ATTRITION – FLOTATION FOR BENEFICIATING OIL SHALE

By

Noura Taha Abd El Tawab Hassan Hussein

A Thesis Submitted to the
Faculty of Engineering at Cairo University
In Partial Fulfillment of the
MASTER OF SCIENCE
In
MINING ENGINEERING

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2019

ATTRITION – FLOTATION FOR BENEFICIATING OIL SHALE

By

Noura Taha Abd El Tawab Hassan Hussein

A Thesis Submitted to the
Faculty of Engineering at Cairo University
In Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE
In
MINING ENGINEERING

Under the Supervision of

Prof. Dr. Ayman A. El-Midany

Professor of Mining Engineering
Faculty of Engineering, Cairo University

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2019

ATTRITION – FLOTATION FOR BENEFICIATING OIL SHALE

By

Noura Taha Abd El Tawab Hassan Hussein

A Thesis Submitted to the
Faculty of Engineering at Cairo University
In Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE
In
MINING ENGINEERING

Approved by the
Examining Committee:

Prof. Dr. Ayman A. El-Midany **Thesis Main Advisor**
Prof. of Mining Engineering Cairo University

_____

Prof. Dr. Eissa M.Maghawry Bayoumy **Internal Examiner**
Prof. of Petroleum Engineering Cairo University

_____

Prof .Dr. Mohammed A.El Dayem A.El Khalek **External Examiner**
Prof.of Mineral Processing Central Metallurgical R&D Institute "CMRDI"

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2019

Engineer's Name: Noura Taha Abd El Tawab Hassan Hussein
Date of Birth: 2/11/1976
Nationality: Egyptian
E-mail: norataha2000@hotmail.com
Phone: 01113760911
Address: Haram/Cairo/ Egypt

Registration Date: 1/3/2014
Awarding Date: /2019
Degree: Master of Science
Department: Mining, Petroleum, and Metallurgy Engineering

Supervisors:
Prof. Dr. Ayman Abdel-Hamid El-Midany
Prof. of Mining Engineering Cairo University

Examiners:
Prof. Dr. Mohammed A.El dayem (External examiner)
Prof.of Mineral Processing Central Metallurgical R&D Institute
Prof. Dr. Eissa Maghawry Bayoumy (Internal examiner)
Prof. of Petroleum Engineering Cairo University
Prof. Dr. Ayman A. El-Midany (Thesis main advisor)
Prof. of Mining Engineering Cairo University

Title of Thesis:

ATTRITION – FLOTATION FOR BENEFICIATING OIL SHALE

Key Words:
Oil shale, Attrition, Flotation, Kerogen, Fine grinding.

Summary:
Oil shale represents an alternative energy source. Beneficiation before retorting is effective in improving its kerogen% .Improper fine grinding of oil shale leads to the appearance of smearing phenomenon which results in flotation deficiency. Attrition scrubbing represents good solution to avoid such phenomenon. A statistical design was used to study the attrition of oil shale in terms of soaking, attrition times and pH. Oil shale flotation was conducted using pine oil and sodium oleate for both conventionally ground and attrited samples. results indicated the attrited samples gave higher kerogen%.

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 : Noura Taha Abdel Tawab Hassan Hussein Date :

Signature

Acknowledgments

Foremost, I would like to express my sincere gratitude to my main supervisor Prof. Dr. Ayman A. El-Midany for the continuous support of my Master's study and research, for his patience, motivation, enthusiasm, and his knowledge. His guidance helped me in all the time of research and writing of this thesis.

I am using this opportunity also to express my gratitude to my colleagues and assistants in the Mining Engineering department who helped me a lot on various issues during my work.

Finally, this Master's thesis would not have been successful without the patience and immense support of my family; I dedicate this work to the soul of my parents, also to my sisters and my husband for everything they have done for me.

TABLE OF CONTENTS

DISCLAIMER……...I
ACKNOWLEDGMENTS……II

TABLE OF CONTENTS III

LIST OF TABLES.....VI

LIST OF FIGURES VII

ABSTRACT IX

CHAPTER 1 : INTRODUCTION…… .1

1.1 INTRODUCTION…… 1

CHAPTER 2 : LITERATURE REVIEW …… 3

2.1. GEOLOGY OF OIL SHALE 3
2.2. ORIGIN OF OIL SHALE 4
2.3. CLASSIFICATION OF OIL SHALE 5
2.4. PARAMETERS OF OIL SHALE'S EXISTENCE 6
2.5. RECOVERY METHODS.....7

