

**THE RECOVERY OF COPPER BY  
TUBULAR SUPPORTED LIQUID  
MEMBRANES**

**BY**

**MUJAHID AZIZ**

**A THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS FOR THE  
DEGREE IN MASTER OF TECHNOLOGY IN CHEMICAL ENGINEERING AT THE  
CAPE PENINSULA UNIVERSITY OF TECHNOLOGY.**

**SUPERVISOR: J.W. COETZEE**

**THE CAPE PENINSULA UNIVERSITY OF TECHNOLOGY**

**SEPTEMBER 2006**

---

## **DECLARATION**

---

I hereby certify that this thesis is my own original work, except where specifically acknowledged in the text. Neither the present thesis nor any part thereof has previously been submitted at any other University.

**MUJAHID AZIZ**

**30<sup>TH</sup> SEPTEMBER 2006**

---

## EXTENDED ABSTRACT

---

During recent years, the use of liquid membranes has gained general interest in the treatment of effluents where solute concentrations are low and large volumes of solutions should be processed, and, if possible, without generating any secondary waste. Liquid membrane processes have been proposed as a clean technology, owing to their characteristics, i.e. high specificity, low energy and utilization. Two liquid membrane processes have been used in metal recovery, which are the liquid surfactant membrane (LSM), which corresponds to double water-in-oil emulsion and solid supported liquid membranes (SLM), which are made by dispersing or impregnating the extractant within the pores of inert solid support.

Previously, the recovery of Cu (II) in a SLM system was conducted by other membrane models such as hollow fibre, spiral and flat sheet. Only a small measure of success on scale-up and industrialization of these models has been attained. One of the disadvantages of the hollow fibre system was the small lumen size through which the feed needed to pass. Pores became clogged by suspended particles because the pressure drop over the small diameter augments lower flow rates and therefore, pre-filtering is necessary (Rathore, *et al.*, 2001).

In this study the behaviour of a tubular SLM reactor with an inner diameter of the lumen approximately fifty times bigger than that of the hollow fibre are used in order to solve the problem of clogging. This tubular reactor was incorporated in to a bench scale plant and proved successful in copper extraction. By observing transient data, mass transport coefficients were determined and compared to published values.

---

## DEDICATION

---

The Almighty, My Creator, Sustainer, Protector...

My Mother, the pillar of encouragement and beacon of light to me,

My Father, a scholar in his own right, deprived of an education, yet a resonant symbol of perpetual learning,

My Wife, the edifice behind my every endeavour, my cloaked teacher of life,

My children, the coolness of my eyes and the equanimity of my heart,

The oppressed of the world, which are always in my supplication, and my heart, shall eternally lie.

And finally

The Teacher of Humanity

*“He who learns for the sake of pretentiousness, dies an ignorant; he who learns to forth words devoid of action, dies a hypocrite; He who learns for the mere sake of altercation, dies sanctimonious; He who learns for the sake of wealth, dies an atheist; and he who learns for the sake of effectuation, dies a Gnostic”*

{The Final Prophet (p.b.u.h.) Of Islam}

---

## ACKNOWLEDGEMENTS

---

The work described in this thesis was carried out within the Chemical Engineering Department at the Cape Peninsula University of Technology (Cape Town Campus) between March 2004 and March 2006.

I hereby wish to thank the following persons and organizations for their contributions towards the completion of this thesis.

Willie Coetzee, for his overall supervision of this project, assistance with the preparation of this manuscript and the valuable input he has given me.

Allan Nesbitt, for his guidance, suggestions, advice of technical commentary, that enabled me to maintain a pristine focus.

The National Research Foundation (NRF) for their financial contribution.

Siyasanga Mnenso and Bongani Kosani, for their assistance in the experimental work conducted.

My wife Muneyba, an academic connoisseur in the field of computer programming, for her love, support and positive influence, not only throughout the duration of this project, but with everything I try to achieve.

Lastly, my parents, for their support and faith in me and for allowing me to further my education.

---

## TABLE OF CONTENTS

---

<b>DECLARATION</b>	<b>II</b>
<b>EXTENDED ABSTRACT</b>	<b>III</b>
<b>DEDICATION</b>	<b>V</b>
<b>ACKNOWLEDGEMENTS</b>	<b>VI</b>
<b>TABLE OF CONTENTS</b>	<b>VII</b>
<b>LIST OF FIGURES</b>	<b>XVII</b>
<b>LIST OF TABLES</b>	<b>XI</b>
<b>LIST OF PHOTOGRAPHS</b>	<b>XXII</b>
<b>CHAPTER 1 : INTRODUCTION</b>	<b>1</b>
<b>1.1 BACKGROUND</b>	<b>1</b>
<b>1.2 RESEARCH OBJECTIVES</b>	<b>3</b>
<b>CHAPTER 2 : LITERATURE REVIEW</b>	<b>4</b>
<b>2.1 COPPER</b>	<b>4</b>
<b>2.2. MEMBRANES</b>	<b>7</b>
<b>2.3. MEMBRANE TECHNOLOGY</b>	<b>9</b>
2.3.1. Developed Processes	10
2.3.1.1 Micro Filtration (MF)	11
2.3.1.2 Ultra Filtration (UF)	12

2.3.1.3	Reverse osmosis (RO)	13
2.3.1.4	Pervaporations	15
2.3.2.	Under-developed processes	15
2.3.2.1	Carrier facilitated transport	16
2.3.2.2	Membrane contactors	16
2.3.2.3	Piezodialysis	16
<b>2.4.</b>	<b>TYPE OF MEMBRANE STRUCTURES</b>	<b>18</b>
2.4.1	Isotropic (Symmetric)	19
2.4.1.1	Micro porous	19
2.4.1.2	Nonporous (Dense)	19
2.4.1.3	Electrically charge	20
2.4.2	Anisotropic (Asymmetric)	20
2.4.2.1	Phase inversion	21
2.4.2.2	Thin film composite	21
<b>2.5.</b>	<b>MEMBRANE MATERIALS</b>	<b>22</b>
<b>2.6.</b>	<b>MEMBRANE MODULES</b>	<b>23</b>
2.6.1	Spiral wound	23
2.6.2	Tubular	25
2.6.3	Hollow fibre	26
2.6.4	Plate and frame (Flat plate /sheet)	27
<b>2.7.</b>	<b>POTENTIAL INDUSTRIAL APPLICATION SLM</b>	<b>29</b>
<b>CHAPTER 3</b>	<b>: THEORY</b>	<b>31</b>
<b>3.1</b>	<b>COUPLED SUPPORTED LIQUID MEMBRANES (SLM)</b>	<b>31</b>
3.1.1	Introduction	31
3.1.2	Passive transport	31
3.1.3	Active (Facilitated) transport	31
3.1.3.1.	Coupled transport (Emulsion supported liquid membrane - ELM)	33
3.1.3.2.	Coupled transport (Solid supported liquid membrane - SLM)	34
<b>3.2</b>	<b>BACKGROUND</b>	<b>36</b>
3.2.1	Transport	38
3.2.2	Extraction equilibrium	40
3.2.3	Modelling of copper transport	41
3.2.4	Permeability definition	42
3.2.5	Measurements of permeability coefficients	42
3.2.6	Mass transfer modelling	43
3.2.7	Membrane Diffusion	45
3.2.8	Mass transfer rate parameters	46



<b>CHAPTER 4 : EXPERIMENTAL</b>	<b>49</b>
<b>4.1 SOLVENT EXTRACTION</b>	<b>49</b>
4.1.1. Distribution (partitioning) coefficients of Cu (II)	50
4.1.2. Permeation Measurements (SLM)	50
<b>4.2. CHARACTERISTICS OF PVDF MEMBRANE</b>	<b>51</b>
<b>4.3. CARRIER AGENT</b>	<b>58</b>
<b>4.4. STRIPPANT</b>	<b>59</b>
<b>4.5 EXPERIMENTAL SET-UP</b>	<b>60</b>
4.5.1. Module Assembly	60
4.5.2. Reagents and solutions	61
4.5.3. Membranes	61
4.5.4. General experimental procedure	62
4.5.5 Transport (permeation) experiments	64
<b>4.6 PERMEATION STUDY</b>	<b>64</b>
<b>CHAPTER 5 : RESULTS AND DISCUSSION</b>	<b>65</b>
<b>5.1. REPRODUCIBILITY OF TUBULAR SLM SYSTEM</b>	<b>65</b>
<b>5.2. EQUILIBRIUM DISTRIBUTIONS</b>	<b>67</b>
<b>5.3. MASS BALANCE OF TRANSIENT TESTS</b>	<b>69</b>
<b>5.4. QUALITATIVE ASSESSMENT OF RESULTS</b>	<b>70</b>
5.4.1 Effect of carrier concentration on permeability	70
5.4.2 Effect of stripping concentration on permeability	72
5.4.3 Effect of Feed concentration on permeability	76
5.4.4 Effect of pH's	82
5.4.5 Effect of pH=2	85
5.4.6 Influence of flow rate	88
<b>5.5. LOCATING THE MASS TRANSFER COEFFICIENT (<math>k_i</math>)</b>	<b>91</b>
<b>5.6. THE EFFECT OF FLOW RATE ON THE FEED MASS TRANSFER COEFFICIENT (<math>k_i</math>)</b>	<b>93</b>
<b>CONCLUSION</b>	<b>97</b>

<b>BIBLIOGRAPHY</b>	<b>99</b>
<b>APPENDIX A</b>	<b>102</b>
<b>APPENDIX B</b>	<b>112</b>
<b>APPENDIX C</b>	<b>123</b>
<b>APPENDIX D</b>	<b>133</b>
<b>APPENDIX E</b>	<b>143</b>
<b>APPENDIX F</b>	<b>153</b>
<b>APPENDIX G</b>	<b>161</b>
<b>APPENDIX H</b>	<b>168</b>
<b>APPENDIX I</b>	<b>184</b>
<b>APPENDIX J</b>	<b>196</b>
<b>APPENDIX K</b>	<b>203</b>
<b>APPENDIX L</b>	<b>210</b>
<b>NOMANCLATURE</b>	<b>214</b>
<b>GREEK SYMBOLS</b>	<b>215</b>
<b>SUBSCRIPTS</b>	<b>216</b>
<b>GLOSSARY</b>	<b>217</b>
<b>ABBREVIATIONS</b>	<b>218</b>

---

## LIST OF FIGURES

---

FIGURE 2.1:	APPLICATION SIZE RANGES OF MEMBRANE FILTRATION PROCESSES	9
FIGURE 2.2:	SEPARATION BY ULTRA FILTRATION	12
FIGURE 2.3:	SEPARATION BY REVERSE OSMOSIS	14
FIGURE 2.4:	SCHEMATIC DIAGRAM OF THE PRINCIPAL TYPES OF MEMBRANE	18
FIGURE 2.5:	ASYMMETRIC THIN FILM COMPOSITE MEMBRANE STRUCTURE	21
FIGURE 2.6:	A EXPLODED VIEW AND CROSS-SECTION DRAWINGS OF A SPIRAL-WOUND MODULE	24
FIGURE 2.7:	A TUBULAR ULTRA FILTRATION SYSTEM IN WHICH 30 TUBES ARE CONNECTED IN SERIES	25
FIGURE 2.8:	A SCHEMATIC REPRESENTATION OF THE PRINCIPAL TYPES OF HOLLOW FIBRE MEMBRANES	26
FIGURE 2.9:	SCHEMATIC PLATE AND FRAME MODULE	28
FIGURE 2.10:	A SCHEMATIC FLOW DIAGRAM, WHICH SHOWS THE PLACE OF COUPLED TRANSPORT MEMBRANE IN THE COPPER EXTRACTION SCHEME	30
FIGURE 3.1:	DIAGRAM SHOWING CARRIER SUPPORTED LIQUID MEMBRANE	32
FIGURE 3.2:	FACILITATED TRANSPORT	33
FIGURE 3.3:	EMULSION LIQUID MEMBRANE TRANSPORT	34
FIGURE 3.4:	CARRIER AGENT CONCENTRATION GRADIENTS THAT FORM IN COUPLED TRANSPORT MEMBRANE	35
FIGURE 3.5:	SLM SHOW HOW THE PORES ARE FILLED WITH LIQUID	35
FIGURE 3.6:	CROSS SECTIONAL AREA OF SLM SYSTEM	39
FIGURE 3.7:	SUGGESTED ALGORITHM FOR LOCATING THE MASS TRANSFER COEFFICIENT IN THE LIQUID PHASE OF THE LUMEN.	48
FIGURE 4.1:	SCHEMATIC REPRESENTATION OF A TUBULAR MEMBRANE	51
FIGURE 4.3:	SCHEMATIC REPRESENTATION OF A TUBULAR MEMBRANE	53

FIGURE 4.4:	SEM SHOWING THE SMOOTH, COATED LAYER, INSIDE SURFACE AREA OF MEMBRANE (MAGNIFIED BY 1000)	54
FIGURE 4.5:	SEM SHOWING THE DISTRIBUTION OF PORES ON THE OUTER SURFACE OF MEMBRANE (MAGNIFIED BY 100)	55
FIGURE 4.6:	SEM SHOWING THE DISTRIBUTION OF PORES ON THE OUTER SURFACE OF MEMBRANE (MAGNIFIED BY 500)	55
FIGURE 4.7:	SEM SHOWING THE DISTRIBUTION OF PORES ON THE OUTER SURFACE OF MEMBRANE (MAGNIFIED BY 1000)	56
FIGURE 4.8:	SEM SHOWING A CROSS-SECTION OF MEMBRANE (MAGNIFIED BY 226)	56
FIGURE 4.9:	SEM SHOWING A CROSS-SECTION OF MEMBRANE (MAGNIFIED BY 318)	57
FIGURE 4.10:	SCHEMATIC VIEW OF TUBULAR SLM OPERATED IN RECYCLE MODE FOR THE RECOVERY OF Cu (II) FROM AQUEOUS MEDIA	62
FIGURE 5.1:	EXPERIMENTAL COURSES OF Cu (II) CONCENTRATION IN THE FEED RESERVOIR. FOUR CONSECUTIVE BATCH EXPERIMENTS WITHOUT INITIAL RE-IMPREGNATION OF THE MEMBRANE	66
FIGURE 5.2:	Cu (II) PARTITIONING BETWEEN THE AQUEOUS AND ORGANIC PHASES WHEN THERE IS A CHANGE IN THE REACTANT AND STRIPPANT CONCENTRATION.	68
FIGURE 5.3:	EXPERIMENTAL COURSES OF Cu (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF EXTRACTANT CONCENTRATION WITH SHELL SOL D70 AS CARRIER ON PERMEATION	70
FIGURE 5.4:	EXPERIMENTAL COURSES OF Cu (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF EXTRACTANT CONCENTRATION WITH SHELL SOL D70 AS CARRIER ON THE FLUX	71
FIGURE 5.5:	EXPERIMENTAL COURSES OF Cu (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF CARRIER CONCENTRATION ON PERMEABILITY	71
FIGURE 5.6:	EXPERIMENTAL COURSES OF Cu (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF H <sub>2</sub> SO <sub>4</sub> CONCENTRATION ON THE PERMEABILITY AT A 5 AND 20% H <sub>2</sub> SO <sub>4</sub> STRIP CONCENTRATION	72

FIGURE 5.7:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE STRIP RESERVOIR. THE EFFECT OF H <sub>2</sub> SO <sub>4</sub> CONCENTRATION ON PERMEABILITY AT A 5 AND 20% H <sub>2</sub> SO <sub>4</sub> STRIP CONCENTRATION	73
FIGURE 5.8:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF H <sub>2</sub> SO <sub>4</sub> CONCENTRATION ON THE PERMEABILITY	75
FIGURE 5.9:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF CU <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> CONCENTRATION ON THE PERMEATION	76
FIGURE 5.10:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF CU <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> CONCENTRATION ON THE FLUX	77
FIGURE 5.11:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF CU <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> CONCENTRATION OF 100PPM AND 400PPM ON THE FLUX	78
FIGURE 5.12:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED AND STRIP RESERVOIRS. THE EFFECT OF CU <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> CONCENTRATION ON PERMEABILITY AT 100PPM CU <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> FEED CONCENTRATION	79
FIGURE 5.13:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED AND STRIP RESERVOIRS. THE EFFECT OF CU <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> CONCENTRATION ON PERMEABILITY AT 400PPM CU <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> FEED CONCENTRATION	80
FIGURE 5.14:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF CU <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> CONCENTRATION ON PERMEABILITY.	81
FIGURE 5.15:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF CONSTANT PH ON PERMEATION	82
FIGURE 5.16:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF CONSTANT PH ON THE FLUX	83
FIGURE 5.17:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF CONSTANT PH ON PERMEABILITY	84
FIGURE 5.18:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF PH=2 AT DIFFERENT FEED CONCENTRATIONS HAS ON PERMEATION	85

FIGURE 5.19:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF PH=2 AT DIFFERENT FEED CONCENTRATION ON THE FLUX	86
FIGURE 5.20:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF PH=2 AT DIFFERENT FEED CONCENTRATIONS HAVE ON PERMEABILITY	87
FIGURE 5.21:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF FLOW RATE ON PERMEATION. FEED LINEAR FLOW VELOCITY $0.167\text{CM}^3\text{SEC}^{-1}$	88
FIGURE 5.22:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF FLOW RATE ON PERMEATION. FEED LINEAR FLOW VELOCITY $0.333\text{CM}^3\text{SEC}^{-1}$	89
FIGURE 5.23:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF THE LINEAR VELOCITY IN THE FEED HAS ON THE PERMEABILITY.	90
FIGURE 5.24:	SCHEMATIC ALGORITHM DESCRIBING THE COMPUTER CALCULATION FOR THE AQUEOUS MASS TRANSFER COEFFICIENT IN THE FEED ( $K_f$ )	95
FIGURE 5.25:	SHOWS THE COMPARISON BETWEEN THE DIFFERENT MASS TRANSFER COEFFICIENTS.	96
FIGURE B.1:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF FEED CONCENTRATION ON PERMEABILITY. THE RESULTS OF EXPERIMENT 1.1 – 1.7 SHOWS ON THE GRAPH HOW THE GRADIENT CAN BE OBTAINED ( $S_p$ ) BY PLOTTING $V_f \ln(C/C_0)$ VS TIME	122
FIGURE C.1:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF STRIP CONCENTRATION ON PERMEABILITY. THE RESULTS OF EXPERIMENT 2.1 – 2.6 SHOWS ON THE GRAPH HOW THE GRADIENT CAN BE OBTAINED ( $S_p$ ) BY PLOTTING $V_f \ln(C/C_0)$ VS TIME	132
FIGURE D.1:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF REACTANT CONCENTRATION ON PERMEABILITY. THE RESULTS OF	

	EXPERIMENT 3.1 – 3.6 SHOWS ON THE GRAPH HOW THE GRADIENT CAN BE OBTAINED ( $S_p$ ) BY PLOTTING $V_F \ln(C/C_0)$ VS TIME	142
FIGURE E.1:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF FEED FLOW RATES ON PERMEABILITY. THE RESULTS OF EXPERIMENT 4.1 – 4.6 SHOWS ON THE GRAPH HOW THE GRADIENT CAN BE OBTAINED ( $S_p$ ) BY PLOTTING $V_F \ln(C/C_0)$ VS TIME	152
FIGURE F.1:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF CONSTANT PH ON THE PERMEABILITY. THE RESULTS OF EXPERIMENT 5.1 – 5.5 SHOWS ON THE GRAPH HOW THE GRADIENT CAN BE OBTAINED ( $S_p$ ) BY PLOTTING $V_F \ln(C/C_0)$ VS TIME	160
FIGURE G.1:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR. THE EFFECT OF VARYING PH ON THE PERMEABILITY. THE RESULTS OF EXPERIMENT 6.1 – 3.4 SHOWS ON THE GRAPH HOW THE GRADIENT CAN BE OBTAINED ( $S_p$ ) BY PLOTTING $V_F \ln(C/C_0)$ VS TIME	167
FIGURE H.1.1:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR AT DIFFERENT FEED CONCENTRATIONS.	169
FIGURE H.1.2:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE STRIP RESERVOIR AT DIFFERENT FEED CONCENTRATIONS.	170
FIGURE H.2.1:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR AT DIFFERENT STRIP CONCENTRATIONS.	171
FIGURE H.2.2:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE STRIP RESERVOIR AT DIFFERENT STRIP CONCENTRATIONS.	172
FIGURE H.3.1:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR AT DIFFERENT CARRIER CONCENTRATIONS.	176
FIGURE H.3.2:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE STRIP RESERVOIR AT DIFFERENT CARRIER CONCENTRATIONS.	177
FIGURE H.4.1:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR AT DIFFERENT FEED/STRIP VELOCITIES.	178
FIGURE H.4.2:	EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE STRIP RESERVOIR AT DIFFERENT FEED/STRIP VELOCITIES.	179

<b>FIGURE H.5.1:</b>	<b>EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR AT DIFFERENT FEED CONCENTRATIONS AT A pH=2</b>	<b>180</b>
<b>FIGURE H.5.2:</b>	<b>EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE STRIP RESERVOIR AT DIFFERENT FEED CONCENTRATIONS AT A pH=2</b>	<b>181</b>
<b>FIGURE H.6.1:</b>	<b>EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE FEED RESERVOIR AT DIFFERENT FEED CONCENTRATIONS AT A CONSTANT FEED pH</b>	<b>182</b>
<b>FIGURE H.6.2:</b>	<b>EXPERIMENTAL COURSES OF CU (II) CONCENTRATION IN THE STRIP RESERVOIR AT DIFFERENT FEED CONCENTRATIONS AT A CONSTANT FEED pH</b>	<b>183</b>



---

## LIST OF TABLES

---

TABLE 2.1:	PHYSICAL PROPERTIES OF COPPER:	5
TABLE 4.1:	CHARACTERISTICS OF A SINGLE TUBULAR MEMBRANE:	57
TABLE 4.2:	PROPERTIES OF LIX 984N:	58
TABLE 4.3:	PROPERTIES OF SHELL SOL D70:	59
TABLE 4.4:	PROPERTIES OF SULPHURIC ACID (H <sub>2</sub> SO <sub>4</sub> ):	59
TABLE 5.2:	THE PERMEATION OF CU (II) AS A FUNCTION OF SULPHURIC ACID CONCENTRATION AT THE 50% MARK	74
TABLE 5.3:	SELECT MASS TRANSFER COEFFICIENT ACHIEVED WHILE TESTING DIFFERENT STRIP CONCENTRATIONS	92
TABLE 5.4:	FLOW RATE OF CU (II) AS A FUNCTION OF LINEAR VELOCITY AND THE MASS TRANSFER COEFFICIENT (K <sub>i</sub> )	93
TABLE 5.5:	COEFFICIENT AND EXPONENTIAL VALUES A FUNCTION OF THE FEED MASS TRANSFER COEFFICIENT (K <sub>i</sub> )	94
TABLE A.1:	EXPERIMENTAL PARAMETERS AND CALCULATED VALUES	111
TABLE B.1:	RESULTS FROM EXPERIMENT 1.1	114
TABLE B.2:	RESULTS FROM EXPERIMENT 1.2	115
TABLE B.3:	RESULTS FROM EXPERIMENT 1.3	116
TABLE B.4:	RESULTS FROM EXPERIMENT 1.4	117
TABLE B.5:	RESULTS FROM EXPERIMENT 1.5	118
TABLE B.6:	RESULTS FROM EXPERIMENT 1.6	119
TABLE B.7:	RESULTS FROM EXPERIMENT 1.7	120
TABLE B.8:	RESULTS FROM EXPERIMENT 1.1 -1.7	121

TABLE C.1:	RESULTS FROM EXPERIMENT 2.1	125
TABLE C.2:	RESULTS FROM EXPERIMENT 2.2	126
TABLE C.3:	RESULTS FROM EXPERIMENT 2.3	127
TABLE C.4:	RESULTS FROM EXPERIMENT 2.4	128
TABLE C.5:	RESULTS FROM EXPERIMENT 2.5	129
TABLE C.6:	RESULTS FROM EXPERIMENT 2.6	130
TABLE C.7:	RESULTS FROM EXPERIMENT 2.1 -2.6	131
TABLE D.1:	RESULTS FROM EXPERIMENT 3.1	135
TABLE D.2:	RESULTS FROM EXPERIMENT 3.2	136
TABLE D.3:	RESULTS FROM EXPERIMENT 3.3	137
TABLE D.4:	RESULTS FROM EXPERIMENT 3.4	138
TABLE D.5:	RESULTS FROM EXPERIMENT 3.5	139
TABLE D.6:	RESULTS FROM EXPERIMENT 3.6	140
TABLE D.7:	RESULTS FROM EXPERIMENT 3.1 -3.6	141
TABLE E.1:	RESULTS FROM EXPERIMENT 4.1	145
TABLE E.2:	RESULTS FROM EXPERIMENT 4.2	146
TABLE E.3:	RESULTS FROM EXPERIMENT 4.3	147
TABLE E.4:	RESULTS FROM EXPERIMENT 4.4	148
TABLE E.5:	RESULTS FROM EXPERIMENT 4.5	149
TABLE E.6:	RESULTS FROM EXPERIMENT 4.6	150
TABLE E.7:	RESULTS FROM EXPERIMENT 4.1 -4.6	151
TABLE F.1:	RESULTS FROM EXPERIMENT 5.1	155
TABLE F.2:	RESULTS FROM EXPERIMENT 5.2	156
TABLE F.3:	RESULTS FROM EXPERIMENT 5.3	157
TABLE F.4:	RESULTS FROM EXPERIMENT 5.4	158
TABLE F.5:	RESULTS FROM EXPERIMENT 5.5	159
TABLE G.1:	RESULTS FROM EXPERIMENT 6.1	163
TABLE G.2:	RESULTS FROM EXPERIMENT 6.2	164

TABLE G.3:	RESULTS FROM EXPERIMENT 6.3	165
TABLE G.4:	RESULTS FROM EXPERIMENT 6.4	166
TABLE H.1.1:	RAW DATA FROM EXPERIMENTS 1.1 – 1.7 IN THE FEED SIDE.	169
TABLE H.1.2:	RAW DATA FROM EXPERIMENTS 1.1 – 1.7 IN THE STRIP SIDE.	170
TABLE H.2.1:	RAW DATA FROM EXPERIMENTS 2.1 – 2.6 IN THE FEED SIDE.	171
TABLE H.2.2:	RAW DATA FROM EXPERIMENTS 2.1 – 2.6 IN THE STRIP SIDE.	172
TABLE H.2.3:	RAW DATA FROM EXPERIMENTS 2.1 AND 2.6 IN THE FEED SIDE.	173
TABLE H.2.4:	RAW DATA FROM EXPERIMENTS 2.1 AND 2.6 IN THE STRIP SIDE.	174
TABLE H.2.5:	RAW DATA FROM EXPERIMENTS 2.1 AND 2.4 IN THE FEED SIDE.	175
TABLE H.2.6:	RAW DATA FROM EXPERIMENTS 2.1 AND 2.4 IN THE STRIP SIDE.	175
TABLE H.3.1:	RAW DATA FROM EXPERIMENTS 3.1 – 3.6 IN THE FEED SIDE.	176
TABLE H.3.2:	RAW DATA FROM EXPERIMENTS 3.1 – 3.6 IN THE STRIP SIDE.	177
TABLE H.4.1:	RAW DATA FROM EXPERIMENTS 4.1 – 4.6 IN THE FEED SIDE.	178
TABLE H.4.2:	RAW DATA FROM EXPERIMENTS 4.1 – 4.6 IN THE STRIP SIDE.	179
TABLE H.5.1:	RAW DATA FROM EXPERIMENTS 5.1 – 5.5 IN THE FEED SIDE.	180
TABLE H.5.2:	RAW DATA FROM EXPERIMENTS 5.1 – 5.5 IN THE STRIP SIDE	181
TABLE H.6.1:	RAW DATA FROM EXPERIMENTS 6.1 – 6.4 IN THE FEED SIDE.	182
TABLE H.6.2:	RAW DATA FROM EXPERIMENTS 6.1 – 6.4 IN THE STRIP SIDE	183
TABLE I.1.1:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 5% STRIP	186
TABLE I.1.2:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 10% STRIP	186
TABLE I.1.3:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 15% STRIP	186
TABLE I.1.4:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 20% STRIP	187
TABLE I.1.5:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 25% STRIP	187
TABLE I.1.6:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 30% STRIP	187
TABLE I.1.7:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 5% STRIP	188
TABLE I.1.8:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 10% STRIP	188
TABLE I.1.9:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 15% STRIP	188
TABLE I.1.10:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 20% STRIP	189

TABLE I.1.11:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 25% STRIP	189
TABLE I.1.12:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 30% STRIP	189
TABLE I.2.1:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 5% REACTANT	191
TABLE I.2.2:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 10% REACTANT	191
TABLE I.2.3:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 15% REACTANT	191
TABLE I.2.4:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 20% REACTANT	192
TABLE I.2.5:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 25% REACTANT	192
TABLE I.2.6:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 30% REACTANT	192
TABLE I.2.7:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 40% REACTANT	193
TABLE I.2.8:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 5% REACTANT	193
TABLE I.2.9:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 10% REACTANT	194
TABLE I.2.10:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 15% REACTANT	194
TABLE I.2.11:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 20% REACTANT	194
TABLE I.2.12:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 25% REACTANT	195
TABLE I.2.13:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 30% REACTANT	195
TABLE I.2.14:	DISTRIBUTION COEFFICIENT ( $M_{Cu}$ ) USING 40% REACTANT	195
TABLE J.1.1:	PERMEATION COEFFICIENT CALCULATIONS AT DIFFERENT FEED CONCENTRATIONS AT EQUILIBRIUM SHOWN IN APPENDIX A.1	197
TABLE J.1.2:	PERMEATION COEFFICIENT CALCULATIONS AT DIFFERENT STRIP CONCENTRATIONS AT EQUILIBRIUM SHOWN IN APPENDIX A.2	198
TABLE J.1.3:	PERMEATION COEFFICIENT CALCULATIONS AT DIFFERENT FLOW RATES AT EQUILIBRIUM SHOWN IN APPENDIX A.3	199
TABLE J.1.4:	PERMEATION COEFFICIENT CALCULATIONS AT REACTANT CONCENTRATIONS AT EQUILIBRIUM SHOWN IN APPENDIX A.4	200
TABLE J.1.5:	PERMEATION COEFFICIENT CALCULATIONS AT CONSTANT pH AT EQUILIBRIUM SHOWN IN APPENDIX A.5	201
TABLE J.1.6:	PERMEATION COEFFICIENT CALCULATIONS AT pH = 2 AT EQUILIBRIUM SHOWN IN APPENDIX A.6	202

TABLE K.1.1:	LOCATING OF THE MASS TRANSFER COEFFICIENT ( $K_L$ ) USING EQUATION 17 AND SHOWN IN FIGURE 2.25 AT DIFFERENT FEED CONCENTRATIONS	204
TABLE K.1.2:	LOCATING OF THE MASS TRANSFER COEFFICIENT ( $K_L$ ) USING EQUATION 17 AND SHOWN IN FIGURE 2.25 AT DIFFERENT STRIPPANT CONCENTRATIONS	205
TABLE K.1.3:	LOCATING OF THE MASS TRANSFER COEFFICIENT ( $K_L$ ) USING EQUATION 17 AND SHOWN IN FIGURE 2.25 AT DIFFERENT REACTANT CONCENTRATIONS	206
TABLE K.1.4:	LOCATING OF THE MASS TRANSFER COEFFICIENT ( $K_L$ ) USING EQUATION 17 AND SHOWN IN FIGURE 2.25 AT DIFFERENT FLOW RATES	207
TABLE K.1.5:	LOCATING OF THE MASS TRANSFER COEFFICIENT ( $K_L$ ) USING EQUATION 17 AND SHOWN IN FIGURE 2.25 AT A CONSTANT PH	208
TABLE K.1.6:	LOCATING OF THE MASS TRANSFER COEFFICIENT ( $K_L$ ) USING EQUATION 17 AND SHOWN IN FIGURE 2.25 AT PH = 2	209
TABLE L.1.1:	MASS TRANSFER CALCULATIONS AT DIFFERENT FEED CONCENTRATIONS	211
TABLE L.1.2:	MASS TRANSFER CALCULATIONS AT DIFFERENT STRIPPANTS CONCENTRATIONS	211
TABLE L.1.3:	MASS TRANSFER CALCULATIONS AT DIFFERENT FLOW RATES	212
TABLE L.1.4:	MASS TRANSFER CALCULATIONS AT DIFFERENT REACTANT CONCENTRATIONS	212
TABLE L.1.5:	MASS TRANSFER CALCULATIONS AT CONSTANT PH	213
TABLE L.1.6:	MASS TRANSFER CALCULATIONS AT PH = 2	213

---

## LIST OF PHOTOGRAPHS

---

PHOTOGRAPH 4.2:	SINGLE TUBULAR MEMBRANE WITH A 190MM LENGTH	52
PHOTOGRAPH 4.3:	SINGLE TUBULAR SLM MEMBRANE SET-UP	60
PHOTOGRAPH 4.4:	PHOTOGRAPH OF A SINGLE TUBULAR MEMBRANE SLM SET-UP SHOWING THE COUNTER CURRENT FLOW OF FEED AND STRIP IN THE TUBE AND SHELL SIDE	63

---

---

# CHAPTER 1 : INTRODUCTION

---

## 1.1 BACKGROUND

During the past twenty years membrane technology has had an impressive growth that has confirmed its potential to contribute to the solving of topical challenges in hydrometallurgy.

Systematic studies of membrane phenomena can be traced back to the eighteenth century philosopher scientists. Throughout the nineteenth and early twentieth centuries, membranes had no industrial or commercial uses, but were used as laboratory tools to develop physical and chemical theories. By 1960, the elements of modern membrane science had developed, but membranes were used in only a few laboratories and specialized industrial applications. No significant membrane industries existed and the total annual sales of membranes for all industrial applications probably did not exceed US\$20 million in 2003. Membranes suffered from four problems that prohibited their widespread use as a separation process. These were: unreliability, slow reaction rates, non-selectivity and cost. Solutions to each of these problems have been developed during the last 30 years and membrane-based separation processes are presently commonplace (Baker, 2004).

Undoubtedly, the feasibility of the separation and concentration of metals with liquid membranes should be considered as one of the most promising technological advances produced in the field of hydrometallurgical processes. Particularly, the use of solid supported liquid membranes in a hollow fibre and flat sheet configuration has been successfully tested for the recovery of metallic ions from aqueous solutions and therefore compete with solvent extraction (SX) and ion-exchange (IX) processes. However, a tubular solid supported liquid membrane, as reported in this study, remains a novelty and hence the necessity for this study.

It is well documented that the employment of liquid membrane technology would offer several advantages as compared with the current solvent extraction process in mixer-settlers, in particular cost savings in the inventory of an expensive solvent and smaller reactor size. As no direct mixing between the aqueous or the organic phase takes place, crud formation and phase entrapment difficulties can be avoided. Many papers concerned with the selective separation and concentration of metallic ions with liquid membranes have recently been reported (Marchese, *et al.*, 2004).

According to Baker (2004), carrier facilitated transport processes (SLM's) often achieve spectacular separations between closely related species because of the selectivity of the carriers. However, no coupled transport process has advanced to the commercial stage despite a steady stream of papers within academic literature. The marginal improvement in economics that is offered by coupled transport processes, over conventional technology such as solvent extraction or ion exchange is clearly an advantage of the SLM. Major breakthroughs in performance are required to make coupled transport technology commercially competitive as facilitated transport membranes are a long way from the commercialization and are plagued by many difficult technical problems. However, the economic rationale for developing facilitated transport membranes is at least clear. Research in tubular membrane technology has therefore, become significant.



## **1.2 RESEARCH OBJECTIVES**

To evaluate an alternative to hollow fibre, spiral and flat sheet supported liquid membrane systems for the extraction of copper and the development of an experimental scale-up procedure.

**The objectives for this study were:**

- To construct and commission an experimental bench scale SLM reactor for the extraction of metal ions.
- To investigate the use of a novel SLM reactor for the extraction and concentration of copper ions in a closed batch system.
- To identify the variables that affects the extraction rate of copper.
- Locate mass transfer coefficients by applying published models.
- Utilize the located mass transfer coefficient to investigate the controlling mechanism of the system.

---

## CHAPTER 2 : LITERATURE REVIEW

---

### 2.1 COPPER

Copper and some of its alloys have been used by humanity since the Bronze Age. As one of the first metals known to humans, free copper was probably mined in the Tigris-Euphrates valley as early as the fifth century BC. Cyprus, from which the metal's name originally comes, was the primary source of copper in the ancient world ([www.encyclopedia.com](http://www.encyclopedia.com)).

However, there is evidence that every ancient metal culture at some stage discovered and used the red metal. The early age of copper probably had its greatest development in Egypt. The most important copper ores during those times could be found in Sinai, Syria, Afghanistan, Cyprus and Central Europe. European copper mines of the Bronze Age are known in Austria, Germany, France, Spain, Portugal and Greece. The world's copper industry is confronted with many technical and economical problems. Currently, one of the biggest challenges is to prevent the loss of markets to substitute materials such as aluminium, steel and plastics, as its price has increased dramatically in the early 21<sup>st</sup> century ([www.nautilus.fis.uc.pt](http://www.nautilus.fis.uc.pt)).

Copper is widely spread in many parts of the world mainly as mineral combinations with iron, sulphur, carbon and oxygen. Over 160 copper minerals have been identified, of which only a dozen are commercially important. Copper is divided into three groups namely: (i) Primary, which is represented by compounds such as bornite, chalcopyrite, enargite and others; (ii) Oxidized copper minerals, cuprite, malachite, azurite and chrysocolla and (iii) Secondary sulphides such as chalcocite and covellite. The commercially more important minerals are chalcocite with 79,8% copper and chalcopyrite with 34,5% copper ([www.nautilus.fis.uc.pt](http://www.nautilus.fis.uc.pt)). Some physical properties of copper are provided in Table 2.1 ([www.scescape.net](http://www.scescape.net)).

**Table 2.1: Physical properties of Copper:**

Property	Value
Atomic number	29
Atomic weight	63.546
Density @ 293K (g.cm <sup>-3</sup> )	8.96
Atomic volume (cm <sup>3</sup> .mol <sup>-1</sup> )	7.1
State	Solid
Melting point (K)	1356.6
Boiling point (K)	2843
Heat of fusion (kJ.mol <sup>-1</sup> )	13.050
Heat of vaporization (kJ.mol <sup>-1</sup> )	300.30
1 <sup>ST</sup> Ionization energy (kJ.mol <sup>-1</sup> )	745.4
2 <sup>ND</sup> Ionization energy (kJ.mol <sup>-1</sup> )	1957.9
3 <sup>RD</sup> Ionization energy (kJ.mol <sup>-1</sup> )	3553.5
Heat atomization (kJ.mol.atoms <sup>-1</sup> )	338
Electro negativity	1.95
Electron affinity (kJ.mol <sup>-1</sup> )	118.5
Specific heat J.gK <sup>-1</sup>	0.38
Hardness (mohs)	2.75
Thermal conductivity (J.m-sec-deg <sup>-1</sup> )	401
Electrical conductivity (l.mohm-cm <sup>-1</sup> )	595.8
Polarizability (A <sup>3</sup> )	6.7

Copper is reddish in colour, takes on a bright metallic lustre and is malleable, ductile and a good conductor of heat and electricity. It is second only to silver in electrical conductivity, while it is softer than iron but harder than zinc and can be polished to a bright finish. Copper has a low chemical reactivity ([www.encyclopedia.com](http://www.encyclopedia.com)).

Copper metal is prepared commercially in various ways. Copper sulphide ores, which usually contains 1 to 2% copper, are concentrated to 20 to 40% copper by flotation and are then roasted to remove some of the sulphur and impurities. It is then smelted with iron oxide in either a blast furnace or reverberatory furnace in order to produce copper matte. The matte is transferred to a converter where it is treated by blowing air through it to remove sulphur as sulphur dioxide and the iron as a slag of ferrous oxide. The resulting copper is 98 to 99% pure. The copper is further purified by electrolysis. Copper oxide ores are usually treated by a leaching process, the copper in the ore is dissolved by a diluted sulphuric acid solution. Pure copper is recovered by electrolysis ([www.encyclopedia.com](http://www.encyclopedia.com)).

The main commercial use of copper is based on its electrical conductivity. Half the total annual output amount is employed in the manufacture of electrical appliances and wire. Copper is used as roofing, making copper utensils and coins and metalwork. Other uses of copper appear as tubing in the plumbing industry, heat exchangers, refrigerators and air conditioning coils, owing to its high heat conductivity ([www.encyclopedia.com](http://www.encyclopedia.com)).

## 2.2. MEMBRANES

A membrane is a permeable or semi-permeable phase, often a thin polymeric solid, which restricts the motion of certain species. This added phase is essentially a barrier between a feed stream and product stream. The performance of a membrane is defined by Scott *et al.*, (1990), in terms of two simple factors, namely flux and selectivity. Flux or permeation rate is the volumetric (mass or molar) flow rate of fluid that passes through the membrane per unit area of membrane per unit time. The selectivity of solutes and particulates in liquids and gases are the retention of solutes by the membrane.

According to Scott *et al.*, (1996), the main uses of membranes in industry are:

- The filtration of micron and submicron size dependent solids (and dispersed liquid) from liquid and gases, which contain dissolved solids.
- The removal of macromolecules and colloids from liquids which contain ionic species.
- The separation of mixtures of miscible liquids.
- The selective separation of gases and vapours from gas and vapour streams.
- The selective transport of ionic species only.
- The virtually complete removal of all material suspended and dissolved in water.

The membrane is clearly the most important part of the separation process. Membrane material science has rapidly developed over recent years to produce a wide range of materials of different structures and with different ways of functioning. Scott *et al.*, (1996) classified membrane materials into three types:

- Synthetic polymers; which are a vast source of perfluoro polymers, silicone rubbers, polyamides and poly sulphones are prominent.
- Modified natural products.
- Miscellaneous, which include inorganic, ceramic, metals, dynamic and liquid membranes.

According to Scott *et al.*, (1996) membrane materials should possess the following properties to be effective for separation.

- Chemical resistance (to both feed and cleaning fluids).
- Mechanical stability.
- Thermal stability.
- High permeability.
- High selectivity.
- Stable operation.

These properties are relative in terms of individual processes and the respective capital and operating costs. Chemical resistance, for example, relates more to the operating lifetime of the membrane.

A number of techniques are available to prepare synthetic membranes according to the membrane material selected. Membrane preparation processes, include (Baker, 2004)

- Phase separation (phase inversion) process.
- Loeb-Sourirajan technique/process.
- Interfacial polymerization process.
- Solution-coating process.

According to Baker (2004) membrane materials with the appropriate chemical, mechanical and permeation properties should be selected, determined by the specific transport process. Once the membrane material has been selected, the technology required to fabricate this material into a robust, thin, defect-free membrane, is similar for all membrane processes.

### 2.3. MEMBRANE TECHNOLOGY

According to Scott *et al.*, (1996) improvements and advances in membrane technology over the last two decades have seen applications expand in many industrial sectors, namely chemical, petrochemical, mineral and metallurgical, food, biotechnology, pharmaceutical, electronics, paper and pulp and water. Membrane separations are in competition with physical methods of separation such as selective adsorption, absorption, solvent extraction, distillation, crystallisation and cryogenic gas separation. The feature, which distinguishes membrane separation from the other separation techniques, is the provision of a third phase and that is the membrane. This phase whether solid liquid or gaseous, introduces an interface(s) between the two bulk phases between which molecular exchanges occur and gives the advantages of efficiency and selectivity. The membrane can be neutral or charged and porous or non-porous and acts as a perm selective barrier.

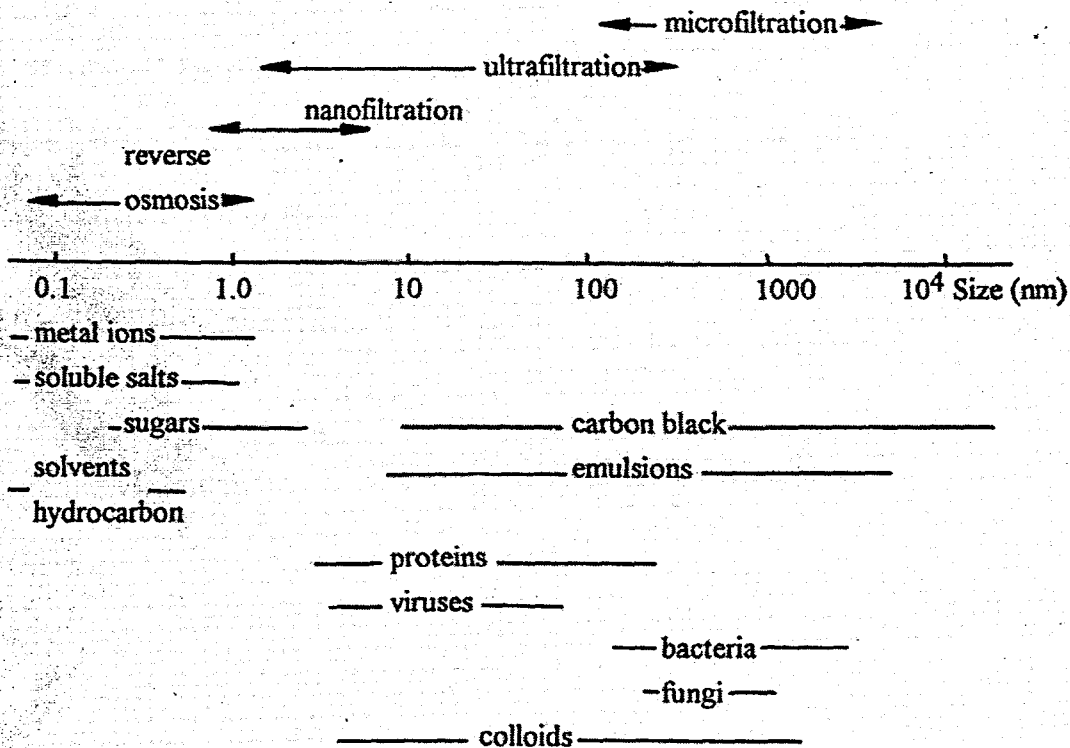


Figure 2.1: Application size ranges of membrane filtration processes

The transport of selected species through the membrane is achieved by a driving force across the membrane. This provides a broad classification of membrane separations in the way of a mechanism by which material is transported across a membrane. The flow of material across a membrane should be kinetically driven, by the application of mechanical, chemical or electrical work (Scott *et al.*, 1996).

The driving forces are pressure, concentration, temperature or electrical potential. In many cases the transport rate (permeation) is proportional to the driving force and the membrane can be categorised in terms of an appropriate permeability coefficient (Scott *et al.*, 1996).

According to Baker (2004), membrane technology is divided into two main processes, namely developed and under developed processes.

### **2.3.1. Developed Processes**

Developed processes are applied in industry through the use of six methods:

- Micro Filtration (MF);
- Ultra Filtration (UF);
- Reverse Osmosis (RO);
- Electrolysis;
- Gas Separation; and
- Pervaporation.



Some of these methods are described by Scott *et al.*, (1996) as follows:

### 2.3.1.1 Micro Filtration (MF)

Filtration is a means of removing unwanted solids from a liquid or a gas stream by mechanical sieving. A pressure gradient is maintained across the filter to maintain the fluid flow through the filtration media. The filtrate or permeate, which flows through the filter should ideally be devoid of suspended solid. With convectional filters, particle fragments and filter media can escape during filtration (Scott *et al.*, 1996).

In membrane micro filtration (MF), the filter is generally made from a thin polymer film with a uniform pore size and a high pore density of approximately 80%. The principle method of particle retention is characterised as sieving although the separation is influenced by interactions between the membrane surface and the solution (Scott *et al.*, 1996).

Micro filtration is most widely applied in a dead-end mode of operation. Here the feed flow is perpendicular to the membrane surface and the retained (filtered) particles accumulate on the surface, which forms a filter cake. The thickness of this cake, increases with time and the permeation rate correspondingly decreases. Eventually, the membrane filter reaches an impractical or uneconomic low filtration rate and is either cleaned or replaced. In order to reduce the effect of a build-up of solid particle cake on the membrane surface, an alternative cross-flow operation of filtration can be used (Scott *et al.*, 1996).

The technologically important applications of micro filtration are summarized below:

- Removal of particles from liquid and gas streams for chemical, biological, pharmaceutical and food industries.
- Clarification and sterile filtration of heat sensitive solutions and beverages.
- Production of pure water in the electronics industry.

- Product purification, gas filtration and process solvent recovery in the chemical industry.
- Waste water treatment (Scott *et al.*, 1996).

### 2.3.1.2 Ultra Filtration (UF)

Ultra filtration (UF) is the third membrane separation processes, which are grouped together under pressure-driven processes. UF covers the region between MF and RO and is used to remove particles in the size range  $0.001\text{-}0.02\ \mu\text{m}$ . Solvents and salts of low molecular weight will pass through the membranes, while larger molecules are retained. Thus the principal application of UF is in the separation of macromolecules with a size retention in the molar mass range of 300 to 300 000. UF membranes are permeable to molecules of molar masses of 1000 and exhibit a low rejection rate of salts (Scott *et al.*, 1996).

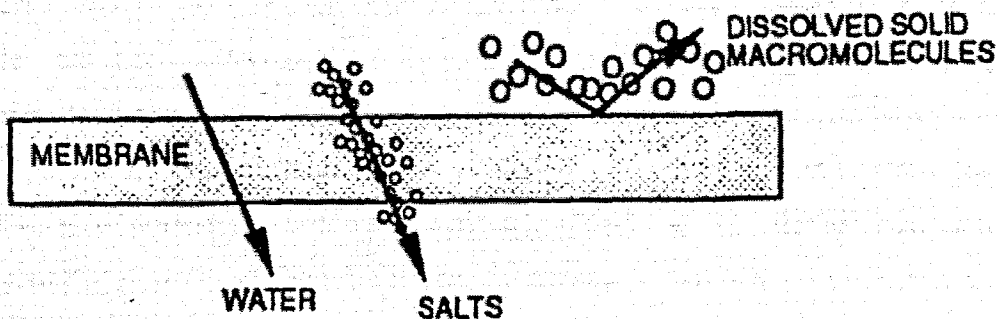


Figure 2.2: Separation by ultra filtration

Ultra filtration is typically applied in the separation of macromolecular solutes and colloidal material from macromolecular solutes and solvents. There are many analytical applications on laboratory scale, which include the concentration of proteins, enzymes and hormones as well as in biochemical and clinical analysis (Scott *et al.*, 1996).

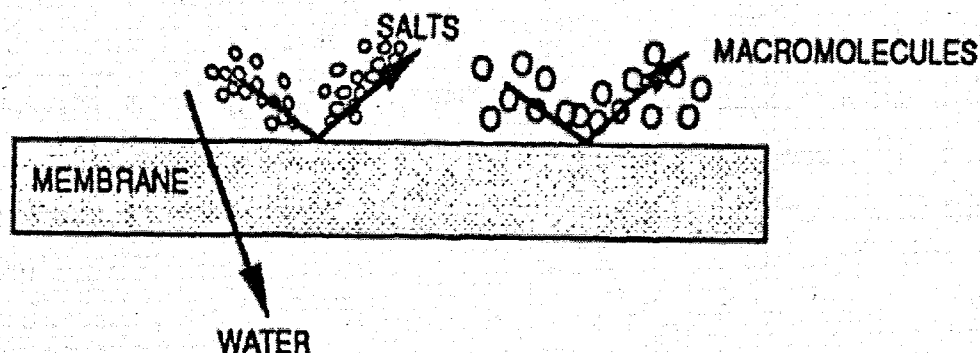
The wide variety of applications includes the following industries:

- Chemical and nuclear; in the treatment of waste water and effluents.
- Automobile; for recovery and recycling in electro paint baths.
- Pulp and paper.
- Food and dairy; for the clarification of juices and wines and milk concentration sterile filtration.
- Biological and pharmaceutical: for the manufacture of antibiotics, the removal of pyrogens and the treatment of blood plasma (Scott *et al.*, 1996).

### 2.3.1.3 Reverse osmosis (RO)

Reverse osmosis (RO) is a pressure driven process, which is aimed at the separation of ionic solutes and macromolecules from aqueous streams. The method of dissolved salt removal is different to that of micro filtration and is not merely a physical process based on size difference of solute and solvent. Such species are of similar molecular size and of a size comparable to the wide range of pore spaces in the polymeric RO membrane. In order to visualize the RO process, the process of osmosis should first be considered. Osmosis occurs when a suitable semi-permeable membrane is used to separate two solutions of equal volume, one being water and the other a dilute salt solution. Water is transferred from the water side of the membrane to the dilute solution side until an osmotic equilibrium is reached, at which point a hydrostatic pressure, which is the osmotic pressure, has built up in the solute solution side. By applying a pressure to the salt solution side, the flow of water, through the membrane, can be stopped and if the pressure exceeds the osmotic pressure, the flow is reversed (Scott *et al.*, 1996).

This is termed reverse osmosis or hyper filtration in which the concentration of salt is increased by the flow of water (or solvent) from a more concentrated solution to a dilute solution. Reverse osmosis membranes can essentially separate all solute species, both inorganic and organic from solution (Figure 2.4). The mechanisms of the separation of species are based on processes, which relates to their size and shape, their ionic charge, as well as interactions with the membrane itself.



**Figure 2.3: Separation by reverse osmosis**

RO has principally seen a wide range of applications during the processing of aqueous solutions in the following areas:

- Desalination of brackish water and sea water.
- Production of pure water for a variety of industries.
- Concentration of solutions of food products, pharmaceutical solutions and chemical streams.
- Waste water treatment (Scott *et al.*, 1996).

The use of RO is generally increasing as more resilient membranes emerge (Scott *et al.*, 1990).

#### 2.3.1.4 Pervaporations

Pervaporation (PV) is a membrane process for the separation of miscible liquid mixtures into more concentrated products of the constituents. Interest in this process is growing owing to the practical limitations of reverse osmosis in many potential separations where otherwise extreme pressures would be required. Separation is achieved by applying a lower pressure (vacuum) to the permeate side of the membrane, whilst the other side is exposed to the liquid which will be separated (Scott *et al.*, 1996).

The commercial application of PV is currently being investigated in the chemical and biochemical industries. The recovery of low concentrations of organics, e.g. alcohols from fermentation broths and the removal of small quantities of solvents from water, is typical (Scott *et al.*, 1996).

#### 2.3.2. Under-developed processes

The under-developed processes can be divided into two groups, namely Industrial and Medical processes, which are described by Scott *et al.*, (1996) as follows:

Under-developed processes are further divided into six methods:

##### **Industrial under-developed processes:**

- Carrier facilitated transport.
- Membrane contactors.
- Piezodialysis.

##### **Medical under-developed processes:**

- Artificial kidneys.
- Blood oxygenators.
- Controlled release pharmaceuticals.

Some of these methods are described by Scott *et al.*, (1996) as follows:

### **2.3.2.1 Carrier facilitated transport**

Separation, using liquid membranes, can be likened to that of conventional solvent extraction and stripping in which a thin liquid film is used to transport the solute from the feed to the product side. The use of a liquid film offers the possibility of much higher separation rates than in polymer films because of the higher diffusion rates in the former (Scott *et al.*, 1990). Prime industrial targets for the acceptance of liquid membranes are in extraction processes for recovery of aromatic and aliphatic hydrocarbons and metal ions. Research into a number of hydrometallurgical applications is particularly active. This process will be discussed in detail in the chapters that follow (Scott *et al.*, 1996).

### **2.3.2.2 Membrane contactors**

Methods of phase contact usually involve the dispersion of one fluid phase as droplets and bubbles into another phase. After mass transport the dispersed phases are then separated by a method which utilizes the difference in their phase density (Scott *et al.*, 1996). There are many applications of hollow fibre membrane technology in phase contacting, which ranges from waste recovery, food and pharmaceutical industries to analytical and medical applications (Scott *et al.*, 1996).

