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LEACHING IN REACTIVE FROTH OF ZINC SULPHIDE CONCENTRATE

Daniel Phillip Obeng

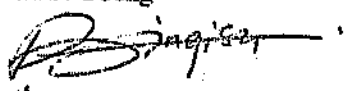
A dissertation submitted to the Faculty of Engineering, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the Degree of Master of Science in Engineering.

Johannesburg, 1997.

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Daniel P. Obeng



27th day of November, 1997.

ABSTRACT

Laboratory experimentation were conducted to investigate the regeneration and recycling of nitric acid during leaching in froth (L/F) processing of Gamsberg zinc sulphide concentrate.

Two experiments were performed in a mechanically stirred batch reactor at 80-90°C to determine the leaching kinetics of the zinc sulphide concentrate. 93 to 97% of zinc was extracted into spent zinc sulphate electrolyte containing 30 to 40g/l nitric acid during 40 to 60 minutes of leaching without regeneration of nitric acid.

Between 60.72 and 97.79% of the consumed nitric acid was regenerated after 45 minutes of batch L/F experiments carried out at 80-90°C and 50kPa. The results show that the degree of nitric acid regeneration is inversely proportional to the concentration of nitric acid in the leaching solution. Zinc extraction ranged between 56.31 and 78.37% whilst 40.29 to 50.99% of the initial sulphide sulphur was oxidised to elemental sulphur. In the continuous L/F experiments conducted at 80-90°C and 100-200kPa, the degree of nitric acid regeneration varied from 33.63 to 97.22%. Overall zinc extraction was about 62% whilst 47% of the sulphide sulphur reported as elemental sulphur after 60 minutes of processing .

A five-stage L/F processing of the concentrate was carried out in which the flotation phenomenon was used for selective separation of the floatable fraction from the non-floatable fraction. About 40 to 80% of the consumed nitric acid was regenerated, 88.94% of zinc was extracted whilst 55.65% of the sulphide sulphur reported as elemental sulphur after 77 minutes of processing. The recoveries of zinc and elemental sulphur increased to over 92% and 58% respectively when the leach residue was subsequently leached in the batch reactor.

To my parents, brothers, sisters and friends.

To God be all the glory.

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CONTENTS Page

DECLARATION		I
ABSTRACT		II
DEDICATION		III
ACKNOWLEDGEMENTS		IV
CONTENTS		V
LIST OF FIGURES		VIII
LIST OF TABLES		IX
1.0	**INTRODUCTION**	1
2.0	**STATE OF KNOWLEDGE**	5
2.1	The Leaching in froth (L/F) process	5
2.2	The reactive froth with nitric acid/nitric oxides/oxygen system	8
2.3	Regeneration of nitric acid in reactive froth	9
2.4	Other distinguishing attributes of the L/F process	14
2.5	Some observations made in the L/F process	14
3.0	**EXPERIMENTAL**	16
3.1	Description of materials and reagents used	16
3.2	Methods of chemical analysis	16
3.3	Determination of zinc concentration in the size fractions	19
3.4	Experimental apparatus	20
3.4.1	The batch reactor	20
3.4.2	The leaching in froth reactor	22
3.5	Experimental procedures	25
3.5.1	Kinetics of zinc sulphide concentrate leaching with nitric acid	25

3.5.2	Leaching in froth experiments	27
3.5.3	Leaching of residues obtained from the L/F experiments in the batch reactor	33
3.5.4	Digestion of leach residues	34
3.5.5	Determination of elemental sulphur	35
4.0	**RESULTS**	37
4.1	Results of experiments on kinetics of leaching	37
4.2	Results of leaching in froth experiments	39
4.2.1	Results of batch leaching in froth experiments	39
4.2.2	Results of continuous leaching in froth experiments	44
4.2.3	Results of five-stage leaching in froth processing	47
4.3	Results of leaching of residues obtained from the L/F experiments in the batch reactor	51
5.0	**DISCUSSION**	54
5.1	Leaching kinetics of zinc sulphide concentrate with nitric acid	55
5.2	Zinc sulphide concentrate leaching in froth	56
5.2.1	Regeneration and recycling of nitric acid in the reactive froth	57
5.2.2	Froth stability	59
5.2.3	Zinc extraction	60
5.2.4	Elemental sulphur extraction and its role	63
5.3	Two-stage leaching in froth processing	65
6.0	**SUMMARY AND CONCLUSIONS**	68
APPENDICES		71
APPENDIX A		71

A.1 DATA USED FOR THE CALCULATION OF DEGREE OF NITRIC ACID REGENERATION IN THE BATCH L/F EXPERIMENTS 71
A.2 SAMPLE CALCULATION OF THE DEGREE OF NITRIC ACID REGENERATION IN THE BATCH L/F EXPERIMENTS 73

APPENDIX B 76

B.1 HNO_3 CONCENTRATION IN FILTRATES AND WASH WATER OBTAINED FROM CONTINUOUS L/F EXPERIMENTS 76
B.2 CALCULATION OF DEGREE OF HNO_3 REGENERATION IN THE CONTINUOUS L/F EXPERIMENTS 77

APPENDIX C 81

C.1 CONDITIONS AND RESULTS OF THE 5-STAGE L/F EXPERIMENTS 81
C.2 SAMPLE CALCULATION OF HNO_3 REGENERATION IN THE 5-STAGE L/F EXPERIMENTS 87

REFERENCES 89

LIST OF FIGURES

Figure		Page
2.1	Schematic representation of a cross-section of the reactive froth fragment	7
2.2	Simplified model of nitric acid recycling and zinc sulphide decomposition in froth	12
2.3	Reduction of nitrates from leach solution by fresh concentrate in the froth	13
3.1	Experimental set-up of the batch reactor	21
3.2	The leaching in froth reactor with auxiliary equipment	23
3.3	The modified leaching in froth reactor with auxiliary equipment	24
4.1	Zinc extraction during leaching with 40g/l and 30g/l nitric acid	38
4.2	Zinc extraction into spent electrolyte containing 31.63g/l, 24.57g/l and 12.28g/l nitric acid	41
4.3	Nitric acid regeneration during zinc extraction into spent electrolyte containing 31.63g/l, 24.57g/l and 12.28g/l nitric acid	41
4.4	Variation of nitric acid regeneration with initial conc. of nitric acid	42
4.5	Variation of zinc extraction with initial conc. of nitric acid	42
4.6	Variation of elemental sulphur generated with initial conc. of nitric acid	43
4.7	Zinc extraction and regeneration of nitric acid during continuous leaching in froth	46
4.8	Cumulative percentage zinc extraction and elemental sulphur generated during the 5-stage leaching in froth processing	49
4.9	Simplified flowsheet of the 5-stage L/F processing	50
4.10	Zinc extraction during leaching of residues obtained from the L/F experiments in the batch reactor	52
5.1	Simplified flowsheet of leaching in froth processing of zinc sulphide concentrate	66

LIST OF TABLES

Table		Page
3.1	Chemical composition of the Gamsberg zinc sulphide concentrate	17
3.2	Particle size distribution of the Gamsberg concentrate	18
3.3	Distribution of zinc in the size fractions	19
3.4	Experimental conditions of the batch L/F experiments with simultaneous regeneration of nitric acid	28
3.5	Experimental conditions of the continuous L/F processing	29
3.6	Conditions of the 5-stage L/F processing	32
3.7	Experimental conditions of leaching of the L/F residues in the batch reactor	34
4.1	Tests on leaching kinetics of the zinc sulphide concentrate	37
4.2	Batch leaching in froth experiments with simultaneous nitric acid regeneration	40
4.3	Tests on continuous leaching in froth with simultaneous HNO_3 regeneration	44
4.4	Five-stage leaching in froth processing with simultaneous regeneration of HNO_3	48
4.5	Leaching of residues obtained from the L/F tests in the batch reactor	51
B.1	HNO_3 conc. in filtrates and wash water of stage 1	76
B.2	HNO_3 conc. in filtrates and wash water of stage 2	76
B.3	HNO_3 conc. in filtrates and wash water of stage 3	76
C 1	Results of experiment 1 of L/F 1	81
C.2	Results of experiment 2 of L/F 1	82
C.3	Results of experiment 3 of L/F 1	82
C.4	Results of experiment 4 of L/F 1	83
C.5	Results of experiment 5 of L/F 1	84
C.6	Results of L/F 2	84
C.7	Results of L/F 3	85

C.8 Results of L/F 4 86
C.9 Results of L/F 5 86

1.0 INTRODUCTION

The two processes today accepted as viable technologies of zinc sulphide concentrate processing are :

(i) a roasting process followed by acid leaching of the calcine

and

(ii) the direct pressure leaching of the concentrate.

Practically, almost all raw materials for zinc leaching carry the metal in the form of sulphide which is insoluble in any commercial solvent. Hence roasting is required as a preliminary treatment to leaching to convert the sulphide to oxide and render as large a proportion of the zinc as possible, soluble in dilute solutions of sulphuric acid. The basic reaction for the roasting process can be summarised as:

$$ZnS + 1.5O_2 = ZnO + SO_2 \qquad (1.1)$$

Due to environmental constraints, sulphur dioxide (SO_2) emitted from the roaster is converted to sulphuric acid and hence a nexus exists between the production of zinc and acid production. A substantial proportion of the plant capital cost is attributed to the acid plant and much of the running costs is due to the roasting step. With the production of sulphuric acid, the zinc plant must be located at a restricted distance from the acid markets to ensure sale and delivery at an economically viable rate[1,2]. In addition, with conventional fluid bed roasters, fine particle size and impurities such as copper and lead are a major impediment to efficient roaster performance[3]. With the depletion of good quality coarse concentrates and new deposits tend to be of fine grain, coupled with the aforementioned disadvantages, the need to develop alternative processing options

such as the direct pressure leaching increases.

Oxidative or direct pressure leaching of zinc sulphide concentrates requires oxygen as an oxidant in acidic solution to oxidise sulphide sulphur to elemental sulphur and extract zinc into solution. The equation for the reaction can be expressed as:

$$ZnS + 0.5O_2 + H_2SO_4 = ZnSO_4 + S^o + H_2O \quad (1.2)$$

The process is applicable to a wide variety of zinc sulphide concentrates ranging from high-grade marmatitic or sphaleritic material to complex zinc-lead concentrates. Treatment of concentrates with high iron content by the roast-leach process is difficult because of zinc ferrite formation. The production of elemental sulphur rather than SO_2 breaks the link between zinc and acid production and therefore offers considerable flexibility in the processing of zinc sulphide ores. However, the low solubility of oxygen in water result in operating conditions of 180-210°C and 1500-3000kPa in order to achieve acceptable reaction rates[4] which make the process technically difficult.

Mizoguchi and Habashi[5] also indicated that the use of high pressure equipment results in high capital investment, operation complexity, maintenance difficulties and loss of lead in a form of lead jarosite which cannot be recovered by known leachants such as chloride or ammonium acetate solution. Subsequently, a number of researchers have searched for an alternative process in which high pressure is not required. Of these, H_2SO_4-$Fe_2(SO_4)_2$ and HCl-$FeCl_3$ leaching systems have received the most attention[6,7,8,9,10,11]. In the former system however, a passivation film may form on the surface of the particle, leading to low zinc extraction[12]. Also in the latter system, although a much more

expensive acid, HCl, which has the corrosive capacity to solubilise the contained metal values is used, selectivity is poor. Recovery of lead and precious metals can be difficult and electrolytic recovery of zinc cannot be achieved without the use of either precipitation or solvent extraction[3,13].

Further attempts to develop an alternative process to existing technologies of zinc extraction from sulphide concentrates have recently been focused on taking advantage of the oxidative property of nitric acid[3,14]. The use of nitric acid as a hydrometallurgical leach medium for metal sulphides has been proposed since the beginning of this century[15]. Bjorling et al[16,17,18] made publications on the use of nitric acid as a catalyst in oxidising sulphide concentrates. Nitric acid is known to be a powerful oxidant, capable of dissolving a substantial range of metals, minerals, metallurgical intermediates and processing wastes. It is an efficient carrier of oxygen and much more efficient than the direct oxidation with either high-pressure air or oxygen itself[19].

Laboratory experimentation conducted by the Electrolytic Zinc Company of Australasia Limited in 1978 showed that nitric oxide mixtures reacted readily with zinc sulphide concentrates in dilute sulphuric acid[3]. Zinc extraction during two hours of leaching exceeded 80%, while 90% of the sulphide sulphur reported as elemental sulphur. Following this, numerous workers have presented flow sheets, varying in application, from total dissolution of concentrates[20,21] to partial chemical fracture of refractory ores[4,22] which include the two well-known processes, namely, the NITROX Process and REDOX Technology (formerly called the ARSENO Process).

Although the hydrometallurgical potential of nitric acid application to sulphide ore and concentrate leaching has been known for decades, commercial

exploitation of a nitric acid based leaching system is yet to materialise. This has been mainly ascribed to the set backs which have existed with respect to efficient regeneration and recycling of nitric acid, and in the case of the base metals industry, the total removal of nitrates from the leach solution[3]. The latter is generally required due to environmental constraints[3,23]. In the case of zinc processing, the harmful action of nitrate ions on the cathodic process and quality of the cathodic deposit constitutes an important additional requirement[24,25]. Quite a number of biological and chemical systems can be utilised for the reduction of nitrates from leach solutions[3,26,27]. The reduction of NO_3^- to NH_4^+ or N_2 by metallic zinc also decreases the concentration of nitrates to 5mg/l. However this happens only after forty-eight (48) hours[3].

The improvement in the efficiency of regeneration and recycling of nitric acid[3] has been the motivation for this study. This is of great importance because nitric acid is expensive and therefore any small loss can adversely affect the economics of the process. Generally, the regeneration of nitric acid does not deviate from the standard methods of its production and nitrosyl compounds absorption in the old technologies of sulphuric acid production. However, in almost all cases, a separate plant is required for this purpose. To this day, it is only the high temperature REDOX technology which has been developed for the decomposition of refractory sulphides prior to cyanidation, regenerates nitric acid "in situ" during pressure leaching[4].

This study therefore aims at investigating the regeneration and recycling of nitric acid during leaching in froth (L/F) processing of Gamsberg zinc sulphide concentrate as an alternative route to the Ronst-Leach and Sherrit-Cominco Direct Pressure Leaching processes.

2.0 STATE OF KNOWLEDGE

2.1 The Leaching in Froth (L/F) Process

Leaching in Froth is a proposed process which combines flotation with leaching by using a reactive gaseous reagent as a flotation carrier and a leaching solution as the reactive liquid medium to form a foam or froth in which the leached solid particles are suspended[28]. This way, the extraction of values is transferred from the continuous liquid phase to the froth phase.

Leaching in froth is distinguished from the conventional leaching in continuous liquid phase due to the commonly known distinctive physical properties of solid, liquid and gas phases as well as the surface phenomena of gas-liquid-solid interfaces. The low solubility of oxygen and some other gases in aqueous medium, their low densities and high molar volumes, usually cause stringent conditions to be applied in hydrometallurgical processes which make use of these gases. These "arduous" conditions include elevated temperature and pressure, high dispersion of the gases and vigorous agitation of the three-phase suspension. In froth however, these aggressive conditions are replaced by a large gas-liquid interfacial area and the leaching process takes place in a thin film i.e. the bubble wall.

Due to the generally low density of gases, the upward flow of bubbles to the surface of the continuous liquid phase shortens the gas-liquid contact time. In the froth phase, the gaseous reagents are encapsulated in the liquid cells so that their premature removal from the reactive environment is suppressed. Stoichiometrically, the volume proportions of the reacting gases, liquids and solids are usually of the order 100:10:1. Thus froth is probably the best balanced state in which the volumetric proportions of the reactants correspond to the

considerably differentiated molar volumes of the gas, liquid and solid phases[28].

The physico-chemical basis of the foam state and their various applications have been summarised[29]. The use of a two-phase cellular foam has been applied in chemical engineering, particularly in gas cleaning, oxidation and other absorption processes[30,31]. Stangle et and Mahalingam[32] published the modelling of a three-phase foam-slurry reactor. The authors investigated the absorption of carbon dioxide in aqueous foam with suspended fine particles of calcium oxide.

The foam state is defined as the transformation of spherical bubbles of gas into foam cells[33]. This state is unstable and the lifespan of foam cells is short with respect to the generally long time required for a number of three-phase processes. Basically, the formed foam is characterised by[33,34,35,36]:

(i) rearrangement of the cell sizes as a result of capillary suction as differences in pressure in the froth cells of various sizes;
(ii) mobility of the liquid wall interfaces;
(iii) drainage of liquid due to gravitation
(iv) bursting of cell walls which is a function of the physico-chemical properties of liquids and the surface phenomena on the liquid/gas or liquid/solid interphase.

Figure 2.1 shows a simplified model of a cross-section of the reactive froth cells. Each cell of the froth can be regarded as a "micro-batch leaching reactor"[28] which is linked to other cells by an active mass transfer. Capillary suction causes liquid to flow from the thin walls of the froth (or foam, i.e. when solid particles are present) cells into regions in which edges of at least three cells come together. Thus a greater part of the liquid content in the foam is contained in these regions which have been identified as the "Plateau Borders"[35]. Gravitational drainage,

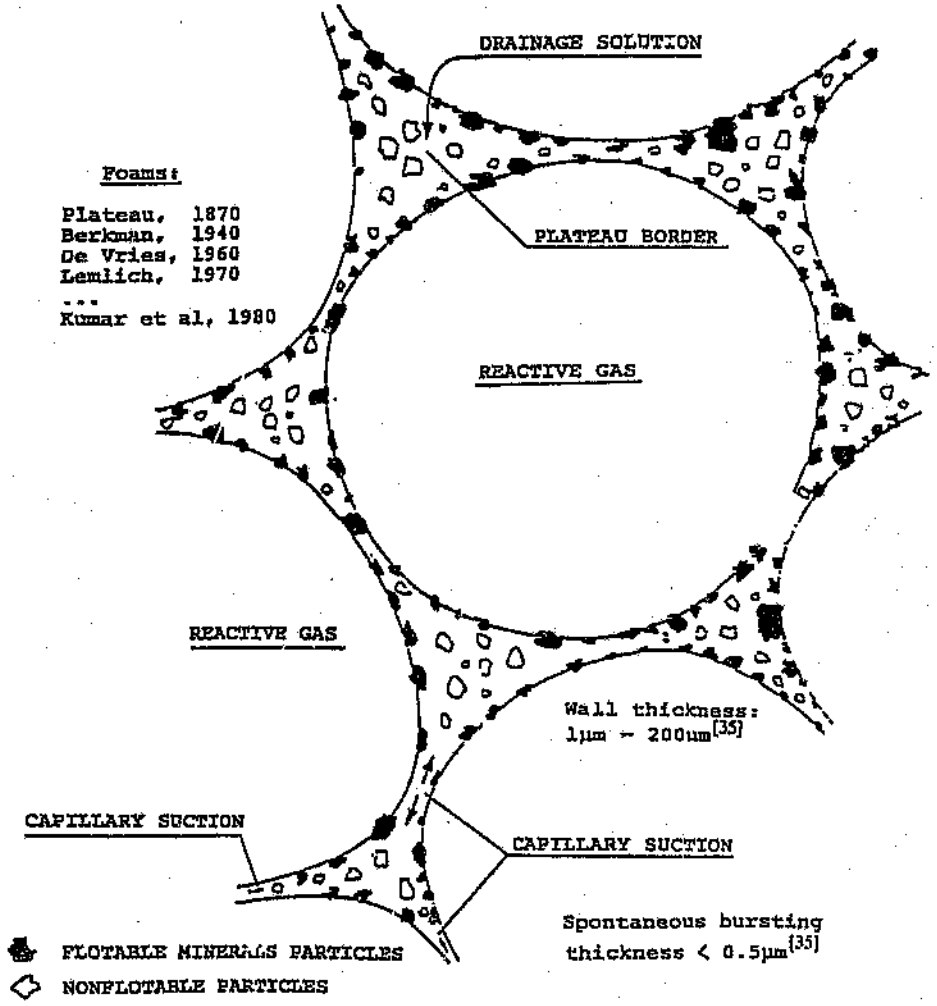


Figure 2.1 Schematic representation of a cross-section of the reactive froth fragment[28]

capillary suction and fluidity of the gas-liquid interfaces create a network of liquid streams in the froth[35]. Such a network constitutes conducive hydrodynamic conditions for leaching in a column flotation-type of reactor, provided fresh leaching solution trickles from the top of the reactor, through the froth bed, to replace the solution which becomes saturated as a result of the spontaneous reaction with the gaseous reagent encapsulated in the froth.