2.5.1.EXTRACTION OF OIL FROM OIL SHALE…. ……. ……... 7

2.5.2.MINING AND EXTRACTION METHODS … . . 7

2.5.3.HYDROGENATION AND THERMAL DISSOLUTION PROCESSES..... 10

2.5.4.RETORTING PROCESS 10

2.5.5.SURFACE RETORTING 10

2.5.6.IN-SITU PROCESSING 11

2.6. OIL SHALE ECONOMICS 11
2.7. OIL SHALE IN THE WORLD 12

2.7.1. WORLD ESTIMATION OF OIL SHALE …… 12

2.7.2. OIL SHALE IN EGYPT 13

2.7.2.1 THE FUTURE OF OIL SHALE IN EGYPT.....14

2.8. INTRODUCTION TO THE BENEFICIATION OF OIL SHALE 14

2.8.1.ASSOCIATED PROBLEMS OF OIL SHALE RETORTING.....15

2.8.2.THE IMPORTANCE OF OIL SHALE BENEFICIATION 16

2.8.3.THE BENEFICIATION PRINCIPLE 17

2.8.4.SIZE REDUCTION STEP 18

2.8.5.CHEMICAL AND PHYSICAL BENEFICIATION METHODS 19

2.8.6. MECHANICAL FLOTATION 20

2.8.7.COLUMN FLOTATION 20

2.8.8.FROTH FLOTATION..... 20

2.9.ATTRITION..... 23

CHAPTER 3 EXPERIMENTAL 24
3.1. COLLECTION OF THE OIL SHALE SAMPLES 24
3.2. PREPARATION 25
3.2.1. CRUSHING 25
3.2.2. SAMPLING 26
3.2.2.1.CONING AND QUARTERING 26
3.2.3. GRINDING 27
3.2.3.1. MODERATE GRINDING 27
3.2.3.2. FINE GRINDING 27
3.2.4. SCREENING 28
3.3. SAMPLE CHARACTERIZATION 28
3.3.1. MICROSCOPIC ANALYSIS 28
3.3.2. CHEMICAL ANALYSIS 28
3.3.3. ORE CHARACTERISTICS ANALYSIS 29
3.3.4. DTA AND DTG ANALYSIS 29
3.3.5. FTIR 29
3.4. SOAKING 29
3.5. ATTRITION 30
3.5.1 STATISTICAL DESIGN 31
3.5.1.1 EL BEIDA STATISTICAL DESIGN 31
3.5.1.2 EL NAKHEIL STATISTICAL DESIGN 33
3.6. KEROGEN AND CARBONATE (LOI) DETERMINATION 34
3.7. FLOTATION 34
3.7.1 FROTH FLOTATION 34
3.7.1.1 FLOTATION OF OIL SHALE GROUND BY THE BALL MILL 35
3.7.1.2 FLOTATION USING ATTRITED SAMPLES 36
CHAPTER 4 RESULTS AND DISCUSSION 37
4.1.CHEMICAL ANALYSIS 37
4.2. MINERALOGICAL INVESTIGATION 37
4.2.1. EL-NAKHEIL OIL SHALE 37
4.2.2. EL BEIDA OIL SHALE 39
4.3. ORE CHARACTERISTICS 40
4.4. THERMAL AND GRAVIMETRIC ANALYSIS (DTA & TGA) 41
4.4.1. EL-NAKHEIL OIL SHALE 41
4.4.2. EL-BEIDA OIL SHALE 42
4.5. PRELIMINARY ATTRITION TESTS 44
4.5.1. ATTRITION OF EL-BEIDA SAMPLE 44

