

Ain Shams University Faculty of Science

EXTRACTTION OF URANIUM AND COPPER FROM CALCAREOUS SHALE, UM BOGMA FORMATION, G. ALLOUGA, SOUTH WESTERN, SINAI-EYGPT.

A Ph.D. Thesis Submitted

To

Chemistry Department Faculty of Science Ain Shams University

By

Soaad Mohamed Sabry Ahmed Elashry

M. Sc. (**Inorganic Chemistry**) Nuclear Materials Authority



Ain Shams University Faculty of Science

EXTRACTTION OF URANIUM AND COPPER FROM CALCAREOUS SHALE, UM BOGMA FORMATION, G. ALLOUGA, SOUTH WESTERN, SINAI-EYGPT.

Ph.D. Thesis Submitted

By

Soaad Mohamed Sabry Ahmed Elashry M. Sc. (Inorganic Chemistry)

To

Chemistry Department Faculty of Science-Ain Shams University

For the requirements

Degree of Doctor of Philosophy (Ph.D.) in Science (Chemistry)

Under Supervision of

Prof. Dr. Mohamed M. Abo-Aly

Prof. of Inorganic Chemistry Faculty of Science, Ain Shams University Prof. Dr. Sofia Yahia Afifi

Prof. of Geochemistry
Vice Chairman of Nuclear Materials
Authority

ACKNOWLEDGEMENT

Thanks God for your blessing and help during this study

I would like to thank and appreciate **Prof. Dr. Mohamed Mahmoud Abo -Aly**, Professor of inorganic Chemistry, Faculty of Science, Ain Shams University for his supervision, guidance and continuous encouragement and critical review for the present work.

My deep thanks and gratitude to **Prof. Dr. Sofia Yahia Afifi Mohamed,** Prof. of Geochemistry, the vice chairman of Nuclear Materials Authority (NMA) for suggesting the point of research, her direct supervision and guidance, fruitful scientific discussion, valuable advises, help offering during the progress of the study, reading, her insight on both the professional and personal levels which gave me the greatest helps to accomplish this study

My thanks and gratitude is also due to **Dr. Mohamed Mohamed Goda**, lecturer of Geochemistry, NMA for his help, encouragement and fruitful discussion.

Thanks are also for **prof. Dr. Ibrahim E. Elassy**, Prof. of field geology and former vice chairman of Nuclear Materials Authority (NMA) for his interesting discussion and continuous interest.

I am deeply indebted to all my colleagues and staff members of Major Chemical Analysis Lab. (Inshas), Nuclear Materials Authority for their help and encouragement.

I express my deep thanks to my family for the continuous encouragement during all stages of this work.

Soaad M. El-Ashry

Abbreviations used

ADU Ammonium diuranate

AMP Ammonium molybdophosphate

BSE Back scatter electronic

Cuprizone Oxalic acid bis(cyclohexylidene hydrazide)

