

شبكة المعلومات الجامعية التوثيق الإلكتروني والميكروفيلو

بسم الله الرحمن الرحيم





MONA MAGHRABY



شبكة المعلومات الجامعية التوثيق الإلكتروني والميكروفيلو



شبكة المعلومات الجامعية التوثيق الالكتروني والميكروفيلم



MONA MAGHRABY



شبكة المعلومات الجامعية التوثيق الإلكترونى والميكروفيلم

جامعة عين شمس التوثيق الإلكتروني والميكروفيلم قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها علي هذه الأقراص المدمجة قد أعدت دون أية تغيرات



يجب أن

تحفظ هذه الأقراص المدمجة بعيدا عن الغبار



MONA MAGHRABY





OPTIMIZING THE PROCESS PARAMETERS IN THE PRODUCTION OF ALUMINA

By

Sohair Taha Aly

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY
in
Chemical Engineering

OPTIMIZING THE PROCESS PARAMETERS IN THE PRODUCTION OF ALUMINA

By **Sohair Taha Aly**

A Thesis Submitted to the Faculty of Engineering at Cairo University in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

in

Chemical Engineering

Under the Supervision of

Prof. Dr. Magdi Fouad Abadir

Prof. Dr. Ibrahim Ahmed Ibrahim

Professor of Inorganic Industries Chemical Engineering Department Faculty of Engineering, Cairo University Professor of Material Science Central Metallurgical Research and Development Institute

OPTIMIZING THE PROCESS PARAMETERS IN THE PRODUCTION OF ALUMINA

By Sohair Taha Aly

A Thesis Submitted to the Faculty of Engineering at Cairo University in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

in **Chemical Engineering**

Approved by the Examining Committee	
Prof. Dr. Magdi Fouad A	Abadir, Thesis Main Advisor
Prof. Dr. Mahmoud Abde	 el Hakim El-Rifai, Internal Examiner
Prof. Dr. Shereen Kamel Research Professor	Amin Kamel, External Examiner

Research Professor Engineering Research Division National Research Centre Engineer's Name: Sohair Taha Aly
Date of Birth: 19/5/ 1977
Nationality: Egyptian

E-mail: sohair@eaeat.edu.eg

Phone: 01148935932

Address: Okba Ib Nafe St,El-Obour City, No#19...

Registration Date: 1 /3 /2017 **Awarding Date:** 1 /3 /2020

Degree: Doctor of Philosophy **Department:** Chemical Engineering

Supervisors:

Prof. Dr. Magdi Fouad Abadir Prof. Dr. Ibrahim Ahmed Ibrahim

Examiners:

Prof. Dr. Magdi Fouad Abadir (Thesis main advisor)
Prof. Dr. Mahmoud Abdel Hakim El-Rifai (Internal examiner)
Prof. Dr. Shereen Kamel Amin Kamel (External Examiner)

Research Professor

Engineering Research Division National Research Centre

Title of Thesis:

OPTIMIZING THE PROCESS PARAMETERS IN THE PRODUCTION OF ALUMINA

Key Words:

Acid Leaching, Statistical Study, Aluminum chloride, Alumina

Summary:

Three parameters were optimized using HCl (32%) to obtain aluminum chloride hexa- hydrate. Three parameters were optimized using response surface methodology approach. Alumina recovery of 83.2% was predicted on using 1.4 stoichiometric acid to solid ratio, a reaction temperature of 104°C and a reaction time of 3 hours. This result was then assessed experimentally. The obtained hexa hydrate was prepared in crystalline form through injection of hydrogen chloride in the saturated solution of aluminum chloride. The hexahydrate crystals obtained were subsequently purified in a three stage process to increase their purity to 99.961%. Roasting of these crystals up to 800°C under flow of argon steam then roasting the produced amorphous aluminum oxide at 1250°C in a continuous flowing of Ar gas and keeping at this temperature for 4 hours, then cooling down to room temperature. Highly crystalline alumina was produced with purity 99.9%.



Disclaimer

I hereby declare that this thesis is my own original work and that no part of it has been submitted for a degree qualification at any other university or institute.

I further declare that I have appropriately acknowledged all sources used and have cited them in the references section.

Name: Sohair Taha Aly	Date:	/	/
Signature:			

Dedication

I dedicate my dissertation work to my dear husband who is the main partner in this work in each step. His words of encouragement and push were always giving me the force to complete this work.

I also dedicate my dissertation work to my loving parents, my sister Kawther and my brother Saad who are not in our world today. Their words of encouragement and push for tenacity ring in my ears. I also dedicate this dissertation to my brothers Mohamed and Kamal and to my family who have supported me throughout the process.

