



**Studies on the Extraction of Lanthanides and
Preparation of Pure Calcium Carbonate from
Egyptian Phosphogypsum Produced during
Phosphoric Acid Production Process**

By

Osama El-Sayed Mohamed Roushdy

M. Sc. Chemistry 2014

For the Degree of Doctor of Philosophy (Ph. D.) in
Chemistry

A Thesis Presented

To Chemistry Dept., Faculty of science

Ain Shams University

2018



AIN SHAMS UNIVERSITY
Faculty of science
Chemistry Department

**Studies on the Extraction of Lanthanides and Preparation of
Pure Calcium Carbonate from Egyptian Phosphogypsum
Produced during Phosphoric Acid Production Process**

*A Thesis Presented
To Chemistry Department, Faculty of science
Ain Shams University*

By

Osama El-Sayed Mohamed Roushdy

M.Sc. Inorganic & Analytical Chemistry 2014

For the Degree of Doctor of Philosophy (Ph. D.) in Chemistry

Supervised by

Prof. Dr. Saad Abdel-Wahab Mohamed
Professor of Physical Chemistry
Faculty of Science-Ain shams University

Prof. Dr. Hady Soliman Gado
Professor of Geochemistry
Nuclear Materials Authority, Cairo

Ass. Prof. Mohamed Helmy Taha
Assistant Professor of Physical chemistry
Nuclear Materials Authority, Cairo

2018

ACKNOWLEDGEMENT

I am in greatest thankful to **allah** The Most Merciful, The Most Gracious, by the grace of whom the progress and success of the present work.

It is my pleasure to express my deepest thanks to **Prof. Dr. Saad Abdel-Wahab**, *Prof. of Physical Chemistry, Chemistry Department, Faculty of Science, Ain- Shams University*, for his direct supervising of the work, valuable discussions, encouragement, kind help given throughout this work, and careful revision of the manuscript.

It is my pleasure to express my deep thanks, appreciation and gratitude to **Prof. Dr. Hady S. Gado**, *Professor of Geochemistry, Nuclear Materials Authority, Cairo*, for his support, direct supervision, encouragement, valuable discussions throughout the work. I am greatly indebted for granting me for early stage research training and for his generous help for supervision.

My deep thanks to **Dr. Mohamed H. Taha**, *Assistant Professor of Physical Chemistry, Nuclear Materials Authority, Cairo*, for his direct supervision of the work, encouragement, careful revision of the manuscript and kind help given throughout this work.

My thanks and best wishes extend to all members of the Phosphoric Acid Purification Pilot Plant (**PAPPP**), for

their support and huge facilities offered in different ways during the progress of this work.

My thanks and best wishes extend to ***Dr. K. Ahmed***, *Department of Radiological Protection, Nuclear Materials Authority, Cairo*, for his huge help given throughout this work.

*Last but not Least, my thanks are due to **my parents, my wife, my sister, my children** and all my friends for their love, support and encouragement which gave me the strength to overcome many obstacles. I cannot thank them enough.*

Osama El-Sayed Mohamed Roushdy

ABSTRACT

The utilization of phosphogypsum (PG) as a raw material for the production of valuable products is interesting. In this contribution, Rare earth elements (REEs) leaching from dihydrate phosphogypsum using sulfuric acid was investigated using One-factor-at-a-time (OFAT) methodology and Design of Experiment (DoE) methodology. Based on the OFAT methodology, the influence of various factors affecting the leaching process such as; reaction time, sulfuric acid concentration, liquid to solid ratio, leaching temperature, and stirring speed have been examined terms of high REEs leaching efficiency and low impurities.

In regards to DoE methodology, the multivariate 2^3 full factorial design is used to study the effect of sulfuric acid concentration, liquid/ solid ratio, leaching time on the REEs leaching process. The normal first order model (fitted model) between significant factors and the response was developed by the Design Expert 11.0 software. The obtained results clarify that REEs leaching efficiency was 72.3% under the following optimal conditions; 4 % sulfuric acid concentration, liquid/ solid ratio, ml/ g, 5/1, and reaction time of 3 hrs.

Dihydrate phosphogypsum, treated with sulfuric acid, has been converted into calcium carbonate and sodium sulfate using sodium carbonate. Phosphogypsum conversion process has been investigated using One-factor-at-a-time (OFAT) procedure and Design of Experiment (DoE) procedure. Regards to the OFAT procedure, the effect of different factors such as; stirring time, sodium carbonate concentration, liquid to solid ratio, reaction

temperature, and stirring speed on the conversion process using sodium carbonate have been investigated.