Research on the L/F process was first carried out by Letowski et al[37]. The authors investigated the "Leaching/Flotation Process" for the processing of complex sulphide ore using ferric sulphate solution as the reactive liquid medium. The ferric sulphate solution was continuously regenerated in froth by oxygen under elevated pressure which was simultaneously the flotation carrier. Later, the process was investigated for complex sulphide ore leaching in chloride solutions under elevated oxygen pressure, with simultaneous precipitation and separation of the products of iron hydrolysis[38]. The most important finding of these research work was that, the process can be used for the continuous selective transportation of suspensions or the floatable particles from one step of leaching to another without recourse to the routine solid-liquid separation, while the non-floatable particles are gravitationally transported in the opposite direction.

2.2 The Reactive Froth with Nitric Acid/Nitrogen Oxides/Oxygen System

Alhough the selective segregation of the leached particles according to their floatability during the Leaching/Flotation processing[37,38] is an advantage of the process, it was found that the oxidative reactions of leaching of the sulphides were relatively slow. Hence progress of leaching in froth was not the rest correlated with fast flotation. This resulted in the quest for a more vigorous oxidative conditions. Eventually, the nitric acid/nitrogen oxides/oxygen system was selected based on the knowledge that nitric acid is a powerful oxidising

agent, decomposes all non-ferrous sulphides and is easy to regenerate.

The use of nitric acid/nitrogen oxides/oxygen system during L/F processing has been investigated for mineral graphite concentration and purification[38], zinc sulphide leaching[39] as well as the recovery of gold from refractory minerals[40]. In the former, the conducted experiments demonstrated that the beneficiation and purification of the mineral graphite can be carried out in one process which combines flotation with simultaneous leaching. However, this research did not supply quantitative data on multiple regeneration and recycling of nitric acid.

During the zinc sulphide leaching[39] and the recovery of gold from refractory minerals[40], attempts were made to regenerate and recycle the consumed nitric acid. As found in the mineral graphite concentration and purification, in these cases also, it was found that the nitric acid/nitrogen oxides/oxygen system has an exceptional self-regenerating ability when acting in froth. However, some problems associated with recycling of the regenerated nitric acid were encountered and therefore the results were not specifically conclusive. Also in a previous study on zinc sulphide concentrate leaching in reactive froth, Letowski and Obeng[41] observed that the particles lost their floatability periodically. This was later found to be due to a mechanical problem which was resolved after some modifications to the L/F reactor had been made.

2.3 Regeneration of Nitric Acid in Reactive Froth

Although it is commonly known that nitric acid is a powerful oxidising agent, decomposes all non-ferrous sulphides and easy to regenerate, this expensive acid is not practically regenerated in the continuous liquid phase. This is because of the low solubility of the product of its reduction (nitric oxide) and oxygen. Thus in aqueous solutions, the oxidative capacity of nitric acid is limited to a single

action after which the gaseous NO escapes from the solution. However, in the froth in which oxygen is encapsulated, multiple regeneration of nitric acid proceeds.

A very important and well-known property of the nitric acid-nitrogen oxides system is that immediately after performing its oxidative action, in the case of ZnS decomposition, nitric acid transforms into gaseous nitric oxide as given in equation (2.1) :

$$3ZnS_{(s)} + 2HNO_{3(aq)} + 3H_2SO_{4(aq)} = 3ZnSO_{4(aq)} + 3S^{o}_{(s)} + 2NO_{(g)} + 4H_2O_{(l)} \quad (2.1)$$

Despite its low solubility in water (0.06 litres NO/1 litre of water at 20°C[42]), NO is a very fast carrier of oxygen into solution. Various concepts of its application in leaching processes have been presented[16,20,28,43,44,45,46]. Thus the NO generated in equation (2.1) being virtually insoluble in water abandons the solution very quickly and on coming into contact with oxygen in the froth phase, reacts instantly according to equation (2.2):

$$2NO_{(g)} + O_{2(g)} = 2NO_{2(g)} \quad (2.2)$$

The oxidised NO, i.e. NO_2 or its bimer, N_2O_4, is far more soluble in water than oxygen. As a result, it reacts with water in the liquid walls of the froth cells where it undergoes instantaneous hydrolysis and disproportionation through active intermediate species[17,28] to regenerate HNO_3 and NO, i.e.

$$3NO_{2(g)} + H_2O_{(l)} = 2HNO_{3(aq)} + NO_{(g)} \quad (2.3)$$

By reforming the oxidising agent in this manner, HNO_3 only acts as a catalyst and hence eliminates the need for extensive dissolution of oxygen in the leaching system as done in Direct Pressure leaching. The regenerated nitrate ions oxidise the sphalerite particles in froth and hence reaction (2.1) is repeated. The NO produced in equation (2.3) also reacts with oxygen according to equation (2.2) and the cycle continues. A closed circuit for nitric acid regeneration in the reactive froth is therefore created.

Figure 2.2 shows a schematic diagram of a simplified model of nitric acid regeneration in the reactive froth. As illustrated on the diagram, the solution constituting the thin walls of the froth is very rapidly saturated with NO_2 entering from both sides and hence by the accumulated soluble product (HNO_3) of reaction (2.3). Therefore drainage of saturated solution from the liquid walls into the "Plateau Borders" should be conducive to leaching in froth, on condition that fresh leaching solution is supplied to the froth to replace the saturated solution. According to de Vries[35], the pressure of gas entrapped in the froth is non-uniform and inversely proportional to the dimensions of the froth cells. However, the difference in pressure which can be sustained by the liquid wall of the froth cells prior to its rapture seems to be so small that diffusion of gas through the wall due to the pressure gradient is negligible, compared with the fast rate of NO_2 absorption in the froth. Figure 2.2 also depicts the direct attack of the regenerated nitric acid on a zinc sulphide particle which is suspended in the froth.

A very important condition for zinc sulphide concentrate processing in reactive froth is that the final leach solution should be "nitrate free" and thus ready for purification and zinc electrowinning[14]. Work carried out by Cole and Buson[47]

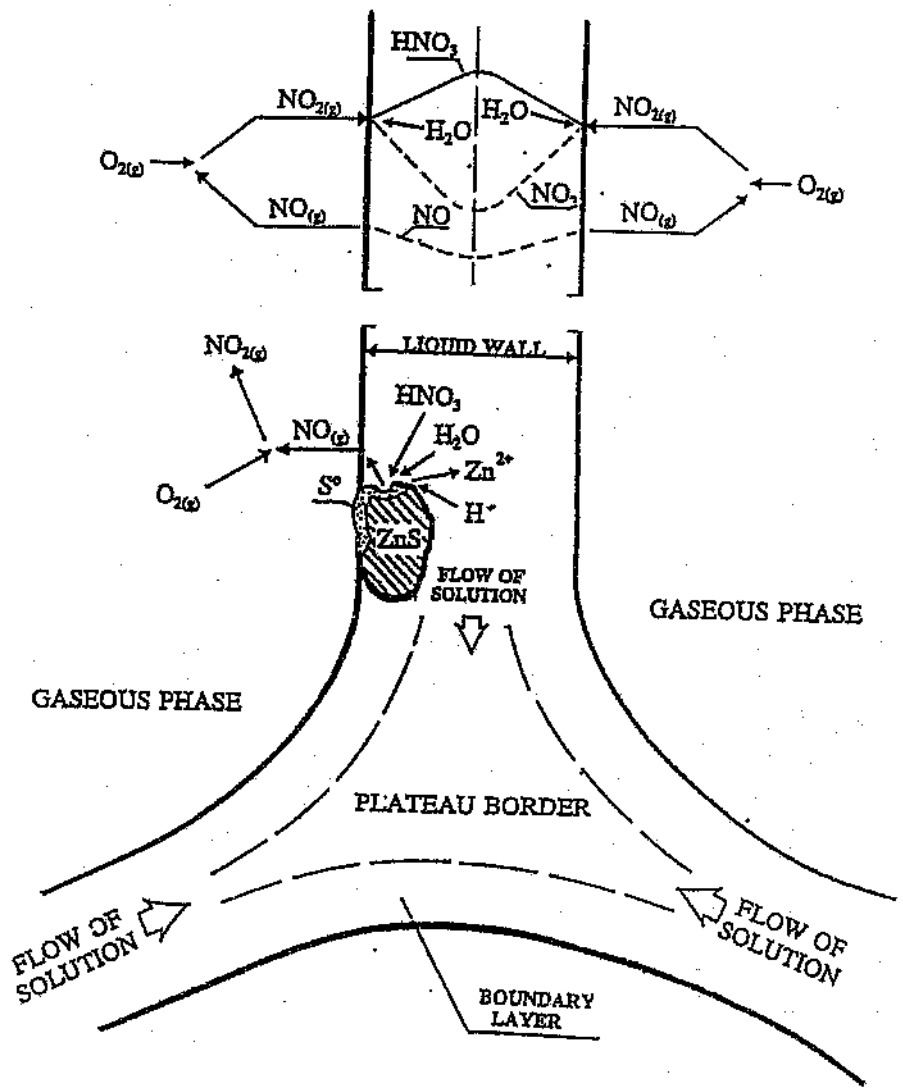


Figure 2.2 Simplified model of nitric acid recycling and zinc sulphide decomposition in froth[39]

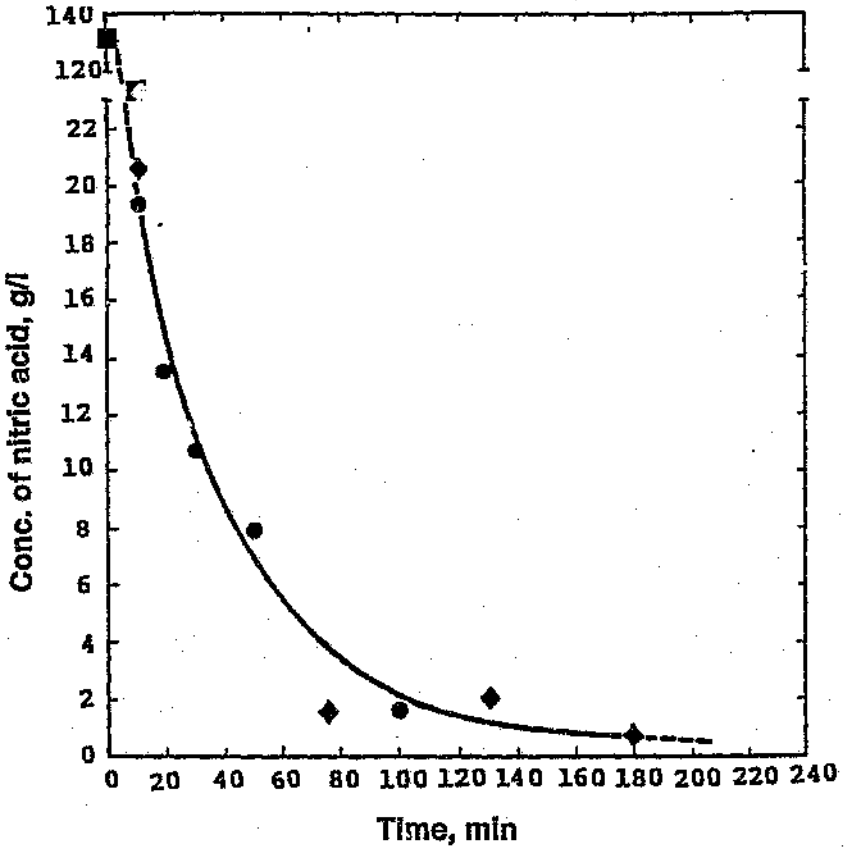


Figure 2.3 Reduction of nitrates from leach solution by fresh concentrate in the froth[47]

showed that the removal of nitrate from concentrated zinc sulphate solution is relatively easy in froth when active oxygen is replaced by gaseous nitrogen which is a non-active flotation carrier. According to their experimental data (figure 2.3), the concentration of nitrate in concentrated zinc sulphate solution can be reduced from about 130 to 0.7g/l after three hours of reducing leaching in froth.

2.4 Other Distinguishing Attributes of the L/F Process

- The leaching in froth process seems to be quite amenable to three-phase leaching processes in which the gaseous reagent is much more expensive than air or cannot be allowed into the atmosphere due to its toxic, explosive or other environmentally unacceptable properties and therefore should be as much as possible recycled to the process.

- The fact that a given volume of reactive gas can be encapsulated in the foam, in which a suitable quantity of particles can be suspended prevents the removal of the gaseous reagents prematurely from the reactive environment. This is a problem which usually occurs in the continuous liquid phase. In the froth, the hydrodynamics of gaseous "bubbles" is the same as liquid and solid reactants.

- The well developed gas/liquid surface area in the froth considerably increases the flow of the reactive gases being transported between the gaseous and liquid phases. According to de vries[35] the gas/liquid surface area in the froth can reach 5000cm^2/cm^3 if the volumetric gas liquid ratio is about 10.

2.5. Some Observations Made in the L/F Process

Some observations made in the L/F process include the following[28];

(i) the components responsible for the floatability of the particles are not at the same time subjected to dissolution or other chemical alterations that would affect the ability of the particles to float. However, during L/F processing, the non floatable solid particles can acquire temporary or stable hydrophobic properties as a result of a chemical modification

of the particles surface.

(ii) the non-floatable leached particles and the solid particles which precipitate or crystallise in the liquid walls of the foam cells can be retained for some time in the froth as a suspension in the leaching solution flowing through the Plateau borders.

3.0 EXPERIMENTAL

3.1 Description of material and reagents used

The sphalerite used in this study was a Garnsberg flotation concentrate obtained from Gold Fields of South Africa (Pty.) Limited. Mineralogically, the concentrate is composed mainly of sphalerite (ZnS), small amounts of pyrrhotite (FeS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), galena (PbS) and others, with quartz (SiO_2) being the main gangue mineral. The chemical composition and particle size distribution of the concentrate as supplied by Gold Fields[48] are presented in tables 3.1 and 3.2 respectively. It can be observed from table 3.2 that over 90% of the particles of the concentrate passed 75μm. This is desirable for both leaching and flotation processes and hence was advantageous for both batch reactor and leaching in froth experiments as it enhanced the leaching kinetics as well as particle floatability.

The spent electrolyte used was also obtained from Gold Fields and contained 50g/l Zn and 180g/l H_2SO_4[48]. Analytical grade nitric acid was used in all the experiments. Distilled water was used in preparation of all reagents.

3.2 Methods of chemical analysis

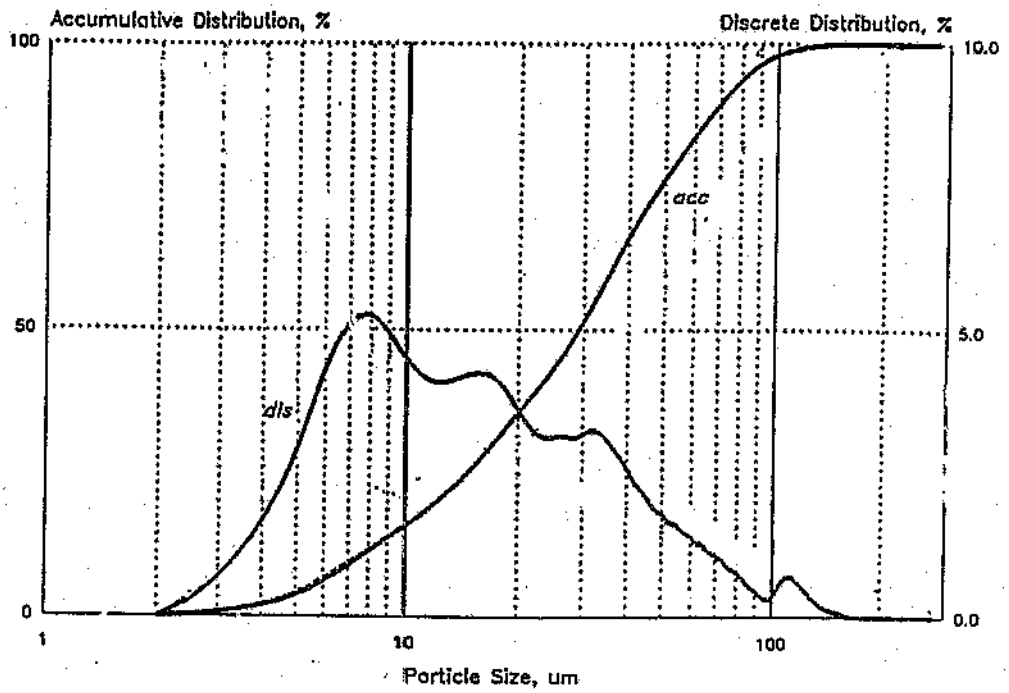
The concentrations of zinc, iron and manganese in solution were measured on a Varian Spectra AA-10 Atomic Absorption Spectrometer (AAS) in the School of Process and Materials Engineering at this University. In the case of zinc, it was found that the analytical results were best when the samples were not diluted. As a result, higher zinc standard solutions than the usual 1000mg/l supplied by the companies had to be prepared. The highest zinc standard used was 14,000mg/l. When these high standards were used for calibration, the samples could be diluted up to 100 times and the results were almost the same as the undiluted

Table 3.1 Chemical composition of the Gamsberg zinc sulphide concentrate[48]

Analysis		Gamsberg Conc
Element		*g/kg*
Zinc	Zn	470
Iron	Fe	74
Lead	Pb	8.9
Manganese	Mn	9.7
Copper	Cu	1.2
Sulfide	S^{2-}	297
Sulfate	SO_4^{2-}	36
Lime	CaO	2.3
Alumina	$AlO_{1.5}$	12
Silica	SiO_2	48
Magnesium	Mg	< 0.500
Silver	Ag	*ca* 0.010
Fluorine	F	*ca* 0.120
Compound		*g/kg*
Total Sphalerite	(Zn,Fe,Mn)S	778
Sphalerite	*ZnS*	*701*
In Sphalerite	*FeS*	*62*
In Sphalerite	*MnS*	*15*
Galena	PbS	10
Pyrite	FeS_2	7
Pyrrhotite	FeS	17
Chalcopyrite	$CuFeS_2$	3
Quartz	SiO_2	48
Microcline	$KAlSi_3O_8$	
BALANCE	Others	136
Accounted for	S^{2-}	95%
Fe in Sphalerite	Fe/Tot Fe	53%
Fe in Sphalerite	Fe/ZnS	56
Mn in Sphalerite	Mn/ZnS	14

Table 3.2 Particle size distribution of the Gamsberg concentrate[48]

Particle Size		
d10	µm	8
d50	µm	29
d90	µm	71
< 75 µm	%	92
< 30 µm	%	52
< 10 µm	%	15



samples.