### **2.3.2.3 Piezodialysis**

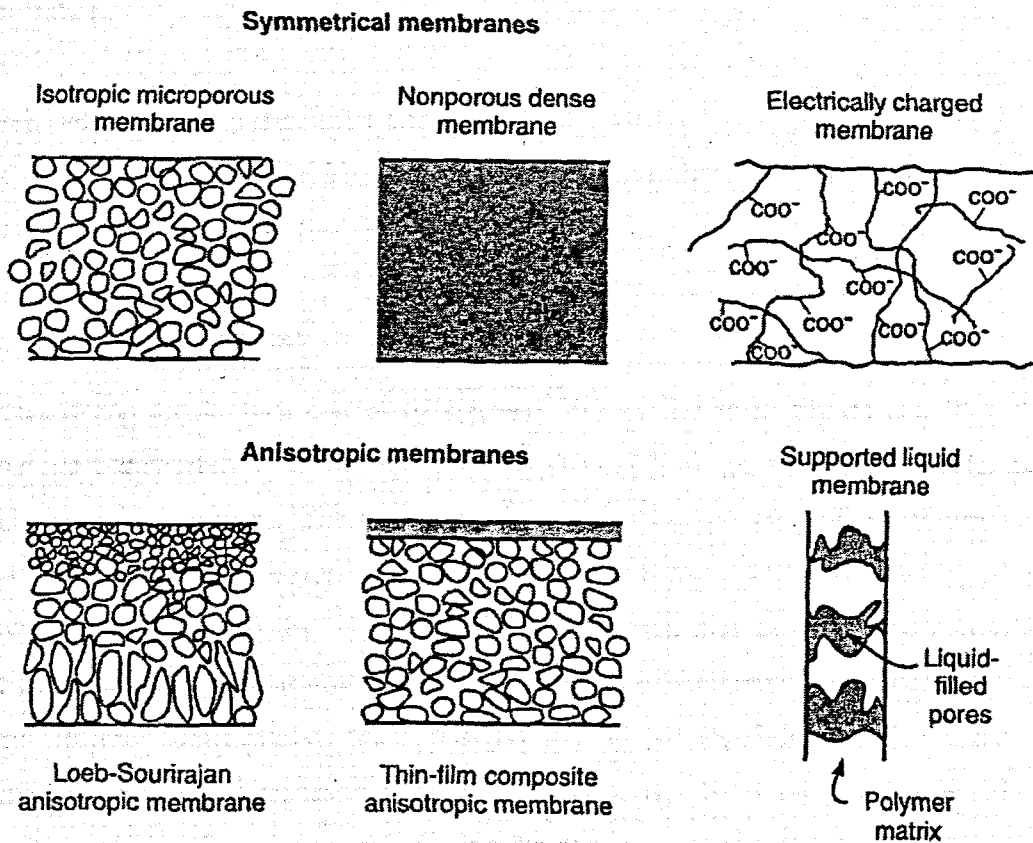
Piezodialysis is a pressure-driven process in which the solute species is forced through a composite, which consists of anionic and cationic permeable elements which are arranged in a mosaic structure. The mode of operation is attributed to its ion-exchange capacity through which it attains a concentration of permeating ions higher than that in the feed solution. The application of a differential pressure discharges (or squeezes) the ions into the permeate. The process thus provides a way of desalting aqueous solutions but it is not known to be practiced commercially (Scott *et al.*, 1996).

According to Scott *et al.* (1996), other processes and devices, which are available include membrane distillation, electrophoresis, dialysis, nano filtration, gas separation, electro dialysis, thermopervaporation, transport depletion, controlled release, thermo-osmosis, membrane electrodes and membrane catalysts.

## 2.4. TYPE OF MEMBRANE STRUCTURES

The functioning of a membrane depends on its structure as this essentially determines the mechanism of separation and, thus, the application. Scott *et al.*, (1996) mentioned that two types of structures are generally found in membranes, namely symmetric and asymmetric. Symmetric membranes are of three general types: approximately cylindrical pores, porous and non-porous (homogeneous). Asymmetric membranes are characterised by a non-uniform structure, which comprises an active top layer or skin supported by a porous support or sub layer.

The principal types of membranes are shown schematically in Figure 2.4 and are described briefly below (Baker 2004).



**Figure 2.4: Schematic diagram of the principal types of membrane**



## **2.4.1 Isotropic (Symmetric)**

### **2.4.1.1 Micro porous**

A micro porous membrane is similar in both structure and function as compared to a conventional filter. It has a rigid, highly voided structure, as shown in Figure 2.4, with randomly distributed interconnected pores. However, these pores differ from those in a conventional filter by being extremely small. All the particles that are larger than the largest pores are completely rejected by the membrane. Particles that are smaller than the largest pores, but larger than the smallest pores, are partially rejected, according to the pore size distribution of the membrane. Particles that is much smaller than the smallest pores will pass through the membrane. Thus, the separation of solutes by micro porous membranes is mainly a function of molecular size and pore size distribution.

In general, only molecules that differ considerably in size can be separated effectively by micro porous membranes, for example, in ultra filtration and micro filtration (Baker 2004).

### **2.4.1.2 Nonporous (Dense)**

Nonporous, dense membranes consist of a dense film as shown in Figure 2.4, through which permeates are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is directly related to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material. Thus, nonporous, dense membranes can separate permeates of a similar size if their concentration in the membrane material (that is, their solubility) differs significantly. Most gas separation, pervaporation and reverse osmosis membranes use dense membranes to perform the separation. These membranes usually have an anisotropic structure to improve the flux (Baker 2004).

### 2.4.1.3 Electrically charge

Electrically charged membranes can be dense or micro porous but are most commonly finely micro porous, with the pore walls carrying fixed positively or negatively charged ions. A membrane with fixed positively charged ions is referred to as an anion-exchange membrane because it binds anions in the surrounding fluid. Similarly, a membrane, which contains fixed negatively charged ions, is called a cation-exchange membrane (Baker 2004).

Separation with charged membranes is mainly achieved by the exclusion of ions of the same charge as the fixed ions of the membrane structure and, to a much lesser extent, by the pore size. The separation is affected by the charge and the concentration of the ions in solution. For example, monovalent ions are excluded less effectively than divalent ions and, in solutions of high ionic strength, selectivity decreases. Electrically charged membranes are used for processing electrolyte solutions in electrodialysis (Baker 2004).

### 2.4.2 Anisotropic (Asymmetric)

The transport rate of a species through a membrane is inversely proportional to the membrane thickness. High transport rates are desirable in membrane separation processes for economic reasons; hence, the membrane should be as thin as possible. Conventional film fabrication technology limits the manufacture of mechanically strong, defect-free films to about 20  $\mu\text{m}$  thickness (Baker 2004).

Asymmetric membranes are produced either by phase inversion from single polymers or as composite structures, as shown by Figure 2.4.

### 2.4.2.1 Phase inversion

Phase inversion incorporates porous structures, which are formed by precipitation from a homogeneous polymer solution. The membranes are made up of a relatively thick porous support layer (0.2 – 0.5mm) with a dense active 'skin' layer ( $<1\mu\text{m}$ ). These are classed as pore membranes and are used in NF and UF (Baker 2004).

Phase inversion is also used in the manufacture of micro porous symmetric membranes.

### 2.4.2.2 Thin film composite

Composite membranes differ from those produced by phase inversion since the skin and support are made of different materials. This enables a certain amount of tailoring of the membranes' function for specific applications and gives potential improvements over phase inversion.

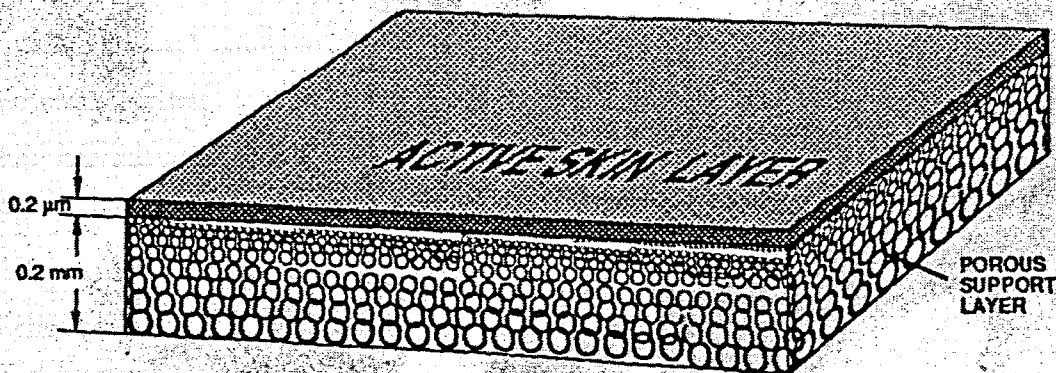


Figure 2.5: Asymmetric thin film composite membrane structure

## **2.5. MEMBRANE MATERIALS**

A number of membrane materials are currently manufactured. According to Baker (2004), most membrane materials are made from organic polymers. However, in recent years, interest in membranes formed from less conventional materials has increased. Ceramic membrane, dense metal and supported liquid membranes are being manufactured with alternative material.

Supported liquid membrane films are being developed for carrier-facilitated transport processes which will be discussed fully in the chapters to follow.

Examples of polymer membrane materials are:

- Cellulose acetate.
- Polyamide thin film composites.
- Polysulphone.
- Sulphonated polysulphone.
- Polyethersulphone.
- Polyvinylidenedifluoride.
- Polyacrylonitrile.
- Polytetrafluoroethylene.
- Other Polymers.

## 2.6. MEMBRANE MODULES

Industrial membrane plants often require hundreds to thousands of square metres of membrane to perform the separation that is required. Before a membrane separation can be performed industrially methods of economical and efficient packaging of large areas of membrane are required. These packages are called membrane modules. The development of the technology to produce low-cost membrane modules was one of the breakthroughs that led to commercial membrane processes in the 1960s and 1970s (Baker 2004).

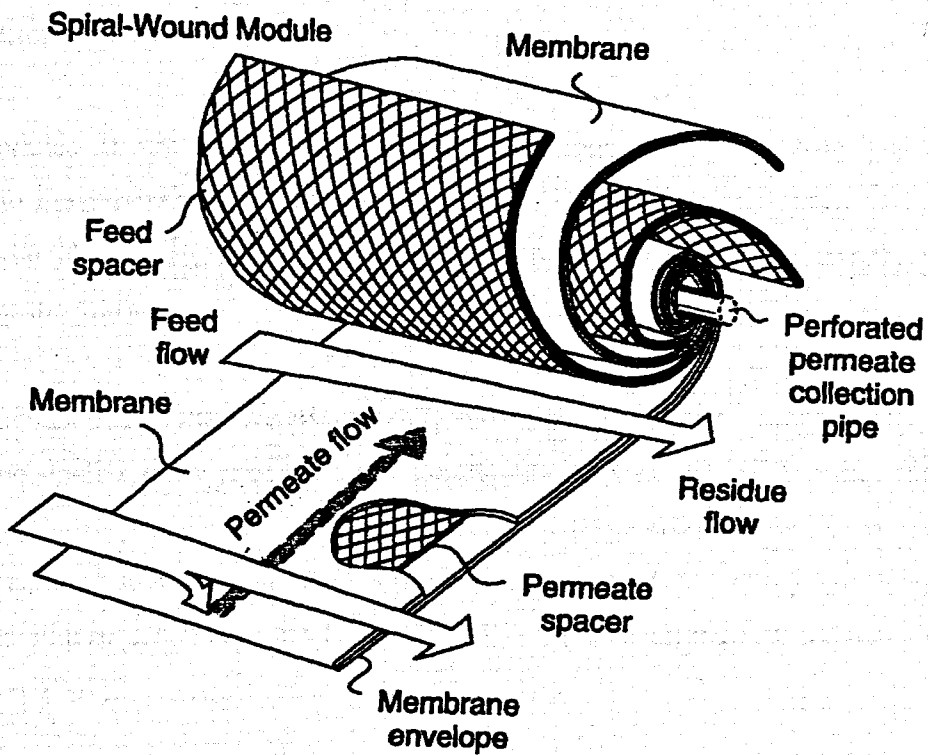
According to Baker (2004), the earliest designs were based on simple filtration technology and consisted of flat sheets of membrane which were held in a type of filter press. These are called plate-and-frame modules. Membranes in the form of 1- to 3-cm-diameter tubes were developed at the same time. Both designs are still used, but because of their relatively high cost these have been largely displaced in most applications by two other designs, namely the spiral-wound module and the hollow fibre module (Baker 2004).

According to Baker (2004), membrane modules are divided into the following types:

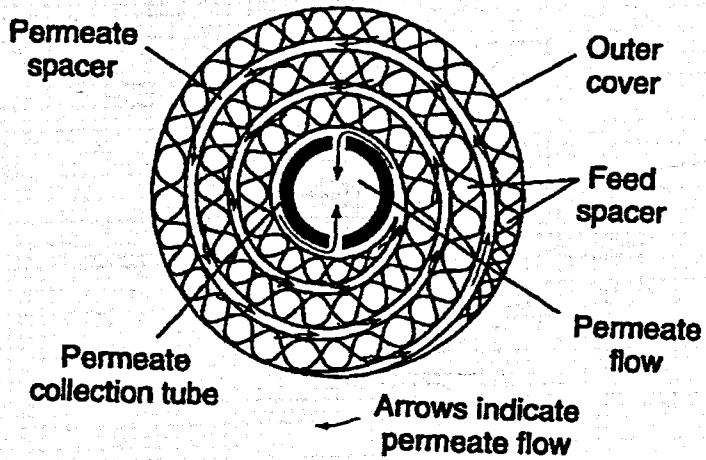
- Spiral wound.
- Tubular.
- Hollow fibre.
- Plate and frame.

### 2.6.1 Spiral wound

Feed solution passes across the membrane surface as shown in Figure 2.6. A portion passes through the membrane and enters the membrane envelope where it spirals inward to the central perforated collection pipe. One solution enters the module (the feed) and two solutions leave (the residue and permeate). Spiral-wound modules are the most common module design for reverse osmosis and ultra filtration, as well as for high-pressure gas separation applications in the natural gas industry (Baker 2004).



### Spiral-Wound Module Cross Section

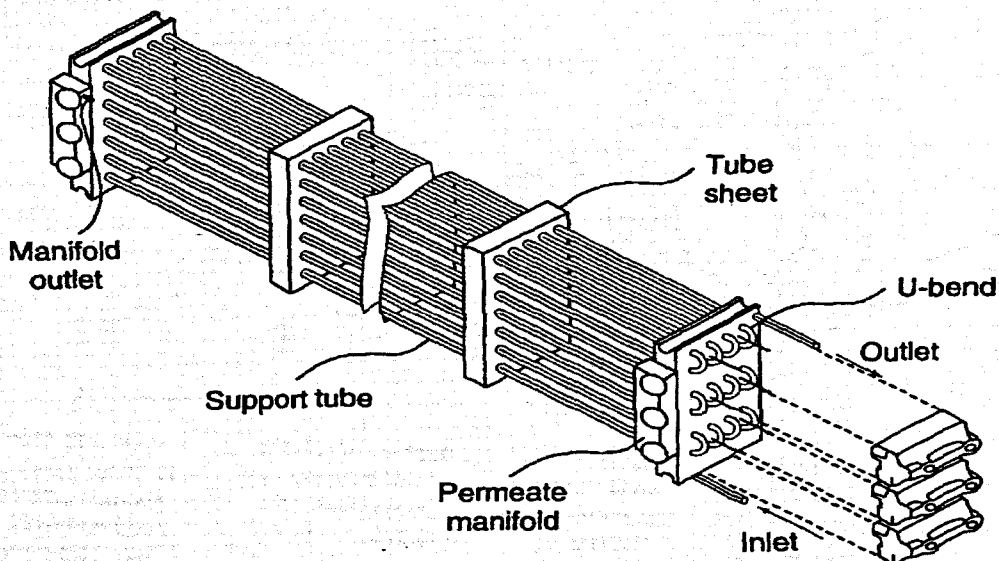


**Figure 2.6:** A exploded view and cross-section drawings of a spiral-wound module

## 2.6.2 Tubular

Tubular modules are now generally limited to ultra filtration applications, for which the benefit of resistance to membrane fouling, owing to good fluid hydrodynamics outweighs their high cost. Typically, the tubes consist of a porous paper or fibreglass support with the membrane formed on the inside of the tubes.

The first tubular membranes were between 2 and 3 cm in diameter. More recently as many as five to seven smaller tubes' each 0.5-1.0 cm in diameter' are nested inside a single larger tube. In a typical tubular membrane system, a large number of tubes are manifold in series. Permeate is removed from each tube and sent to a permeate collection header. A drawing of a 30-tube system is shown in Figure 2.7, where the feed solution is pumped through all 30 tubes connected in series (Baker 2004).



**Figure 2.7:** A tubular ultra filtration system in which 30 tubes are connected in series

### 2.6.3 Hollow fibre

Hollow fibre membrane modules are formed in two basic geometries. The first is the shell-side feed design and is used for hydrogen separations. In such a module, a loop or a closed bundle of fibres is contained in a pressure vessel. The system is pressurized from the shell side. Permeate passes through the fibre wall and exits through the open fibre ends. This design is easy to make and allows very large membrane areas to be contained in an economical system. Because the fibre wall should support considerable hydrostatic pressure, the fibres usually have small diameters and thick walls, typically 50- $\mu\text{m}$  internal diameter and 100- to 200- $\mu\text{m}$  outer diameter (Baker 2004).

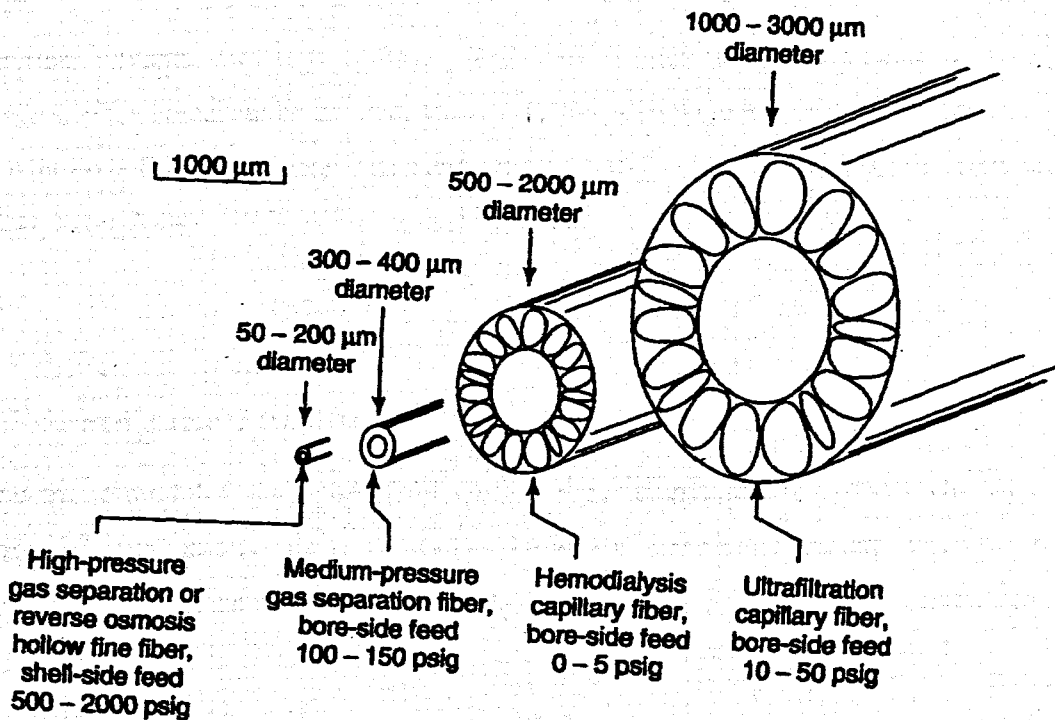


Figure 2.8: A schematic representation of the principal types of hollow fibre membranes



The second type of hollow fibre module is the bore-side feed type. The fibres in this type of unit are open at both ends, while the feed fluid is circulated through the bore of the fibres. In order to minimize pressure drop inside the fibres, the diameters are usually larger than those of the fine fibres that are used in the shell-side feed system and are generally made by solution spinning. These so-called capillary fibres are used in ultra filtration, pervaporation, and some low to medium-pressure gas applications. Feed pressures are usually limited to below 150 psig in this type of module (Baker 2004).

In bore-side feed modules it is important to ensure that all of the fibres have identical fibre diameters and permeances.

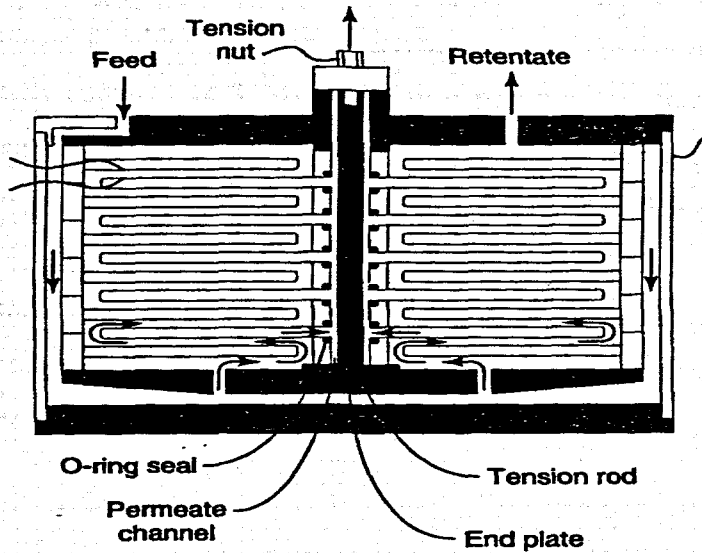
An important advantage of hollow fibre membranes is that compact modules with very high membrane surface areas can be formed. However, this advantage is offset by the generally lower fluxes of hollow fibre membranes, as compared to flat-sheet membranes made from the same materials (Baker 2004).

#### **2.6.4 Plate and frame (Flat plate /sheet)**

Plate-and-frame modules were one of the earliest types of membrane system, which have been developed for some small-scale applications. However, these units are expensive compared to the alternatives and leaks through the gaskets, which are required for each plate, are serious problems.

Membrane, feed spacers, and product spacers are layered together between two end plates. The feed mixture is forced across the surface of the membrane. A portion passes through the membrane, enters the permeate channel and makes its way to a central permeate collection manifold (Baker 2004).

Plate-and-frame modules provide good flow control on both permeate and feed side of the membrane, but the large number of spacer plates and seals lead to high module costs. The feed solution is directed across each plate in series. Permeate enters the membrane envelope and is collected through the central permeate collection channel (Baker 2004).



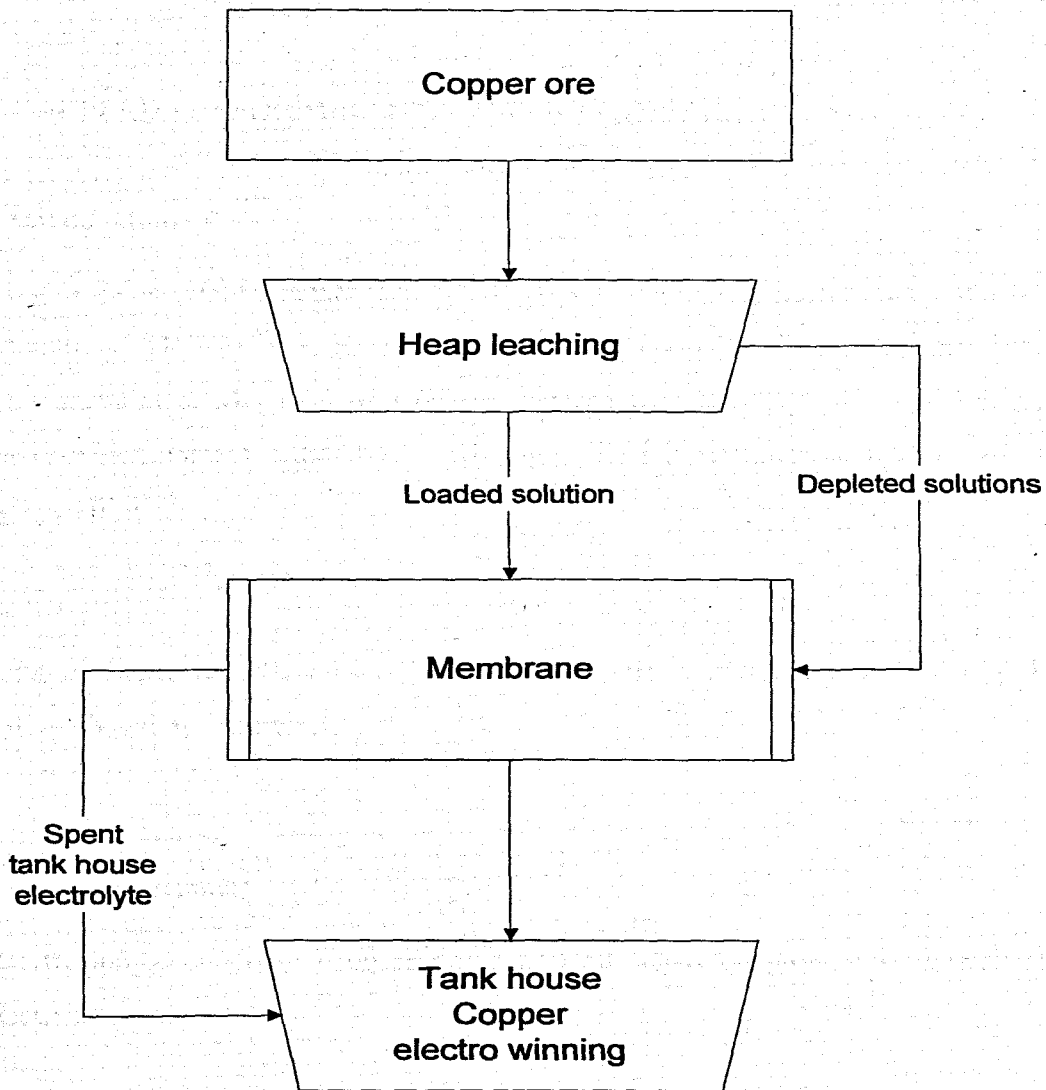
**Figure 2.9: Schematic plate and frame module**

These modules are presently only used in electro dialysis and pervaporation systems and in a limited number of reverse osmosis and ultra filtration applications with highly fouling feeds (Baker 2004).

## 2.7. POTENTIAL INDUSTRIAL APPLICATION SLM

Increased concern of air pollution from smelters and the continuing need for economical extractive processes for low grade ores have resulted in a wide ranging search for new extractive metallurgical techniques. In the copper mining industry, for example, heaped low grade ores are leached with sulphuric acid which produces an impure dilute copper solution. These solutions are acidic and typically contain 1 to 5 grams of copper per litre. One method of recovering the copper from this solution is by cementation with scrap iron. However, industry is turning increasingly to solvent extraction with an organic complexing agent followed by electro winning.

The coupled transport process described here, if used in the right module, could be used to replace the solvent extraction cycle. The overall flow scheme would then appear as illustrated Figure 3.15 (Baker *et al.*, 2004)



**Figure 2.10:** A schematic flow diagram, which shows the place of coupled transport membrane in the copper extraction scheme

---

## CHAPTER 3 : THEORY

---

### 3.1 COUPLED SUPPORTED LIQUID MEMBRANES (SLM)

#### 3.1.1 Introduction

According to Baker (2004), carrier facilitated transport membranes incorporate a reactive carrier in the membrane. The carrier reacts with and helps to transport one of the components of the feed across the membrane. Much of the work on carrier-facilitated transport has employed liquid membranes which contain a dissolved carrier agent held by capillary action in the pores of a micro porous film.

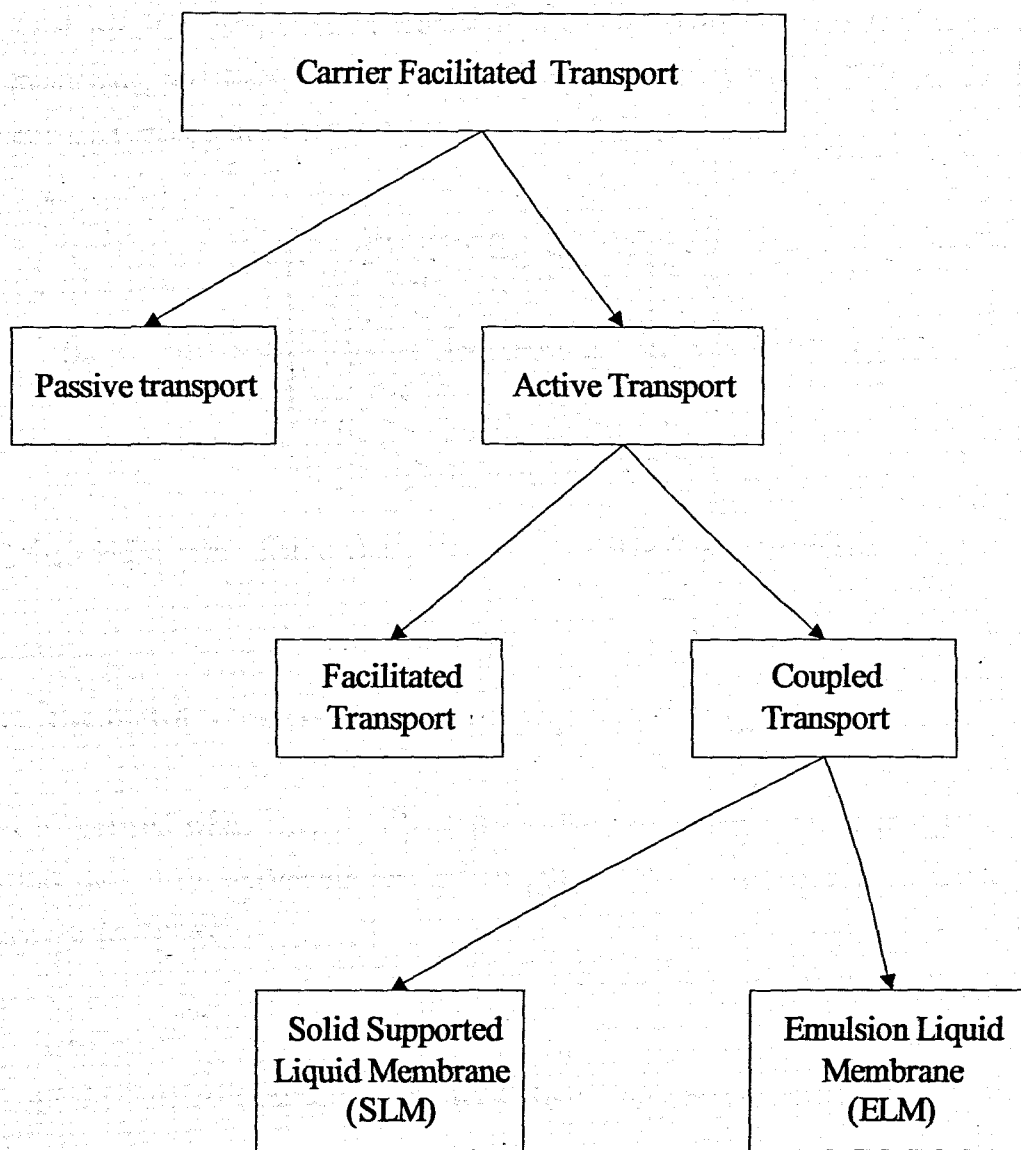
According to Baker (2004), carrier facilitated transport is divided into Passive and Active transport, as shown by Figure 3.1.

#### 3.1.2 Passive transport

Passive diffusion occurs down a concentration gradient, where the process is relatively slow and non-selective.

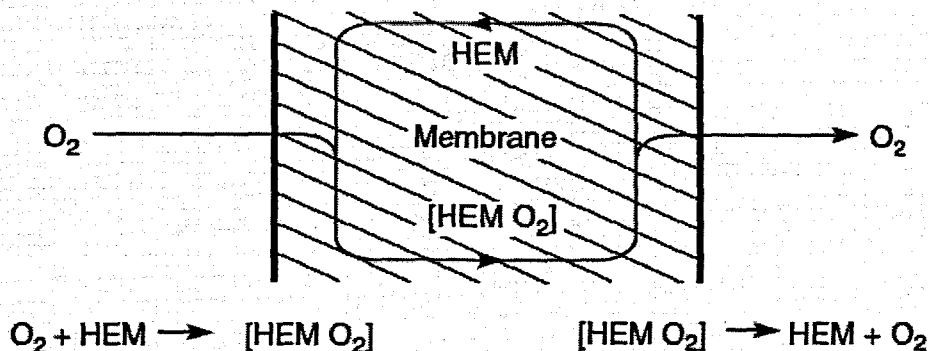
#### 3.1.3 Active (Facilitated) transport

In facilitated transport, the liquid membrane phase contains a carrier agent that chemically combines with the permeant, which will be transported.



**Figure 3.1: Diagram showing carrier supported liquid membrane**

The carrier, as shown in Figure 3.2 is haemoglobin, which transports oxygen. On the upstream side of the membrane, the haemoglobin reacts with oxygen, which then diffuses to the downstream membrane interface (Baker 2004).



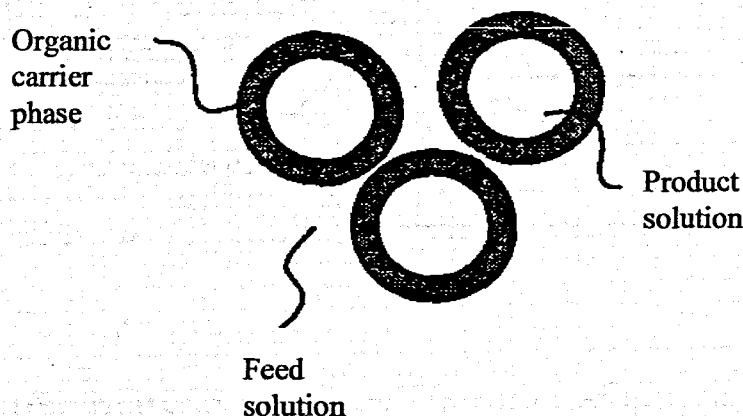
**Figure 3.2: Facilitated transport**

The reaction is reversed when oxygen is liberated to the permeate gas and haemoglobin is reformed. In this case, the haemoglobin acts as a shuttle to selectively transport oxygen through the membrane (Baker 2004).

### 3.1.3.1. Coupled transport (Emulsion supported liquid membrane - ELM)

The immobilized liquid carrier is the emulsion or 'bubble' membrane. This technique employs a surfactant-stabilized emulsion, as shown in Figure 3.3. The organic carrier phase forms the wall of an emulsion droplet, which separates the aqueous feed from the aqueous product solution. Metal ions are concentrated in the interior of the droplets (Baker 2004).

When sufficient metal has been extracted, the emulsion droplets are separated from the feed and the emulsion is broken to liberate a concentrated product solution and an organic carrier phase. The carrier phase is decanted from the product solution and recycled to produce more emulsion droplets.



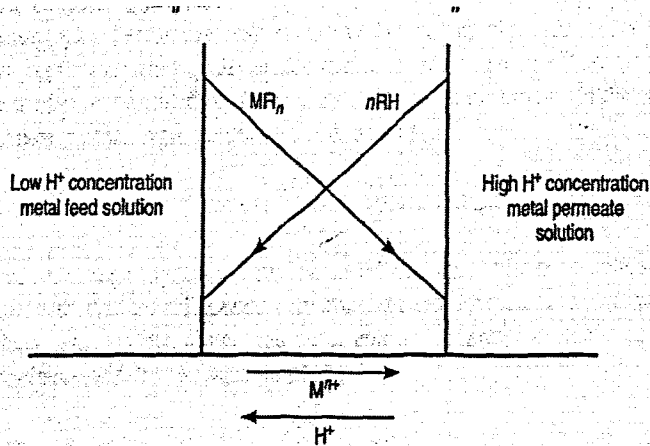
**Figure 3.3: Emulsion liquid membrane transport**

The stability of the liquid membrane remains a technical problem. Ideally, the emulsion membrane would be completely stable during the extraction step to prevent the two aqueous phases from mixing, but would be completely broken and easily separated in the stripping step. However, it has proved difficult to achieve this level of control over emulsion stability (Baker 2004).

### 3.1.3.2. Coupled transport (Solid supported liquid membrane - SLM)

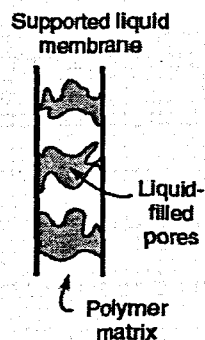
Coupled transport (SLM) resembles facilitated transport since a carrier agent is incorporated in the membrane. However, in coupled transport the carrier agent couples the flow of two species. As a result of coupling, one of the species can be moved against its concentration gradient provided the concentration gradient of the second coupled species is sufficiently large. In Figure 3.4, the carrier is an oxime that forms an organic-soluble complex with metal ions. The reaction is reversed by hydrogen. On the feed side of the membrane, two oxime carrier molecules pick up a metal ion, which liberates two hydrogen ions to the feed solution (Baker 2004).





**Figure 3.4: Carrier agent concentration gradients that form in coupled transport membrane**

The metal-oxime complex then diffuses to the downstream membrane interface where the reaction is reversed because of the higher concentration of hydrogen ions in the permeate solution. The metal ion is liberated to the permeate solution, and two hydrogen ions are picked up. The re-formed oxime molecules diffuse back to the feed side of the membranes (Baker 2004).



**Figure 3.5: SLM show how the pores are filled with liquid**

Carrier facilitated transport has often involved liquid membranes and the process is often called liquid membrane transport (Baker, 2004).

### 3.2 BACKGROUND

Various separation methods including solvent extraction and ion exchange are used for the recovery and concentration of precious metals from dilute solutions according to Kumar *et al.*, (2000). Szpakowska *et al.*, (1996) has mentioned that from a research perspective, supported liquid membranes are presently a topical separation technique as it is relatively cheap and energy efficient compared to solvent extraction.

Recently, publications have shown that a greater interest has developed specifically into copper recovery using SLM's. Various membrane systems, which use solutions from different origins and a number of selective commercial reagents, utilizing a number of solvents, have been reported (Szpakowska *et al.*, 1996; Sarangi *et al.*, 2004; Arous *et al.*, 2004; Alguacil, 1999; Valenzuela *et al.*, 1999).

Various organic carriers that are used for the membrane transport of copper (II), are hydroxime derivatives, LIX 54, sulphonamide derivative, thiourea derivatives and LIX 973N (Alguacil, 2001).

One of the promising techniques is the use of micro-porous hollow fibre modules as the interface in a liquid/liquid contactor. The basic principle of hollow fibre SLM is the immobilization of organic extractant in the pores of hydrophobic membranes that uses the wetting characteristics of the membrane. The aqueous feed is introduced on the lumen side (tube) because of the hydrophobic nature of the membrane (Yang *et al.*, 2000) that prevents the aqueous solution from displacing carrier extractant.

The main advantages of this technique are no entrainment, no flooding and a large interfacial area. In addition, this system provides a large ratio of membrane area to the volume of circulating process solutions.

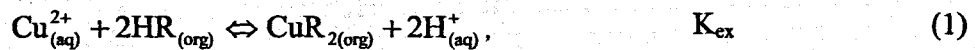
A disadvantage of this system could be the clogging of the hollow fiber membrane pores by suspended particles in the feed, requiring pre-filtration. Alternatively, the feed could be passed through the shell side instead of the minute lumen (tube) side of the membrane allowing for higher flow rates and hence minimizing particle settle out (Rathore *et al.*, 2001). Another approach is to adjust the inner diameter of the membrane allowing the feed to pass through the lumen (tube) side at a higher velocity. This is the main advantage of this novel method of using a tubular (id=0.0127m) SLM as apposed to the hollow fibre (id=0.0006 – 0.0008m) SLM (Valenzuela *et al.*, 1996; Danesi, 1984).

The advantage of a lower clogging rate can be offset against the lower surface area to process the fluid ratio. In the treatment of liquids which contain suspended solids, the SLM may prove superior and ultimately also results in a lower pressure drop.

In this study, the flux of copper across the tubular SLM was investigated in a closed circuit configuration for the purposes of determining the permeation of copper (II) under various conditions such as a varying flow rate and different concentrations of copper and strip pant. The strip pant that was used was sulphuric acid. Studies were also conducted to judge the reproducibility and stability of the proposed system for the direct recovery of copper (II). The feed used was a synthetic solution of copper sulphate.

### 3.2.1 Transport

The process of copper extraction by using a tubular membrane as solid support with salicylaldoximic-type extractants, proceeds by the diffusion of copper ions from the bulk feed solution in the tube through the membrane and out into the strip solution, with a stoichiometric quantity of hydrogen ions that move in the opposite direction. As the fibre's pore structure is completely impregnated with the protonated carrier of solvent, Equation 1 (Valenzuela *et al.*, 1999) shows the reversible reaction that is present to varying degrees between the bulk feed, through the membrane to the bulk strip.



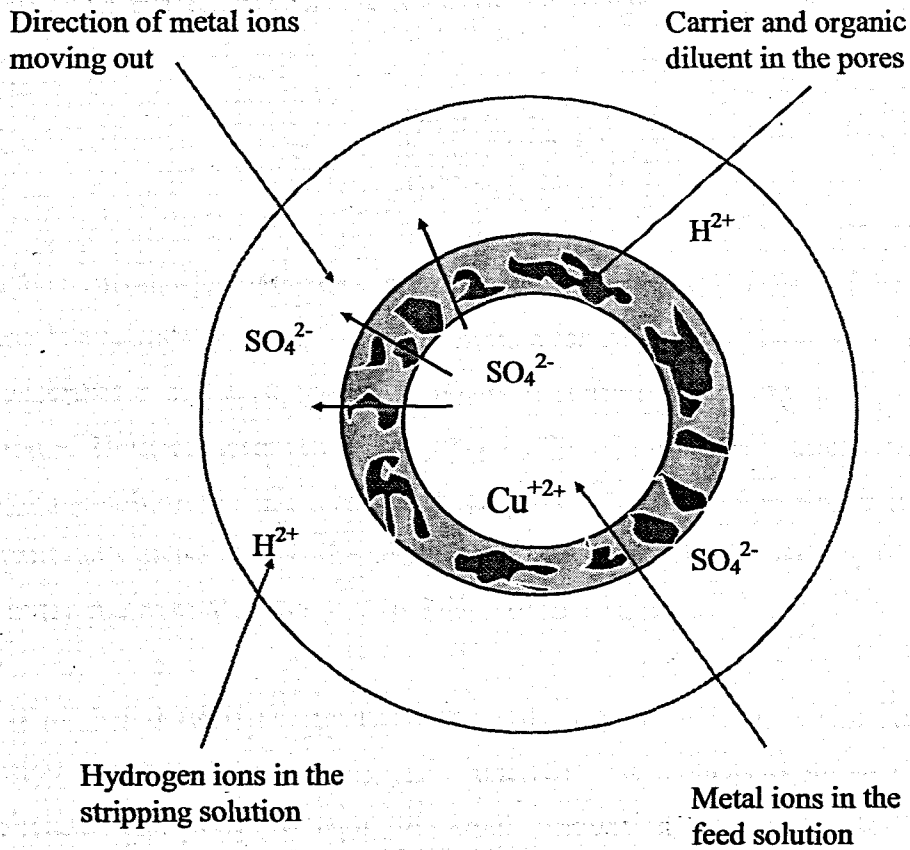
Where:  $HR$  is the acidic extractant

$\text{CuR}_2$  is the metal complex extracted into the organic phase

The subscript "aq" and "org" denote aqueous and organic solutions adjacent to the interface.

The copper ions diffuse through the bulk feed solution to the feed-membrane interface through the boundary layer, tube side, which forms a complex with the extractant. This extractant then diffuses through the membrane to the opposite surface (strip phase), where it exchanges the copper ion for a hydrogen ion, which effectively releases the copper into the strip phase, (Figure 3.6.).

The hydrogen form of the extractant then diffuses back through the membrane to the feed phase. The driving force for the exchange process is the concentration gradient of the hydrogen ions over the membrane (Breembroek *et al.*, 1998).



**Figure 3.6: Cross sectional area of SLM system**

### 3.2.2 Extraction equilibrium

This reaction is characterized by the equilibrium constant

$$K_{ex} = \frac{[\text{CuR}_2]_{org} [\text{H}^+]_{aq}^2}{[\text{HR}]_{org}^2 [\text{Cu}^{+2}]_{aq}} \quad (2)$$

where the terms in square brackets represents the molar concentrations of the particular chemical species. The equilibrium equation can be written for the organic phase or the aqueous phase.

The subscripts  $o$  and  $l$  represent the position of the feed and the permeate interfaces of the membrane. Thus, the term  $[\text{CuR}_n]_o$  represents the molar concentration of component  $\text{CuR}$  in the aqueous solution at the feed/membrane interface. The subscript  $m$  is used to represent the membrane phase. Thus, the term  $[\text{CuR}_n]_{o(m)}$  is the molar concentration of component  $\text{CuR}_n$  in the membrane at the feed interface (point  $o$ ).

Only  $[\text{CuR}_n]$  and  $[\text{RH}]$  are measurable in the organic phase, where  $[\text{H}^+]$  and  $[\text{Cu}^{2+}]$  are negligibly small. Similarly, only  $[\text{H}^+]$  and  $[\text{Cu}^{2+}]$  are measurable in the aqueous phase, where  $[\text{CuR}_n]$  and  $[\text{RH}]$  are negligibly small. Equation (2) can therefore be written for the feed solution interface as (Baker, 2004):

$$K' = \frac{[\text{MR}_n]_{o(m)} [\text{H}]_o^2}{[\text{RH}]_o^2 [\text{M}]_o} = \frac{k_m}{k_a} \cdot K \quad (3)$$

where  $k_m$  and  $k_a$  are the partition coefficients of  $\text{Cu}^{2+}$  and  $\text{H}^+$  between the aqueous and organic phases. This form of Equation 2 is preferred because all the quantities are easily measured experimentally. For example,  $[\text{MR}_n]_{o(m)}/[\text{M}]_o$  is easily recognizable as the distribution coefficient of metal between the organic and aqueous phases (Baker, 2004).

The same equilibrium applies at the permeate-solution interface, while Equation 3 can be recast to

$$K' = \frac{[MR_n]_{\ell(m)} [H]_{\ell}^n}{[RH]_{\ell(m)}^n [M]_{\ell}} \quad (4)$$

The distribution (partitioning) coefficient can also be written as follows where  $m_{Cu,feed}$  is the distribution coefficient:

$$K_{ex} = m_{Cu,feed} \frac{[H^+]_{aq}^2}{[HR]_{org}^2} \quad (5)$$

where R is LIX984 dissolved on Shellsol D70.

$K_{ex} = 0.85$  (Teramoto *et al.*, 1983; De Haan *et al.*, 1989; Breembroek *et al.*, 1998).

### 3.2.3 Modelling of copper transport

Models of Danesi (1984); De Haan *et al.* (1989) and Breembroek *et al.* (1998), are used to determine mass transport coefficients of the SLM system and are then checked against similar coefficients located by other researchers such as Kumar *et al.* (2000).

### 3.2.4 Permeability definition

The mass transfer rate through the liquid membrane can be characterized by the permeability coefficient the driving force of the extraction that depends on the concentrations on both sides of the membrane. If the driving force is high, only the concentration in the feed phase suffices to describe the process. Equation 6 describes this parameter as a function of flux  $J$  from a batch of feed phase (Danesi, 1984).

$$P = \frac{J}{C} = - \frac{dC}{Cdt} \frac{V}{A} \quad (6)$$

Where  $C$  is the feed metal concentration at time  $t$ ,  $V$  is the volume of the feed solution, while  $A$  is the total membrane surface area. This equation is applicable for a flat-sheet membrane.

### 3.2.5 Measurements of permeability coefficients

Assuming linear concentration gradients, fast interfacial reactions and the distribution coefficient of Cu (II) between the tubular fibre membrane phase and the stripping phase is much lower than that between the feed phase and the membrane, the final equation obtained for permeability (Equation 7) could be expressed as suggested by Danesi, (1984); Breembroek *et al.* (1998); Kumar *et al.*, 2000) and Rathore *et al.*, 2001. This model holds for low metal concentration in a recycle mode (Danesi, 1984).

$$V_f \ln \left( \frac{C_f}{C_s} \right) = A P_{Cu} \frac{f}{f+1} t \quad (7)$$



$$f = \frac{Q_f}{P_{Cu} L \epsilon N r_i} \text{ when } f = 1 \quad (8)$$

$P_{Cu}$  is a modified permeability coefficient which equals the permeability coefficient measured for a flat-sheet membrane (equation 6), when  $d_a < R$  and membranes, which have the same tortuosity factor, porosity, thickness and aqueous boundary layers of equal thickness, are compared.  $C_f$  and  $C_{f0}$  are metal concentrations at times  $t$  and  $0$ , respectively.

$A$  and  $V_f$  are effective area of membrane and volume of the feed respectively.  $Q_f$  is the volumetric flow rate ( $\text{cm}^3 \cdot \text{s}^{-1}$ ) of feed solution which flowed through the tube side. If  $V_f \ln(C_f/C_0)$  versus  $t$  slope is  $S_p$  then  $P_{Cu}$  could be obtained by the following relation (Danesi, 1984; Rathore *et al.*, 2001; Kumar *et al.*, 2000).

$$P_{Cu} = \frac{S_p r_i v_f}{2\pi r_i^2 L N v_f - S_p L \epsilon} \quad (9)$$

Where  $N$ ,  $L$ ,  $r_i$ ,  $\epsilon$ ,  $v_f$  are the numbers of fibre in the module, length of fibre, internal radius of tubular fibre membrane, porosity of tubular fibre and linear feed flow velocity respectively.

### 3.2.6 Mass transfer modelling

The design of tubular supported liquid membranes (TSLM) modules for the separation-concentration of copper by using permeability coefficient  $P_{Cu}$  centres on three mass transfer resistances (Rathore *et al.*, 2001; Kumar *et al.*, 2000):

- The first occurs in the liquid which flows through the tubular lumen.
- The second corresponds to the copper-complex diffusion across the liquid membrane, which is immobilized on the porous wall of the fibre.

- The third resistance is due to the aqueous interface that is created on the outside of the fibre.

The reciprocal of the overall permeability coefficient is given by the sum of resistances thus:

$$\frac{1}{P_{Cu}} = \frac{1}{k_i} + \frac{r_i}{r_{lm}} \frac{1}{P_m} + \frac{r_i}{r_o} \frac{1}{k_s} \quad (10)$$

where  $r_{lm}$  is the tubular fibre log mean radius,  $k_i$  and  $k_s$  are the aqueous feed and stripping mass transfer coefficients in the tube side and in the shell side respectively.  $P_m$  is the membrane permeability, which is related to the distribution coefficient of copper ( $m_{Cu,feed}$ ) with LIX984 +D70 by:

$$P_m = m_{Cu,feed} k_m = \frac{K_{ex} [HR]_{org}^2}{[H^+]_{aq}^2} k_m \quad (11)$$

where  $k_m$  is the membrane mass transfer coefficient, and  $m_{Cu,feed}$  is the distribution coefficient which is defined as:

$$m_{Cu,feed} = \frac{[CuR_2]_{org}}{[Cu^{2+}]_{aq}} \quad (12)$$

Substituting equation 11 into 10 (Rathore *et al.*, 2001; Kumar *et al.*, 2000) provides  $P_{Cu}$

$$P_{Cu} = \frac{S_p r_i v_f}{2\pi_i^2 L N v_f - S_p L \epsilon} \quad (13)$$

when the reaction is instantaneous at the stripping phase side, the contribution of the outer aqueous phase resistance is removed from Equation 10 and  $P_{Cu}$  is determined from

$$\frac{1}{P_{Cu}} = \frac{1}{k_i} + \frac{r_i}{r_{lm}} \frac{[H^+]_{aq}^2}{K_{ex} [HR]_{org}^2} \frac{1}{k_m} \quad (14)$$

### 3.2.7 Membrane Diffusion

The diffusion coefficient ( $D_{org}$ ) of copper extractant complexes through the organic membrane phase was determined in previous work. According Breembroek *et al* (1998), the  $D_{org}$  value should not be less than  $1 \times 10^{-11} \text{ cm}^2 \cdot \text{sec}^{-1}$ . In this study a value of  $9 \times 10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}$  was used. The effect of this value is to alter the  $P_m$  and therefore the resistance through the membrane. In this study it will be important to determine the overall impact of membrane resistance on overall mass transport. If it plays a major role, a better estimate of  $D_{org}$  will be required.

The effective diffusion coefficient ( $D_{eff}$ ) of copper through the supported liquid membrane depends upon the diffusion coefficient ( $D_{org}$ ) as well as the tortuosity ( $t_m$ ) and the porosity ( $\epsilon_m$ ) of the support.

$$D_{eff} = \frac{\epsilon_m D_{org}}{t_m} \quad (15)$$

The tortuosity is often taken to be approximately 2 (Breembroek *et al.*, 1998; Baker, 2004). The fibre geometry is known however, for the purposes of mass transfer calculation, the membrane thickness ( $d_m$ ) can be calculated by the equation given by De Haan *et al.*(1989); Breembroek *et al.*(1998).

$$\delta_m = r_{feedside} \ln \frac{r_o}{r_i} \quad (16)$$

where  $r_{feedside}$  is the radius of the fibre on the feed side and  $r_o$  and  $r_i$  refers to the outer and inner diameter of the fibre, respectively.

### 3.2.8 Mass transfer rate parameters

For the calculation of the permeability's from Equation 14, the mass transfer rate parameters should be known. This includes the mass transfer through the aqueous lumen feed phase and the diffusion through the liquid membrane. The mass transfer rate equations through the aqueous feed and membrane are derived from literature (De Haan *et al.*, 1989; Breembroek *et al.*, 1998).

The aqueous mass transfer coefficient ( $k_{aq,i}$ ) on the tube side of the membrane at low velocities, can be determined assuming laminar flow.

$$\frac{k_{aq,i} d_i}{D_{Cu, aq}} = 1.62 \left( \frac{d_i^2 \langle v \rangle}{LD_{Cu, aq}} \right)^{0.33} \quad (17)$$

where  $d_i$  is the internal tubular diameter,  $L$  is the length of the tube and  $v$  is the mean liquid velocity through the tube.

The diffusion of the chelate complex and the carrier through the membrane wall can be approximated by diffusion through a cylinder wall (De Haan *et al.*, 1989; Breembroek *et al.*, 1998).

$$k_m = \frac{2\pi D_{eff}}{\ln \left( \frac{r_o}{r_i} \right)} \quad (18)$$

The only parameters of the system that can not be located through calculation are the mass transfer coefficients in the aqueous feed ( $k_i$ ) and aqueous strip ( $k_s$ ), the location of which normally occupies mass transport studies such as these.

Assuming that  $k_s$  can be ignored, which is not an unreasonable assumption given the very high concentration of electrolyte on the strip side of the membrane (Kumar *et al.*, 2000), the location of  $k_i$  could be determined using the algorithm in Figure 3.7. Ultimate location of  $k_i$  would be by iterative calculation and once located, its value could be compared to other published values and its alteration to system variables i.e. feed flow rate, could be checked.

