorbed species with the upper layer being vulnerable to removal by washing whilst the lower component is firmly bonded to the adsorbent surface. The absorption spectra strongly indicate that the OPD molecule interacts with the mineral through the C-N functional group where the nitrogen free-electron pair overlaps with the metal ions of the sulfide mineral lattice leading to the formation of an amine-related surface species. At the same time, the hydrogen atoms of the -NH₂ functional group interact with the aqueous phase by forming hydrogen bonds, thus ensuring that the solid surface is continuously hydrophilic. This process tends to render the solid surface more hydrophilic than sulphophilic and causes an increase in the contact angle of the three-phase system [55].

⁴⁰This is only a speculation.

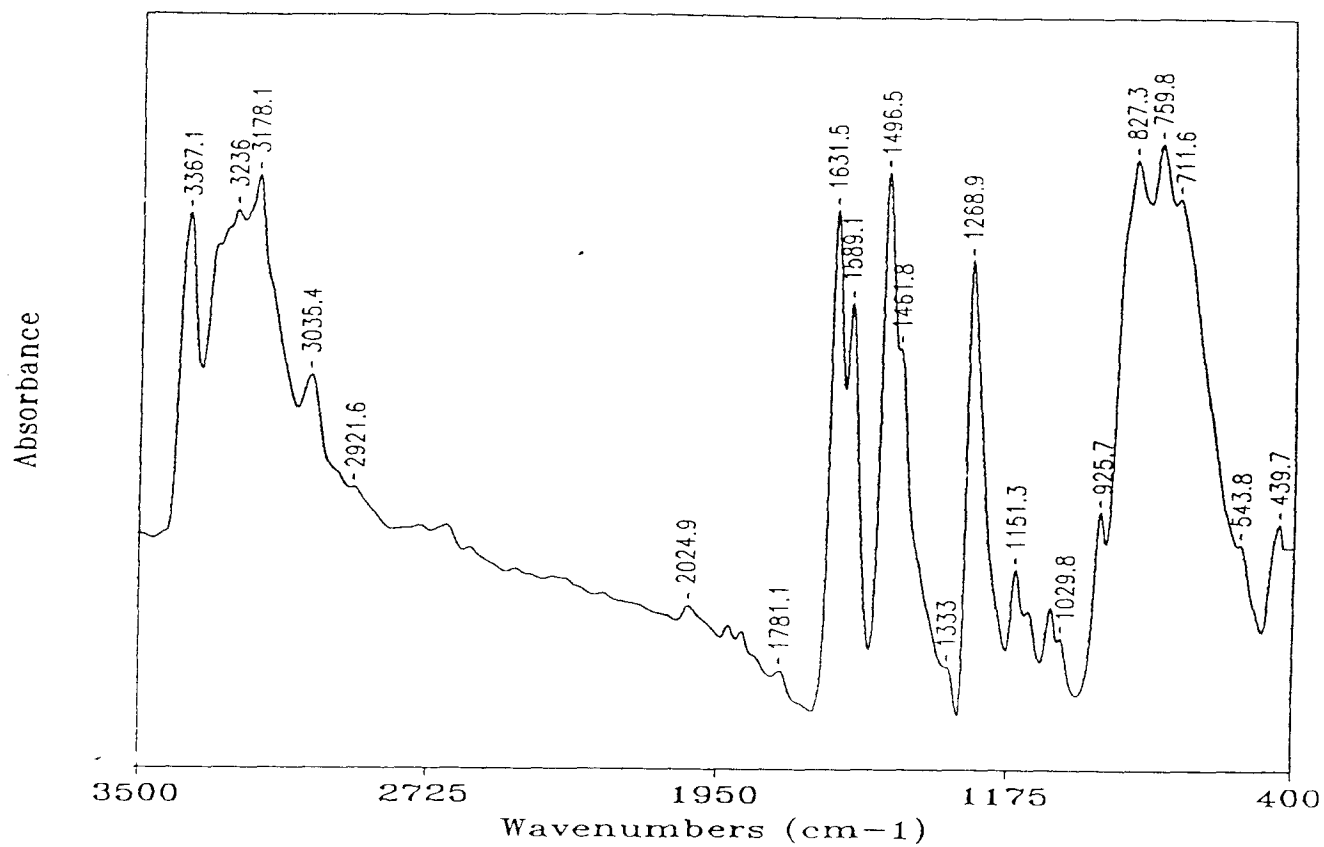


Figure 5.50: KBr pellet spectrum of OPD.

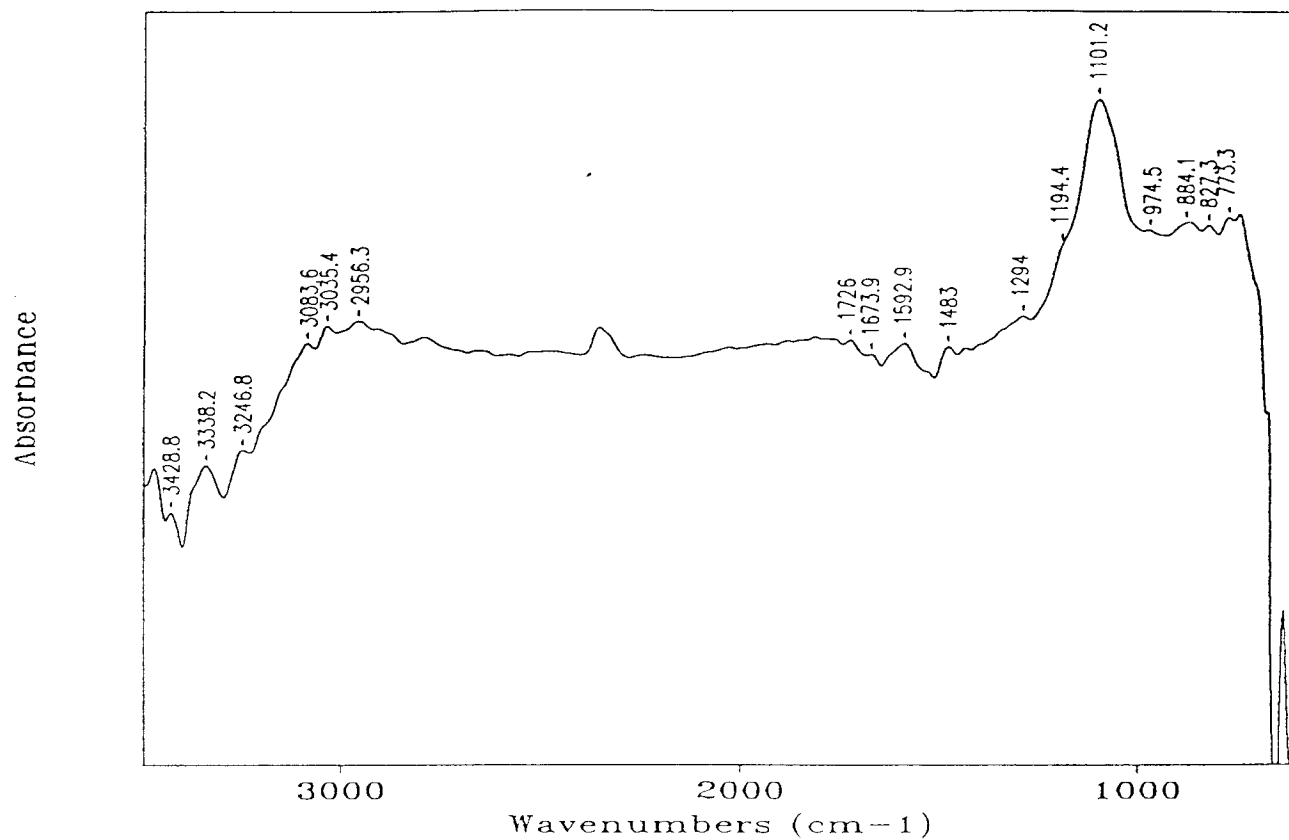
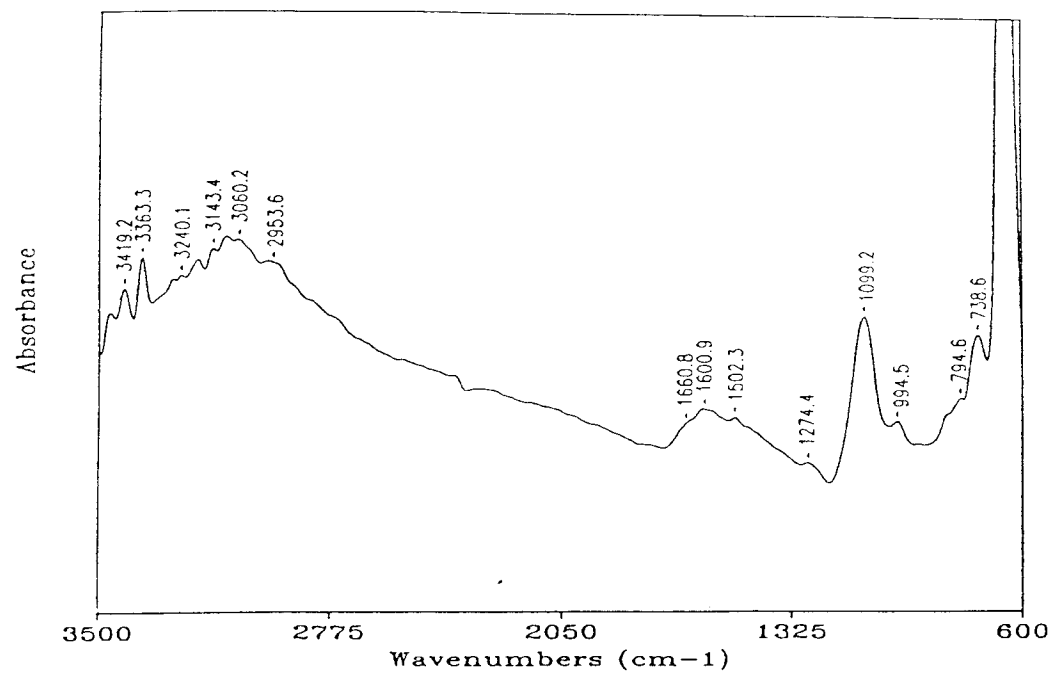
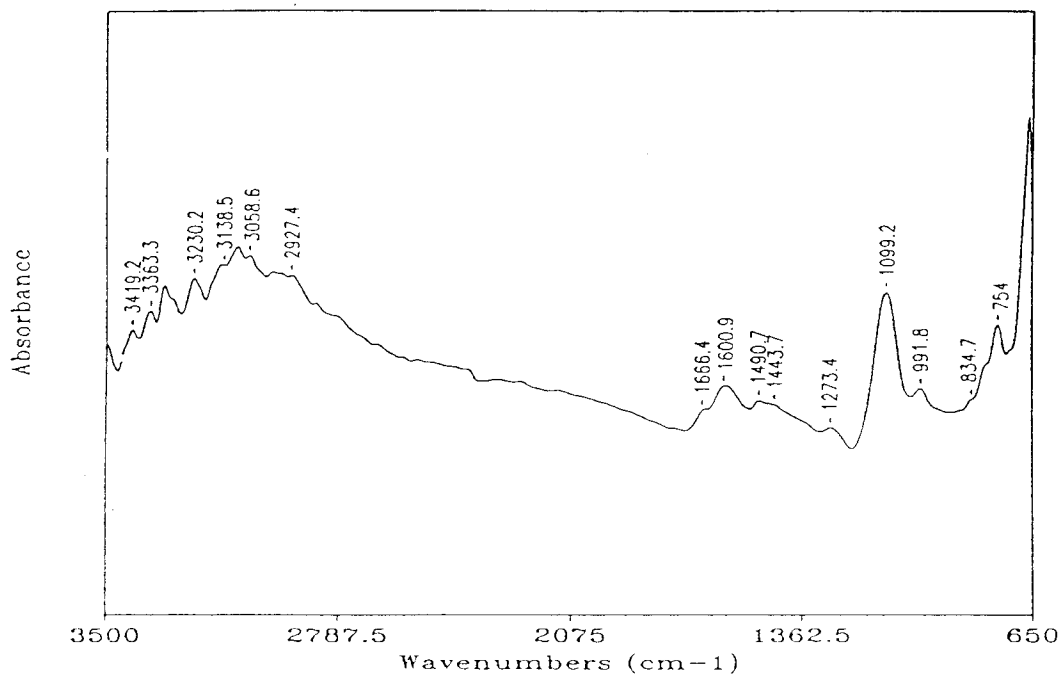


