

STUDIES ON THE ELECTROWINNING OF COPPER FROM DILUTE SOLUTIONS

A Thesis

submitted by

ELSAYED MOSTAFA ELSAYED

(B. SC., HONS, 1990, AIN SHAMS UNIVERSITY)

Under the Supervision of

5413432
E. M.
Prof. Dr. Ahmed Mohamed Azzam

Professor of Physical Chemistry

Faculty of Science

Ain Shams University

63251
Prof. Dr. Ahmed ElSaid Saba

Professor of Extractive

Metallurgy and Head of the

Electro metallurgy Laboratory

CMRDI

To

CHEMISTRY DEPARTMENT

FACULTY OF SCIENCE

AIN SHAMS UNIVERSITY

In partial fulfilment of
the requirements of the award
of the degree of Master of
Science in Chemistry

1997

STUDIES ON THE ELECTROWINNING OF COPPER FROM DILUTE SOLUTIONS

Thesis Advisors

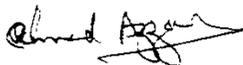
Prof. Dr. Ahmed Mohamed Azzam

Professor of Physical Chemistry,

Faculty of Science,

Ain Shams University

Approved



Prof. Dr. Ahmed Elsaid Saba

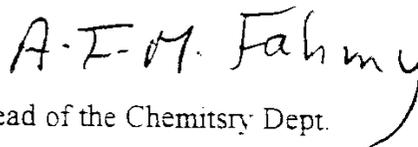


Professor of Extractive Metallurgy

and Head of Electrometallurgy Laboratory,

CMRDI

Prof. Dr. A. F. M. Fahmy



Head of the Chemistry Dept.



ACKNOWLEDGMENT

ACKNOWLEDGMENT

The author wishes to express his deepest gratitude to Prof. Dr. A.M. Azzam, Prof. of Physical Chemistry, Faculty of Science, Ain Shams University for his Sponsorship Interest, and kind help in completion of this work.

I am greatly indebted to Prof. Dr. A. E. Saba, Prof. of Extractive Metallurgy and Head of Electrometallurgy Laboratory, Central Metallurgical Research and Development Institute (CMRDI), for sincere advice, helpful guidance and valuable discussions throughout this work.

I would like to submit my gratitude and deep thanks to Dr. A. E. El-Sherief, Assoc. Prof., Electrometallurgy Lab. (CMRDI), for his continuous support as well as his helpful discussions and interpretation of the results.

Thanks are also due to my colleagues in the Electrometallurgy Lab. for their encouragement and good companionship.

Thanks should be forwarded to the Academy of Scientific Research and Technology for helping me in the preparation of the Thesis.

PREFACE

PREFACE

The present thesis is submitted to the Faculty of Science, Ain Shams University in Partial fulfillment for the requirements of Master of Science in Chemistry. Beside the research work present in this thesis, the candidate attended ten postgraduate courses for one academic year in the following topics

- 1 Corrosion Chemistry
- 2 Electrochemistry
- 3 Catalysis Chemistry
- 4 Surface Chemistry
- 5 Computer
- 6 Thermodynamics
- 7 Quantum Mechanics
- 8 Cement
- 9 Kinetic of Reaction
- 10 Physical Polymers

He has successfully passed the final examination of these courses, besides an English language course.

Head of the Department of chemistry

Prof. Dr. A.F. M. Fahmy

CONTENTS

	Page
ABSTRACT	1
LIST OF FIGURES	2
LIST OF TABLES	12
LIST OF SYMBOLS	15
PROBLEM ORIENTATION AND AIM OF WORK	17
I LITERATURE SURVEY	19
1.1. Sources of Dilute Copper Waste Solutions	19
1.2. Waste Water Treatment Methods	20
1.2.1. Physical processes	20
1.2.1.1 Heat supply (heating) and heat removal (chilling) processes	20
1.2.1.2 Membrane techniques (Reverse Osmosis process)	21
1.2.2. Chemical Processes	21
1.2.2.1 Cementation process	22
1.2.2.2. Precipitation process	24
1.2.2.3. Solvent extraction process	25
1.2.2.4 Ion exchange process	26
1.2.3. Electrolytic processes	29
1.2.3.1. Three-dimensional electrode cells	32
1.2.3.1.1. Fixed bed electrode	33
1.2.3.1.2. Fluidized bed electrode (FBE) cell	34
1.2.3.2. Extended two-dimensional electrode cell "Swiss-roll (S R) cell"	37

	Page	
II	EXPERIMENTAL	39
2.1.	Electrolytes	39
2.2.	The Electrolysis System	40
2.2.1.	Electrolytic cells	40
2.2.1.1.	The fluidized bed electrode cell 'Three-dimensional particulated electrode cell with separator'	40
2.2.1.2.	The Swiss-roll cell	41
2.2.2.	Measuring instruments	41
2.2.3.	Recirculating pump	45
2.2.4.	Visual and photographic investigations	45
2.2.5.	Potentiodynamic measurements	45
2.2.6.	Performance of experiments	45
2.2.6.1.	Electrode pretreatments	45
2.2.6.2.	Cathodic current efficiency calculation	46
2.2.6.3.	Current density measurements	47
2.2.6.4.	Limiting current density measurements	47
III	RESULTS AND DISCUSSION	48
3.1.	Preliminary Work on Copper Electrodeposition from Dilute Copper Sulphate Solutions Using Glassy Carbon Electrode.	48
3.1.1.	Cyclic voltammetry and Potentiodynamic studies	48
3.1.1.1.	Effect of copper ion concentration	50
3.1.1.2.	Effect of flow rate	51
3.1.1.3.	Effect of the presence of foreign cations	55