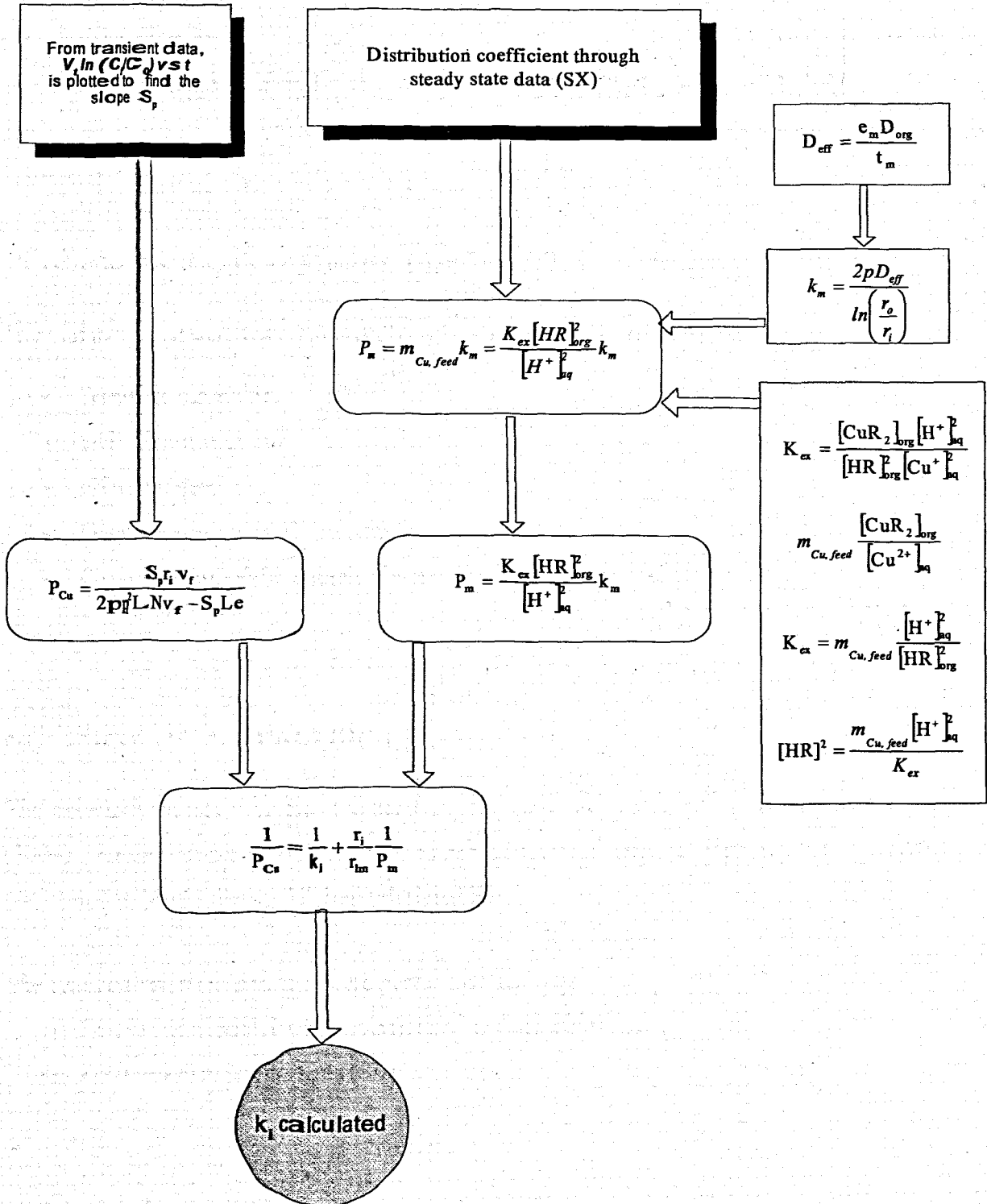


Figure 3.7: Suggested algorithm for locating the mass transfer coefficient in the liquid phase of the lumen.

---

## CHAPTER 4 : EXPERIMENTAL

---

This chapter describes the experimental procedures followed in this study.

The variables that were tested in order to achieve the set objectives were:

- Feed Concentration.
- Strip Concentration.
- pH of the feed.
- Flow rates of the feed and strip.
- Concentration of the organic phase.

### 4.1 SOLVENT EXTRACTION

The chemistry involved in SLM is basically the same as that of SX according to Juang *et al.*, (2004). In this work, batch SX experiments of Cu (II) with LIX984 in Shell sol D70 were performed to obtain the equilibrium relationship.

The types of batch experiments were performed, namely:

- Distribution (partitioning) coefficient measurements (SX).
- Permeation measurements (SLM).

#### 4.1.1. Distribution (partitioning) coefficients of Cu (II)

Equal volumes of 10 cm<sup>3</sup> Cu (II) and an organic extractant LIX984 dissolved in Shell sol D70 were pipetted into a 30 cm<sup>3</sup> glass stoppered equilibration vial and stirred mechanically for 30 minutes at room temperature (25 °C).

After phase separation, the copper concentration was determined by a standard absorption spectrometry technique. The distribution (partitioning) coefficient ( $m_{\text{Cu,feed}}$ ) of Cu (II), defined as the ratio of concentration of the copper species in the organic phase and in the aqueous phase, was calculated. Initially, a mass balance was performed by analyzing both phases. This was done to test the accuracy of the analytical techniques. However, in most cases only the aqueous phase was analyzed with the organic phase concentration determined by mass balance.

Distribution (partitioning) coefficients were measured over a broad range of concentrations of the feed, strip and organic complexing agent. In order to study the back extraction of Cu (II), the loaded organic solution was withdrawn into an equilibration tube and back extracted for approximately 30 minutes with the same volume of the strip pant (H<sub>2</sub>SO<sub>4</sub>). The Cu (II) content, after stripping the metal ion, was then analyzed. All the measurements were done in duplicate and agreement of the  $m_{\text{Cu,feed}}$  values that were obtained was within 3% with the accuracy of the mass balance within 95%. ALL calculations and test results are shown in APPENDIX I.

#### 4.1.2. Permeation Measurements (SLM)

A SLM module was design to extract and strip Copper ions simultaneously. Solvent extraction was achieved in one step through permeation of Copper using a solid support.



#### 4.2. CHARACTERISTICS OF PVDF MEMBRANE

A thin tubular hydrophobic micro-porous polyvinylidenedifluoride (PVDF) membrane support was used for this research. The characteristics of this membrane are summarized in Table 1.

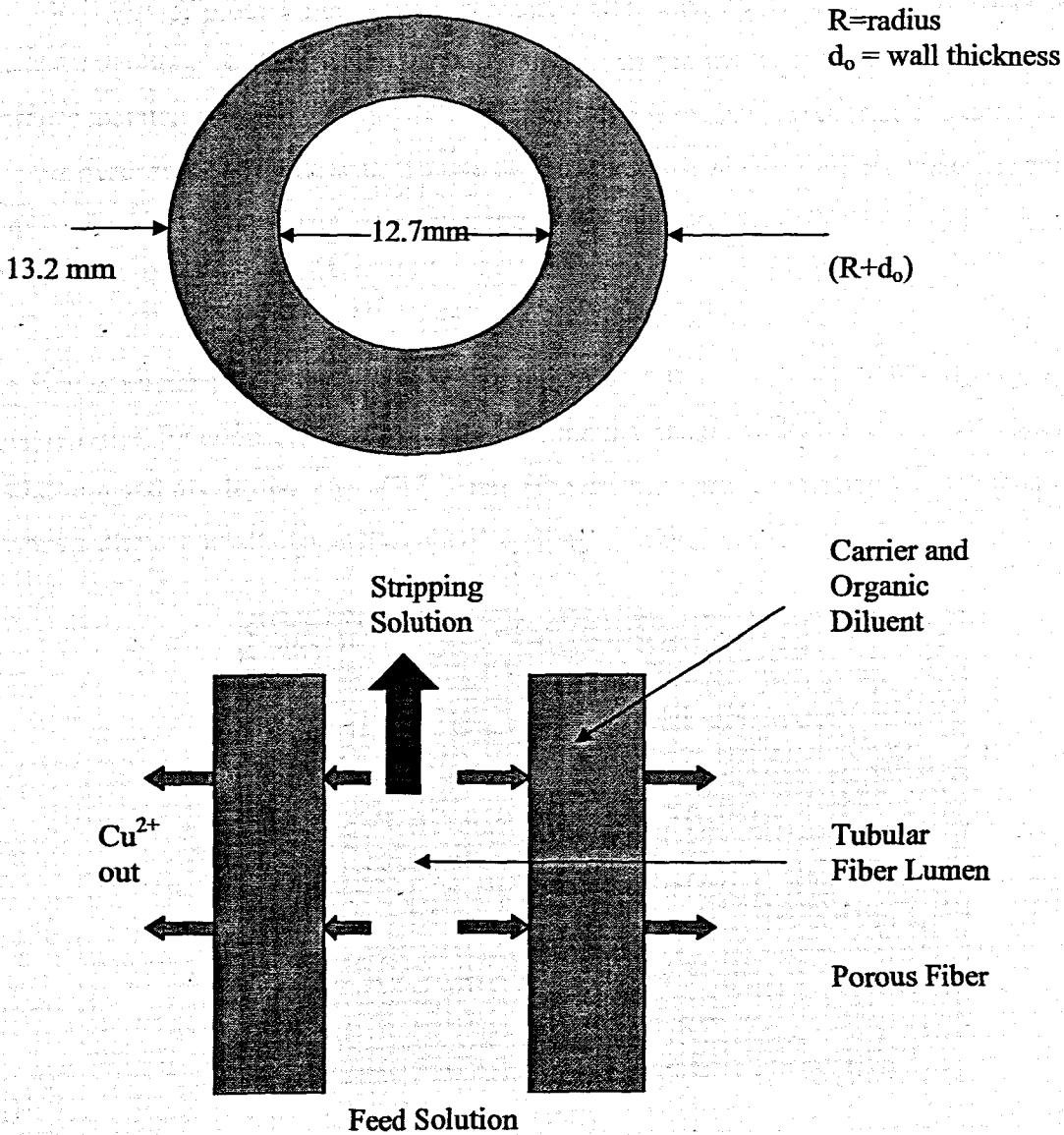
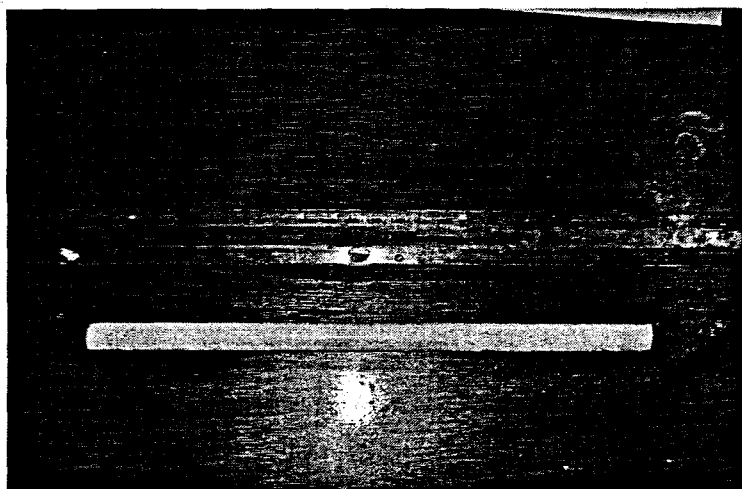


Figure 4.1: Schematic representation of a tubular membrane

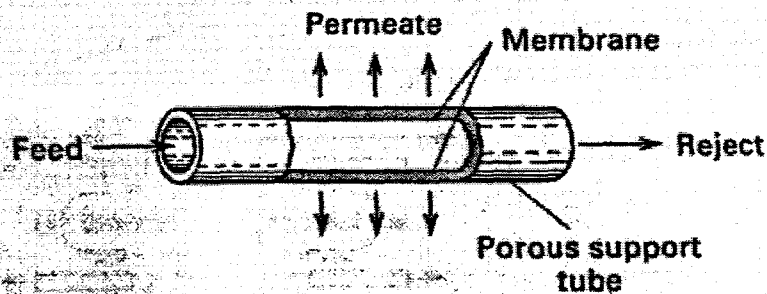
PVDF materials offer the same pH and temperature limits as PS, but has a higher tolerance to oxidizing agents such as chlorine while the PS materials they tend to crack after a prolonged exposure to high concentrations of chlorine. 'Cracking or fouling of the membrane film usually result to loss of process flux in PS materials, while with PVDF materials, particles are retained at the membrane surface which virtually eliminates fouling of the internal pore structure. With proper maintenance and storage, these membranes are reusable. According to Scott *et al.* (1996), better performance results with the use of PVDF as compared to the PS material, with fluxes of up to double those of similar membranes, and they are available as asymmetric membranes formed by phase inversion'.

A single tubular PVDF membrane with a length of 180mm is shown in Photograph 4.1. Tubular membranes, by definition, have a large-bore tubular shape, typically with an outside diameter of 13.2 mm and inside diameter of 12.7 mm, (Figure 4.2), unlike the narrow-bore tubular membrane types with very small diameters, called capillary membranes.



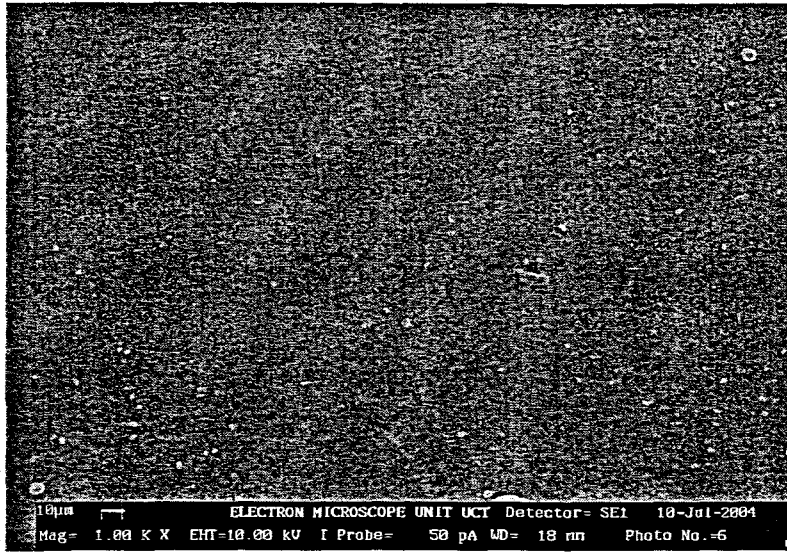
**Photograph 4.2: Single tubular membrane with a 180mm length**

The tubular membrane described in this report belongs to in the category of anisotropic membranes. According to Baker *et al.* (2004), anisotropic or asymmetric membranes consist of an extremely thin surface layer which is supported on a much thicker, porous substructure, as mentioned before.



**Figure 4.3:** Schematic representation of a tubular membrane

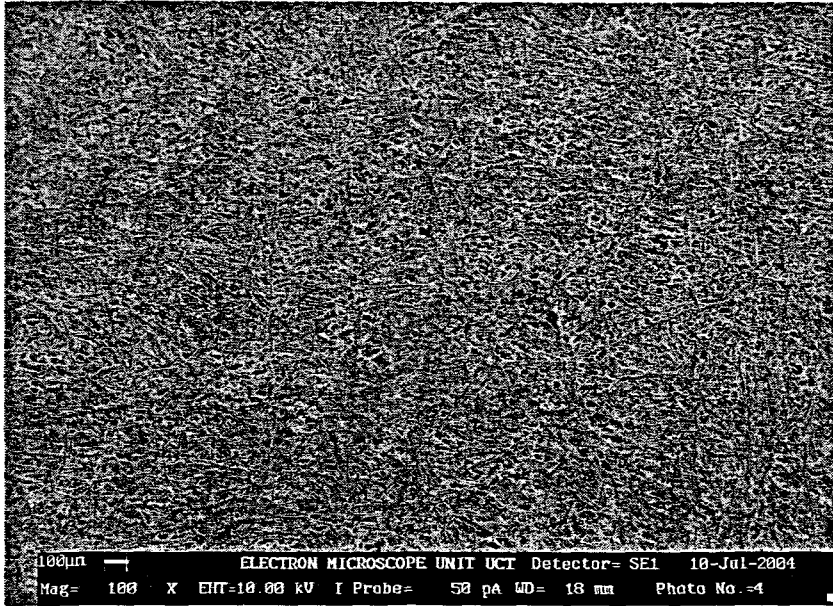
Micro porous membranes are characterized by their tortuosity, porosity and average pore size (diameter) Baker *et al.*, (2004). Pore size can be evaluated by microscopic observation. The optical microscope can be used for macro-porous materials with pore diameters down to 50  $\mu\text{m}$ . Scanning electron microscopy (SEM) is more convenient and more useful than optical microscopy. Pore diameter can be measured by using SEM and image techniques, which are useful as SEM images of pore structure can be analyzed numerically by computer software.



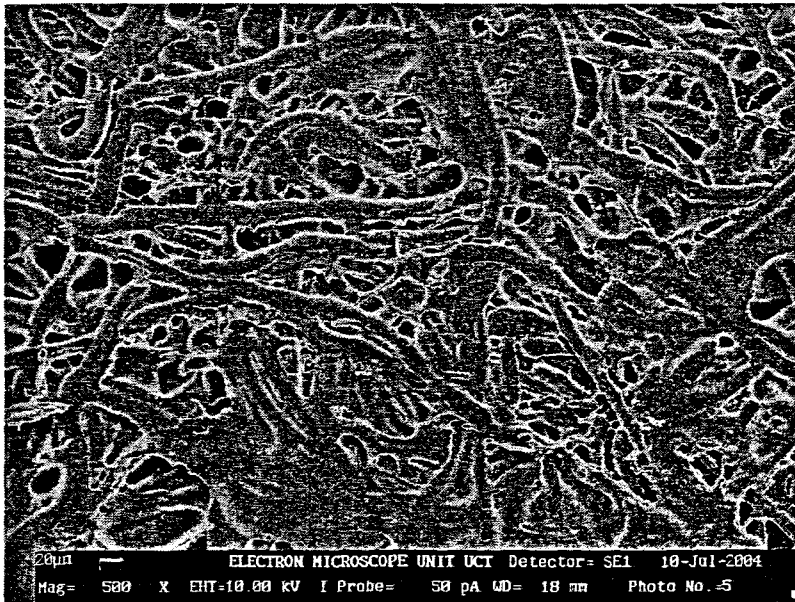
**Figure 4.4:** SEM showing the smooth, coated layer, inside surface area of membrane (magnified by 1000)

Average pore diameter has been calculated by taking 10 pore size samples which measures the size using the scale from an SEM. Membrane porosity ( $\epsilon$ ) is the fraction of the total membrane volume that is porous. A typical micro porous membrane has an average porosity of 0.3-0.7. SEM images of pore structure have been analyzed numerically by a computer package, which concluded that the porosity of this PVDF membrane is 0.6 or 60%.

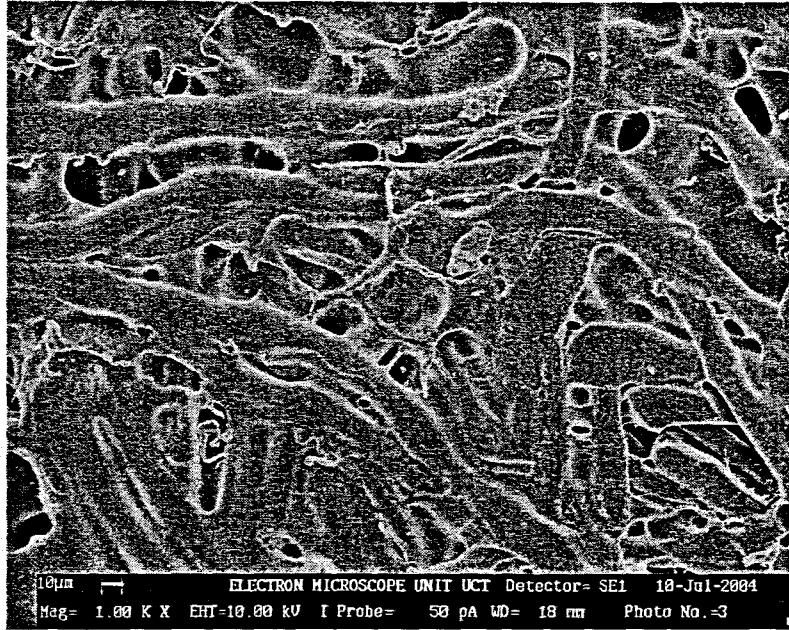
According to Baker *et al.* (2004), the membrane tortuosity ( $t$ ) reflects the length of the average pore compared to the membrane thickness. Simple cylindrical pores at a right angle to the membrane surface have a tortuosity of one, which means that the average length of the pore is the membrane thickness. Pores usually take a more meandering path through the membrane, rendering typical tortuosities in the range 1.5-2.5. From the above mentioned information structure of this membrane, it may be concluded that this membrane's tortuosity is 2.



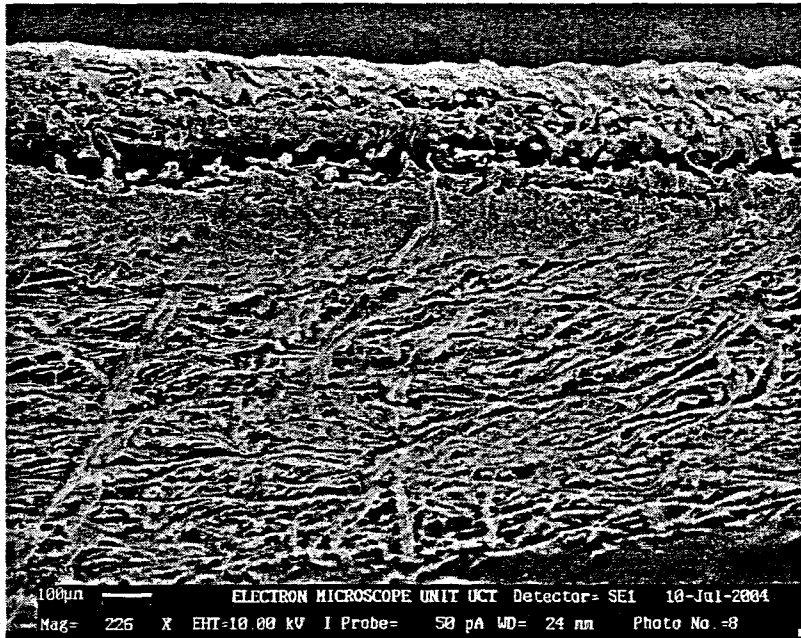
**Figure 4.5:** SEM showing the distribution of pores on the outer surface of membrane (magnified by 100)



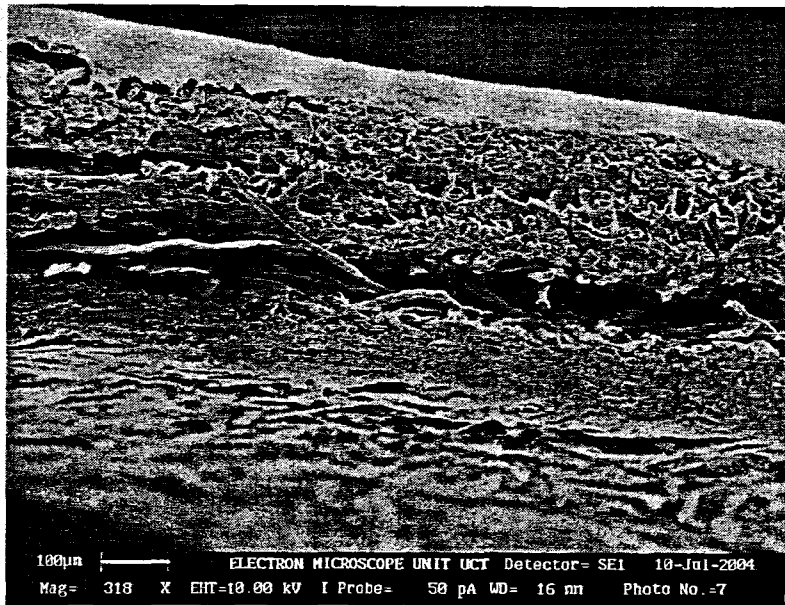
**Figure 4.6:** SEM showing the distribution of pores on the outer surface of membrane (magnified by 500)



**Figure 4.7:** SEM showing the distribution of pores on the outer surface of membrane (magnified by 1000)



**Figure 4.8:** SEM showing a cross-section of membrane (magnified by 226)



**Figure 4.9:** SEM showing a cross-section of membrane (magnified by 318)

**Table 4.1:** Characteristics of a single tubular membrane:

Membrane material	Polivinyldenedifluoride (PVDF)
Type of membrane	Tubular
Outer diameter ( $d_o$ )	0.0132 m
Inner diameter ( $d_i$ )	0.0127 m
Wall thickness ( $d_{wall}$ )	0.00025 m
Average pore size ( $d_p$ )	2 $\mu\text{m}$
Length of tube ( $L$ )	0.190 m
Number of tubes ( $N$ )	1
Porosity ( $\epsilon_{mem}$ )	60 %
Tortuosity ( $\tau$ )	2
Shell diameter ( $d_{module}$ )	0.22 m
Surface area ( $A_{surface}$ )	0.002413 $\text{m}^2$
Cutt off, approx.	18 000 Dalton
Operating pH	2 – 10

### 4.3. CARRIER AGENT

The carrier agent which was tested in this study is the latest of the oxime family. These oximes are all currently used in copper solvent extraction processes. The commercial extractant, LIX 984N (product from Cognis) is the mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime, which was supplied by Cognis Corporation Mining Chemicals Technology Division, Arizona, USA, Cognis *et al.*, (2002).

**Table 4.2: Properties of LIX 984N:**

<b>Physical Properties</b>	
Extractant appearances	Fluid Amber Liquid
Specific Gravity (25 <sup>0</sup> C/25 <sup>0</sup> C)	0.90-0.92
Flash Point	Greater than 160 <sup>0</sup> F
Copper Complex Solubility	0.30g/l Cu at 25 <sup>0</sup> C

<b>Performance Specifications</b>	
Maximum Copper Loading	5.1 to 5.4 g/l Cu
Extraction Isotherm Point	>4.40 g/l Cu
Extraction kinetics	>95% (30 seconds)
Extraction Cu/Fe selectivity	>2000
Extraction phase separation	<70 seconds
Strip Isotherm Point	<1.8 g/l Cu
Net Copper Transfer	>2.70 g/l Cu
Strip Kinetics	>95% (30 seconds)
Strip Phase Separation	<80 seconds

The carrier agent was diluted with a diluent, Shell sol D70, which is a product from Shell (PTY) Ltd. This mixture of carrier agent, LIX 984N, with the solvent Shell sol D70, forms an organic solution called the extractant.



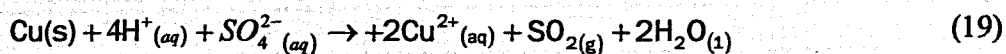
The diluent, Shell sol D70, consists predominantly of C<sub>11+</sub> paraffin and naphthenics.

**Table 4.3: Properties of Shell sol D70:**

Density @ 15°C	0.788 kg/L
Boiling range	193 - 245 °C
Flash point	73 °C
Aromatic content	0.03%.

#### 4.4. STRIPPANT

The strippant utilised in this research was sulphuric acid. It is a strong acid, with great oxidizing characteristics. In aqueous solution it is largely changed to hydrogen ions (H<sup>+</sup>) and sulphate ions (SO<sub>4</sub><sup>2-</sup>), each molecule gives two (H<sup>+</sup>) ions, thus sulphuric acid is dibasic. Concentrated sulphuric acid is a strong enough oxidizing agent to dissolve copper. Sulphur dioxide is produced by reduction of the sulphuric acid; the chemical reaction that takes place is shown in the equation below.



**Table 4.4: Properties of Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>):**

Density @ 15°C	1.82 kg.L <sup>-1</sup>
Viscosity	0.0267 Pa.s
Molar mass	98.08 kg.kmol <sup>-1</sup>

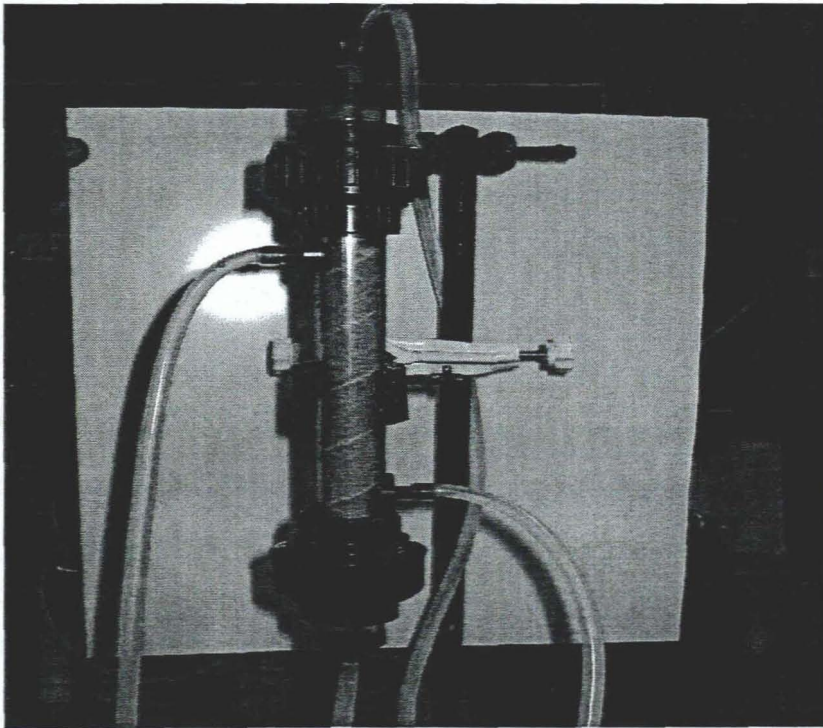
(www.Wikipedia.com).

## 4.5 EXPERIMENTAL SET-UP

### 4.5.1. Module Assembly

The tubular supported liquid membrane module was fabricated from a perspex tube with a diameter of 22mm in which a single tube (SLM) was fixed and sealed by epoxy quickset glue.

The module in Photograph 4.3 was designed to prevent any mixing between the strip and feed solution. In all test work, a thin hydrophobic micro-porous polyvinylidenedifluoride (PVDF) tubular membrane, which was supplied by Koch (USA), was used. The specifications for this material is given in Table 4.1



**Photograph 4.3: Single tubular SLM membrane set-up**

#### 4.5.2. Reagents and solutions

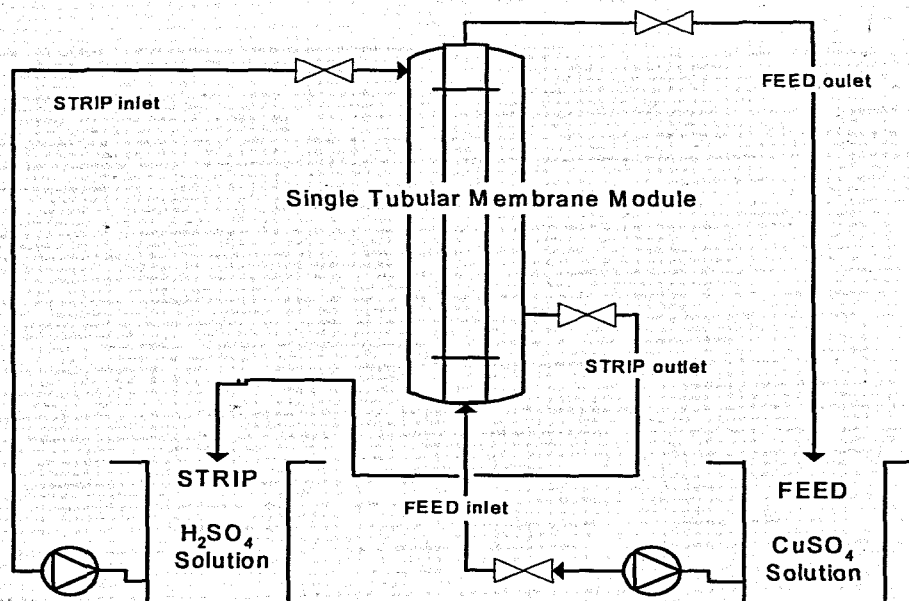
The commercial extractant LIX 984N (product from Cognis) is mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime, which was supplied by Cognis Corporation Mining Chemicals Technology Division, Arizona, USA . The reagent was used as received from the manufacturer and diluted in Shell sol D70 (consists predominantly of C<sub>11+</sub> paraffins and naphthenics).

The aqueous feed phase was made up by using a copper sulphate solution. Approximately 3.46g of CuSO<sub>4</sub>·5H<sub>2</sub>O salt (AR grade) was weighed and placed into a 1000ml bottom flask. Distilled water was then added to make up the stock solution. From the stock solution concentrations of 100, 150, 200 and 250 ppm, were produced to conduct the various experiments.

Concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) solutions were used as metal-acceptor stripping agents. 98% Sulphuric acid was added to the distilled water to form concentrations of 5, 10, 15, 20 and 25% to conduct the various experiments. All other chemicals were of an analytical grade.

#### 4.5.3. Membranes

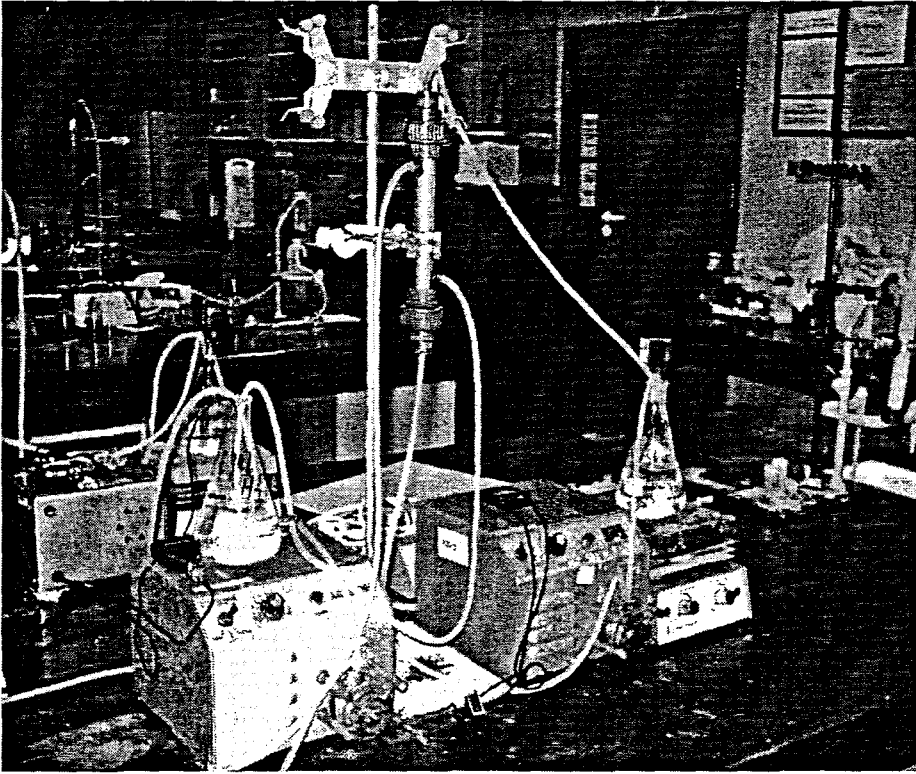
The tubular supported liquid membranes were impregnated with carrier solution, which contained the extractant dissolved in the diluents Shell sol D70, by soaking it in the organic solution and placing it in a dessicator under a vacuum for at least 2 hours. According to Ma *et al.*, (2000), the vacuum enhances the overall permeation of the organic phase into the pores of the membranes. After soaking, the membrane was removed from the dessicator, taken out of the organic solution, wiped with a piece of tissue paper and rinsed with water to ensure the removal of excess carrier (and solvent). The membrane was then fixed inside the SLM apparatus.



**Figure 4.10: Schematic view of tubular SLM operated in recycle mode for the recovery of Cu (II) from aqueous media**

#### 4.5.4. General experimental procedure

Figure 4.10 shows the experimental set-up where the feed and strip phases flow parallel along the fibre wall. The single tubular membrane, with an average pore diameter of  $10\mu\text{m}$ , 18cm length and  $24\text{cm}^2$  surface area, was operated at a flow rate of  $0.167$  to  $0.833\text{cm}^3\text{sec}^{-1}$  in recycle mode. All experiments were carried out at ambient temperature. Both the feed and strip solutions from  $200\text{cm}^3$  reservoirs were counter currently recycled. It was chosen to run the aqueous feed in the lumen side and the aqueous strip in the shell side.



**Photograph 4.4:** Photograph of a single tubular membrane SLM set-up showing the counter current flow of feed and strip in the tube and shell side

#### 4.5.5 Transport (permeation) experiments

The batch transport experiments were carried out in the tubular SLM module. The geometrical membrane area was  $24\text{cm}^2$  and the volume of the feed and stripping solution was  $200\text{ cm}^3$ .

Experiments were conducted by testing the aqueous feed solutions, which contained different concentrations of Cu (II) at 100, 150, 200, 250, 300, 350 and 400ppm. Experiments were conducted testing the aqueous strip solutions, which contained concentrations of 5, 10, 15, 20 and 25%  $\text{H}_2\text{SO}_4$ . Experiments at different reagent concentration of 10, 15, 20, 25, 30 and 40% were tested. The last parameter that was tested involved different feed and strip flow rates at 10, 15, 20, 30, 40 and 50 ml/min. Batch experiments lasted for 50 hours per run. At the end of all the batch experiments, an optimum condition to increase the permeation of Cu (II) for this system was achieved.

#### 4.6 PERMEATION STUDY

The feed and strip solutions were re-circulated by means of calibrated peristaltic pumps (re-circulating mode), which operated in stirred regime. Samples of  $1\text{cm}^3$  were taken out at the outlets of the feed and strip phases at regular intervals. Membrane permeabilities were determined by monitoring Cu (II) concentration by a Varian Techtron AA-1275 absorbance spectrophotometer in the feed as a function of time. The pH of the aqueous feed was also taken at regular intervals.

---

## CHAPTER 5 : RESULTS AND DISCUSSION

---

The experimentally determined permeability's  $P_{Cu}$  were calculated from kinetic data, interfacial area of the membrane volume of the feed circuit and Equation 14 (Table 3.1). Only tests which were successfully completed are shown. Unsuccessful experimental runs were deemed to be so when one of the following occurred:

- tube rupture as a result of exposure to sulphuric acid;
- O-ring fatigue;
- Incorrect assembly (design problems);
- Membrane ruptures as a result of incorrect handling or deterioration of solid support.

Leakages in the system could easily be detected by a change in the volume of the feed and strip reservoirs and the volume inside the shell and membrane.

Preliminary experiments indicated that a tubular SLM unit was:

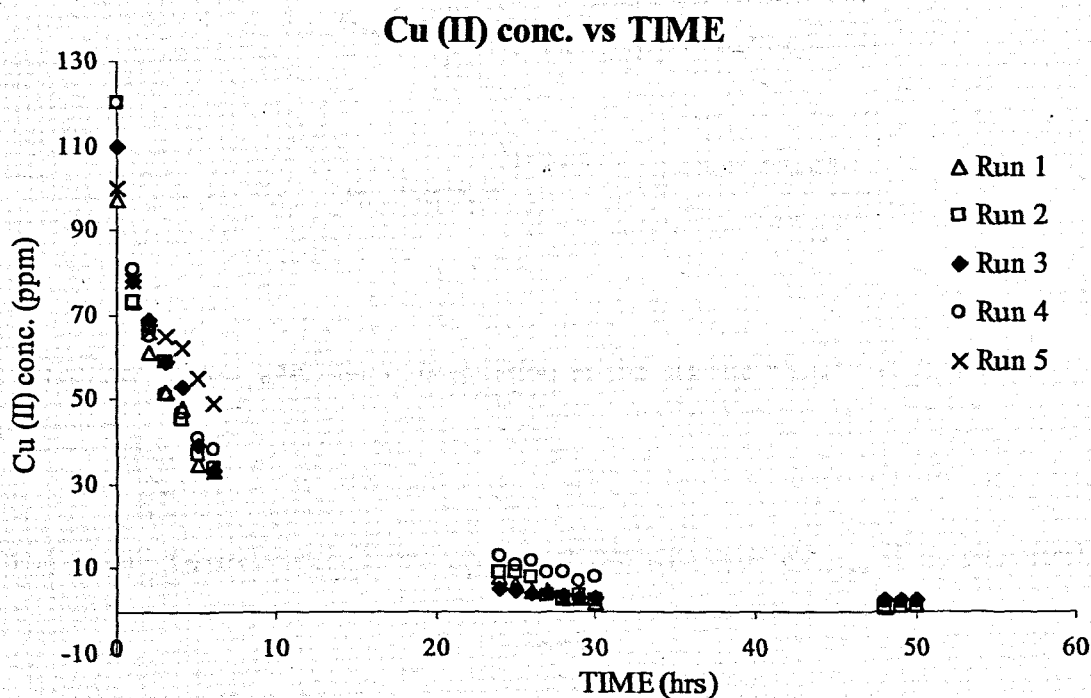
- Capable of reducing Cu (II) concentration to low levels in the feed;
- Capable of generating a concentrated solution of Cu (II) in the strip; and
- Capable of stable operation for more than four batch experiments.

### 5.1. REPRODUCIBILITY OF TUBULAR SLM SYSTEM

To prove that the system employed in this test work was stable and rendered reproducible results, an applicably designed experiment rendered the following results. The experiment used a membrane that was loaded to the optimum concentration of carrier i.e. 20%, acid concentration at 25%, and a feed flow rate and concentration of  $0.333\text{cm}^3.\text{s}^{-1}$  and 100ppm respectively.

This system was then subjected to continual cycles of fresh feed and strippant. The kinetics of each test was measured and is presented in Figure 5.1.

As seen from Figure 5.1, stability of the TSLM was quite remarkable when four consecutive experiments were performed without re-impregnation. The fifth run was aborted half way through the experiment, because of the TSLM started to leak which was due to the tearing of the fibre membrane material. The results obtained from these experiments were quite reproducible and no significant reduction in permeability was observed.



**Figure 5.1: Experimental courses of Cu (II) concentration in the feed reservoir. Four consecutive batch experiments without initial re-impregnation of the membrane**



## 5.2. EQUILIBRIUM DISTRIBUTIONS

A very important aspect of the test work was to determine the partition curve of the copper distribution between the organic and aqueous phases and the results of these tests are given in this section.

From the test results the distribution coefficient, ( $m_{Cu}$ ), for both the extraction and stripping could theoretically be calculated as mentioned in chapter 4. Because equal volumes of aqueous and organic solutions were used:

$$m_{Cu}(\text{feed}) = \frac{[\text{Conc.}]_{\text{organic after extraction}}}{[\text{Conc.}]_{\text{feed after extraction}}} \quad (20)$$

$$m_{Cu}(\text{strip}) = \frac{[\text{Conc.}]_{\text{organic after stripping}}}{[\text{Conc.}]_{\text{strip after stripping}}} \quad (21)$$

As per (Kumar *et al* , 2000) the concentration in the organic phase was determined by mass balance.

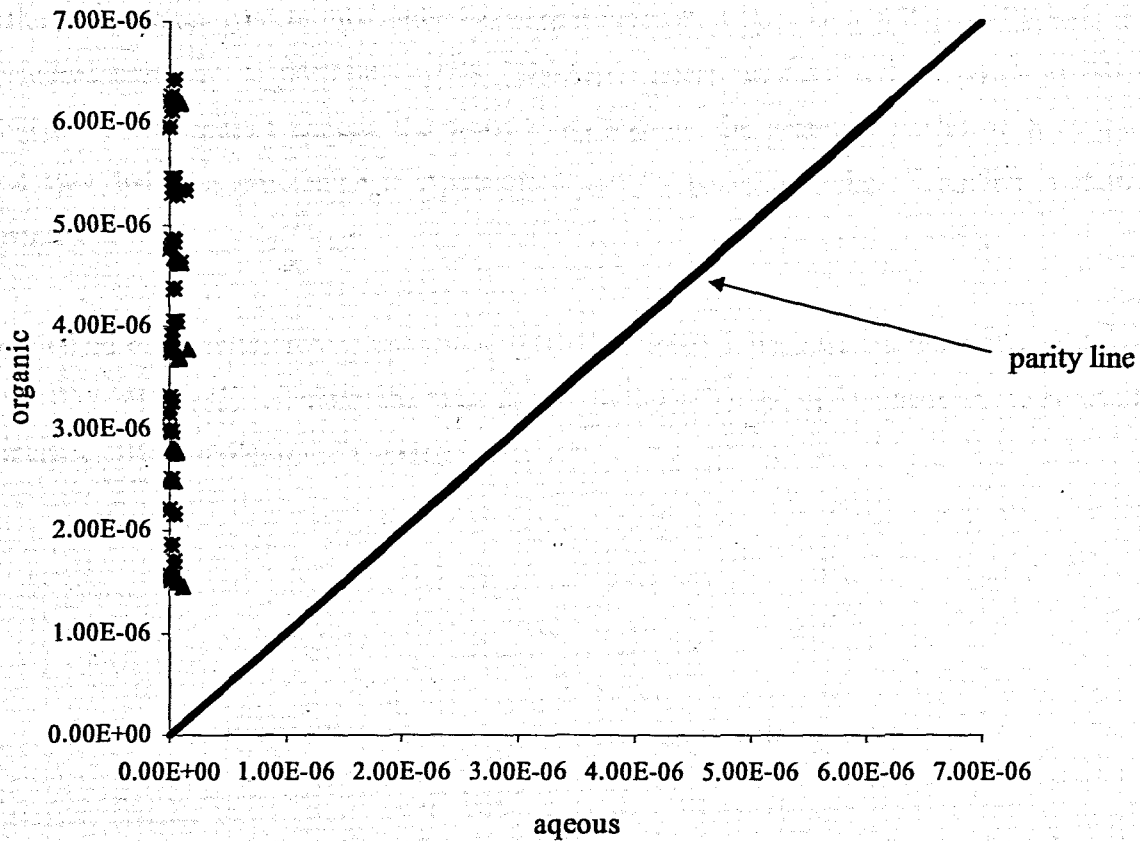
$$[\text{Conc.}]_{\text{organic after extraction}} = [\text{Conc.}]_{\text{feed before extraction}} - [\text{Conc.}]_{\text{feed after extraction}} \quad (22)$$

and

$$[\text{Conc.}]_{\text{organic after extraction}} = [\text{Conc.}]_{\text{feed before stripping}} - [\text{Conc.}]_{\text{feed after stripping}} \quad (23)$$

Equations (22) and (23) hold true only if equal volumes of aqueous and organic solutions are used as mentioned in chapter 4, and the strip solution is initially free of the copper ions used.

To give some idea of the partition of copper between the two phases Figure 5.2 indicates the distribution.



**Figure 5.2: Cu (II) partitioning between the aqueous and organic phases when there is a change in the reactant and strippant concentration.**

It can be observed that the copper ions tend to be intensely close to the y axis, proving it to be overwhelmingly soluble in the organic phase. In light of this and average  $m_{Cu}$  (distribution coefficient) of 0.9873 was used for all calculations and to show the accuracy of this average as representative of the equilibrium of the system, a variance of 0.000162 is calculated.

### **5.3. MASS BALANCE OF TRANSIENT TESTS**

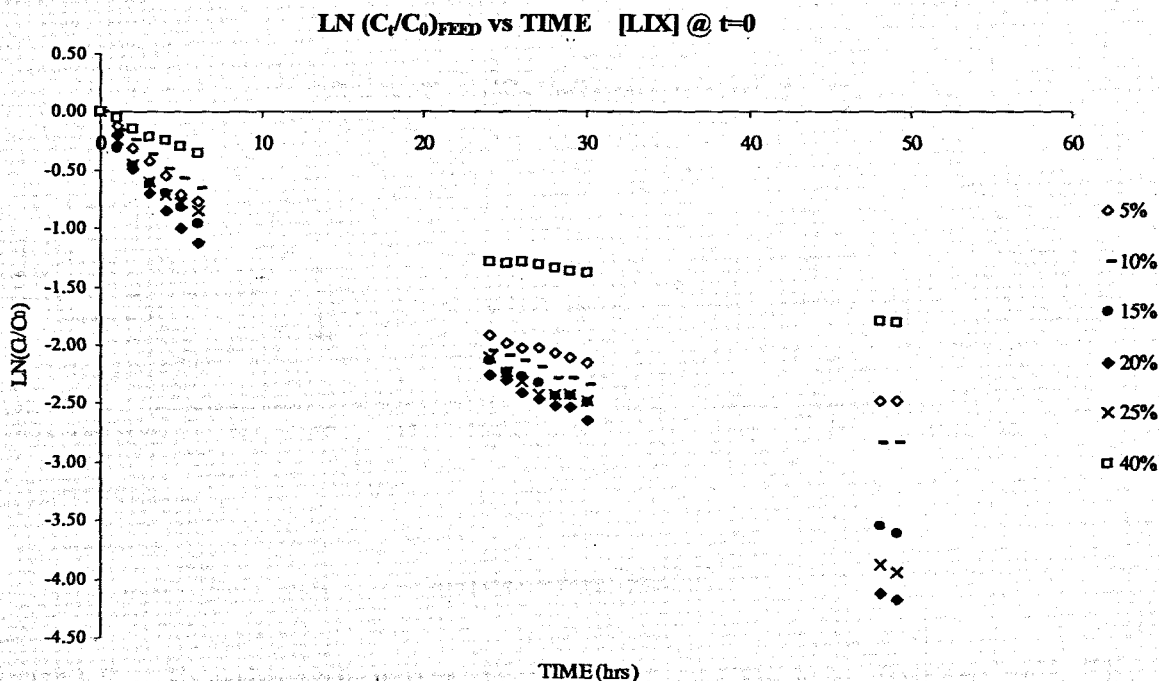
As the system employed in this study was entirely closed, it became possible, and indeed it was considered pertinent to perform a mass balance in every test. An average error of 5% was calculated on the mass balances, the worst being 9% and the best 1%. Tables of the results of these mass balances are shown in Appendix J and an example of the calculation is shown in Appendix A.

The method of calculation was to assume that all atomic copper mass in the feed could pass to one of three places; 1) remain in the feed, 2) pass to the strippant, or 3) remain in the pores of the membrane after completion of the kinetic test.

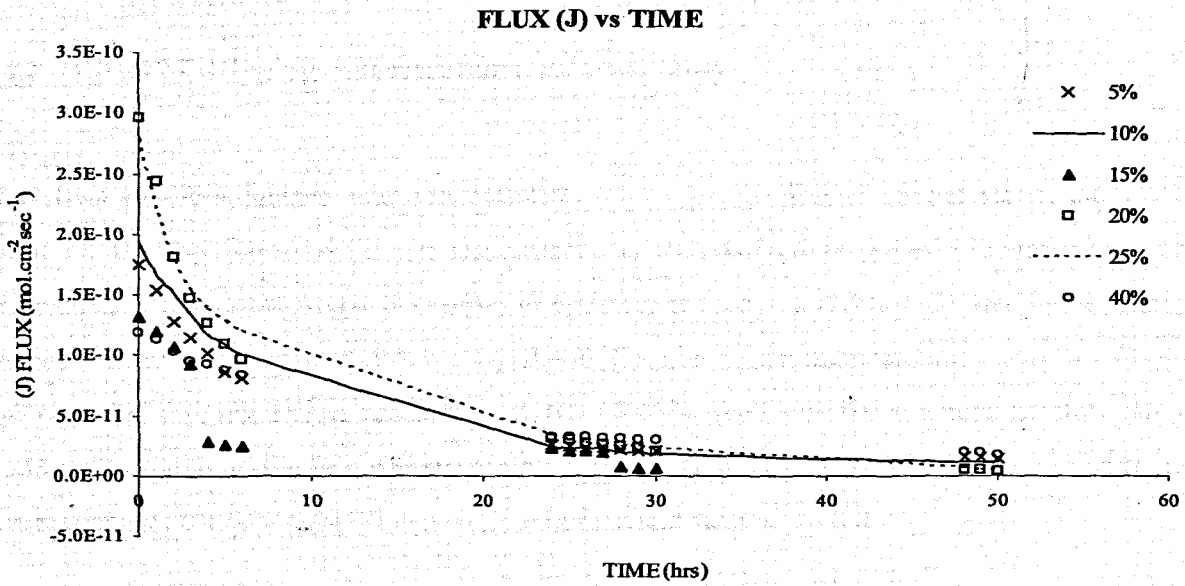
## 5.4. QUALITATIVE ASSESSMENT OF RESULTS

### 5.4.1 Effect of carrier concentration on permeability

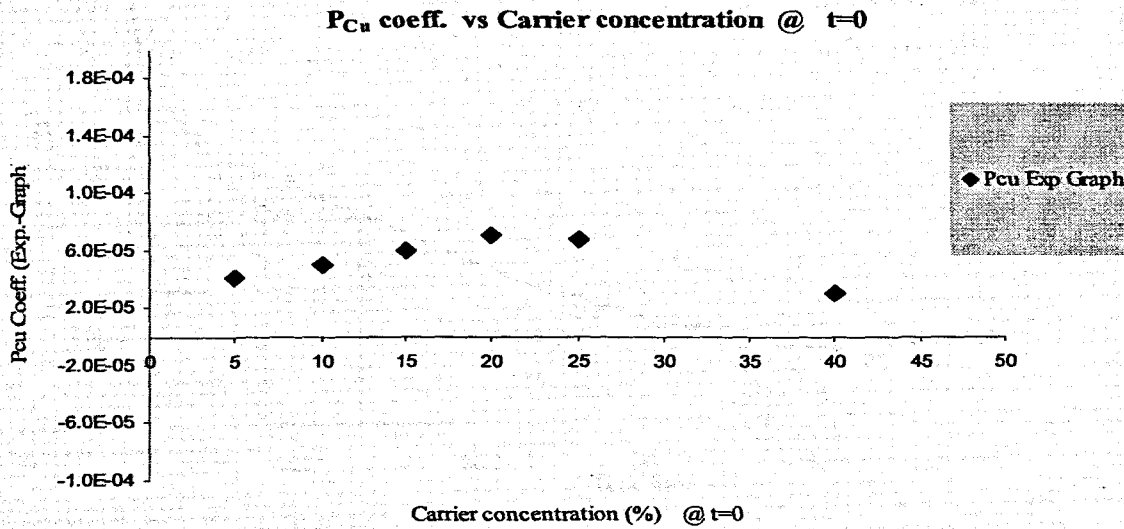
The effect of the carrier concentration on the transport of copper between the feed and stripping, from here on referred to as the overall permeation coefficient ( $P_{Cu}$ ), based on the feed concentration measurements as summarized in pages 177 and 178. Figures 5.3, 5.4 and 5.5 shows that the overall permeation coefficient increases with an increase carrier concentration up to a 20%. At higher concentrations the coefficients starts decreasing. This may be due to the increased viscosity at higher concentration of carrier, which in turn adversely affects the transport kinetics of copper ions. Thus, from these results 20% carrier concentration would appear to be the optimum carrier concentration for further experiments to evaluate various parameters.



**Figure 5.3:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of extractant concentration with Shell sol D70 as carrier on permeation



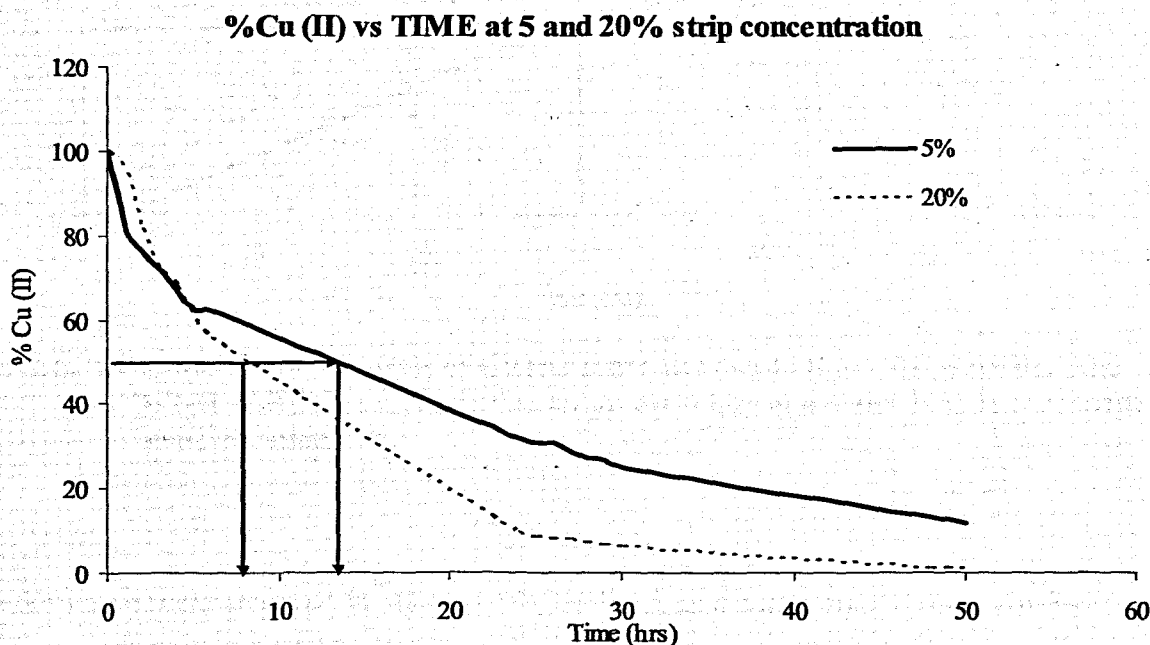
**Figure 5.4:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of extractant concentration with Shell sol D70 as carrier on the flux



**Figure 5.5:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of carrier concentration on permeability

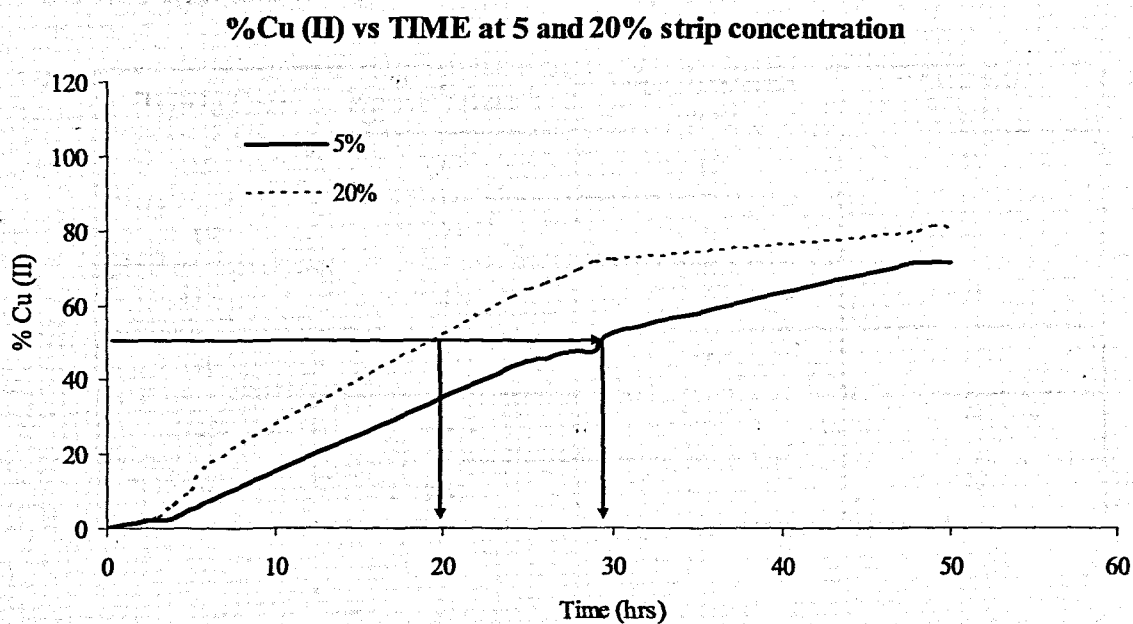
#### 5.4.2 Effect of stripping concentration on permeability

The effect of the sulphuric acid concentration on the permeation of copper across the TSLM based on the feed concentration measurements as summarized in pages 172 and 173. The strippant  $H_2SO_4$  was investigated in order to optimize the Copper (II) transfer rate in the reactor. Results of Cu (II) transport from a synthetic Copper (II)sulphate solution with a 200ppm concentration through TSLM consisting of 20% LIX984/Shell sol D70 at a constant flow rate of  $0.333\text{cm}^3\text{sec}^{-1}$  in both the feed and strip in a counter current recycle mode is shown in Figure 5.6. The percentage Cu (II) transport versus time in feed and strip is plotted.