Figure 5.51: ATR spectrum of 5 g/L solution of OPD; solution condition: $[\text{H}_2\text{SO}_4] = 0.036 \text{ M}$, Temperature = 25°C ; reference spectrum: solvent.



(a)



(b)

Figure 5.52: ATR spectrum of sphalerite conditioned in OPD solution (no ferric pre-treatment) for 20 minutes; solution condition: $[\text{H}_2\text{SO}_4] = 0.036 \text{ M}$, Temp. = 25 °C. (a) reference spectrum: solvent (b) less solution spectrum.

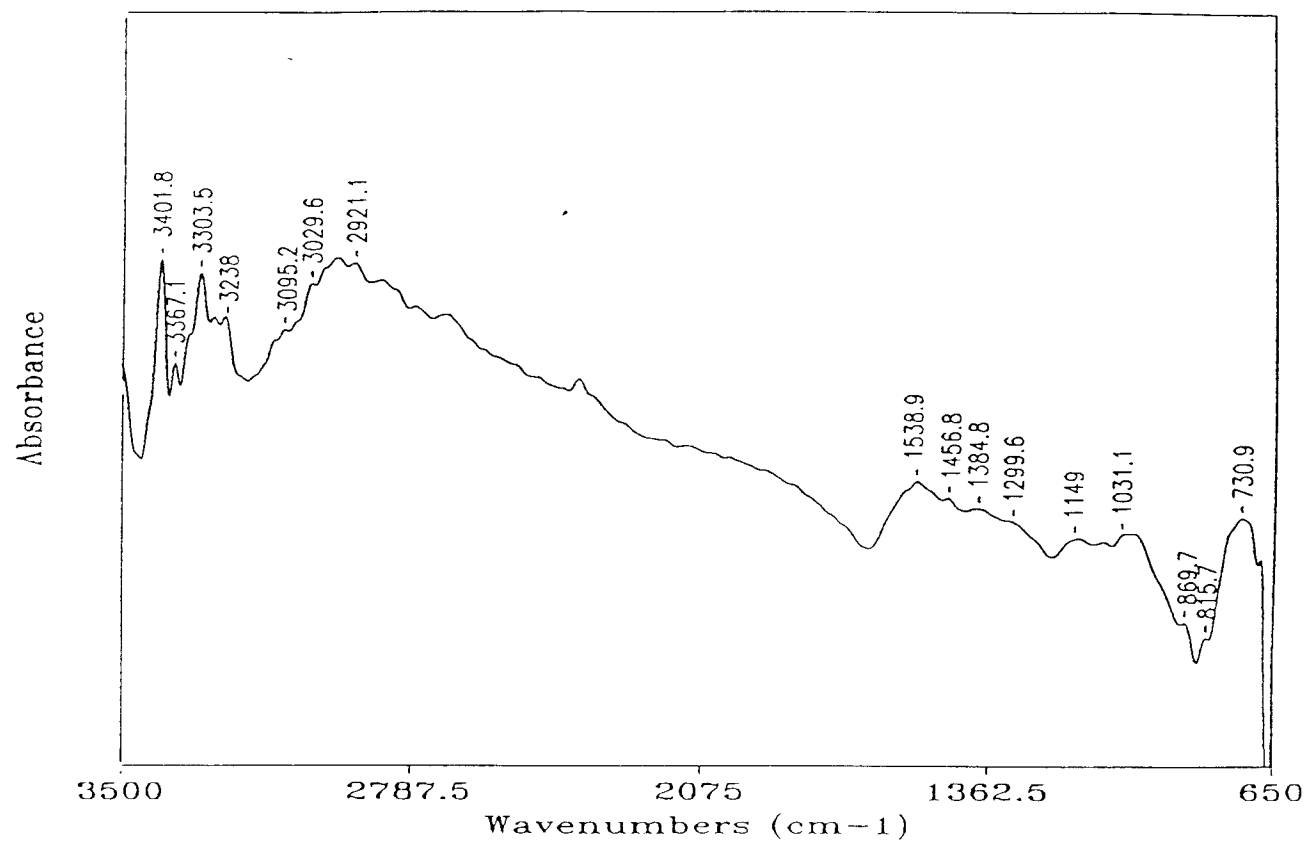
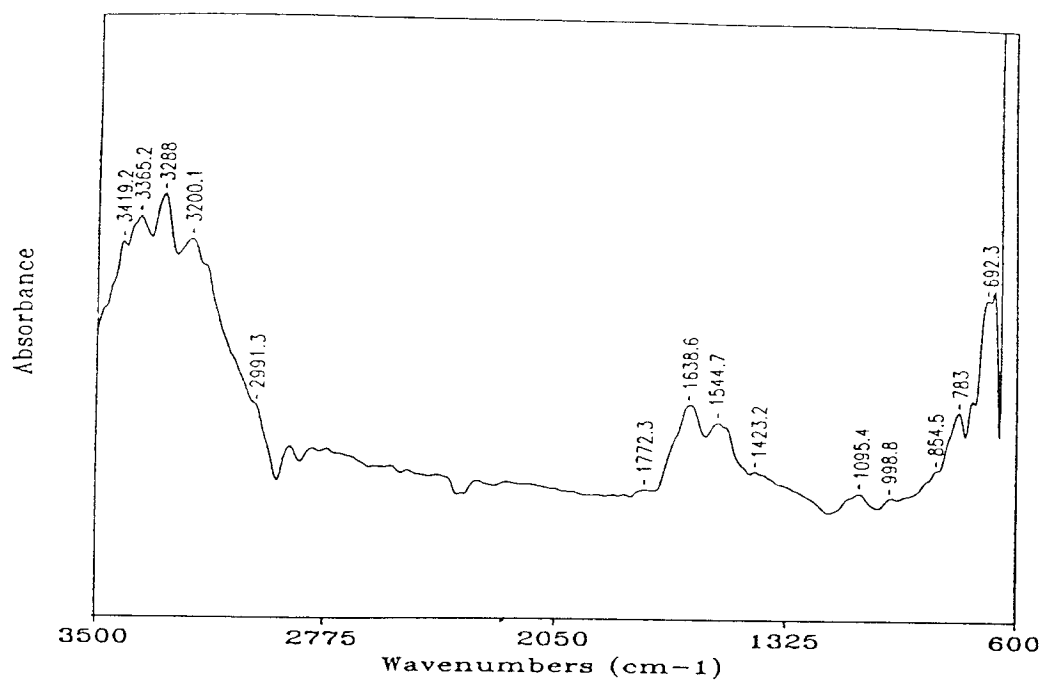
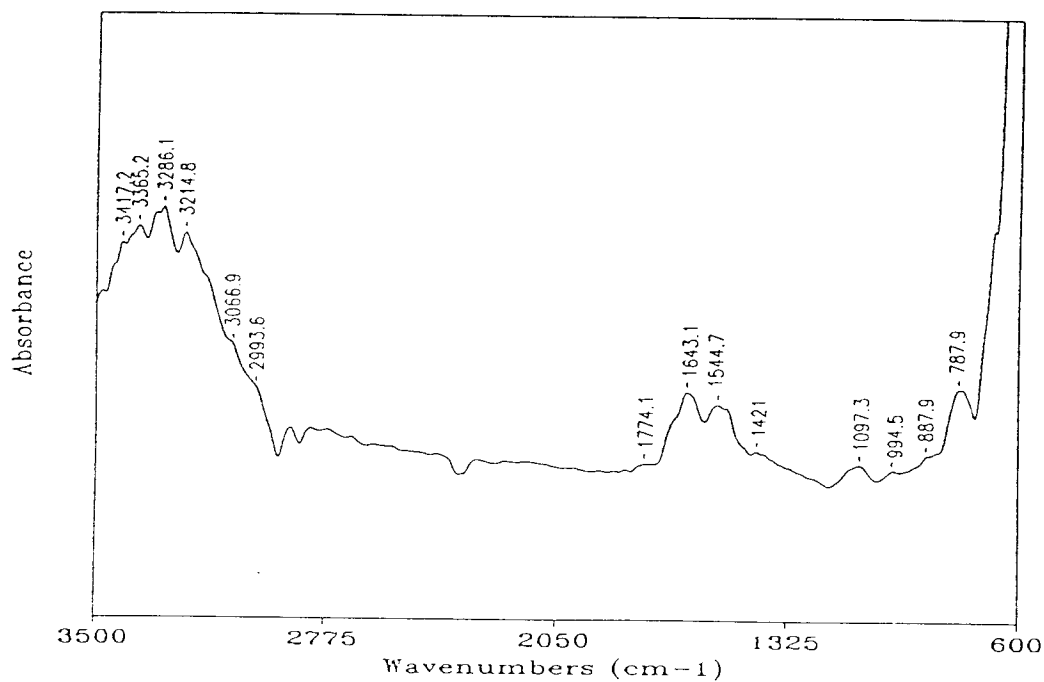


Figure 5.53: ATR spectrum of sphalerite washed after conditioning in 5 g/L OPD solution for 20 minutes, reference spectrum: solvent.