The full factorial design has been performed to optimize the conversion of phosphogypsum to carbonate using sodium carbonate. Four factors were taken into consideration in the experimental planning: time, solid/ liquid ratio, sodium carbonate concentration, and temperature. The analysis of variance (ANOVA) has been used to determine the main effects and interactions between the studied factors. The optimum conditions have been determined as, sodium carbonate concentration of 30 %, reaction time of 10 min and solid/ liquid ratio, g/ ml of 1:2. Under these optimum conditions, the phosphogypsum conversion to carbonate efficiency performance is 95.2 %. The characterization of the produced calcium carbonate has been achieved using XRF, XRD and FT-IR.

The environmental radiation impact as well as radiation hazard indices factors (exposure rate and absorbed dose rate, effective dose rate, the radium equivalent activity (Ra_{eq}), external hazard, internal hazard and (level index) I-gamma) have been measured and calculated in phosphogypsum working sample, phosphogypsum leached with sulfuric acid, produced calcium carbonate, and sodium sulfate. The obtained results clear that, the produced calcium carbonate, and sodium sulfate have normal level of natural background where these values are within the world permissible limits. This means that the produced sodium carbonate and sodium sulfate are acceptable for use in industrial applications.

Keywords: phosphogypsum, Rare earths, calcium carbonate, full factorial design, optimization

CONTENTS	Page
ACKNOWLEDGMENTS	i
ABSTRACT	iii
CONTENTS	v
LIST OF FIGURES	ix
LIST OF TABLES	xiii
ABBREVIATIONS	xvii
CHAPTER 1 INTRODUCTION	
1.1. Background	1
1.2. Geology of Phosphate Rocks	1
1.3. Phosphoric Acid Production	3
1.3.1. Production by Thermal Process	3
1.3.2. Production by Wet Process	3
1.3.2.1. Dihydrate (DH) Process	4
1.3.2.2. Hemihydrate (HH) Process	6
1.3.2.3. Di-hydrate-hemi-hydrate.....	8
1.3.2.4. Hemi-hydrate-di-hydrate with Intermediate Filtration (HDH)	8
1.3.2.5. Re-pulping Process	8
1.4. Production of Phosphogypsum.....	9
1.4.1. Characterization of Phosphogypsum	11
1.4.2. Phosphogypsum Disposal	14
1.5. Environmental Impacts Associated with Phosphogypsum Dumping Yards	16
1.6. Procedures and Costs of Stacking of Phosphogypsum	17
1.7. Phosphogypsum Uses and Conversion	19
1.7.1. Application of PG in Agriculture	19

1.7.2. Phosphogypsum as a Building Material.....	20
1.7.3. Phosphogypsum Conversion.....	21
1.8. Rare Earth Elements in Phosphogypsum.....	24
1.9. Aim of Work.....	32
CHAPTER 2 EXPERIMENTAL	
2.1. Chemical and Reagents	33
2.1.1. Chemicals	33
2.1.2. Reagents	35
2.2. Materials and Apparatus	37
2.3. Measurement Instruments and Equipments	37
2.4. Samples Preparations	39
2.4.1. Solid Samples Preparations	39
2.4.2. Preparation of Some Ions Stock Synthetic Solutions.....	40
2.5. Analytical Procedures.....	41
2.5.1. Phosphorus Determination	41
2.5.2. Sulfate Determination	42
2.5.3. Determination of Uranium Concentration.....	42
2.5.4. Determination of Total Rare Earth Elements	43
2.5.5. Determination of Total Iron.....	44
2.5.6. Calcium determination	44
2.6. Materials	45
2.6.1. Preparation of phosphogypsum working Sample.....	45
2.6.2. Characteristics of phosphogypsum.....	45
2.7. Experimental Procedures	47
2.7.1. Rare Earth Elements (REEs) Leaching Procedure.....	47
2.7.2. Phosphogypsum conversion to calcium carbonate Procedure.....	48
2.8. Design of Experiments	49

2.9. Measurement of Radionuclide Concentrations (^{238}U , ^{226}Ra , ^{232}Th and ^{40}K) with Gamma-Ray Spectroscopy.....	51
---	----