**Figure 5.6:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of  $H_2SO_4$  concentration on the permeability at a 5 and 20%  $H_2SO_4$  strip concentration

The 50% extraction was achieved in 13hrs at 5% sulphuric acid concentration shown in Figure 5.6, whereas the equivalent extraction in the 20% sulphuric acid concentration was achieved after 8 hours.



**Figure 5.7: Experimental courses of Cu (II) concentration in the strip reservoir. The effect of  $H_2SO_4$  concentration on permeability at a 5 and 20%  $H_2SO_4$  strip concentration**

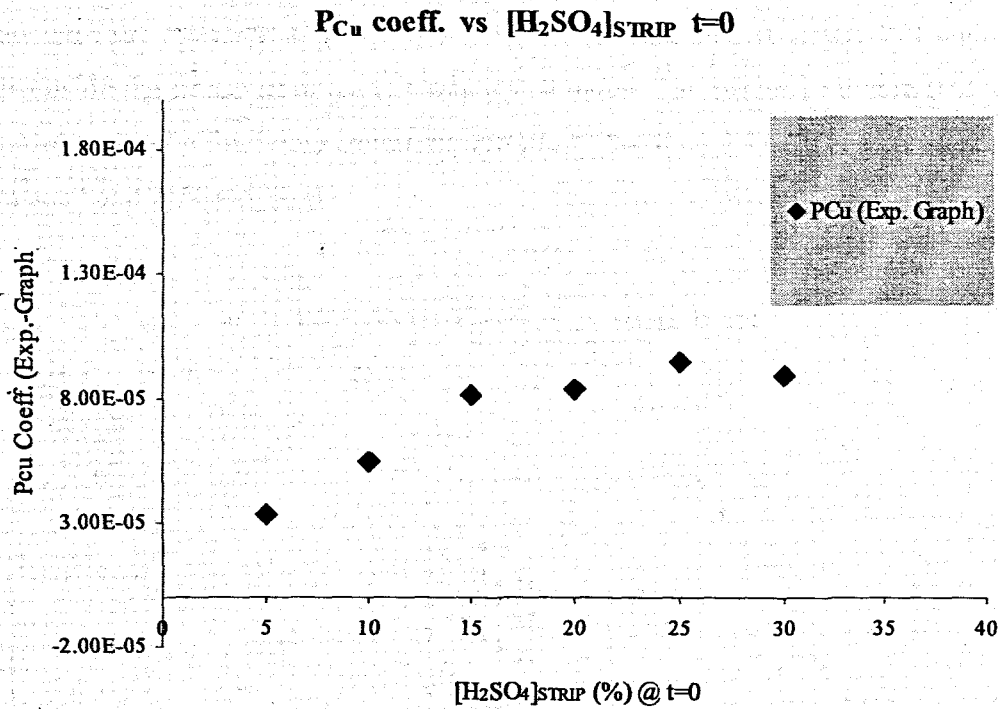
The 50% strip were achieved in 30hrs at 5% sulphuric acid concentration shown in Figure 5.7, whereas the equivalent extraction in the 20% sulphuric acid concentration was achieved after 20 hours. This implies that higher overall permeation coefficient is achieved at the higher sulphuric acid concentration.

Table 5.2 and Figure 5.8 present the influence of sulphuric acid concentration on the permeability of copper under the above mentioned conditions.

**Table 5.2: The Permeation of Cu (II) as a function of Sulphuric acid concentration at the 50% mark**

[H <sub>2</sub> SO <sub>4</sub> ] (%)	P <sub>Cu</sub> (10 <sup>-5</sup> ) (cm.s <sup>-1</sup> )	50% extraction (hrs)	50% strip (hrs)
5	3.82	13	30
10	5.71	6	27
15	9.34	6	23
20	9.66	5	20
25	10.48	5	18
30	9.47	5	18



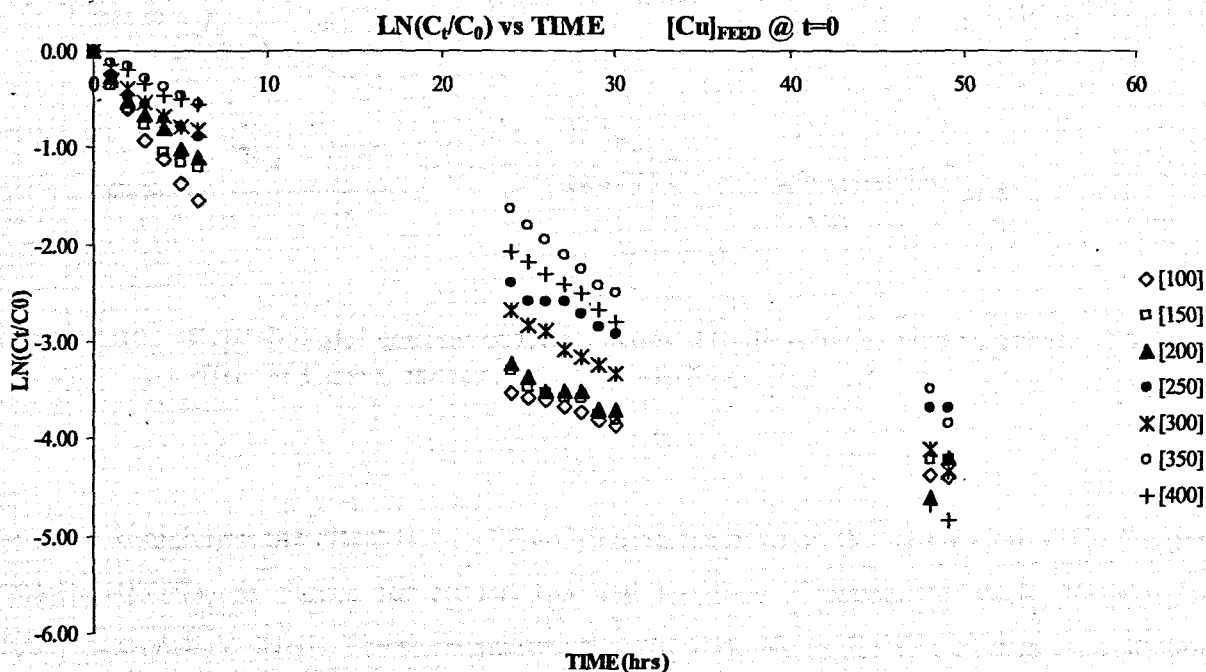


**Figure 5.8: Experimental courses of Cu (II) concentration in the feed reservoir. The effect of  $H_2SO_4$  concentration on the permeability**

From Figure 5.8 it would appear that the overall permeation coefficient is not generally affected by the change in acid concentration in the strippant. However, for excessively low concentrations of acid in the strippant > 15% there would appear to be some drop off in the overall permeation coefficient, indicating that the reaction occurring at the strippant membrane interface is not so instantaneous. However above 15 % it would appear that acid concentration has no effect and therefore no resistance to mass transfer on the strippant side.

### 5.4.3 Effect of Feed concentration on permeability

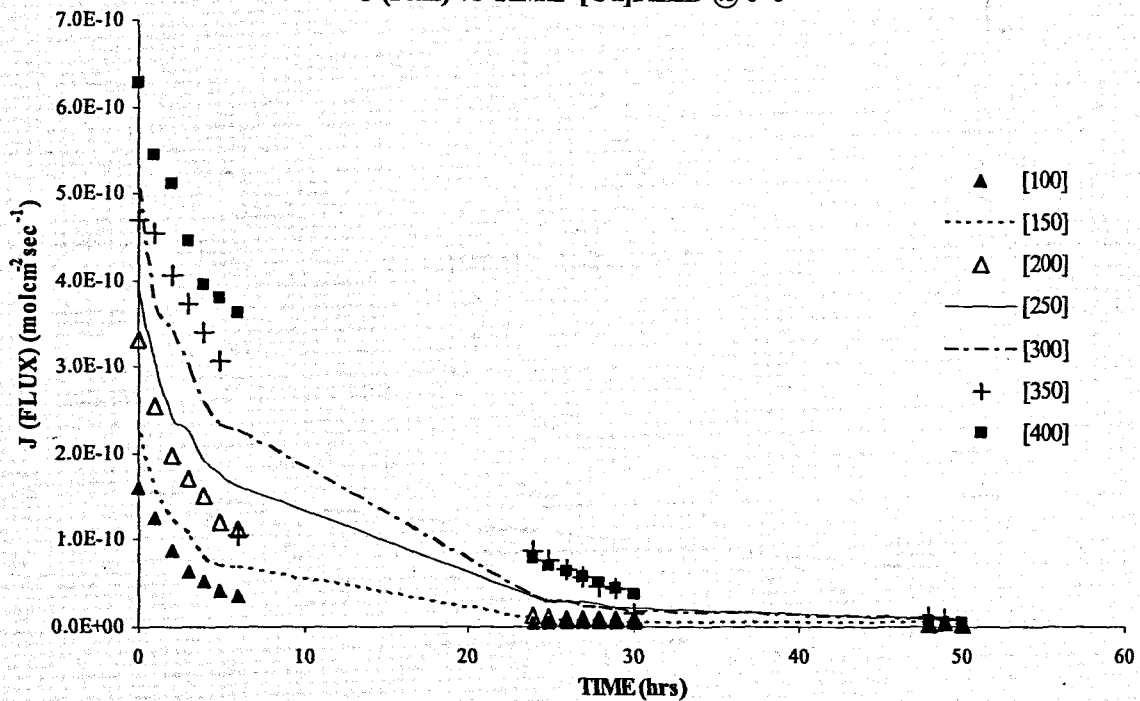
The effect of the initial feed copper concentration on the permeation of copper across the TSLM based on the feed concentration measurements are summarized in pages 170 and 1171. The effect of this on the transport of Cu (II) was investigated. The results in Figure 5.8, 5.9 and 5.10 was attained under the following condition: 20% LIX984/Shell sol D70 at a constant flow rate of  $0.333\text{cm}^3\text{sec}^{-1}$  and 25% strippant.



**Figure 5.9: Experimental courses of Cu (II) concentration in the feed reservoir. The effect of  $\text{CuSO}_4$  concentration on the permeation**

The flux for the different concentrations is shown in Figure 5.9 and 5.10, indicating the different fluxes attained for the different starting Cu (II) concentrations.

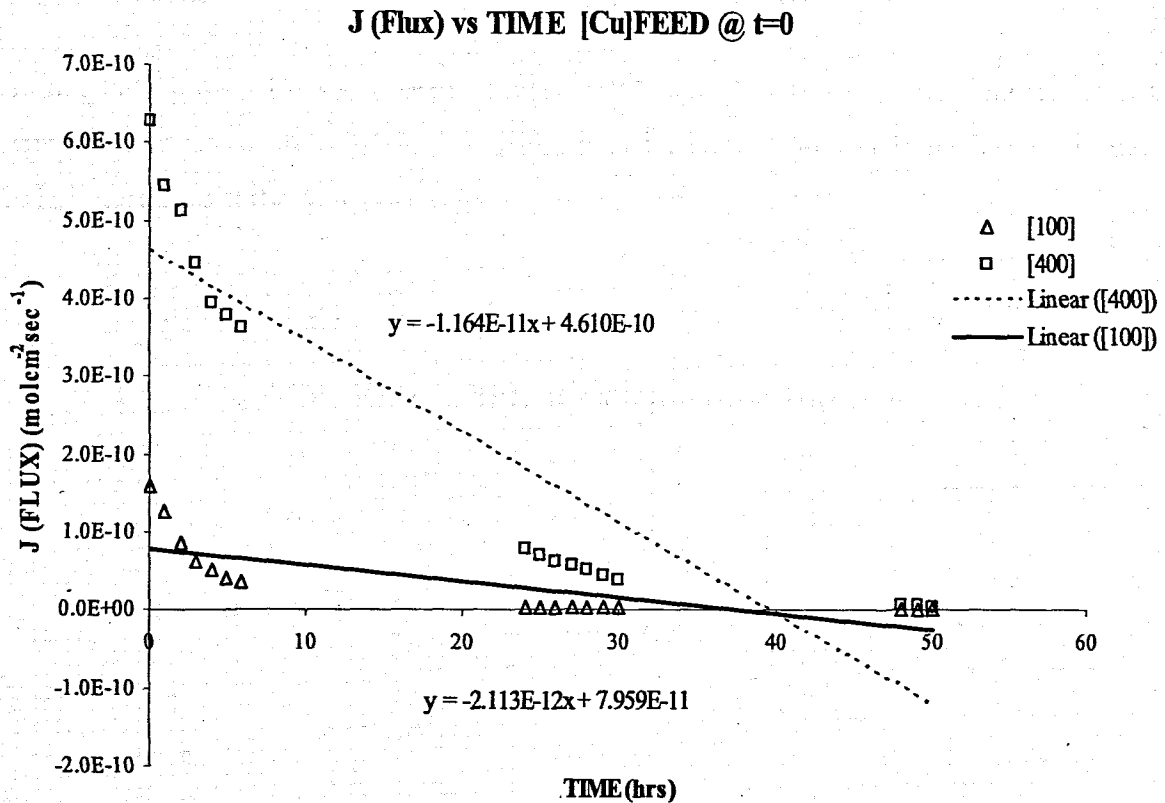
## J (Flux) vs TIME [Cu]FEED @ t=0



**Figure 5.10: Experimental courses of Cu (II) concentration in the feed reservoir. The effect of  $\text{CuSO}_4$  concentration on the flux**

In order to highlight the effect that metal concentrations have on the permeation of Cu (II), two concentrations were chosen for comparison and the flux of copper for each (100ppm and 400ppm) were calculated. The slope analysis technique shown in Figure 5.11 was used (Rathore *et al.*, 2001).

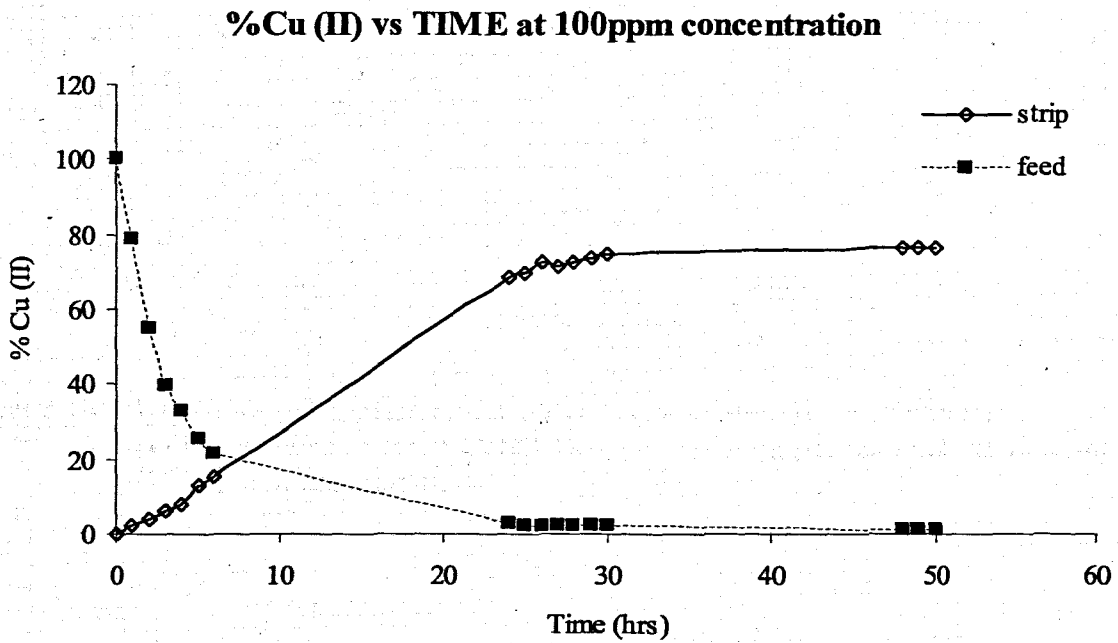
From this method, the average flux for Cu (II) at 100ppm was found to be  $2.1 \times 10^{-12} \text{ mol.cm}^{-2}.\text{s}^{-1}$  and for Cu (II) at 400ppm was found to be  $11.7 \times 10^{-12} \text{ mol.cm}^{-2}.\text{s}^{-1}$ . Higher the copper concentration results in a higher flux. Again, this is the result of a higher concentration driving force.



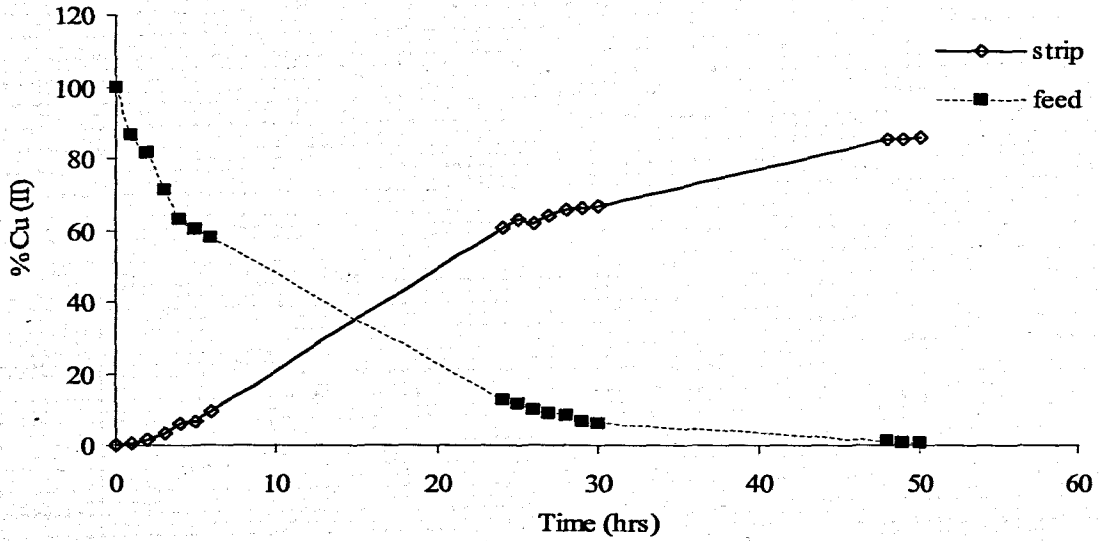
**Figure 5.11: Experimental courses of Cu (II) concentration in the feed reservoir. The effect of CuSO<sub>4</sub> concentration of 100ppm and 400ppm on the flux**

Figure 5.12 and 5.13, shows the copper concentration in the feed decreasing with time and the concentration in the strip phase increasing. For the 100ppm feed concentration the result of copper permeation after 6 hours from the feed phase was found to be 21% and in the strip phase 15% at the metal concentration of 100ppm, whereas the copper transport for the 400ppm concentration was 58% in the feed and 9% in the strip phase.

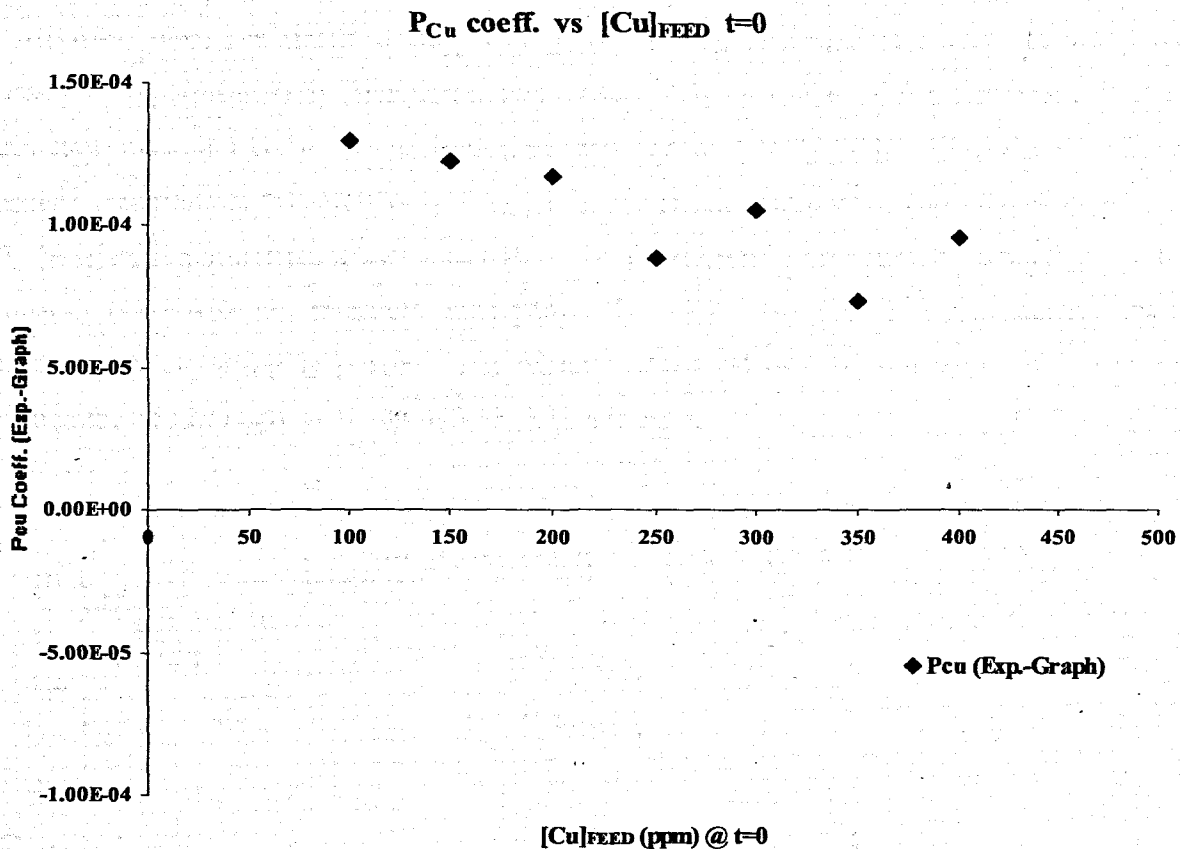
According to Figure 5.13, the 400ppm concentration shows a faster permeation rate than the 100ppm concentration. Equilibrium is reached after 30 hours, whereas extraction is still taking place in Figure 5.12 at the same interval.



**Figure 5.12: Experimental courses of Cu (II) concentration in the feed and strip reservoirs. The effect of  $\text{CuSO}_4$  concentration on permeability at 100ppm  $\text{CuSO}_4$  feed concentration**

**%Cu (II) vs TIME at 400ppm concentration**

**Figure 5.13: Experimental courses of Cu (II) concentration in the feed and strip reservoirs. The effect of CuSO<sub>4</sub> concentration on permeability at 400ppm CuSO<sub>4</sub> feed concentration**

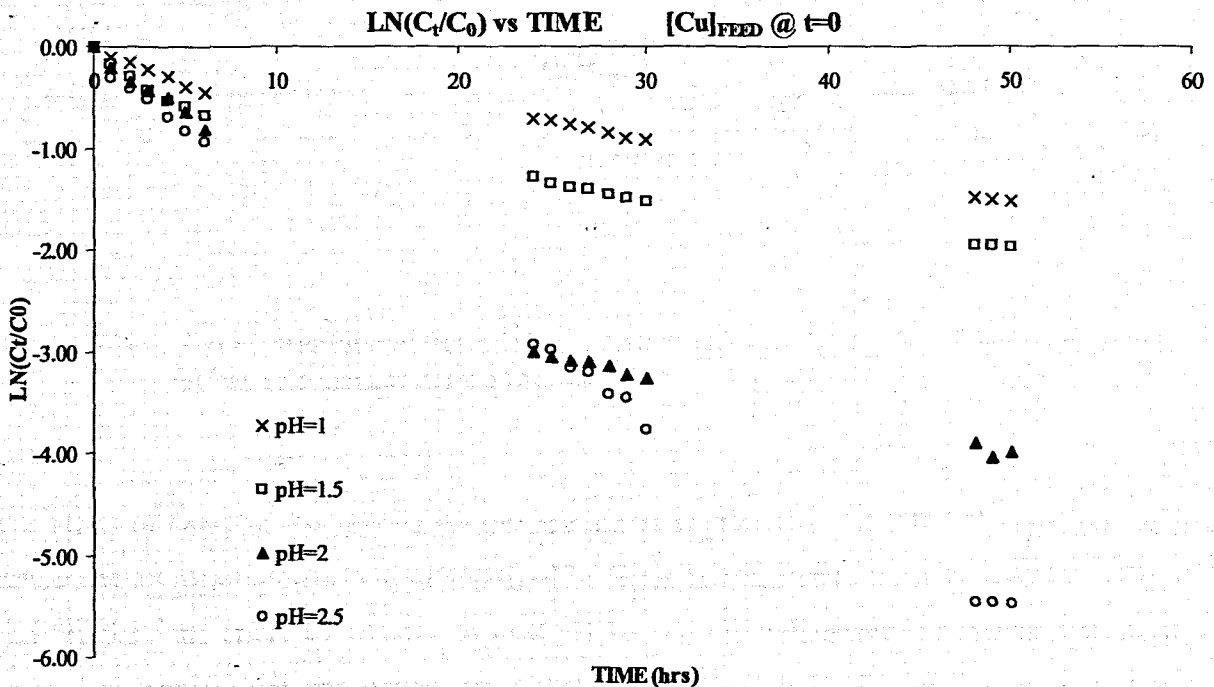


**Figure 5.14: Experimental courses of Cu (II) concentration in the feed reservoir. The effect of  $CuSO_4$  concentration on permeability.**

Figure 5.14 shows the effect that different feed copper concentrations have on the permeation coefficient. The results fluctuate as the concentrations are changed. A kind of straight line trend is observed, indicating that the metal concentration does not have such a huge effect on the coefficient.

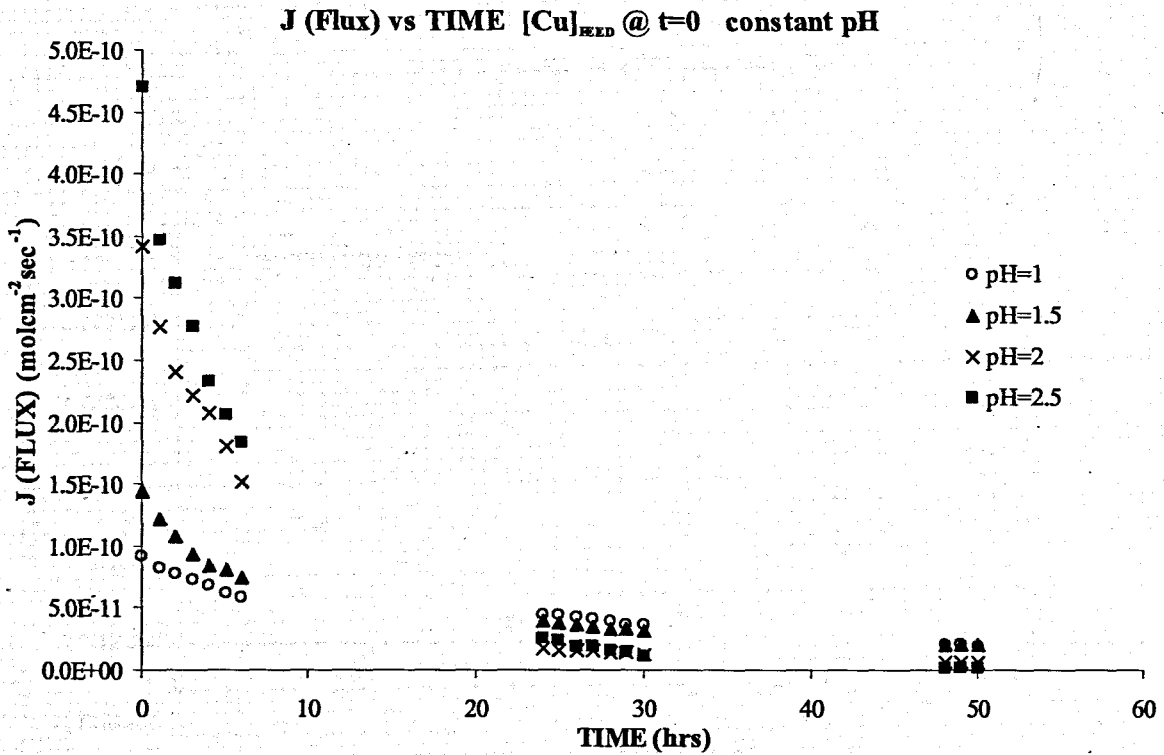
#### 5.4.4 Effect of pH's

Experiments were performed in the pH range of 1-2.5 to investigate the effect of pH of feed phase on the permeation by keeping the hydrogen ion concentration of the strip phase, feed and strip flow rates and carrier concentration all constant at 25%  $\text{H}_2\text{SO}_4$ ,  $0.333\text{cm}^3\text{sec}^{-1}$  and 20% carrier concentration. The effect of feed phase pH on the transport of copper ions through the TSLM is an important parameter because of the equilibrium limitations of extraction reaction (equation (1)). Also, the transport driving force for acidic extractants is a pH gradient between the feed and the stripping phases. The effect of feed pH on the permeation of copper ions through the TSLM is given in Figure 5.15, 5.16 and 5.17.



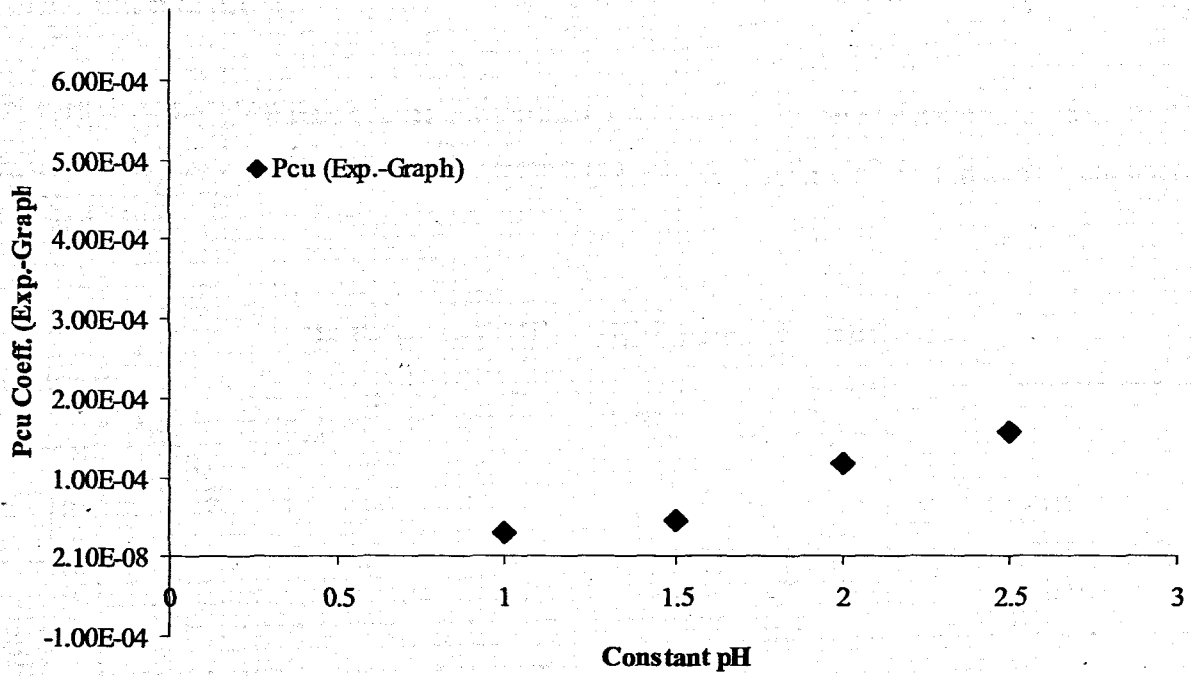
**Figure 5.15: Experimental courses of Cu (II) concentration in the feed reservoir. The effect of constant pH on permeation**





**Figure 5.16: Experimental courses of Cu (II) concentration in the feed reservoir. The effect of constant pH on the flux**

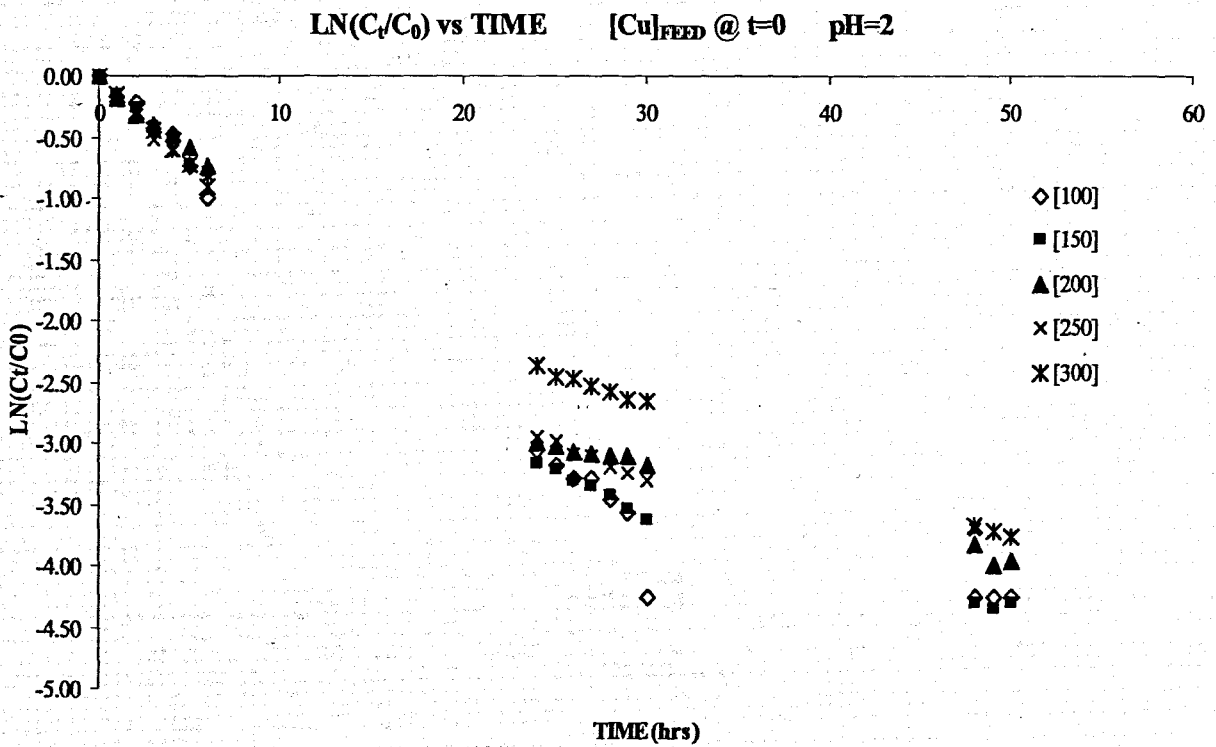
The effect of constant feed pH on the permeation of copper across the TSLM based on the feed concentration measurements are summarized in pages 179 and 180. It can be seen from Fig 5.15 and Fig 5.17 the effect the change in feed pH has on the permeation coefficient and the flux. From Equation 5.17 it can be observed that the permeation coefficient increases as the pH decreases.

**$P_{Cu}$  coeff. vs Constant pH**

**Figure 5.17: Experimental courses of Cu (II) concentration in the feed reservoir. The effect of constant pH on permeability**

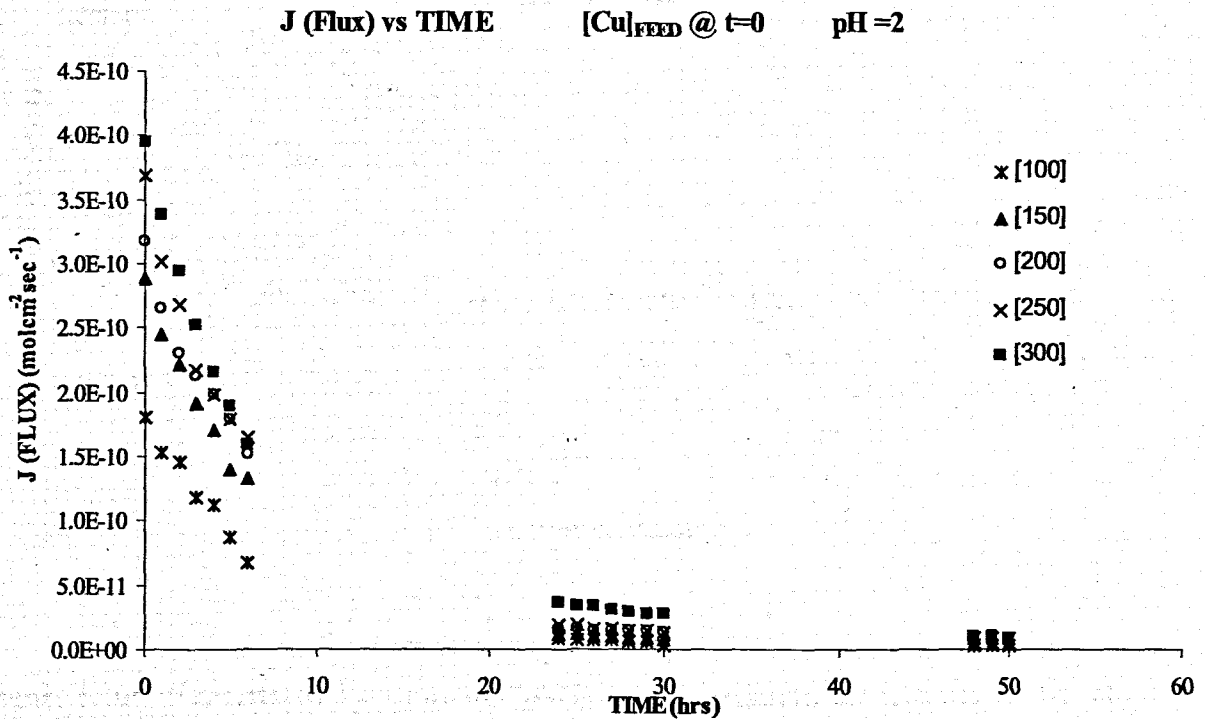
### 5.4.5 Effect of pH=2

The effect of the initial feed copper concentration on the permeation of copper across the TSLM based on the feed concentration measurements at a constant feed pH=2 are summarized in pages 181 and 182.

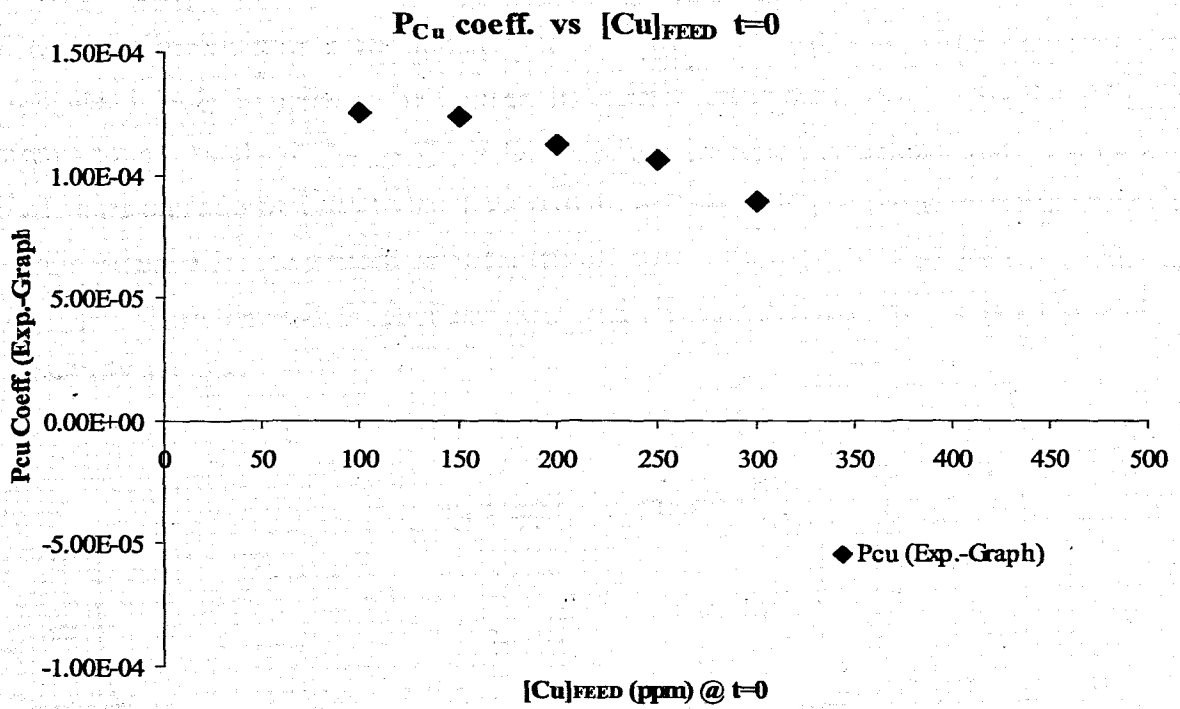


**Figure 5.18:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of pH=2 at different feed concentrations has on permeation

In Figure 5.18, 5.19 and 5.20 it can be observed that there is no significant change in the permeation of copper. The driving force for the transport of copper is the hydrogen ions in the system. If it is kept constant in the feed, no real changes will take place as can be seen on the permeation coefficient in Figure 5.21.



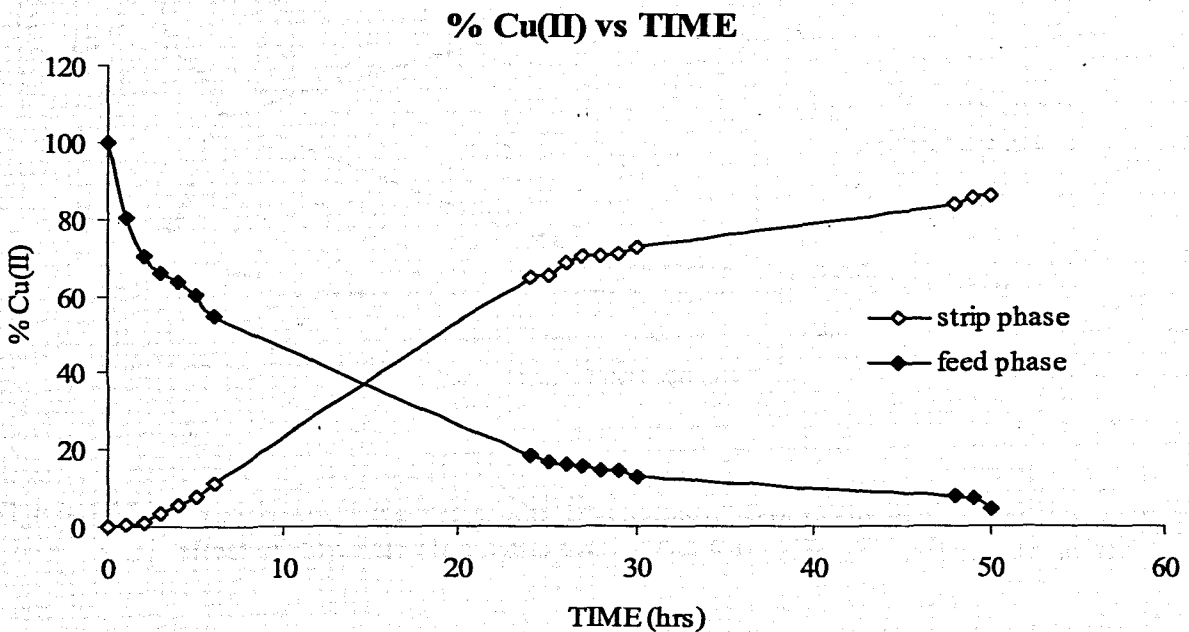
**Figure 5.19:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of pH=2 at different feed concentration on the flux



**Figure 5.20:** Experimental courses of  $Cu(II)$  concentration in the feed reservoir. The effect of  $pH=2$  at different feed concentrations have on permeability

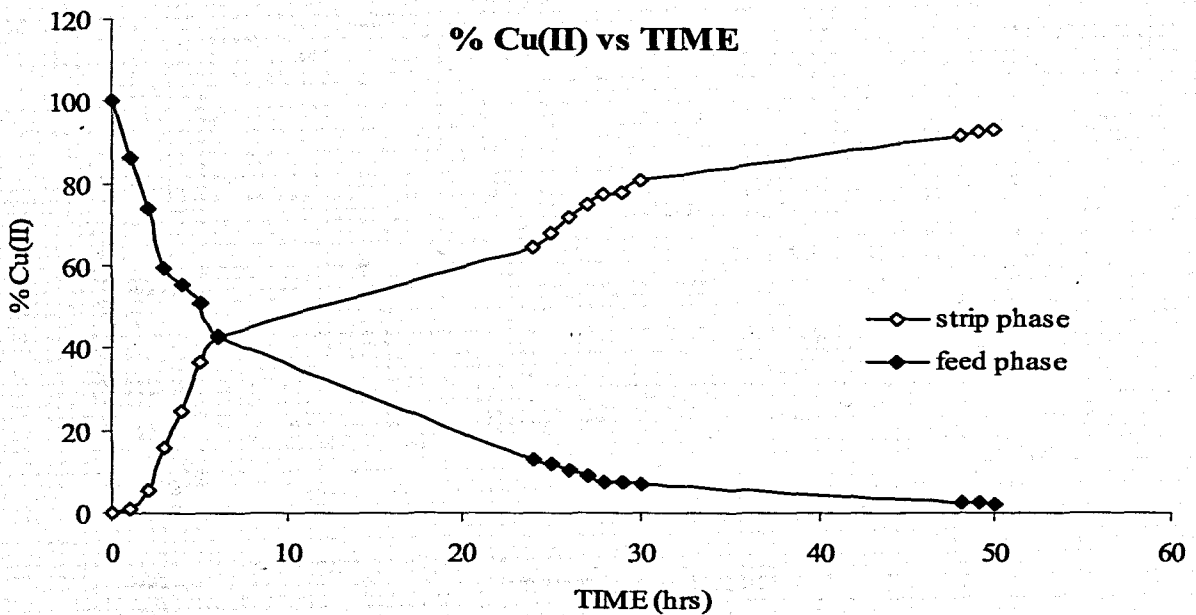
#### 5.4.6 Influence of flow rate

The effect of flow rate on the permeation of copper across the TSLM based on the feed concentration measurements are summarized in pages 179 and 180. The flow rate was investigated in order to optimize the Copper (II) transfer rate in the tube side. Results of Cu (II) transport from a synthetic Copper (II) sulphate solution with a 200ppm concentration through TSLM consisting of 20% LIX984/Shell sol D70 using 25% H<sub>2</sub>SO<sub>4</sub> strippant, in recycle mode, is shown in Figure 5.21, the percentage of Cu (II) transport versus time in feed and strip is plotted. The Copper concentration in the feed decreases with time and the concentration in the strip phase continuously increase.



**Figure 5.21: Experimental courses of Cu (II) concentration in the feed reservoir. The effect of flow rate on permeation. Feed linear flow velocity  $0.167\text{cm}^3\text{sec}^{-1}$**

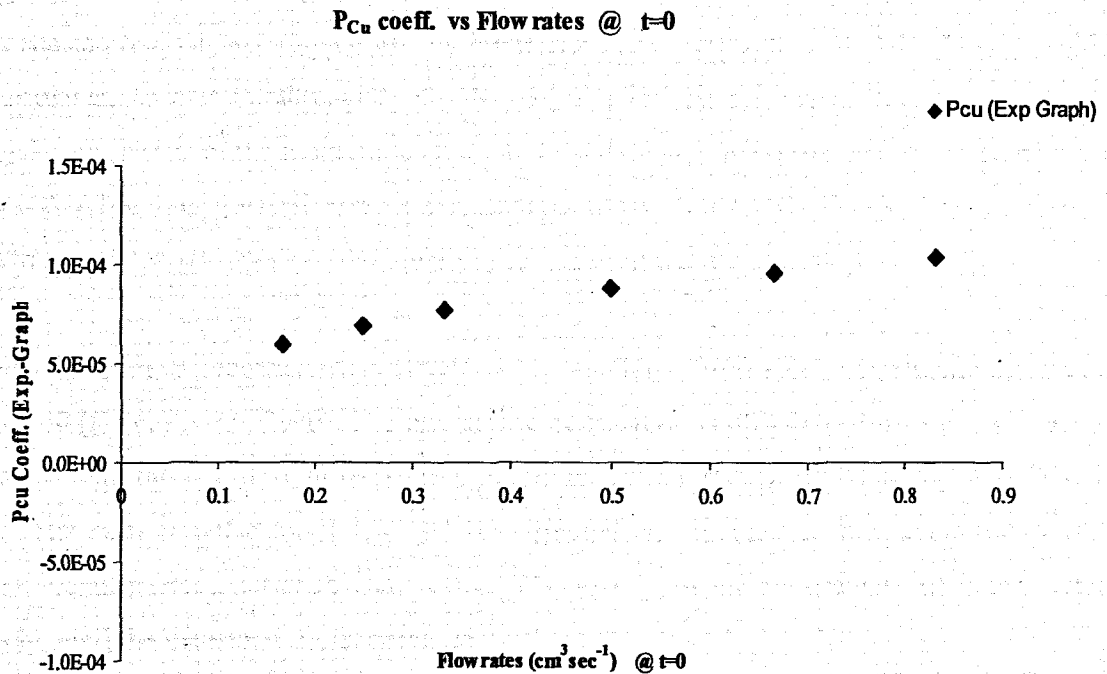
After 6 hours, the permeation of Copper from the feed phase was found to be 54% and to the strip phase was found to be 11% at the flow rate of  $0.167\text{cm}^3\text{sec}^{-1}$ , whereas the copper transport from feed phase was more than 43% and in the strip phase approximately 44% when the feed rate was increased to  $0.333\text{cm}^3\text{sec}^{-1}$ .



**Figure 5.22:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of flow rate on permeation. Feed linear flow velocity  $0.333\text{cm}^3\text{sec}^{-1}$

Figure 5.22 shows the permeation of Cu(II) with increased flow rate, and indicated that the higher flow rate ( $0.333\text{cm}^3\text{sec}^{-1}$ ) was more suitable for Cu(II) transport compared to a lower flow rate ( $0.167\text{cm}^3\text{sec}^{-1}$ )

Figure 5.23 shows the influence of linear flow velocity on the copper permeability. The  $P_{Cu}$  values increases with linear flow velocity ranging between  $0.167$  and  $0.333\text{cm}^3.\text{sec}^{-1}$  and with the permeability unchanged at higher velocities. Hence, the optimal flow rate for a tubular SLM of diameter  $12.7\text{cm}$  is approximately  $0.333\text{cm}^3.\text{sec}^{-1}$  at a linear velocity of  $0.004\text{cm}.\text{sec}^{-1}$ .



**Figure 5.23: Experimental courses of Cu (II) concentration in the feed reservoir. The effect of the linear velocity in the feed has on the permeability.**



## 5.5. LOCATING THE MASS TRANSFER COEFFICIENT ( $k_i$ )

As mentioned in the section 3.2.8 the feed side mass transfer coefficient, ( $k_i$ ) value can be located by iteration providing all the values of all the other system variables are known. Figure 3.7 gives an analytical method of locating the  $k_i$  value. Given the reliability and repeatability of the results, it was deemed possible that a mass transfer coefficient ( $k_i$ ) on the inside tubular lumen could be back calculated. As the overall coefficient of mass transfer can be located from kinetic data and the singular resistance of the membrane ( $P_m$ ) can be calculated using the method of Kumar *et al.* (2000); it then becomes possible to back calculate the mass transfer coefficient  $k_i$ , (Breembroek *et al.*, 1998) associated with the laminar layer in the lumen of the membrane.

The overall permeation coefficient ( $P_{Cu}$ ) values are calculated from kinetic data using the gradient ( $Sp$ ) method (Kumar *et al.*, 2000). The membrane permeation coefficient ( $P_m$ ) is calculated from Equation 13 and the equilibrium data through the model equations published by Kumar *et al.*, (2000). The mass transfer coefficient ( $k_i$ ) is estimated and substituted into equation 14 which gives an overall permeation coefficient value. The mass transfer coefficient ( $k_i$ ) it then altered iteratively, until the measured  $P_{Cu}$  is obtained.

A reasonable assumption made is that the only effective resistances to mass transfer are the laminar layer and the membrane permeation. The resistance in the laminar layer on the strippant (acid) side is deemed to be negligible (Kumar *et al.*, 2000). In Table 5.3 it is possible to see the overall dominance of the resistance by mass transfer coefficient in the aqueous feed ( $k_i$ ) compared to the resistance in the membrane ( $P_m$ ). This ultimately shows that the control of mass transfer would appear to ultimately be in the laminar layer of the lumen.

**Table 5.3: Select mass transfer coefficient achieved while testing different strip concentrations**

$P_{Cu}$	$P_m$	$k_f$	$P_m/k_f$
3.82E-05	4.39E-03	3.85E-05	114
5.71E-05	4.17E-03	5.79E-05	72
9.34E-05	4.39E-03	9.54E-05	46
9.66E-05	4.39E-03	9.87E-05	45
1.05E-04	4.36E-03	1.07E-04	41
9.47E-05	4.39E-03	9.68E-05	45

## 5.6. THE EFFECT OF FLOW RATE ON THE FEED MASS TRANSFER COEFFICIENT ( $k_i$ )

One could expect that when the flow rate is changed, it will have a direct impact on the aqueous feed mass transfer coefficient ( $k_i$ ) through the expected change fluid dynamics. The changing trend in the flow rate, indicating that resistance in the tubular lumen (laminar layer) is the controlling factor of this unit shown by Equation 14. This shows the change in the mass transfer coefficient ( $k_i$ ) compared to that of the resistance in the membrane. In Table 5.4 we compare  $k_i$  values determined by measurement and back calculation and those calculated from a published model (Breembroek *et al.*, 1998; Kumar *et al.*, 2000).