DEHPA Diethylhexyl-phosphoric acid

Ea Activation energy

EDTA Ethylene di amine tetra acetic acid

EDX Energy dispersive X-ray

ESEM Environmental scanning electron microscope

g/L Gram per litre

HCHO Formaldehyde

hr Hour

IAEA International Atomic Energy Agency

ICP-AES Inductively coupled plasma mass spectrometer

ICP-OES Inductively coupled plasma optical emission spectrometer

IRA-400 Amberlit IRA-400 resin

ISL Insitu leaching

K_d Distribution constant

L.O.I Loss on ignition

LIX984N 2- hydroxy-5-nonylacetophenone oxime

NMA Nuclear Materials Authority

ppm Part per million

R Universal gas constant, 8.314 Jmol⁻¹ K⁻¹

REEs Rare earth elements

RIa-mag Glycidyl methacrylate chelating resin

rpm Round per minute

List of Abbreviations

S/L Solid- liquid ratio

T Reaction temperature, K^o

TBP Tributyl phosphate

TPPO Triphenyl phosphine oxide

w.s.r Wet settled resin

XRD X-ray diffraction

XRF X-ray fluorescence

ΔH Enthalpy change

ΔS Entropy change

CONTENTS

| Abbreviations List of Tables List of Figures Abstract | | Page VI VIII IX XII |
|--|---|---------------------------------|
| | CHAPTER –I INTRODUCTION AND LITERATURE SURVEY | |
| 1.1. | General outlook and aim of work | 1 |
| 1.2. | Some aspects of the elements under study | 3 |
| 1.2.1 | Uranium | 3 |
| 1.2.1.1. | Chemistry of uranium | 4 |
| 1.2.1.2. | Uses of uranium | 5 |
| 1.2.2 | Copper | 5 |
| 1.2.2.1. | Chemistry of copper | 6 |
| 1.2.2.2. | Uses of copper | 6 |
| 1.3. | Uranium and copper ore processing technologies | 7 |
| 1.3.1. | Ore preliminary concentration and treatment | 7 |
| 1.3.2. | Pre - concentration operations | 8 |
| 1.3.2.1. | Floatation | 8 |
| 1.3.2.2. | Roasting | 9 |
| 1.4. | Extractive hydrometallurgy of uranium and copper | |
| 1.1. | rocks | 9 |
| 1.4.1. | Uranium - copper leaching | 9 |
| 1.4.1.1 | Conventional techniques | 9 |
| 1.4.1.1.1 | Atmospheric agitation leaching | 9 |
| 1.4.1.1.2 | Pressure leaching | 10 |
| 1.4.1.1.3 | Strong acid pugging and curing | 10 |
| 1.4.1.1.4 | Percolation leaching | 10 |
| 1.4.1.2 | Non-conventional techniques | 11 |
| 1.4.1.2.1 | In-Situ leaching | 11 |
| 1.4.1.2.2 | Bacterial leaching | 11 |
| 1.4.1.2.3 | Heap leaching | 13 |
| 1.5. | Leaching reagents for leaching uranium and copper | |
| | from their rocks | 13 |
| 1.5.1. | Acidic leaching | 13 |
| 1.5.2. | Alkaline leaching | 15 |

| | CO | NTENTS |
|------------|---|--------|
| 1.6. | Separation methods of uranium and copper | 17 |
| 1.6.1. | Precipitation method | 17 |
| 1.6.2. | Co-precipitation | 18 |
| 1.6.3. | Solvent extraction | 18 |
| 1.6.4. | Ion exchange | 21 |
| 1.6.4.1. | Chemistry of ion exchange process | 22 |
| 1.6.4.1.1. | Sorption reactions | 23 |
| 1.6.4.1.2. | Elution reaction | 23 |
| 1.7. | Concentrated uranium production | 24 |
| 1.8. | Literature review | 26 |
| | CHAPTER II | |
| | EXPERIMENTAL WORK | |
| 2.1. | Materials | 37 |
| 2.1.1. | Chemicals and reagent | 37 |
| 2.1.2. | Lewatit mono plus M-500 Resin for uranium | 37 |
| 2.1.2. | separation. | 31 |
| 2.1.2.1. | Characterization of Lewatit Resin | 37 |
| 2.1.2.2. | Properties of Lewatit Resin | 39 |
| 2.1.3. | LIX-984N Extractant for copper separation. | 39 |
| 2.1.3.1. | LIX-984N characterization | 39 |
| 2.1.3.2. | Main advantages of LIX-984N | 39 |
| 2.2. | Instrumentation and equipment. | 40 |
| 2.2.1. | General | 40 |
| 2.2.2. | pH measurement | 41 |
| 2.2.3. | U.V. Visible spectrophotometeric measurements. | 41 |
| 2.2.4. | Flame photometer | 41 |
| 2.2.5. | X-ray diffraction | 42 |
| 2.2.6. | X-ray fluorescence. | 42 |
| 2.2.7. | Environmental Scanning Electron Microscope | 42 |
| 2.2.8. | Atomic absorption spectrometer | 42 |
| 2.2.9. | Inductively Coupled Plasma-Optical Emission | |
| | Spectrometer | 43 |
| 2.3. | Material preparations | 43 |
| 2.3.1. | Preparation of uranium stock synthetic solution | 43 |
| 2.4. | Analytical methods | 43 |
| 2.4.1. | Chemical analysis of major oxides | 43 |
| 2.4.2. | Trace elements determination. | 44 |
| 2.4.3. | Control chemical analysis of uranium | 44 |
| 2.4.3.1. | Spectrophotometric technique | 44 |
| 2.4.3.2. | Oxidometric titration | 45 |
| 2.4.4. | Control chemical analysis of copper | 45 |