Acknowledgments

Grateful to "Allah"; the most merciful and the most gratuitous.

I'm deeply indebted and grateful to Prof. Magdi Fouad Abadir; who played the basic role for this work to come to light.

I also wish to express my thanks to Prof. Ibrahim Ahmed Ibrahim for his opinions and guidance through all steps in implementation of practical work in this study.

I also wish to express my thanks to Prof. Shereen Mohamed Samir in EA& EAT for her continuous support.

I also wish to express my thanks to my friends, Eng. Kareem Hossam in EA&EAT and Dr Hamdi Mamoun in CMRDI for their continuous support.

.

Table of Content

DISCLAIMER	1
DEDICATION	ii
ACKNOWLEDGMENTS	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
NOMENCLATURE	xi
ABSTRACT	xii
Chapter One: Introduction	
1.1 Alumina	1
1.2 Aim of the present work	3
1.3 Organization of thesis	3
Chapter Two: Literature Review	
2.1. Introduction	5
2.2 Properties of aluminum oxide	5
2.2.1 General outlook	5
2.2.2 Crystal Structure of aluminum oxide	5
2.2.2.1 Introduction	5
2.2.2.2 The θ -alumina phase	6
2.2.2.3 The γ -alumina phase	7
2.2.2.4 The α -alumina phase	7
2.3 Uses of α–alumina	8
2.4. Industrial preparation of aluminum oxide	9
2.4.1 Introduction	9
2.4.2 Extraction of alumina from bauxite ores (Bayer Process)	11
2.4.2.1 Introduction	11
2.4.2.2 Process description.	11
2.4.3 Extraction of alumina from non-bauxite ores	13
2.4.3.1 Introduction	13
2.4.3.2 Thermal activation of non-bauxite ores	14
2.4.3.3 Mechanical activation of non-bauxite ores	15
2.4.3.4 Acid leaching process.	16
2.4.3.5 Leaching using different mineral acids	18
2.4.4 Hydrochloric acid leaching of kaolin clay	18
2.4.4.1 Factors affecting the leaching process	18
2.4.4.2 Optimization of leaching parameters using response surface methodology (RSM)	19
2.4.4.3 Types of experimental design using RSM	20
2.4.5 Purification of aluminum chloride	22

2.4.5.1 Introduction	22
2.4.5.2 Crystallization of aluminum chloride hexa-hydrate	22
2.4.6 Calcination of aluminum chloride hexa- hydrate (ACH) crystals	24
2.5. Kinetics of heterogeneous phase reactions	24
2.5.1 Introduction	24
2.5.2 Kinetic equations	25
2.5.2.1 The progressive reaction model	25
2.5.2.2 The shrinking core model	26
2.5.2.3 Effect of temperature on the rate of reaction	27
2.5.3 Isothermal vs non – isothermal methods	27
2.5.3.1 Introduction.	27
2.5.3.2 Non – isothermal analysis tools	28
2.5.3.3 Non-isothermal kinetic methods	28
Chanton Thuas Evranimental Work	
Chapter Three: Experimental Work 3.1. Materials	31
3.2. Characterization techniques.	31
3.2.1 X – Ray diffraction analysis (XRD).	31
3.2.2 X – Ray fluorescence (XRF)	31
3.2.3 Particle size distribution (PSD)	32
3.2.4 Thermal analysis.	33
·	
3.3 Experimental methods	33
3.3.3.1 Analysis of titanium dioxide	33
3.3.1.2 Analysis of iron oxide	33
3.3.1.3 Analysis of alumina	33 34
3.3.1.4 Statistical analysis of the results of acid leaching	34
3.3.3 Purification of aluminum chloride.	_
3.3.4 Calcination of purified aluminum chloride	35
3.3.4 Calcination of purmed aluminum emoride	37
Chapter Four: Results and Discussion	
4.1. Characterization of kaolin	39
4.1.1 Chemical analysis (XRF)	39
4.4.2Mineralogical analysis (XRD)	39
4.1.3 Thermogravimetric analysis (TGA)	40
4.1.4 Particle size distribution (PSD)	41
4.2 Experimental results of the leaching process	41
4.2.1 First statistical model	41
4.2.1.1 The design matrix	41
4.2.1.2 Statistical analysis of variance	42
4.2.1.3 Interaction between the studied parameters	45
4.2.1.4 Concluding remarks for the first model	49
4.2.2Second statistical model	50
4.2.2.1 The design matrix	50