**Table 5.4: Flow rate of Cu (II) as a function of linear velocity and the mass transfer coefficient ( $k_i$ )**

Flow rate (cm <sup>3</sup> .sec <sup>-1</sup> )	Linear vel. (cm.sec <sup>-1</sup> )	$k_i$ (Equ.17)	$k_i$ (measured)
0.17	2.23E-03	4.45E-05	6.10E-05
0.25	3.33E-03	5.09E-05	7.03E-05
0.33	4.44E-03	5.60E-05	7.79E-05
0.50	6.67E-03	6.41E-05	9.00E-05
0.67	8.89E-03	7.06E-05	9.96E-05
0.83	1.11E-02	7.60E-05	1.08E-04

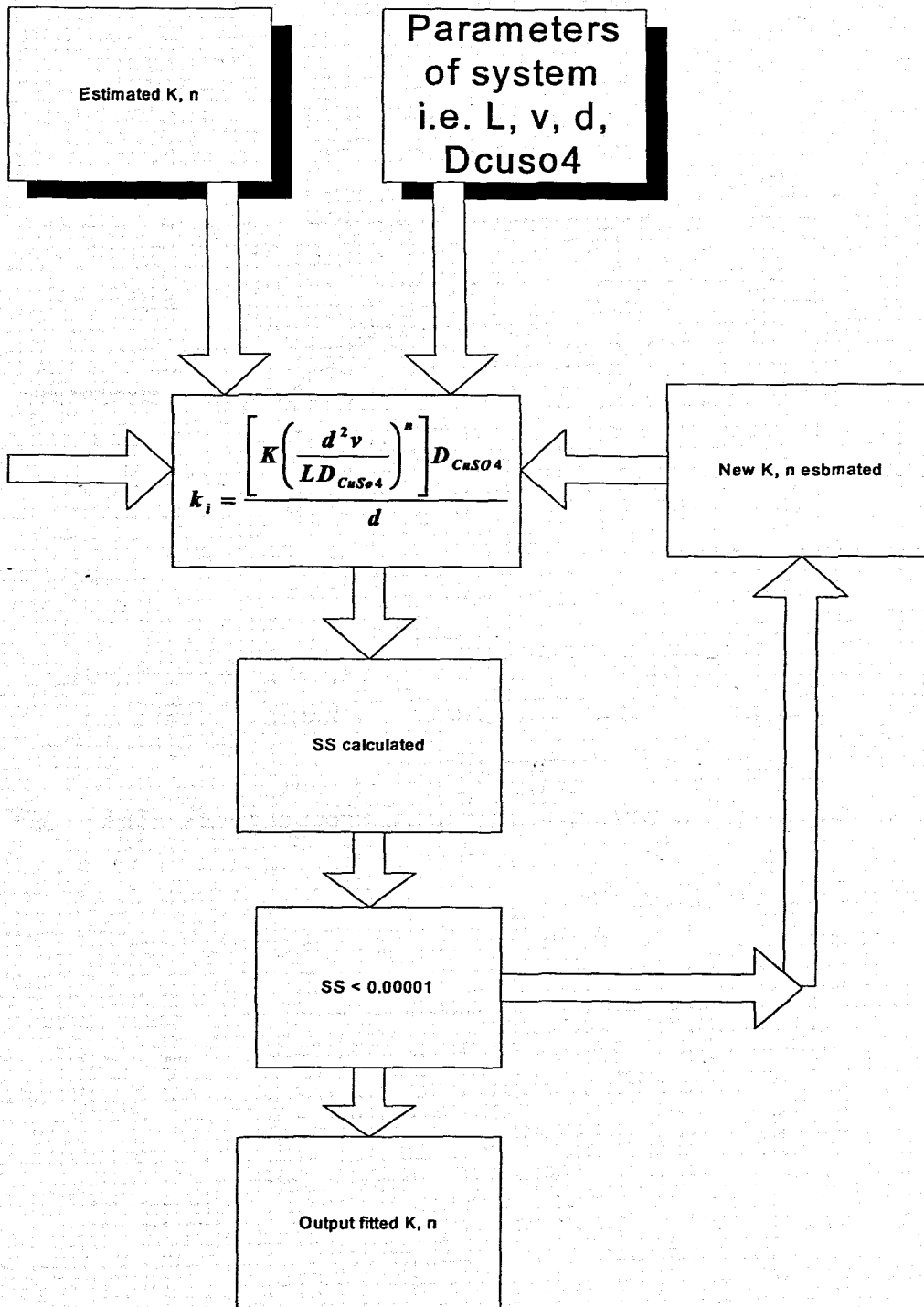
To improve the fit of the Breembroek *et al.* (1998) model (Equ.17), to the  $k_i$  values obtained, a two parameter fit was done in which the coefficient and the exponential values ( $K$ ,  $n$ ) of the Breembroek equation were searched for.

Location of the constants was achieved by the application of the algorithm described in Figure 5.24. The located constants were found to be reasonable and well within range of those achieved by other researchers, vindicating the mass transfer mechanism assumed in this thesis. Table 5.5 compares the located coefficients and exponents.

The values obtained were 2.10 and 0.34 respectively which compares very well with values in the literature (Breembroek *et al.*, 1998). Figure 5.25 shows the calculated mass transfer coefficient according to Equation 17, and the line shows the new calculated mass transfer coefficient describing the system.

**Table 5.5: Coefficient and exponential values a function of the feed mass transfer coefficient ( $k_i$ )**

	Coefficient	Exponential value
Sieder <i>et al</i>	1.86	0.33
Leveque <i>et al</i>	1.62	0.33
<b>Model</b>	<b>2.10</b>	<b>0.34</b>



**Figure 5.24:** Schematic algorithm describing the computer calculation for the aqueous mass transfer coefficient in the feed ( $k_i$ )

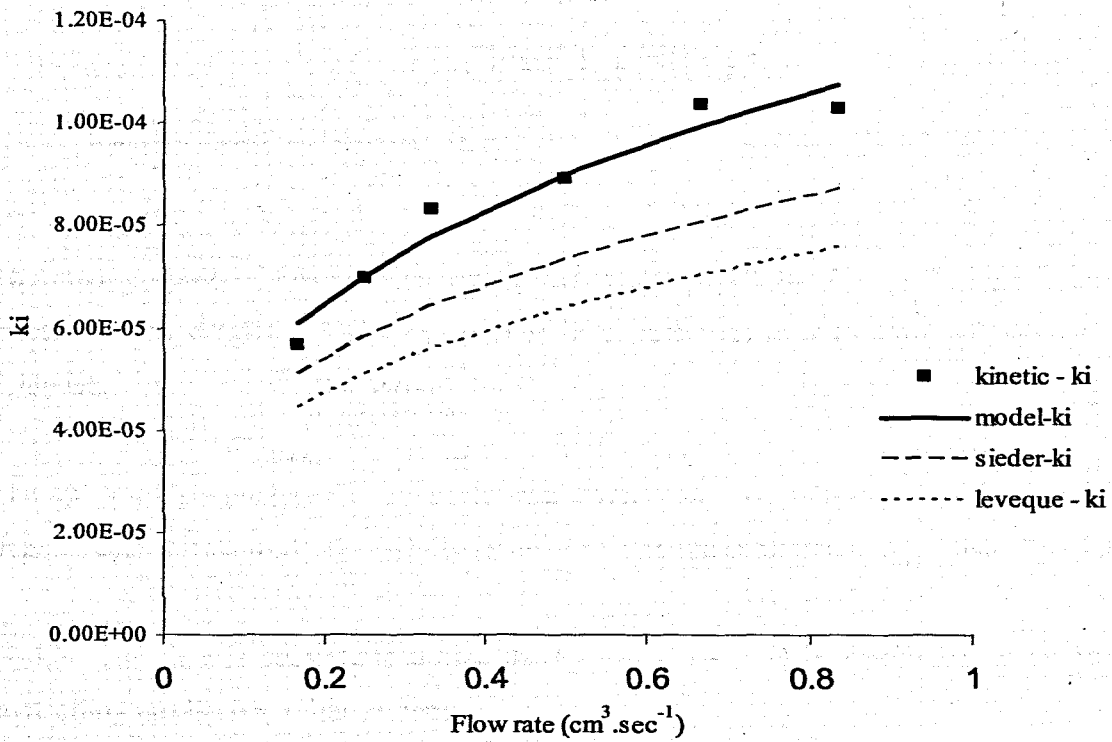


Figure 5.25: Shows the comparison between the different mass transfer coefficients.

---

## CONCLUSION

---

The main purpose of this research which was to investigate the use of the novel tubular SLM reactor for the extraction and concentration of copper ions in a closed batch system has been achieved.

The operating parameters that affect the extraction rate of copper were identified and the mass transfer coefficients were successfully located through the application of published models.

In this study it was possible to utilize the located mass transfer coefficient to investigate the controlling mechanism of the system.

A successful design and commission of a TSLM bench scale reactor system was achieved. A quantitative study of the copper permeation was carried out on this system. Optimum operating condition was achieved assisting the permeation of copper through this system.

The successful operation of TSLM units over extended periods of time has proved that by the proper selection of extractant and diluent, the problems of instability can be minimized. Maintaining of the lowest possible pressure gradient across the TSLM must also be adhered to in order to minimize catastrophic destruction of the membrane.

The closeness of the parameters located in the application of the model of Kumar *et al.*, (2000) and Breembroek *et al.*, (1998) to the  $k_i$  values calculated from kinetic data can be seen as a vindication of the modelling approach to understanding the mechanism of mass transfer in this system.

**It is hoped that this research will have served to prove that tubular SLM's can be successfully used to selectively recover copper and other metals from aqueous solutions in a cost effective manner. Further investigation however needs to be done, specifically a better permeation model for the TSLM.**



---

## BIBLIOGRAPHY

---

**Alguacil, F.J.**, *Recovery of copper from ammoniacal/ammonium carbonate medium by LIX 973N*, Hydrometallurgy 52 (1999) 55-61.

**Alguacil, F.J.**, *Mechanistic study of active transport of copper (II) from ammoniacal/ammonium carbonate medium using LIX 973N as a carrier across a liquid membrane*, Hydrometallurgy 61 (2001) 177-183.

**Arous, O., Gherrou, A., Kerdjoudj, H.**, *Removal of Ag (I), Cu (II) and Zn (II) ions with a supported liquid membrane containing cryptands as carriers*, Desalination 161 (2004) 295-303

**Baker W. Richard**, *Membrane Technology and Applications*, 2004, John Wiley & Sons, Ltd, 2<sup>nd</sup> Edition, pp 1-2

**Breembroek, G.R.M., Van Straalen, A., Witkamp, G.J., Van Rosmalen, G.M.**, *Extraction of cadmium and copper using hollow fibre supported liquid membranes*, J. of Membrane Science 146 (1998) 185 – 195.

Cognis Corporation, *LIX 984N Material Safety Data Sheet*, Cognis Ireland Ltd. (2002).

**Danesi, R. Pier**, *A simplified model for the coupled transport of metal ions through Hollow-fibre supported liquid membranes*. J. Of Membrane Sci., 20 (1984) 231-248

**De Haan, A.B., Bartels, P.V., De Graauw, J.,** *Extraction of metal ions from waste water. Modelling of the mass transfer in a supported liquid membrane process, J. of Membrane Science, 45 (1989) 281-297.*

**Juang, R., Kao, H., Wu, W.,** *Analysis of liquid membrane extraction of binary Zn(II) and Cd(II) from chloride media with Aliquat 336 based on thermodynamic equilibrium models, J. of Membrane Sci. 228 (2004) 169-177.*

**Kumar, A., Haddad, R., Benzal, G., Ninou, R., Sastre, A.M.,** *Use of modified membrane carrier system for the recovery of gold cyanide from alkaline Cyanide media using hollow fiber supported liquid membranes: feasibility Studies and mass transfer modeling, J. Membrane Sci. 174 (2000) 17-30*

**Ma, P., X. Dong Chen, X., Monwar Hossain, M.D.,** *Lithium extraction from a multi component mixture using supported liquid membranes, Sep. Sci. and Tech., 35 (15), 2000, 2513-2533.*

**Marchese, J., Valenzuela, F., Basualto, C., Acosta, A.,** *Transport of molybdenum with Alamine 336 using supported liquid membrane, Hydrometallurgy 72 (2004) 309-317.*

**Rathore, N.S., Sonawane, J.V., Kumar, A., Venugopalan, A.K., Singh, R.K., Badjpai, D.D., Shukla, J.P.** *Hollow fiber supported liquid membrane: a novel technique for separation And recovery of plutonium from aqueous acidic wastes, J. of Membrane Sci. 189 (2001) 119-128.*

**Saranghi, K., Das, R.P.,** *Separation of copper and zinc by supported liquid membrane using TOPS-99 as mobile carrier, Hydrometallurgy 71 (2004) 335-242.*

**Sastre, A.M., Madi, A., Alquacil, F.J.,** *Solvent extraction of Au (CN)<sup>-</sup> and application to Facilitated supported liquid membrane transport, Hydrometallurgy 54 (2000) 171-184*

**Scott K. and Hughes R.** *Industrial Membrane Separation technology*, Blackie Academic and professional: London (1996).

**Szpakowska, M.**, *Coupled transport of copper through different types of liquid membranes containing Acorga P-50 as carrier*, J. of Membrane Sci. 109 (1996) 77-86

**Teramoto, M. and Tanimoto, H.**, *Mechanism of Copper permeation through hollow fibre liquid membranes*, Separation science and Technology, 18 (10), (1983) 871 – 892.

**Valenzuela, F.R., Basualto, C., Tapia, C., Sapag, J.**, *Application of hollow-fibre supported liquid membranes technique to the selective recovery of a low content of copper from a Chilean mine water*, J. of Membrane Sci. 155 (1999) 163-168.

**Valenzuela, F.R., Basualto, C., Tapia, C., Sapag, J., and Parotori, C.** *Recovery of copper from leaching residual solutions by means of a hollow-fibre membrane extractor*, Minerals Engineering, Vol 9, No. 1, (1996) 15-22.

[www.encyclopedia.com/printable.aspx?id=1E1:copper](http://www.encyclopedia.com/printable.aspx?id=1E1:copper)

[www.nautilus.fis.uc.pt/st2.5/scenes-e/eleme/e02900.html](http://www.nautilus.fis.uc.pt/st2.5/scenes-e/eleme/e02900.html)

[www.scescape.net/-woods/elements/copper.html](http://www.scescape.net/-woods/elements/copper.html)

[www.wikopedia.com](http://www.wikopedia.com)

**Yang, C., Cussler, E.L.** *Reaction dependant extraction of copper and nickel using hollow fibres*. J.of Membrane Sci. 166 (2000) 229 – 238.

---

## APPENDIX A

---

### A.1 Measured Permeation Coefficient (Experimental)

If  $V_t \ln (C_f/C_0)$  versus  $t$  slope is  $S_p$  then  $P_{Cu}$  could be obtained by the following relation in Equation (7) and (9) (Danesi, 1984; Rathore *et al.*, 2001; Kumar *et al.*, 2000).

$$P_{Cu} = \frac{S_p r_i v_f}{2\pi r_i^2 L N v_f - S_p L e}$$

From the gradient ( $S_p$ ) =  $6.43163 \times 10^{-3}$  (100ppm  $CuSO_4$  Feed)

$$P_{Cu} = \frac{(6.543163 \times 10^{-3})(0.635)(0.00444)}{2\pi(0.635)^2(19)(1)(0.00444) - (6.43163 \times 10^{-3})(19)(1)(0.6)}$$

$$P_{Cu} = 1.2976 \times 10^{-4} \text{ cm}\cdot\text{sec}^{-1}$$

## A.2 Deriving Permeation Coefficient (Model)

Membrane thickness ( $d_m$ ): from equation (16)

$$d_{mem} = r_{feedside} \ln \frac{r_o}{r_i}$$

$$\delta_{mem} = 0.635 \text{ cm} \ln \left( \frac{0.66 \text{ cm}}{0.635 \text{ cm}} \right)$$

$$d_{mem} = 0.025 \text{ cm}$$

Membrane effective diffusion coefficient ( $D_{eff}$ ): from equation (15)

$$D_{eff} = \frac{e_m D_{org}}{t_m}$$

$$D_{eff} = \frac{(0.6)(9 \times 10^{-6})}{(2)}$$

$$D_{eff} = 2.7 \times 10^{-6} \text{ cm} \cdot \text{sec}^{-1}$$

Volumetric Flow rate (Q):

$$20\text{ml}\cdot\text{min}^{-1} = 0.333\text{ cm}^3\cdot\text{sec}^{-1}$$

Surface area of membrane (A) - Tube:

$$\begin{aligned} A &= 2\pi RLN \\ &= 2\pi (0.625\text{cm})(19\text{cm})(1) \\ &= 75\text{ cm}^2 \end{aligned}$$

Surface area of membrane (A) - Shell:

$$\begin{aligned} A &= 2\pi RLN \\ &= 2\pi (0.635\text{cm})(19\text{cm})(1) \\ &= 76\text{ cm}^2 \end{aligned}$$

Effective membrane area:

$$\begin{aligned} A &= 2\pi RLNe \\ &= 2\pi (0.635\text{cm})(19\text{cm})(1)(0.6) \\ &= 45.5\text{ cm}^2 \end{aligned}$$

Shell (housing diameter):

Shell diameter – membrane outer diameter

$$\text{shell diameter} = 2.2\text{cm} - 1.32\text{cm} = 0.88\text{cm}$$

Linear flow velocity inside (v)

$$v = \frac{Q}{A}$$

$$v = \frac{0.333 \text{ cm}^3 \cdot \text{sec}^{-1}}{75 \text{ cm}^2}$$

$$v = 0.0044 \text{ cm} \cdot \text{sec}^{-1}$$

Mass transfer rate in the feed side ( $k_{\text{Cu, aq}}$ ) from equation (17)

$$\frac{k_{\text{aq, i}} d_i}{D_{\text{Cu, aq}}} = 1.62 \left( \frac{d_i^2 v}{LD_{\text{Cu, aq}}} \right)^{0.33}$$

$$\frac{k_{\text{q, Cu}} d_{\text{Cu}}}{D_{\text{Cu, aq}}} = 1.62 \left( \frac{d_{\text{Cu}}^2 v}{LD_{\text{Cu, aq}}} \right)^{0.33}$$

$$k_{\text{Cu, aq}} = \left\{ \frac{\left[ 1.62 \left( \frac{\{1.27 \times 1.27\} 0.0044}{19 \{1.5 \times 10^{-5}\}} \right)^{0.33} \right] 1.5 \times 10^{-5}}{1.27} \right\}$$

$$k_{\text{Cu, aq}} = 5.53 \times 10^{-5} \text{ cm} \cdot \text{sec}^{-1}$$

Mass transfer rate in the feed side ( $k_{H_2SO_4, aq}$ ): from equation (17)

$$k_{H_2SO_4, aq} = \left\{ \frac{\left[ 1.62 \left( \frac{\{0.88 \times 0.88\} 0.0044}{19 \{1.73 \times 10^{-5}\}} \right)^{0.33} \right] 1.73 \times 10^{-5}}{0.88} \right\}$$

$$k_{H_2SO_4, aq} = 6.9 \times 10^{-5} \text{ cm.sec}^{-1}$$

Mass transfer rate in the membrane ( $k_m$ ): from equation (18)

$$k_{mem} = \frac{2\pi D_{eff}}{\ln\left(\frac{r_o}{r_i}\right)}$$

$$k_{mem} = \frac{2\pi(2.7 \times 10^{-6})}{\ln\left(\frac{0.66}{0.635}\right)}$$

$$k_{mem} = 4.393 \times 10^{-4} \text{ cm.sec}^{-1}$$



From equation (5):

At 25% H<sub>2</sub>SO<sub>4</sub>, from table (K1.1) =  $2.105 \times 10^{-5}$

$$K_{ex} = D_{Cu} \frac{[H^+]_{aq}^2}{[HR]_{org}^2}$$

$$0.85 = (0.99) \times \frac{(1.45 \times 10^{-4})}{[HR]_{org}^2}$$

$$[HR]_{org}^2 = 1.68 \times 10^{-4}$$

From equation (14)

$$\frac{1}{P_{Cu}} = \frac{1}{k_i} + \frac{r_i}{r_{lm}} \frac{[H^+]_{org}^2}{K_{ex} [HR]_{org}^2} \frac{1}{k_m}$$

$$\frac{1}{P_{Cu}} = \frac{1}{(1.075 \times 10^{-4})} + \frac{(0.635)}{(0.647)} \left[ \frac{(1.68 \times 10^{-4})}{(0.85)} \right] (4.39 \times 10^{-4})$$

$$P_{Cu} = 1.0475 \times 10^{-4} \text{ cm.sec}^{-1}$$

Example of calculations of a free  $[H^+]$  when the pH is 2

$$\begin{aligned} \text{pH} &= -\log [H^+] \\ 2 &= -\log [H^+] \\ [H^+] &= 10^{-2} \\ [H^+] &= 0.01 \text{ mol.dm}^{-3} \end{aligned}$$

**A.3 Mass Balance calculation**

$$\text{Feed}_{\text{Cu}(t=0)} = \text{Strip}_{\text{Cu, equilibrium}} + \text{Feed}_{\text{Cu, equilibrium}} + \text{Membrane}_{\text{Cu, equilibrium}}$$

$$\begin{aligned} \text{Feed}_{\text{Cu}: (t=0)} \quad m_t &= V_{\text{feed}} \times \rho_{\text{H}_2\text{O}} \\ &= 200 \text{ cm}^3 \times 1 \text{ g.cm}^{-3} \\ m_t &= 200\text{g} \end{aligned}$$

$$\begin{aligned} m_f &= 200\text{g} \times 98\text{ppm} \\ m_f &= 0.0196\text{g} \end{aligned}$$

$$\begin{aligned} \text{Strip}_{\text{Cu}: (t=\text{eq})} \quad m_t &= V_{\text{feed}} \times \rho_{\text{H}_2\text{SO}_4} \\ &= 200 \text{ cm}^3 \times 1.13 \text{ g.cm}^{-3} \\ m_t &= 226\text{g} \end{aligned}$$

$$m_s = 226 \text{ g} \times 75 \text{ ppm}$$

$$m_s = 0.01695 \text{ g}$$

$$\begin{aligned} \text{Feed Cu: (t=eq)} \quad m_t &= V_{\text{feed}} \times \rho_{\text{H}_2\text{O}} \\ &= 200 \text{ cm}^3 \times 1 \text{ g.cm}^{-3} \end{aligned}$$

$$m_t = 200 \text{ g}$$

$$m_f = 200 \text{ g} \times 1 \text{ ppm}$$

$$m_f = 0.0002 \text{ g}$$

$$\begin{aligned} \text{Mem Cu: (t=eq)} \quad m_t &= V_{\text{feed}} \times \rho_{\text{H}_2\text{SO}_4} \\ &= 25 \text{ cm}^3 \times 1.13 \text{ g.cm}^{-3} \end{aligned}$$

$$m_t = 28.25 \text{ g}$$

$$m_f = 28.25 \text{ g} \times 5 \text{ ppm}$$

$$m_f = 0.0034 \text{ g}$$

$$\begin{aligned} \text{Feed Cu(t=0)} &= \text{Strip Cu, equilibrium} + \text{Feed Cu, equilibrium} + \text{Membrane Cu, equilibrium} \\ &= 0.01695 + 0.0002 + 0.034 \\ &= 0.01749 \text{ g} \end{aligned}$$

89% recovery for this variable

Effective membrane area	45.5	cm <sup>2</sup>
Surface area of membrane	75	cm <sup>2</sup>
Volume of feed tank	200	cm <sup>3</sup>
membrane inner radius (r <sub>i</sub> )	0.635	cm
membrane outer radius (r <sub>o</sub> )	0.66	cm
membrane (r <sub>lm</sub> )	0.65554	cm
Radius (inside)	0.625	cm
shell diameter	0.88	cm
membrane inner diameter (id)	1.27	cm
membrane outer diameter (od)	1.32	cm
shell diameter (d)	2.2	cm
tube volume (d)	2.5	cm <sup>3</sup>
shell volume	3	cm <sup>3</sup>
porosity	0.6	
phi	3.1415927	
membrane thickness (l)	0.02500	cm
D <sub>CuSO<sub>4</sub></sub> in H <sub>2</sub> O	1.50x10 <sup>-5</sup>	cm <sup>2</sup> .sec <sup>-1</sup>
D <sub>H<sub>2</sub>SO<sub>4</sub></sub> in H <sub>2</sub> O	1.73x10 <sup>-5</sup>	cm <sup>2</sup> .sec <sup>-1</sup>
Viscosity of fluid (μ)	0.25	Pa.sec
density of fluid (ρ)	1.175	g.cm <sup>-3</sup>
membrane thickness (l)	0.02500	cm
Re no.	3.130x10 <sup>-7</sup>	

$k_{\text{feed}}$	$1.075 \times 10^{-4}$	$\text{cm} \cdot \text{sec}^{-1}$
$k_{\text{strip}}$	$6.9 \times 10^{-5}$	$\text{cm} \cdot \text{sec}^{-1}$
$k_{\text{membrane}}$	$4.393 \times 10^{-4}$	$\text{cm} \cdot \text{sec}^{-1}$
$D_{\text{eff}}$	$2.700 \times 10^{-6}$	$\text{cm}^2 \cdot \text{sec}^{-1}$
tortuosity	2	
$K_{\text{ex}}$	0.85	
$D_{\text{org}}$	$9.00 \times 10^{-6}$	$\text{cm}^2 \cdot \text{sec}^{-1}$

**Table A.1: Experimental parameters and calculated values**

---

**APPENDIX B**

---

DATA  
FROM  
BATCH  
EXPERIMENTS

**AQUEOUS FEED CONCENTRATIONS (CuSO<sub>4</sub>)**

The effect different aqueous feed ( $\text{CuSO}_4$ ) concentrations have on the permeation of Copper (II) at the following experimental conditions.

**Experimental parameters:**

Volume of aqueous feed phase:	$200\text{cm}^3$
Volume of aqueous strip phase:	$200\text{cm}^3$
Membrane length:	19cm
Feed concentration ( $\text{CuSO}_4$ ):	100ppm – 400ppm
Strip concentration ( $\text{H}_2\text{SO}_4$ ):	25%
Extractant concentration (Lix 984):	20%
Feed flow rate ( $\text{CuSO}_4$ ):	$20\text{ml}\cdot\text{min}^{-1} / 0.33\text{cm}^3\cdot\text{sec}^{-1}$
Strip flow rate ( $\text{H}_2\text{SO}_4$ ):	$20\text{ml}\cdot\text{min}^{-1} / 0.33\text{cm}^3\cdot\text{sec}^{-1}$
Time:	50hours / 180 000sec

---

**EXPERIMENT 1.1**


---

Variable: Feed concentration (CuSO<sub>4</sub>): 100 ppm,

t (hr)	t (sec)	[100]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>f</sub> ln (C/C <sub>o</sub> )	ln (C/C <sub>o</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	98	9.8E-05	1.5E-06	3.1E-04	0.0E+00	0.0E+00	2.0E-10
1	3600	77	7.7E-05	1.2E-06	2.4E-04	4.8E+01	-2.4E-01	1.6E-10
2	7200	54	5.4E-05	8.4E-07	1.7E-04	1.2E+02	-6.0E-01	1.1E-10
3	10800	39	3.9E-05	6.1E-07	1.2E-04	1.9E+02	-9.3E-01	7.9E-11
4	14400	32	3.2E-05	5.1E-07	1.0E-04	2.2E+02	-1.1E+00	6.6E-11
5	18000	25	2.5E-05	4.0E-07	7.9E-05	2.7E+02	-1.4E+00	5.1E-11
6	21600	21	2.1E-05	3.3E-07	6.6E-05	3.1E+02	-1.5E+00	4.3E-11
24	86400	3	2.9E-06	4.5E-08	9.1E-06	7.0E+02	-3.5E+00	5.9E-12
25	90000	3	2.7E-06	4.3E-08	8.5E-06	7.2E+02	-3.6E+00	5.5E-12
26	93600	3	2.7E-06	4.2E-08	8.4E-06	7.2E+02	-3.6E+00	5.5E-12
27	97200	2	2.5E-06	3.9E-08	7.8E-06	7.3E+02	-3.7E+00	5.1E-12
28	100800	2	2.4E-06	3.7E-08	7.4E-06	7.5E+02	-3.7E+00	4.8E-12
29	104400	2	2.1E-06	3.4E-08	6.7E-06	7.6E+02	-3.8E+00	4.4E-12
30	108000	2	2.0E-06	3.2E-08	6.4E-06	7.8E+02	-3.9E+00	4.1E-12
48	172800	1	1.2E-06	1.9E-08	3.8E-06	8.8E+02	-4.4E+00	2.5E-12
49	176400	1	1.2E-06	1.9E-08	3.8E-06	8.8E+02	-4.4E+00	2.5E-12
50	180000	1	1.2E-06	1.9E-08	3.8E-06	8.8E+02	-4.4E+00	2.5E-12

**Table B.1: Results from experiment 1.1**



---

**EXPERIMENT 1.2**


---

Variable: Feed concentration (CuSO<sub>4</sub>): 150 ppm,

t (hr)	t (sec)	[150]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>f</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	136	1.4E-04	2.1E-06	4.3E-04	0.0E+00	0.0E+00	2.6E-10
1	3600	96	9.6E-05	1.5E-06	3.0E-04	7.1E+01	-3.6E-01	1.9E-10
2	7200	75	7.5E-05	1.2E-06	2.4E-04	1.2E+02	-6.0E-01	1.4E-10
3	10800	64	6.4E-05	1.0E-06	2.0E-04	1.5E+02	-7.6E-01	1.2E-10
4	14400	48	4.8E-05	7.6E-07	1.5E-04	2.1E+02	-1.0E+00	9.3E-11
5	18000	43	4.3E-05	6.8E-07	1.4E-04	2.3E+02	-1.2E+00	8.4E-11
6	21600	41	4.1E-05	6.4E-07	1.3E-04	2.4E+02	-1.2E+00	7.9E-11
24	86400	5	5.0E-06	7.9E-08	1.6E-05	6.6E+02	-3.3E+00	9.7E-12
25	90000	4	4.2E-06	6.7E-08	1.3E-05	6.9E+02	-3.5E+00	8.2E-12
26	93600	4	4.0E-06	6.3E-08	1.3E-05	7.1E+02	-3.5E+00	7.8E-12
27	97200	4	3.8E-06	5.9E-08	1.2E-05	7.2E+02	-3.6E+00	7.3E-12
28	100800	4	3.8E-06	6.0E-08	1.2E-05	7.2E+02	-3.6E+00	7.3E-12
29	104400	3	3.2E-06	5.0E-08	9.9E-06	7.5E+02	-3.8E+00	6.1E-12
30	108000	3	3.0E-06	4.7E-08	9.5E-06	7.6E+02	-3.8E+00	5.8E-12
48	172800	2	2.0E-06	3.2E-08	6.3E-06	8.4E+02	-4.2E+00	3.9E-12
49	176400	2	2.0E-06	3.1E-08	6.3E-06	8.4E+02	-4.2E+00	3.9E-12
50	180000	2	1.9E-06	3.0E-08	5.9E-06	8.6E+02	-4.3E+00	3.7E-12

**Table B.2: Results from experiment 1.2**

---

**EXPERIMENT 1.3**


---

Variable: Feed concentration (CuSO<sub>4</sub>): 200 ppm,

t (hr)	t (sec)	[200]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>r</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec
0	0	203	2.0E-04	3.2E-06	6.4E-04	0.0E+00	0.0E+00	3.7E-10
1	3600	156	1.6E-04	2.5E-06	4.9E-04	5.3E+01	-2.6E-01	2.9E-10
2	7200	121	1.2E-04	1.9E-06	3.8E-04	1.0E+02	-5.2E-01	2.2E-10
3	10800	105	1.1E-04	1.7E-06	3.3E-04	1.3E+02	-6.6E-01	1.9E-10
4	14400	92	9.2E-05	1.4E-06	2.9E-04	1.6E+02	-7.9E-01	1.7E-10
5	18000	74	7.4E-05	1.2E-06	2.3E-04	2.0E+02	-1.0E+00	1.4E-10
6	21600	68	6.8E-05	1.1E-06	2.1E-04	2.2E+02	-1.1E+00	1.3E-10
24	86400	8	8.0E-06	1.3E-07	2.5E-05	6.5E+02	-3.2E+00	1.5E-11
25	90000	7	7.0E-06	1.1E-07	2.2E-05	6.7E+02	-3.4E+00	1.3E-11
26	93600	6	6.0E-06	9.4E-08	1.9E-05	7.0E+02	-3.5E+00	1.1E-11
27	97200	6	6.0E-06	9.4E-08	1.9E-05	7.0E+02	-3.5E+00	1.1E-11
28	100800	6	6.0E-06	9.4E-08	1.9E-05	7.0E+02	-3.5E+00	1.1E-11
29	104400	5	5.0E-06	7.9E-08	1.6E-05	7.4E+02	-3.7E+00	9.2E-12
30	108000	5	5.0E-06	7.9E-08	1.6E-05	7.4E+02	-3.7E+00	9.2E-12
48	172800	2	2.0E-06	3.1E-08	6.3E-06	9.2E+02	-4.6E+00	3.7E-12
49	176400	3	3.0E-06	4.7E-08	9.4E-06	8.4E+02	-4.2E+00	5.5E-12
50	180000	2	2.0E-06	3.1E-08	6.3E-06	9.2E+02	-4.6E+00	3.7E-12

**Table B.3: Results from experiment 1.3**

---

**EXPERIMENT 1.4**


---

Variable: Feed concentration (CuSO<sub>4</sub>): 250 ppm,

t (hr)	t (sec)	[250]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>f</sub> ln (C/C <sub>o</sub> )	ln (C/C <sub>o</sub> )	J molem <sup>-2</sup> sec
0	0	242	2.4E-04	3.8E-06	7.6E-04	0.0E+00	0.0E+00	3.4E-10
1	3600	190	1.9E-04	3.0E-06	6.0E-04	4.8E+01	-2.4E-01	2.6E-10
2	7200	150	1.5E-04	2.4E-06	4.7E-04	9.6E+01	-4.8E-01	2.1E-10
3	10800	140	1.4E-04	2.2E-06	4.4E-04	1.1E+02	-5.5E-01	1.9E-10
4	14400	120	1.2E-04	1.9E-06	3.8E-04	1.4E+02	-7.0E-01	1.7E-10
5	18000	110	1.1E-04	1.7E-06	3.5E-04	1.6E+02	-7.9E-01	1.5E-10
6	21600	100	1.0E-04	1.6E-06	3.1E-04	1.8E+02	-8.8E-01	1.4E-10
24	86400	22	2.2E-05	3.5E-07	6.9E-05	4.8E+02	-2.4E+00	3.1E-11
25	90000	18	1.8E-05	2.8E-07	5.7E-05	5.2E+02	-2.6E+00	2.5E-11
26	93600	18	1.8E-05	2.8E-07	5.7E-05	5.2E+02	-2.6E+00	2.5E-11
27	97200	18	1.8E-05	2.8E-07	5.7E-05	5.2E+02	-2.6E+00	2.5E-11
28	100800	16	1.6E-05	2.5E-07	5.0E-05	5.4E+02	-2.7E+00	2.2E-11
29	104400	14	1.4E-05	2.2E-07	4.4E-05	5.7E+02	-2.8E+00	1.9E-11
30	108000	13	1.3E-05	2.0E-07	4.1E-05	5.8E+02	-2.9E+00	1.8E-11
48	172800	6	6.0E-06	9.4E-08	1.9E-05	7.4E+02	-3.7E+00	8.3E-12
49	176400	6	6.0E-06	9.4E-08	1.9E-05	7.4E+02	-3.7E+00	8.3E-12
50	180000	5	5.0E-06	7.9E-08	1.6E-05	7.8E+02	-3.9E+00	7.0E-12

**Table B.4: Results from experiment 1.4**

---

**EXPERIMENT 1.5**


---

Variable:      Feed concentration (CuSO<sub>4</sub>): 300 ppm,

t (hr)	t (sec)	[300]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>t</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molecm <sup>-2</sup> sec
0	0	308	3.1E-04	4.8E-06	9.7E-04	0.0E+00	0.0E+00	5.1E-10
1	3600	226	2.3E-04	3.6E-06	7.1E-04	6.2E+01	-3.1E-01	3.8E-10
2	7200	208	2.1E-04	3.3E-06	6.5E-04	7.9E+01	-3.9E-01	3.5E-10
3	10800	181	1.8E-04	2.8E-06	5.7E-04	1.1E+02	-5.3E-01	3.0E-10
4	14400	156	1.6E-04	2.5E-06	4.9E-04	1.4E+02	-6.8E-01	2.6E-10
5	18000	141	1.4E-04	2.2E-06	4.4E-04	1.6E+02	-7.8E-01	2.4E-10
6	21600	137	1.4E-04	2.2E-06	4.3E-04	1.6E+02	-8.1E-01	2.3E-10
24	86400	21	2.1E-05	3.3E-07	6.6E-05	5.4E+02	-2.7E+00	3.5E-11
25	90000	18	1.8E-05	2.8E-07	5.7E-05	5.7E+02	-2.8E+00	3.0E-11
26	93600	17	1.7E-05	2.7E-07	5.4E-05	5.8E+02	-2.9E+00	2.8E-11
27	97200	14	1.4E-05	2.2E-07	4.4E-05	6.2E+02	-3.1E+00	2.3E-11
28	100800	13	1.3E-05	2.0E-07	4.1E-05	6.3E+02	-3.2E+00	2.2E-11
29	104400	12	1.2E-05	1.9E-07	3.8E-05	6.5E+02	-3.2E+00	2.0E-11
30	108000	11	1.1E-05	1.7E-07	3.5E-05	6.7E+02	-3.3E+00	1.8E-11
48	172800	5	5.0E-06	7.9E-08	1.6E-05	8.2E+02	-4.1E+00	8.3E-12
49	176400	4	4.0E-06	6.3E-08	1.3E-05	8.7E+02	-4.3E+00	6.7E-12
50	180000	4	4.0E-06	6.3E-08	1.3E-05	8.7E+02	-4.3E+00	6.7E-12

**Table B.5: Results from experiment 1.5**

---

**EXPERIMENT 1.6**


---

Variable: Feed concentration (CuSO<sub>4</sub>): 350 ppm,

t (hr)	t (sec)	[350]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>r</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	331	3.3E-04	5.2E-06	1.0E-03	0.0E+00	0.0E+00	3.8E-10
1	3600	290	2.9E-04	4.6E-06	9.1E-04	2.6E+01	-1.3E-01	3.4E-10
2	7200	280	2.8E-04	4.4E-06	8.8E-04	3.3E+01	-1.7E-01	3.2E-10
3	10800	250	2.5E-04	3.9E-06	7.9E-04	5.6E+01	-2.8E-01	2.9E-10
4	14400	230	2.3E-04	3.6E-06	7.2E-04	7.3E+01	-3.6E-01	2.7E-10
5	18000	210	2.1E-04	3.3E-06	6.6E-04	9.1E+01	-4.6E-01	2.4E-10
6	21600	190	1.9E-04	3.0E-06	6.0E-04	1.1E+02	-5.6E-01	2.2E-10
24	86400	65	6.5E-05	1.0E-06	2.0E-04	3.3E+02	-1.6E+00	7.5E-11
25	90000	54	5.4E-05	8.5E-07	1.7E-04	3.6E+02	-1.8E+00	6.2E-11
26	93600	47	4.7E-05	7.4E-07	1.5E-04	3.9E+02	-2.0E+00	5.4E-11
27	97200	40	4.0E-05	6.3E-07	1.3E-04	4.2E+02	-2.1E+00	4.6E-11
28	100800	35	3.5E-05	5.5E-07	1.1E-04	4.5E+02	-2.2E+00	4.1E-11
29	104400	29	2.9E-05	4.6E-07	9.1E-05	4.9E+02	-2.4E+00	3.4E-11
30	108000	27	2.7E-05	4.2E-07	8.5E-05	5.0E+02	-2.5E+00	3.1E-11
48	172800	10	1.0E-05	1.6E-07	3.1E-05	7.0E+02	-3.5E+00	1.2E-11
49	176400	7	7.0E-06	1.1E-07	2.2E-05	7.7E+02	-3.9E+00	8.1E-12
50	180000	6	6.0E-06	9.4E-08	1.9E-05	8.0E+02	-4.0E+00	6.9E-12

**Table B.6: Results from experiment 1.6**

---

**EXPERIMENT 1.7**


---

Variable: Feed concentration (CuSO<sub>4</sub>): 400 ppm,

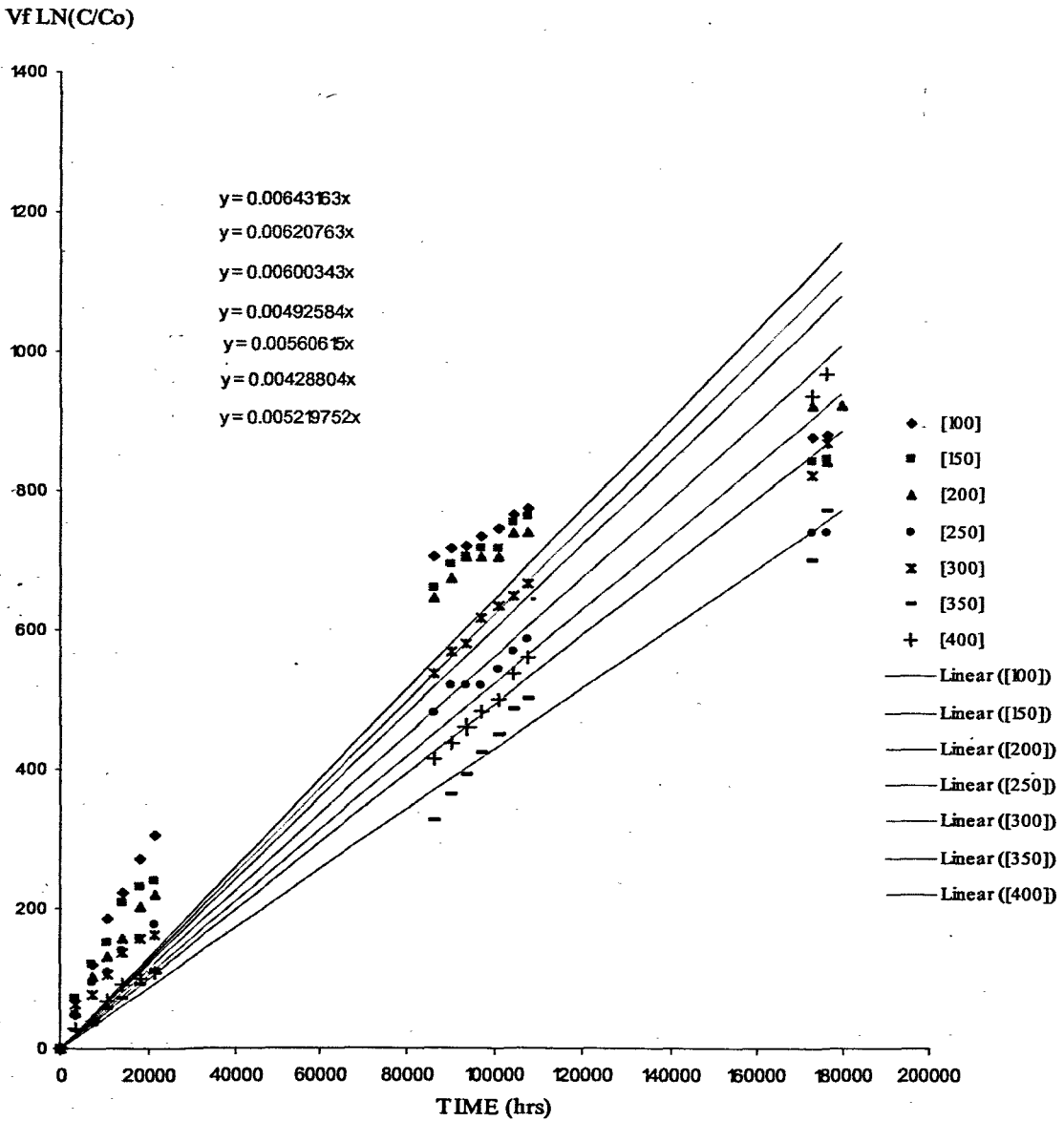
t (hr)	t (sec)	[400]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>r</sub> ln (C/C <sub>o</sub> )	ln (C/C <sub>o</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	380	3.8E-04	6.0E-06	1.2E-03	0.0E+00	0.0E+00	5.7E-10
1	3600	330	3.3E-04	5.2E-06	1.0E-03	2.8E+01	-1.4E-01	5.0E-10
2	7200	310	3.1E-04	4.9E-06	9.8E-04	4.1E+01	-2.0E-01	4.7E-10
3	10800	270	2.7E-04	4.2E-06	8.5E-04	6.8E+01	-3.4E-01	4.1E-10
4	14400	240	2.4E-04	3.8E-06	7.6E-04	9.2E+01	-4.6E-01	3.6E-10
5	18000	230	2.3E-04	3.6E-06	7.2E-04	1.0E+02	-5.0E-01	3.5E-10
6	21600	220	2.2E-04	3.5E-06	6.9E-04	1.1E+02	-5.5E-01	3.3E-10
24	86400	48	4.8E-05	7.6E-07	1.5E-04	4.1E+02	-2.1E+00	7.2E-11
25	90000	43	4.3E-05	6.8E-07	1.4E-04	4.4E+02	-2.2E+00	6.5E-11
26	93600	38	3.8E-05	6.0E-07	1.2E-04	4.6E+02	-2.3E+00	5.7E-11
27	97200	34	3.4E-05	5.4E-07	1.1E-04	4.8E+02	-2.4E+00	5.1E-11
28	100800	31	3.1E-05	4.9E-07	9.8E-05	5.0E+02	-2.5E+00	4.7E-11
29	104400	26	2.6E-05	4.1E-07	8.2E-05	5.4E+02	-2.7E+00	3.9E-11
30	108000	23	2.3E-05	3.6E-07	7.2E-05	5.6E+02	-2.8E+00	3.5E-11
48	172800	4	3.5E-06	5.5E-08	1.1E-05	9.4E+02	-4.7E+00	5.3E-12
49	176400	3	3.0E-06	4.7E-08	9.4E-06	9.7E+02	-4.8E+00	4.5E-12
50	180000	3	2.7E-06	4.2E-08	8.5E-06	9.9E+02	-4.9E+00	4.1E-12

**Table B.7:** Results from experiment 1.7

pH values at different Feed concentration (CuSO<sub>4</sub>)

TIME(hrs)	TIME(sec)	100	150	200	250	300	350	400
0	0	3.56	3.41	2.79	3.46	3.3	3.14	3.09
1	3600	3.03	3.05	2.56	3.03	2.89	3.01	2.73
2	7200	3.04	2.76	2.42	3.04	2.67	2.79	2.66
3	10800	2.92	2.64	2.34	2.92	2.43	2.71	2.56
4	14400	2.89	2.62	2.24	2.89	2.35	2.65	2.17
5	18000	2.82	2.58	2.23	2.82	2.21	2.41	2.01
6	21600	2.82	2.56	2.22	2.82	2.16	2.23	1.99
24	86400	2.23	2.04	1.9	2.41	1.92	1.9	1.83
25	90000	2.23	2.04	1.89	2.4	1.92	1.89	1.83
26	93600	2.22	2.02	1.88	2.32	1.93	1.89	1.86
27	97200	2.2	2.01	1.85	2.3	1.91	1.88	1.84
28	100800	2.19	2.03	1.89	2.09	1.9	1.87	1.83
29	104400	2.18	1.99	1.87	2.01	1.89	1.87	1.82
30	108000	2.19	1.99	1.86	2.01	1.89	1.86	1.82
48	172800	1.93	1.88	1.8	1.76	1.73	1.71	1.68
49	176400	1.92	1.88	1.81	1.76	1.74	1.71	1.66
50	180000	1.92	1.88	1.81	1.76	1.73	1.7	1.68

Table B.8: Results from experiment 1.1 -1.7



**Figure B.1:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of feed concentration on permeability. The results of experiment 1.1 – 1.7 shows on the graph how the gradient can be obtained ( $S_p$ ) by plotting  $V_f \ln(C/C_0)$  vs TIME



---

**APPENDIX C**

---

DATA  
FROM  
BATCH  
EXPERIMENTS

**AQUEOUS STRIP CONCENTRATIONS (H<sub>2</sub>SO<sub>4</sub>)**

The effect different aqueous strip ( $\text{H}_2\text{SO}_4$ ) concentrations have on the extraction of Copper (II)

at the following experimental conditions.