| | CO | ONTENTS |
|------------|--|------------|
| 2.4.4.1. | Spectrophotometric technique | 45 |
| 2.4.5. | Determination of thorium using Arsenazo III | |
| | reagent | 47 |
| 2.4.6. | Determination of total rare earth elements | 47 |
| 2.5. | Leaching process | 48 |
| 2.6. | Recovery studies for both uranium and copper | 50 |
| 2.6.1. | Sorption of uranium using column technique by | |
| | Lewatit mono Plus M500 resin (Solid - liquid | |
| | extraction). | 50 |
| 2.6.2. | Uranium elution from the loaded anion exchange | |
| | resin | 51 |
| 2.7. | Precipitation of uranium concentrate | 51 |
| 2.8. | Extraction of copper | 51 |
| 2.8.1. | Extraction of copper from carbonate leach liquor | 51 |
| 2.8.2. | Extraction of copper using LIX 984N from sulfate | 7 1 |
| 2021 | leach liquor (Liquid- liquid extraction). | 51 |
| 2.8.2.1. | Extraction process | 52 53 |
| 2.8.2.2. | Stripping process Procinitation of compar from strip Solution | 53 54 |
| 2.9. | Precipitation of copper from strip Solution | 34 |
| | CHAPTER III | |
| | RESULTS AND DISCUSSION | |
| 3.1. | Chemical characterization of the study calcareous | |
| 5.1. | shale | 55 |
| 3.2. | Mineralogical characteristics of the studied sample | 57 |
| 3.3. | Leaching processes | 62 |
| 3.3.1. | Alkaline leaching of uranium and copper from | 02 |
| 0.0.1 | calcareous shale sample | 63 |
| 3.3.1.1. | Chemistry of carbonate leaching process | 63 |
| 3.3.1.2. | Batch Leaching | 64 |
| 3.3.1.2.1. | Effect of different alkaline reagents | 65 |
| 3.3.1.2.2. | Effect of the ammonium carbonate concentration | 66 |
| 3.3.1.2.3. | Effect of the ammonium bicarbonate concentration | 67 |
| 3.3.1.2.4. | Effect of calcareous shale grain size. | 69 |
| 3.3.1.2.5. | Effect of solid/liquid ratio (S/L) | 70 |
| 3.3.1.2.6. | Effect of oxidant addition | 70 |
| 3.3.1.2.7. | Effect of agitation time | 72 |
| 3.3.1.2.8. | Effect of temperature | 73 |
| 3.3.1.3. | Preparation of alkaline leach liquor | 74 |
| 3.3.2. | Acidic leaching of uranium and copper | 75 |