(a)



(b)

Figure 5.54: ATR spectrum of sphalerite conditioned in 5 g/L OPD solution (after ferric pre-treatment) for 20 minutes; solution condition: $[\text{H}_2\text{SO}_4] = 0.036 \text{ M}$, Temp. = 25°C (a) Reference spectrum: solvent (b) less the solution spectrum.

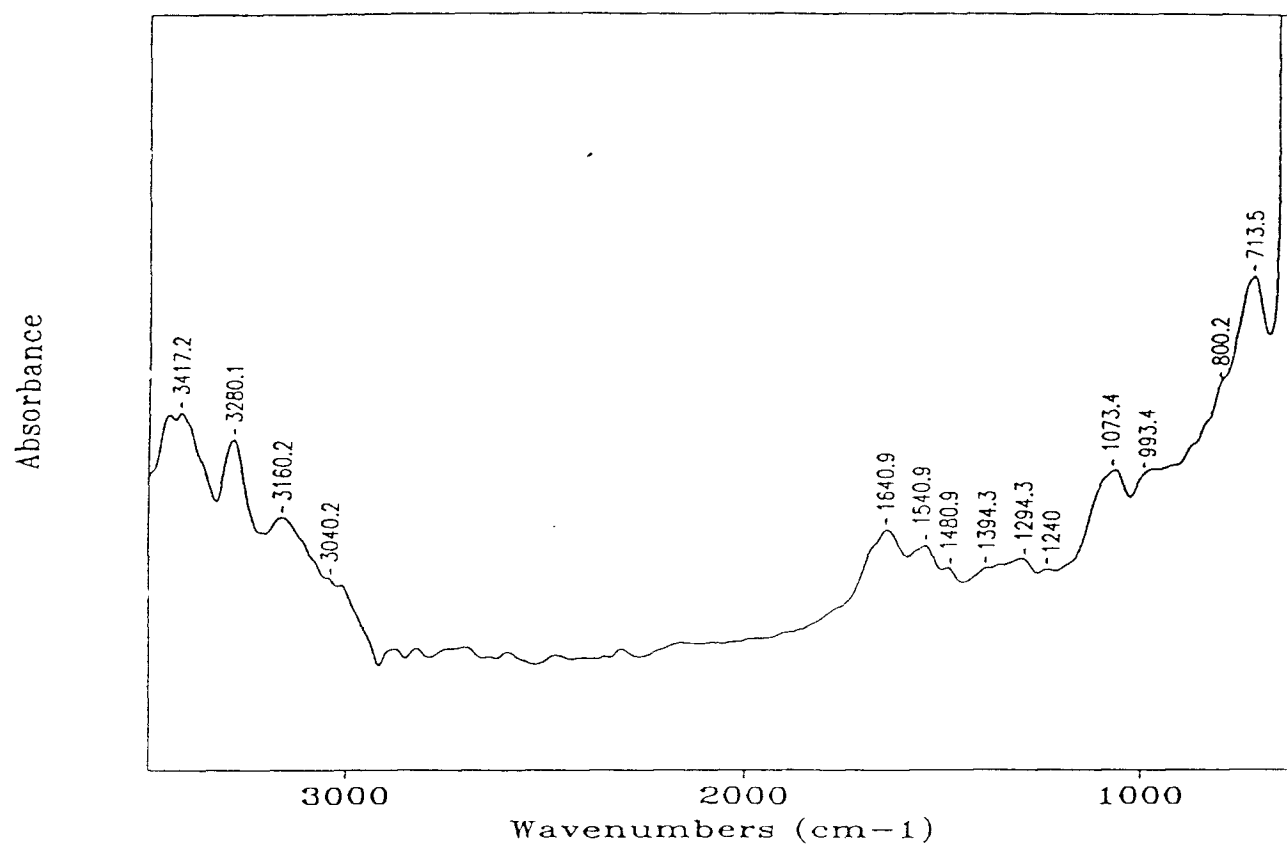


Figure 5.55: ATR spectrum of washed sphalerite after contact with ferric/OPD solution, reference spectrum: solvent.

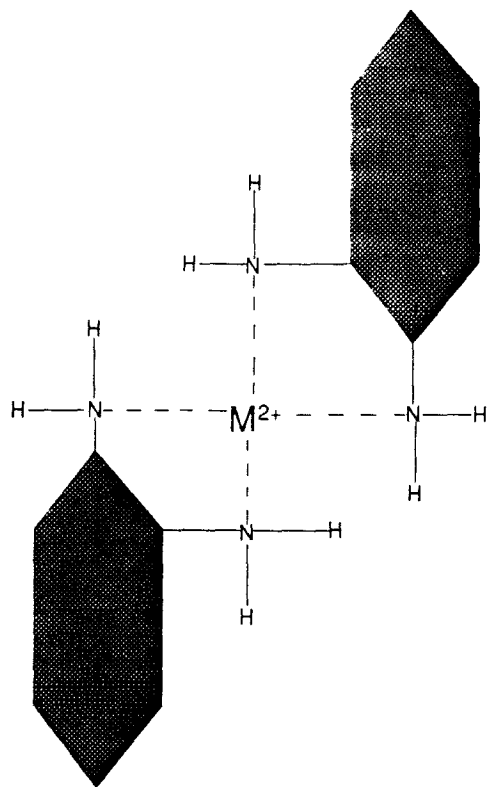


Figure 5.56: Metal-OPD complex on interaction.

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The studies conducted have measured the interfacial activity of various surface active agents and how these interfacial characteristics are related to the usefulness of these reagents as dispersants for liquid sulphur in the oxidative pressure leaching of sphalerite. The fact that a surfactant can be very efficient in terms of interfacial tension reductions and contact angle increases is no guarantee that the surfactant can be efficient in the leaching process. Besides the interfacial properties exhibited by the different surface active agents other variables such as reagent stability come into play if a surfactant is to be effective under the zinc pressure leaching conditions. The following are the conclusions from the present studies:

- In terms of interfacial tension reductions, OPD was the least effective. It effected virtually no change in the liquid sulphur–aqueous phase interfacial tension but acted to increase the sulphur–mineral contact angle. This implies the surfactant is not adsorbed at the liquid sulphur–aqueous interface but adsorbed at the liquid–mineral interface. All other surfactants adsorbed at both interfaces, naphthalene sulphonic acid–formaldehyde condensates being the most reactive reagent at the interfaces. It effected the highest change in the interfacial tension and the contact angle at a concentration of about 0.1 g/L. CAHSB exhibited about the same effect as lignin

sulphonic acid up to about 0.3 g/L. However, unlike the behaviour of lignin sulphonic acid, the interfacial tension decreased further when CAHSB concentration was increased to about 0.5 g/L beyond which the interface was insensitive to any further increase in surfactant concentration. TAHSB and CAB effected an interfacial tension decrease to a lesser extent than the other reagents with the exception of OPD.

- Just like the interfacial tension effects, lignin sulphonic acid, naphthalene sulphonic acid-formaldehyde condensates, and CAHSB effected the most contact angle increase from 80 to 145–155°; OPD effected an increase to 125–135°.
- Without adsorption at the mineral-liquid interface, γ_{MA} and γ_{MS} will not be affected by the presence of any surfactant and hence $\gamma_{SA} \cos \theta$ (or $\gamma_{MA} - \gamma_{MS}$) should remain constant; however, $\gamma_{SA} \cos \theta$ varies with surfactant addition. From Table 5.9, γ_{MS} far exceeds the value of γ_{MA} (compared to that obtained in the absence of any surfactant), since a surfactant can only act (or accumulate) at an interface to lower the interfacial free energy, and not raise it. Thus γ_{MS} cannot be raised in the presence of the surfactants. Hence the surfactants act to lower γ_{MA} and the result is an increase in the contact angle. The effect of lowering γ_{MA} and γ_{SA} (except for OPD), and hence increasing the contact angle, increases the tendency for liquid sulphur to detach (or roll) from the mineral surface, making the mineral accessible to the aqueous phase.
- Under leaching conditions, the effectiveness of the surfactants (used as dispersants for liquid sulphur) does not necessarily exhibit the same behavioural pattern as their interfacial activities. Thus, naphthalene sulphonic acid-formaldehyde condensates, CAHSB, CAB, and TAHSB were poor dispersants even under low pulp density conditions. On the other hand, OPD was a very good dispersant for liquid sulphur.

the results being comparable to those obtained with lignin sulphonic acid under both low and high pulp density leaching conditions. This indicates that the most important criterion for a surfactant to be effective under leaching conditions is for the surfactant to be able to increase the liquid sulphur–mineral contact angle (by being adsorbed on the mineral–liquid interface). The angle does not necessarily need to be very high provided a certain *critical angle* (greater than 90°) is exceeded.