**Experimental parameters:**

Volume of aqueous feed phase:	200cm <sup>3</sup>
Volume of aqueous strip phase:	200cm <sup>3</sup>
Membrane length:	18cm
Feed concentration ( $\text{CuSO}_4$ ):	200ppm
Strip concentration ( $\text{H}_2\text{SO}_4$ ):	5% - 30%
Extractant concentration (Lix 984):	20%
Feed flow rate ( $\text{CuSO}_4$ ):	20ml.min <sup>-1</sup> / 0.33cm <sup>3</sup> .sec <sup>-1</sup>
Strip flow rate ( $\text{H}_2\text{SO}_4$ ):	20ml.min <sup>-1</sup> / 0.33cm <sup>3</sup> .sec <sup>-1</sup>
Time:	50hours / 180 000sec

## EXPERIMENT 2.1

Variable: Strip concentration (H<sub>2</sub>SO<sub>4</sub>): 5%

t (hr)	t (sec)	5%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>r</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	210	2.1E-04	3.3E-06	6.6E-04	0.0E+00	0.0E+00	8.0E-09
1	3600	170	1.7E-04	2.7E-06	5.4E-04	4.2E+01	-2.1E-01	6.5E-09
2	7200	160	1.6E-04	2.5E-06	5.0E-04	5.4E+01	-2.7E-01	6.1E-09
3	10800	150	1.5E-04	2.4E-06	4.7E-04	6.7E+01	-3.4E-01	5.7E-09
4	14400	140	1.4E-04	2.2E-06	4.4E-04	8.1E+01	-4.1E-01	5.3E-09
5	18000	130	1.3E-04	2.0E-06	4.1E-04	9.6E+01	-4.8E-01	5.0E-09
6	21600	130	1.3E-04	2.0E-06	4.1E-04	9.6E+01	-4.8E-01	5.0E-09
24	86400	67	6.7E-05	1.1E-06	2.1E-04	2.3E+02	-1.1E+00	2.6E-09
25	90000	65	6.5E-05	1.0E-06	2.0E-04	2.3E+02	-1.2E+00	2.5E-09
26	93600	65	6.5E-05	1.0E-06	2.0E-04	2.3E+02	-1.2E+00	2.5E-09
27	97200	60	6.0E-05	9.4E-07	1.9E-04	2.5E+02	-1.3E+00	2.3E-09
28	100800	57	5.7E-05	9.0E-07	1.8E-04	2.6E+02	-1.3E+00	2.2E-09
29	104400	56	5.6E-05	8.8E-07	1.8E-04	2.6E+02	-1.3E+00	2.1E-09
30	108000	52	5.2E-05	8.2E-07	1.6E-04	2.8E+02	-1.4E+00	2.0E-09
48	172800	27	2.7E-05	4.2E-07	8.5E-05	4.1E+02	-2.1E+00	1.0E-09
49	176400	26	2.6E-05	4.1E-07	8.2E-05	4.2E+02	-2.1E+00	9.9E-10
50	180000	25	2.5E-05	3.9E-07	7.9E-05	4.3E+02	-2.1E+00	9.5E-10

**Table C.1: Results from experiment 2.1**

## EXPERIMENT 2.2

Variable: Strip concentration (H<sub>2</sub>SO<sub>4</sub>): 10%

t (hr)	t (sec)	10%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>t</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molem <sup>-2</sup> sec <sup>-1</sup>
0	0	203.88	2.0E-04	3.2E-06	6.4E-04	0.0E+00	0.0E+00	1.2E-08
1	3600	191.58	1.9E-04	3.0E-06	6.0E-04	1.2E+01	-6.2E-02	1.1E-08
2	7200	132.3	1.3E-04	2.1E-06	4.2E-04	8.6E+01	-4.3E-01	7.6E-09
3	10800	116.26	1.2E-04	1.8E-06	3.7E-04	1.1E+02	-5.6E-01	6.6E-09
4	14400	112.58	1.1E-04	1.8E-06	3.5E-04	1.2E+02	-5.9E-01	6.4E-09
5	18000	101.78	1.0E-04	1.6E-06	3.2E-04	1.4E+02	-6.9E-01	5.8E-09
6	21600	89.08	8.9E-05	1.4E-06	2.8E-04	1.7E+02	-8.3E-01	5.1E-09
24	86400	44.38	4.4E-05	7.0E-07	1.4E-04	3.0E+02	-1.5E+00	2.5E-09
25	90000	41.14	4.1E-05	6.5E-07	1.3E-04	3.2E+02	-1.6E+00	2.4E-09
26	93600	40.66	4.1E-05	6.4E-07	1.3E-04	3.2E+02	-1.6E+00	2.3E-09
27	97200	40.12	4.0E-05	6.3E-07	1.3E-04	3.3E+02	-1.6E+00	2.3E-09
28	100800	37.16	3.7E-05	5.8E-07	1.2E-04	3.4E+02	-1.7E+00	2.1E-09
29	104400	34.94	3.5E-05	5.5E-07	1.1E-04	3.5E+02	-1.8E+00	2.0E-09
30	108000	33.96	3.4E-05	5.3E-07	1.1E-04	3.6E+02	-1.8E+00	1.9E-09
48	172800	11.96	1.2E-05	1.9E-07	3.8E-05	5.7E+02	-2.8E+00	6.8E-10
49	176400	7.3	7.3E-06	1.1E-07	2.3E-05	6.7E+02	-3.3E+00	4.2E-10
50	180000	6.02	6.0E-06	9.5E-08	1.9E-05	7.0E+02	-3.5E+00	3.4E-10

Table C.2: Results from experiment 2.2

---

**EXPERIMENT 2.3**


---

**Variable:** Strip concentration (H<sub>2</sub>SO<sub>4</sub>): 15%

t (hr)	t (sec)	15%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>t</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	205.64	2.1E-04	3.2E-06	6.5E-04	0.0E+00	0.0E+00	1.9E-08
1	3600	185.35	1.9E-04	2.9E-06	5.8E-04	2.1E+01	-1.0E-01	1.7E-08
2	7200	158.19	1.6E-04	2.5E-06	5.0E-04	5.2E+01	-2.6E-01	1.5E-08
3	10800	142.26	1.4E-04	2.2E-06	4.5E-04	7.4E+01	-3.7E-01	1.3E-08
4	14400	116.58	1.2E-04	1.8E-06	3.7E-04	1.1E+02	-5.7E-01	1.1E-08
5	18000	110.23	1.1E-04	1.7E-06	3.5E-04	1.2E+02	-6.2E-01	1.0E-08
6	21600	92.16	9.2E-05	1.5E-06	2.9E-04	1.6E+02	-8.0E-01	8.6E-09
24	86400	17.66	1.8E-05	2.8E-07	5.6E-05	4.9E+02	-2.5E+00	1.6E-09
25	90000	13.22	1.3E-05	2.1E-07	4.2E-05	5.5E+02	-2.7E+00	1.2E-09
26	93600	12.43	1.2E-05	2.0E-07	3.9E-05	5.6E+02	-2.8E+00	1.2E-09
27	97200	11.63	1.2E-05	1.8E-07	3.7E-05	5.7E+02	-2.9E+00	1.1E-09
28	100800	10.9	1.1E-05	1.7E-07	3.4E-05	5.9E+02	-2.9E+00	1.0E-09
29	104400	9.06	9.1E-06	1.4E-07	2.9E-05	6.2E+02	-3.1E+00	8.5E-10
30	108000	7.69	7.7E-06	1.2E-07	2.4E-05	6.6E+02	-3.3E+00	7.2E-10
48	172800	5.82	5.8E-06	9.2E-08	1.8E-05	7.1E+02	-3.6E+00	5.4E-10
49	176400	4.83	4.8E-06	7.6E-08	1.5E-05	7.5E+02	-3.8E+00	4.5E-10
50	180000	3.52	3.5E-06	5.5E-08	1.1E-05	8.1E+02	-4.1E+00	3.3E-10

**Table C.3: Results from experiment 2.3**

---

**EXPERIMENT 2.4**


---

Variable: Strip concentration (H<sub>2</sub>SO<sub>4</sub>): 20%

t (hr)	t (sec)	20%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>f</sub> ln (C/C <sub>s</sub> )	ln (C/C <sub>s</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	233	2.3E-04	3.7E-06	7.3E-04	0.0E+00	0.0E+00	2.2E-08
1	3600	220.34	2.2E-04	3.5E-06	6.9E-04	1.1E+01	-5.6E-02	2.1E-08
2	7200	190.68	1.9E-04	3.0E-06	6.0E-04	4.0E+01	-2.0E-01	1.8E-08
3	10800	166.1	1.7E-04	2.6E-06	5.2E-04	6.8E+01	-3.4E-01	1.6E-08
4	14400	158.71	1.6E-04	2.5E-06	5.0E-04	7.7E+01	-3.8E-01	1.5E-08
5	18000	139.24	1.4E-04	2.2E-06	4.4E-04	1.0E+02	-5.1E-01	1.3E-08
6	21600	129.83	1.3E-04	2.0E-06	4.1E-04	1.2E+02	-5.8E-01	1.3E-08
24	86400	21.82	2.2E-05	3.4E-07	6.9E-05	4.7E+02	-2.4E+00	2.1E-09
25	90000	20.37	2.0E-05	3.2E-07	6.4E-05	4.9E+02	-2.4E+00	2.0E-09
26	93600	19.1	1.9E-05	3.0E-07	6.0E-05	5.0E+02	-2.5E+00	1.8E-09
27	97200	18.18	1.8E-05	2.9E-07	5.7E-05	5.1E+02	-2.6E+00	1.8E-09
28	100800	16.37	1.6E-05	2.6E-07	5.2E-05	5.3E+02	-2.7E+00	1.6E-09
29	104400	14.95	1.5E-05	2.4E-07	4.7E-05	5.5E+02	-2.7E+00	1.4E-09
30	108000	14.52	1.5E-05	2.3E-07	4.6E-05	5.6E+02	-2.8E+00	1.4E-09
48	172800	2.69	2.7E-06	4.2E-08	8.5E-06	8.9E+02	-4.5E+00	2.6E-10
49	176400	2.31	2.3E-06	3.6E-08	7.3E-06	9.2E+02	-4.6E+00	2.2E-10
50	180000	2	2.0E-06	3.1E-08	6.3E-06	9.5E+02	-4.8E+00	1.9E-10

**Table C.4:** Results from experiment 2.4

---

**EXPERIMENT 2.5**


---

Variable: Strip concentration (H<sub>2</sub>SO<sub>4</sub>): 25%

t (hr)	t (sec)	25%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>t</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	225	2.3E-04	3.5E-06	7.1E-04	0.0E+00	0.0E+00	2.4E-08
1	3600	202.5	2.0E-04	3.2E-06	6.4E-04	2.1E+01	-1.1E-01	2.1E-08
2	7200	178.3	1.8E-04	2.8E-06	5.6E-04	4.7E+01	-2.3E-01	1.9E-08
3	10800	159	1.6E-04	2.5E-06	5.0E-04	6.9E+01	-3.5E-01	1.7E-08
4	14400	143.7	1.4E-04	2.3E-06	4.5E-04	9.0E+01	-4.5E-01	1.5E-08
5	18000	136.5	1.4E-04	2.1E-06	4.3E-04	1.0E+02	-5.0E-01	1.4E-08
6	21600	121.5	1.2E-04	1.9E-06	3.8E-04	1.2E+02	-6.2E-01	1.3E-08
24	86400	15	1.5E-05	2.4E-07	4.7E-05	5.4E+02	-2.7E+00	1.6E-09
25	90000	12.2	1.2E-05	1.9E-07	3.8E-05	5.8E+02	-2.9E+00	1.3E-09
26	93600	12.6	1.3E-05	2.0E-07	4.0E-05	5.8E+02	-2.9E+00	1.3E-09
27	97200	10.5	1.1E-05	1.7E-07	3.3E-05	6.1E+02	-3.1E+00	1.1E-09
28	100800	9.5	9.5E-06	1.5E-07	3.0E-05	6.3E+02	-3.2E+00	1.0E-09
29	104400	9.5	9.5E-06	1.5E-07	3.0E-05	6.3E+02	-3.2E+00	1.0E-09
30	108000	9.5	9.5E-06	1.5E-07	3.0E-05	6.3E+02	-3.2E+00	1.0E-09
48	172800	3.2	3.2E-06	5.0E-08	1.0E-05	8.5E+02	-4.3E+00	3.4E-10
49	176400	3.1	3.1E-06	4.9E-08	9.8E-06	8.6E+02	-4.3E+00	3.2E-10
50	180000	3	3.0E-06	4.7E-08	9.4E-06	8.6E+02	-4.3E+00	3.1E-10

**Table C.5: Results from experiment 2.5**

---

**EXPERIMENT 2.6**


---

Variable: Strip concentration (H<sub>2</sub>SO<sub>4</sub>): 30%

t (hr)	t (sec)	30%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>t</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	231	2.3E-04	3.6E-06	7.3E-04	0.0E+00	0.0E+00	2.2E-08
1	3600	215	2.2E-04	3.4E-06	6.8E-04	1.4E+01	-7.2E-02	2.0E-08
2	7200	190	1.9E-04	3.0E-06	6.0E-04	3.9E+01	-2.0E-01	1.8E-08
3	10800	160.6	1.6E-04	2.5E-06	5.1E-04	7.3E+01	-3.6E-01	1.5E-08
4	14400	141	1.4E-04	2.2E-06	4.4E-04	9.9E+01	-4.9E-01	1.3E-08
5	18000	134	1.3E-04	2.1E-06	4.2E-04	1.1E+02	-5.4E-01	1.3E-08
6	21600	123.7	1.2E-04	1.9E-06	3.9E-04	1.2E+02	-6.2E-01	1.2E-08
24	86400	24	2.4E-05	3.8E-07	7.6E-05	4.5E+02	-2.3E+00	2.3E-09
25	90000	19.3	1.9E-05	3.0E-07	6.1E-05	5.0E+02	-2.5E+00	1.8E-09
26	93600	15	1.5E-05	2.4E-07	4.7E-05	5.5E+02	-2.7E+00	1.4E-09
27	97200	13.2	1.3E-05	2.1E-07	4.2E-05	5.7E+02	-2.9E+00	1.3E-09
28	100800	12	1.2E-05	1.9E-07	3.8E-05	5.9E+02	-3.0E+00	1.1E-09
29	104400	10.4	1.0E-05	1.6E-07	3.3E-05	6.2E+02	-3.1E+00	9.9E-10
30	108000	9.1	9.1E-06	1.4E-07	2.9E-05	6.5E+02	-3.2E+00	8.6E-10
48	172800	5	5.0E-06	7.9E-08	1.6E-05	7.7E+02	-3.8E+00	4.7E-10
49	176400	4.2	4.2E-06	6.6E-08	1.3E-05	8.0E+02	-4.0E+00	4.0E-10
50	180000	3.3	3.3E-06	5.2E-08	1.0E-05	8.5E+02	-4.2E+00	3.1E-10

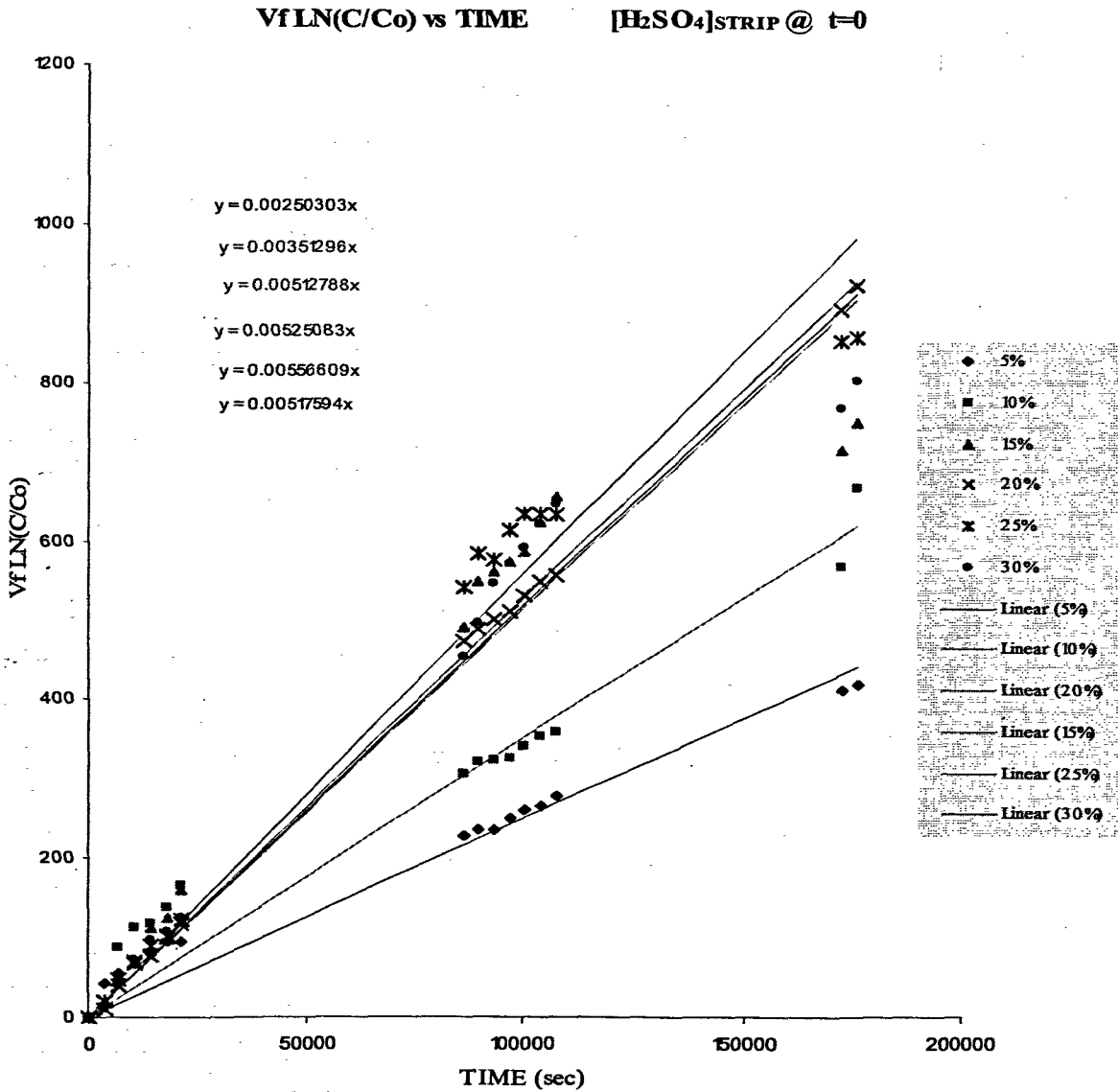
**Table C.6: Results from experiment 2.6**



pH values at different strip concentration ( $H_2SO_4$ )

t (hr)	t (sec)	5%	10%	15%	20%	25%	30%
0	0	3.58	3.19	3.24	2.90	3.28	3.35
1	3600	2.99	2.89	2.98	2.72	2.77	2.81
2	7200	2.83	2.75	2.81	2.61	2.63	2.59
3	10800	2.78	2.67	2.69	2.53	2.57	2.50
4	14400	2.72	2.62	2.66	2.33	2.44	2.41
5	18000	2.70	2.58	2.53	2.30	2.30	2.31
6	21600	2.67	2.54	2.48	2.26	2.12	2.18
24	86400	2.42	2.38	2.35	1.95	1.88	1.91
25	90000	2.41	2.37	2.34	1.94	1.85	1.90
26	93600	2.37	2.36	2.33	1.93	1.87	1.88
27	97200	2.36	2.35	2.32	1.91	1.86	1.86
28	100800	2.36	2.34	2.29	1.89	1.85	1.86
29	104400	2.33	2.34	2.32	1.88	1.84	1.83
30	108000	2.34	2.33	2.31	1.89	1.83	1.82
48	172800	2.18	2.12	2.04	1.43	1.40	1.38
49	176400	2.19	2.13	2.04	1.42	1.41	1.38
50	180000	2.19	2.12	2.04	1.43	1.41	1.38

Table C.7: Results from experiment 2.1 -2.6



**Figure C.1:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of strip concentration on permeability. The results of experiment 2.1 – 2.6 shows on the graph how the gradient can be obtained ( $S_p$ ) by plotting  $V_f \ln(C/C_0)$  vs TIME

---

**APPENDIX D**

---

DATA  
FROM  
BATCH  
EXPERIMENTS

**EXTRACTANT (CARRIER) CONCENTRATIONS  
(LIX984)**

The effect different extractant (CARRIER), LIX984C concentrations have on the permeation of Copper (II) at the following experimental conditions.

**Experimental parameters:**

Volume of aqueous feed phase:	200cm <sup>3</sup>
Volume of aqueous strip phase:	200cm <sup>3</sup>
Membrane length:	18cm
Feed concentration (CuSO <sub>4</sub> ):	200ppm
Strip concentration (H <sub>2</sub> SO <sub>4</sub> ):	25%
Extractant concentration (Lix 984):	5% - 40%
Feed flow rate (CuSO <sub>4</sub> ):	20ml.min <sup>-1</sup> / 0.333cm <sup>3</sup> .sec <sup>-1</sup>
Strip flow rate (H <sub>2</sub> SO <sub>4</sub> ):	20ml.min <sup>-1</sup> / 0.333cm <sup>3</sup> .sec <sup>-1</sup>
Time:	50hours / 180 000sec

### EXPERIMENT 3.1

**Variable:** Reactant (carrier) concentration (LIX984): 5%

t (hr)	t (sec)	5%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	Vf ln (C/C <sub>0</sub> )	ln(C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	190	1.9E-04	3.0E-06	6.0E-04	0.0E+00	0.0E+00	1.7E-10
1	3600	168	1.7E-04	2.6E-06	5.3E-04	2.5E+01	-1.2E-01	1.5E-10
2	7200	139	1.4E-04	2.2E-06	4.4E-04	6.3E+01	-3.1E-01	1.3E-10
3	10800	125	1.3E-04	2.0E-06	3.9E-04	8.4E+01	-4.2E-01	1.1E-10
4	14400	111	1.1E-04	1.7E-06	3.5E-04	1.1E+02	-5.4E-01	1.0E-10
5	18000	93	9.3E-05	1.5E-06	2.9E-04	1.4E+02	-7.1E-01	8.6E-11
6	21600	88	8.8E-05	1.4E-06	2.8E-04	1.5E+02	-7.7E-01	8.1E-11
24	86400	28	2.8E-05	4.4E-07	8.8E-05	3.8E+02	-1.9E+00	2.6E-11
25	90000	26	2.6E-05	4.1E-07	8.2E-05	4.0E+02	-2.0E+00	2.4E-11
26	93600	25	2.5E-05	3.9E-07	7.9E-05	4.1E+02	-2.0E+00	2.3E-11
27	97200	25	2.5E-05	3.9E-07	7.9E-05	4.1E+02	-2.0E+00	2.3E-11
28	100800	24	2.4E-05	3.8E-07	7.6E-05	4.1E+02	-2.1E+00	2.2E-11
29	104400	23	2.3E-05	3.6E-07	7.2E-05	4.2E+02	-2.1E+00	2.1E-11
30	108000	22	2.2E-05	3.5E-07	6.9E-05	4.3E+02	-2.2E+00	2.0E-11
48	172800	16	1.6E-05	2.5E-07	5.0E-05	4.9E+02	-2.5E+00	1.5E-11
49	176400	16	1.6E-05	2.5E-07	5.0E-05	4.9E+02	-2.5E+00	1.5E-11
50	180000	15	1.5E-05	2.4E-07	4.7E-05	5.1E+02	-2.5E+00	1.4E-11

**Table D.1: Results from experiment 3.1**

---

**EXPERIMENT 3.2**


---

**Variable:** Reactant (carrier) concentration (LIX984): 10%

t (hr)	t (sec)	10%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	Vf ln (C/C <sub>0</sub> )	ln(C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	187	1.9E-04	2.9E-06	5.9E-04	0.0E+00	0.0E+00	1.9E-10
1	3600	160	1.6E-04	2.5E-06	5.0E-04	3.1E+01	-1.6E-01	1.7E-10
2	7200	146	1.5E-04	2.3E-06	4.6E-04	5.0E+01	-2.5E-01	1.5E-10
3	10800	130	1.3E-04	2.0E-06	4.1E-04	7.3E+01	-3.6E-01	1.3E-10
4	14400	114	1.1E-04	1.8E-06	3.6E-04	9.9E+01	-4.9E-01	1.2E-10
5	18000	106	1.1E-04	1.7E-06	3.3E-04	1.1E+02	-5.7E-01	1.1E-10
6	21600	97	9.7E-05	1.5E-06	3.1E-04	1.3E+02	-6.6E-01	1.0E-10
24	86400	24	2.4E-05	3.8E-07	7.6E-05	4.1E+02	-2.1E+00	2.5E-11
25	90000	23	2.3E-05	3.6E-07	7.2E-05	4.2E+02	-2.1E+00	2.4E-11
26	93600	22	2.2E-05	3.5E-07	6.9E-05	4.3E+02	-2.1E+00	2.3E-11
27	97200	21	2.1E-05	3.3E-07	6.6E-05	4.4E+02	-2.2E+00	2.2E-11
28	100800	19	1.9E-05	3.0E-07	6.0E-05	4.6E+02	-2.3E+00	2.0E-11
29	104400	19	1.9E-05	3.0E-07	6.0E-05	4.6E+02	-2.3E+00	2.0E-11
30	108000	18	1.8E-05	2.8E-07	5.7E-05	4.7E+02	-2.3E+00	1.9E-11
48	172800	11	1.1E-05	1.7E-07	3.5E-05	5.7E+02	-2.8E+00	1.1E-11
49	176400	11	1.1E-05	1.7E-07	3.5E-05	5.7E+02	-2.8E+00	1.1E-11
50	180000	11	1.1E-05	1.7E-07	3.5E-05	5.7E+02	-2.8E+00	1.1E-11

**Table D.2: Results from experiment 3.2**

---

**EXPERIMENT 3.3**


---

Variable:      Reactant (carrier) concentration (LIX984): 15%

t (hr)	t (sec)	15%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	Vf ln (C/C <sub>0</sub> )	ln(C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	195	2.0E-04	3.1E-06	6.1E-04	0.0E+00	0.0E+00	2.4E-10
1	3600	143	1.4E-04	2.3E-06	4.5E-04	6.2E+01	-3.1E-01	1.8E-10
2	7200	123	1.2E-04	1.9E-06	3.9E-04	9.2E+01	-4.6E-01	1.5E-10
3	10800	106	1.1E-04	1.7E-06	3.3E-04	1.2E+02	-6.1E-01	1.3E-10
4	14400	97	9.7E-05	1.5E-06	3.1E-04	1.4E+02	-7.0E-01	1.2E-10
5	18000	86	8.6E-05	1.4E-06	2.7E-04	1.6E+02	-8.2E-01	1.1E-10
6	21600	75	7.5E-05	1.2E-06	2.4E-04	1.9E+02	-9.6E-01	9.3E-11
24	86400	23	2.3E-05	3.6E-07	7.2E-05	4.3E+02	-2.1E+00	2.8E-11
25	90000	21	2.1E-05	3.3E-07	6.6E-05	4.5E+02	-2.2E+00	2.6E-11
26	93600	20	2.0E-05	3.1E-07	6.3E-05	4.6E+02	-2.3E+00	2.5E-11
27	97200	19	1.9E-05	3.0E-07	6.0E-05	4.7E+02	-2.3E+00	2.4E-11
28	100800	17	1.7E-05	2.7E-07	5.4E-05	4.9E+02	-2.4E+00	2.1E-11
29	104400	17	1.7E-05	2.7E-07	5.4E-05	4.9E+02	-2.4E+00	2.1E-11
30	108000	16	1.6E-05	2.5E-07	5.0E-05	5.0E+02	-2.5E+00	2.0E-11
48	172800	6	5.6E-06	8.8E-08	1.8E-05	7.1E+02	-3.6E+00	6.9E-12
49	176400	5	5.2E-06	8.2E-08	1.6E-05	7.2E+02	-3.6E+00	6.4E-12
50	180000	5	5.1E-06	8.0E-08	1.6E-05	7.3E+02	-3.6E+00	6.3E-12

**Table D.3: Results from experiment 3.3**

---

**EXPERIMENT 3.4**


---

Variable:      Reactant (carrier) concentration (LIX984): 20%

t (hr)	t (sec)	20%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	Vf ln (C/C <sub>0</sub> )	ln(C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	211	2.1E-04	3.3E-06	6.6E-04	0.0E+00	0.0E+00	3.0E-10
1	3600	174	1.7E-04	2.7E-06	5.5E-04	3.9E+01	-1.9E-01	2.4E-10
2	7200	129	1.3E-04	2.0E-06	4.1E-04	9.8E+01	-4.9E-01	1.8E-10
3	10800	105	1.1E-04	1.7E-06	3.3E-04	1.4E+02	-7.0E-01	1.5E-10
4	14400	90	9.0E-05	1.4E-06	2.8E-04	1.7E+02	-8.5E-01	1.3E-10
5	18000	78	7.8E-05	1.2E-06	2.5E-04	2.0E+02	-1.0E+00	1.1E-10
6	21600	69	6.9E-05	1.1E-06	2.2E-04	2.2E+02	-1.1E+00	9.7E-11
24	86400	22	2.2E-05	3.5E-07	6.9E-05	4.5E+02	-2.3E+00	3.1E-11
25	90000	21	2.1E-05	3.3E-07	6.6E-05	4.6E+02	-2.3E+00	2.9E-11
26	93600	19	1.9E-05	3.0E-07	6.0E-05	4.8E+02	-2.4E+00	2.7E-11
27	97200	18	1.8E-05	2.8E-07	5.7E-05	4.9E+02	-2.5E+00	2.5E-11
28	100800	17	1.7E-05	2.7E-07	5.4E-05	5.0E+02	-2.5E+00	2.4E-11
29	104400	17	1.7E-05	2.6E-07	5.3E-05	5.1E+02	-2.5E+00	2.3E-11
30	108000	15	1.5E-05	2.4E-07	4.7E-05	5.3E+02	-2.6E+00	2.1E-11
48	172800	3	3.4E-06	5.4E-08	1.1E-05	8.3E+02	-4.1E+00	4.8E-12
49	176400	3	3.2E-06	5.0E-08	1.0E-05	8.4E+02	-4.2E+00	4.5E-12
50	180000	3	3.0E-06	4.7E-08	9.4E-06	8.5E+02	-4.3E+00	4.2E-12

**Table D.4: Results from experiment 3.4**



---

**EXPERIMENT 3.5**


---

Variable:      Reactant (carrier) concentration (LIX984): 25%

t (hr)	t (sec)	25%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	Vf ln (C/C <sub>0</sub> )	ln(C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	214	2.1E-04	3.4E-06	6.7E-04	0.0E+00	0.0E+00	2.8E-10
1	3600	167	1.7E-04	2.6E-06	5.3E-04	5.0E+01	-2.5E-01	2.2E-10
2	7200	137	1.4E-04	2.2E-06	4.3E-04	8.9E+01	-4.5E-01	1.8E-10
3	10800	118	1.2E-04	1.9E-06	3.7E-04	1.2E+02	-6.0E-01	1.5E-10
4	14400	106	1.1E-04	1.7E-06	3.3E-04	1.4E+02	-7.0E-01	1.4E-10
5	18000	99	9.9E-05	1.6E-06	3.1E-04	1.5E+02	-7.7E-01	1.3E-10
6	21600	92	9.2E-05	1.4E-06	2.9E-04	1.7E+02	-8.4E-01	1.2E-10
24	86400	26	2.6E-05	4.1E-07	8.2E-05	4.2E+02	-2.1E+00	3.4E-11
25	90000	23	2.3E-05	3.6E-07	7.2E-05	4.5E+02	-2.2E+00	3.0E-11
26	93600	21	2.1E-05	3.3E-07	6.6E-05	4.6E+02	-2.3E+00	2.7E-11
27	97200	19	1.9E-05	3.0E-07	6.0E-05	4.8E+02	-2.4E+00	2.5E-11
28	100800	19	1.9E-05	3.0E-07	6.0E-05	4.8E+02	-2.4E+00	2.5E-11
29	104400	19	1.9E-05	3.0E-07	6.0E-05	4.8E+02	-2.4E+00	2.5E-11
30	108000	18	1.8E-05	2.8E-07	5.7E-05	5.0E+02	-2.5E+00	2.3E-11
48	172800	4	4.4E-06	6.9E-08	1.4E-05	7.8E+02	-3.9E+00	5.7E-12
49	176400	4	4.1E-06	6.5E-08	1.3E-05	7.9E+02	-4.0E+00	5.3E-12
50	180000	4	4.0E-06	6.3E-08	1.3E-05	8.0E+02	-4.0E+00	5.2E-12

**Table D.5: Results from experiment 3.5**

---

**EXPERIMENT 3.6**


---

Variable:      Reactant (carrier) concentration (LIX984): 40%

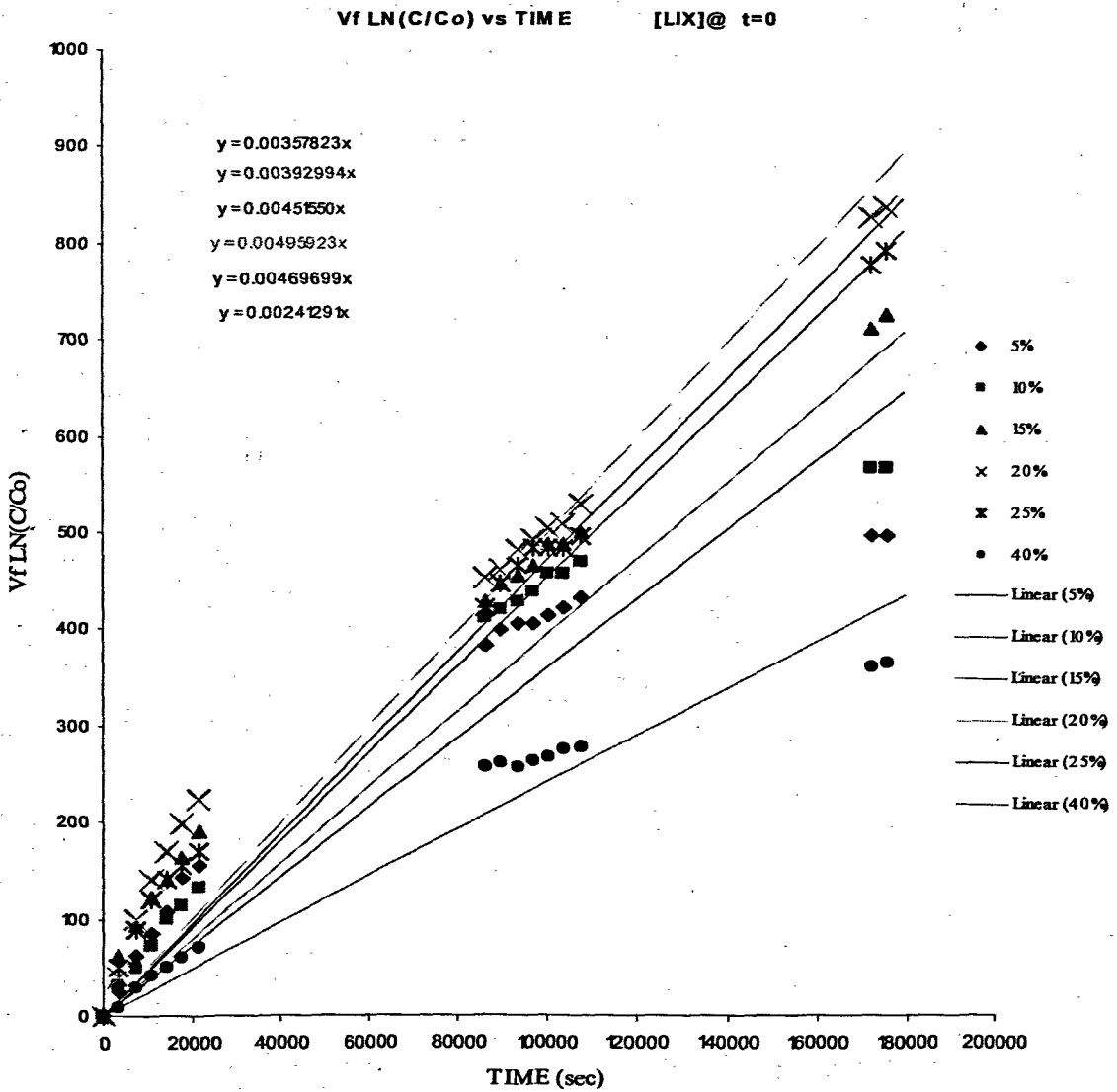
t (hr)	t (sec)	40%	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	Vf ln (C/C <sub>0</sub> )	ln(C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	205	2.1E-04	3.2E-06	6.5E-04	0.0E+00	0.0E+00	1.2E-10
1	3600	196	2.0E-04	3.1E-06	6.2E-04	9.0E+00	-4.5E-02	1.1E-10
2	7200	178	1.8E-04	2.8E-06	5.6E-04	2.8E+01	-1.4E-01	1.0E-10
3	10800	166	1.7E-04	2.6E-06	5.2E-04	4.2E+01	-2.1E-01	9.6E-11
4	14400	160	1.6E-04	2.5E-06	5.0E-04	5.0E+01	-2.5E-01	9.2E-11
5	18000	152	1.5E-04	2.4E-06	4.8E-04	6.0E+01	-3.0E-01	8.8E-11
6	21600	145	1.5E-04	2.3E-06	4.6E-04	6.9E+01	-3.5E-01	8.3E-11
24	86400	57	5.7E-05	9.0E-07	1.8E-04	2.6E+02	-1.3E+00	3.3E-11
25	90000	56	5.6E-05	8.8E-07	1.8E-04	2.6E+02	-1.3E+00	3.2E-11
26	93600	57	5.7E-05	9.0E-07	1.8E-04	2.6E+02	-1.3E+00	3.3E-11
27	97200	55	5.5E-05	8.7E-07	1.7E-04	2.6E+02	-1.3E+00	3.2E-11
28	100800	54	5.4E-05	8.5E-07	1.7E-04	2.7E+02	-1.3E+00	3.1E-11
29	104400	52	5.2E-05	8.2E-07	1.6E-04	2.7E+02	-1.4E+00	3.0E-11
30	108000	52	5.2E-05	8.1E-07	1.6E-04	2.8E+02	-1.4E+00	3.0E-11
48	172800	34	3.4E-05	5.4E-07	1.1E-04	3.6E+02	-1.8E+00	2.0E-11
49	176400	33	3.3E-05	5.3E-07	1.1E-04	3.6E+02	-1.8E+00	1.9E-11
50	180000	30	3.0E-05	4.7E-07	9.4E-05	3.8E+02	-1.9E+00	1.7E-11

**Table D.6: Results from experiment 3.6**

## pH values at different reactant concentration (LIX984)

t (hr)	t (sec)	5%	10%	15%	20%	25%	40%
0	0	3.20	3.54	3.45	3.50	2.73	2.98
1	3600	2.80	3.08	3.06	3.12	2.51	2.53
2	7200	2.71	2.95	2.82	2.98	2.39	2.42
3	10800	2.67	2.84	2.60	2.88	2.31	2.42
4	14400	2.55	2.74	2.57	2.80	2.24	2.40
5	18000	2.49	2.67	2.42	2.60	2.28	2.36
6	21600	2.42	2.51	2.22	2.56	2.27	2.32
24	86400	2.11	2.03	1.90	1.89	1.98	2.12
25	90000	2.13	2.00	1.88	1.86	1.98	2.10
26	93600	2.10	1.98	1.87	1.86	1.96	2.06
27	97200	2.09	1.96	1.85	1.84	1.94	2.02
28	100800	2.08	1.95	1.86	1.83	1.95	2.02
29	104400	2.07	1.93	1.91	1.82	1.93	1.98
30	108000	2.05	1.91	1.89	1.81	1.93	1.98
48	172800	1.87	1.84	1.77	1.71	1.69	1.89
49	176400	1.87	1.84	1.77	1.72	1.69	1.88
50	180000	1.85	1.84	1.77	1.71	1.68	1.89

Table D.7: Results from experiment 3.1 -3.6



**Figure D.1:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of reactant concentration on permeability. The results of experiment 3.1 – 3.6 shows on the graph how the gradient can be obtained ( $S_p$ ) by plotting  $V_f \ln(C/C_0)$  vs TIME

---

**APPENDIX E**

---

**DATA  
FROM  
BATCH  
EXPERIMENTS**

**FEED and STRIP FLOW RATES**

The effect different feed and strip flow rates have on the permeation of Copper (II) at the following experimental conditions.

**Experimental parameters:**

Volume of aqueous feed phase:	200cm <sup>3</sup>
Volume of aqueous strip phase:	200cm <sup>3</sup>
Membrane length:	18cm
Feed concentration (CuSO <sub>4</sub> ):	200ppm
Strip concentration (H <sub>2</sub> SO <sub>4</sub> ):	25%
Extractant concentration (Lix 984):	20%
Feed flow rate (CuSO <sub>4</sub> ):	0.167cm <sup>3</sup> .sec <sup>-1</sup> - 0.833cm <sup>3</sup> .sec <sup>-1</sup>
Strip flow rate (H <sub>2</sub> SO <sub>4</sub> ):	0.167cm <sup>3</sup> .sec <sup>-1</sup> - 0.833cm <sup>3</sup> .sec <sup>-1</sup>
Time:	50hours / 180 000sec

---

**EXPERIMENT 4.1**


---

Variable:      Feed and Strip flow rates:       $0.167\text{cm}^3.\text{sec}^{-1}$

0	0	224	2.2E-04	3.5E-06	7.1E-04	0.0E+00	0.0E+00	2.0E-10
1	3600	180	1.8E-04	2.8E-06	5.7E-04	4.4E+01	-2.2E-01	1.6E-10
2	7200	158	1.6E-04	2.5E-06	5.0E-04	7.0E+01	-3.5E-01	1.4E-10
3	10800	147	1.5E-04	2.3E-06	4.6E-04	8.4E+01	-4.2E-01	1.3E-10
4	14400	143	1.4E-04	2.3E-06	4.5E-04	9.0E+01	-4.5E-01	1.3E-10
5	18000	135	1.4E-04	2.1E-06	4.2E-04	1.0E+02	-5.1E-01	1.2E-10
6	21600	122	1.2E-04	1.9E-06	3.8E-04	1.2E+02	-6.1E-01	1.1E-10
24	86400	41	4.1E-05	6.5E-07	1.3E-04	3.4E+02	-1.7E+00	3.6E-11
25	90000	37	3.7E-05	5.8E-07	1.2E-04	3.6E+02	-1.8E+00	3.3E-11
26	93600	36	3.6E-05	5.7E-07	1.1E-04	3.7E+02	-1.8E+00	3.2E-11
27	97200	35	3.5E-05	5.5E-07	1.1E-04	3.7E+02	-1.9E+00	3.1E-11
28	100800	32	3.2E-05	5.0E-07	1.0E-04	3.9E+02	-1.9E+00	2.8E-11
29	104400	32	3.2E-05	5.0E-07	1.0E-04	3.9E+02	-1.9E+00	2.8E-11
30	108000	29	2.9E-05	4.6E-07	9.1E-05	4.1E+02	-2.0E+00	2.6E-11
48	172800	17	1.7E-05	2.7E-07	5.4E-05	5.2E+02	-2.6E+00	1.5E-11
49	176400	16	1.6E-05	2.5E-07	5.0E-05	5.3E+02	-2.6E+00	1.4E-11
50	180000	10	1.0E-05	1.6E-07	3.1E-05	6.2E+02	-3.1E+00	8.8E-12

**Table E.1: Results from experiment 4.1**

---

**EXPERIMENT 4.2**


---

Variable:      Feed and Strip flow rates:       $0.250\text{cm}^3.\text{sec}^{-1}$

t (hr)	t (sec)	0.250	$\text{g.cm}^{-3}$	$\text{mol.cm}^{-3}$	$\text{mole (cm}^3)$	$V_r \ln (C/C_0)$	$\ln (C/C_0)$	$J \text{ mol.cm}^{-2}.\text{sec}^{-1}$
0	0	215	2.2E-04	3.4E-06	6.8E-04	0.0E+00	0.0E+00	2.3E-10
1	3600	205	2.1E-04	3.2E-06	6.5E-04	9.5E+00	-4.8E-02	2.2E-10
2	7200	155	1.6E-04	2.4E-06	4.9E-04	6.5E+01	-3.3E-01	1.7E-10
3	10800	145	1.5E-04	2.3E-06	4.6E-04	7.9E+01	-3.9E-01	1.6E-10
4	14400	135	1.4E-04	2.1E-06	4.2E-04	9.3E+01	-4.7E-01	1.5E-10
5	18000	125	1.3E-04	2.0E-06	3.9E-04	1.1E+02	-5.4E-01	1.3E-10
6	21600	115	1.2E-04	1.8E-06	3.6E-04	1.3E+02	-6.3E-01	1.2E-10
24	86400	36	3.6E-05	5.7E-07	1.1E-04	3.6E+02	-1.8E+00	3.9E-11
25	90000	34	3.4E-05	5.4E-07	1.1E-04	3.7E+02	-1.8E+00	3.7E-11
26	93600	32	3.2E-05	5.0E-07	1.0E-04	3.8E+02	-1.9E+00	3.5E-11
27	97200	28	2.8E-05	4.4E-07	8.8E-05	4.1E+02	-2.0E+00	3.0E-11
28	100800	27	2.7E-05	4.2E-07	8.5E-05	4.1E+02	-2.1E+00	2.9E-11
29	104400	27	2.7E-05	4.2E-07	8.5E-05	4.1E+02	-2.1E+00	2.9E-11
30	108000	24	2.4E-05	3.8E-07	7.6E-05	4.4E+02	-2.2E+00	2.6E-11
48	172800	7	6.9E-06	1.1E-07	2.2E-05	6.9E+02	-3.4E+00	7.4E-12
49	176400	6	6.3E-06	9.9E-08	2.0E-05	7.1E+02	-3.5E+00	6.8E-12
50	180000	6	5.9E-06	9.3E-08	1.9E-05	7.2E+02	-3.6E+00	6.4E-12

**Table E.2:**      Results from experiment 4.2



### EXPERIMENT 4.3

Variable: Feed and Strip flow rates:  $0.333\text{cm}^3.\text{sec}^{-1}$

t (hr)	t (sec)	0.333	$\text{g.cm}^{-3}$	$\text{mol.cm}^{-3}$	mole ( $\text{cm}^3$ )	$V_1 \ln(C/C_0)$	$\ln(C/C_0)$	$J \text{ mol.cm}^{-2}.\text{sec}^{-1}$
0	0	222	2.2E-04	3.5E-06	7.0E-04	0.0E+00	0.0E+00	2.9E-10
1	3600	192	1.9E-04	3.0E-06	6.0E-04	2.9E+01	-1.5E-01	2.5E-10
2	7200	164	1.6E-04	2.6E-06	5.2E-04	6.1E+01	-3.0E-01	2.1E-10
3	10800	132	1.3E-04	2.1E-06	4.2E-04	1.0E+02	-5.2E-01	1.7E-10
4	14400	123	1.2E-04	1.9E-06	3.9E-04	1.2E+02	-5.9E-01	1.6E-10
5	18000	113	1.1E-04	1.8E-06	3.6E-04	1.4E+02	-6.8E-01	1.5E-10
6	21600	96	9.6E-05	1.5E-06	3.0E-04	1.7E+02	-8.4E-01	1.2E-10
24	86400	29	2.9E-05	4.6E-07	9.1E-05	4.1E+02	-2.0E+00	3.7E-11
25	90000	26	2.6E-05	4.1E-07	8.2E-05	4.3E+02	-2.1E+00	3.3E-11
26	93600	23	2.3E-05	3.6E-07	7.2E-05	4.5E+02	-2.3E+00	3.0E-11
27	97200	20	2.0E-05	3.1E-07	6.2E-05	4.8E+02	-2.4E+00	2.5E-11
28	100800	16	1.6E-05	2.5E-07	5.1E-05	5.2E+02	-2.6E+00	2.1E-11
29	104400	16	1.6E-05	2.5E-07	5.0E-05	5.3E+02	-2.6E+00	2.1E-11
30	108000	15	1.5E-05	2.4E-07	4.7E-05	5.4E+02	-2.7E+00	1.9E-11
48	172800	6	6.0E-06	9.4E-08	1.9E-05	7.2E+02	-3.6E+00	7.7E-12
49	176400	5	5.0E-06	7.9E-08	1.6E-05	7.6E+02	-3.8E+00	6.4E-12
50	180000	5	4.5E-06	7.1E-08	1.4E-05	7.8E+02	-3.9E+00	5.8E-12

**Table E.3: Results from experiment 4.3**

---

**EXPERIMENT 4.4**


---

Variable:      Feed and Strip flow rates:       $0.500\text{cm}^3.\text{sec}^{-1}$

t (hr)	t (sec)	0.500	$\text{g.cm}^{-3}$	$\text{mol.cm}^{-3}$	$\text{mole (cm}^3)$	$V_f \ln (C/C_0)$	$\ln (C/C_0)$	$J \text{ molcm}^{-2}\text{sec}^{-1}$
0	0	211	2.1E-04	3.3E-06	6.6E-04	0.0E+00	0.0E+00	2.9E-10
1	3600	189	1.9E-04	3.0E-06	5.9E-04	2.2E+01	-1.1E-01	2.6E-10
2	7200	161	1.6E-04	2.5E-06	5.1E-04	5.4E+01	-2.7E-01	2.2E-10
3	10800	130	1.3E-04	2.0E-06	4.1E-04	9.7E+01	-4.8E-01	1.8E-10
4	14400	120	1.2E-04	1.9E-06	3.8E-04	1.1E+02	-5.6E-01	1.7E-10
5	18000	114	1.1E-04	1.8E-06	3.6E-04	1.2E+02	-6.2E-01	1.6E-10
6	21600	92	9.2E-05	1.4E-06	2.9E-04	1.7E+02	-8.3E-01	1.3E-10
24	86400	22	2.2E-05	3.5E-07	6.9E-05	4.5E+02	-2.3E+00	3.0E-11
25	90000	21	2.1E-05	3.3E-07	6.6E-05	4.6E+02	-2.3E+00	2.9E-11
26	93600	20	2.0E-05	3.1E-07	6.2E-05	4.7E+02	-2.4E+00	2.7E-11
27	97200	18	1.8E-05	2.8E-07	5.6E-05	4.9E+02	-2.5E+00	2.5E-11
28	100800	15	1.5E-05	2.4E-07	4.7E-05	5.3E+02	-2.6E+00	2.1E-11
29	104400	14	1.4E-05	2.2E-07	4.3E-05	5.5E+02	-2.7E+00	1.9E-11
30	108000	12	1.2E-05	1.9E-07	3.8E-05	5.7E+02	-2.9E+00	1.7E-11
48	172800	4	4.2E-06	6.6E-08	1.3E-05	7.8E+02	-3.9E+00	5.8E-12
49	176400	4	4.0E-06	6.3E-08	1.3E-05	7.9E+02	-4.0E+00	5.5E-12
50	180000	4	3.8E-06	6.0E-08	1.2E-05	8.0E+02	-4.0E+00	5.2E-12

**Table E.4: Results from experiment 4.4**

---

**EXPERIMENT 4.5**


---

Variable: Feed and Strip flow rates:  $0.667\text{cm}^3.\text{sec}^{-1}$

t (hr)	t (sec)	0.667	$\text{g.cm}^{-3}$	$\text{mol.cm}^{-3}$	mole ( $\text{cm}^3$ )	$V_r \ln (C/C_0)$	$\ln (C/C_0)$	$J \text{ molem}^{-2}\text{sec}^{-1}$
0	0	218	2.2E-04	3.4E-06	6.9E-04	0.0E+00	0.0E+00	3.5E-10
1	3600	180	1.8E-04	2.8E-06	5.7E-04	3.8E+01	-1.9E-01	2.9E-10
2	7200	156	1.6E-04	2.5E-06	4.9E-04	6.7E+01	-3.3E-01	2.5E-10
3	10800	124	1.2E-04	2.0E-06	3.9E-04	1.1E+02	-5.6E-01	2.0E-10
4	14400	101	1.0E-04	1.6E-06	3.2E-04	1.5E+02	-7.7E-01	1.6E-10
5	18000	81	8.1E-05	1.3E-06	2.5E-04	2.0E+02	-9.9E-01	1.3E-10
6	21600	68	6.8E-05	1.1E-06	2.1E-04	2.3E+02	-1.2E+00	1.1E-10
24	86400	16	1.6E-05	2.5E-07	5.0E-05	5.2E+02	-2.6E+00	2.6E-11
25	90000	15	1.5E-05	2.4E-07	4.7E-05	5.4E+02	-2.7E+00	2.4E-11
26	93600	14	1.4E-05	2.2E-07	4.4E-05	5.5E+02	-2.7E+00	2.2E-11
27	97200	13	1.3E-05	2.1E-07	4.2E-05	5.6E+02	-2.8E+00	2.1E-11
28	100800	12	1.2E-05	1.9E-07	3.8E-05	5.8E+02	-2.9E+00	1.9E-11
29	104400	10	1.0E-05	1.6E-07	3.1E-05	6.2E+02	-3.1E+00	1.6E-11
30	108000	8	8.0E-06	1.3E-07	2.5E-05	6.6E+02	-3.3E+00	1.3E-11
48	172800	3	3.4E-06	5.4E-08	1.1E-05	8.3E+02	-4.2E+00	5.4E-12
49	176400	3	3.1E-06	4.9E-08	9.8E-06	8.5E+02	-4.3E+00	5.0E-12
50	180000	3	3.0E-06	4.7E-08	9.4E-06	8.6E+02	-4.3E+00	4.8E-12

**Table E.5: Results from experiment 4.5**

## EXPERIMENT 4.6

Variable:      Feed and Strip flow rates:       $0.833\text{cm}^3.\text{sec}^{-1}$

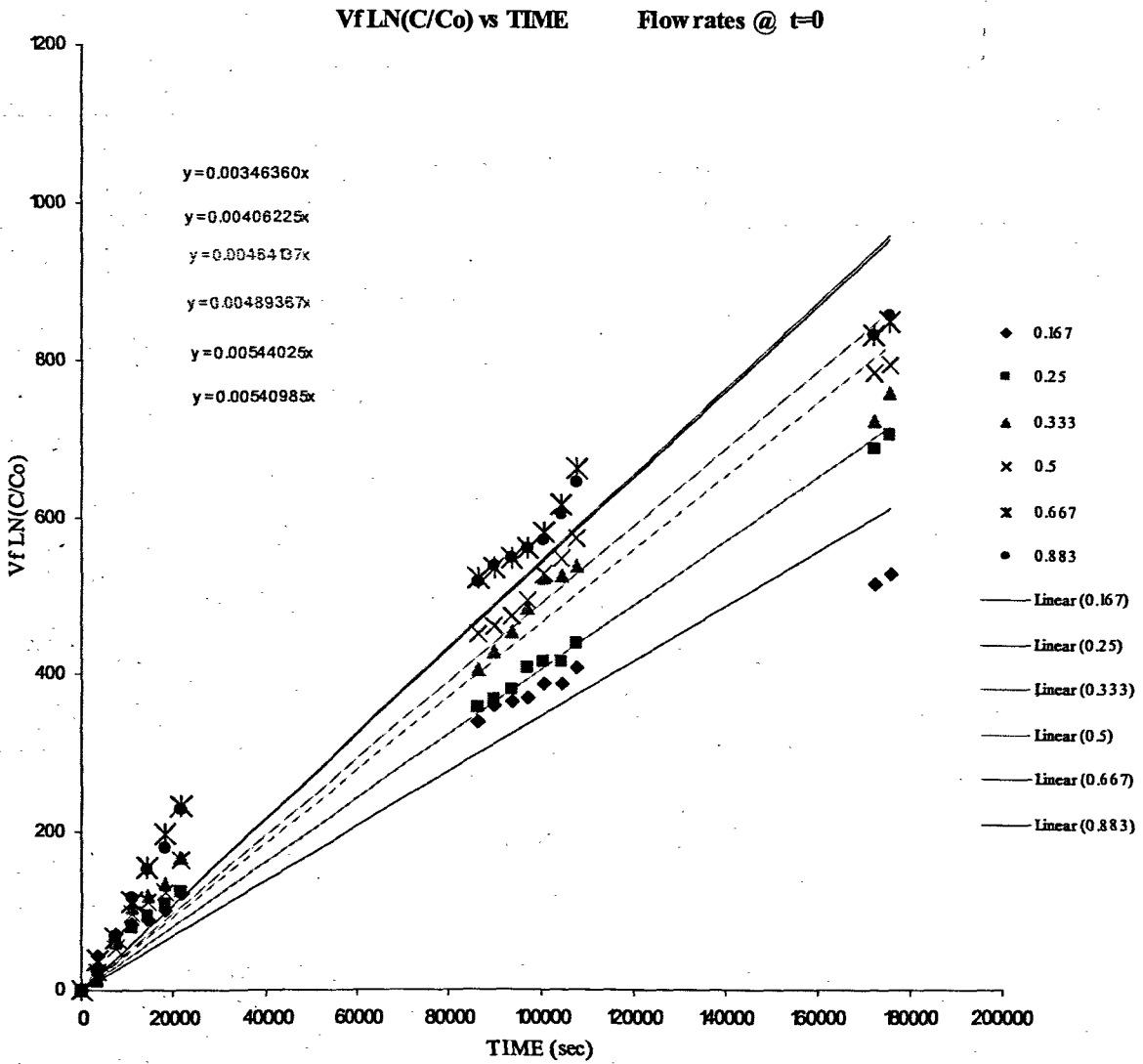
t (hr)	t (sec)	0.833	$\text{g.cm}^{-3}$	$\text{mol.cm}^{-3}$	mole ( $\text{cm}^3$ )	$V_t \ln (C/C_0)$	$\ln (C/C_0)$	$J \text{ molem}^{-2}\text{sec}^{-1}$
0	0	225	2.3E-04	3.5E-06	7.1E-04	0.0E+00	0.0E+00	3.6E-10
1	3600	200	2.0E-04	3.1E-06	6.3E-04	2.4E+01	-1.2E-01	3.2E-10
2	7200	160	1.6E-04	2.5E-06	5.0E-04	6.8E+01	-3.4E-01	2.5E-10
3	10800	126	1.3E-04	2.0E-06	4.0E-04	1.2E+02	-5.8E-01	2.0E-10
4	14400	105	1.1E-04	1.7E-06	3.3E-04	1.5E+02	-7.6E-01	1.7E-10
5	18000	92	9.2E-05	1.4E-06	2.9E-04	1.8E+02	-8.9E-01	1.5E-10
6	21600	72	7.2E-05	1.1E-06	2.3E-04	2.3E+02	-1.1E+00	1.1E-10
24	86400	17	1.7E-05	2.7E-07	5.4E-05	5.2E+02	-2.6E+00	2.7E-11
25	90000	15	1.5E-05	2.4E-07	4.8E-05	5.4E+02	-2.7E+00	2.4E-11
26	93600	15	1.5E-05	2.3E-07	4.6E-05	5.5E+02	-2.7E+00	2.3E-11
27	97200	14	1.4E-05	2.2E-07	4.3E-05	5.6E+02	-2.8E+00	2.2E-11
28	100800	13	1.3E-05	2.0E-07	4.1E-05	5.7E+02	-2.9E+00	2.1E-11
29	104400	11	1.1E-05	1.7E-07	3.5E-05	6.0E+02	-3.0E+00	1.7E-11
30	108000	9	9.0E-06	1.4E-07	2.8E-05	6.4E+02	-3.2E+00	1.4E-11
48	172800	4	3.5E-06	5.5E-08	1.1E-05	8.3E+02	-4.2E+00	5.5E-12
49	176400	3	3.1E-06	4.9E-08	9.8E-06	8.6E+02	-4.3E+00	4.9E-12
50	180000	3	3.0E-06	4.7E-08	9.4E-06	8.6E+02	-4.3E+00	4.8E-12

**Table E.6: Results from experiment 4.6**

## pH values at different feed flow rates

TIME (hrs)	TIME (sec)	0.167 cm <sup>3</sup> .sec <sup>-1</sup>	0.25 cm <sup>3</sup> .sec <sup>-1</sup>	0.333 cm <sup>3</sup> .sec <sup>-1</sup>	0.5 cm <sup>3</sup> .sec <sup>-1</sup>	0.667 cm <sup>3</sup> .sec <sup>-1</sup>	0.833 cm <sup>3</sup> .sec <sup>-1</sup>
0	0	3.41	3.44	3.42	3.45	3.10	3.36
1	3600	3.05	3.08	3.02	2.98	2.63	2.84
2	7200	2.76	2.89	2.81	2.83	2.51	2.71
3	10800	2.72	2.81	2.58	2.73	2.39	2.52
4	14400	2.65	2.76	2.45	2.63	2.28	2.32
5	18000	2.63	2.71	2.42	2.52	2.10	2.22
6	21600	2.51	2.64	2.29	2.42	2.01	2.18
24	86400	2.43	2.33	2.16	2.17	1.91	1.95
25	90000	2.42	2.33	2.15	2.16	1.92	1.94
26	93600	2.43	2.31	2.14	2.15	1.91	1.92
27	97200	2.41	2.29	2.15	2.16	1.90	1.89
28	100800	2.41	2.28	2.14	2.15	1.90	1.90
29	104400	2.42	2.27	2.13	2.15	1.89	1.91
30	108000	2.39	2.28	2.13	2.14	1.88	1.90
48	172800	1.74	1.82	1.93	1.86	1.82	1.78
49	176400	1.74	1.81	1.92	1.86	1.83	1.78
50	180000	1.74	1.82	1.93	1.86	1.81	1.78

Table E.7: Results from experiment 4.1 -4.6



**Figure E.1:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of feed flow rates on permeability. The results of experiment 4.1 – 4.6 shows on the graph how the gradient can be obtained ( $S_p$ ) by plotting  $V_f \ln(C/C_0)$  vs TIME

---

**APPENDIX F**

---

**DATA  
FROM  
BATCH  
EXPERIMENTS**

**AQUEOUS FEED CONCENTRATIONS (CuSO<sub>4</sub>) at  
pH = 2**

The effect different aqueous feed ( $\text{CuSO}_4$ ) concentrations have on the permeation of Copper (II) at the following experimental conditions.