4.5.1.1. EFFECT OF ATTRITION ON PRODUCT WEIGHT %..... 44
4.5.1.2. EFFECT OF PH 46
4.5.1.3. EFFECT OF ATTRITION TIME 48
4.5.1.4. EFFECT OF SOAKING TIME..... 49
4.5.2. PREPARING FINER SIZES 55
4.5.3. EFFECT OF ATTRITION SPEED.....56
4.6. FLOTATION 57
4.6.1. FLOTATION FEED PREPARED BY BALL MILL GRINDING..... 57
4.6.1.1. PINE OIL 57
4.6.1.2. HIGH DOSE EFFECT OF PINE OIL FOR EL BEIDA OIL SHALE FLOTATION PREPARED BY BALL MILL 59
4.6.1.3. SODIUM OLEATE 60
4.6.2. FLOTATION OF FEED PREPARED BY ATTRITION 62
4.6.2.1. SODIUM OLEATE…… 62
4.6.2.2 PINE OIL……. 64
4.6.2.3. EFFECT OF HIGHER DOSE OF PINE OIL FOR FLOTATION OF ATTRITION PRODUCT…… 66
4.6.2.4. FLOTATION OF EL BEIDA OIL SHALE RESULTED FROM THE ATTRITION USING THE SCREENED SIZE (- 0.1 MM +0.045MM) AT PH 10.5.. 67
4.6.3. RELATION BETWEEN KEROGEN % AFTER FLOTATION ,PH AND METHOD OF GRINDING 69
4.6.3.1. KEROGEN % GRAPH VERSUS DIFFERENT PH VALUES OF FLOATED ATTRITED OIL SHALE WITH 7.5 KG/T. OF PINE OIL 69
4.6.3.2 KEROGEN % GRAPH VS DIFFERENT PH VALUES OF FLOATED GROUND OIL SHALE WITH 7.5 KG/T. OF PINE OIL. 70
4.6.4. CONDITIONED FLOTATION EXPERIMENTS 72
4.7. EL NAKHEIL DESIGN 73
4.7.1. EFFECT OF STUDIED FACTORS ON KEROGEN %.....74
4.7.2. EFFECT OF STUDIED FACTORS ON LOI % 76
4.7.3 . FLOTATION OF EL-NAKHIEL SAMPLE.....79
4.7.3.1. COMPARISON BETWEEN THE FLOTATION RESULTS OF GROUND SAMPLES BY THE BALL MILL AND THE ATTRITED SAMPLES OF EL NAKHEIL OIL SHALE…….. .. 80
4.8 DISCUSSION AND CONCLUSIONS..... 81
REFERENCES 82
APPENDIX I …… 87
APPENDIX II…….. . 93

List of Tables

Table 2.1. Top Ten Ranked Countries by Oil Shale Resource Volume 13
Table 3.1. The factors levels of El-beida design 31
Table 3.2:El-beida Design matrix of factors 32
Table 3.3. The factors levels of El-Nakheil design 33
Table 3.4. El-Nakheil Design matrix of factors 34
Table 4.1. Chemical analysis of studied oil shale samples.....37
Table 4.2. Ore characteristics of oil shale samples 41
Table 4.3. Statistical design results in terms of Wt%.....44
Table 4.4. The attrition results in terms of - 2.36 mm size fraction 45
Table 4.5. Results of El Nakheil experimental design 74
Table 4.6. Results of flotation of the attrition products.....80

List of Figures

Fig. 2.1. Oil shale sedimentary rock....3
Fig. 2.2. General scheme of the oil shale component 3
Fig. 2.3. Average chemical composition of Green River oil shale, Riffle, Colorado 4
Fig. 2.4 Hutton's classification of oil shale 6
Fig 2.5. Scheme for the extraction of shale oil....8
Fig. 2.6. Stages of oil shale production 9
Fig. 2.7. Economic comparison between oil shale exploitation technologies. 11
Fig. 2.8. Oil shale Market Size in the world. 12
Fig. 2.9. Organic and inorganic composition of oil shale 15
Fig. 2.10.Schematic diagram of a froth flotation cell....21
Fig. 2.11.Effect of collector dosage on USA oil shale froth flotation 222
Fig. 3.1. El-Nakheil and El-Beida mines location....24
Fig. 3.2. (a) El-Beida mine, (b) El-Nakheil mine....25
Fig. 3.3. A laboratory Jaw crusher, (a) front view, (b) top view....26
Fig. 3.4. Coning and quartering....27
Fig. 3.5 (a) A tumbling ball mill, (b) Grinding steel balls....27
Fig. 3.6. Vibrating screens....28
Fig. 3.7 The Attrition equipment....30
Fig. 3.8. Flotation cell....35
Fig. 4.1. Thin sections of El-Nakheil oil shale containing kerogen 38
Fig. 4.2. Polished section of El-Nakheil oil shale 39
Fig. 4.3. Thin sections of El-Beida oil shale containing kerogen....40
Fig. 4.4. DTA of El-Nakheil oil shale 41
Fig. 4.5. TGA of El- Nakheil oil shale 42
Fig. 4.6. DTA of El-Beida oil shale....43
Fig. 4.7. TGA of El-Beida oil shale....43
Fig. 4.8. Effect of pH on the -2.36 mm weight percent, a) no soaking,
b) Soaking 120 min 47
Fig. 4.9. Effect of attrition time on the -2.36 mm weight percent,
a) no soaking, b) 120 min soaking time 48
Fig. 4.10. Effect of soaking time on the -2.36 mm wt %, ...50
a) no attrition, b) 120 min attrition time....
Fig. 4.11. Cube graph for the effect of studied factors on producing…….51
fines by attrition....
Fig. 4.12 Effect of attrition on the kerogen % in -2.36 mm attrition product 53
a) No soaking, b) 60 min, and c) 120 min soaking time ....
Fig. 4.13. Effect of attrition on LOI % in -2.36 mm attrition product ……..55
a) No soaking, b) 60 min, and c) 120 min soaking time ....
Fig. 4.14. Effect of pH on LOI% in -0.2mm and +0.2mmparticle sizes....56
Fig. 4.15. Effect of attrition speed on LOI % in attrited product 56
Fig. 4.16. Effect of pine oil dose on the kerogen%....58
Figure 4.17. Effect of pine oil dose on the recovery %....58
Figure 4.18 . Effect of pine oil higher dose on the kerogen %....59
Figure 4.19. Effect of pine oil higher dose on the recovery % of the ground oil shale..60