The concentration of nitrate in solution samples was determined by the use of a Double Beam Spectrophotometer (model U-2000) at the Department of Chemistry, and Merckoquant Analytical Nitrate Test Strips procured from Merck (Pty) Limited, South Africa.

3.3 Determination of zinc concentration in the size fractions

Although the overall zinc content of the Gamsberg concentrate was supplied by Gold Fields, it was important to determine the concentration of zinc in the various size fractions as this would help in analysing the results. A known weight of the concentrate was therefore subjected to wet screening. A representative sample of each size fraction was taken by means of a sample splitter. About 1g of the representative sample of each fraction was digested with aqua regia ($3HCl:1HNO_3$). To ensure accurate and reliable results, the digestion was done thrice for each fraction. The resulting solids were thoroughly washed with distilled water and filtered. The filtrates were analysed for zinc on the AAS and the average of the results for each size fraction was calculated. The solid residues

Table 3.3 Distribution of zinc in the size fractions

Size Fraction (µm)	Zinc Content (%)
+ 75	43.20
+ 53	46.93
+ 45	48.74
+ 25	49.26
- 25	46.60

were dried in an oven after which the loss in weight of the samples were determined. This somehow served as a check against the results obtained from the AAS analysis, since the total weight of zinc extracted cannot be greater than the loss in sample weight. The distribution of zinc in the various size fractions is presented in table 3.3.

It can be seen from table 3.3 that below 75µm, the concentration of zinc is about the same in all the fractions. Taking into consideration the fact that about 92% of the concentrate passed 75µm (table 3.2) and zinc concentration in the +75µm fraction is over 43% (table 3.3), it can be assumed that zinc is evenly disseminated in the concentrate.

3.4 Experimental apparatus

Two sets of apparatus namely, a one-litre mechanically stirred batch reactor and the leaching in froth reactor were used. The former was used for the experiments on leaching kinetics as well as leaching of residues obtained from the leaching in froth experiments. The latter was used for the leaching in froth experiments with simultaneous regeneration of nitric acid. These sets of apparatus are described below.

3.4.1 The Batch Reactor

Figure 3.1 shows the experimental set-up of the batch reactor. It comprised two 1-litre mechanically stirred batch reactors, each with a cover, mounted in a heating mantle and equipped with other auxiliary parts and necessary control equipment. During leaching, the overflow of froth from the main reactor was channelled through a tubing into the overflow reactor from which it was recycled to the main reactor by means of the Masterflex peristaltic pump equipped with

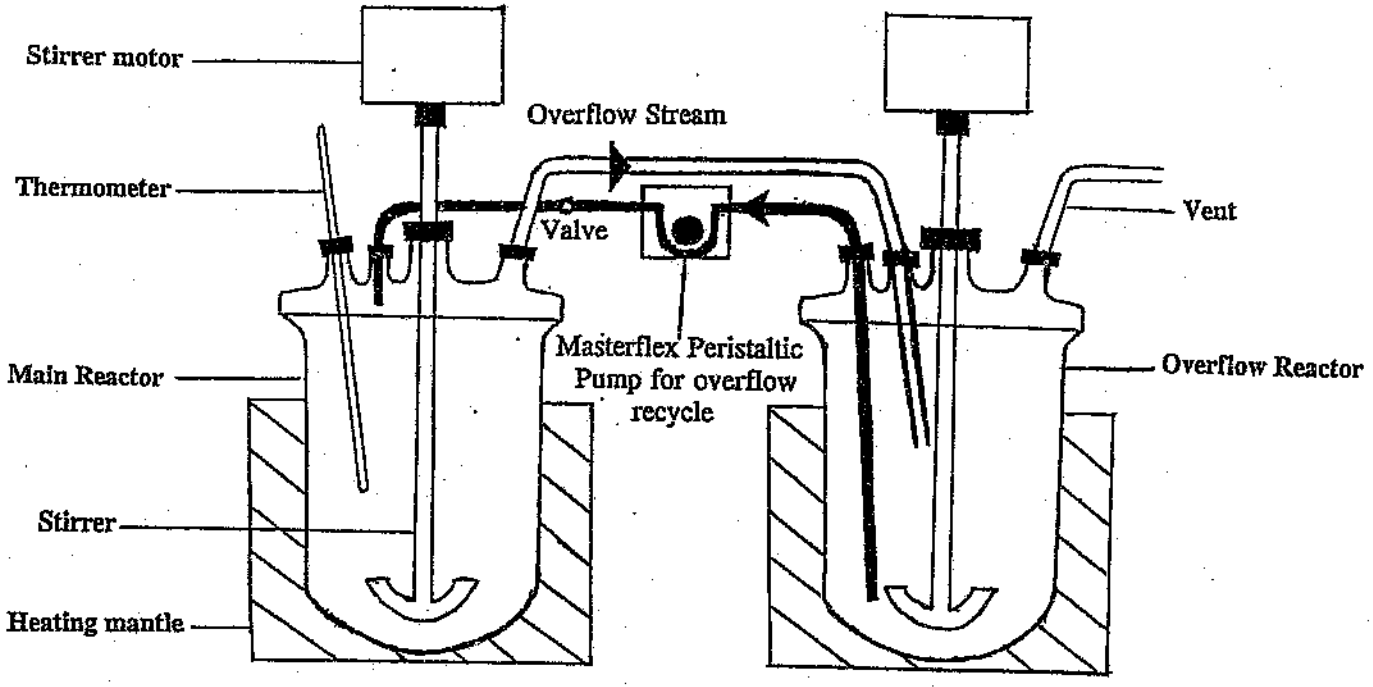


Figure 3.1 Experimental set-up of the batch reactor

Norprene tubing and a teflon valve. Heating of the contents of the reactor to the desired temperature was effected by a variable voltage transformer connected to the heating mantle and the temperature was constantly monitored by means of a thermometer fixed on the main reactor. Gaseous products which evolved in the course of leaching were evacuated from the circuit via the vent on the overflow reactor.

3.4.2 · The Leaching in Froth Reactor

The leaching in froth reactor is shown schematically in figure 3.2. A 2.6-litre Corning-glass tubular reactor, 126cm high and 5cm in diameter together with a 7-litre teflon-lined steel froth collector and gas-solid/liquid separator constitute the main components of the installation. Three Masterflex peristaltic pumps equipped with Norprene tubing as well as valves and tubes made of teflon, were used for feeding or recycling of solid-liquid suspension and reagents into the reactor. For safety reasons, a safety valve which releases gas at a pressure of 320kPa was mounted on the reactor although the reactor can sustain a maximum working pressure of 360kPa. The heating equipment comprised three variable voltage transformers equipped with insulated heating tapes wound around the reactor (not shown in the figure) and a heating plate with a magnetic stirrer (HM) at the bottom of the main reactor. Mixing of the contents of the main reactor was effected by the stirrer at the bottom and sparging of the gaseous reagents and products.

After several trial tests, the leaching in froth reactor was modified. The teflon-lined steel froth collector and gas-solid/liquid separator was replaced with a 2-litre Corning glass column. A second sparger was also introduced into the section of reactive gas dispersion in the solid/liquid suspension. These were done to facilitate increase in the rate of transportation of gaseous reactants and products

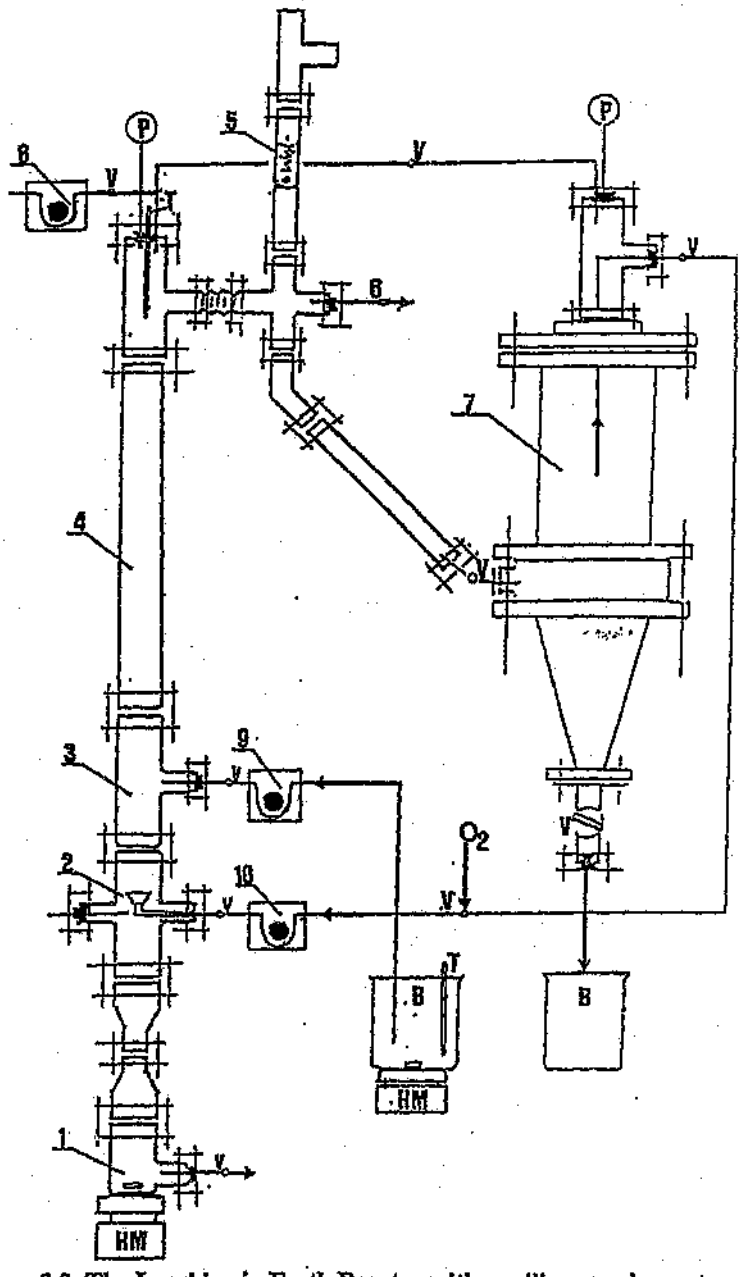


Figure 3.2 The Leaching in Froth Reactor with auxiliary equipment:
(1) The non-floatable fraction collector; (2) Section of the reactive gas dispersion in the solid/liquid suspension; (3) Section of feeding of solid/liquid suspension; (4) The reactive froth section; (5) Safety valve; (6) Froth sampling valve; (7) Separator of gas and solid/liquid suspension; (8), (9) and (10) Masterflex peristalstic pumps for transportation of reactants and products; (P) Pressure gauge; (T) Thermometer; (B) Beaker; (V) Valve; (HM) Heating plate with a magnetic stirrer.
***The electrical heating and thermal insulation are not shown in the figure.

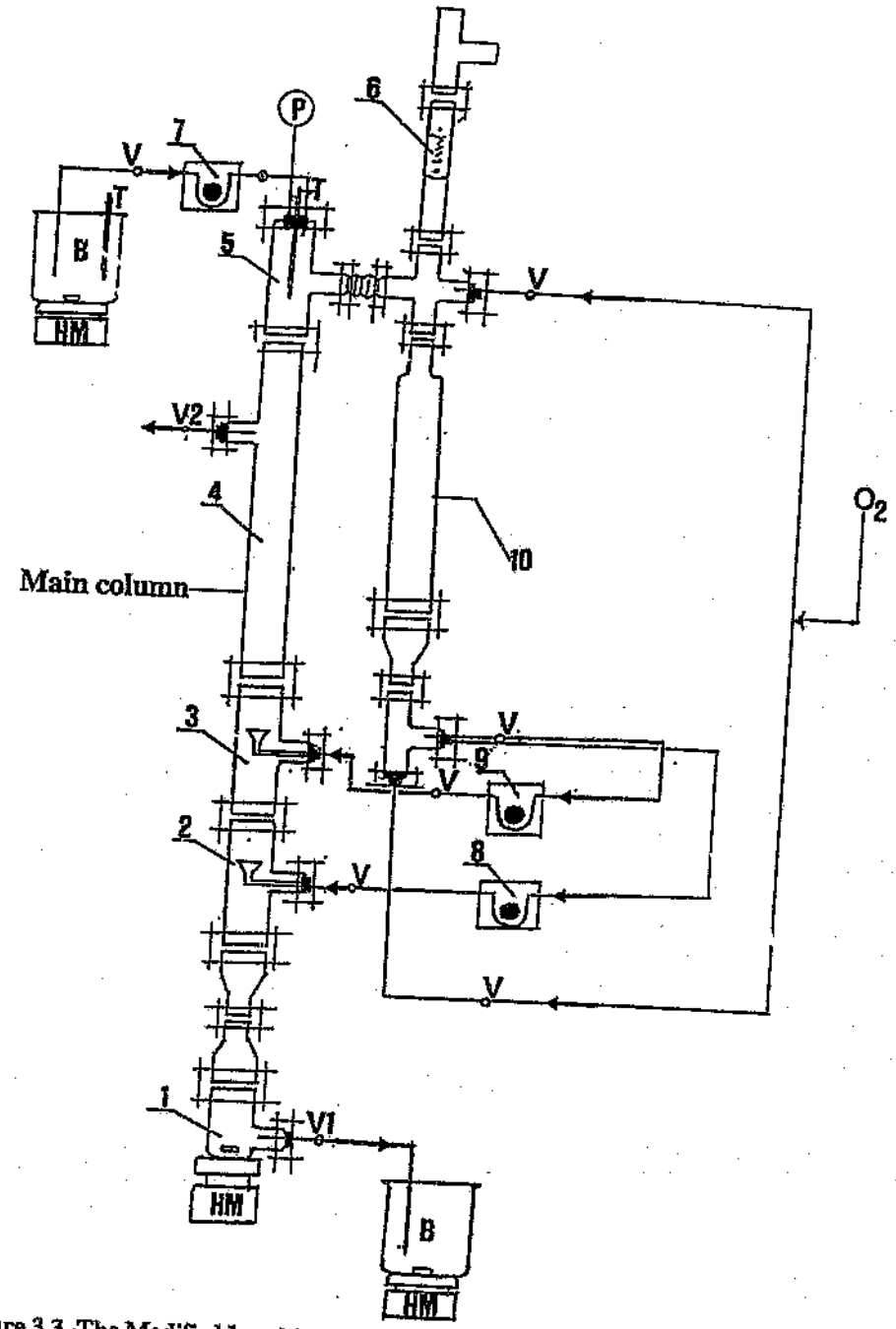


Figure 3.3 The Modified Leaching in Froth Reactor with auxiliary equipment:
(1) Non-floatable fraction collector; (2) and (3) Section of the reactive gas dispersion in the solid/liquid suspension; (4) The reactive froth section; (5) Section of feeding of solid/liquid suspension; (6) Safety valve; (7), (8) and (9) Masterflex peristalstic pumps for transportation of reactants and products; (10) Column for the conversion of excess NO to NO_2 and recycling; (P) Pressure gauge; (T) Thermometer; (B) Beaker; (V) Valve; (HM) Heating plate with magnetic stirrer.
***The electrical heating and thermal insulation are not shown in the figure.

through the reactor and hence increase the rate of nitric acid regeneration. The modified L/F reactor which was used for all the experiments is shown in figure 3.3.

3.5 Experimental procedures

3.5.1 Kinetics of zinc sulphide concentrate leaching with nitric acid

Two different experiments were conducted to determine the leaching kinetics of the zinc sulphide concentrate decomposition in zinc sulphate spent electrolyte by nitric acid. These were performed in the batch reactor shown in figure 3.1. Both experiments were carried out at temperatures between 80 and 90°C. under ambient pressure and in a fume cupboard. Stirrer speed was kept at about 400rpm to prevent the solids from settling and enhance the rate of leaching by increasing the rate of diffusion of the products from the reaction zone and unreacted substances towards the reaction zone.

In the first experiment, one litre of the spent electrolyte was heated to an initial temperature of 80°C in the main reactor. Pulp containing 150g of the zinc sulphide concentrate was then added. This was followed by addition of 40g of 55% HNO_3 which initiated the spontaneous reaction. Additional portions of nitric acid were subsequently added at short time intervals such that its concentration remained at a relatively stable level of about 40g/l throughout the experimental period of 45 minutes. This was done to prevent overshooting of the temperature due to the highly exothermic nature of the reaction between nitric acid and the sulphidic concentrate as well as avoid excessive overflow of froth from the main reactor. Total volume of nitric acid added amounted to about 0.2 litres. The froth which formed spontaneously on addition of nitric acid flowed via the tubing into the overflow reactor from which the solid/liquid suspension

was recycled to the main reactor by means of the Masterflex peristaltic pump. Gaseous nitric oxide which evolved during the experiment escaped from the circuit via the vent.

In the second experiment, approximately 30g of 55% HNO_3 was added into the main leaching reactor after heating one litre of the spent electrolyte to 80°C and adding pulp containing 100g of the zinc sulphide concentrate. Successive amounts of nitric acid were added to a total volume of about 0.1 litres until about 60 minutes of leaching when mechanical agitation and heating were stopped. This way, nitric acid concentration was kept at about 30g/l. 40g of nitric acid was thereafter added to the contents of the reactor and allowed to stand for over 40 minutes. As in the first experiment, the spontaneously formed froth which flowed into the overflow reactor was recycled.

In both experiments, 20mls samples of the solid/liquid suspension were taken at specific time intervals and filtered into tablet tubes. At the end of each experiment, the resulting slurry was allowed to cool to about 40°C and then filtered under vacuum. The solid residue was washed several times with distilled water until pH of wash water dropping from the funnel indicated a value of about 4.5 on : pH paper indicator. Each residue of the 20mls samples taken during the experiments was washed in the same way. Samples of the final filtrates as well as the wash water were taken. These together with the filtrates of the intermediate samples were analysed for zinc on the AAS. The residues were dried in the oven, weighed to find the weight loss and subsequently ground in a mortar. Representative samples of the ground residues were digested and analysed for zinc on the AAS. The amount of elemental sulphur generated in each experiment was also determined.

3.5.2 Leaching in Froth experiments

(a) Batch leaching in froth experiments

Three different experiments were conducted in the L/F reactor using the same concentration of sulphuric acid (72.13g/l) but different amounts of nitric acid to determine the effects of varying the concentration of the latter on

- the degree of nitric acid regeneration
- elemental zinc extraction into solution
- conversion of the initial sulphide sulphur to elemental sulphur.

In each experiment, 600mls of the spent electrolyte was diluted to 1.5litres and heated together with a known volume of nitric acid to about 80°C in the L/F reactor. A known weight of the zinc sulphide concentrate was mixed with distilled water, heated to about the same temperature and pumped into the main column of the reactor from the top using pump 7. Oxygen was simultaneously sparged into the reactor to maintain the pressure at the required level. The froth state began to form at about half way up the main column and maximum froth height was about 70cm. The pressure gauge indicated an increase to about 50kPa and then started to drop due to the oxidation of NO to NO_2 by the supplied oxygen. NO_2 formed in column 10 which was highly visible by its intense reddish-brown colour was continuously sparged into the main column using pumps 8 and 9. Samples were taken at specific time intervals and filtered into tablet tubes.