**Experimental parameters:**

Volume of aqueous feed phase:	$200\text{cm}^3$
Volume of aqueous strip phase:	$200\text{cm}^3$
Membrane length:	19cm
Feed concentration ( $\text{CuSO}_4$ ):	100ppm – 400ppm
Strip concentration ( $\text{H}_2\text{SO}_4$ ):	25%
Extractant concentration (Lix 984):	20%
Feed flow rate ( $\text{CuSO}_4$ ):	$20\text{ml}\cdot\text{min}^{-1} / 0.33\text{cm}^3\cdot\text{sec}^{-1}$
Strip flow rate ( $\text{H}_2\text{SO}_4$ ):	$20\text{ml}\cdot\text{min}^{-1} / 0.33\text{cm}^3\cdot\text{sec}^{-1}$
Time:	50hours / 180 000sec
pH:	2



## EXPERIMENT 5.1

Variable: Feed concentration (CuSO<sub>4</sub>): 100 ppm,

t (hr)	t (sec)	[100]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>r</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	92	9.2E-05	1.4E-06	2.9E-04	0.0E+00	0.0E+00	1.8E-10
1	3600	78	7.8E-05	1.2E-06	2.5E-04	3.3E+01	-1.7E-01	1.5E-10
2	7200	74	7.4E-05	1.2E-06	2.3E-04	4.4E+01	-2.2E-01	1.5E-10
3	10800	60	6.0E-05	9.4E-07	1.9E-04	8.5E+01	-4.3E-01	1.2E-10
4	14400	57	5.7E-05	9.0E-07	1.8E-04	9.6E+01	-4.8E-01	1.1E-10
5	18000	44	4.4E-05	6.9E-07	1.4E-04	1.5E+02	-7.4E-01	8.7E-11
6	21600	34	3.4E-05	5.4E-07	1.1E-04	2.0E+02	-1.0E+00	6.7E-11
24	86400	4	4.3E-06	6.8E-08	1.4E-05	6.1E+02	-3.1E+00	8.5E-12
25	90000	4	3.8E-06	6.0E-08	1.2E-05	6.4E+02	-3.2E+00	7.5E-12
26	93600	3	3.4E-06	5.4E-08	1.1E-05	6.6E+02	-3.3E+00	6.7E-12
27	97200	3	3.4E-06	5.4E-08	1.1E-05	6.6E+02	-3.3E+00	6.7E-12
28	100800	3	2.9E-06	4.6E-08	9.1E-06	6.9E+02	-3.5E+00	5.7E-12
29	104400	3	2.6E-06	4.1E-08	8.2E-06	7.1E+02	-3.6E+00	5.1E-12
30	108000	1	1.3E-06	2.0E-08	4.1E-06	8.5E+02	-4.3E+00	2.6E-12
48	172800	1	1.3E-06	2.0E-08	4.1E-06	8.5E+02	-4.3E+00	2.6E-12
49	176400	1	1.3E-06	2.0E-08	4.1E-06	8.5E+02	-4.3E+00	2.6E-12
50	180000	1	1.3E-06	2.0E-08	4.1E-06	8.5E+02	-4.3E+00	2.6E-12

**Table F.1: Results from experiment 5.1**

## EXPERIMENT 5.2

Variable: Feed concentration (CuSO<sub>4</sub>): 150 ppm,

t (hr)	t (sec)	[150]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>t</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	148	1.5E-04	2.3E-06	4.7E-04	0.0E+00	0.0E+00	2.9E-10
1	3600	126	1.3E-04	2.0E-06	4.0E-04	3.2E+01	-1.6E-01	2.4E-10
2	7200	114	1.1E-04	1.8E-06	3.6E-04	5.2E+01	-2.6E-01	2.2E-10
3	10800	98	9.8E-05	1.5E-06	3.1E-04	8.2E+01	-4.1E-01	1.9E-10
4	14400	88	8.8E-05	1.4E-06	2.8E-04	1.0E+02	-5.2E-01	1.7E-10
5	18000	72	7.2E-05	1.1E-06	2.3E-04	1.4E+02	-7.2E-01	1.4E-10
6	21600	68	6.8E-05	1.1E-06	2.1E-04	1.6E+02	-7.8E-01	1.3E-10
24	86400	6	6.2E-06	9.8E-08	2.0E-05	6.3E+02	-3.2E+00	1.2E-11
25	90000	6	5.9E-06	9.3E-08	1.9E-05	6.4E+02	-3.2E+00	1.1E-11
26	93600	5	5.4E-06	8.5E-08	1.7E-05	6.6E+02	-3.3E+00	1.0E-11
27	97200	5	5.2E-06	8.2E-08	1.6E-05	6.7E+02	-3.3E+00	1.0E-11
28	100800	5	4.8E-06	7.6E-08	1.5E-05	6.9E+02	-3.4E+00	9.3E-12
29	104400	4	4.3E-06	6.8E-08	1.4E-05	7.1E+02	-3.5E+00	8.4E-12
30	108000	4	3.9E-06	6.1E-08	1.2E-05	7.3E+02	-3.6E+00	7.6E-12
48	172800	2	2.0E-06	3.1E-08	6.3E-06	8.6E+02	-4.3E+00	3.9E-12
49	176400	2	1.9E-06	3.0E-08	6.0E-06	8.7E+02	-4.4E+00	3.7E-12
50	180000	2	2.0E-06	3.1E-08	6.3E-06	8.6E+02	-4.3E+00	3.9E-12

**Table F.2: Results from experiment 5.2**

---

**EXPERIMENT 5.3**


---

Variable: Feed concentration (CuSO<sub>4</sub>): 200 ppm,

t (hr)	t (sec)	[200]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>r</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	180	1.8E-04	2.8E-06	5.7E-04	0.0E+00	0.0E+00	3.2E-10
1	3600	150	1.5E-04	2.4E-06	4.7E-04	3.6E+01	-1.8E-01	2.7E-10
2	7200	130	1.3E-04	2.0E-06	4.1E-04	6.5E+01	-3.3E-01	2.3E-10
3	10800	120	1.2E-04	1.9E-06	3.8E-04	8.1E+01	-4.1E-01	2.1E-10
4	14400	112	1.1E-04	1.8E-06	3.5E-04	9.5E+01	-4.7E-01	2.0E-10
5	18000	101	1.0E-04	1.6E-06	3.2E-04	1.2E+02	-5.8E-01	1.8E-10
6	21600	86	8.6E-05	1.4E-06	2.7E-04	1.5E+02	-7.4E-01	1.5E-10
24	86400	9	8.9E-06	1.4E-07	2.8E-05	6.0E+02	-3.0E+00	1.6E-11
25	90000	9	8.7E-06	1.4E-07	2.7E-05	6.1E+02	-3.0E+00	1.5E-11
26	93600	8	8.3E-06	1.3E-07	2.6E-05	6.2E+02	-3.1E+00	1.5E-11
27	97200	8	8.2E-06	1.3E-07	2.6E-05	6.2E+02	-3.1E+00	1.4E-11
28	100800	8	8.1E-06	1.3E-07	2.5E-05	6.2E+02	-3.1E+00	1.4E-11
29	104400	8	8.0E-06	1.3E-07	2.5E-05	6.2E+02	-3.1E+00	1.4E-11
30	108000	7	7.4E-06	1.2E-07	2.3E-05	6.4E+02	-3.2E+00	1.3E-11
48	172800	4	3.9E-06	6.1E-08	1.2E-05	7.7E+02	-3.8E+00	6.9E-12
49	176400	3	3.3E-06	5.2E-08	1.0E-05	8.0E+02	-4.0E+00	5.8E-12
50	180000	3	3.4E-06	5.4E-08	1.1E-05	7.9E+02	-4.0E+00	6.0E-12

**Table F.3: Results from experiment 5.3**

---

**EXPERIMENT 5.4**


---

Variable: Feed concentration (CuSO<sub>4</sub>): 250 ppm,

t (hr)	t (sec)	[250]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>r</sub> ln (C/C <sub>o</sub> )	ln (C/C <sub>o</sub> )	J molem <sup>-2</sup> sec
0	0	220	2.2E-04	3.5E-06	6.9E-04	0.0E+00	0.0E+00	3.7E-10
1	3600	180	1.8E-04	2.8E-06	5.7E-04	4.0E+01	-2.0E-01	3.0E-10
2	7200	160	1.6E-04	2.5E-06	5.0E-04	6.4E+01	-3.2E-01	2.7E-10
3	10800	130	1.3E-04	2.0E-06	4.1E-04	1.1E+02	-5.3E-01	2.2E-10
4	14400	118	1.2E-04	1.9E-06	3.7E-04	1.2E+02	-6.2E-01	2.0E-10
5	18000	107	1.1E-04	1.7E-06	3.4E-04	1.4E+02	-7.2E-01	1.8E-10
6	21600	98	9.8E-05	1.5E-06	3.1E-04	1.6E+02	-8.1E-01	1.6E-10
24	86400	11	1.1E-05	1.8E-07	3.6E-05	5.9E+02	-3.0E+00	1.9E-11
25	90000	11	1.1E-05	1.7E-07	3.5E-05	6.0E+02	-3.0E+00	1.9E-11
26	93600	10	1.0E-05	1.6E-07	3.1E-05	6.2E+02	-3.1E+00	1.7E-11
27	97200	10	9.8E-06	1.5E-07	3.1E-05	6.2E+02	-3.1E+00	1.6E-11
28	100800	9	9.0E-06	1.4E-07	2.8E-05	6.4E+02	-3.2E+00	1.5E-11
29	104400	9	8.6E-06	1.4E-07	2.7E-05	6.5E+02	-3.2E+00	1.4E-11
30	108000	8	8.0E-06	1.3E-07	2.5E-05	6.6E+02	-3.3E+00	1.3E-11
48	172800	5	5.4E-06	8.5E-08	1.7E-05	7.4E+02	-3.7E+00	9.0E-12
49	176400	5	5.3E-06	8.3E-08	1.7E-05	7.5E+02	-3.7E+00	8.9E-12
50	180000	5	5.1E-06	8.0E-08	1.6E-05	7.5E+02	-3.8E+00	8.5E-12

**Table F.4: Results from experiment 5.4**

---

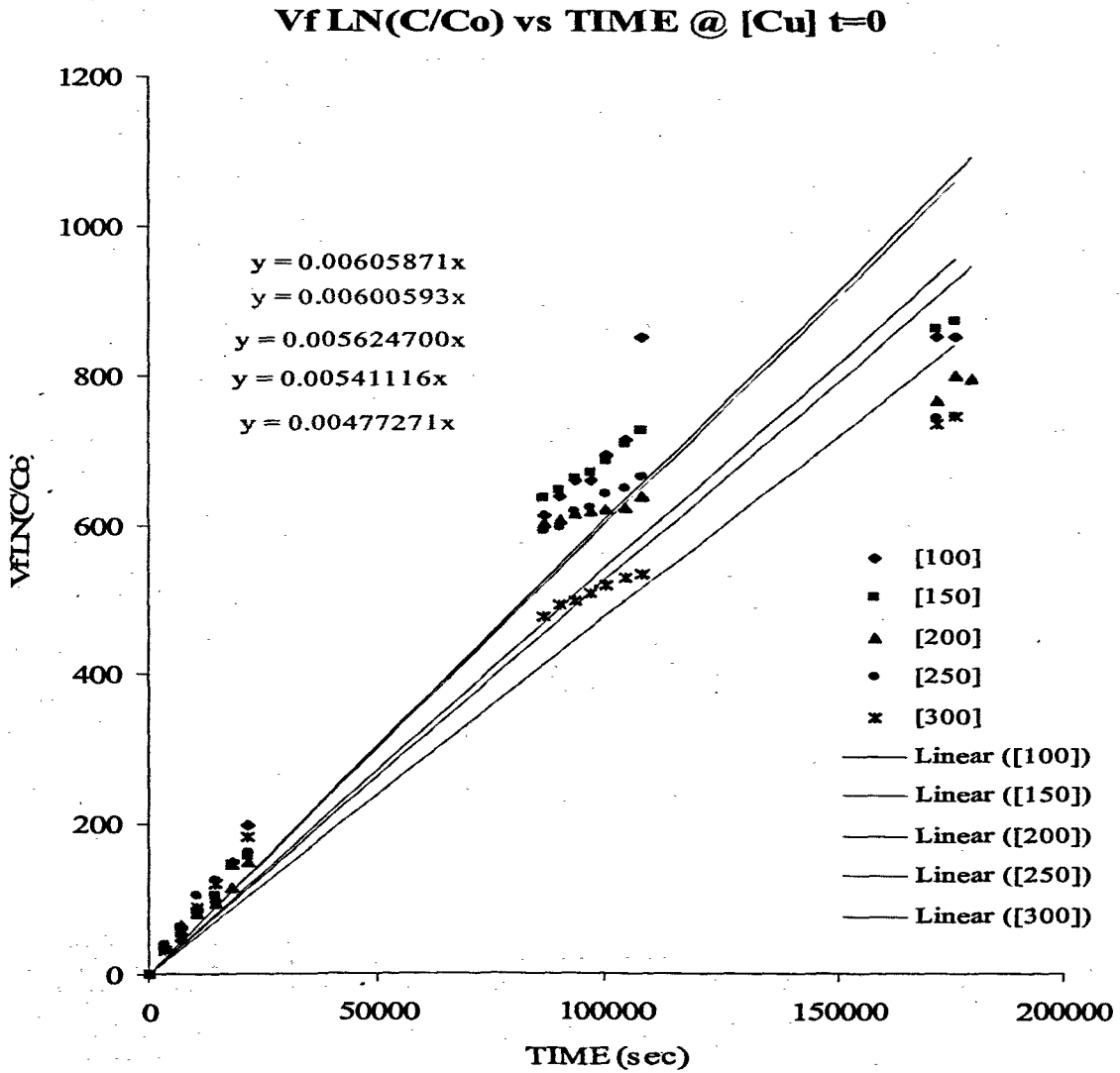
**EXPERIMENT 5.5**


---

Variable: Feed concentration (CuSO<sub>4</sub>): 300 ppm,

t (hr)	t (sec)	[300]	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>r</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	280	2.8E-04	4.4E-06	8.8E-04	0.0E+00	0.0E+00	3.9E-10
1	3600	240	2.4E-04	3.8E-06	7.6E-04	3.1E+01	-1.5E-01	3.4E-10
2	7200	209	2.1E-04	3.3E-06	6.6E-04	5.8E+01	-2.9E-01	2.9E-10
3	10800	179	1.8E-04	2.8E-06	5.6E-04	8.9E+01	-4.5E-01	2.5E-10
4	14400	153	1.5E-04	2.4E-06	4.8E-04	1.2E+02	-6.0E-01	2.2E-10
5	18000	135	1.4E-04	2.1E-06	4.2E-04	1.5E+02	-7.3E-01	1.9E-10
6	21600	113	1.1E-04	1.8E-06	3.6E-04	1.8E+02	-9.1E-01	1.6E-10
24	86400	26	2.6E-05	4.1E-07	8.2E-05	4.8E+02	-2.4E+00	3.7E-11
25	90000	24	2.4E-05	3.8E-07	7.6E-05	4.9E+02	-2.5E+00	3.4E-11
26	93600	23	2.3E-05	3.7E-07	7.4E-05	5.0E+02	-2.5E+00	3.3E-11
27	97200	22	2.2E-05	3.5E-07	6.9E-05	5.1E+02	-2.5E+00	3.1E-11
28	100800	21	2.1E-05	3.3E-07	6.6E-05	5.2E+02	-2.6E+00	3.0E-11
29	104400	20	2.0E-05	3.1E-07	6.3E-05	5.3E+02	-2.6E+00	2.8E-11
30	108000	20	2.0E-05	3.1E-07	6.1E-05	5.3E+02	-2.7E+00	2.7E-11
48	172800	7	7.1E-06	1.1E-07	2.2E-05	7.3E+02	-3.7E+00	1.0E-11
49	176400	7	6.8E-06	1.1E-07	2.1E-05	7.4E+02	-3.7E+00	9.6E-12
50	180000	7	6.5E-06	1.0E-07	2.0E-05	7.5E+02	-3.8E+00	9.1E-12

**Table F.5: Results from experiment 5.5**



**Figure F.1:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of constant pH on the permeability. The results of experiment 5.1 – 5.5 shows on the graph how the gradient can be obtained ( $S_p$ ) by plotting  $V_f \ln(C/C_0)$  vs TIME

---

**APPENDIX G**

---

**DATA  
FROM  
BATCH  
EXPERIMENTS**

**AQUEOUS FEED CONCENTRATION ( $\text{CuSO}_4$ ) at  
various feed pH**

The effect different pH values have on the permeation of Copper (II) at the following experimental conditions.

**Experimental parameters:**

Volume of aqueous feed phase:	200cm <sup>3</sup>
Volume of aqueous strip phase:	200cm <sup>3</sup>
Membrane length:	19cm
Feed concentration (CuSO <sub>4</sub> ):	100ppm
Strip concentration (H <sub>2</sub> SO <sub>4</sub> ):	25%
Extractant concentration (Lix 984):	20%
Feed flow rate (CuSO <sub>4</sub> ):	20ml.min <sup>-1</sup> / 0.33cm <sup>3</sup> .sec <sup>-1</sup>
Strip flow rate (H <sub>2</sub> SO <sub>4</sub> ):	20ml.min <sup>-1</sup> / 0.33cm <sup>3</sup> .sec <sup>-1</sup>
Time:	50hours / 180 000sec
pH:	1, 1.5, 2



---

**EXPERIMENT 6.1**


---

Variable:     pH : 1

t (hr)	t (sec)	I	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>t</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	200	2.0E-04	3.1E-06	6.3E-04	0.0E+00	0.0E+00	8.3E-11
1	3600	180	1.8E-04	2.8E-06	5.7E-04	2.1E+01	-1.1E-01	7.5E-11
2	7200	170	1.7E-04	2.7E-06	5.4E-04	3.3E+01	-1.6E-01	7.1E-11
3	10800	160	1.6E-04	2.5E-06	5.0E-04	4.5E+01	-2.2E-01	6.6E-11
4	14400	150	1.5E-04	2.4E-06	4.7E-04	5.8E+01	-2.9E-01	6.2E-11
5	18000	135	1.4E-04	2.1E-06	4.2E-04	7.9E+01	-3.9E-01	5.6E-11
6	21600	127	1.3E-04	2.0E-06	4.0E-04	9.1E+01	-4.5E-01	5.3E-11
24	86400	98	9.8E-05	1.5E-06	3.1E-04	1.4E+02	-7.1E-01	4.1E-11
25	90000	96	9.6E-05	1.5E-06	3.0E-04	1.5E+02	-7.3E-01	4.0E-11
26	93600	93	9.3E-05	1.5E-06	2.9E-04	1.5E+02	-7.7E-01	3.9E-11
27	97200	90	9.0E-05	1.4E-06	2.8E-04	1.6E+02	-8.0E-01	3.7E-11
28	100800	86	8.6E-05	1.4E-06	2.7E-04	1.7E+02	-8.4E-01	3.6E-11
29	104400	81	8.1E-05	1.3E-06	2.5E-04	1.8E+02	-9.0E-01	3.4E-11
30	108000	79	7.9E-05	1.2E-06	2.5E-04	1.9E+02	-9.3E-01	3.3E-11
48	172800	45	4.5E-05	7.1E-07	1.4E-04	3.0E+02	-1.5E+00	1.9E-11
49	176400	44	4.4E-05	6.9E-07	1.4E-04	3.0E+02	-1.5E+00	1.8E-11
50	180000	43	4.3E-05	6.8E-07	1.4E-04	3.1E+02	-1.5E+00	1.8E-11

**Table G.1: Results from experiment 6.1**

## EXPERIMENT 6.2

Variable:     pH : 1.5

t (hr)	t (sec)	1.5	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>r</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	202	2.0E-04	3.2E-06	6.4E-04	0.0E+00	0.0E+00	1.4E-10
1	3600	170	1.7E-04	2.7E-06	5.4E-04	3.4E+01	-1.7E-01	1.1E-10
2	7200	150	1.5E-04	2.4E-06	4.7E-04	6.0E+01	-3.0E-01	1.0E-10
3	10800	130	1.3E-04	2.0E-06	4.1E-04	8.8E+01	-4.4E-01	8.7E-11
4	14400	118	1.2E-04	1.9E-06	3.7E-04	1.1E+02	-5.4E-01	7.9E-11
5	18000	112	1.1E-04	1.8E-06	3.5E-04	1.2E+02	-5.9E-01	7.5E-11
6	21600	103	1.0E-04	1.6E-06	3.2E-04	1.3E+02	-6.7E-01	6.9E-11
24	86400	56	5.6E-05	8.8E-07	1.8E-04	2.6E+02	-1.3E+00	3.8E-11
25	90000	52	5.2E-05	8.2E-07	1.6E-04	2.7E+02	-1.4E+00	3.5E-11
26	93600	50	5.0E-05	7.9E-07	1.6E-04	2.8E+02	-1.4E+00	3.4E-11
27	97200	49	4.9E-05	7.7E-07	1.5E-04	2.8E+02	-1.4E+00	3.3E-11
28	100800	47	4.7E-05	7.4E-07	1.5E-04	2.9E+02	-1.5E+00	3.2E-11
29	104400	46	4.6E-05	7.2E-07	1.4E-04	3.0E+02	-1.5E+00	3.1E-11
30	108000	44	4.4E-05	6.9E-07	1.4E-04	3.0E+02	-1.5E+00	3.0E-11
48	172800	28	2.8E-05	4.5E-07	8.9E-05	3.9E+02	-2.0E+00	1.9E-11
49	176400	28	2.8E-05	4.4E-07	8.8E-05	3.9E+02	-2.0E+00	1.9E-11
50	180000	28	2.8E-05	4.4E-07	8.7E-05	4.0E+02	-2.0E+00	1.9E-11

**Table G.2: Results from experiment 6.2**

---

**EXPERIMENT 6.3**


---

Variable:     pH : 2

t (hr)	t (sec)	Z	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>r</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	185	1.9E-04	2.9E-06	5.8E-04	0.0E+00	0.0E+00	3.0E-10
1	3600	150	1.5E-04	2.4E-06	4.7E-04	4.2E+01	-2.1E-01	2.4E-10
2	7200	130	1.3E-04	2.0E-06	4.1E-04	7.1E+01	-3.5E-01	2.1E-10
3	10800	120	1.2E-04	1.9E-06	3.8E-04	8.7E+01	-4.3E-01	2.0E-10
4	14400	112	1.1E-04	1.8E-06	3.5E-04	1.0E+02	-5.0E-01	1.8E-10
5	18000	98	9.8E-05	1.5E-06	3.1E-04	1.3E+02	-6.4E-01	1.6E-10
6	21600	82	8.2E-05	1.3E-06	2.6E-04	1.6E+02	-8.1E-01	1.3E-10
24	86400	9	9.2E-06	1.4E-07	2.9E-05	6.0E+02	-3.0E+00	1.5E-11
25	90000	9	8.7E-06	1.4E-07	2.7E-05	6.1E+02	-3.1E+00	1.4E-11
26	93600	8	8.3E-06	1.3E-07	2.6E-05	6.2E+02	-3.1E+00	1.4E-11
27	97200	8	8.2E-06	1.3E-07	2.6E-05	6.2E+02	-3.1E+00	1.3E-11
28	100800	8	7.9E-06	1.2E-07	2.5E-05	6.3E+02	-3.2E+00	1.3E-11
29	104400	7	7.3E-06	1.1E-07	2.3E-05	6.5E+02	-3.2E+00	1.2E-11
30	108000	7	7.0E-06	1.1E-07	2.2E-05	6.5E+02	-3.3E+00	1.1E-11
48	172800	4	3.7E-06	5.8E-08	1.2E-05	7.8E+02	-3.9E+00	6.0E-12
49	176400	3	3.2E-06	5.0E-08	1.0E-05	8.1E+02	-4.1E+00	5.2E-12
50	180000	3	3.4E-06	5.4E-08	1.1E-05	8.0E+02	-4.0E+00	5.5E-12

**Table G.3: Results from experiment 6.3**

---

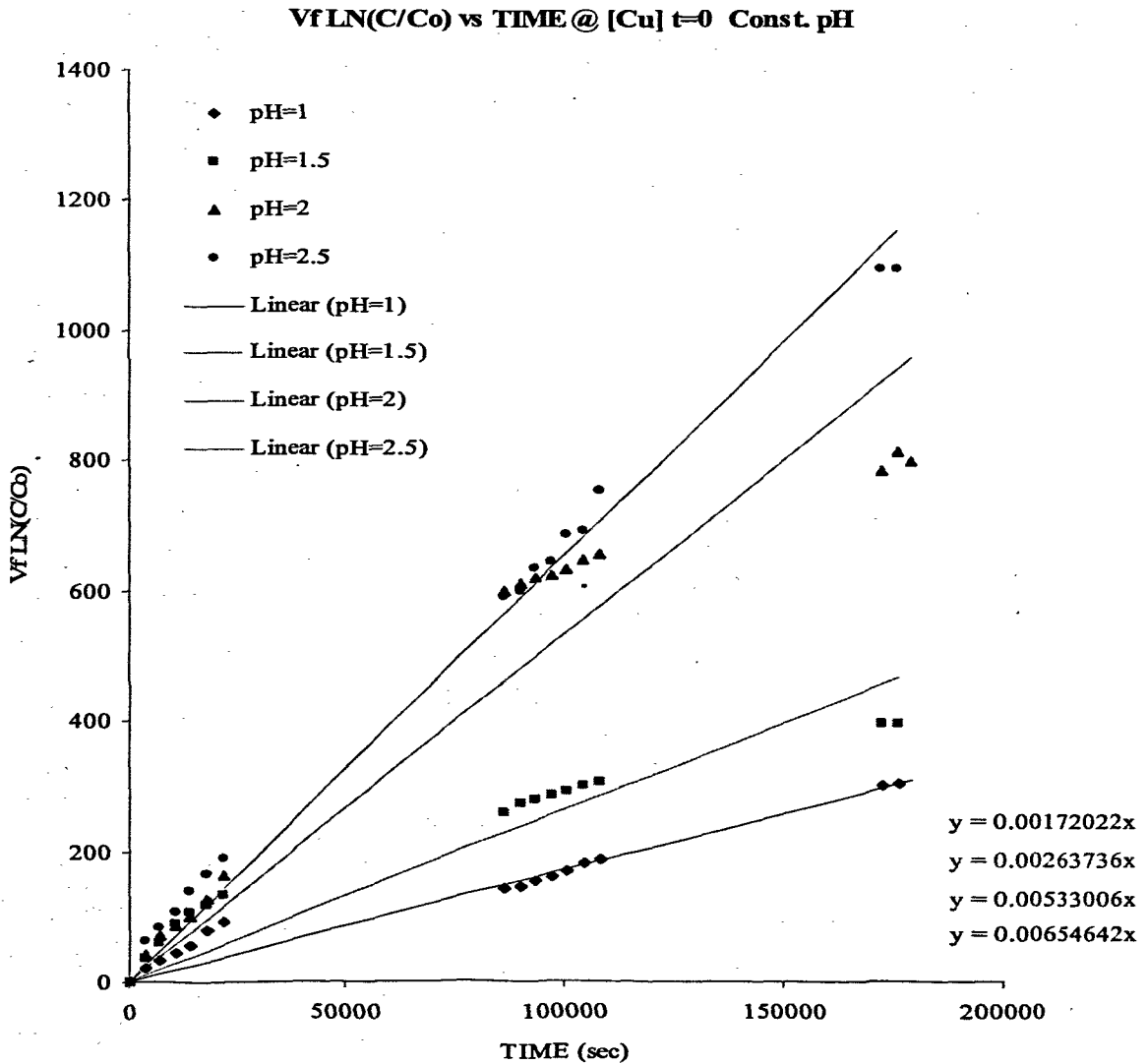
**EXPERIMENT 6.4**


---

Variable:     pH : 2.5

t (hr)	t (sec)	2.5	g.cm <sup>-3</sup>	mol.cm <sup>-3</sup>	mole (cm <sup>3</sup> )	V <sub>r</sub> ln (C/C <sub>0</sub> )	ln (C/C <sub>0</sub> )	J molcm <sup>-2</sup> sec <sup>-1</sup>
0	0	190	1.9E-04	3.0E-06	6.0E-04	0.0E+00	0.0E+00	4.2E-10
1	3600	140	1.4E-04	2.2E-06	4.4E-04	6.1E+01	-3.1E-01	3.1E-10
2	7200	126	1.3E-04	2.0E-06	4.0E-04	8.2E+01	-4.1E-01	2.8E-10
3	10800	112	1.1E-04	1.8E-06	3.5E-04	1.1E+02	-5.3E-01	2.5E-10
4	14400	94	9.4E-05	1.5E-06	3.0E-04	1.4E+02	-7.0E-01	2.1E-10
5	18000	83	8.3E-05	1.3E-06	2.6E-04	1.7E+02	-8.3E-01	1.8E-10
6	21600	74	7.4E-05	1.2E-06	2.3E-04	1.9E+02	-9.4E-01	1.6E-10
24	86400	10	1.0E-05	1.6E-07	3.1E-05	5.9E+02	-2.9E+00	2.2E-11
25	90000	10	9.5E-06	1.5E-07	3.0E-05	6.0E+02	-3.0E+00	2.1E-11
26	93600	8	8.0E-06	1.3E-07	2.5E-05	6.3E+02	-3.2E+00	1.8E-11
27	97200	8	7.6E-06	1.2E-07	2.4E-05	6.4E+02	-3.2E+00	1.7E-11
28	100800	6	6.2E-06	9.8E-08	2.0E-05	6.8E+02	-3.4E+00	1.4E-11
29	104400	6	6.0E-06	9.4E-08	1.9E-05	6.9E+02	-3.5E+00	1.3E-11
30	108000	4	4.4E-06	6.9E-08	1.4E-05	7.5E+02	-3.8E+00	9.7E-12
48	172800	1	8.0E-07	1.3E-08	2.5E-06	1.1E+03	-5.5E+00	1.8E-12
49	176400	1	8.0E-07	1.3E-08	2.5E-06	1.1E+03	-5.5E+00	1.8E-12
50	180000	1	7.8E-07	1.2E-08	2.5E-06	1.1E+03	-5.5E+00	1.7E-12

**Table G.4: Results from experiment 6.4**



**Figure G.1:** Experimental courses of Cu (II) concentration in the feed reservoir. The effect of varying pH on the permeability. The results of experiment 6.1 – 3.4 shows on the graph how the gradient can be obtained ( $S_p$ ) by plotting  $V_f \ln(C/C_0)$  vs TIME

---

**APPENDIX H**

---

**RAW DATA  
FROM  
BATCH  
EXPERIMENTS**

### H.1. Copper permeation at different Copper feed concentrations in (ppm) $\text{mg.dm}^{-3}$ :

FEED

TIME (hrs)	TIME (sec)	100	150	200	250	300	350	400
0	0	98	135	203	242	308	320	380
1	3600	77	96	156	190	226	290	330
2	7200	54	75	121	150	208	280	310
3	10800	39	64	105	140	181	250	270
4	14400	32	48	92	120	156	230	240
5	18000	25	43	74	110	141	210	230
6	21600	21	41	68	100	137	190	220
24	86400	3	5	8	22	21	65	48
25	90000	2	4	7	18	18	54	43
26	93600	2	4	6	18	17	47	38
27	97200	2	4	6	18	14	40	34
28	100800	2	4	6	16	13	35	31
29	104400	2	3	5	14	12	29	26
30	108000	2	3	5	13	11	27	23
48	172800	1	2	2	6	5	10	4
49	176400	1	2	3	6	4	7	3
50	180000	1	2	2	5	4	6	3

Table H.1.1: Raw data from Experiments 1.1 – 1.7 in the FEED side.

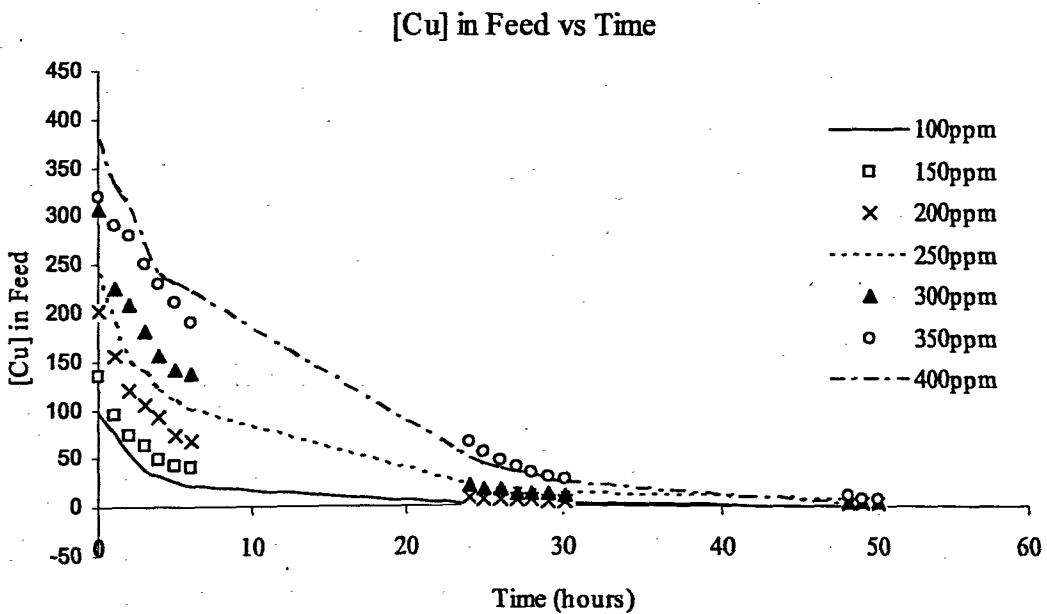


Figure H.1.1: Experimental courses of Cu (II) concentration in the feed reservoir at different feed concentrations.

## STRIP

TIME (hrs)	TIME (sec)	100	150	200	250	300	350	400
0	0	0	0	0	0	0	0	0
1	3600	2	2	4	1	1	4	3
2	7200	4	4	9	3	2	9	7
3	10800	6	5	26	7	10	15	12
4	14400	8	10	29	15	15	24	23
5	18000	13	19	35	24	26	29	25
6	21600	15	22	58	31	30	36	35
24	86400	67	103	140	165	179	211	231
25	90000	68	100	140	169	182	218	240
26	93600	71	105	140	173	184	219	236
27	97200	70	107	150	177	190	228	244
28	100800	71	108	150	189	187	229	249
29	104400	72	107	150	193	190	233	251
30	108000	73	108	160	194	199	235	255
48	172800	75	116	184	226	240	284	325
49	176400	75	117	185	226	250	285	325
50	180000	75	117	185	226	250	286	327

Table H.1.2: Raw data from Experiments 1.1 – 1.7 in the STRIP side.

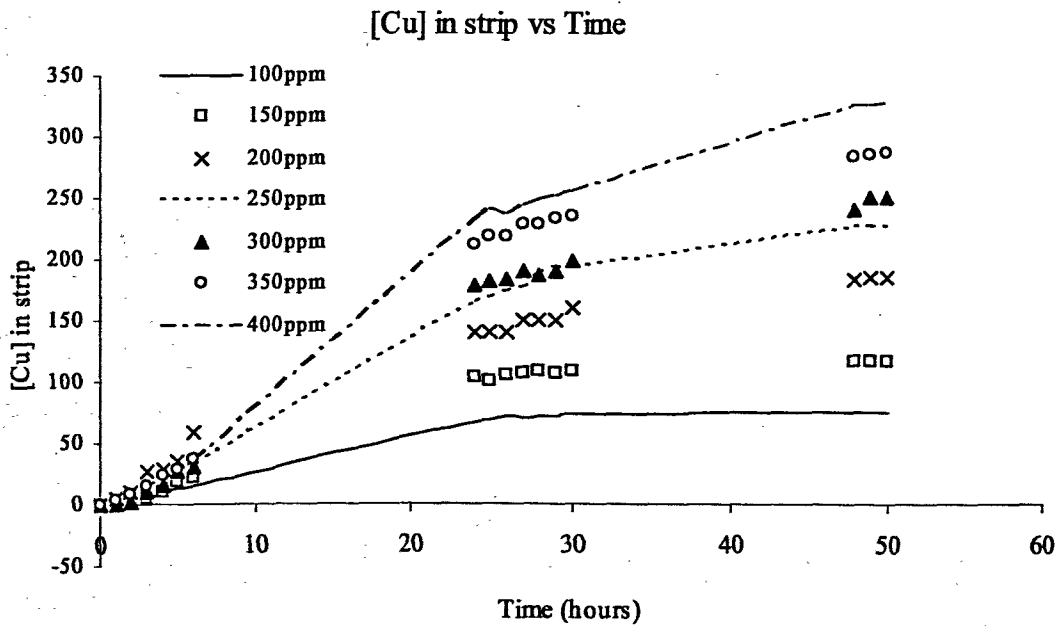


Figure H.1.2: Experimental courses of Cu (II) concentration in the strip reservoir at different feed concentrations.



## H.2. Copper permeation at different Sulphuric acid concentrations in (ppm) $\text{mg.dm}^{-3}$ :

FEED

TIME (hrs)	TIME (sec)	5%	10%	15%	20%	25%	30%
0	0	210	204	206	233	225	231
1	3600	170	192	185	220	203	215
2	7200	160	132	158	191	178	190
3	10800	150	116	142	166	159	161
4	14400	140	113	117	159	144	141
5	18000	130	102	110	139	137	134
6	21600	130	89	92	130	122	124
24	86400	67	44	18	42	15	24
25	90000	65	41	13	40	12	19
26	93600	65	41	12	35	13	15
27	97200	60	40	12	35	11	13
28	100800	57	37	11	31	10	12
29	104400	56	35	9	28	10	10
30	108000	52	34	8	25	10	9
48	172800	27	12	6	6	3	5
49	176400	26	7	5	4	3	4
50	180000	25	6	4	2	3	3

Table H.2.1: Raw data from Experiments 2.1 – 2.6 in the FEED side.

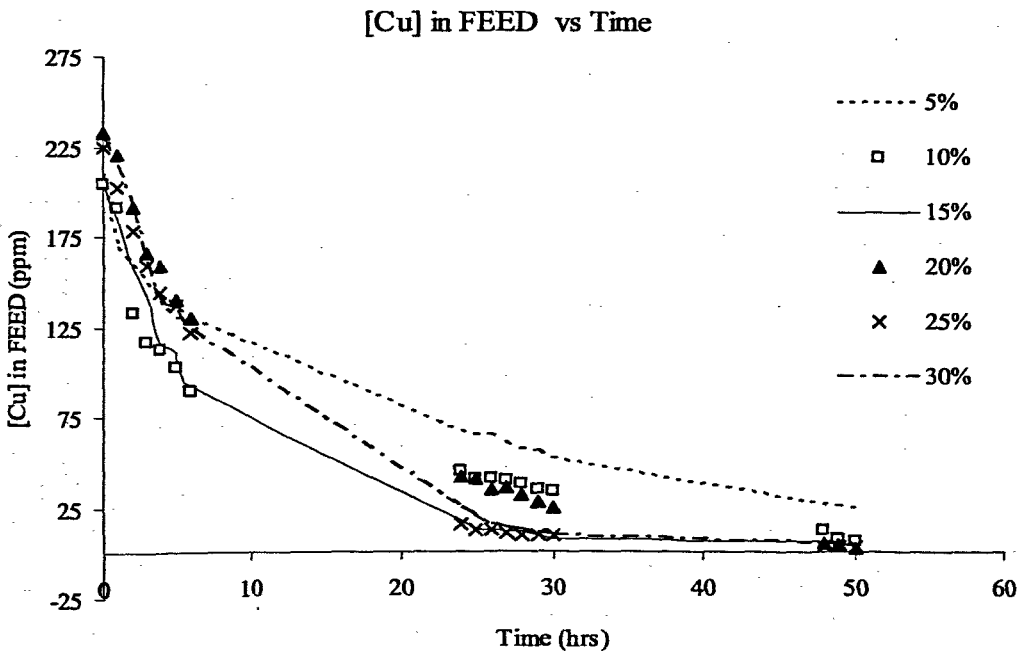


Figure H.2.1: Experimental courses of Cu (II) concentration in the feed reservoir at different strip concentrations.

## STRIP

TIME (hrs)	TIME (sec)	5%	10%	15%	20%	25%	30%
0	0	0	0	0	0	0	0
1	3600	2	8	4	3	3	1
2	7200	3	9	6	3	7	4
3	10800	4	13	10	6	14	6
4	14400	6	16	14	13	23	11
5	18000	11	17	19	24	35	18
6	21600	15	18	26	41	47	23
24	86400	91	98	110	144	176	181
25	90000	94	101	114	149	179	187
26	93600	96	105	121	153	183	188
27	97200	99	104	128	157	185	192
28	100800	100	111	132	161	185	197
29	104400	100	114	138	166	185	199
30	108000	110	116	144	167	185	204
48	172800	150	143	168	185	199	214
49	176400	150	144	171	188	200	215
50	180000	150	146	171	187	202	215

Table H.2.2: Raw data from Experiments 2.1 – 2.6 in the STRIP side.

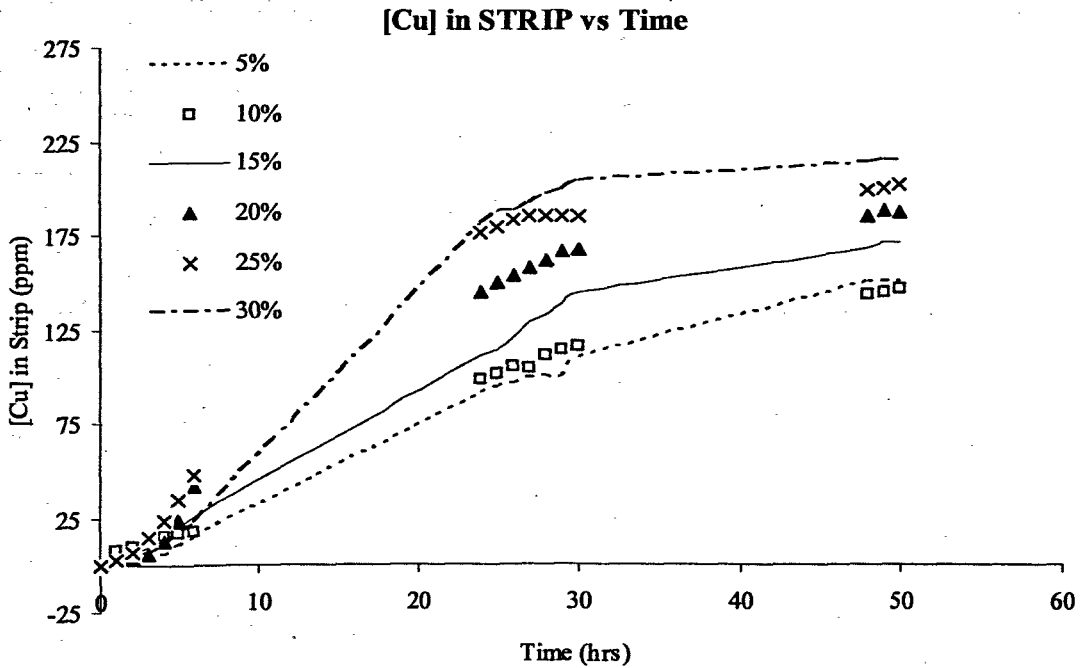


Figure H.2.2: Experimental courses of Cu (II) concentration in the strip reservoir at different strip concentrations.

The effect of  $\text{CuSO}_4$  concentration on the permeability at 100, 200, 300 and 400ppm concentrations:

TIME (hrs)	TIME (sec)	100	%	200	%	300	%	400	%
0	0	98	100	203	100	308	100	380	100
1	3600	77	79	156	77	226	73	330	87
2	7200	54	55	121	60	208	68	310	82
3	10800	39	40	105	52	181	59	270	71
4	14400	32	33	92	45	156	51	240	63
5	18000	25	26	74	36	141	46	230	61
6	21600	21	21	68	33	137	44	220	58
24	86400	3	3	8	4	21	7	48	13
25	90000	2	2	7	3	18	6	43	11
26	93600	2	2	6	3	17	6	38	10
27	97200	2	2	6	3	14	5	34	9
28	100800	2	2	6	3	13	4	31	8
29	104400	2	2	5	2	12	4	26	7
30	108000	2	2	5	2	11	4	23	6
48	172800	1	1	2	1	5	2	4	1
49	176400	1	1	3	1	4	1	3	1
50	180000	1	1	2	1	4	1	3	1

**Table H.2.3: Raw data from Experiments 2.1 and 2.6 in the FEED side.**

TIME (hrs)	TIME (sec)	100	%	200	%	300	%	400	%
0	0	0	0	0	0	0	0	0	0
1	3600	2	2	4	2	1	0	3	1
2	7200	4	4	9	5	2	0	7	2
3	10800	6	6	26	13	10	3	12	3
4	14400	8	8	29	14	15	5	23	6
5	18000	13	13	35	17	26	8	25	7
6	21600	15	15	58	29	30	10	35	9
24	86400	67	68	140	69	179	58	231	61
25	90000	68	69	140	69	182	59	240	63
26	93600	71	72	140	69	184	60	236	62
27	97200	70	71	150	74	190	62	244	64
28	100800	71	72	150	74	187	61	249	66
29	104400	72	73	150	74	190	62	251	66
30	108000	73	74	160	79	199	65	255	67
48	172800	75	77	184	91	240	78	325	86
49	176400	75	77	185	91	250	81	325	86
50	180000	75	77	185	91	250	81	327	86

**Table H.2.4: Raw data from Experiments 2.1 and 2.6 in the STRIP side.**

The effect of H<sub>2</sub>SO<sub>4</sub> concentration on the permeability at 5 and 20% strip concentrations

**FEED**

TIME (hrs)	TIME (sec)	5%	%	20%	%
0	0	210	100	233	100
1	3600	170	81	220	95
2	7200	160	76	191	82
3	10800	150	71	166	71
4	14400	140	67	159	68
5	18000	130	62	139	60
6	21600	130	62	130	56
24	86400	67	32	42	18
25	90000	65	31	40	17
26	93600	65	31	35	15
27	97200	60	29	35	15
28	100800	57	27	31	13
29	104400	56	27	28	12
30	108000	52	25	25	11
48	172800	27	13	6	2
49	176400	26	12	4	2
50	180000	25	12	2	1

**Table H.2.5: Raw data from Experiments 2.1 and 2.4 in the FEED side.**

**STRIP**

TIME(hrs)	TIME (sec)	5%	%	20%	%
0	0	0	0	0	0
1	3600	2	1	3	1
2	7200	3	1	3	1
3	10800	4	2	6	3
4	14400	6	3	13	6
5	18000	11	5	24	10
6	21600	15	7	41	18
24	86400	91	43	144	62
25	90000	94	45	149	64
26	93600	96	46	153	66
27	97200	99	47	157	67
28	100800	100	48	161	69
29	104400	100	48	166	71
30	108000	110	52	167	72
48	172800	150	71	185	79
49	176400	150	71	188	81
50	180000	150	71	187	80

**Table H.2.6: Raw data from Experiments 2.1 and 2.4 in the STRIP side.**

### H.3. Copper permeation at different Carrier concentrations in (ppm) $\text{mg.dm}^{-3}$ :

FEED

TIME(hrs)	TIME(sec)	5%	10%	15%	20%	25%	40%
0	0	190	187	195	211	214	205
1	3600	168	160	143	174	167	196
2	7200	139	146	123	129	137	178
3	10800	125	130	106	105	118	166
4	14400	111	114	97	90	106	160
5	18000	93	106	86	78	99	152
6	21600	88	97	75	69	92	145
24	86400	28	24	23	22	26	57
25	90000	26	23	21	21	23	56
26	93600	25	22	20	19	21	57
27	97200	25	21	19	18	19	55
28	100800	24	19	17	17	19	54
29	104400	23	19	17	17	19	52
30	108000	22	18	16	15	18	52
48	172800	16	11	6	3	4	34
49	176400	16	11	5	3	4	33
50	180000	15	11	5	3	4	30

Table H.3.1: Raw data from Experiments 3.1 – 3.6 in the FEED side.

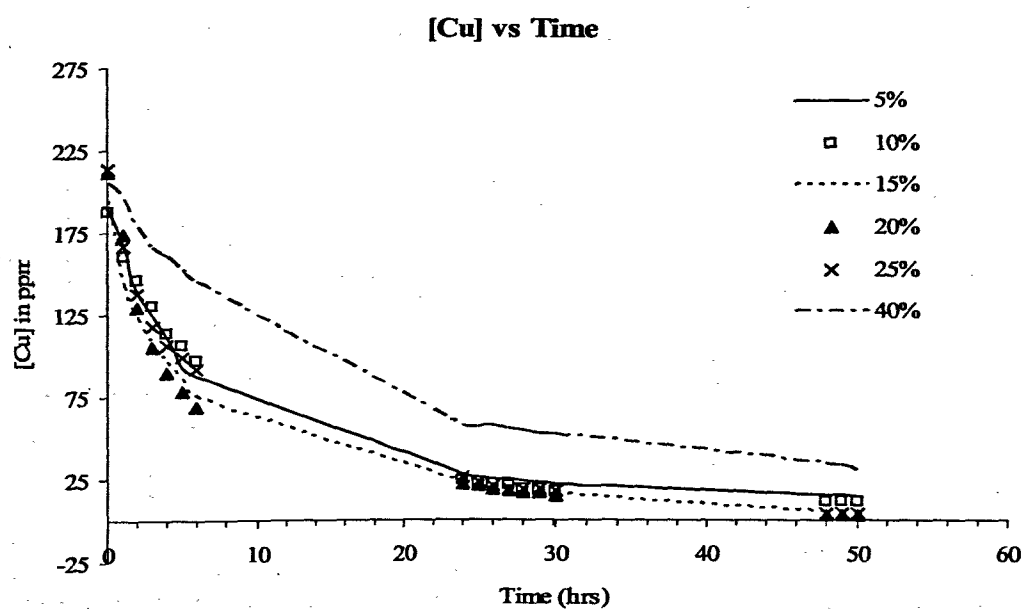


Figure H.3.1: Experimental courses of Cu (II) concentration in the feed reservoir at different carrier concentrations.

## STRIP

TIME(hrs)	TIME(sec)	5%	10%	15%	20%	25%	40%
0	0	0	0	0	0	0	0
1	3600	2	1	2	2	3	5
2	7200	4	5	6	5	8	12
3	10800	8	9	14	14	17	15
4	14400	15	20	22	24	24	21
5	18000	21	26	35	32	33	26
6	21600	28	34	40	42	40	32
24	86400	132	138	148	158	134	112
25	90000	134	145	152	157	137	113
26	93600	138	147	155	155	139	120
27	97200	142	150	158	164	144	121
28	100800	145	155	159	153	145	121
29	104400	150	159	155	161	148	129
30	108000	152	161	160	162	151	128
48	172800	174	173	178	180	177	163
49	176400	176	172	178	180	175	166
50	180000	177	172	179	181	176	166

Table H.3.2: Raw data from Experiments 3.1 – 3.6 in the STRIP side.

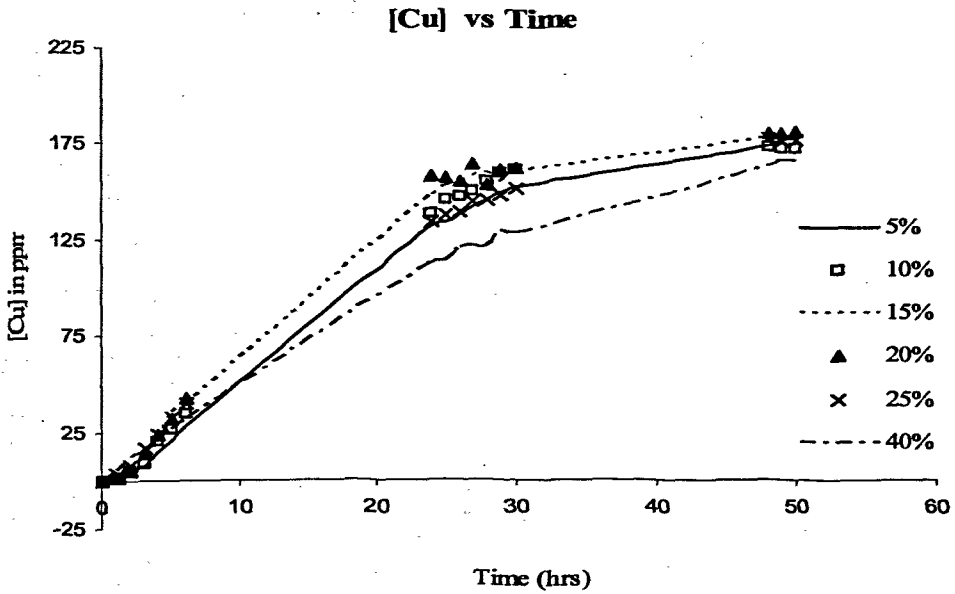


Figure H.3.2: Experimental courses of Cu (II) concentration in the strip reservoir at different carrier concentrations.

#### H.4. Copper permeation at different feed and strip flow rates in (ppm) $\text{mg.dm}^{-3}$ :

FEED

TIME(hrs)	TIME(sec)	0.167 $\text{cm}^3.\text{sec}^{-1}$	0.25 $\text{cm}^3.\text{sec}^{-1}$	0.333 $\text{cm}^3.\text{sec}^{-1}$	0.5 $\text{cm}^3.\text{sec}^{-1}$	0.667 $\text{cm}^3.\text{sec}^{-1}$	0.833 $\text{cm}^3.\text{sec}^{-1}$
0	0	224	215	222	211	218	225
1	3600	180	205	192	189	180	200
2	7200	158	155	164	161	156	160
3	10800	147	145	132	130	124	126
4	14400	143	135	123	120	101	105
5	18000	135	125	113	114	81	92
6	21600	122	115	96	92	68	72
24	86400	41	36	29	22	16	17
25	90000	37	34	26	21	15	15
26	93600	36	32	23	20	14	15
27	97200	35	28	20	18	13	14
28	100800	32	27	16	15	12	13
29	104400	32	27	16	14	10	11
30	108000	29	24	15	12	8	9
48	172800	17	7	6	4	3	4
49	176400	16	6	5	4	3	3
50	180000	10	6	5	4	3	3

Table H.4.1: Raw data from Experiments 4.1 – 4.6 in the FEED side.

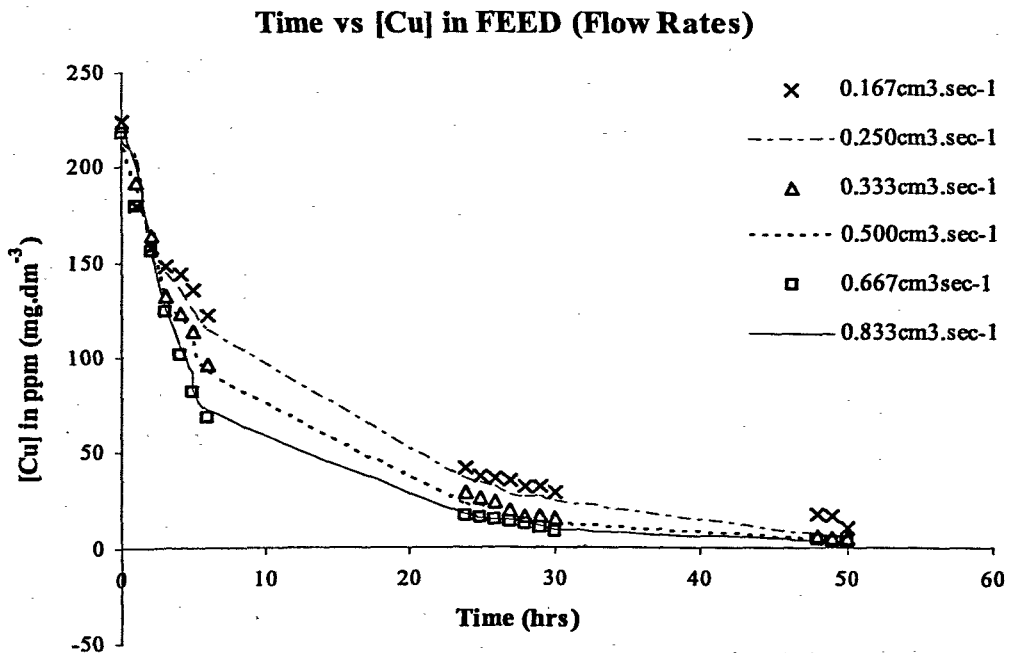


Figure H.4.1: Experimental courses of Cu (II) concentration in the feed reservoir at different feed/strip velocities.



## STRIP

TIME (hrs)	TIME (sec)	0.167 $\text{cm}^3.\text{sec}^{-1}$	0.25 $\text{cm}^3.\text{sec}^{-1}$	0.333 $\text{cm}^3.\text{sec}^{-1}$	0.5 $\text{cm}^3.\text{sec}^{-1}$	0.667 $\text{cm}^3.\text{sec}^{-1}$	0.833 $\text{cm}^3.\text{sec}^{-1}$
0	0	0	0	0	0	0	0
1	3600	1	1	2	1	3	2
2	7200	3	2	12	13	17	15
3	10800	7	6	35	34	44	38
4	14400	12	12	55	60	66	58
5	18000	17	14	71	70	76	72
6	21600	25	28	82	84	90	88
24	86400	145	150	143	145	168	166
25	90000	146	150	151	146	173	173
26	93600	154	155	160	154	178	175
27	97200	157	160	166	161	181	176
28	100800	158	160	171	168	182	178
29	104400	159	165	173	171	186	178
30	108000	162	165	179	175	189	181
48	172800	188	195	204	200	201	197
49	176400	191	198	206	202	202	197
50	180000	193	200	207	202	201	198

Table H.4.2: Raw data from Experiments 4.1 – 4.6 in the STRIP side.