- The presence of oxidizing ionic species such as ferric ions can have an adverse effect on how the surfactants function. Such species can enhance the kinetics of degradation of the surfactants e.g. the effect of ferric/ferrous ions on the interfacial activity of naphthalene sulphonic acid–formaldehyde condensates and the low % zinc extraction (even under low pulp density leaching conditions) in the presence of CAB, CAHSB, TAHSB and naphthalene sulphonic acid–formaldehyde condensates.
- The adsorption of lignin sulphonic acid proceeds through both physical and chemical mechanisms. The surfactant interacts with the mineral through the hydrophilic groups and acts as a bridge between the mineral and the aqueous phase. The interaction results in the formation of a bulk-like Zn(II)–surfactant complex having an organic portion similar to the bulk surfactant structure.
- OPD is adsorbed onto the solid mineral adsorbent through chemical interaction and this adsorption is independent of the pre-adsorption surface characteristics of the mineral. The infrared spectra suggest the formation of amine–related surface species through the C–N functional group of the surfactant. The nitrogen free electron pair possibly overlaps with the metal ions of the sulphide lattice, with the hydrogen atoms of the –NH_2 group interacting with the aqueous phase through hydrogen bonding, rendering the mineral surface hydrophilic. MPD possibly interacts through a similar mechanism.

- It is believed that the formation of pockets of metal–surfactant species/complexes on the mineral surface is probably enough to make the mineral particle sufficiently hydrophilic.

6.2 RECOMMENDATIONS

These studies have shown that OPD (and MPD) can be potential surfactants (or dispersants) for the zinc pressure leach process. This finding could lead to the commercial application of OPD for zinc pressure leaching. However, more investigations need to be carried out on the use of such surfactants. The impact of residual OPD and MPD on the subsequent purification and electrowinning stages of zinc recovery are two areas of concern that need to be addressed before any full scale commercial application is initiated. The environmental effects of these reagents are also very important and require extensive investigations. It is believed that lignin sulphonic acid degrades before the zinc sulphate leach solution reaches the tank house, thus, not interfering with the process. The current study should be expanded to include other surfactants not mentioned in this study.

This thesis was designed to address the role of surfactants in the liquid sulphur–aqueous zinc sulphate interfacial system. The effect of interactions between the surfactants and precipitated solids such as jarosite, lead sulphate, silica, etc. on the coalescence (or dispersion) of liquid sulphur was not studied (or considered) and hence nothing can be said about the role of such precipitated solid materials on the coalescence of sulphur in the presence of the surfactants under leaching conditions, e.g. though OPD was ineffective on the liquid sulphur–aqueous solution interface, it produced sulphur particles of very fine sizes while lignin sulphonic acid which effected a reduction in the interfacial tension (i.e. sulphur dispersion) gave rise unexpectedly to coarse size sulphur particles

in the leaching. Thus a thorough study needs to be conducted on the effect of precipitated solids (on interaction with surfactants) on the coalescence (or dispersion) of liquid sulphur droplets.

The pressure leaching of copper sulphide and pyrrhotite minerals above the melting point of sulphur also experiences the sulphur occlusion problem which tends to reduce the extent of metal extraction. This has prevented the development of a high temperature process (above the melting point of elemental sulphur) for copper recovery from concentrates. It is strongly recommended that future research be directed towards identifying surfactants that disperse liquid sulphur from the surface of industrially important copper minerals. Surface tension and contact angle measurements, leaching studies and ATR-FTIR investigations will be required to develop a complete picture for the copper system.

Bibliography

- [1] M.E. Wadsworth *Heterogeneous Rate Processes in the Leaching of Base Metal Sulphides*, in *Hydrometallurgical Process Fundamentals*, ed. R.G. Bautista, Plenum Press, N.Y. 1982, pp.41-76.
- [2] R.T. Shuey *Semi-Conducting Ore Minerals*, Elsevier Scientific Publishing Co., N.Y. 1975, pp.4-5, 319-320.
- [3] J. Li, Ting-Ke Zhong and M.E. Wadsworth, *Application of Mixed Potential Theory in Hydrometallurgy*, in *Hydrometallurgy, Theory and Practice*, Proceedings of Ernest Peters Int. Symposium, Vancouver, B.C, June 14-18, 1992, eds. W.C. Cooper and D.B. Dreisinger, 29 (1992), pp.47-60.
- [4] K. Osseo-Asare, *Semiconductor Electrochemistry and Hydrometallurgical Processes*, in *Hydrometallurgy, Theory and Practice*, Proceedings of Ernest Peters Int. Symposium, Vancouver, B.C, June 14-18, 1992 eds. W.C. Cooper and D.B. Dreisinger, 29 (1992), pp.61-90.
- [5] L.K. Bailey, *Oxygen Pressure Leaching of Pyrite in Sulfuric Acid*, M.A.Sc. Thesis, UBC., Vancouver, Dec 1974
- [6] L.K Bailey and E. Peters, *Decomposition of Pyrite in Acids by Pressure Leaching and Anodization: the case for an electrochemical Mechanism*, Canadian Metall. Quart., vol.15, 1976, pp.333-344
- [7] E. Peters, *Leaching of Sulphides*, in *Advances in Mineral Processing*, Arbiter Symposium, AIME - SME, 1986, ed. P. Somasundaran, pp.445-462.

- [8] J.E. Dutrizac, *The Leaching of Sulphide Minerals in Chloride Media*, in Hydrometallurgy, Theory and Practice, Proceedings of Ernest Peters Int. Symposium, Vancouver, B.C, June 14–18, 1992 eds. W.C. Cooper and D.B. Dreisinger, 29 (1992), pp.1-45.
- [9] E. Peters and F.M. Doyle, *Leaching and Decomposition of Sulphide Minerals*, in Challenges in Mineral Processing, Proceedings of AIME - SME Symposium Berkeley, California, Dec. 1988, eds. K.V.S. Sastry and M.C. Fuerstenau, pp.509-526.
- [10] E. Peters and H. Majima, *Electrochemical Reactions of Pyrite in Acid Perchlorate Solutions*, Canadian Metall. Quart., vol.7, 1968 pp. 111-117.
- [11] E. Peters, *Electrochemistry of Sulphide Minerals: Trends in Electrochemistry*, eds. J.O'M. Bockris, D.A.J. Rand and B.J. Welch, Plenum Publishing Corp., N.Y. 1977, pp.267-290.
- [12] D.R. McKay and J. Halpern, *A Kinetic Study of the Oxidation of Pyrite in Aqueous Suspension*, Trans. of TMS-AIME, June 1958 pp.301-309.
- [13] J.O'M. Bockris *Modern Aspects of Electrochemistry No.2* Academic Press Inc. Publishers, N.Y. 1959.
- [14] J.O'M. Bockris, B.E. Conway, Ernest Yeager, *Comprehensive Treatise of Electrochemistry*, vol.1, Plenum Press, N.Y., 1980.
- [15] H. Majima, Y. Awakura and N. Misaki, *A Kinetic Study on Nonoxidative Dissolution of Sphalerite in Aqueous Hydrochloric Acid*, Metall. Trans B, vol.12B, Dec 1981 pp.645-649.
- [16] H. Majima, Y. Awakura, T. Hirato, and T. Tanaka, *Leaching of Chalcopyrite in*

- Ferric Chloride and Ferric Sulphate Solutions*, Canadian Metall. Quart., vol.24, 1985, pp.283-291
- [17] M.H. Mao and E. Peters *Acid Pressure Leaching of Chalcocite*, in *Hydrometallurgy-Research, Development and Plant Practice*, eds. K. Osseo-Asare and J.D. Miller, March 6–10, 1983, pp.243-260.
- [18] F.K. Crundwell, *The Influence of the Electronic Structure of Solids on the Anodic Dissolution and Leaching of Semiconducting Sulphide Minerals*, *Hydrometallurgy*, 21 (1988) pp.155-190.
- [19] B. Veerban and F.K. Crundwell, *An Electrochemical Model for the Leaching of a Sphalerite Concentrate*, *Hydrometallurgy*, 16 (1986) pp.345-359.
- [20] J.P. Lotens and E. Wesker, *The Behaviour of Sulphur in the Oxidative Leaching of Sulphidic Minerals*, *Hydrometallurgy*, vol.18, 1987, pp.39-54.
- [21] W.E. King, Jr. and J.A. Lewis, *Simultaneous Effects of Oxygen and Ferric Iron on Pyrite Oxidation in an Aqueous Slurry*, *Industrial and Eng. Chemistry - Process Design and Development*, vol.19, Oct. 1980.
- [22] H. Majima and E. Peters, in *Proceedings of IUPAC Conference*, Sydney, Australia, 1969.
- [23] M.B. Goldhaber, *Geological Survey*, Open Report, 1980, p.80.
- [24] R.E.J. Meyer, *Electroanalytical Chemistry*, *Interfacial Electrochemistry*, 101 (1979), p.59.
- [25] G.B. Brual, J.J. Byerley and G.L. Rempel, *Hydrometallurgy*, 9 (1983), pp.307–331.

- [26] J.E. Dutrizac, *Elemental Sulphur Formation during the Ferric Sulphate Leaching of Chalcopyrite*, Canadian Metall. Quart., vol.28, 1989, pp.337-344.
- [27] J.E. Dutrizac, *Elemental Sulphur Formation during the Ferric Chloride Leaching of Chalcopyrite*, Hydrometallurgy, 23 (1990), pp.153-176.
- [28] J.C. Paytner, *Journal of S. African Institute of Min. & Metall.*, 74 1974, pp.158-170.
- [29] R.T. Lowson, *Chem. Review*, 82, 1982, pp.461-499.
- [30] T. Biegler and D.A. Swift, *Anodic Behaviour of Pyrite in Acid Solutions*, Electrochim Acta, vol.24, 1979, p.415.
- [31] J.P. Corrion and T. Kikindai, *The Aqueous Oxidation of Elemental Sulphur and Different Chemical Properties of the Allotropic Forms S_λ and S_μ* , Journal of Inorganic Nuclear Chemistry, vol.43, 1981, pp.9-15.
- [32] I.G. Reilly, *Ammoniacal Leaching of Copper Sulphides with Sulphur Recovery*, Reprints of AIME-SME Annual Meeting, Denver, Colorado, Feb. 1978, no 78-B-28.
- [33] G. Valensi, in *Atlas of Electrochemical Equilibria in Aqueous Solutions*, ed. M. Pourbaix, Pergamon Press, Oxford, 1974, pp.56-67.
- [34] I.P. Perez and J.E. Dutrizac, *The Effect of the Iron Content of Sphalerite on its Rate of Dissolution in Ferric Sulphate and Ferric Chloride Media*, Hydrometallurgy, 26 (1991), pp.211-232.
- [35] P.D. Scott and M.J. Nicol, *Kinetics of the Leaching of ZnS Concentrate in Acid Solutions containing Ferric Sulfate*, National Institute for Metallurgy, Randburg, South Africa, Report No.1949 (1978).