At the end of each experimental period of 45 minutes, the solid/liquid suspension was discharged from the reactor, allowed to cool to about 40°C under the fume cupboard and then filtered under vacuum. Distilled water was pumped into the main column to wash it. It also served as a medium into which the remaining

NO_2 in column 10 was sparged until no NO_2 was visible. The water was subsequently discharged from the reactor and used as part of water for washing the final residues. Samples of the final filtrates and wash water were taken. These together with those taken during the experiment were analysed for zinc and nitrates. The residues were dried in the oven, weighed to find the weight loss and

Table 3.4 Experimental conditions of the batch L/F experiments with simultaneous regeneration of nitric acid

Experiment	1	2	3
Mass of concentrate, g	100.43	100.64	100.29
Volume of leaching solution, l	1.50	1.50	1.50
Initial HNO_3 concentration, g/l	31.94	24.57	12.28

H_2SO_4 concentration: 72.13g/l; temperature:80-90°C; pressure:50kPa; time: 45 minutes.

then ground in a mortar. Representative samples of the ground residues were weighed, digested with royal water (aqua regia) and then analysed for zinc, iron and manganese. The amount of elemental sulphur generated in each case was also determined. Table 3.4 gives the experimental conditions of the three experiments.

(b) **Continuous leaching in froth experiments**

Approximately 614g of the Gamsberg concentrate was subjected to a 3-stage continuous leaching in froth processing in the L/F reactor. This was done with the objective of investigating:

- nitric acid regeneration, i.e. if it occurs
- zinc extraction into solution
- how much sulphide sulphur is converted to the elemental state

under continuous leaching in froth conditions as most existing zinc plants operate on continuous basis and because of the possibility of the Leaching in Froth Process being one day operated on a commercial scale.

In the first stage, a mixture of 1.5 litres of the spent electrolyte and 50ml of 55% nitric acid were heated to an initial temperature of about 85°C in the main column. The concentrate was pulped with distilled water, heated on a heating plate to about 80°C and then pumped into the reactor from the top using pump 7. Oxygen was simultaneously sparged into the reactor to maintain the pressure at the required level. The pressure increased to about 150kPa and then started to drop due to the conversion of NO to NO_2. Excess NO which escaped from the main reactor into column 10 reacted with the oxygen supplied to this column to form NO_2 which was highly visible by its intense reddish-brown colour. This

Table 3.5 Experimental conditions of the continuous L/F processing

Processing Stage	Mass of solid used (g)	Zinc content (%)	Temp. (°C)	Pressure (kPa)
1	614.197	47.00	85 - 90	150
2	403.224	46.90	80 - 90	200
3	322.821	42.90	80 - 90	150

Volume of spent electrolyte: 1.5l; Initial conc. of HNO_3: 24.57g/l; time of leaching in each stage: 20 minutes.

NO_2 was continuously pumped by recycling pumps 8 and 9 into the main column for nitric acid regeneration. Maximum froth height was about 50cm.

When the non-floatable particles began reporting to the bottom of the main column and were well mixed by the stirrer, valve V1 was opened such that the rate of outflow of pulp into the outflow beaker was approximately equal to that of the inflow of feed from the top. This way, a continuous leaching in froth process was ensured. The outflow beaker was removed and replaced simultaneously with a new one at appropriate time intervals. After discharging the remaining pulp into the last outflow beaker at the end of the experiment, the main column was washed with distilled water in the same way as done in the batch leaching in froth experiments.

Pulp collected into the different beakers was filtered separately. The residues were washed in the same manner as described under the batch leaching in froth experiments. The volumes of each filtrate and its corresponding wash water were measured, noted and samples taken for zinc and nitrate analyses. The same procedure as described under the batch leaching in froth experiments was followed to obtain a representative sample of each residue for the determination of zinc and elemental sulphur contents.

The remaining ground residues were combined, mixed thoroughly and a representative sample taken for the determination of zinc and elemental sulphur contents. About 403g of this c· ·nposite residue was used for the second stage. A little over 10 minutes into this experiment however, recycling pump 8 seized to work and all attempts to restart it proved futile. Thus only pump 9 was used for gas recycling during the remaining part of the experiment.

In the third or final stage, about 323g of the composite residue from the second stage was used. The same procedure as in stage one was followed in both the second and third stages. Volumes of spent electrolyte and nitric acid used in stages two and three were also the same as in stage one. Each processing stage lasted 20 minutes. It was observed that the floatability of the mineral particles improved considerably from one processing stage to the next. Table 3.5 gives the experimental conditions at the various stages.

(c) **Five - stage L/F processing with simultaneous regeneration of nitric acid**

About 780g of the Gamsberg concentrate was subjected to a five-stage L/F processing in the L/F reactor with each stage lasting 15 to 16 minutes. The main aim of these experiments was to investigate the feasibility of one of the practical applications of the leaching in froth process. In this application, the flotation phenomenon is used for the selective separation of the floatable fraction (FF) from the non-floatable fraction (NF), from one step of leaching to another, at the same time, regenerate nitric acid in the reactive froth.

The first stage is a combination of five separate experiments conducted under similar conditions as presented in appendix C.1. These five experiments had to be carried out in order to obtain adequate feed for the subsequent stages. In each of these experiments, known volumes of the spent electrolyte and 55% nitric acid were heated together to about 80°C in the main reactor. The concentrate was pulped with distilled water and the same procedure as in the batch L/F experiments was followed. At the end of each experiment, the floatable fraction was collected from the reactive froth section by opening valve V2 while the non-floatable fraction was discharged from valve V1. To ensure a good separation, the non-floatable fraction was recycled once into the reactor in the course of the experiment. The reactor was washed with distilled water in the same way as done

in the batch leaching in froth experiments. The floatable and non-floatable fractions were then filtered separately after which samples of the filtrates were taken for zinc and nitrate analyses. The same procedure as described under the batch leaching in froth experiments was followed to obtain a representative sample of each residue for the determination of zinc and elemental sulphur contents.

The remaining non-floatable fractions of the five experiments (L/F 1) were combined and used for the second, L/F 2 stage after a representative sample of the composite had been analysed for zinc and elemental sulphur. Known weights of the floatable fractions of L/F 1 (experiments 1-5) and L/F 2 stages were mixed thoroughly and used for the L/F 3 stage. The non-floatable fraction of L/F 2 was

Table 3.6 Conditions of the 5-stage L/F processing

Process. stage	Mass of solid used, g	Zinc content, %	Elemental sulphur content, %	Nitric acid used, g	Press., kPa	Leaching time, min
LF/1	779.51	47.00	-	117.00	80-85*	15
LF/2	361.10	35.65	21.78	66.33	150	16
LF/3	123.30	18.77	35.52	36.85	100	15
LF/4	115.81	30.89	26.97	36.85	100	15
LF/5	83.05	13.42	54.10	29.48	80	16

*Pressure range for the five experiments constituting L/F 1 (appendix C.1); Temperature: 80-90°C; volume of spent electrolyte used in each stage is given in appendix C.1.

further processed in L/F 4 stage. The floatable fraction of L/F 4 was combined with that of L/F 3 and used for the last, L/F 5 stage. The same experimental procedure as described for L/F 1 was followed in all the subsequent stages. As in the case of the feed used for L/F 2, in all the subsequent stages, a representative sample of the feed was analysed for zinc and elemental sulphur. The temperature ranged between 80 and 90°C in all the experiments and maximum froth height averaged about 70cm. The experimental conditions of the 5-stage L/F processing are presented in table 3.6.

3.5.3 Leaching of residues obtained from the L/F experiments in the batch reactor

Residues obtained from all the L/F experiments were thoroughly mixed in a mortar to form a composite residue from which a representative sample was taken to determine the concentrations of zinc and elemental sulphur. The remainder of the composite residue was divided into two portions using a sample splitter. One portion was labelled A. The other was digested with xylene or di-methyl benzene [$C_6H_4(CH_3)_2$] and filtered while still hot to ensure that the dissolved elemental sulphur did not recrystallize into the residue. The residue was subsequently washed with fresh hot xylene to dissolve and filter any elemental sulphur that might still be present. This residue was allowed to dry and labelled B. Leaching of residues A and B were conducted in the batch reactor shown in figure 3.1 to determine:

(i) whether the remaining zinc can be totally extracted

(ii) the effect(s) of the presence or absence of elemental sulphur on the surface of the solid particles on the leaching kinetics.

Although the main objective of this research was to investigate the regeneration and recycling of nitric acid in the reactive froth, it is also important that high zinc

extractions are achieved to make the process economically attractive and hence highly competitive with the conventional methods.

Table 3.7 Experimental conditions of leaching of the L/F residues in the batch reactor

Experiment	Zinc content, %	S^o content, %	S/L ratio, g/l	Temp., °C
1 (Residue A)	36.89	19.22	50.90	80 - 95
2 (Residue B)	42.93	-	50.86	82 - 95

Volume of spent electrolyte: 1 litre; volume of HNO_3: 150ml; time of leaching: 60 minutes; pressure: atmospheric; stirrer speed: 400rpm.

In each experiment, approximately 51g of the respective residue was used. The same procedure as in the experiments on kinetics of leaching was followed. Total volume of nitric acid used and time of leaching in each case were 150ml and 60 minutes respectively. The formation of froth, though spontaneous, was not as intense as observed in the experiments on kinetics of leaching in which case fresh zinc sulphide concentrate was used. Table 3.7 gives the experimental conditions of the experiments.

3.5.4 Digestion of leach residues

To confirm the accuracy and hence reliability of results obtained from AAS analysis of the solution samples, the solid residues were digested to determine the total zinc extraction. In the case of the batch L/F experiments, the iron and manganese contents of the residues were determined as well. These were used in the calculation of the degree of nitric acid regeneration (see appendix A). In the continuous and five stage L/F experiments however, the iron and manganese

contents of the residues were not determined. This was due to the fact that these sets of experiments were mainly focused on some of the practical applications of the L/F process. Hence the fact that some degree of regeneration occurs with only the amount of nitric acid consumed for zinc extraction used in the calculation, should be sufficient to prove the applicability of the process in the real situation.

Digestion was accomplished by weighing about 1g of the representative sample of the residue into a beaker, adding about 20mls of freshly prepared aqua regia and heating the mixture on a heating plate to dryness. The resulting solids were washed thoroughly with distilled water and filtered into a volumetric flask. The filtrate was then analysed for the appropriate elements using the AAS. The solid residue obtained after filtration was also dried in the oven after which the loss in weight was determined. This also served as a check against the AAS results of the filtrate. Zinc extractions calculated from the results of the digested residues were then compared with those obtained from the results of the corresponding solution samples.

3.5.5 Determination of elemental sulphur

This was carried out by digesting a known weight of the residue (up to about 10g) with concentrated xylene. The mixture was heated on a heating plate until all the elemental sulphur has been dissolved. The resulting slurry was filtered while still hot to prevent the elemental sulphur from recrystallising into the solids. The residue was washed with hot concentrated xylene to dissolve and simultaneously filter any elemental sulphur that might still be present. The yellowish filtrate was evaporated in the fume cupboard by placing it on a warm heating plate and blowing compressed air at a moderate rate into it to avoid spilling. The resulting bright yellow crystals of elemental sulphur were then weighed together with the beaker and the weight of the latter subtracted from the total to give the actual

weight of elemental sulphur contained in the digested residue. The amount of elemental sulphur in the total residue was then calculated by proportion.

4.0 RESULTS

4.1 Results of experiments on kinetics of leaching

Results obtained from the experiments carried out in the batch reactor to determine the leaching kinetics of the zinc sulphide decomposition in the spent electrolyte by nitric acid are presented in table 4.1 and figure 4.1. Zinc extractions in table 4.1 were obtained from AAS analysis of the digested leach residues while those in figure 4.1 were obtained from analysis of the solution samples.

Table 4.1 Tests on leaching kinetics of the zinc sulphide concentrate

Expt.	S/L ratio, g/l	HNO_3 conc., mol/l	Leaching time, min	Zinc extraction, %	Loss in sample wt, %	S^o in residue, %
1	150	0 63	45	99.10	58.47	40.00
2	100	0.48	103*	93.81	63.75	39.80

* Mechanical agitation and heating were stopped after 60 minutes of leaching; Temp.:80-90°C; pressure: atmospheric; volume of spent electrolyte: 1 litre; mixing: 400rpm.

Rapid and high extraction of zinc were observed in both experiments 1 and 2 with those of the former being faster and higher than the latter (figure. 4.1). As shown in the figure, about 97% of zinc was extracted after 45 minutes of leaching in experiment 1. However, analysis of filtered and washed residue which remained in contact with the leaching solution for several minutes without mechanical agitation and heating revealed that over 99% of zinc was eventually extracted from the concentrate (table 4.1). In experiment 2, zinc extraction attained a level of about

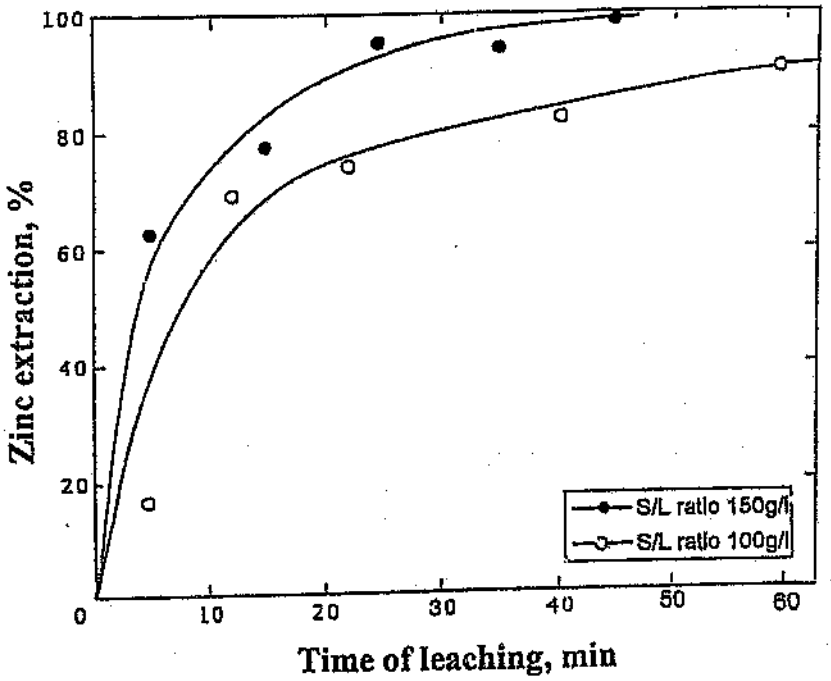


Figure 4.1 Zinc extraction during leaching with 40g/l and 30g/l nitric acid. Temp.: 80-90°C; pressure: atmospheric; stirrer speed: 400rpm.

90% after 60 minutes of leaching when mechanical agitation and heating were stopped (figure 4.1). The degree of zinc extraction increased further to 93.81% (table 4.1) when additional 40g of nitric acid was added to the slurry and allowed to stand for over 40 minutes.

The loss in weight of the samples are also given in table 4.1. It can be observed that the amount of zinc extracted is consistent with the loss in weight of the sample for each experiment. As indicated in the table, the concentration of elemental sulphur in the leach residues was found to be about the same (approximately 40%) in both cases which corresponds to 24.92g and 14.43g for experiments 1 and 2 respectively. In both experiments, about 50% of the initial sulphide sulphur was

converted to the elemental state.

4.2 Results of Leaching in Froth experiments

4.2.1 Results of batch leaching in froth experiments

Results of the batch leaching in froth experiments are presented in table 4.2 and figures 4.2 to 4.6.

Rapid and high extraction of zinc were obtained in experiments 1 (72.00%) and 2 (78.37%) than in experiment 3 (56.31%) probably due to the low initial nitric acid concentration of 12.28g/l used in the latter. It can be seen from table 4.2 that the percentage zinc extraction is consistent with the loss in weight of the initial sample. The ratio of the amount of zinc extracted to the amount of nitric acid used is also given in the table and it increases with decrease in the concentration of nitric acid in the leaching solution. It can also be observed from the table that although the highest concentration of nitric acid was used in experiment 1, the degree of zinc extraction and nitric acid regeneration were lower than those of experiment 2 in which a lower concentration of nitric acid (24.57g/l) was used. The highest regeneration of nitric acid was obtained in experiment 3 in which the initial nitric acid concentration was the lowest (12.28g/l). Figure 4.2 shows the rate of decomposition of the zinc sulphide concentrate at different concentrations of nitric acid whilst figure 4.3 depicts their corresponding nitric acid regeneration curves. It

can be seen that all the regeneration curves indicate an initial drop in the concentration of nitric acid, and thereafter attain a relatively stable level. Data used for the calculation of degree of nitric acid regeneration in each experiment and sample calculation are given in appendices A.1 and A.2 respectively.

Table 4.2 Batch leaching in froth tests with simultaneous nitric acid regeneration

Experiment	1	2	3
Zinc extraction, %	72.00	78.37	56.31
Loss in weight of sample, %	56.09	59.18	45.63
HNO_3 used, mol	0.76	0.59	0.29
Zinc extracted per HNO_3 used, mol/mol	0.68	0.97	1.39
HNO_3 concentration in final solution, g/l	25.51	20.25	9.23
Regeneration of nitric acid, %	60.72	88.59	97.79
Elemental sulphur in residue, %	30.40	37.10	22.01
Initial sulphide sulphur converted to S^o, %	44.96	50.99	40.29
Amount of elemental sulphur converted to SO_4^{2-}, %	19.41	16.45	7.64

Volume of leaching solution: 1.5l; H_2SO_4 concentration: 72.13g/l; temperature:80-90°C; pressure:50kPa; time: 45 minutes.

The amount of elemental sulphur generated which was further oxidised to the sulphate ion increased with increase in concentration of nitric acid in the leaching solution. As can be seen from the table, the amount of elemental sulphur converted to the sulphate ion was highest in experiment 1 (19.41%) and lowest in experiment 2 (7.64%) in which the highest and lowest concentrations of nitric acid were used respectively.

During experiment 3, it was observed that most of the mineral particles lost their

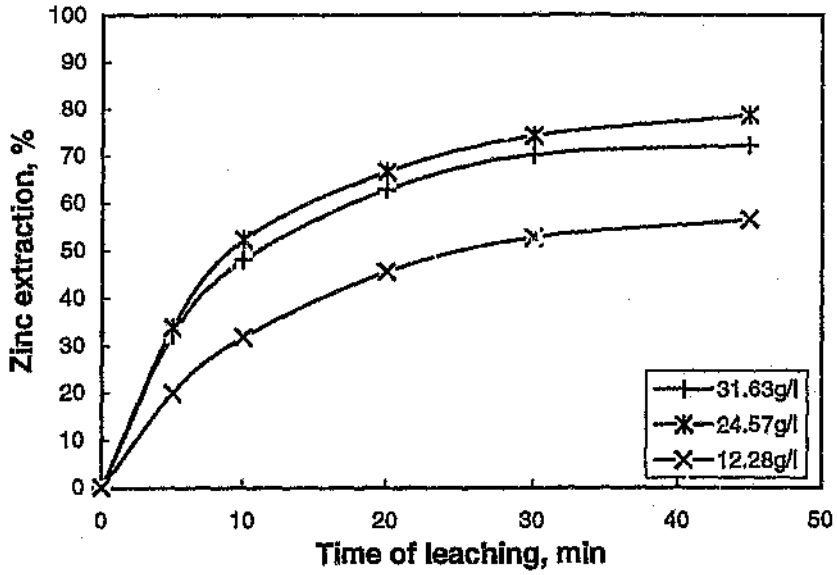


Figure 4.2 Zinc extraction into spent electrolyte containing 31.63g/l, 24.57g/l and 12.28g/l nitric acid. Conc. of H_2SO_4 : 72.13g/l; Temp.: 80-90°C; pressure: 50kPa.