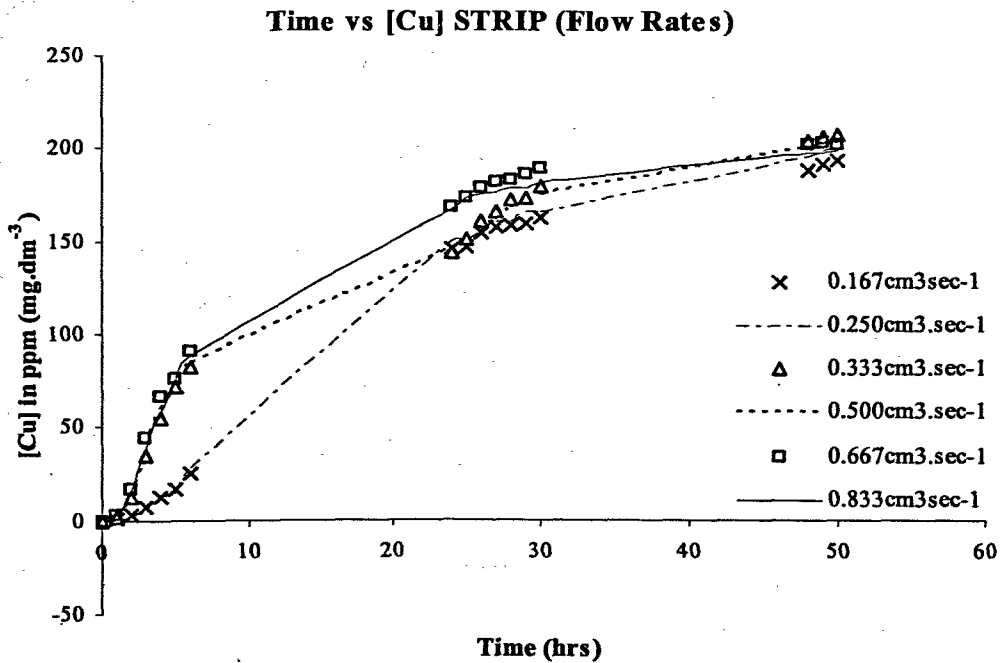


Figure H.4.2: Experimental courses of Cu (II) concentration in the strip reservoir at different feed/strip velocities.

### H.5. Copper permeation at different Copper feed conc. in (ppm) $\text{mg.dm}^{-3}$ at $\text{pH}=2$ :

FEED

TIME(hrs)	TIME(sec)	100	150	200	250	300
0	0	92	148	180	220	280
1	3600	78	126	150	180	240
2	7200	74	114	130	160	209
3	10800	60	98	120	130	179
4	14400	57	88	112	118	153
5	18000	44	72	101	107	135
6	21600	34	68	86	98	113
24	86400	4	6	9	11	26
25	90000	4	6	9	11	24
26	93600	3	5	8	10	23
27	97200	3	5	8	10	22
28	100800	3	5	8	9	21
29	104400	3	4	8	9	20
30	108000	1	4	7	8	20
48	172800	1	2	4	5	7
49	176400	1	2	3	5	7
50	180000	1	2	3	5	7

Table H.5.1: Raw data from Experiments 5.1 – 5.5 in the FEED side.

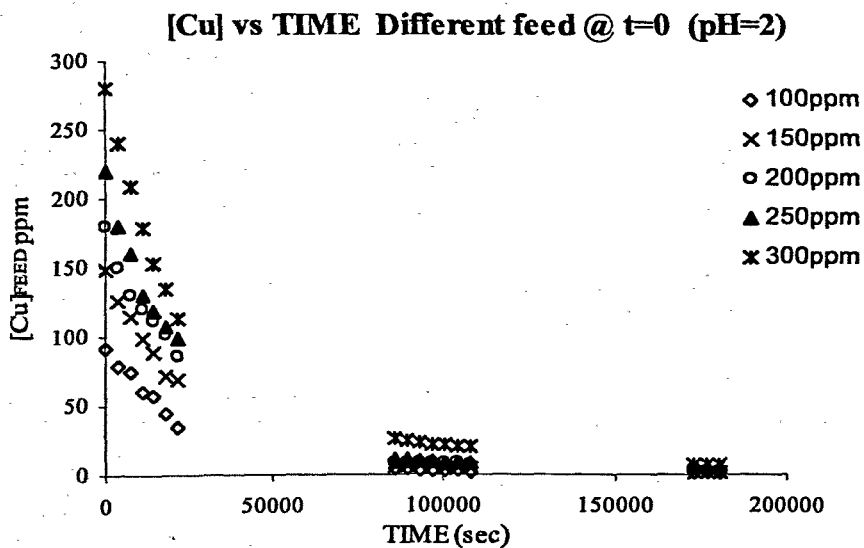


Figure H.5.1: Experimental courses of Cu (II) concentration in the feed reservoir at different feed concentrations at a  $\text{pH}=2$

## STRIP

TIME(hrs)	TIME(sec)	100	150	200	250	300
0	0	0	0	0	0	0
1	3600	2	2	8	9	10
2	7200	2	4	9	10	12
3	10800	2	5	16	16	17
4	14400	3	7	18	19	21
5	18000	5	8	20	23	28
6	21600	8	13	23	28	34
24	86400	54	81	120	148	173
25	90000	58	87	120	150	174
26	93600	59	89	126	151	176
27	97200	60	90	127	152	180
28	100800	64	93	129	154	184
29	104400	64	96	133	154	190
30	108000	65	98	132	155	192
48	172800	78	125	160	188	237
49	176400	78	125	160	188	237
50	180000	78	125	160	188	238

Table H.5.2: Raw data from Experiments 5.1 – 5.5 in the STRIP side

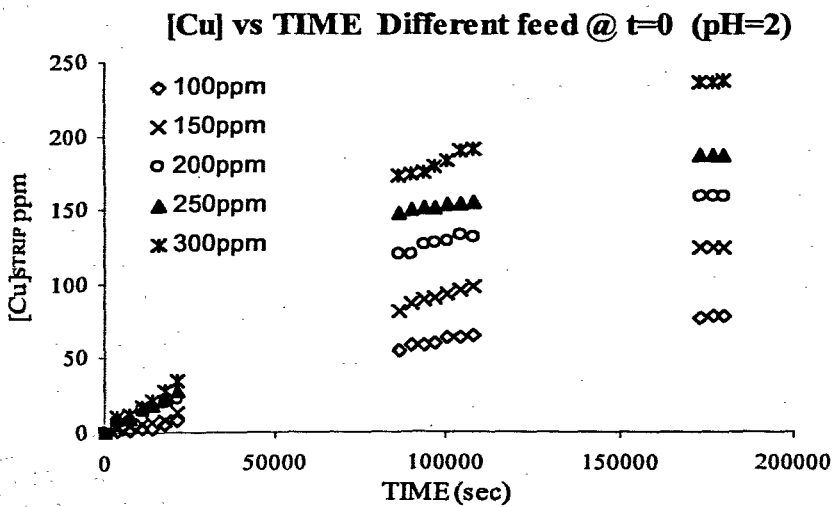
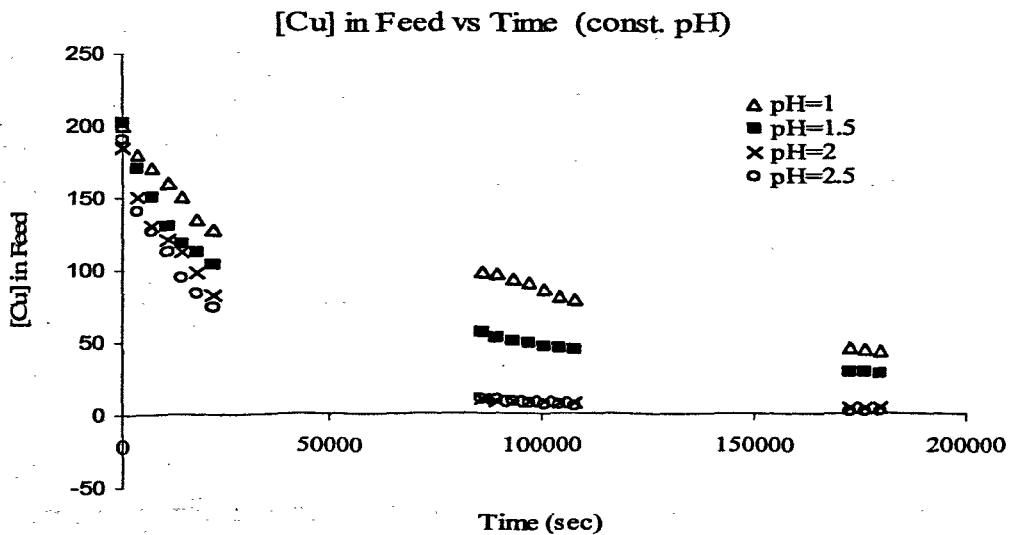


Figure H.5.2: Experimental courses of Cu (II) concentration in the strip reservoir at different feed concentrations at a pH=2

**H.6. Copper permeation at different Copper feed conc. in (ppm)  $\text{mg.dm}^{-3}$  at A constant feed pH:**

TIME(hrs)	TIME(sec)	1	1.5	2	2.5
0	0	200	202	185	190
1	3600	180	170	150	140
2	7200	170	150	130	126
3	10800	160	130	120	112
4	14400	150	118	112	94
5	18000	135	112	98	83
6	21600	127	103	82	74
24	86400	98	56	9	10
25	90000	96	52	9	10
26	93600	93	50	8	8
27	97200	90	49	8	8
28	100800	86	47	8	6
29	104400	81	46	7	6
30	108000	79	44	7	4
48	172800	45	28	4	1
49	176400	44	28	3	1
50	180000	43	28	3	1

**Table H.6.1: Raw data from Experiments 6.1 – 6.4 in the FEED side.**



**Figure H.6.1: Experimental courses of Cu (II) concentration in the feed reservoir at different feed concentrations at a constant feed pH**

TIME(hrs)	TIME(sec)	1	1.5	2	2.5
0	0	0	0	0	0
1	3600	3	3	8	1
2	7200	5	4	9	2
3	10800	6	5	16	3
4	14400	7	8	23	3
5	18000	7	14	28	4
6	21600	8	19	37	5
24	86400	41	77	118	38
25	90000	47	80	120	42
26	93600	52	84	124	46
27	97200	54	86	130	48
28	100800	56	89	132	52
29	104400	60	90	135	55
30	108000	63	92	137	58
48	172800	112	130	148	98
49	176400	114	130	148	98
50	180000	115	130	148	98

Table H.6.2: Raw data from Experiments 6.1 – 6.4 in the STRIP side

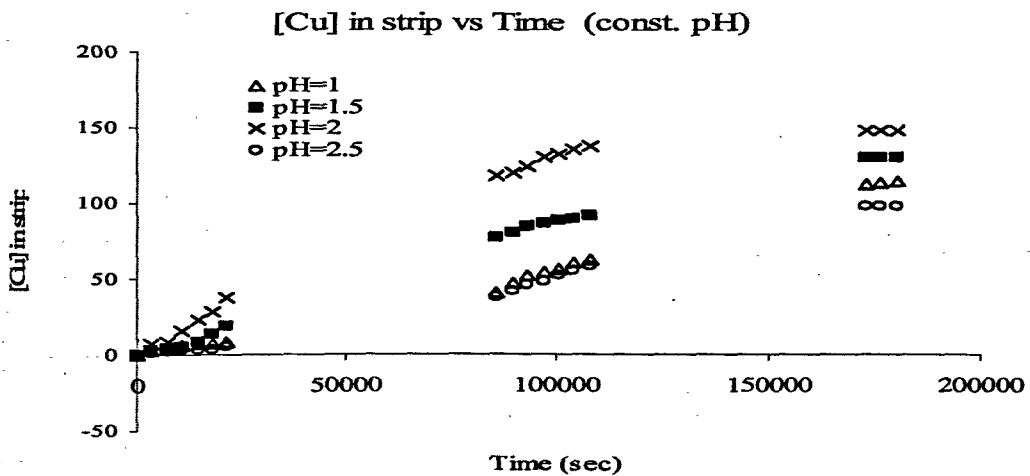


Figure H.6.2: Experimental courses of Cu (II) concentration in the strip reservoir at different feed concentrations at a constant feed pH

---

## APPENDIX I

---

**Calculating and test results of the**

**Distribution coefficient**

**(partitioning coefficient)  $m_{Cu}$**

**Distribution coefficient ( $m_{Cu}$ ) at different  $H_2SO_4$  concentrations:**

The results of solvent extraction tests are presented in this appendix in tables I.1.1 – I.1.12.

The results in I.1.1-I.1.6 represent the testing in the feed and I.1.7-I.1.12 in the strip. The  $m_{Cu}$  values are calculated by equation I.1 for the feed and equation I.2 for the strip.

The reported concentration of the copper in the organic phase is calculated from mass balance equations I.1.3 and I.1.4.

The extraction percentage of the system was calculated.

**Experimental parameters:**

Volume of aqueous feed phase:	20cm <sup>3</sup>
Volume of aqueous strip phase:	20cm <sup>3</sup>
Volume of organic phase:	20cm <sup>3</sup>
Feed concentration (CuSO <sub>4</sub> ):	100, 150, 200, 250, 300, 350 and 400ppm
Strip concentration (H <sub>2</sub> SO <sub>4</sub> ):	5, 10, 15, 20, 25 and 30%
Extractant concentration (Lix 984):	20%

Distribution coefficient ( $m_{Cu}$ ) in FEED

ppm	Aqueous before		Aqueous after		Organic after		Extraction	$m_{Cu(t)}$
	[Cu] <sub>t=0</sub>	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	
100	90	1.42E-06	1.80	2.83E-08	88.20	1.39E-06	98.00	0.9800
150	160	2.52E-06	2.10	3.30E-08	157.90	2.48E-06	98.69	0.9869
200	200	3.15E-06	1.60	2.52E-08	198.40	3.12E-06	99.20	0.9920
250	260	4.09E-06	0.80	1.26E-08	259.20	4.08E-06	99.69	0.9969
300	300	4.72E-06	1.40	2.20E-08	298.60	4.70E-06	99.53	0.9953
350	350	5.51E-06	0.20	3.15E-09	349.80	5.50E-06	99.94	0.9994
400	390	6.14E-06	1.60	2.52E-08	388.40	6.11E-06	99.59	0.9959

Table I.1.1: Distribution coefficient ( $m_{Cu}$ ) using 5% strip

ppm	Aqueous before		Aqueous after		Organic after		Extraction	$m_{Cu(t)}$
	[Cu] <sub>t=0</sub>	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	
100	100	1.57E-06	0.00	0.00E+00	100.00	1.57E-06	100.00	1.0000
150	140	2.20E-06	0.20	3.15E-09	139.80	2.20E-06	99.86	0.9986
200	210	3.30E-06	1.80	2.83E-08	208.20	3.28E-06	99.14	0.9914
250	240	3.78E-06	1.70	2.68E-08	238.30	3.75E-06	99.29	0.9929
300	310	4.88E-06	2.10	3.30E-08	307.90	4.85E-06	99.32	0.9932
350	350	5.51E-06	2.60	4.09E-08	347.40	5.47E-06	99.26	0.9926
400	390	6.14E-06	1.30	2.05E-08	388.70	6.12E-06	99.67	0.9967

Table I.1.2: Distribution coefficient ( $m_{Cu}$ ) using 10% strip

ppm	Aqueous before		Aqueous after		Organic after		Extraction	$m_{Cu(t)}$
	[Cu] <sub>t=0</sub>	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	
100	120	1.89E-06	1.40	2.20E-08	118.60	1.87E-06	98.83	0.9883
150	160	2.52E-06	1.10	1.73E-08	158.90	2.50E-06	99.31	0.9931
200	190	2.99E-06	0.00	0.00E+00	190.00	2.99E-06	100.00	1.0000
250	240	3.78E-06	0.60	9.44E-09	239.40	3.77E-06	99.75	0.9975
300	300	4.72E-06	5.90	9.28E-08	294.10	4.63E-06	98.03	0.9803
350	340	5.35E-06	3.10	4.88E-08	336.90	5.30E-06	99.09	0.9909
400	380	5.98E-06	0.50	7.87E-09	379.50	5.97E-06	99.87	0.9987

Table I.1.3: Distribution coefficient ( $m_{Cu}$ ) using 15% strip



ppm	Aqueous before		Aqueous after		Organic after		Extraction	$m_{Cu(t)}$
	$[Cu]_{t=0}$	$mol.cm^{-3}$	$[Cu]$	$mol.cm^{-3}$	$[Cu]$	$mol.cm^{-3}$	%	
100	98	1.54E-06	1.60	2.52E-08	96.40	1.52E-06	98.37	0.9837
150	160	2.52E-06	0.90	1.42E-08	159.10	2.50E-06	99.44	0.9944
200	200	3.15E-06	0.00	0.00E+00	200.00	3.15E-06	100.00	1.0000
250	260	4.09E-06	2.00	3.15E-08	258.00	4.06E-06	99.23	0.9923
300	304	4.78E-06	0.40	6.29E-09	303.60	4.78E-06	99.87	0.9987
350	348	5.48E-06	8.80	1.38E-07	339.20	5.34E-06	97.47	0.9747
400	410	6.45E-06	2.40	3.78E-08	407.60	6.41E-06	99.41	0.9941

Table I.1.4: Distribution coefficient ( $m_{Cu}$ ) using 20% strip

ppm	Aqueous before		Aqueous after		Organic after		Extraction	$m_{Cu(t)}$
	$[Cu]_{t=0}$	$mol.cm^{-3}$	$[Cu]$	$mol.cm^{-3}$	$[Cu]$	$mol.cm^{-3}$	%	
100	110	1.73E-06	2.00	3.15E-08	108.00	1.70E-06	98.18	0.9818
150	140	2.20E-06	2.70	4.25E-08	137.30	2.16E-06	98.07	0.9807
200	190	2.99E-06	1.40	2.20E-08	188.60	2.97E-06	99.26	0.9926
250	250	3.93E-06	1.60	2.52E-08	248.40	3.91E-06	99.36	0.9936
300	280	4.41E-06	1.90	2.99E-08	278.10	4.38E-06	99.32	0.9932
350	340	5.35E-06	1.80	2.83E-08	338.20	5.32E-06	99.47	0.9947
400	400	6.29E-06	1.60	2.52E-08	398.40	6.27E-06	99.60	0.9960

Table I.1.5: Distribution coefficient ( $m_{Cu}$ ) using 25% strip

ppm	Aqueous before		Aqueous after		Organic after		Extraction	$m_{Cu(t)}$
	$[Cu]_{t=0}$	$mol.cm^{-3}$	$[Cu]$	$mol.cm^{-3}$	$[Cu]$	$mol.cm^{-3}$	%	
100	100	1.57E-06	1.80	2.83E-08	98.20	1.55E-06	98.20	0.9820
150	140	2.20E-06	0.00	0.00E+00	140.00	2.20E-06	100.00	1.0000
200	210	3.30E-06	0.00	0.00E+00	210.00	3.30E-06	100.00	1.0000
250	260	4.09E-06	3.20	5.04E-08	256.80	4.04E-06	98.77	0.9877
300	310	4.88E-06	1.60	2.52E-08	308.40	4.85E-06	99.48	0.9948
350	348	5.48E-06	0.80	1.26E-08	347.20	5.46E-06	99.77	0.9977
400	396	6.23E-06	0.40	6.29E-09	395.60	6.23E-06	99.90	0.9990

Table I.1.6: Distribution coefficient ( $m_{Cu}$ ) using 30% strip

Distribution coefficient ( $m_{Cu}$ ) strip

ppm	Organic before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	$m_{Cu(s)}$
100	88.20	1.39E-06	61	9.60E-07	27	4.28E-07	69.16	0.6916
150	157.90	2.48E-06	96	1.51E-06	62	9.74E-07	60.80	0.6080
200	198.40	3.12E-06	120	1.89E-06	78	1.23E-06	60.48	0.6048
250	259.20	4.08E-06	160	2.52E-06	99	1.56E-06	61.73	0.6173
300	298.60	4.70E-06	180	2.83E-06	119	1.87E-06	60.28	0.6028
350	349.8	5.50E-06	210	3.30E-06	140	2.20E-06	60.03	0.6003
400	388.4	6.11E-06	230	3.62E-06	158	2.49E-06	59.22	0.5922

Table I.1.7: Distribution coefficient ( $m_{Cu}$ ) using 5% strip

ppm	Organic before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	$m_{Cu(s)}$
100	100.00	1.57E-06	76	1.20E-06	24	3.78E-07	76.00	0.7600
150	139.80	2.20E-06	103	1.62E-06	37	5.79E-07	73.68	0.7368
200	208.20	3.28E-06	150	2.36E-06	58	9.16E-07	72.05	0.7205
250	238.30	3.75E-06	180	2.83E-06	58	9.17E-07	75.54	0.7554
300	307.90	4.85E-06	240	3.78E-06	68	1.07E-06	77.95	0.7795
350	347.4	5.47E-06	260	4.09E-06	87	1.38E-06	74.84	0.7484
400	388.7	6.12E-06	290	4.56E-06	99	1.55E-06	74.61	0.7461

Table I.1.8: Distribution coefficient ( $m_{Cu}$ ) using 10% strip

ppm	Organic before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	$m_{Cu(s)}$
100	118.60	1.87E-06	86	1.35E-06	33	5.13E-07	72.51	0.7251
150	158.90	2.50E-06	113	1.78E-06	46	7.22E-07	71.11	0.7111
200	190.00	2.99E-06	140	2.20E-06	50	7.87E-07	73.68	0.7368
250	239.40	3.77E-06	200	3.15E-06	39	6.20E-07	83.54	0.8354
300	294.10	4.63E-06	250	3.93E-06	44	6.94E-07	85.01	0.8501
350	336.9	5.30E-06	295	4.64E-06	42	6.59E-07	87.56	0.8756
400	379.5	5.97E-06	340	5.35E-06	40	6.22E-07	89.59	0.8959

Table I.1.9: Distribution coefficient ( $m_{Cu}$ ) using 15% strip

ppm	Organic before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	$m_{Cu(s)}$
100	96.40	1.52E-06	86	1.35E-06	10	1.64E-07	89.21	0.8921
150	159.10	2.50E-06	145	2.28E-06	14	2.22E-07	91.14	0.9114
200	200.00	3.15E-06	190	2.99E-06	10	1.57E-07	95.00	0.9500
250	258.00	4.06E-06	240	3.78E-06	18	2.83E-07	93.02	0.9302
300	303.60	4.78E-06	280	4.41E-06	24	3.71E-07	92.23	0.9223
350	339.2	5.34E-06	276	4.34E-06	63	9.95E-07	81.37	0.8137
400	407.6	6.41E-06	340	5.35E-06	68	1.06E-06	83.42	0.8342

**Table I.1.10: Distribution coefficient ( $m_{Cu}$ ) using 20% strip**

ppm	Organic before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	$m_{Cu(s)}$
100	108.00	1.70E-06	94	1.48E-06	14	2.20E-07	87.04	0.8704
150	137.30	2.16E-06	120	1.89E-06	17	2.72E-07	87.40	0.8740
200	188.60	2.97E-06	170	2.68E-06	19	2.93E-07	90.14	0.9014
250	248.40	3.91E-06	240	3.78E-06	8	1.32E-07	96.62	0.9662
300	278.10	4.38E-06	260	4.09E-06	18	2.85E-07	93.49	0.9349
350	338.2	5.32E-06	310	4.88E-06	28	4.44E-07	91.66	0.9166
400	398.4	6.27E-06	375	5.90E-06	23	3.68E-07	94.13	0.9413

**Table I.1.11: Distribution coefficient ( $m_{Cu}$ ) using 25% strip**

ppm	Organic before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	$m_{Cu(s)}$
100	98.20	1.55E-06	84	1.32E-06	14	2.23E-07	85.54	0.8554
150	140.00	2.20E-06	115	1.81E-06	25	3.93E-07	82.14	0.8214
200	210.00	3.30E-06	170	2.68E-06	40	6.29E-07	80.95	0.8095
250	248.40	3.91E-06	210	3.30E-06	38	6.04E-07	84.54	0.8454
300	308.40	4.85E-06	270	4.25E-06	38	6.04E-07	87.55	0.8755
350	347.2	5.46E-06	320	5.04E-06	27	4.28E-07	92.17	0.9217
400	395.6	6.23E-06	368	5.79E-06	28	4.34E-07	93.02	0.9302

**Table I.1.12: Distribution coefficient ( $m_{Cu}$ ) using 30% strip**

**Distribution coefficient ( $m_{Cu}$ ) at different reactant (LIX) concentrations:**

The results of solvent extraction tests are presented in this appendix in tables I.2.1 – I.2.12.

The results in I.2.1-I.2.6 represent the testing in the feed and I.2.7-I.2.12 in the strip. The  $m_{Cu}$  values are calculated by equation I.1 for the feed and equation I.2 for the strip.

The reported concentration of the copper in the organic phase is calculated from mass balance equations I.1.3 and I.1.4.

The extraction percentage of the system was calculated.

**Experimental parameters:**

Volume of aqueous feed phase:	20cm <sup>3</sup>
Volume of aqueous strip phase:	20cm <sup>3</sup>
Volume of organic phase:	20cm <sup>3</sup>
Feed concentration (CuSO <sub>4</sub> ):	100, 150, 200, 250, 300, 350 and 400ppm
Strip concentration (H <sub>2</sub> SO <sub>4</sub> ):	25%
Extractant concentration (Lix 984):	5, 10, 15, 20, 25, 30, 40%

Distribution coefficient ( $m_{Cu}$ ) in FEED

ppm	Aqueous before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	D <sub>Cu (f)</sub>
100	100	1.57E-06	0.00	0.00E+00	100.00	1.57E-06	100.00	1.0000
150	160	2.52E-06	1.80	2.83E-08	158.20	2.49E-06	98.88	0.9888
200	180	2.83E-06	2.60	4.09E-08	177.40	2.79E-06	98.56	0.9856
250	250	3.93E-06	9.40	1.48E-07	240.60	3.79E-06	96.24	0.9624
300	300	4.72E-06	3.20	5.04E-08	296.80	4.67E-06	98.93	0.9893
400	400	6.29E-06	3.80	5.98E-08	396.20	6.23E-06	99.05	0.9905

Table I.2.1: Distribution coefficient ( $m_{Cu}$ ) using 5% reactant

ppm	Aqueous before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	D <sub>Cu (f)</sub>
100	100	1.57E-06	0.10	1.57E-09	99.90	1.57E-06	99.90	0.9990
150	160	2.52E-06	0.00	0.00E+00	160.00	2.52E-06	100.00	1.0000
200	180	2.83E-06	3.10	4.88E-08	176.90	2.78E-06	98.28	0.9828
250	240	3.78E-06	4.80	7.55E-08	235.20	3.70E-06	98.00	0.9800
300	300	4.72E-06	2.40	3.78E-08	297.60	4.68E-06	99.20	0.9920
400	400	6.29E-06	4.90	7.71E-08	395.10	6.22E-06	98.78	0.9878

Table I.2.2: Distribution coefficient ( $m_{Cu}$ ) using 10% reactant

ppm	Aqueous before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	D <sub>Cu (f)</sub>
100	100	1.57E-06	7.60	1.20E-07	92.40	1.45E-06	92.40	0.9240
150	160	2.52E-06	2.40	3.78E-08	157.60	2.48E-06	98.50	0.9850
200	180	2.83E-06	3.80	5.98E-08	176.20	2.77E-06	97.89	0.9789
250	240	3.78E-06	4.30	6.77E-08	235.70	3.71E-06	98.21	0.9821
300	300	4.72E-06	5.40	8.50E-08	294.60	4.64E-06	98.20	0.9820
400	400	6.29E-06	3.90	6.14E-08	396.10	6.23E-06	99.03	0.9903

Table I.2.3: Distribution coefficient ( $m_{Cu}$ ) using 15% reactant

ppm	Aqueous before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	D <sub>Cu</sub> (f)
100	100	1.57E-06	0.00	0.00E+00	100.00	1.57E-06	100.00	1.0000
150	160	2.52E-06	1.40	2.20E-08	158.60	2.50E-06	99.13	0.9913
200	180	2.83E-06	2.80	4.41E-08	177.20	2.79E-06	98.44	0.9844
250	240	3.78E-06	4.90	7.71E-08	235.10	3.70E-06	97.96	0.9796
300	300	4.72E-06	4.60	7.24E-08	295.40	4.65E-06	98.47	0.9847
400	400	6.29E-06	5.10	8.03E-08	394.90	6.21E-06	98.73	0.9873

Table I.2.4: Distribution coefficient ( $m_{Cu}$ ) using 20% reactant

ppm	Aqueous before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	D <sub>Cu</sub> (f)
100	100	1.57E-06	0.00	0.00E+00	100.00	1.57E-06	100.00	1.0000
150	160	2.52E-06	0.00	0.00E+00	160.00	2.52E-06	100.00	1.0000
200	180	2.83E-06	2.30	3.62E-08	177.70	2.80E-06	98.72	0.9872
250	240	3.78E-06	4.80	7.55E-08	235.20	3.70E-06	98.00	0.9800
300	300	4.72E-06	3.70	5.82E-08	296.30	4.66E-06	98.77	0.9877
400	400	6.29E-06	4.70	7.40E-08	395.30	6.22E-06	98.83	0.9883

Table I.2.5: Distribution coefficient ( $m_{Cu}$ ) using 25% reactant

ppm	Aqueous before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	D <sub>Cu</sub> (f)
100	100	1.57E-06	4.40	6.92E-08	95.60	1.50E-06	95.60	0.9560
150	160	2.52E-06	0.30	4.72E-09	159.70	2.51E-06	99.81	0.9981
200	180	2.83E-06	1.90	2.99E-08	178.10	2.80E-06	98.94	0.9894
250	240	3.78E-06	5.40	8.50E-08	234.60	3.69E-06	97.75	0.9775
300	300	4.72E-06	4.80	7.55E-08	295.20	4.65E-06	98.40	0.9840
400	400	6.29E-06	3.60	5.67E-08	396.40	6.24E-06	99.10	0.9910

Table I.2.6: Distribution coefficient ( $m_{Cu}$ ) using 30% reactant

ppm	Aqueous before		Aqueous after		Organic after		Extraction	$D_{Cu(f)}$
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	
100	100	1.57E-06	0.00	0.00E+00	100.00	1.57E-06	100.00	1.0000
150	160	2.52E-06	0.00	0.00E+00	160.00	2.52E-06	100.00	1.0000
200	180	2.83E-06	1.80	2.83E-08	178.20	2.80E-06	99.00	0.9900
250	240	3.78E-06	5.30	8.34E-08	234.70	3.69E-06	97.79	0.9779
300	300	4.72E-06	6.00	9.44E-08	294.00	4.63E-06	98.00	0.9800
400	400	6.29E-06	5.80	9.13E-08	394.20	6.20E-06	98.55	0.9855

**Table I.2.7: Distribution coefficient ( $m_{Cu}$ ) using 40% reactant**

Distribution coefficient ( $m_{Cu}$ ) strip

ppm	Organic before		Aqueous after		Organic after		Extraction	$m_{Cu(f)}$
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	
100	100.00	1.57E-06	95	1.49E-06	5	7.87E-08	95.00	0.9500
150	158.20	2.49E-06	150	2.36E-06	8	1.29E-07	94.82	0.9482
200	177.40	2.79E-06	170	2.68E-06	7	1.16E-07	95.83	0.9583
250	240.60	3.79E-06	240	3.78E-06	1	9.44E-09	99.75	0.9975
300	296.80	4.67E-06	280	4.41E-06	17	2.64E-07	94.34	0.9434
400	396.2	6.23E-06	360	5.67E-06	36	5.70E-07	90.86	0.9086

**Table I.2.8: Distribution coefficient ( $m_{Cu}$ ) using 5% reactant**

ppm	Organic before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	$m_{Cu(s)}$
100	99.90	1.57E-06	91	1.43E-06	9	1.40E-07	91.09	0.9109
150	160.00	2.52E-06	150	2.36E-06	10	1.57E-07	93.75	0.9375
200	176.90	2.78E-06	172	2.71E-06	5	7.71E-08	97.23	0.9723
250	235.20	3.70E-06	220	3.46E-06	15	2.39E-07	93.54	0.9354
300	297.60	4.68E-06	270	4.25E-06	28	4.34E-07	90.73	0.9073
400	395.1	6.22E-06	355	5.59E-06	40	6.31E-07	89.85	0.8985

Table I.2.9: Distribution coefficient ( $m_{Cu}$ ) using 10% reactant

ppm	Organic before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	$m_{Cu(s)}$
100	92.40	1.45E-06	90	1.42E-06	2	3.78E-08	97.40	0.9740
150	157.60	2.48E-06	140	2.20E-06	18	2.77E-07	88.83	0.8883
200	176.20	2.77E-06	175	2.75E-06	1	1.89E-08	99.32	0.9932
250	235.70	3.71E-06	230	3.62E-06	6	8.97E-08	97.58	0.9758
300	294.60	4.64E-06	280	4.41E-06	15	2.30E-07	95.04	0.9504
400	396.1	6.23E-06	360	5.67E-06	36	5.68E-07	90.89	0.9089

Table I.2.10: Distribution coefficient ( $m_{Cu}$ ) using 15% reactant

ppm	Organic before		Aqueous after		Organic after		Extraction	
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	$m_{Cu(s)}$
100	100.00	1.57E-06	92	1.45E-06	8	1.26E-07	92.00	0.9200
150	158.60	2.50E-06	130	2.05E-06	29	4.50E-07	81.97	0.8197
200	177.20	2.79E-06	170	2.68E-06	7	1.13E-07	95.94	0.9594
250	235.10	3.70E-06	220	3.46E-06	15	2.38E-07	93.58	0.9358
300	295.40	4.65E-06	280	4.41E-06	15	2.42E-07	94.79	0.9479
400	394.9	6.21E-06	365	5.74E-06	30	4.71E-07	92.43	0.9243

Table I.2.11: Distribution coefficient ( $m_{Cu}$ ) using 20% reactant



ppm	Organic before		Aqueous after		Organic after		Extraction	$m_{Cu(s)}$
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	
100	100.00	1.57E-06	89	1.40E-06	11	1.73E-07	89.00	<b>0.8900</b>
150	160.00	2.52E-06	140	2.20E-06	20	3.15E-07	87.50	<b>0.8750</b>
200	177.70	2.80E-06	175	2.75E-06	3	4.25E-08	98.48	<b>0.9848</b>
250	235.20	3.70E-06	220	3.46E-06	15	2.39E-07	93.54	<b>0.9354</b>
300	296.30	4.66E-06	270	4.25E-06	26	4.14E-07	91.12	<b>0.9112</b>
400	395.3	6.22E-06	370	5.82E-06	25	3.98E-07	93.60	<b>0.9360</b>

**Table I.2.12: Distribution coefficient ( $m_{Cu}$ ) using 25% reactant**

ppm	Organic before		Aqueous after		Organic after		Extraction	$m_{Cu(s)}$
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	
100	95.60	1.50E-06	87	1.37E-06	9	1.35E-07	91.00	<b>0.9100</b>
150	159.70	2.51E-06	120	1.89E-06	40	6.25E-07	75.14	<b>0.7514</b>
200	178.10	2.80E-06	170	2.68E-06	8	1.27E-07	95.45	<b>0.9545</b>
250	234.60	3.69E-06	210	3.30E-06	25	3.87E-07	89.51	<b>0.8951</b>
300	295.20	4.65E-06	265	4.17E-06	30	4.75E-07	89.77	<b>0.8977</b>
400	396.4	6.24E-06	355	5.59E-06	41	6.51E-07	89.56	<b>0.8956</b>

**Table I.2.13: Distribution coefficient ( $m_{Cu}$ ) using 30% reactant**

ppm	Organic before		Aqueous after		Organic after		Extraction	$m_{Cu(s)}$
	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	[Cu]	mol.cm <sup>-3</sup>	%	
100	100.00	1.57E-06	84	1.32E-06	16	2.52E-07	84.00	<b>0.8400</b>
150	160.00	2.52E-06	120	1.89E-06	40	6.29E-07	75.00	<b>0.7500</b>
200	178.20	2.80E-06	165	2.60E-06	13	2.08E-07	92.59	<b>0.9259</b>
250	234.70	3.69E-06	200	3.15E-06	35	5.46E-07	85.22	<b>0.8522</b>
300	294.00	4.63E-06	260	4.09E-06	34	5.35E-07	88.44	<b>0.8844</b>
400	394.2	6.20E-06	350	5.51E-06	44	6.96E-07	88.79	<b>0.8879</b>

**Table I.2.14: Distribution coefficient ( $m_{Cu}$ ) using 40% reactant**

---

## APPENDIX J

---

**Permeation coefficient ( $P_{Cu}$ )**

**Calculations using**

**Equation 14**

ppm	pH	$[H^+]_{\text{feed}}$	$[H^+]^2_{\text{feed}}$	$[HR]_{\text{org}}$	$[HR]^2_{\text{org}}$	$m_{\text{Cu}}$	Pm	1/Pm	1/Pcu	Pcu
100	1.92	1.20E-02	1.45E-04	1.30E-02	1.68E-04	0.9873	4.34E-04	2.31E+03	9.55E+03	1.05E-04
150	1.88	1.32E-02	1.74E-04	1.42E-02	2.02E-04	0.9873	4.34E-04	2.31E+03	9.55E+03	1.05E-04
200	1.81	1.55E-02	2.40E-04	1.67E-02	2.79E-04	0.9873	4.34E-04	2.31E+03	9.55E+03	1.05E-04
250	1.76	1.74E-02	3.02E-04	1.87E-02	3.51E-04	0.9873	4.34E-04	2.31E+03	9.55E+03	1.05E-04
300	1.73	1.86E-02	3.47E-04	2.01E-02	4.03E-04	0.9873	4.34E-04	2.31E+03	9.55E+03	1.05E-04
350	1.70	2.00E-02	3.98E-04	2.15E-02	4.62E-04	0.9873	4.34E-04	2.31E+03	9.55E+03	1.05E-04
400	1.69	2.04E-02	4.17E-04	2.20E-02	4.84E-04	0.9873	4.34E-04	2.31E+03	9.55E+03	1.05E-04

**Table J.1.1: Permeation coefficient calculations at different feed concentrations at equilibrium shown in Appendix A.1**

%	pH	$[H^+]_{feed}$	$[H^+]^2_{feed}$	$[HR]_{org}$	$[HR]^2_{org}$	$m_{Cu}$	Pm	1/Pm	1/Pcu	Pcu
5	2.19	6.46E-03	4.17E-05	6.96E-03	4.84E-05	0.9873	4.34E-03	2.31E+02	1.24E+04	8.09E-05
10	1.12	7.59E-02	5.75E-03	8.18E-02	6.68E-03	0.9873	4.34E-03	2.31E+02	1.24E+04	8.09E-05
15	2.04	9.12E-03	8.32E-05	9.83E-03	9.66E-05	0.9873	4.34E-03	2.31E+02	1.24E+04	8.09E-05
20	1.43	3.72E-02	1.38E-03	4.00E-02	1.60E-03	0.9873	4.34E-03	2.31E+02	1.24E+04	8.09E-05
25	1.41	3.89E-02	1.51E-03	4.19E-02	1.76E-03	0.9873	4.34E-03	2.31E+02	1.24E+04	8.09E-05
30	1.38	4.17E-02	1.74E-03	4.49E-02	2.02E-03	0.9873	4.34E-03	2.31E+02	1.24E+04	8.09E-05

**Table J.1.2: Permeation coefficient calculations at different strip concentrations at equilibrium shown in Appendix A.2**

FLOW RATE	pH	$[H^+]_{feed}$	$[H^+]^2_{feed}$	$[HR]_{org}$	$[HR]^2_{org}$	$m_{Cu}$	Pm	1/Pm	1/Pcu	Pcu
0.167	1.74	1.82E-02	3.31E-04	1.96E-02	3.85E-04	0.9873	4.34E-03	2.31E+02	1.66E+04	6.01E-05
0.25	1.82	1.51E-02	2.29E-04	1.63E-02	2.66E-04	0.9873	4.34E-03	2.31E+02	1.44E+04	6.92E-05
0.333	1.93	1.17E-02	1.38E-04	1.27E-02	1.60E-04	0.9873	4.34E-03	2.31E+02	1.31E+04	7.65E-05
0.5	1.86	1.38E-02	1.91E-04	1.49E-02	2.21E-04	0.9873	4.34E-03	2.31E+02	1.13E+04	8.82E-05
0.667	1.81	1.55E-02	2.40E-04	1.67E-02	2.79E-04	0.9873	4.34E-03	2.31E+02	1.03E+04	9.74E-05
0.833	1.78	1.66E-02	2.75E-04	1.79E-02	3.20E-04	0.9873	4.34E-03	2.31E+02	9.50E+03	1.05E-04

**Table J.1.3: Permeation coefficient calculations at different flow rates at equilibrium shown in Appendix A.3**

[LIX] %	pH	[H <sup>+</sup> ] <sub>feed</sub>	[H <sup>+</sup> ] <sup>2</sup> <sub>feed</sub>	[HR] <sub>org</sub>	[HR] <sup>2</sup> <sub>org</sub>	<i>m</i> <sub>Cu</sub>	P <sub>m</sub>	1/P <sub>m</sub>	1/P <sub>cu</sub>	P <sub>cu</sub>
5	1.85	1.41E-02	2.00E-04	1.52E-02	2.32E-04	0.9873	4.34E-03	2.31E+02	1.46E+04	6.87E-05
10	1.84	1.45E-02	2.09E-04	1.56E-02	2.43E-04	0.9873	4.34E-03	2.31E+02	1.46E+04	6.87E-05
15	1.77	1.70E-02	2.88E-04	1.83E-02	3.35E-04	0.9873	4.34E-03	2.31E+02	1.46E+04	6.87E-05
20	1.71	1.95E-02	3.80E-04	2.10E-02	4.42E-04	0.9873	4.34E-03	2.31E+02	1.46E+04	6.87E-05
25	1.68	2.09E-02	4.37E-04	2.25E-02	5.07E-04	0.9873	4.34E-03	2.31E+02	1.46E+04	6.87E-05
40	1.89	1.29E-02	1.66E-04	1.39E-02	1.93E-04	0.9873	4.34E-03	2.31E+02	1.46E+04	6.87E-05

**Table J.1.4: Permeation coefficient calculations at reactant concentrations at equilibrium shown in Appendix A.4**

pH	$[H^+]_{\text{feed}}$	$[H^+]_{\text{feed}}^2$	$[HR]_{\text{org}}$	$[HR]_{\text{org}}^2$	$m_{\text{Cu}}$	Pm	1/Pm	1/Pcu	Pcu
1	0.100	1.00E-02	9.94E-01	1.15E+00	0.9873	4.31E-01	2.32E+00	1.28E+04	7.82E-05
1.5	0.032	1.00E-03	9.94E-01	9.94E-01	0.9873	3.71E+00	2.70E-01	1.28E+04	7.82E-05
2	0.010	1.00E-04	9.94E-01	9.94E-01	0.9873	3.71E+01	2.70E-02	1.28E+04	7.82E-05
2.5	0.003	1.00E-05	9.94E-01	9.94E-01	0.9873	3.71E+02	2.70E-03	1.28E+04	7.82E-05

**Table J.1.5: Permeation coefficient calculations at constant pH at equilibrium shown in Appendix A.5**

	pH	$[H^+]_{\text{feed}}$	$[H^+]_{\text{feed}}^2$	$[HR]_{\text{org}}$	$[HR]_{\text{org}}^2$	$m_{\text{Cu}}$	Pm	1/Pm	1/Pcu	Pcu
100	2	1.00E-02	1.00E-04	1.08E-02	1.16E-04	0.9873	4.34E-03	2.31E+02	8.98E+03	1.11E-04
150	2	1.00E-02	1.00E-04	1.08E-02	1.16E-04	0.9873	4.34E-03	2.31E+02	8.98E+03	1.11E-04
200	2	1.00E-02	1.00E-04	1.08E-02	1.16E-04	0.9873	4.34E-03	2.31E+02	8.98E+03	1.11E-04
250	2	1.00E-02	1.00E-04	1.08E-02	1.16E-04	0.9873	4.34E-03	2.31E+02	8.98E+03	1.11E-04
300	2	1.00E-02	1.00E-04	1.08E-02	1.16E-04	0.9873	4.34E-03	2.31E+02	8.98E+03	1.11E-04

**Table J.1.6: Permeation coefficient calculations at pH = 2 at equilibrium shown in Appendix A.6**



---

## APPENDIX K

---

**Locating of mass transfer coefficient ( $k_i$ )**

(ppm)	Sp	Pcu	1/Pcu	Pm	1/Pm	1/ki	ki
100	6.43E-03	1.30E-04	7.71E+03	4.34E-04	2.31E+03	5.45E+03	1.84E-04
150	6.21E-03	1.23E-04	8.13E+03	4.34E-04	2.31E+03	5.87E+03	1.70E-04
200	6.00E-03	1.17E-04	8.55E+03	4.34E-04	2.31E+03	6.29E+03	1.59E-04
250	4.93E-03	8.84E-05	1.13E+04	4.34E-04	2.31E+03	9.05E+03	1.11E-04
300	5.61E-03	1.06E-04	9.44E+03	4.34E-04	2.31E+03	7.18E+03	1.39E-04
350	4.29E-03	7.35E-05	1.36E+04	4.34E-04	2.31E+03	1.13E+04	8.82E-05
400	5.22E-03	9.58E-05	1.04E+04	4.34E-04	2.31E+03	8.18E+03	1.22E-04

**Table K.1.1: Locating of the mass transfer coefficient ( $k_i$ ) using Equation 17 and shown in Figure 2.25 at different feed concentrations**

(ppm)	Sp	PCu*	1/PCu*	Pm	1/Pm	1/ki	ki
5	2.50E-03	3.82E-05	2.62E+04	4.34E-03	2.31E+02	2.60E+04	3.85E-05
10	3.51E-03	5.71E-05	1.75E+04	4.34E-03	2.31E+02	1.73E+04	5.79E-05
15	5.13E-03	9.34E-05	1.07E+04	4.34E-03	2.31E+02	1.05E+04	9.54E-05
20	5.25E-03	9.66E-05	1.04E+04	4.34E-03	2.31E+02	1.01E+04	9.87E-05
25	5.57E-03	1.05E-04	9.54E+03	4.34E-03	2.31E+02	9.31E+03	1.07E-04
30	5.18E-03	9.47E-05	1.06E+04	4.34E-03	2.31E+02	1.03E+04	9.68E-05

**Table K.1.2: Locating of the mass transfer coefficient ( $k_i$ ) using Equation 17 and shown in Figure 2.25 at different strippant concentrations**

(ppm)	Sp	Pcu	1/Pcu	Pm	1/Pm	1/ki	ki
5	3.46E-03	5.62E-05	1.78E+04	4.34E-03	2.31E+02	1.76E+04	5.69E-05
10	4.06E-03	6.86E-05	1.46E+04	4.34E-03	2.31E+02	1.44E+04	6.97E-05
15	4.64E-03	8.16E-05	1.23E+04	4.34E-03	2.31E+02	1.20E+04	8.31E-05
20	4.89E-03	8.76E-05	1.14E+04	4.34E-03	2.31E+02	1.12E+04	8.94E-05
25	5.44E-03	1.01E-04	9.85E+03	4.34E-03	2.31E+02	9.63E+03	1.04E-04
30	5.41E-03	1.01E-04	9.93E+03	4.34E-03	2.31E+02	9.71E+03	1.03E-04

**Table K.1.3: Locating of the mass transfer coefficient ( $k_i$ ) using Equation 17 and shown in Figure 2.25 at different reactant concentrations**

(ppm)	Sp	Pcu	1/Pcu	Pm	1/Pm	1/ki	ki
5	3.58E-03	5.85E-05	1.71E+04	4.34E-03	2.31E+02	1.69E+04	5.92E-05
10	3.93E-03	6.57E-05	1.52E+04	4.34E-03	2.31E+02	1.50E+04	6.67E-05
15	4.52E-03	7.87E-05	1.27E+04	4.34E-03	2.31E+02	1.25E+04	8.01E-05
20	4.96E-03	8.92E-05	1.12E+04	4.34E-03	2.31E+02	1.10E+04	9.11E-05
25	4.70E-03	8.29E-05	1.21E+04	4.34E-03	2.31E+02	1.18E+04	8.45E-05
40	2.41E-03	3.66E-05	2.73E+04	4.34E-03	2.31E+02	2.71E+04	3.69E-05

**Table K.1.4: Locating of the mass transfer coefficient ( $k_i$ ) using Equation 17 and shown in Figure 2.25 at different flow rates**

pH	Sp	PCu*	1/PCu*	Pm	1/Pm	1/ki	ki
1.00	1.72E-03	2.64E-05	3.79E+04	4.31E-01	2.32E+00	3.79E+04	2.64E-05
1.50	2.64E-03	4.27E-05	2.34E+04	3.71E+00	2.70E-01	2.34E+04	4.27E-05
2.00	5.33E-03	1.04E-04	9.64E+03	3.71E+01	2.70E-02	9.64E+03	1.04E-04
2.50	6.55E-03	1.40E-04	7.14E+03	3.71E+02	2.70E-03	7.14E+03	1.40E-04

**Table K.1.5: Locating of the mass transfer coefficient ( $k_i$ ) using Equation 17 and shown in Figure 2.25 at a constant pH**

(ppm)	$S_p$	$P_{Cu}$	$1/P_{Cu}$	$P_m$	$1/P_m$	$1/k_i$	$k_i$
100	6.06E-03	1.25E-04	7.99E+03	2.26E+02	1.25E-04	5.93E-03	1.69E+02
150	6.01E-03	1.24E-04	8.09E+03	2.26E+02	1.24E-04	5.88E-03	1.70E+02
200	5.62E-03	1.12E-04	8.90E+03	2.26E+02	1.12E-04	5.51E-03	1.81E+02
250	5.41E-03	1.06E-04	9.41E+03	2.26E+02	1.06E-04	5.30E-03	1.89E+02
300	4.77E-03	8.94E-05	1.12E+04	0.00E+00	8.94E-05	4.68E-03	2.14E+02

**Table K.1.6: Locating of the mass transfer coefficient ( $k_i$ ) using Equation 17 and shown in Figure 2.25 at pH = 2**

---

**APPENDIX L**

---

**Mass balance calculations**



ppm	100	150	200	250	300	350	400
Feed(t=0)	0.01960	0.02700	0.04060	0.04840	0.06160	0.06400	0.07600
Feed(t=0)	0.00020	0.00040	0.00040	0.00100	0.00080	0.00120	0.00054
Strip	0.01695	0.02644	0.04181	0.05108	0.05650	0.06464	0.07390
Membrane	0.00034	0.00031	0.00025	0.00023	0.00093	0.00059	0.00082
Total	0.01749	0.02715	0.04246	0.05230	0.05823	0.06643	0.07526
% Recovery	89	101	105	108	95	104	99
	116	0	21	65	30	14	1
mass error	11	1	5	8	5	4	1
average error	5	%					

**Table L.1.1: Mass transfer calculations at different feed concentrations**

(H <sub>2</sub> SO <sub>4</sub> )	5%	10%	15%	20%	25%	30%
Feed(t=0)	0.04200	0.04078	0.04113	0.04660	0.04500	0.04620
Feed(t=0)	0.00500	0.00120	0.00070	0.00040	0.00060	0.00066
Strip	0.03390	0.03300	0.03865	0.04226	0.04556	0.04859
Membrane	0.00073	0.00054	0.00059	0.00099	0.00048	0.00034
Total	0.03963	0.03474	0.03994	0.04365	0.04664	0.04959
% Recovery	94	85	97	94	104	107
	32	219	8	40	13	54
mass error	6	15	3	6	4	7
average error	7	%				

**Table L.1.2: Mass transfer calculations at different strippants concentrations**

	0.167 cm <sup>3</sup> .sec <sup>-1</sup>	0.25 cm <sup>3</sup> .sec <sup>-1</sup>	0.333 cm <sup>3</sup> .sec <sup>-1</sup>	0.5 cm <sup>3</sup> .sec <sup>-1</sup>	0.667 cm <sup>3</sup> .sec <sup>-1</sup>	0.833 cm <sup>3</sup> .sec <sup>-1</sup>
Feed(t=0)	0.04480	0.04300	0.04440	0.04220	0.04360	0.04500
Feed(t=0)	0.00200	0.00118	0.00090	0.00076	0.00060	0.00060
Strip	0.04362	0.04520	0.04678	0.04574	0.04543	0.04475
Membrane	0.00068	0.00076	0.00031	0.00105	0.00034	0.00048
Total	0.04630	0.04714	0.04799	0.04755	0.04637	0.04583
% Recovery	103	101	105	108	95	104
	11	0	21	65	30	14
mass error	3	1	5	8	5	4
average error	4	%				

**Table L.1.3: Mass transfer calculations at different flow rates**

	5%	10%	15%	20%	25%	40%
Feed(t=0)	0.03800	0.03740	0.03900	0.04220	0.04280	0.04100
Feed(t=0)	0.00300	0.00220	0.00102	0.00060	0.00080	0.00600
Strip	0.04000	0.03887	0.04045	0.04091	0.03978	0.03752
Membrane	0.00028	0.00031	0.00034	0.00059	0.00048	0.00048
Total	0.04328	0.04138	0.04181	0.04210	0.04106	0.04400
% Recovery	114	111	107	100	96	107
	116	0	21	65	30	14
mass error	14	11	7	0	4	7
average error	7	%				

**Table L.1.4: Mass transfer calculations at different reactant concentrations**

	1	1.5	2	2.5
Feed(t=0)	0.04000	0.04040	0.03700	0.03800
Feed(t=0)	0.00860	0.00554	0.00068	0.00016
Strip	0.02599	0.02938	0.03345	0.02215
Membrane	0.00096	0.00107	0.00059	0.00102
Total	0.03555	0.03599	0.03472	0.02332
% Recovery	89	89	94	61
	116	0	21	65
mass error	11	11	6	9
average error	9	%		

**Table L.1.5: Mass transfer calculations at constant pH**

	100	150	200	250	300
Feed(t=0)	0.01840	0.02960	0.03600	0.04400	0.05600
Feed(t=0)	0.00026	0.00040	0.00068	0.00102	0.00130
Strip	0.01763	0.02825	0.03616	0.04249	0.05379
Membrane	0.00020	0.00045	0.00028	0.00051	0.00068
Total	0.01809	0.02910	0.03712	0.04402	0.05577
% Recovery	98	98	103	100	100
	116	0	21	65	30
mass error	2	2	3	0	0
average error	1	%			

**Table L.1.6: Mass transfer calculations at pH = 2**

---

## NOMANCLATURE

---

A	total internal area of TSLM module (cm <sup>2</sup> )
R	membrane radius (cm)
N	number of tubes
L	tube length
C	copper concentration (g/cm <sup>3</sup> )
d	diameter of one fibre (cm)
$r_i$	inner fibre radius
$r_o$	outer fibre radius
$r_{lm}$	logarithmic mean radius of one fibre
$d_o$	outer fibre diameter
$m_{Cu,feed}$	distribution coefficient in aqueous feed
$m_{Cu,strip}$	distribution coefficient in aqueous strip
$D_{aq,CuSO_4}$	diffusion coefficient of copper complex in feed
$D_{aq,H_2SO_4}$	diffusion coefficient of sulphuric acid complex in strip
$D_{org}$	diffusion coefficient of organic reactant in membrane
$D_{eff}$	effective diffusion coefficient of organic reactant in membrane
$k_i$	mass transfer coefficient of aqueous feed (cm.s <sup>-1</sup> )
$k_m$	membrane mass transfer coefficient (cm.s <sup>-1</sup> )
$k_s$	mass transfer coefficient of aqueous strip (cm.s <sup>-1</sup> )
$k_{org}$	organic mass transfer coefficient for stripping (cm.s <sup>-1</sup> )
$K_{ex}$	extraction constant
$t_m$	thickness of the fibre membrane (cm)
$V_f$	volume of feed tank (cm <sup>3</sup> )
$V_s$	volume of stripping tank (cm <sup>3</sup> )

---

## GREEK SYMBOLS

---

$\varepsilon$	porosity of the membrane
$\tau$	tortuosity of the membrane
$\delta$	membrane thickness
$v_t$	velocity of liquid on tube side (cm/s)
$v_s$	velocity of liquid on shell side (cm/s)

---

## SUBSCRIPTS

---

m	membrane
f	feed side
s	strip side
i	inner
o	outer
t	tube side
aq	aqueous

---

## GLOSSARY

---

- Solvent extraction** A term used to describe a liquid-liquid extraction process that involves a transfer of ionic species from the extractant to the aqueous phase in exchange for ions from the aqueous phase.
- Permeability** The rate of flow of a liquid through a porous material
- Flux** The rate of flow of copper ions through the membrane porous material per unit time per unit area.
- Feed** The stream that flows into any membrane module
- Retentate** That part of the feed retained by the membrane
- Permeate** That part of the feed that crosses the membrane
- Extractant** A viscous chemical solution used to load a metal ion from the aqueous phase. An extractant is usually mixed with a diluent to comprise the organic phase.
- Aqueous phase** The water portion of a system consisting of two liquid phases, one that is primarily water and a second that is a liquid immiscible ( $\text{CuSO}_4$ ) with water

---

## ABBREVIATIONS

---

SLM	Supported liquid membrane
PVDF	Polivinyldenedifluoride
SEM	Scanning electron microscopy
SX	Solvent extraction
IX	Ion exchange
TSLM	Tubular supported liquid membrane
PS	Polysolphone