- [36] F.K. Crundwell, *Kinetics and Mechanism of the Oxidative Dissolution of a Zinc Sulphide Concentrate in Ferric Sulphate Solutions*, Hydrometallurgy, 19 (1987), pp.227–242.
- [37] J.E. Dutrizac and R.J.C. MacDonald, *Ferric Ion as a Leaching Medium*, Minerals Science and Eng., vol. 6, no. 2, April 1974, pp.59–100.
- [38] F.K. Crundwell, *Refractory Behaviour of Two Sphalerite Concentrates to Dissolution in Ferric Sulphate Solutions*, Hydrometallurgy, 19 (1987), pp.253–258.
- [39] F.K. Crundwell, *The Effect of Flocculant Addition to the Leaching solution on the Kinetics of Oxidative Dissolution of Sphalerite*, Mintek Report M298, 1987, South Africa
- [40] S. Zhang, W.K. Choi and A.E. Torma, *Metall.*, 42 (1988), pp.881–884.
- [41] N.V. Ngoc, M. Shamsuddin and P.M. Prasad, *Oxidative Leaching of an Off-grade/Complex Copper Concentrate in Chloride Lixiviant*, Metall. Trans. B, vol. 21B, 1990, pp.611–620.
- [42] L.D. Romankiv and P.L. deBruyn, *Unit Operations in Hydrometallurgy*, Gordon and Breach (1965), p.45.
- [43] L.D. Locker and P.L. deBruyn, *Journal of Electrochem. Society*, (1969) vol. 116, p. 1659.
- [44] F.K. Crundwell and B. Verbaan, *Kinetics and Mechanism of the Nonoxidative Dissolution of Sphalerite (Zinc Sulphide)*, Hydrometallurgy, 17 (1987), pp. 369–384.

- [45] J.E. Dutrizac and R.J.C. MacDonald, *The Dissolution of Sphalerite in Ferric Chloride Solutions*, Metall. Trans. B, vol.9B, 1978, pp.543-551.
- [46] Z. Jin, G.W. Warren, H. Henein, *Reaction Kinetics of the Ferric Chloride Leaching of Sphalerite - An Experimental Study*, Metall. Trans. B, vol.15B, 1984, pp.5-12.
- [47] G.E. Bobeck and H. Su, *The Kinetics of Dissolution of Sphalerite in Ferric Chloride Solution*, Metall. Trans B, vol.16B, 1985, pp.413-424.
- [48] Y. Venkataswamy and P.R. Khangaonkar, *Ferric Chloride Leaching of Sphalerite in the Presence of an Organic Solvent for Sulphur*, Hydrometallurgy, 7 (1981), pp. 1-5.
- [49] P.C. Rath, R.K. Paramguru and P.K. Jena, *Hydrometallurgy*, 6 (1981), pp. 219-225.
- [50] P. Neou-Singouna and F. Fourlaris, *A Kinetic Study of the Ferric Chloride Leaching of an Iron-Activated Bulk Sulfide Concentrate*, Hydrometallurgy, 23 (1990), pp. 203-220.
- [51] G. Bjorling, *Leaching of Sulfide Minerals under Pressure*, Erzmetall. vol 8, 1954, pp.781-784.
- [52] F.A. Forward and H. Veltman *Direct Leaching of ZnS Concentrate*, Journal of Metals, Dec. 1954, pp.836-840.
- [53] R.J. Jan, M.T. Hepworth and V.G. Fox, *A Kinetic Study on the Pressure Leaching of Sphalerite*, Metall. Trans. B, vol.7B, Sept. 1976, pp.353-361.
- [54] D. Dreisinger, E. Peters, M. Talaba, K.B. DeGraaf, G. Owusu, and R. Swiniarski, *Kinetics of the Sherritt Gordon Zinc Pressure Leach Process*, in Lead-Zinc 1990,

- AIME - TMS Annual Meeting, CA., Feb.,1990, pp.313-333.
- [55] G. Owusu, E. Peters and D.B. Dreisinger, *Surface Tensions and Contact Angles due to Lignin Sulfonates in the System: Liquid Sulfur, Aqueous Zinc Sulfate and Zinc Sulfide*, The Canadian Journal of Chemical Engineering, vol.70, 1992, pp.173-180.
- [56] G. Owusu, *Interfacial Studies in the Zinc Pressure Leach Technology*, M.A.Sc Thesis, University of British Columbia, Vancouver, Sept. 1989.
- [57] D.B. Dreisinger (U.B.C.) and G. Parker (Cominco Metals Ltd), *Private Discussion*, 1989.
- [58] P. Kawulka, W.J. Haffenden, V.N. Mackiw, *Recovery of Zinc from Zinc Sulphides by Direct Pressure Leaching*, Canadian Patent No. 971368, July 22, 1975.
- [59] H. Veltman, J.W. Gulyas, P.T. O'Kane, W.R. Middagh, *Hydrometallurgical Process for Treating Sulphides Containing Non-ferrous and Ferrous Metal Values*, Canadian Patent No. 904591, July 11, 1972.
- [60] H. Veltman, G.J.J. Mould, P. Kawulka, *Two Stage Pressure Leaching Process for Zinc and Iron-Bearing Mineral Sulphides*, Canadian Patent No. 1049953, June 3, 1979.
- [61] H.E. Hirsch, J.F. Higginson, E.G. Parker, G.M. Swinkels, *Leaching of Metal Sulphides*, US Patent No. 4192851, March 1980.
- [62] X. Guang-Xiang, L. Jin-jia, S. Hui-juan, Y. Ke-ning and C. Chang-lin, *Preliminary Studies on the Physical Chemistry of the Acid Pressure Leaching of ZnS Concentrate*, in Separation Processes in Hydrometallurgy, ed. G.A. Davies, Ellis Horwood-SCI, London, 1987, pp.125-132.

- [63] M.T. Martin and W.A. Jankola, *Cominco's Trail Zinc Pressure Leach Operation*, CIM Bulletin, April 1985, pp.77-81.
- [64] D. Dreisinger and E. Peters *The Mathematical Modelling of the Zinc Pressure Leach Process*, in *The Mathematical Modelling of Metal Processing Operations*, ed. J. Szekely, AIME - TMS, 1987, pp.347-369.
- [65] J.E. Bernal, *Kinetic Study on Direct Leaching of Sphalerite in Sulfuric Acid Solution using Ferrous Sulfate as the Catalyst* - Masters Thesis, Montana College of Mineral Science and Tech., Butte, 1982.
- [66] T.R. Scott and N.I. Dyson, Trans. TMS-AIME, 1968, vol. 242, pp. 1815.
- [67] T. de Nys and F. Terwinghe, *Integration of Direct Leaching of Zinc-Based Sulphidic Concentrates*, in *Lead-Zinc 1990*, eds. T.S. Mackey and R.D. Prengaman, AIME-TMS Annual Meeting, CA. Feb. 1990, pp.335-350.
- [68] F.K. Crundwell, *Effect of Iron Impurity in Zinc Sulphide Concentrate on the Rate of Dissolution*, Am. Inst. of Chemical Eng. Journal, 34(7) (1988), pp. 1128-1134.
- [69] K. Tozawa and S.Y. Piao, Metall. Rev.,- Min. Metall. Inst. Japan, 4 (1987), pp.89-105.
- [70] H. Kametani and M. Kobayashi, Metall. Trans. B, vol. 19B (1988), pp. 25-36.
- [71] R. Kammel, F. Pawlek, M. Simon and L. Xi-Ming, Metall., 41 (1987), pp. 158-161.
- [72] F. Pawlek, *Hydrometallurgical Process for Extracting Copper from Chalcopyrite or Bornite Concentrate*, US Patent No. 3949051, April 1976.
- [73] Dowa Mining Co Ltd, *Flotation of Complex Sulfide Ores*, Japan Patent No.59/160558 A2, Sept 11, 1984.

- [74] A. Vizsolyi, H. Veltman, I.H. Warren and V.N. Mackiw, *Copper and Elemental Sulphur from Chalcopyrite by Pressure Leaching* Journal of Metals, Nov. 1967, pp.52-59.
- [75] H. Veltman, S. Pellegrini, V.N. Mackiw, *Direct Acid Pressure Leaching of Chalcocite Concentrate*, Journal of Metals, Feb. 1967, pp.21-25.
- [76] K. Tozawa et.al *Effect of Addition of Na Lignin Sulfonate on the Direct Pressure Leaching of ZnS*, Tohoku Daigaku Senko Seiren Kenkyusho Iho, 36(2), 1981, pp.123-128.
- [77] G. Nickless, *Inorganic Sulfur Chemistry*, Elsevier Publishing Company, 1968, pp.248-249.
- [78] W. N. Tuller *The Sulfur Data Book*, McGraw-Hill Book Company, 1954.
- [79] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience Publishers, N.Y., 1962, p.407.
- [80] A.M. Kellas, *Journal of Chemical Society*, vol.113, 1918, p.903.
- [81] T. Moeller, *Inorganic Chemistry, An Advanced Textbook*, John Wiley & Sons, 1952, pp.487-491.
- [82] R. Fanelli, *The Surface Tension of Sulphur*, Journal of Am. Chemical Society, vol.72, 1950, pp.4016-4018.
- [83] M.J. Rosen, *Surfactants and Interfacial Phenomena*, John Wiley & Sons, N.Y., 1978, pp.149-171.
- [84] C. A. Miller and P. Neogi, *Interfacial Phenomena*, Marcel Dekker, Inc., N.Y., 1985, pp.1-16, 140-142.