| | | CONTENTS |
|------------|--|----------|
| 3.3.2. 1. | Chemistry of uranium leaching using H ₂ SO ₄ | 76 |
| 3.3.2.2. | Batch Leaching | 77 |
| 3.3.2.2.1. | Effect of grain size on leaching efficiency of coppe | r |
| | and uranium | 77 |
| 3.3.2.2.2. | Effect of sulfuric acid concentration on leaching | |
| | efficiency of copper and uranium | 78 |
| 3.3.2.2.3. | Effect of solid / liquid ratio on the leaching | |
| | efficiency of uranium and copper | 79 |
| 3.3.2.2.4. | Effect of contact time on the leaching efficiency of | |
| | uranium and copper | 81 |
| 3.3.2.2.5. | Effect of temperature on the leaching efficiency of | 82 |
| | uranium and copper | |
| 3.3.3.3. | Preparation of acidic leach liquor | 83 |
| 3.4. | Recovery of uranium and copper from alkaline | |
| | leach liquor | 85 |
| 3.4.1. | Recovery of uranium from carbonate leach liquor | 85 |
| 3.4.1.1. | Sorption of uranium | 86 |
| 3.4.1.1.1 | Effect of pH on uranium recovery from carbonate | |
| | media | 86 |
| 3.4.1.1.2. | Uranium loading | 87 |
| 3.4.1.1.3. | Uranium elution profile | 88 |
| 3.4.1.2. | Preparation and qualification of the final uranium | |
| | concentrate from carbonate media | 89 |
| 3.4.2. | Recovery of copper from carbonate leach liquor | 90 |
| 3.5. | Recovery of uranium and copper from acidic leach | |
| | liquor. | 91 |
| 3.5.1. | Recovery of uranium from acidic leach liquor | 91 |
| 3.5.1.1. | Effect of pH on uranium extraction from sulfate | |
| | media | 91 |
| 3.5.1.2. | Sorption of uranium | 92 |
| 3.5.1.2.1. | Uranium loading | 92 |
| 3.5.1.2.2. | Uranium elution profile | 94 |
| 3.5.1.2. | Preparation and qualification of the final uranium | |
| | concentrate from sulfate media | 94 |
| 3.5.1.3. | Purification of the uranium concentrate produced | |
| | from acidic media | 95 |
| 3.5.2. | Recovery of copper from sulfate leach liquor | |
| | (Liquid- liquid extraction). | 96 |
| 3.5.2.1. | Factors affecting the extraction of copper | 97 |
| 3.6.2.1.1. | Effect of different diluents | 97 |
| 3.6.2.1.2. | Effect of equilibrium pH on Cu extraction | 99 |
| 3.6.2.1.3. | Effect of LIX-984N concentration | 100 |

| | CONTENTS |
|---|--|
| Effect of shaking time. | 101 |
| _ | 101 |
| Effect of aqueous to organic (A/O) phase ratio | 104 |
| Copper stripping | 105 |
| Factors affect the stripping of copper | 105 |
| Effect of H ₂ SO ₄ acid concentration on copper | |
| stripping | 105 |
| Effect of contact time on copper stripping | 106 |
| Effect of organic /aqueous (O/A) phase ratio | 107 |
| Preparation and quantification of the copper | |
| concentrate product | 108 |
| Proposed flow sheets for alkaline and acidic | |
| recovery of uranium and copper from calcareous | |
| shale sample, Um Bogma formation, G. Allouga, | |
| South western, Sinai, Egypt. | 109 |
| - | |
| | 110 |
| ± • | |
| copper using acidic leaching. | 112 |
| ND CONCLUCION | 114 |
| SUMMARY AND CONCLUSION | |
| REFERENCES ARABEC SUMMARY | |
| | Factors affect the stripping of copper Effect of H ₂ SO ₄ acid concentration on copper stripping Effect of contact time on copper stripping Effect of organic /aqueous (O/A) phase ratio Preparation and quantification of the copper concentrate product Proposed flow sheets for alkaline and acidic recovery of uranium and copper from calcareous shale sample, Um Bogma formation, G. Allouga, South western, Sinai, Egypt. Proposed flow sheet for recovery of uranium and copper using alkaline leaching. Proposed flow sheet for recovery of uranium and copper using acidic leaching. |

LIST OF TABLES

| Table (1) | The Chemicals and reagents | 38 |
|-------------------|---|-----|
| Table (2) | The studied factors affect the agitation leaching of the calcareous shale sample. | 49 |
| Table (2) | • | 47 |
| Table (3) | Chemical analysis of average major oxides in (Wt %), | |
| | calcareous shale samples, Um Bogma Formation, | ~ ~ |
| T. 11 (4) | Gabel Allouga, Sinai, Egypt. | 56 |
| Table (4) | Average concentration of U, Th, and \sum REEs (ppm), | |
| | of calcareous shale sample, Um Bogma Formation, | |
| | Gabel Allouga, Sinai, Egypt. | 57 |
| Table (5) | X-ray diffraction data of studied calcareous shale | |
| | minerals, Um Bogma formation, G. Allouga, south | |
| | western, Sinai, Egypt. | 61 |
| Table (6) | Leaching of Cu and U from calcareous shale by | |
| | different alkaline mixture. | 65 |
| Table (7) | Chemical analysis of prepared leach liquor using | |
| | alkaline leaching of calcareous shale sample. | 75 |
| Table (8) | Chemical analysis of prepared sulfate leach liquor | |
| . , | using acidic leaching of calcareous shale sample. | 84 |
| Table (9) | Comparison between factors controlling alkaline and | |
| () | acidic leaching processes on calcareous shale, Um | |
| | Bogma formation, G. Allouga, South western, Sinai, | |
| | Egypt | 85 |
| Table (10) | Affect the dielectric constant of the diluent on copper | |
| | extraction efficiency from sulfate leach liquor. | 98 |
| Table (11) | Thermodynamic parameters of copper extraction from | , 0 |
| 14610 (11) | sulfate leach liquor using LIX 984N as extractant. | 103 |
| Table (12) | Effect of A/O phase ratio on copper extraction by | 105 |
| 1 abic (12) | 4% LIX 983N in kerosene | 104 |
| Table (13) | Effect of O/A phase ratio on copper stripping from | |
| 1 abic (10) | loaded 4% LIX 984N in kerosene by 3M H ₂ SO ₄ with | |
| | shaking time 4min | 108 |
| | shaking time. | 100 |