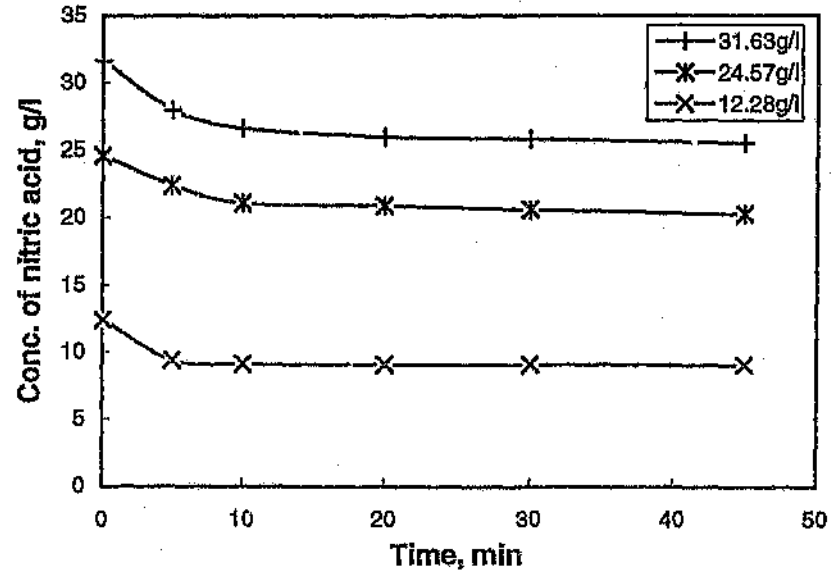


Figure 4.3 Nitric acid regeneration during zinc extraction into spent electrolyte containing 31.63g/l, 24.57g/l and 12.28g/l nitric acid. Temp.: 80-90°C; conc. of H_2SO_4: 72.13g/l; pressure: 50kPa.

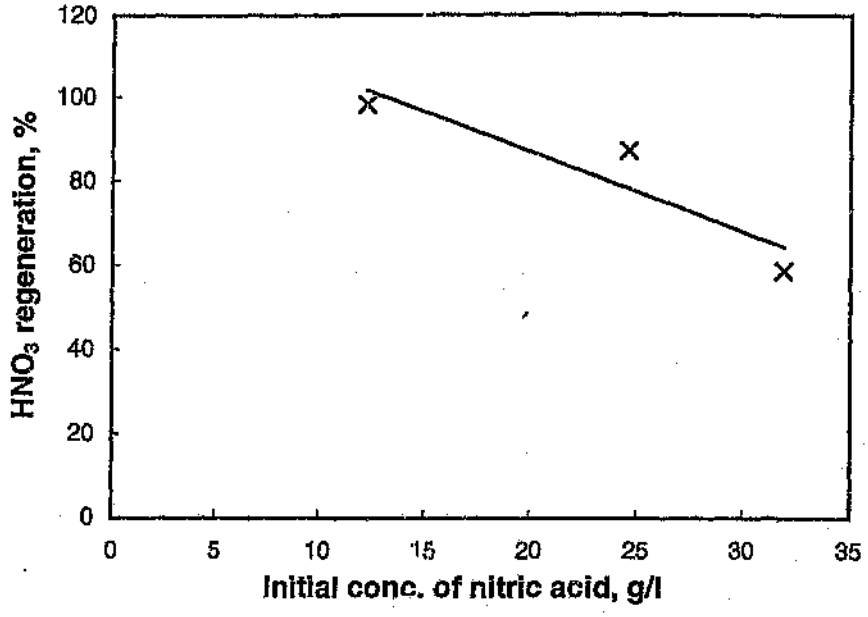


Figure 4.4 Variation of nitric acid regeneration with initial conc. of nitric acid. Temp.: 80-90°C; pressure: 50kPa.

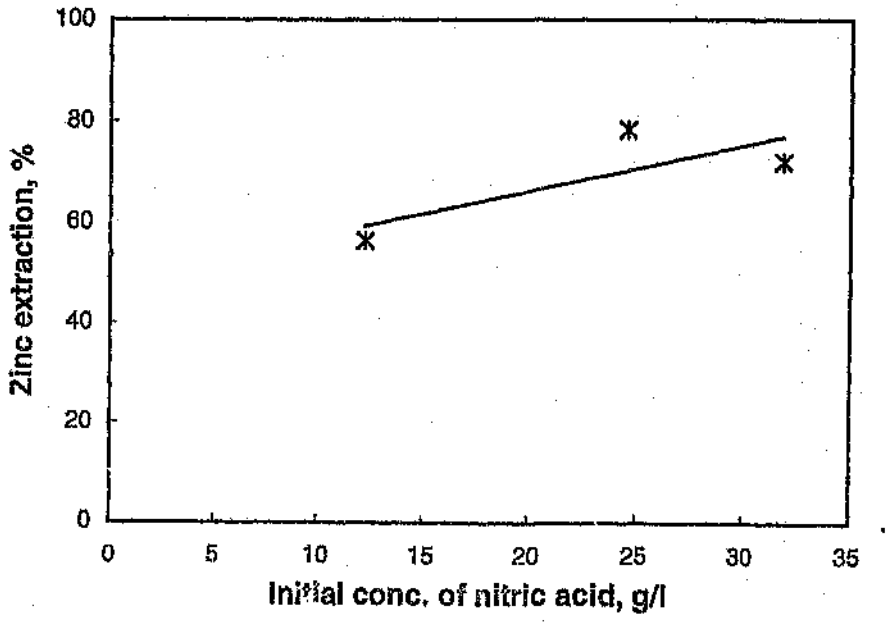


Figure 4.5 Variation of zinc extraction with initial conc. of nitric acid. Temp.: 80-90°C; pressure: 50kPa.

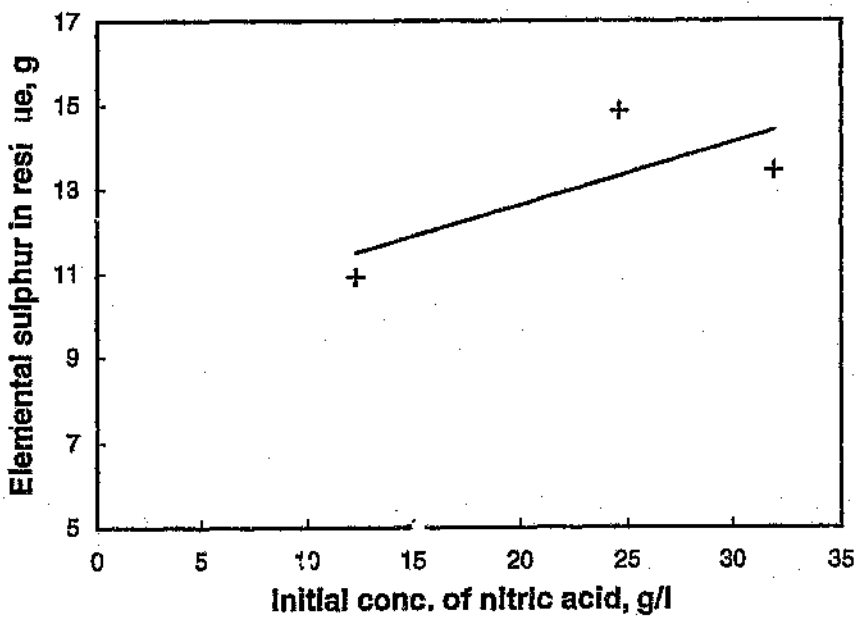


Figure 4.6 Variation of elemental sulphur generated with initial conc. of nitric acid. Temp.: 80-90°C; pressure: 50kPa.

floatability initially, but after collecting them from the bottom and re-introducing them into the main column in the course of the experiment, the particle floatability improved. This can be ascribed to the fact that due to the low nitric acid concentration, the amount of elemental sulphur initially generated was not enough to render most of the particles sufficiently hydrophobic or aerophillic. However, with the regeneration of the consumed nitric acid, more sulphide sulphur was converted to the elemental state which made the particles floatable when they were recycled once into the reactor.

Figure 4.4 shows the variation of the degree of nitric acid regeneration with the initial concentration of nitric acid as observed in the three experiments. It can be seen from the figure that the degree of nitric acid regeneration varies inversely as

the concentration of nitric acid in the leaching solution. The variations of total zinc extracted and elemental sulphur generated with the initial concentration of nitric acid are also presented in figures 4.5 and 4.6 respectively. It is observed from these figures that the percentage zinc and sulphur extractions increased with increase in initial concentration of nitric acid.

4.2.2 Results of continuous leaching in froth experiments

Results of the continuous leaching in froth experiments are presented in table 4.3 and figure 4.7(a and b). The degree of zinc extraction obtained in each processing stage is given in the table. Due to different zinc contents of the solids used in each stage, the corresponding mass of zinc extracted is also presented in the table. The percentage loss in weight of the sample as given in the table agrees with the respective amount of zinc extracted. It can be seen from the table that the degree of nitric acid regeneration varied between 33.63 and 97.22. The comparatively low

Table 4.3 Tests on continuous Leaching in Froth with simultaneous HNO_3 regeneration

Stage of processing	1	2	3
Zinc extraction, %	25.26	20.89	38.43
Mass of Zn extracted, g	72.92	39.51	53.22
Loss in sample weight, %	25.10	13.52	23.14
HNO_3 regeneration, %	97.22	33.63	88.06
Zn extracted per HNO_3 used, mol/mol	1.91	1.03	1.39
S^o in residue, %	7.47	13.60	26.40

Temperature:80-90°C; pressure:150-200kPa; time of leaching in each stage:20 minutes. The concentrations of nitric acid in sample solutions and wash water are given in appendix B.1.

value of 33.63% regeneration obtained in the second stage can be attributed to the low rate of transportation of NO_2 into the main column when gas recycling pump 8 seized in the course of the experiment. The concentrations of nitric acid in the filtrates and wash water and calculation of the degree of nitric acid regeneration in each stage are given in appendices B.1 and B.2 respectively.

The ratio of the amount of zinc extracted to that of nitric acid used in each stage is also presented in the table. It can be seen that the ratio decreased from 1.91 in stage 1 to 1.03 in the second stage. This was expected because in the latter, some nitric acid needed for zinc extraction first reacted with the elemental sulphur coating before coming into contact with the unreacted zinc sulphide. The same trend was expected to be observed from stage 2 to stage 3. However, a reversed trend was observed with the ratio increasing from 1.03 to 1.39 in the third stage. This can be attributed to the comparatively slow rate of transportation of gases in the second stage when recycling pump 8 failed to function.

The percentage elemental sulphur in the leach residue as shown in the table, increased from one processing stage to the next. This explains why the particle floatability increased considerably from one stage to the next during the experiments. 47.1% of the initial sulphide sulphur was converted to elemental sulphur.

Figure 4.7a shows the cumulative zinc extraction with time during the continuous L/F processing. It can be seen from the figure that in all the processing stages, the rate of zinc extraction into solution attained a relatively constant level after about 10 to 15 minutes of leaching. This was expected as it is typical of continuous processes to attain a steady state after running for sometime. The retention time of the particles in the froth can therefore be estimated to be between 10 and 15

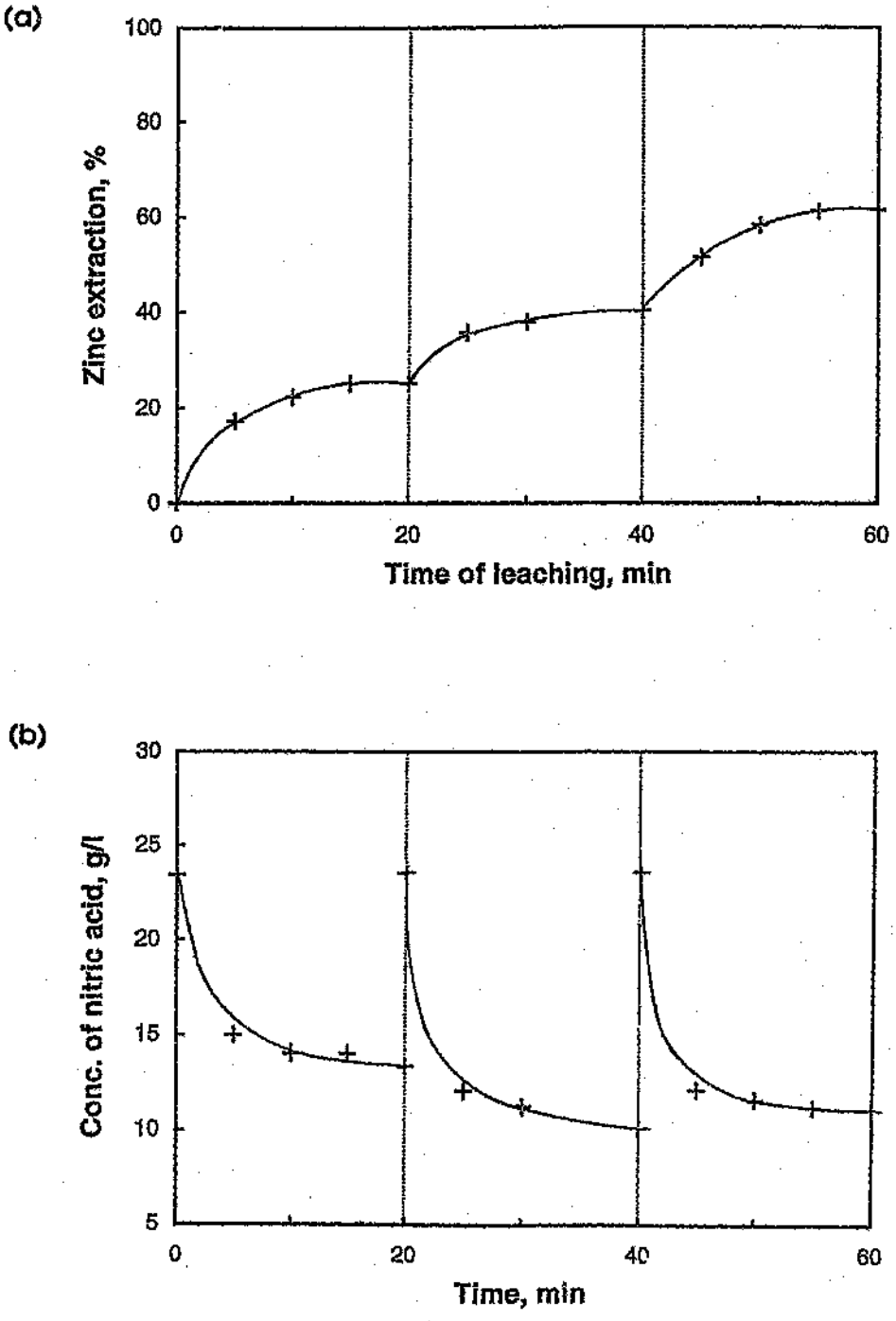


Figure 4.7 (a) Zinc extraction and (b) regeneration of nitric acid during continuous leaching in froth. Temp.: 80-90°C; pressure: 150-200kPa.

minutes. Approximately 62% of zinc was extracted from the concentrate after 60 minutes of continuous leaching in froth .

Figure 4.7b shows the concentration of nitric acid in the leaching solution with time in each stage. The graphs indicate a rapid drop in the concentration of nitric acid during the first 5 to 10 minutes after which it attains a relatively stable level due to its regeneration in the reactive froth. Due to the seizure of gas recycling pump 8 during the second processing stage, only three data points were obtained as compared to four in the first and third stages (figure 4.7).

4.2.3 Results of five-stage leaching in froth processing

Results of the five-stage leaching in froth processing are presented in table 4.4 and figures 4.8 and 4.9. The results for L/F 1 given in the table are based on the assumption that all the 5 experiments (appendix C.1) were carried out as a single experiment. For example, the percentage zinc extraction equals the total mass of zinc extracted in all the five experiments divided by the sum total of the initial masses of zinc in the feed used in the five experiments etc. However, the concentration of nitric acid in final the solution and degree of nitric acid regeneration are given as a range. The argument is that if the five experiments were conducted as a single experiment in a larger L/F reactor, the nitric acid concentration and degree of regeneration could be within or even greater than the respective range of values stated.

It can be observed from the table that the ratio of zinc extracted to the amount of nitric acid used decreased with increase in the elemental sulphur content of the feed used (elemental sulphur content of feed used is given in figure 4.9). Due to the fact that nitric acid regeneration occurs mainly in the froth, it was expected that the

Table 4.4 Five-stage le.. ing in froth processing with simultaneous regeneration of HNO_3

Stage of processing		LF/1	LF/2	LF/3	LF/4	LF/5
Zinc extraction, %		60.84	41.62	66.20	57.45	67.25
Loss in sample weight, %		46.21	21.53	26.62	25.60	15.87
HNO_3 used, mol		2.81	1.05	0.59	0.59	0.47
Zn extracted per HNO_3 used, mol/mol		1.21	0.78	0.40	0.53	0.25
HNO_3 conc. in final solution, g/l	FF	10.00	20.00	20.00	10.00	20.00
	NF	10.00 - 5.00	20.00	20.00	10.00	20.00
HNO_3 regeneration, %		46.10 - 80.39	57.09	51.50	48.90	39.37
Zinc content, %	FF	18.42	21.90	7.26	20.13	4.90
	NF	35.65	30.89	10.95	14.26	5.80
Elemental sulphur, %	FF	35.52	41.12	64.18	42.08	74.76
	NF	21.78	26.97	49.29	39.76	56.00

Temperature: 80-90°C; Pressure: 100-200kPa.

concentration of nitric acid in the FF would be greater than that in the NF. However, the results in the table indicate that nitric acid concentration was almost the same in both fractions at each stage. This can be ascribed to the interdependence of the froth and continuous liquid phases.

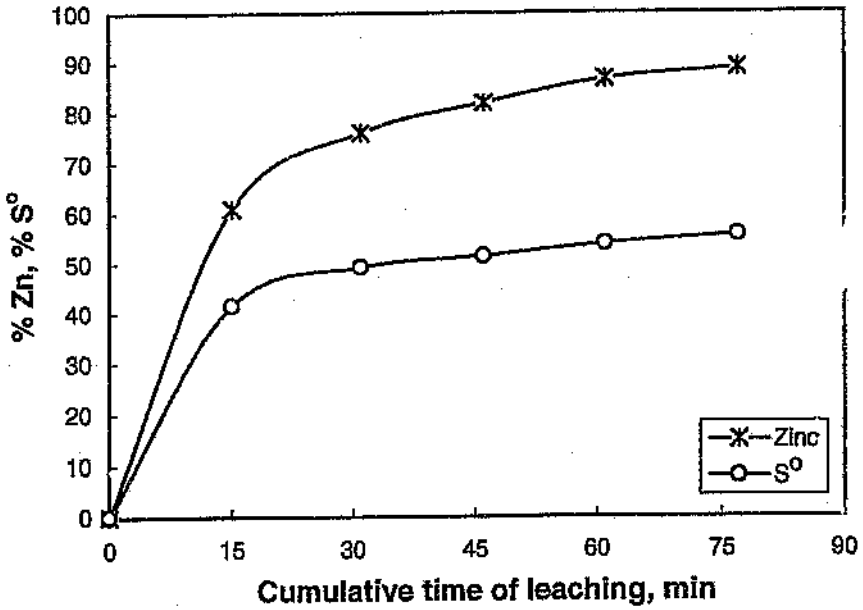


Figure 4.8 Cumulative percentage zinc extraction and elemental sulphur generated during 5-stage leaching in froth processing. Temp.: 80-90°C; pressure: 100-200kPa.