- [85] A.M. Schwartz and J.W. Perry, *Surface Active Agents, Their Chemistry and Technology*, Interscience Publishers, Inc., N.Y., 1949.
- [86] I.A. Pearl, *Chemistry of Lignin*, Marcel Dekker, Inc. N.Y., 1967.
- [87] L.E. Wise and E.C. Jahn, *Wood Chemistry*, Reinold Publishing Corp., N.Y., 1952, pp.453-482.
- [88] W.C.Browing, *Surface Active Properties of Lignosulfonates*, in *Chemistry, Physics and Applications of Surface Active Substances: Proceedings of the 4th Int. Congress on Surface Active Substances*, Brussels, Sept. 1964, vol.1, ed. F. Asinger, Gordon and Breach Science Publishers, 1967, pp.142-153.
- [89] W.M. Linfield, *Anionic Surfactant Pt II : Surfactant Science Series*, vol.7, Marcel Dekker, Inc., N.Y., 1976, pp.335-337.
- [90] S.L.H. Chan, C.G. Baker and J.M. Beeckmans, *Powder Technology*, vol.13, 1976, pp.223-230.
- [91] *Chem. Abstracts* CAS 95-54-5
- [92] *Dupont Chemicals Manual on OPD*, 1990, Wilmington, DE
- [93] R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Allyn and Bacon, Inc., Boston, 1966, pp. 387, 701.
- [94] W.R. Noble and W.M. Linfield, *Soap-Based Detergent Formulation: XXVI Hard Water Detergency of Soap-Lime Dispersant Combinations with Builders and Inorganic Salts*, *Journal of Am. Oil Chemical Society*, Oct.1980, p.369.
- [95] G.W. Fernley, *Zwitterionic Surfactants: Structure and Performance*, *Journal of Am. Oil Chemical Society*, Jan 1978, vol.55. p.98-103.

- [96] M.J. Rosen, *Surfactants and Interfacial Phenomena*, John Wiley & Sons, N.Y., 1978, pp.3-24
- [97] B.R. Bluestein and Clifford L. Hilton, *Amphoteric Surfactants - Surfactant Science Series*, vol.12, Marcel Dekker, Inc., N.Y.
- [98] V.S. Brunel, G. Laurent, L.P. Pierre, and S. Bernard, *Surface Active Compounds of the Sulphobetaines Family, their Manufacture and Use, particularly for Enhanced Oil Recovery*, US Patent no. 4704229, Nov. 3, 1987.
- [99] K. Helmut Wagner *Processes for the Preparation of Sulphobetaines*, US Patent no.4259191, March 31, 1981.
- [100] R. Ohme, B. Detlef, G. Kristina, K. Gunter, R. Jochen and S. Herst, *Sulphobetaines*, US Patent no.4410709, Oct. 18, 1983.
- [101] R. Ernst *Processes for Producing Acyclic Surfactant Sulphobetaines*, US Patent no. 3280179, Oct. 18th, 1966
- [102] T.J. Micich and W.M. Linfield *Soap-Based Detergent Formulations: XXII Sulphobetaine Derivatives of N-Alkylglutaramides and Adipamides*, Journal of Am. Oil Chemical Society, vol.54, 1977
- [103] L.R. Plitt and M.K. Kim, *Adsorption Mechanism of Fatty Acid Collectors on Barite*, Trans. AIME - SME, vol.256, 1974, pp.188-193.
- [104] G.W. Poling and J. Leja, *Infrared Spectroscopy Studies of Xanthate and their Adsorption on Nickel*, Canadian Metall.Quart., vol.1, 1962, pp.109-128.
- [105] R.E. Coleman, H.E. Powell and A.A. Cochran, *Infrared Studies of Products of the*

- Reaction between Activated Zinc Sulphide and Potassium Ethyl Xanthate*, Trans.-SME, Dec. 1967, pp.408-412
- [106] I. Persson, P. Persson, M. Valli, S. Fozo, and B. Malmensten, *Reactions on Sulfide Mineral Surfaces in Connection with Xanthate Flotation Studied by Diffuse Reflectance FTIR Spectroscopy, Atomic Absorption Spectrophotometry and Calorimetry*, Unpublished.
- [107] J. Mielczarski, P. Nowak, and J.W. Strojcek, *Spectrophotometric Investigation on Products of Potassium Ethyl Xanthate Sorption on Lead Sulfide and Galena Surface: Part I Oxidized Samples*, Polish Journal of Chemistry, 54 (1980), pp.279-291.
- [108] T. Davidson and B. Stanley Pons, *Vibrational Spectroscopy of the Electrode/Electrolyte Interface: Use of FTIR Spectroscopy*, Journal of Electroanalytical Chemistry, 125 (1981), pp.237-241.
- [109] J.W. Strojek and J.A. Mielczarski, *Infrared Reflection Spectroscopy for Investigations of Sorption on Powders*, Roczniki Chemii, 48 (1974), pp. 1747-1750.
- [110] J. Iskra and M. Kielkowska, *Application of ATR Technique to Fluorite-Oleate-Quebracho Systems*, Trans. Inst. of Min. and Metall., 89 (1980), pp. C87-90.
- [111] R.T. Yang, M.J.D. Low, G.L. Haller and J. Fenn, *Infrared Study of Adsorption In-Situ at the Liquid/Solid Interface IV*, Journal of Colloid and Int. Science, vol.44, 1973, p.249
- [112] M. Hasegawa and M.J.D. Low, *Infrared Study of Adsorption In-Situ at the Liquid-Solid Interface II*, Journal of Colloid and Int. Science, vol.30, 1969, pp.378-386.
- [113] S.C. Termes and P.E Richardson, *Application of FTIR Spectroscopy for In-Situ*

- Studies of Sphalerite with Aqueous Solutions of Potassium Ethyl Xanthate and with Diethyl Xanthate*, Int. Journal of Mineral Processing, 18 (1986), pp. 167-178.
- [114] V.M. Lovell, L.A. Goold and N.P. Finkelstein, *Infrared Studies of the Adsorption of Oleate Species on Calcium Fluoride* Int. Journal of Mineral Processing, 1 (1974), pp.183-192.
- [115] J.J. Kellar, W.M. Cross and J.D. Miller, *Adsorption Density Calculation from In-Situ FT-IR/IRS: Data at Dilute Surfactant Concentration*, Applied Spectroscopy, vol.43, 1989, pp.1456-1459.
- [116] E.W. Giesekke, *A Review of Spectroscopic Techniques Applied to the Study of Interactions between Minerals and Reagents in Flotation Systems*, Int. Journal of Mineral Processing, 11(1983), pp.19-58.
- [117] J.J. Kellar, C.A. Young, K. Knutson and J.D. Miller, *Thermotropic Phase Transition of Adsorbed Oleate Species at a Fluorite Surface by In-Situ FTIR/IRS Spectroscopy*, Journal of Colloid and Interface Science, vol.144, 1991, pp.381-389.
- [118] J.M. Cases and P. de Donato, *FTIR Analysis of Sulfide Mineral Surfaces before and after Collection: Galena*, Unpublished.
- [119] J.O. Leppinen, C.I. Basilio and R.H. Yoon, *In-Situ FTIR Study of Ethyl Xanthate Adsorption on Sulfide Minerals Under Conditions of Controlled Potential*, Int. Journal of Mineral Processing, 26 (1989) pp.259-274.
- [120] J.O. Leppinen, *FTIR and Flotation Investigations of the Adsorption of Ethyl Xanthate on Activated and Non-activated Sulfide Minerals*, Int. Journal of Mineral Processing, 30 (1990) pp.245-263.

- [121] M.L. Hair, *Infrared Spectroscopy in Surface Chemistry*, Marcel Dekker, Inc., New York, 1967.
- [122] C.E. Meloan, *Elementary Infrared Spectroscopy*, Macmillan Company, New York, 1963.
- [123] N.L. Alpert, W.E. Keiser and H.A. Szymanski, *IR: Theory and Practice of Infrared Spectroscopy*, Plenum Press, New York, 1970.
- [124] I. Fleming and D.H. Williams, *Spectroscopic Methods in Organic Chemistry*, McGraw Hill Publishing Co. Ltd., London
- [125] P.R. Gomes Brandao, *Oleate Adsorption and Magnesite Flotation*, PhD. Thesis, University of British Columbia, Vancouver, 1982.
- [126] B. George and P. McIntyre, *Infrared Spectroscopy*, John Wiley & Sons, London, 1987.
- [127] N.J. Harrick, *Internal Reflection Spectroscopy*, Interscience Publishers, N.Y., 1967.
- [128] J.W. Strojek and J. Mielczarski, *Advances in Colloid and Interface Science*, 19 (1983), pp.309-327.
- [129] *Internal Reflection Spectroscopy*, vol.1, Instructions for Operation of Wilks Scientific Internal Reflection Infrared Spectrophotometers and Accessories, 1965.
- [130] J.D. Miller, and Jon J. Kellar, *Quantitative In-Situ Analysis of Collector Adsorption Reactions by FTIR Internal Reflection Spectroscopy*, in Challenges in Mineral Processing, Proceedings of AIME - SME Symposium in honour of Douglas W. Fuerstenau, Berkeley, California, Dec. 7-9, 1988, eds. K.V.S. Sastry and M.C. Fuerstenau, pp.109-128.

- [131] G. Haller and R.W. Rice, *A Study of Adsorption on Single Crystals by Internal Reflection Spectroscopy*, Journal of Physical Chemistry, vol.74 (1970), pp.4386-4393.
- [132] J.F. Paddy, in *Surface and Colloid Science*, ed. Egon Matijevic, vol.1 Wiley-Interscience, N.Y., 1969, pp.111-113.
- [133] A.W. Adamson, *Physical Chemistry of Surfaces*, Interscience Publishers, N.Y., 1967.
- [134] J.M. Andreas, E.A. Hauser and W.B. Tucker, *Boundary Tension by Pendant Drops*, Journal of Physical Chemistry, vol.42, 1938, pp.1001-1017.
- [135] D.I. Jon, H.L. Rosano and H.Z. Cummins, *Toluene/Water/1-Propanol Interfacial Tension Measurement by means of Pendant Drop, Spinning Drop, and Laser Light-Scattering Methods*, Journal of Colloid and Interface Science, vol.114 no.2, 1986, pp.330-339.
- [136] C. Jho and A.D. King Jr., *Interfacial Tensions of n-Hexane with Aqueous Solutions of Na Dodecyl Sulfonate in Equilibrium with Dimethyl Ether at Elevated Pressures*, Journal of Colloid and Interface Science, vol.79, 1981, pp.365-371.
- [137] A.S. Michaels and E.A. Hauser, *Interfacial Tension at Elevated Pressure and Temperature II*, Journal of Physical and Colloid Chemistry, vol.55, 1951, pp.408-421.
- [138] W.E. Rose and W.F. Seyer, *The Interfacial Tension of Some Hydrocarbons against Water*, Journal of Physical and Colloid Chemistry, vol.55, 1951, pp.439-447.
- [139] P. Joos and E. Rillaerts, *Theory on the Determination of the Dynamic Surface Tension with the Drop Volume and Maximum Bubble Pressure Methods*, Journal of Colloid and Interface Science, vol.79 no.1, 1981, pp.96-100.