4.2.2.2 Statistical Analysis of Variance	51
4.2.2.3 Interaction between the studied parameters	53
4.2.2.4 Concluding remarks for the second model	58
4.3 Alumina purification process	59
4.3.1 First trials of purification (three crystallization stages)	59
4.3.2 Second trial of purification process (four crystallization stages)	60
4.3.3 Material balance on different stages of crystallization	61
4.4 Decomposition of AlCl ₃ .6H ₂ O (ACH) to α-Al ₂ O ₃	63
4.4.1 Thermal analysis of aluminum chloride hexa-hydrate	64
4.4.2 Kinetics of decomposition of ACH	66
4.4.3 Effect of calcination temperature on the decomposition products	68
4.5.4 Effect of calcination time	70
4.5.5 Effect of the type of carrier gas	72
4.5.6 Production of chlorine free corundum (α-Al ₂ O ₃)	74
4.5.6.1 Experimental procedure	74
4.5.6.2 First run	75
4.5.6.3Second run.	75
4.5.6.4Third run.	76
4.5.6.5Fourth run	76
4.5.6.6Fifth run	76
4.5.6.2 Concluding remarks	79
Chapter Five: Conclusions	
5.1. Introduction	80
5.2. Leaching process results	80
5.2.1 First model.	80
5.2.2 Second model	80
5.3 Purification Stage	81
5.3.1 Three stages trial	81
5.3.2 Four stages trial	81
5.4. Calcination ACH to alumina	81
5.4.1Kinetic results	82
5.4.2 Calcination parameters	82
5.4.2.1 Temperature effect	82
5.4.2.2 Time effect	82
5.4.2.3 Carrier gas effect	82
5.4.3 Free chlorine alumina	83
References	85

List of Tables

Title	Page. No
Table (2.1): Properties of alumina	5
Table (2.2): Selected properties of some alumina phases	6
Table (2.3): High purity alumina grades (> 99%) and their applications	9
Table (2.4): Low purity alumina $(80 - 90\%)$ 23	9
Table (2.5): Main minerals of bauxite ore deposits	10
Table (2.6): Main bauxite producing countries	11
Table (2.7): Most common non-bauxite minerals	13
Table (2.8): Potential of alumina extraction from non-bauxite ores	14
Table (2.9): Box- Behnken design matrix for three factors	21
Table (2.10): Different forms of the kinetic function $g(\alpha) = k.t$	27
Table (3.1): Standard screen openings	32
Table (3.2): Experimental conditions for the first optimization of the	35
leaching step	
Table (3.3): Experimental conditions for the second optimization of the	35
leaching step	30
Table (4.1): XRF Chemical composition of Kalabsha kaolin	39
Table (4.2): Levels of design (model 1)	42
Table (4.3): Experimental 3 ³ Box-Behnken design for the leaching	43
experiments (model1)	13
Table (4.4): Results of alumina recovery (model 1)	44
Table (4.5): Analysis of variance (ANOVA) table of alumina recovery	45
(model 1)	13
Table (4.6): Correlation table for alumina conversion (model 1)	49
Table (4.7): Chosen levels of variables (model 2)	50
Table (4.8): Experimental 33 Box-Behnken design for the leaching	51
experiments	31
(model 2)	
Table (4.9): Results of alumina recovery (model 2)	53
Table (4.10): Correlation table for alumina conversion (model 2)	58
Table (4.11): ICP Analysis for HCl and water used in crystallization	59
process	39
Table (4.12): ICP Analysis for crystals obtained from the three Stages	60
Table (4.12). ICF Analysis for crystals obtained from the four stages	61
	62
Table (4.14): Material balance of crystallization run for first Stage	02
(average values) Table (4.15): Material belongs of anystallization man for Second Stage	61
Table (4.15): Material balance of crystallization run for Second Stage	64
(average values)	
Table (4.16): Temperatures of decomposition of the hexa-hydrate at	66
different conversion levels	
Table (4.17): Activation energies at different conversion levels	66
Table (4.18): Phases identified on calcination of ACH at different	70
temperatures in argon	
Table (4.19): Peak broadening at $2\theta = 67^{\circ}$ and maximum grain size	70

List of Tables

Title	Page. No
Table (4.20): Effect of holding time on the weight loss, phases present	71
and chlorine content in samples calcined at 1100°C in argon atmosphere	
Table (4.21): Effect of type of gas carrier on the weight loss, phases	75
identified and chlorine content in samples calcined at 1100°C for 5 hours.	
Table (5.1): Stages of preparation of high purity alumina	84