The concentrations of zinc and elemental sulphur in the floatable (FF) and non-floatable (NF) fractions determined after each stage are also shown in the table. An important observation is that with the exception of L/F 4, zinc concentration in the FF was lower than that of the NF. It can also be seen that the trend of elemental sulphur concentration in the FF and NF is directly opposite to that of zinc concentration in the residues.

Figure 4.8 depicts the cumulative zinc and sulphur extractions during the five-stage processing. The fast reaction with nitric acid resulted in about 75% zinc extraction after 30 minutes of leaching in froth after which the degree of extraction increased gradually to 88.94% during the next 47 minutes of leaching. The conversion of sulphide sulphur to elemental sulphur followed the trend of zinc extracted into solution. 55.65% of the initial sulphide sulphur reported as

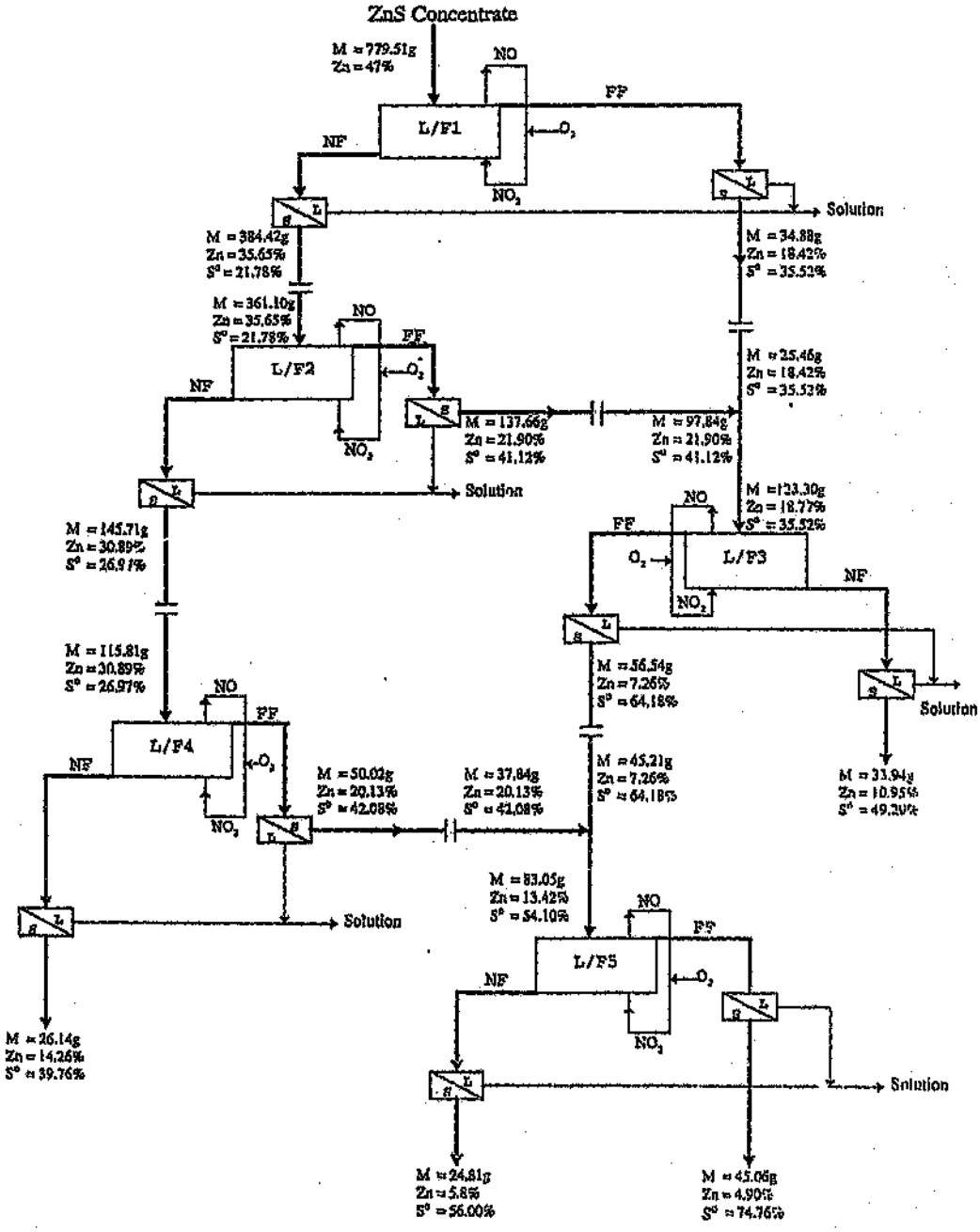


Figure 4.9 Simplified flowsheet of the 5-stage L/F processing

elemental sulphur at the end of the five stage processing. A simplified flowsheet of the five-stage L/F processing is presented in figure 4.9.

4.3 Results of leaching of residues obtained from the L/F experiments in the batch reactor

These results are presented in table 4.5 and figure 4.10. For the sake of clarity, the percentage zinc extraction as well as the mass of zinc extracted are both indicated in the table. It must be noted that the concentration of zinc in residue B in which case elemental sulphur was extracted prior to leaching was higher (42.93%) than that of residue A (36.89%). Hence the 93.4% zinc extraction obtained from leaching of residue B corresponded to a greater mass of zinc than 98% in the case of residue A. The loss in weight of the sample as presented in the table is consistent with the mass of zinc extracted. This suggests that the elemental sulphur layer on particles of residue A was porous and therefore the leaching solution diffused through it and reacted with the zinc sulphide resulting in 98% zinc extraction and converting more sulphide sulphur into the elemental state. It can be seen from

Table 4.5 Leaching of residues obtained from the L/F tests in the batch reactor

Experiment	Zinc extraction, %	Mass of zinc extracted, g	Loss in sample weight, %	S^o in residue, %
Residue A	98.0	18.40	53.28	66.7
Residue B	93.4	20.39	58.39	40.0

S/L ratio: 51g/l; temperature: 80-95°C; pressure: atmospheric; time of leaching: 60 minutes; stirrer speed: 400rpm.

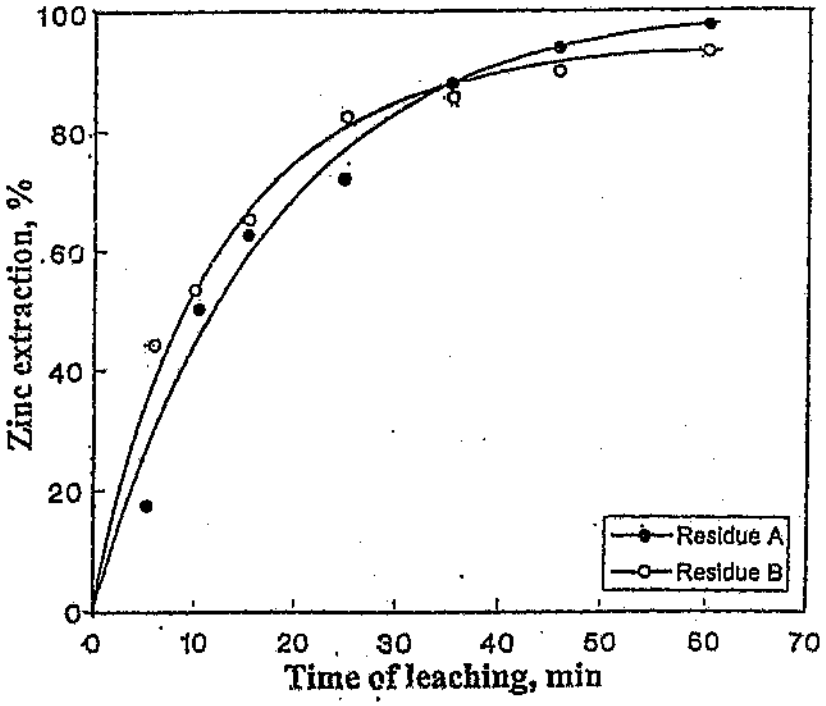


Figure 4.10 Zinc extraction during leaching of residues obtained from L/F experiments in the batch reactor. S/L ratio: 51g/l; Temp.: 80-95°C; pressure: atmospheric; stirrer speed: 400rpm.

tables 3.7 and 4.5 that the elemental sulphur content of residue A increased from 19.22% to 66.7% whilst that of B increased from 0% to 40%. These increments correspond to 6.08g and 8.46g for residues A and B respectively. Thus the amounts of zinc and elemental sulphur produced in the case of residue B correspond respectively to 1.11 and 1.39 times those of residue A.

It can also be seen from figure 4.10 that the rate of zinc extraction for residue B was higher than that of residue A during the first 35 minutes of leaching. This could be ascribed to the fact that the elemental sulphur coating on particles of

residue A served as a boundary layer through which the leaching solution had to diffuse before coming into contact with the unreacted zinc sulphide whereas in the case of residue B, there was no such layer at the beginning of the experiment.

5.0 DISCUSSION

The direct leaching of zinc sulphide concentrate requires oxygen as an oxidant in acidic medium to convert the sulphide sulphur to elemental sulphur and extract zinc into solution as zinc sulphate for subsequent recovery. The equation for the reaction has already been given in equation 1.2, which is:

$$ZnS_{(s)} + 0.5O_{2(g)} + H_2SO_{4(aq)} = ZnSO_{4(aq)} + S^o_{(s)} + H_2O_{(l)}$$

However, the above reaction is relatively slow and controlled by the limited solubility of oxygen in aqueous solutions at moderate temperature and low oxygen pressure[49]. As a result, high temperatures and pressures, high rate of oxygen dispersion, as well as vigorous agitation are applied in order to obtain acceptable reaction rates[4]. These stringent conditions make the leaching process technically difficult. Fortunately, however, nitric acid is one of the most efficient carriers of oxygen into solution, being much more efficient than direct oxidation with either high-pressure air or oxygen itself[19] and is also easy to regenerate. Thus oxygen in equation 1.2 can be substituted by nitric acid to give equation 2.1, which is :

$$3ZnS_{(s)} + 2HNO_{3(aq)} + 3H_2SO_{4(aq)} = 3ZnSO_{4(aq)} + 3S^o_{(s)} + 2NO_{(g)} + 4H_2O_{(l)}$$

The above explains why sulphuric acid (the spent electrolyte) and nitric acid were used in all the experiments. Thus the spent electrolyte provided the necessary acidic medium whilst nitric acid acted as a better oxidant than oxygen itself. Equation 2.1 therefore represents the basic reaction in all the experimentation conducted in this study.

5.1 Leaching kinetics of zinc sulphide concentrate with nitric acid

The reaction kinetics of zinc sulphide concentrate decomposition in spent zinc sulphate electrolyte with the catalytic action of nitric acid has not yet been exactly investigated. It is known however, that initiation and sustenance of the vigorous reaction of nitric acid with metal sulphides require a minimum level of its concentration which in turn, depends on the leach material and other conditions[47]. In the Arseno-Process, the concentration of nitric acid ranges between 70 and 110g/l and decomposition of refractory sulphide is complete after 8 to 10 minutes at 90-100°C or even after 2-5 minutes at 180°C, provided oxygen is continuously supplied in excess for the oxidation of NO[4]. Also in the Nitrox Process, decomposition of refractory sulphides is complete after 20 minutes at 80-90°C[43]. However, with regard to zinc sulphide leaching, some problems with the lowering of NO_2 dissolution rate in solution containing 25g/l nitric acid were observed[3]. Canterford et al[14] also observed nearly total decomposition of ZnS after 30 minutes of high-temperature (180-210°C) leaching and 360 minutes of low-temperature (85-95°C) experiments using near stoichiometric amounts of nitric acid. However, no information was supplied by the authors on the concentration of nitric acid and leaching kinetics.

In the present study, experiments on the leaching kinetics of the Gamsberg zinc sulphide concentrate decomposition by nitric acid have been carried out. Results obtained from these experiments (figure 4.1) suggest that during the first 20 - 30 minutes of leaching, the rate of zinc sulphide decomposition is controlled by the fast reaction with nitric acid provided nitric acid is available in a suitable quantity. Subsequently, the gradual diminishing of the leaching rate could be ascribed to diffusion through the boundary layer of the generated elemental sulphur which had not yet been oxidised further to the sulphate ion. This was particularly visible during the first experiment in which the degree of zinc

extraction increased from 97% to over 99% after the leach residue remained in contact with the leaching solution under mild conditions for a few minutes.

The results obtained were not fitted into in any of the existing kinetic leaching models as this was outside the scope of the present study. However, it could be said from these results that the first 85-90% of zinc sulphide decomposition is controlled by the fast reaction with nitric acid and the last 10-15%, equally by diffusion and chemical reaction. In both experiments, calculations showed that the amount of elemental sulphur which remained in the leach residues corresponded to merely about 50% of the oxidised sulphide sulphur. This suggests that the other 50% was oxidised further to the sulphate ion.

5.2 Zinc sulphide concentrate leaching in froth

As mentioned earlier (page 8), research on the Leaching in Froth process by Letowski et al[37,38] revealed that the oxidative reactions of sulphide leaching were relatively slow and therefore the rate of leaching in froth was not the best correlated with fast flotation. Consequently, nitric acid was selected based on the knowledge that it is one of the most efficient carriers of oxygen and can be effective through the active intermediate species of the O_2-NO-NO_2/H_2O-HNO_3-HNO_2 system. In this study, the process has been applied to the leaching of Gamsberg zinc sulphide concentrate with the consumed nitric acid being regenerated and recycled. The reactive froth was formed by the spent electrolyte containing nitric acid, a mixture of gaseous oxygen and NO_x encapsulated in the foam and particles of the concentrate suspended in the foam. The following sections discuss the regeneration and recycling of nitric acid, froth stability, zinc and elemental sulphur extraction as well as the role of the latter in the conducted experiments.

5.2.1 Nitric acid regeneration and recycling in the reactive froth

The function of nitric acid used in the conducted experiments is probably the best illustration of the unique advantages of the Leaching in Froth process. Nitric acid is not practically regenerated in the continuous liquid phase. However in the froth in which oxygen is encapsulated, multiple regeneration of nitric acid proceeds as explained earlier (page 10).

According to results of the batch leaching in froth experiments, between 60.72 and 97.79% (table 4.2) of the consumed nitric acid was regenerated after 45 minutes of leaching in reactive froth. All the regeneration curves (figure 4.3) indicate an initial drop in the concentration of nitric acid in the leaching solution during the first 10 minutes, after which it attains a relatively stable level. The initial drop in nitric acid concentration is due to the rapid oxidation of the concentrate by nitric acid. Subsequently, multiple regeneration of the consumed nitric acid in froth resulted in its attainment of the relatively constant concentration. This is evident from the fact that during the first 10 minutes, between 30 and 50% of zinc was extracted into solution (figure 4.2) when nitric acid concentration attained a relatively stable level. The increase in zinc extraction to about 72.00, 78.37 and 56.31% in experiments 1, 2 and 3 respectively was due to the multiple regeneration and recycling of nitric acid in the reactive froth.

Figure 4.4 shows that the degree of nitric acid regeneration is inversely proportional to the initial concentration of nitric acid used in the three experiments. This can be explained by the fact that with a high initial concentration of nitric acid, comparatively more elemental sulphur is generated during the first few minutes of leaching, which serves as a boundary layer

through which the leaching solution must diffuse before it comes into direct contact with the unreacted core. This possibly explains why in experiments 1 and 2, the concentration of nitric acid in solution showed a gradual decrease after the first 10 minutes as compared to an almost straight line in the case of experiment 3 (figure 4.3). The presence of a relatively large boundary layer formed by the elemental sulphur coating generated in experiment 1 could have therefore slowed down the rate of transportation of reactants and products to and from the reaction zone even though the reaction between the leaching solution and the unreacted core could still be very fast. This is also visible from the experiment on the kinetics of leaching (section 4.1) when the degree of zinc extraction increased from 97 to over 99% after the leach residue remained in contact the leaching solution under mild conditions for several minutes. Results of the leaching of residues obtained from the leaching in froth experiments (figure 4.10) also indicate that residue B in which elemental sulphur was extracted prior to leaching, had a faster initial rate of leaching than residue A.

During the three-stage continuous leaching in froth experiments, between 33.63 and 97.22% (table 4.3) of the consumed nitric acid was regenerated. The comparatively low degree of nitric acid regeneration (33.63%) during the second leaching stage is attributed to the relatively slow rate of transportation of NO_2 into the main column due to seizure of gas recycling pump 8. This illustrates the importance of the rate of transportation of gases with regard to the efficiency of nitric acid regeneration. In all the conducted experiments the speed of pumps 8 and 9 was kept at about 1.0l/min to maintain a balance between high rate of gas transportation and a stable froth. The latter is of great importance as regeneration occurs mainly in the reactive froth due to the encapsulated oxygen.

In the five-stage leaching in froth experiments, about 46 to 80% of the consumed nitric acid was regenerated after 15 to 16 minutes of processing in each stage. It can be observed from these results and those of the other L/F tests that the degree of nitric acid regeneration generally decreases with increase in the elemental sulphur content of the feed used. This is because with a larger elemental sulphur coating, the boundary layer is increased which in turn results in the rate of transportation of reactants and products to and from the reaction zone being slowed down.

Due to the interdependence of the froth and continuous liquid phases, it was difficult to confirm whether nitric acid regeneration was better in the former than the latter in the conducted experiments. It can be seen from the results in table 4.4 that the concentrations of nitric acid in both the FF and NF fractions were about the same in each stage.

The direct recycling of nitric acid is of great importance because this aspect of the L/F process presents a vast improvement over the other leaching processes that utilise nitric acid as an oxidant. The known methods of nitric acid regeneration do not deviate from the standard techniques applied in the production of nitric acid and absorption of nitrosyl compounds into sulphuric acid in the old technologies of sulphuric acid production. However, a separate plant is generally required for this purpose. To this end, it is only the high temperature (180-210°C) REDOX technology which regenerates nitric acid in-situ[4], i.e. directly during pressure leaching.

5.2.2 Froth stability

Due to the fact that multiple regeneration of nitric acid occurs in the froth in which oxygen is encapsulated, it was necessary to ensure a stable froth in the

conducted experiments. Advantage was also taken of the fact that zinc sulphate solution supports a natural froth upon aeration[2]. Maximum froth height ranged between 50 and 70cm. It has been established from this study that in order to obtain a stable froth during L/F processing of the zinc sulphide concentrate, the following should be ensured:

- The feed should be introduced from the top of the main column
- The overall pressure should not exceed 200kPa. As observed in the experiments, once this threshold value was exceeded, the froth completely disappeared.
- The speed of gas recycling pumps 8 and 9 should be about 1.0l/min.
- Sparger of porosity 1 or 2 should be used.

5.2.3 Zinc extraction

The rate of zinc sulphide decomposition in the conducted experiments was high and varied according to the concentration of nitric acid in the leaching solution, retention time of the particles in froth as well as the presence or absence of elemental sulphur on the surface of the mineral particles.