CHAPTER 3 RESULTS AND DISCUSSIONS

3.1 Rare Earth Elements Leaching Investigation	53
3.1.1. One-factor-at-a-time methodology	53
3.1.1.1 Effect of Sulfuric Acid Concentration	54
3.1.1.2 Effect of Reaction Time.....	56
3.1.1.3 Effect of Sulfuric Acid/ Phosphogypsum, v/ m, Ratio.....	58
3.1.1.4 Effect of Reaction Temperature.....	60
3.1.1.5 Effect of Mixing Stirring Speed.....	62
3.1.2. Statistical design of experiments method.....	64
3.1.2.1. The Significant Parameters.....	65
3.1.2.2. The Statistical Analysis for the Proposed Model.....	75
3.1.2.3. Influence of Main factors on the leaching process.....	77
3.1.2.3.1. Effect of sulfuric acid concentrations.....	77
3.1.2.3.2. Effect of liquid/ solid mass ratio.....	79
3.1.2.3.3. Effect of reaction time.....	80
3.1.2.4. Influence of factor Interaction on the leaching process.....	82
3.1.3. Optimization the leaching process.....	86
3.1.4. Validation of the model	89
3.1.5 Specification of Leached Acidulate Solution.....	91
3.2. Phosphogypsum conversion to calcium carbonate investigation	94
3.2.1. One-factor-at-a-time method.....	94
3.2.1.1. Effect of Reaction Stirring Time.....	95
3.2.1.2. Effect of Sodium Carbonate Concentration.....	97
3.2.1.3. Effect of sodium carbonate to phosphogypsum mass ratio ml / g.....	99
3.2.1.4. Effect of Reaction Temperature.....	101

3.2.1.5. Effect of Stirring speed	103
3.2.2. Statistical design of experiments method.....	105
3.2.2.1. The Significant Parameters.....	106
3.2.2.2. The Statistical Analysis for the Proposed Model.....	113
3.2.2.3. Influence of Main Factors on Phosphogypsum Conversion Process.....	117
3.2.2.3.1. Effect of sodium carbonate concentration.....	117
3.2.2.3.2. Effect of liquid/ solid ratio.....	118
3.2.2.3.3. Effect of stirring time.....	119
3.2.2.3.4. Effect of temperature.....	120
3.2.2.4. Influence of Factor Interaction on Phosphogypsum conversion process.....	121
3.2.3. Validation of the model.....	126
3.3. Characterization of the produced solid.....	127
3.4. Natural radioactive level and radiation Hazards Measurements.....	131
3.4.1. The specific activities of ^{238}U , ^{232}Th , ^{226}Ra and ^{40}K	132
3.4.2. Dose assessment and Radiological effects.....	133
3.4.2.1. Radium Equivalent Activity (Ra_{eq}).....	133
3.4.2.2. The external and internal hazard index (H_{ex} & H_{in}).....	135
3.4.2.3. Radioactivity level index (I_{γ}).....	136
3.4.2.4. Gamma-absorbed dose rate (D).....	137
3.4.2.5. Annual effective dose equivalent, AEDE.....	138
3.4.2.6. Exposure rate (ER).....	139
SUMMARY AND COCLUSTION.....	141
REFERENCES	147
ARABIC SUMMARAY	

List of Figures

Figure		Page
1.1	Dihydrate process	5
1.2	Hemihydrate process	7
1.3	Dependence of calcium sulfate hydrate crystallization on temperature and P_2O_5	10
1.4	Dependence of calcium sulfate Dihydrate/Hemihydrate equilibrium on sulfuric acid concentration.....	10
2.1	Phosphorus calibration curve.....	41
2.2	Sulfate calibration curve	42
2.3	Uranium calibration curve	43
2.4	REEs calibration curve.....	44
2.5	X-ray diffraction pattern of phosphogypsum sample.....	46
2.6	IR spectra of phosphogypsum sample.....	47
3.1	Effect of acid concentration on REEs and Fe_2O_3 leaching efficiency from phosphogypsum (particle size: 100 μm ; v/ m ratio: 9 ml/ 1.0 g; rpm: 400; time: 60 min; temperature: 25 $^{\circ}C$).....	55
3.2	Effect of reaction time on REEs and Fe_2O_3 leaching efficiency from phosphogypsum (particle size: 100 μm ; v/ m ratio: 5 ml/ 1.0 g; rpm: 400; H_2SO_4 concentration: 6.0 %; temperature: 25 $^{\circ}C$).....	57