Figure 4.20. Effect of sodium oleate dose on the kerogen % of the ground oil shale at different pH.....61
Figure 4.21. Effect of sodium oleate on recovery % of the ground oil shale at different pH.....61
Figure 4.22. Effect of sodium oleate on the kerogen of the attrited oil shale % at pH 3 and pH 9.....63
Figure 4.23. Effect of sodium oleate on the recovery % of the attrited oil shale at pH 3 and pH 9.....63
Figure 4.24. Effect of pine oil on the kerogen % of attrited oil shale at pH 3 & pH 9 ..65
Figure 4.25. Effect of pine oil on the Recovery % of the attrited oil shale at pH3&pH9 65
Fig 4.26 . Effect of pine oil higher doses on kerogen% of attrited oil shale 66
Fig. 4.27. Effect of pine oil concentration on the recovery of attrited oil shale.....67
Fig. 4.28. Effect of higher doses of pine oil on kerogen% of the attrited oil shale.....68
Fig 4.29. effect of higher dose of pine oil on the recovery of the attrited oil shale 68
Fig 4.30 . Effect of pH on kerogen% of attritioned oil shale 69
Fig 4.31. Effect of pH on the recovery of the attrited oil shale.....70
Fig.4.32Effect of pHon kerogen% of oil shale ground by ball mill…… …. 71
Fig 4.33. Recovery% of ground oil shale with pine oil at different pH 71
Fig .4.34. Effect of number of stirring stages on kerogen % before and after flotation.73
Fig. 4.35. Effect of attrition time and pH on kerogen % at no stirring.....75
Fig.4.36. Effect of attrition time and pH on kerogen % at 30 min stirring 75
Fig.4.37. Effect of studied factors on kerogen %.....76
Fig .4.38. Effect of attrition time and pH on LOI % at different stirring times …… 78 (a),(b), (c)
Fig.4.39. Effect of studied factors on LOI% 79

Abstract

Petroleum is considered the main conventional natural resource of energy in the world. It is being rapidly consumed in a depleting trend of its reserves due to the great growth in the industrial production all over the world. The oil shale large reserves are considered as a very promising alternative source of petroleum.

This thesis aims to find solutions to the problems associated with the beneficiation and retorting of the oil shale. Samples used were obtained from two localities, namely; El Beida and El Nakheil mines in the Qusier area, Eastern Desert.

There are several studies regarding the beneficiation of the oil shale deposits indicating that the flotation techniques is the most promising. Among several problems facing the separation of the valuable content "kerogen" from oil shale by flotation, the smearing effect is most deteriorating. It appears due to fine grinding of oil shale particles that leads to the release of oil phase as well as the coating of large particles with smaller ones. Such smearing phenomenon leads to deficiency in the flotation selectivity and results in a decrease in the desired organic matter “kerogen” grade and recovery percentages.

Attrition is used as a cleaning technique for the surface of particles as well as a size reduction technique. It is used not only to dispose of the inorganic minerals that decrease the kerogen and its recovery but also used to avoid the smearing effect. Experimental design of the attrition process was used for both samples El beida and El Nakheil to optimize the process in terms of the main affecting variables. The main factors are soaking time, attrition time, and pH. In addition, the flotation behavior of the samples was studied with respect to collectors type and dosage.