As in the experiments on kinetics of leaching, the rate of zinc sulphide decomposition during the leaching in froth experiments was controlled by the fast reaction with nitric acid for the first 20 to 30 minutes during which about 40-80% of zinc was extracted from the concentrate (figures 4.2, 4.7a and 4.8). Subsequently, the gradual decrease in the rate of leaching can also be attributed to diffusion of the leaching solution through the boundary layer of the generated elemental sulphur. As observed from the results, particularly those of the continuous and 5-stage L/F experiments (table 4.3 and figure 4.8), the amount of elemental sulphur generated increased with time of leaching, hence increasing

the thickness of the boundary layer.

In the batch leaching in froth experiments, although a higher initial concentration of nitric acid was used in experiment 1 (31.63g/l) than 2 (24.57g/l), the rate of zinc sulphide decomposition was about the same in both cases during the first five minutes (figure 4.2) and thereafter, it was faster in experiment 2 than experiment 1. This suggests that although the amount of zinc extracted generally increases with increase in the initial concentration of nitric acid in solution (figure 4.5), there exists a threshold nitric acid concentration beyond which this general trend does not hold because of the multiple regeneration of nitric acid. The rate of zinc sulphide decomposition in the case of experiment 3 (figure 4.2) also shows that for fast leaching kinetics, the initial concentration of nitric acid must be higher than a certain threshold value. However, in terms of the ratio of total amount of zinc extracted to the amount of nitric acid used, experiment 3 in which the lowest initial nitric acid concentration was used had the highest value of 1.39 which is about twice that of experiment 1 (table 4.2) in which the highest concentration of nitric acid was used. In this respect, it could be said that experiment 3 was the most efficient, followed by experiment 2 and lastly experiment 1. It should also be noted that the degree of nitric acid regeneration followed the same trend as the above mentioned ratio.

The ratio of zinc extracted to the amount of nitric acid used in the case of the continuous and five-stage leaching in froth experiments decreased from one stage of processing to the next. This can be attributed to the elemental sulphur coating on the particles in the second and subsequent stages which served as a boundary layer and therefore retarded the decomposition of the unreacted zinc sulphide by nitric acid. It can be seen that in all the experiments, some amount of the elemental sulphur formed was oxidised further to the sulphate ion. This

shows that some of the nitric acid needed for oxidation of the zinc sulphide reacted with the elemental sulphur and hence resulted in decrease in the said ratio. In these cases also, the degree of nitric acid regeneration followed the same trend as that of the ratio of zinc extracted to the amount of nitric acid used. An exception however, is the second stage of the continuous leaching in froth experiments (table 4.3) during which the rate of transportation of gases was relatively slow due to seizure of gas recycling pump 8.

An important observation from the results of the experiments on five-stage leaching in froth processing is that, with the exception of L/F 4, the zinc concentration in the floatable fraction, FF is lower than that of the non-floatable fraction, NF (table 4.4) in each stage. From the distribution of zinc in table 3.3, it is noted that zinc is almost evenly disseminated in all the size fractions. The fact that zinc concentration in the FF is lower than that of the corresponding NF confirms that leaching is better in the froth phase than in the continuous liquid phase. The anomaly observed in L/F 4 could be due to the fact that it was the second time of processing the non-floatable fraction of the non-floatable fraction of L/F 1 (see figure 4.9).

It is evident from the results that the degree of zinc extraction is a function of retention time of the mineral particles in the reactive froth. Between 56.31 and 78.37% of zinc was extracted after 45 minutes of batch leaching in froth experiments. In the continuous leaching in froth experiments, a total zinc extraction of about 62% was obtained after 60 minutes of leaching with a retention time (time at which zinc extraction attained a relatively stable level) of about 10 to 15 minutes in each stage (figure 4.7a). It is obvious that the degree of zinc extraction would [illegible]ed further after one or more stages of continuous leaching in [illegible]ing. This is supported by the fact that the

highest zinc extraction of 88.94% was obtained after 77 minutes of five-stage leaching in froth processing with an average retention time of about 15 minutes in each stage.

5.2.4 Elemental sulphur extraction and its role

The role of elemental sulphur in the conducted experiments demonstrates how the leaching in froth process makes use of some of the properties acquired by the mineral particles in the course of leaching to carry out certain functions which would otherwise involve the use of expensive reagents. Letowski[28] also made use of the natural hydrophobicity of graphite and the hydrophobicity acquired by sulphides during the mineral graphite purification in reactive froth.

In the routine flotation process, certain chemical reagents such as activators and collectors are used to selectively alter the surface properties of the mineral particles of interest and thus render them sufficiently hydrophobic to be amenable to flotation. In the present study however, none of these reagents were used. The elemental sulphur in reaction (2.1.), once generated, coats the surface of the mineral particles and renders them sufficiently hydrophobic. As a result, they can cling or attach themselves to the rising gas bubbles and undergo a collectorless flotation.

During the batch leaching in froth experiments, between 40.29 and 50.99% (table 4.2) of the initial sulphide sulphur remained in the leach residue as elemental sulphur. In the continuous and five-stage leaching in froth processing, about 47% and 56% of the sulphide sulphur reported as elemental sulphur respectively. As observed in the experiments, particularly those on the continuous and five-stage leaching in froth processing, particle floatability increased considerably from one processing stage to the next due to increase in the amount of elemental sulphur

formed. Figure 4.8 depicts how the concentration of elemental sulphur in the solids increased with time of leaching during the five-stage leaching in froth processing. From the trends of sulphur and zinc recoveries in figure 4.8 and those of figures 4.5 and 4.6 during the batch leaching in froth experiments, it can be concluded that the amount of elemental sulphur generated during the conducted experiments was proportional to the amount of zinc extracted into solution.

Results of the five-stage leaching in froth experiments illustrate further the role of elemental sulphur in the conducted experiments. It can be seen from table 4.4 that the concentration of elemental sulphur in the floatable fraction was higher than that of the corresponding non-floatable fraction which is directly opposite to the general trend of zinc concentration in these fractions. This confirms the fact that the mineral particles attained their hydrophobic or aerophillic property due to the generated elemental sulphur which coated their surfaces.

Evidently, elemental sulphur as the only component responsible for the floatability of the mineral particles should not simultaneously be subjected to dissolution or other chemical transformation which might affect the ability of the particles to float. Forward and Warren[50] separated the factors that may control the rate of dissolution of sulphide minerals into three categories as follows:

(i) mass transfer of reactants or products in the solution,

(ii) chemical reaction at the mineral surface, or in solution and

(iii) coating of insoluble products on the surface of the mineral.

They reported that when oxidation occurs below 118°C, the film of elemental sulphur that is formed is porous and does not inhibit oxidation. However, Brennecke et al[20] also reported that a further gradual oxidation of the generated elemental sulphur to sulphate ion:

$$S^{o} + 2HNO_3 = SO_4^{2-} + 2H^{+} + 2NO \quad (5.1)$$

is inevitable even at the low temperature (80-90°C) of processing. Results obtained from the present study seem to agree with the observation made by Brennecke et al. Approximately 8 to 19% of the oxidised sulphide sulphur was oxidised further to the sulphate ion in the batch L/F experiments (see table 4.2 and appendix A.1). In the continuous L/F experiments, a total of 9.8% of the generated elemental sulphur was converted to sulphate ion (see appendix B.2) whilst during the five-stage L/F experiments a total of 20.59% of the elemental sulphur was oxidised (appendix C.1). The amount of elemental sulphur which is further oxidised to the sulphate ion in the conducted experiments increases with increased retention time of the mineral particles in the leaching medium as well as the concentration of nitric acid in solution.

5.3 Two-stage leaching in froth processing

A simplified flowsheet for zinc sulphide concentrate leaching in froth is presented in figure 5.1. In the first reducing leaching in froth stage, removal of nitric acid from the leach solution directed to standard purification and electrolysis is carried out by its reduction to nitric oxide using fresh zinc sulphide concentrate in froth. Gaseous nitrogen is a carrier which facilitates the removal of nitric oxide from the solution directed to zinc electrolysis. A mixture of gaseous N_2, NO and H_2O is then contacted with under-stoichiometric amount of oxygen and directed to the absorption unit where absorption of the formed NO_2 in the spent electrolyte is carried out. A small amount of NO which is not absorbed and the total amount of the carrier N_2 are recycled to the reducing leaching stage.

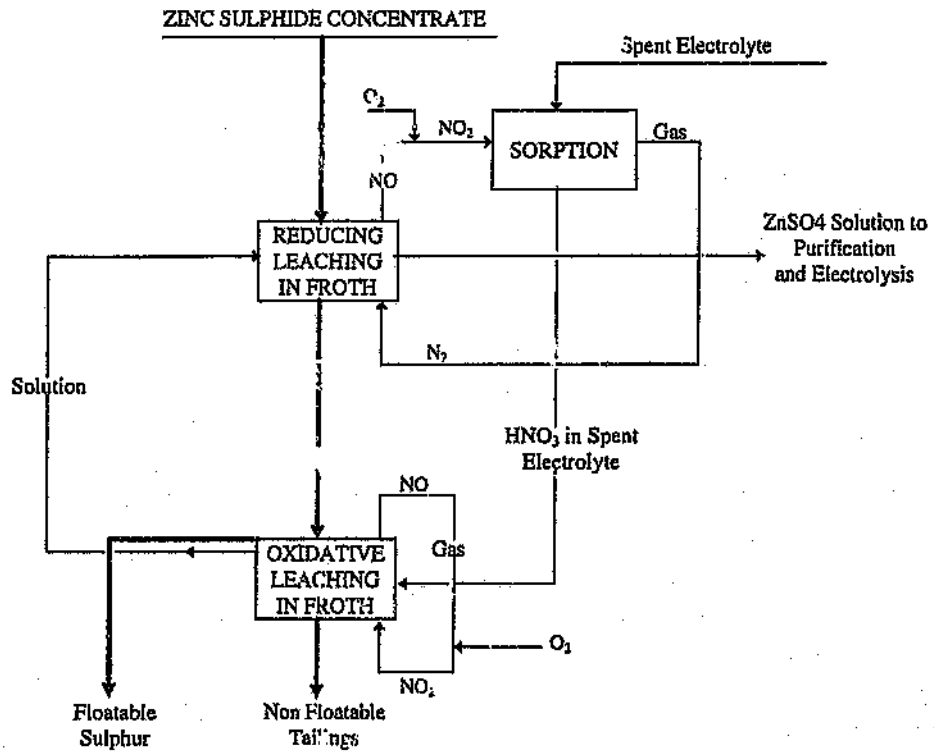


Figure 5.2 Simplified flowsheet of leaching in froth processing of zinc sulphide concentrate[39]

The partially leached concentrate from the first stage is then directed to the second or oxidative leaching in froth stage. In this stage, a substantial part of the zinc is extracted from the solid phase with simultaneous regeneration of nitric acid under elevated oxygen pressure.

Thus in the tests on five-stage L/F processing for example, the final leach solution from all the stages can be combined and subjected to the reducing leaching in froth stage where the solution will be contacted with a calculated amount of fresh concentrate for the removal of residual nitrate and subsequent solution treatment as described above. The solid or partially leached concentrate

from the reducing leaching in froth stage can then be subjected to one or more oxidative leaching in froth stages for the extraction of the remaining zinc with simultaneous regeneration of nitric acid.

Assuming that the residue obtained after oxidative leaching in froth is subsequently leached in the batch reactor (figure 3.1) to recover the remaining zinc as described in section 3.5.3, then the NO which will be produced can be channelled to the NO stream from either the reducing or oxidative leaching in froth stage for the eventual regeneration of nitric acid. Such incorporation into the proposed flowsheet could result in a further considerable reduction in the amount of nitric acid to be used and at the same time, ren[illegible] the process environmentally friendly. In this case also, zinc and elemental sulphur recoveries can be increased to 92.19% and 58.06% respectively if treated as residue A or 92.26% and 59.06% if treated as residue B, according to results obtained from leaching of the L/F residues in the batch reactor (section 4.3).

6.0 SUMMARY AND CONCLUSIONS

The regeneration and recycling of nitric acid during batch and continuous leaching in froth processing of the Gamsberg zinc sulphide concentrate have been investigated. The degree of zinc extraction as well as elemental sulphur recovery with respect to the initial sulphide sulphur content of the feed under different processing conditions have also been determined. The following conclusions can be drawn from the study:

- Leaching of zinc sulphide concentrate in froth allows for the extraction of zinc with simultaneous regeneration and recycling of nitric acid in one unit process which can be carried out at 80-90°C and under 50-200kPa.

- In the L/F process, multiple regeneration of nitric acid occurs in the reactive froth due to the encapsulated oxygen. As a result, the amount of nitric acid used can be considerably lower than in the continuous liquid phase.

- The degree of nitric acid regeneration varies inversely as the initial concentration of nitric acid in solution. However, for rapid reaction kinetics, the initial nitric acid concentration must be greater than a certain threshold value. An initial nitric acid concentration of 22 to 24g/l is therefore suggested.

- The rate of transportation of gases affects the regeneration of nitric acid. For efficient nitric acid regeneration, the gas flow rate into the main reactor should be about 1l/min, i.e. about 300rpm gas recycling pump speed, to maintain a balance between a stable froth and fast rate of

transportation of gases.

- A stable froth which is a requisite for efficient nitric acid regeneration can be ensured by introducing the solid-liquid suspension from the top of the main column into the leaching solution, using a sparger of porosity 1 or 2, maintaining a gas flow rate of about 1l/min. and a total pressure of less than 200kPa.

- The L/F process can be carried out in a continuous or batch mode for the extraction of zinc from its sulphide concentrate with the simultaneous regeneration of nitric acid. Also, during the L/F process, the flotation phenomenon can be used for the selective separation of the floatable particles from the non-floatable particles from one stage of leaching to another and at the same time, regenerate the consumed nitric acid in the froth.

- The degree of zinc extraction and recovery of elemental sulphur with respect to the initial sulphide sulphur increase with increase in concentration of nitric acid in solution as well as the retention time of the particles in the reactive froth. The amounts of zinc and elemental sulphur extracted from the concentrate can be increased further if the leach residue obtained after L/F processing is leached in the batch reactor.

- The presence of elemental sulphur on the surface of the mineral particles decreases the amount of zinc extracted and seems to decrease the efficiency of nitric acid regeneration. These effects increase with increase in the elemental sulphur content of the feed.

- The amount of oxidised sulphide sulphur which is further converted to the sulphate ion increases with increase in the concentration of nitric acid as well as retention time of the mineral particles in the leaching medium.

The results obtained from this study confirm that the $HNO_3/NO_x/O_2$ oxidative system has an exceptional self-regenerating ability if it is acting in froth. The leaching in froth processing of zinc sulphide concentrate can therefore be considered as an alternative to the existing methods of zinc recovery. Due to efficient and multiple regeneration of nitric acid in the reactive froth, the amount used can be considerably lower than in the continuous liquid phase. This together with high zinc extraction as well as the environmentally friendly conditions, among others, represent a potential for substantial savings in capital and operating costs. Although the removal of nitrates from zinc sulphate solution directed to electrolysis still needs to be improved upon, their removal by reducing leaching in froth seems to be relatively easy.

In this study, no investigation on the disappearance of froth after a total pressure of 200kPa has been exceeded was carried out. It is however suspected that this is a mechanical problem which with some more modifications in the leaching in froth installation, could be overcome. Once this is achieved, it is anticipated that better nitric acid regeneration and zinc extraction than those reported in this study could be obtained.

APPENDICES

APPENDIX A

A.1 DATA USED FOR THE CALCULATION OF DEGREE OF NITRIC ACID REGENERATION IN THE BATCH L/F EXPERIMENTS

EXPERIMENT 1

Mass of ZnS concentrate	= 100.43g
Mass of Zn in concentrate	= 100.43g x 47% = 47.20g
Mass of Fe in concentrate	= 100.43g x 7.4% = 7.43g
Mass of Mn in concentrate	= 100.43g x 0.97% = 0.97g
Mass of sulphide sulphur in concentrate	= 100.43g x 29.7% = 29.83g
Volume of leaching solution	= 1.5l
Volume of nitric acid used	= 65ml = 65mlx1.34g/mlx55% = 47.91g
Zn extraction	= 72.00 %
Fe extraction	= 61.23%
Mn extraction	= 57.26%
Mass of final residue	= 44.094g
Elemental sulphur content of final residue	= 30.40%
Mass of elemental sulphur produced	= 13.41g
Mass of elemental sulphur converted to SO_4^{2-}	= 3.23g
Volume of final solution	= 1.5l
HNO_3 concentration in final solution	= 25.71g/l
Volume of wash water	= 5.0l
HNO_3 concentration in wash water	= 0.20g/l

EXPERIMENT 2

Mass of ZnS concentrate	= 100.64g
Mass of Zn in concentrate	= 100.64g x 47% = 47.30g
Mass of Fe in concentrate	= 100.64g x 7.4% = 7.44g
Mass of Mn in concentrate	= 100.64g x 0.97% = 0.98g
Mass of sulphide sulphur in concentrate	= 100.64g x 29.7% = 29.89g
Volume of leaching solution	= 1.5l
Volume of nitric acid used	= 50ml = 36.85g
Zn extraction	= 78.37 %

APPENDIX A CONTINUED

Fe extraction	= 62.30%
Mn extraction	= 58.40%
Mass of final residue	= 41.085g
Elemental sulphur content of residue	= 37.10%
Mass of elemental sulphur produced	= 15.24g
Mass of elemental sulphur converted to SO_4^{2-}	= 3.0g
Volume of final solution	= 1.45l
HNO_3 concentration in final solution	= 20.25g/l
Volume of wash water	= 3.18l
HNO_3 concentration in wash water	= 0.15g/l

EXPERIMENT 3

Mass of ZnS concentrate	= 100.29g	
Mass of Zn in concentrate	= 100.29g x 47%	= 47.14g
Mass of Fe in concentrate	= 100.29g x 7.4%	= 7.42g
Mass of Mn in concentrate	= 100.29g x 0.97%	= 0.97g
Mass of sulphide sulphur in concentrate	= 100.29g x 29.7%	= 29.79g
Volume of leaching solution	= 1.5l	
Volume of nitric acid used	= 25ml = 18.425g	
Zn extraction	= 56.31 %	
Fe extraction	= 43.80%	
Mn extraction	= 35.40%	
Mass of final residue	= 54.525g	
Elemental sulphur of residue	= 22.01%	
Mass of elemental sulphur produced	= 12.00g	
Mass of elemental sulphur converted to SO_4^{2-}	= 0.992g	
Volume of final solution	= 1.45l	
HNO_3 concentration in final solution	= 9.23g/l	
Volume of wash water	= 4.50l	
HNO_3 concentration in wash water	= 0.05g/l	

APPENDIX A CONTINUED

A.2 SAMPLE CALCULATION OF THE DEGREE OF NITRIC ACID REGENERATION IN THE BATCH L/F EXPERIMENTS

The reaction between the major sulphides in the Gamsberg concentrate and nitric acid can be summarised as:

$$3MS + 2HNO_3 + 3H_2SO_4 = 3MSO_4 + 3S^0 + 2NO + 4H_2O \qquad (7.1)$$

Where M = Zn, Fe, Mn

Mass of zinc extracted in experiment 1 = 47.20g x 72% = 33.98g

Number of moles of zinc extracted = $\frac{33.98g}{65.37g/mole}$

= 0.52moles

Mass of Fe extracted = 7.43g x 61.23% = 4.55g

Number of moles of Fe extracted = $\frac{4.55g}{55.85g/mole}$

= 0.082moles

Mass of Mn extracted = 0.97g x 57.26% = 0.56g

Number of moles of Mn extracted = $\frac{0.56g}{54.94g/mole}$

= 0.01moles

Total number of moles of Zn, Fe and Mn extracted = (0.52+0.081+0.01)moles
= 0.612moles