3.3	Effect of sulfuric acid/ phosphogypsum mass ratio on REEs and Fe ₂ O ₃ leaching efficiency from phosphogypsum (particle size: 100 µm; temperature: 25 °C; rpm: 400; time: 4 hrs; sulfuric acid concentration: 6.0 %).	59
3.4	Effect of reaction temperature on REEs and Fe ₂ O ₃ leaching efficiency from phosphogypsum (particle size: 100 µm; v/ m ratio: 60 ml/ 10 g; rpm: 400; time: 4 hrs; sulfuric acid concentration: 6.0 %)	61
3.5	Effect of mixing stirring speed on REEs and Fe ₂ O ₃ leaching efficiency from phosphogypsum (particle size: 100 µm; v/ m ratio: 60 ml/ 10 g; temperature: 25 °C; time: 4 hrs; sulfuric acid concentration: 6.0 %).	63
3.6	Normal probability plot of the standardized effects for REEs leaching.	74
3.7	Normal probability plot of the standardized effects for Fe ₂ O ₃ leaching.	74
3.8A	Effect of sulfuric acid concentrations on REEs leaching process	78
3.8B	Effect of sulfuric acid concentrations on Fe ₂ O ₃ leaching process	78
3.9A	Effect of liquid/ solid ratio on REEs leaching process	79
3.9B	Effect of liquid/ solid ratio on Fe ₂ O ₃ leaching process	80
3.10A	Effect of time on REEs leaching process	81
3.10B	Effect of time on Fe ₂ O ₃ leaching process	81
3.11(i,ii,iii)	Interaction effect plot for REEs leaching efficiency.....	83
3.12(i,ii,iii)	Interaction effect plot for Fe ₂ O ₃ leaching efficiency.....	84
3.13	Surface plots of leached REEs.....	85
3.14	Surface plots of leached Fe ₂ O ₃	86
3.15	Scatter diagram of experimental values versus predicted values by Equations 4.....	89

3.16	Scatter diagram of experimental values versus predicted values by Equations 5.....	90
3.17	Effect of reaction time on the conversion of phosphogypsum to calcium carbonates (Na_2CO_3 (10%)) sodium carbonate to phosphogypsum mass ratio 30 ml / 10 g at room temp., 600 rpm.....	96
3.18	Effect of sodium carbonate concentration on the conversion of phosphogypsum to calcium carbonate, sodium carbonate to phosphogypsum mass ratio 3/1 ml/g, time 30 min. at 600 rpm at room temperature.....	98
3.19	Effect of sodium carbonate to phosphogypsum mass ratio ml / g on the conversion of phosphogypsum to calcium carbonate (Na_2CO_3 (30%), time 30 min., at room temp., 600 rpm.....	100
3.20	Effect of temperature on the conversion of phosphogypsum to calcium carbonate, sodium carbonate to phosphogypsum mass ratio 3/1 ml/g, (Na_2CO_3 (30%), time 30 min. at 600 rpm	102
3.21	Effect of Stirring speed on the conversion of phosphogypsum to calcium carbonate, sodium carbonate to phosphogypsum mass ratio 3/1 ml/g, Na_2CO_3 (30%), time 30 min. at 50 °C.....	104
3.22	Normal probability plot of the standardized effects.....	110
3.23	Pareto Chart of the Standardized Effects.....	111
3.24	Normal Plot of Residuals.....	116
3.25	Plot of residuals versus predicted recoveries.....	117
3.26	Effect of sodium carbonate concentrations on phosphogypsum conversion.....	118
3.27	Effect of aqueous/ organic ratio on phosphogypsum conversion process.....	119
3.28	Effect of time on phosphogypsum conversion process.....	120
3.29	Effect of temperature on phosphogypsum conversion process.....	121
3.30(a-f)	The interaction effect plot of phosphogypsum conversion process	123

3.31	Contour plots of phosphogypsum conversion process.....	124
3.32	Surface plots of phosphogypsum conversion process.....	125
3.33	Scatter diagram of actual values versus predicted values by Equation (11).....	126
3.34	X-ray diffraction pattern of the produced calcium carbonate...	128
3.35	IR spectra of the produced calcium carbonate.....	129
3.36	X-ray diffraction pattern of the produced sodium sulfate.....	130
3.37	IR spectra of the produced sodium sulfate.....	131

List of Tables

Table	Page
1.1 Variations in chemical analysis of various phosphate rocks	2
1.2 Chemical composition of raw PG in percentage.....	12
1.3 Main rare earth elements and heavy metals in PG.....	12
1.4 Radioactive nuclides in PG.....	13
1.5 Rare earth content of phosphate rock.....	25
2.1 List of Utilized Chemicals and Reagents	33
2.2 Chemical analysis of phosphogypsum sample.....	46
3.1 Effect of acid concentration on REEs and Fe ₂ O ₃ leaching efficiency from phosphogypsum (particle size: 100 µm; v/ m ratio: 9 ml/ 1.0 g; rpm: 400; time: 60 min; temperature: 25 °C).....	55
3.2 Effect of reaction time on REEs and Fe ₂ O ₃ recovery efficiency from phosphogypsum (particle size: 100 µm; v/ m ratio: 5 ml/ 1.0 g; rpm: 400; H ₂ SO ₄ concentration: 6.0 %; temperature: 25 °C).....	57
3.3 Effect of sulfuric acid/ phosphogypsum mass ratio on REEs and Fe ₂ O ₃ leaching efficiency from phosphogypsum (particle size: 100 µm; temperature: 25 °C; rpm: 400; time: 4 hrs; sulfuric acid concentration: 6.0 %)	60