Three sizes of El-Beida sample were analyzed (+3 mm, +2.36 mm, -2.36 mm), after being attrited. The most successful size achieved great results was -2.36 mm where it was attrited for 120 min soaking time and 120 min. attrition time consequently at pH 2.

Flotation is conducted to El-Beida attrited sample containing 10% kerogen in the feed that reaches to 18.4% by attrition to achieve 27.7% by flotation with more than 95 % recovery at pH 3 with higher dose of pine oil:7.5 kg/t.

For El Nakheil sample, the statistical design was used in terms of the main affecting factors: stirring time, attrition time, and pH. The design results indicated that the kerogen was effectively improved from 28% to 33.2%. While the usage of flotation on the attrited samples at pH 3, with 7.5kg/t pine oil, the kerogen improved from 33% to 38% with a recovery of 50% .

Attrition achieved better results either for both samples at the acidic medium pH 3 where the kerogen and recovery percentages were improved. It is also worth mentioning that the smearing phenomenon was minimized and that was detected especially when the attrited oil shale achieved better results than the ground in the flotation tests for both samples.

Chapter 1 : Introduction

1.1. Introduction

The petroleum is a natural resource which is rapidly consumed [1]. There are enormous efforts to find possible substitutes for it. The reserves of oil shale.stand out as a very important source of substitutes for .petroleum [2].

Oil shales are fine-grained rocks. These rocks have not been under the necessary heat, pressure, and/or depth for the right length of time required to form conventional crude oil. However, this immature form of petroleum contains refractory organic material that can be refined into fuels [3]. It consists of soluble bitumen fraction represents about 20% of this organic material, whereas the remainder exists as an insoluble kerogen, most of oil shales appear to have been deposited in shallow lakes, marshes, or seas [4].

Oil shale contains materials such as paraffin hydrocarbons. These paraffins are major constituents of natural gas and oil and are called kerogen. When the rock is heated, it releases petroleum-like liquids.

Oil shale is described as a compact, laminated rock of sedimentary origin with the observation that the organic matter is not oily (bituminous), yielding over 33% of ash and containing organic matter that yields oil when distilled.[5]

To distinguish the difference, the term oil shale means kerogen-rich sediments that can produce oil upon retorting or else. The term shale oil means the oil that can be produced from the rock. Oil shale can be described as “composites” of tightly-bound organics and inorganics [6].

Oil shale can be extracted from the ground, but compared to mining crude oil from wells; the process is much more complicated. However, with oil shale, the kerogen is in a solid form and cannot be pumped out of the rock. This means that the rock itself has to be mined first before any attempts to extract the oil can begin. Once the rock has been mined, a process called retorting (in which the rock is heated to a high temperature) is carried out. These results in an oil-like liquid that can be further refined and burned for fuel and energy.

Shale oil is similar to petroleum, and can be refined into many different substances, including diesel fuel, gasoline, and liquid petroleum gas (LPG). Companies can also refine shale oil to produce other commercial products, such as ammonia and sulfur. The spent rock can be used in cement.

A significant amount of inorganic minerals is produced when oil shale is mined , leading to a decrease in the grade and yield of the oil shale , and to increase in the cost of the pyrolysis stage of production ,these factors make oil shale energy less readily usable.

Beneficiation processes have been used in the separation of the organic content from other mineral impurities of the oil shale deposits.

The most promising beneficiating techniques is the flotation technique, where it has been widely used and previous studies indicated that flotation is inexpensive, reduces the amount of ash, and increases the organic content percentage.

Although flotation is an effective method for increasing the grade of an oil shale, previous studies indicated that there are several problems facing the separation of the valuable content "kerogen" from oil shale, one of the major limitations is the smearing effect which appears during the froth flotation due to the fine grinding of oil shale particles produced by ball mill or rod mill and that leads to deficiency in the selectivity of organic matter resulting

in a decrease in the kerogen and recovery percentages through the beneficiation process. Hence this thesis aims to find solutions to the problems associated with the beneficiation and retorting of the oil shale.

This work focuses on the beneficiation of oil shale using the attrition of the oil shale particles followed by flotation. The attrition process was used as a substitute method for grinding instead of conventional grinding methods by ball or rod mills. The selection of attrition technique is due to its effectiveness in disintegrating the oil shale particles as well as cleaning the particle surface because of its erosion, abrasion and friction effect. Thus, the main objectives of this thesis are increasing the separation efficiency in terms of kerogen grade and recovery percentages by scrubbing the particles' surface from impurities and overcoming the smearing phenomenon resulted from grinding using the conventional methods.