LIST OF FIGURES

| Fig. (1) | Geologic map of the studied area | 2 |
|------------------|--|----|
| Fig. (2) | Leaching methods and techniques | 12 |
| Fig. (3) | Generalized processes for production of uranium | |
| O , , | concentrate | 25 |
| Fig. (4) | Structure of anionic resin | 39 |
| Fig. (5) | Reaction between LIX984N and copper | 40 |
| Fig. (6) | The standard curve for uranium spectrophotometric | |
| U () | determination at 655nm by Metertch Single Beam | |
| | spectrophotometer at 25°C | 45 |
| Fig. (7) | Calibration curve of copper using cuprizone reagent | 47 |
| Fig. (8) | EDX and BSE image showing uranophane adsorbed on | 58 |
| | ilmenite | |
| Fig. (9) | EDX and BSE image showing calcopyrite mineral | 58 |
| Fig. (10) | EDX and BSE image showing copper oxide mineral | 59 |
| Fig. (11) | EDX and BSE image showing pyrite mineral | 59 |
| Fig. (12) | EDX and BSE image showing gypsum mineral | 59 |
| Fig. (13) | EDX and BSE image showing HREEs- bearing mineral | 60 |
| Fig. (14) | X-ray diffraction pattern of studied calcareous shale | |
| | minerals, Um Bogma formation, G. Allouga, south western, | |
| | Sinai, Egypt. | 60 |
| Fig. (16) | Effect of (NH ₄) ₂ CO ₃ concentration on U and Cu leaching | |
| | efficiencies, from calcareous shale, Um Bogma formation, | |
| | G. Allouga, Sinai, Egypt. | 67 |
| Fig. (17) | Effect of (NH ₄)HCO ₃ concentration on U and Cu leaching | |
| | efficiencies, from calcareous shale, Um Bogma formation, | |
| 71 (10) | G. Allouga, Sinai, Egypt. | 68 |
| Fig. (18) | Effect of grain size on U and Cu leaching efficiencies, from | |
| | calcareous shale sample, Um Bogma formation, | |
| F: (10) | G. Allouga, South western, Sinai, Egypt. | 69 |
| Fig. (19) | Effect of solid/liquid ratio on U and Cu leaching | |
| | efficiencies, from calcareous shale sample, Um Bogma | 70 |
| E:- (20) | formation, G. Allouga, South western, Sinai, Egypt. | 70 |
| Fig. (20) | Effect of oxidant H ₂ O ₂ on U and Cu leaching efficiencies, | |
| | from calcareous shale sample, Um Bogma formation, | 70 |
| Fig. (21) | G. Allouga, South western, Sinai, Egypt. | 70 |
| Fig. (21) | Effect of leaching time on U and Cu leaching efficiencies, | |
| | from calcareous shale sample, Um Bogma formation, G. Allouga, South western, Sinai, Egypt. | 72 |
| Fig. (22) | Effect of leaching temperature on U and Cu leaching | 12 |
| Fig. (22) | efficiencies from calcareous shale sample Um Bogma | |
| | circleneres from careareous share sample of Dogina | |