	Page
3.1.1.3.a. Effect of the presence of iron cations	55
3.1.1.3.b. Effect of the presence of zinc cations	55
3.1.2. Galvanostatic studies	58
3.1.3. Potentiostatic studies	58
3.2. Copper Electrolysis Using Conventional Planar Electrode	62
3.3. Copper Electrowinning from Dilute Solution Using Fluidized Bed Electrode (FBE) Cell	65
3.3.1. Cell voltage and cathodic polarization	65
3.3.1.1. Effect of flow rate on cell voltage	66
3.3.1.2. Effect of current density on cathodic polarization	66
3.3.1.3.a. Effect of deposition time on the cathodic polarization	69
3.3.1.3.b. Effect of deposition time on cell voltage	73
3.3.1.4. Effect of the presence of iron cations on cathodic polarization and cell voltage	78
3.3.1.5. Effect of the presence of zinc cations on cathodic polarization and cell voltage	78
3.3.2. Current efficiency measurements	84
3.3.2.1. Effect of flow rate	84
3.3.2.2. Effect of current density	85
3.3.2.3. Effect of deposition time	87
3.3.2.4. Effect of sulphuric acid concentration	89
3.3.2.5. Effect of the presence of iron cations	93
3.3.2.6. Effect of the presence of zinc cations	93

	Page
3.3.3.	Energy consumption determinations 97
3.3.4.	A stepwise decreasing current programme 103
3.3.5.	Copper electrowinning from waste waters using FBE cell 108
3.3.6.	Microstructure and morphology 111
3.4.	Copper electrowinning from dilute solutions using Swiss roll (SR) cell. 116
3.4.1.	Cathodic polarization and cell voltage 116
3.4.1.1.a.	Effect of current density on cathodic polarization 116
3.4.1.1.b.	Effect of current density on cell voltage 117
3.4.1.2.a.	Effect of deposition time on cathodic polarization 117
3.4.1.2.b.	Effect of deposition time on cell voltage 121
3.4.1.3.	Effect of sulphuric acid concentration on cell voltage 121
3.4.1.4.	Effect of the presence of iron cations on cathodic polarization and cell voltage 121
3.4.1.5.	Effect of the presence of zinc cations on cathodic polarization and cell voltage 127
3.4.2.	Current efficiency measurements 130
3.4.2.1.	Effect of current density 130
3.4.2.2.	Effect of deposition time 130
3.4.2.3.	Effect of sulphuric acid concentration 133
3.4.2.4.	Effect of the presence of iron cations 134
3.4.2.5.	Effect of the presence of zinc cations 134

	Page
3.4.3. Energy consumption determinations	141
3.4.4. A stepwise decreasing current programme	147
3.4.5. Copper electrowinning from waste waters using (SR) cell	150
3.4.6. Microstructure and morphology	152
SUMMARY AND CONCLUSIONS	157
REFERENCES	167
ARABIC SUMMARY	
ARABIC ABSTRACT	

ABSTRACT

ABSTRACT
STUDIES ON THE ELECTROWINNING OF COPPER
FROM DILUTE SOLUTIONS

ELSAYED MOSTAFA ELSAYED

ELECTROMETALLURGY LABORATORY

**CENTRAL METALLURGICAL RESEARCH AND
DEVELOPMENT INSTITUTE**

Copper electrowinning from dilute solutions continues to attract considerable research efforts. The concentration of the metal ions in these solutions are less than 5 gl^{-1} , which are unsuitable for conventional electrolysis cells. Non conventional cells with relatively large cathodic area are essential.

Fluidized bed electrode (FBE) cell and Swiss-roll (SR) cell have been investigated. The effects of cathodic current densities, initial copper concentrations, free sulphuric acid concentration and rate of flow of the solutions on both the cathodic current efficiency and power consumption were studied. The influence of the initial copper and sulphuric acid concentrations on current efficiency was effective at concentrations less than 0.5 gl^{-1} cupric ions and 5 gl^{-1} H_2SO_4 , where a drastic fall in the efficiency was obtained. The effect of the presence of iron and zinc cations on the copper electrowinning process was studied.

Copper could be removed from synthetic and industrial mixtures of Cu Fe Zn sulphate solutions, with no detectable change in the iron and zinc concentration. On the other hand copper was depleted to less than 5 ppm with a current efficiencies more than 65%.

Keywords: Dilute solution, copper electrowinning Fluidized Bed Electrode (FBE) cell, Swiss-roll (SR) cell, cathodic polarization, cell voltage, current efficiency, energy consumption.



LIST OF FIGURES