From reaction 7.1, HNO_3 required for the extraction of Zn, Fe and Mn
= 2/3 × 0.612moles
= 0.408moles

Also from the reaction 5.1,which is:

$$3ZnS + 2HNO_3 + 3H_2SO_4 = 3ZnSO_4 + 3S^0 + 2NO + 4H_2O$$

APPENDIX A CONTINUED

Number of moles of elemental sulphur generated ≡ number of moles of Zn extracted

⇒ number of moles of elemental sulphur to be generated
= 0.52moles
= 0.52moles × 32g/mole
=16.64g

Mass of elemental sulphur in residue = 13.41g

Mass of elemental sulphur converted to sulphate = (16.64 - 13.41)g
= 3.23g
= $\frac{3.23g}{32g/mole}$

= 0.101moles

From reaction 5.5, which is

$S^0 + 2HNO_3 = SO4^{2-} + 2H^+ + 2NO$

Number of moles of HNO_3 required for the conversion of 0.101moles of elemental sulphur to $SO4^{2-}$
= 2 × 0.101moles
= 0.202moles
= 0.202moles × 63g/mole
= 12.73g

Mass of HNO_3 in final solution = HNO_3 conc. in final solution × volume of solution
= 25.51g/l × 1.5l
=38.27g

Mass of HNO_3 in wash water = HNO_3 conc. in wash water × volume of wash water
= 0.2g/l x 5l
=1.00g

HNO_3 regeneration =(HNO_3 used for Zn, Fe and Mn extraction + HNO_3 used for the conversion of S^0 to SO_4^{2-} + HNO_3 in final solution + HNO_3 in wash water - initial amount of HNO_3) ÷ (initial amount of HNO_3)

APPENDIX A CONTINUED

$$\% \text{ HNO}_3 \text{ regeneration} = \frac{25 + 13.73 + 38.27 + 1.00 - 47.91}{47.91} \times 100\%$$

$$= 60.72\%$$

APPENDIX B

B.1 HNO_3 CONCENTRATION IN FILTRATES AND WASH WATER OBTAINED FROM CONTINUOUS L/F EXPERIMENTS

Table B.1 HNO_3 conc. in filtrates and wash water of stage 1

Sample	Time, min	HNO_3 conc. in filtrate, g/l	Vol. of filtrate, l	HNO_3 conc. in wash H_2O, g/l	Vol. of wash H_2O, l
1	5	15.00	0.32	0.035	2.185
2	10	14.00	0.29	0.080	0.770
3	15	14.00	0.37	0.050	1.290
4	20	13.36	0.40	0.100	2.500

Total HNO_3 in filtrates and wash water = 19.84g

Table B.2 HNO_3 conc. in filtrates and wash water of stage 2

Sample	Time, min	HNO_3 conc. in filtrate, g/l	Vol. of filtrate, l	HNO_3 conc. in wash H_2O, g/l	Vol. of wash H_2O, l
1	5	12.06	0.48	0.250	0.785
2	10	11.23	0.42	0.005	0.915
3	20	10.10	0.50	0.050	3.030

Total HNO_3 in filtrates and wash water = 15.91g

Table B.3 HNO_3 conc. in filtrates and wash water of stage 3

Sample	Time, min	HNO_3 conc. in filtrate, g/l	Vol. of filtrate, l	HNO_3 conc. in wash H_2O, g/l	Vol. of wash H_2O, l
1	5	12.10	0.22	0.250	0.985
2	10	11.60	0.41	0.100	1.065
3	15	11.20	0.43	0.050	0.930
4	20	11.06	0.40	0.100	3.950

Total HNO_3 in filtrates and wash water = 17.45g

APPENDIX B CONTINUED

B.2 CALCULATION OF DEGREE OF HNO_3 REGENERATION IN THE CONTINUOUS L/F EXPERIMENTS

Stage 1

Mass of concentrate = 614.197g
Zn concentration = 47%
Zn extraction = 25.26%
Mass of Zn extracted = 614.197g x 47% x 25.26%
= 72.92g
$= \frac{72.92g}{65.37g/mole}$

= 1.12 moles

From reaction 5.1, HNO_3 required for the above zinc extraction = 2/3 x 1.12 moles

= 0.747 moles
= 0.747 moles x 63g/mole
= 47.04g

Number of moles of elemental sulphur to be generated
= 1.12 moles
= 1.12 moles x 32g/mole
= 35.84g

Mass of elemental sulphur in residue = 460.03g x 7.47%
= 34.36g
Mass of elemental sulphur converted to SO_4^{2-} = (35.84 - 34.36)g
= 1.48g
$= \frac{1.48g}{32g/mole}$

= 0.046 moles

From reaction 5.5, HNO_3 required for the conversion of elemental sulphur to SO_4^{2-}

= 2 x 0.046 moles
= 0.092 moles
= 0.092moles x 63 g/mole
= 5.8g

APPENDIX B CONTINUED

HNO_3 regeneration = (HNO_3 used for Zn extraction + HNO_3 used for the conversion of elemental sulphur to SO_4^{2-} + total HNO_3 in filtrate and wash water of samples - initial amount of HNO_3) ÷ (initial amount of HNO_3)

$$\% HNO_3 \text{ regeneration} = \frac{47.04 + 5.80 + 19.837 - 36.85}{36.85} \times 100\%$$

$$= \frac{35.827 \times 100\%}{36.85}$$

$$= 97.22\%$$

Stage 2

Mass of feed (residue from first stage) = 403.224g
Zu concentration = 46.9%
Zn extraction = 20.89%
Mass of Zn extracted = 403.224 x 46.9% x 20.89%
= 39.51g
$= \frac{39.51g}{65.37g/mole}$

= 0.604 moles

HNO_3 required for the above zinc extraction
= 2/3 x 0.604moles
= 0.403 moles
= 0.403 moles x 63g/mole
= 25.34g

Number of moles of elemental sulphur to be generated
= 0.604 moles
= 0.604 moles x 32g/mole
= 19.328g

APPENDIX B CONTINUED

Mass of elemental sulphur in feed = 403.224g x 7.47%
= 30.12g

Total elemental sulphur to be generated = (19.328 + 30.12)
= 49.448g

Mass of elemental sulphur in final residue = 348.703g x 13.6%
= 47.42g

Mass of elemental sulphur converted to SO_4^{2-} = (49.448 - 47.42)g
= 2.028g
= $\frac{2.028g}{32g/mole}$
= 0.0634 moles

HNO_3 required for the conversion of elemental sulphur to SO_4^{2-}
= 2 x 0.0634 moles
= 0.127 moles
= 0.127moles x 63 g/mole
= 7.99g

$$\% HNO_3 \text{ regeneration} = \frac{25.34 + 7.99 + 15.913 - 36.85}{36.85} \times 100\%$$

$$= \frac{12.393 \times 100\%}{36.85}$$

$$= 33.63\%$$

Stage 3

Mass of feed (residue from second stage) = 322.821g
Zn concentration = 42.90%
Zn extraction = 38.43%
Mass of Zn extracted = 322.821 x 42.90% x 38.43%
= 53.222g
= $\frac{53.222g}{65.37g/mole}$

= 0.814 moles

HNO_3 required for the above zinc extraction = 2/3 x 0.814moles
= 0.543 moles
= 0.543 moles x 63g/mole
= 34.209g

Number of moles of elemental sulphur to be generated
= 0.814 moles
= 0.814 moles x 32g/mole
= 26.048g

Mass of elemental sulphur in feed = 322.821g x 13.60%
= 43.90g

Total elemental sulphur to be generated = (26.048 + 43.90)
= 69.948g

Mass of elemental sulphur in final residue = 248.136g x 26.40%
= 65.51g

Mass of elemental sulphur converted to SO_4^{2-} = (69.948 - 65.51)g
= 4.474g
= $\frac{4.474g}{32g/mole}$

= 0.14 moles

HNO_3 required for the conversion of elemental sulphur to SO_4^{2-}
= 2 x 0.14 moles
= 0.28 moles
= 0.28moles x 63 g/mole
= 17.64g

$$\% HNO_3 \text{ regeneration} = \frac{34.209 + 17.64 + 17.452 - 36.85}{36.85} \times 100\%$$

$$= \frac{32.451 \times 100\%}{36.85}$$

= 88.06%

APPENDIX C

C.1 CONDITIONS AND RESULTS OF THE 5-STAGE L/F EXPERIMENTS

L/F 1 (EXPERIMENTS 1 - 5)

EXPERIMENT 1

Mass of ZnS concentrate = 110.311g
Mass of Zn in concentrate = 110.311g x 47% = 51.846g
Volume of spent electrolyte used = 1.5l
Volume of nitric acid used = 50ml = 50ml x 1.34g/ml x 55% =36.85g
Temperature : 80 - 90°C
Pressure : 80kPa
Time : 15 minutes

Table C.1 Results of experiment 1 of L/F 1

	FF	NF
Mass of solids (g)	4.214	46.385
Zn content (%)	15.470	26.610
Mass of zinc in solids (g)	0.625	12.340
Elemental sulphur content (%)	27.000	32.140
Mass of elemental sulphur (g)	1.138	14.910
Volume of filtrate (l)	0.415	1.125
HNO_3 conc. in filtrate(g/l)	10.000	10.000
Volume of wash water (l)	1.370	2.880
HNO_3 conc. in wash water(g/l)	0.500	0.350
Total HNO_3 in filtrate and w. water (g)	4.835	12.260

Elemental sulphur converted to SO_4^{2-} = 2.99g
Note : Floatable fraction = FF
Non-floatable fraction = NF

EXPERIMENT 2

Mass of ZnS concentrate = 122.234g
Mass of Zn in concentrate = 122.234g x 47% = 57.45g
Volume of spent electrolyte used = 1.5l
Volume of nitric acid used = 50ml = 36.85g
Temperature : 80 - 90°C
Pressure : 80 - 85kPa
Time : 15 minutes

Table C.2 Results of experiment 2 of L/F 1

	FF	NF
Mass of solids (g)	4.011	55.542
Zn content (%)	14.490	30.410
Mass of zinc in solids (g)	0.581	16.890
Elemental sulphur content (%)	25.200	28.450
Mass of elemental sulphur (g)	1.010	15.800
Volume of filtrate (l)	0.620	0.920
HNO_3 conc. in filtrate(g/l)	10.000	10.000
Volume of wash water (l)	2.500	3.080
HNO_3 conc. in wash water(g/l)	0.500	0.350
Total HNO_3 in filtrate and w. water (g)	7.450	10.280

Elemental sulphur converted to SO_4^{2-} = 2.77g

EXPERIMENT 3

Mass of ZnS concentrate = 128.477g
Mass of Zn in concentrate = 128.477g x 47% = 60.384g
Volume of spent electrolyte used = 1.5l
Volume of nitric acid used = 50ml = 36.85g
Temperature : 80 - 90°C
Pressure : 80 - 85kPa
Time : 15 minutes

Table C.3 Results of experiment 3 of L/F 1

	FF	NF
Mass of solids (g)	3.451	45.885
Zn content (%)	7.500	27.280
Mass of zinc in solids (g)	0.259	12.520
Elemental sulphur content (%)	26.010	40.530
Mass of elemental sulphur (g)	0.900	18.600
Volume of filtrate (l)	0.610	1.000
HNO_3 conc. in filtrate(g/l)	10.000	10.000
Volume of wash water (l)	1.280	4.480
HNO_3 conc. in wash water(g/l)	0.025	0.350
Total HNO_3 in filtrate and w. water (g)	6.130	11.570

Elemental sulphur converted to SO_4^{2-} = 3.68g

APPENDIX C CONTINUED

EXPERIMENT 4

Mass of ZnS concentrate	= 120.58g
Mass of Zn in concentrate	= 120.58g x 47% = 56.673g
Volume of spent electrolyte used	= 1.5l
Volume of nitric acid used	= 50ml = 36.85g
Temperature	: 80 - 90°C
Pressure	: 80 - 85kPa
Time	: 15 minutes

Table C.4 Results of experiment 4 of L/F 1

	FF	NF
Mass of solids (g)	10.210	48.110
Zn content (%)	15.160	26.630
Mass of zinc in solids (g)	1.550	12.810
Elemental sulphur content (%)	25.200	31.420
Mass of elemental sulphur (g)	2.570	15.120
Volume of filtrate (l)	0.820	0.945
HNO_3 conc. in filtrate(g/l)	10.000	5.000
Volume of wash water (l)	1.880	3.000
HNO_3 conc. in wash water(g/l)	0.050	0.500
Total HNO_3 in filtrate and w. water (g)	8.294	6.230

Elemental sulphur converted to SO_4^{2-} = 3.11g

EXPERIMENT 5

Mass of ZnS concentrate	= 297.94g
Mass of Zn in concentrate	= 297.94g x 47% = 140.03g
Volume of spent electrolyte used	= 1.5l
Volume of nitric acid used	= 40ml = 40ml x 1.34g/ml x 55% =29.48g
Temperature	: 80 - 90°C
Pressure	: 80 - 85kPa
Time	: 15 minutes

Table C.5 Results of experiment 5 of L/F 1

	FF	NF
Mass of solids (g)	12.990	188.500
Zn content (%)	26.270	43.770
Mass of zinc in solids (g)	3.410	82.500
Elemental sulphur content (%)	5.210	10.190
Mass of elemental sulphur (g)	6.770	19.210
Volume of filtrate (l)	1.040	0.385
HNO_3 conc in filtrate(g/l)	10.000	10.000
Volume of wash water (l)	3.080	3.780
HNO_3 conc. in wash water(g/l)	0.100	0.350
Total HNO_3 in filtrate and w. water (g)	10.710	5.180

Elemental sulphur converted to SO_4^{2-} = 0.58g

L/F 2

Mass of NF residue from L/F 1 (experiments 1 - 5) = 361.103g
Mass of Zn in residue = 361.103g x 35.65%
= 128.73g
Volume of spent electrolyte used = 1.5l
Volume of nitric acid used = 90ml = 66.33g
Temperature : 80 - 90°C
Pressure : 150kPa
Time : 16 minutes

Table C.6 Results of L/F 2

	FF	NF
Mass of solids (g)	137.660	145.710
Zn content (%)	21.900	30.890
Mass of zinc in solids (g)	30.150	45.010
Elemental sulphur content (%)	41.120	26.970
Mass of elemental sulphur (g)	56.610	39.300
Volume of filtrate (l)	0.930	0.620
HNO_3 conc. in filtrate(g/l)	20.000	20.000
Volume of wash water (l)	1.900	2.700
HNO_3 conc. in wash water(g/l)	0.700	0.750
Total HNO_3 in filtrate and w. water (g)	19.93	14.425

Elemental sulphur converted to SO_4^{2-} = 8.99g

APPENDIX C CONTINUED

L/F 3

Mass of FF residue from L/F 1 and L/F 2 combined = 123.296g
Mass of Zn in residue = 123.296g x 18.77%
= 23.143g
Volume of spent electrolyte used = 1.5l
Volume of nitric acid used = 50ml = 36.85g
Temperature : 80 - 90°C
Pressure : 100kPa
Time : 15 minutes

Table C.7 Results of L/F 3

	FF	NF
Mass of solids (g)	56.538	33.938
Zn content (%)	7.260	10.950
Mass of zinc in solids (g)	4.102	3.720
Elemental sulphur content (%)	64.180	49.290
Mass of elemental sulphur (g)	36.290	16.730
Volume of filtrate (l)	0.892	0.706
HNO_3 conc. In filtrate(g/l)	20.000	20.000
Volume of wash water (l)	2.740	0.850
HNO_3 conc. In wash water(g/l)	0.400	0.400
Total HNO_3 in filtrate and w. water (g)	18.940	14.460

Elemental sulphur converted to SO_4^{2-} =3.26g

L/F 4

Mass of NF residue from L/F 2 = 115.805g
Mass of Zn in residue = 115.805g x 30.89%
= 35.770g
Volume of spent electrolyte used = 1.5l
Volume of nitric acid used = 50ml
Temperature : 80 - 90°C
Pressure : 100kPa
Time : 15 minutes

Table C.8 Results of L/F 4

	FF	NF
Mass of solids (g)	50.023	36.142
Zn content (%)	20.130	14.260
Mass of zinc in solids (g)	10.070	5.153
Elemental sulphur content (%)	42.080	39.760
Mass of elemental sulphur (g)	21.050	14.370
Volume of filtrate (l)	0.710	0.920
HNO_3 conc. in filtrate(g/l)	10.000	10.000
Volume of wash water (l)	2.445	2.625
HNO_3 conc. in wash water(g/l)	0.300	0.500
Total HNO_3 in filtrate and w. water (g)	7.830	10.512

Elemental sulphur converted to SO_4^{2-} = 5.871g

L/F 5

Mass of FF residue from L/F 3 and L/F 4 combined = 83.052g
Mass of Zn in residue = 83.052g x 13.42%
= 11.146g

Volume of spent electrolyte used = 1.5l
Volume of nitric acid used = 40ml = 29.48g
Temperature : 80 - 90°C
Pressure : 80kPa
Time : 15 minutes

Table C.9 Results of L/F 5

	FF	NF
Mass of solids (g)	45.063	24.813
Zn content (%)	4.900	5.800
Mass of zinc in solids (g)	2.210	1.440
Elemental sulphur content (%)	74.760	56.000
Mass of elemental sulphur (g)	33.690	13.900
Volume of filtra (l)	0.810	0.740
HNO_3 conc. in filtrate(g/l)	20.000	20.000
Volume of wash water (l)	2.890	2.230
HNO_3 conc. in wash water(g/l)	0.250	0.250
Total HNO_3 in filtrate and w. water (g)	16.920	15.360

Elemental sulphur converted to SO_4^{2-} = 1.02g

APPENDIX C CONTINUED

C.2 SAMPLE CALCULATION OF HNO_3 REGENERATION IN THE 5-STAGE L/F EXPERIMENTS

Using L/F 5,

Mass of zinc extracted and NF residues = Mass of zinc in feed - Mass of zinc in FF

= 11.146 - (2.21 + 1.44)

= 7.496g

Number of moles of zinc extracted = $\frac{7.496}{65.37}$

= 0.115 moles

By a similar argument as in appendix A, number of moles of elemental sulphur to be generated = 0.115moles = 0.115moles x 32g/mole = 3.68

Mass of elemental sulphur in residue used for L/F 5 = 83.052 x 54.10%
= 44.93g

Total elemental sulphur to be produced = (3.68 + 44.93)g
= 48.61g

Mass of elemental sulphur in FF = 45.06g x 74.76%
= 33.69g

Mass of elemental sulphur in NF = 24.813 x 56.00%
= 13.90g

Total elemental sulphur generated = (33.69 + 13.90)
= 47.59g

Mass of elemental sulphur converted to SO_4^{2-} = (48.61 - 47.59)g = 1.02g
= $\frac{1.02g}{32g/mole}$

= 0.032moles

From reaction 5.5, HNO_3 required for this conversion = 2 x 0.032moles
= 0.064moles

= 0.064mol. x 63g/mol.
= 4.032g

Degree of HNO_3 regeneration = (HNO_3 used for Zn, Fe and Mn extractions + HNO_3 used for the conversion of elemental sulphur to SO_4^{2-} + total HNO_3 in filtrates of FF and NF - initial amount of HNO_3)/ initial amount of HNO_3

$$= \frac{4.83 + 4.032 + 16.923 + 15.36 - 29.48}{29.48} \times 100\%$$

$$= \frac{11.665}{29.48} \times 100\%$$

= 39.57%

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