| Fig. (23) | formation, G. Allouga, South western, Sinai, Egypt. Effect of Effect of grain size on U and Cu leaching | 73 |
|------------------|--|-----|
| | efficiencies, from calcareous shale sample, Um Bogma | |
| | formation, G. Allouga, South western, Sinai, Egypt. | 78 |
| Fig. (24) | Effect of sulfuric acid concentrations on and Cu leaching | |
| | efficiencies calcareous shale sample, Um Bogma formation, | |
| | G. Allouga, South western, Sinai, Egypt. | 79 |
| Fig. (25) | Effect of Solid /Liquid phase ratio on uranium and copper | |
| | leaching efficiencies, calcareous shale sample, Um Bogma | |
| | formation, G. Allouga, South western, Sinai, Egypt. | 80 |
| Fig. (26) | Effect of agitation time on uranium and copper leaching | |
| 8 () | efficiencies, calcareous shale sample, Um Bogma formation, | 0.1 |
| | G. Allouga, South western, Sinai, Egypt. | 81 |
| Fig. (27) | Effect of leaching temperature on uranium and copper | |
| 0 () | leaching efficiencies, calcareous shale sample, Um Bogma | |
| | formation, G. Allouga, South western, Sinai, Egypt. | 82 |
| Fig. (28) | Effect of pH on uranium adsorption using Lewatit Mono | |
| | Plus M500 resin from carbonate leach solution. | 87 |
| Fig. (29) | Adsorption curve for uranium extraction from carbonate | |
| | leach liquor of calcareous shale using Lewatit Mono Plus | |
| | M500 (each aliquot sample vol. =150 mL). | 88 |
| Fig. (30) | Elution bell curve for uranium from loaded Lewatit Mono | |
| | plus M500 anion exchange resin. | 89 |
| Fig. (31) | X-ray fluorescence qualitative analysis of the prepared | 90 |
| | sodium diuranate. | |
| Fig. (32) | X-ray fluorescence analysis of the prepared copper oxide. | 91 |
| Fig. (33) | Effect of pH on extraction of uranium using Lewatit | |
| (- 1) | MonoPlus M500 resin from sulfate solution. | 92 |
| Fig. (34) | Adsorption curve for uranium extraction from suphate | |
| | leach solution of calcareous shale using Lewatit Mono Plus | 02 |
| E: (25) | M500 (each aliquot sample vol.=100 mL). | 93 |
| Fig. (35) | Elution bell curve for uranium from loaded Lewatit Mono | 04 |
| Eig (26) | plus M500 anion exchange resin. | 94 |
| Fig. (36) | X-ray diffraction analysis of the prepared uranium oxide UO ₃ . | 95 |
| Fig. (27) | · · | 93 |
| Fig. (37) | X-ray fluorescence analysis of the prepared uranium oxide UO ₃ . | 96 |
| Fig. (38) | Effect of different diluents on copper extraction. | 98 |
| Fig. (39) | Effect of pH on copper extraction efficiency. | 99 |
| Fig. (40) | Effect of LIX-984N conc, on copper extraction efficiency. | 100 |
| Fig. (41) | Effect of shaking time on copper extraction efficiency. | 101 |
| Fig. (42) | Effect of temperature on copper extraction efficiency. | 102 |
| Fig. (43) | | 103 |

| Fig. (44) | Effect of H ₂ SO ₄ acid concentration on copper stripping | |
|--------------|---|-----|
| | efficiency. | 106 |
| Fig. (45) | Effect of shaking time on copper stripping efficiency. | 107 |
| Fig. (46) | XRD diffraction data of copper sulfate product. | 108 |
| Fig. (47) | X-ray fluorescence analysis of the prepared copper oxide | 109 |
| Fig. (48) | Proposed flow sheet for alkaline recovery of uranium and | |
| | copper from calcareous shale, Um Bogma formation, | |
| | G. Allouga, Southwestern, Sinai, Egypt. | 111 |
| Fig. (49) | Proposed flow sheet for acidic recovery of uranium and | |
| O . , | copper from calcareous shale, Um Bogma formation, | |
| | G. Allouga, Southwestern, Sinai, Egypt. | 113 |