- [140] K.Z. Haung, C.P. Chai and J.R. Maa, *Surface Tension and Adsorption of Vapors on Immiscible Liquids*, Journal of Colloid and Interface Science, vol.79 no.1, 1981, pp.1-6.
- [141] J.W. Jennings, Jr. *An Efficient Method for the Determination of Interfacial Tensions from Drop Profiles*, Langmuir, 1988, 4, pp.959-967.
- [142] F.E. Bartell and F.L. Miller, *A Method for the Measurement of Interfacial Tension of Liquid-Liquid Systems*, The Journal of the Am. Chemical Society, vol.50, 1928, pp.1961-1967.
- [143] W.G. Eversole and D.S. Dedrick, *The Effect of Dissolved Electrolytes on the Boundary Tension of Water*, Journal of Physical Chemistry, vol.37, 1933, pp.1205-1214.
- [144] D.S. Dedrick and M.H. Hanson, *The Effect of Sodium Acetate on the Interfacial Tension of the Benzene-Water System at 40°C*, Journal of Physical Chemistry, vol.37, 1933, pp.1215-1221.
- [145] G. Jones and W.A. Ray, *The Surface Tension of Solutions of Electrolytes as a Function of the Concentration: A Differential Method for Measuring Relative Surface Tensions*, The Journal of the Am. Chemical Society, vol.59, 1937, pp.187-198.
- [146] J.C. Speakman, *The Measurement of Surface and Interfacial Tensions*, Journal of the Chemical Society, 1933, pp.1449-1453.
- [147] D.M. Gans and W.D. Harkins, *The Drop Weight Method for the Determination of Surface Tension; The Effect of an Inclination of the Tip Upon the Drop Weight*, The Journal of the Am. Chemical Society, vol.52, 1930, pp.2287-2289.
- [148] D.M. Gans and W.D. Harkins, *The Surface Tension of Aqueous Solutions of Paratoluidine*, The Journal of the Am. Chemical Society, vol.52, 1930, pp.2289-2295.

- [149] D.K. Chattoraj and K.S. Birdi, *Adsorption and the Gibbs Surface Excess*, Plenum Press, N.Y., 1984.
- [150] R. Aveyard and D.A. Haydon, *An Introduction to the Principles of Surface Chemistry*, Cambridge University Press, Cambridge, 1973.
- [151] J.T. Davies and E.K. Rideal, *Interfacial Phenomena*, Academic Press, 1961, pp.1-5.
- [152] R.J. Good and C.J. van Oss, *The Modern Theory of Contact Angles and the Hydrogen Bond Components of Surface Energies*, in *Modern Approaches to Wettability – Theory and Applications*, M.E. Schrader and G.I. Loeb (eds.), Plenum Press, New York, 1992, pp.1-24.
- [153] J.K. Spelt, D. Li and A.W. Neumann, *The Equation of State Approach to Interfacial Tensions*, in *Modern Approaches to Wettability – Theory and Applications*, M.E. Schrader and G.I. Loeb (eds.), Plenum Press, New York, 1992, pp.101-142
- [154] G.D. Parfitt, *Dispersion of Powders in Liquids*, John Wiley & Sons, N.Y., 1969, pp.1-17.
- [155] J. Basset, R.C. Denney, G.H. Jeffrey, J. Mendham, *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th edition, Longman, London, 1978.
- [156] J.S. Fritz and G.H. Schenk, *Quantitative Analytical Chemistry*, Allyn & Bacon, Inc., Boston, 1979.
- [157] L.F. Hamilton and S.G. Simpson, *Quantitative Chemical Analysis*, MacMillan Co., N.Y., 1958.

- [158] R.A. Day, Jr. and A.L. Underwood, *Quantitative Analysis*, Prentice-Hall, New Jersey, 1986.
- [159] A. Doren and P.G. Ronxhet, *Infrared Study of the Adsorption on Silica of a Collector with an Oxyethylene chain*, Int. Journal of Min. Proc., 9(1982), pp.343-351.
- [160] E.J. Purcell, *Calculus with Analytic Geometry*, Appleton-Century Crofts, N.Y., 1965, pp.584-589.
- [161] G.B. Thomas, Jr. *Calculus and Analytic Geometry*, Addison-Wesley Company, Inc., 1960, pp.585-590.
- [162] D.J. Shaw, *Introduction to Colloid and Surface Chemistry*, Butterworths, London, 3rd. ed.
- [163] Manual on Naphthalene Sulfonic Acid-Formaldehyde Condensates supplied by Handy Chemicals Ltd., Laprairie, Quebec, Canada.
- [164] K. Osseo-Asare, *Interfacial Phenomena in Leaching Systems*, in Hydrometallurgical Process Fundamentals, ed. R.G. Bautista, Plenum Press, 1982, pp.227-269.
- [165] H.I. Bolker and N.G. Sommerville, *Infrared Spectroscopy of Lignins. Part II: Lignins in Unbleached Pulp*, Pulp and Paper Magazine, vol. 64, 1963, pp. T-187-193.
- [166] A.N. James and P.A. Tice, *The Presence of Carboxylic Groups in Lignosulfonate preparations*, Tappi, vol.48, 1965, pp.239-244.
- [167] A.J. Michel, A.J. Watson and H.G. Higgins, *An Infrared Spectroscopic Study of Delignification of Eucalyptus Regnans*, Tappi, vol 48, 1965, pp.520-532.

- [168] H.L. Hergert, *Infrared Spectra of Lignin and Related Compounds II. Conifer Lignin and Model Compounds*, Journal of Organic Chemistry, vol. 25, 1960, pp. 405–413.
- [169] K.V. Sarkanen and C.H. Ludwig, *Lignins, Occurrence, Formation, Structure and Reactions*, Wiley–Interscience, N.Y.
- [170] L.J. Bellamy, *Infrared Spectra of Complex Molecules*, John Wiley & Sons, N.Y., 1958.
- [171] G. Socrates, *Infrared Characteristic Group Frequencies*, John Wiley & Sons, N.Y., 1980.
- [172] T.W. Healy and M.S. Moignard, *A Review of Electrokinetic Studies of Metal Sulphides*, in Flotation Volume I - AIME New York, 1976, ed. M.C. Fuerstenau, pp.275–297.
- [173] M.J. Moignard, D.R. Dixon and T.W. Healy, *Electrokinetic Properties of the Zinc Sulphide-Water and Nickel Sulphide-Water Interfaces*, in Proceedings of AIMM., Sept. 1977, pp.31–38.
- [174] G. Owusu, D.B. Dreisinger, and E. Peters, *Oxidative Acid Pressure Leaching of Zinc Sulfide Minerals in the Presence of Different Surfactants*, presented at the Canadian Chemical Engineering Conference, Toronto, October 1992.

Appendix A

RADII OF CURVATURE

The derivation of radii of curvature is based purely on analytical geometry and applied to the pendant drop. The curvature, κ , of a curve at a point P(x,y) is the rate of change of ϕ per unit change in arc length along the curve at that point i. e.

$$\kappa = \left| \frac{d\phi}{ds} \right| \quad (\text{A.78})$$

where ϕ is the angle in Figure A.57 and s is the arc length measured along the curve. Radius of curvature is the reciprocal of curvature:

$$\sigma = 1/\kappa \quad (\text{A.79})$$

Thus, if one of these quantities is known, the other can be easily obtained. Consider the equation

$$p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (\text{A.80})$$

where R_1 and R_2 are the radii of curvature. Consider the curve C (i. e. the profile of the pendant drop) to be represented by a twice differentiable function $y = f(x)$. Let P(x,y) be any arbitrary point on the curve, C, and ϕ is the inclination of the tangent to the curve at P (i. e. the angle between a tangent and the horizontal). At P, R_1 can be represented as being in the plane of the paper and R_2 perpendicular to the plane of the paper. R_2 is given by NP (on the diagram) which rotates about OO. At the apex (origin, O) $R_1 = R_2$. In two-dimensional space, x, y, the direction of a line is given by its inclination. The tangent to the curve at any arbitrary point P is given by:

$$\tan \phi = f'(x) = y' \quad (\text{A.81})$$

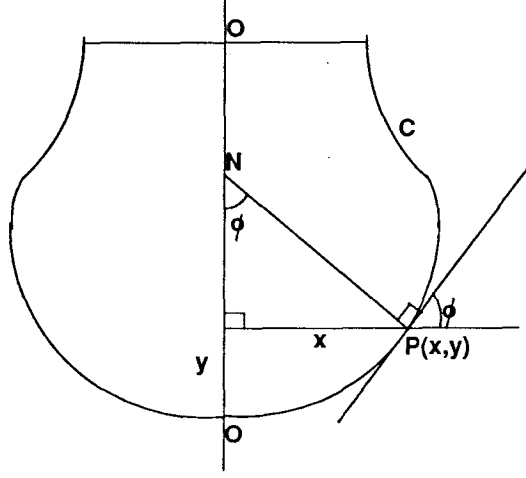


Figure A.57: Section of pendant drop profile

$$\Rightarrow \phi = \tan^{-1} f'(x) \quad (\text{A.82})$$

Therefore, since

$$\kappa = \left| \frac{d\phi}{ds} \right| = \left| \frac{d\phi}{dx} \cdot \frac{dx}{ds} \right| \quad (\text{A.83})$$

$$= \left| \frac{d}{dx} \tan^{-1} f'(x) \right| \left| \frac{dx}{ds} \right| \quad (\text{A.84})$$

However (from calculus),

$$\frac{d}{dx} \tan^{-1} f'(x) = \frac{y''(x)}{1 + (y'(x))^2} \quad (\text{A.85})$$

Meanwhile, $\frac{dx}{ds}$ can be derived from the curve considering the movement of P(x,y) such that

$$\frac{ds}{dx} = \sqrt{1 + (y'(x))^2} \quad (\text{A.86})$$

$$\Rightarrow \kappa = \frac{y''(x)}{1 + (y'(x))^2} \frac{1}{\sqrt{1 + (y'(x))^2}} \quad (\text{A.87})$$

$$= \frac{y''(x)}{\sqrt[3]{1 + (y'(x))^2}} \quad (\text{A.88})$$

The radius of curvature R_1 , can be obtained as the reciprocal of κ .

From Figure A.57

$$R_2 = \frac{x}{\sin \phi} = \frac{x[1 + (y'(x))^2]^{1/2}}{y'(x)} \quad (\text{A.89})$$

Appendix B

CHEMICAL ANALYSIS

B.1 Analysis of Fe^{3+} and Fe^{2+} ions

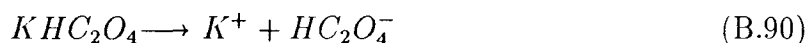
About 55–60 mL of deionized water is added to 5 mL of sample solution (i.e. filtrate). The diluted solution is titrated against 0.1 or 0.05 M ceric sulphate solution (i.e. Ce^{4+}) using an Autotitrator with Pt. and calomel electrodes. The Fe^{2+} ion concentration is then computed once the end point of the titration is reached.

The ferric ion concentration is calculated from the total iron concentration of the sample solution. About 15–25 mL of 6 M HCl solution is added to 2 mL of the sample solution and heated to about 80°C. Any ferric ion is reduced to the ferrous state by adding 0.5 N SnCl_2 solution until the solution turns colourless. Excess SnCl_2 solution is added. The solution is cooled and then diluted with 55–60 mL of deionized water; 10 mL of 5 % HgCl_2 solution is also added and allowed to stand for about 5 minutes and then titrated with the standard ceric sulphate solution to an end point of about 740 mV. The total iron concentration is then computed. The difference between this and the ferrous ion concentration gives the total ferric ion concentration.

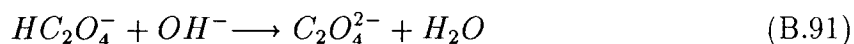
B.2 Total Acidity Analysis

To a 2 mL sample solution, 10 mL potassium hydrogen oxalate solution, KHC_2O_4 , (at $\text{pH} = 5\text{--}6$) is added to complex any metals in solution and then diluted with about 55–60 mL of deionized water. The solution is then titrated against 0.5 M NaOH using

the Autotitrator (with a combination pH electrode - glass+calomel). The volume of the titrant is then read from the chart. A blank titration is done by titrating 10 mL potassium hydrogen oxalate solution against the standard NaOH solution. The difference between the two volumes give the NaOH requirement of the solution acid (H^+) concentration. The total acid concentration of the sample solution is then calculated. The reactions occurring are:



For the blank titration



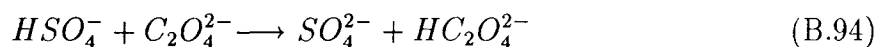
Sulphuric acid dissociates according to



Then

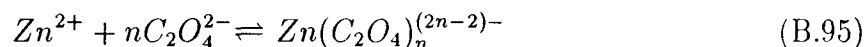


and

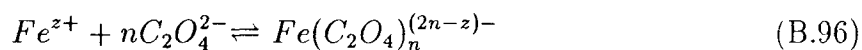


Reaction B.91 then proceeds from reactions B.93 and B.94. This gives the base requirements by the acid.

The metal ions are complexed according to:



and



These two reactions do not make any H^+ .

B.3 Sulphur Analysis

Determination of elemental sulphur in leach residue

Add 50–60 mL of ~ 2.1 mol/L Na_2S to 0.5–0.8 grams of sample (i.e. leach residue) and heat to 70–80°C. After about 15 minutes, filter and wash residue 2–3 times with about 0.5 mol/L NaOH solution followed by distilled water. Dry residue and weigh. The difference between residue and sample weights gives the weight of elemental sulphur.

Determination of sulphate sulphur in leach solution

To 5–10 mL of sample solution, add 50 mL of water and about 1 gm. of hydroxylamine hydrochloride and gently heat to dissolution of salt. Filter into 500 mL beaker and wash thoroughly. Adjust the pH of the filtrate to about 7 using ammonium hydroxide and then add 5 mL of HCl . Dilute the solution to about 300–400 mL, and heat to boiling. Add 25 mL of barium chloride solution while boiling or stirring and allow to stand for several hours or overnight on a low warming plate. The barium chloride solution will precipitate the sulphate sulphur as barium sulphate. Test if solid precipitation is complete through drop-wise addition of barium chloride to the supernatant liquid. If precipitation is complete filter and thoroughly wash residue with 5 to 6 times with hot water. If the precipitation is not complete, add more chloride solution to complete it. Transfer the residue to a ceramic crucible and ignite in muffle furnace at 850–900°C for one hour. Cool the solid, weigh, and calculate sulphur content as follows:

$$\text{Sulphur, \%} = A * 0.13735 * \frac{100}{B}$$

or

$$\text{g/L Sulphur} = A * 0.13735 * \frac{1000}{C} * D$$

where

- A = weight of barium sulphate found (g)
- B = sample weight (g) (if starting material is solid and has to be digested before the sulphur determination)
- C = volume of sample solution used (mL)
- D = dilution (as ratio of diluted volume to initial volume)

Determination of sulphide sulphur in concentrate

About 10 mL each of bottle strength HNO_3 and HCl are added to 0.3–0.5 gram of concentrate sample in a beaker and then heated until contents boil, shaking the beaker from time to time. The beaker is cooled and about 1 mL of liquid bromine is added to oxidize the sulphide sulphur to the sulphate form. The beaker is allowed to stand cold for about 10 minutes with gentle shaking from time to time. The beaker is gently heated to evaporate any residual bromine. The solution is boiled down to 10–15 mL, allowed to cool and then carefully diluted to 50–60 mL and filtered into a 250 mL volumetric flask. The filter is washed several times and the solution made up to volume. The sulphur determination is carried out as described in the previous section.

Appendix C

SURFACE EXCESS

Thermodynamically, the Gibbs adsorption equation for an interface in an i component system is given by [149]:

$$-d\gamma = S_{int}^1 dT + \sum_{i=1}^i \Gamma_i^1 d\mu_i \quad (C.97)$$

where S_{int}^1 = interfacial excess entropy per unit area

T = temperature

μ_i = chemical potential of i th component in the system

At constant temperature

$$-d\gamma = \sum_{i=1}^i \Gamma_i^1 d\mu_i \quad (C.98)$$

The chemical potential, μ_i , of the i th solute in the solution is given by:

$$\mu_i = \mu_i^o + RT \ln a_i \quad (C.99)$$

or

$$\mu_i = \mu_i^o + RT \ln f_i c_i \quad (C.100)$$

where μ_i^o = standard chemical potential of component i .

Differentiating the above equation

$$d\mu_i = RT(d \ln f_i + d \ln c_i) \quad (C.101)$$

$$= RT \left(1 + \frac{d \ln f_i}{d \ln c_i} \right) d \ln c_i \quad (C.102)$$

$$= RT \xi_i(d \ln c_i) \quad (C.103)$$

For i components system, equations C.98 and C.103 give

$$-d\gamma = RT(\Gamma_1^1 \xi_1 d\ln c_1 + \Gamma_2^1 \xi_2 d\ln c_2 + \cdots + \Gamma_i^1 \xi_i d\ln c_i) \quad (\text{C.104})$$

Component 1 is considered to be the solvent whose interfacial excess is assumed be negligible. This means that

$$\Gamma_1^1 = 0$$

and Γ_i^1 can be written as Γ_i . Equation C.104 can thus be simplified to

$$-d\gamma = RT\Gamma_2 \xi_2 d\ln c_2 \left(1 + \frac{\Gamma_3 \xi_3 d\ln c_3}{\Gamma_2 \xi_2 d\ln c_2} + \frac{\Gamma_4 \xi_4 d\ln c_4}{\Gamma_2 \xi_2 d\ln c_2} + \cdots + \frac{\Gamma_i \xi_i d\ln c_i}{\Gamma_2 \xi_2 d\ln c_2} \right) \quad (\text{C.105})$$

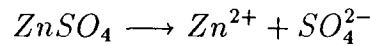
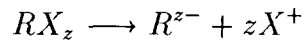
This simplifies to

$$-d\gamma = mRT\Gamma_2 d\ln c_2 \quad (\text{C.106})$$

where

$$m = \xi_2 \cdot \left(1 + \frac{\Gamma_3 \xi_3 d\ln c_3}{\Gamma_2 \xi_2 d\ln c_2} + \frac{\Gamma_4 \xi_4 d\ln c_4}{\Gamma_2 \xi_2 d\ln c_2} + \cdots + \frac{\Gamma_i \xi_i d\ln c_i}{\Gamma_2 \xi_2 d\ln c_2} \right)$$

For a solution containing an organic electrolyte (or surfactant) RX_z and inorganic electrolyte $ZnSO_4$, it can be assumed that they both dissociate completely according to:



where

z = valency of organic surface active anion

R = is the surface active anion.

For a multicomponent solution like this one

$$-d\gamma = \Gamma_{RX_z} d\mu_{RX_z} + \Gamma_{ZnSO_4} d\mu_{ZnSO_4} \quad (\text{C.107})$$

and

$$\mu_{RX_z} = \mu_R + z\mu_{X^+}$$

$$\mu_{ZnSO_4} = \mu_{Zn^{2+}} + \mu_{SO_4^{2-}}$$

Mathematically, it is shown that [149]:

$$\Gamma_{ZnSO_4} = \Gamma_{SO_4^{2-}}$$

Similarly,

$$\Gamma_{RX_z} = \Gamma_R$$

Thus, the relative surface excess of the surfactant can be computed using equation C.106 if the following speciation assignments are made:

c_1 assigned to the solvent (water)

c_2 assigned to R (or RX_z)

c_3 can be assigned to X^+

c_4 represents Zn^{2+} and

c_5 represents SO_4^{2-} .