



بسم الله الرحمن الرحيم

∞∞∞∞

تم رفع هذه الرسالة بواسطة / سلوي محمود عقل

بقسم التوثيق الإلكتروني بمركز الشبكات وتكنولوجيا المعلومات دون أدنى

مسئولية عن محتوى هذه الرسالة.

ملاحظات: لا يوجد





Cairo University

INVESTIGATING THE SURFACE CHANGES UNDER DIFFERENT GRINDING CONDITIONS AND THEIR IMPACT ON OIL SHALE FLOTATION

By

Nesren Mohamed Khairy Abd El-Aziz Khalf

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
MINING ENGINEERING

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2021

INVESTIGATING THE SURFACE CHANGES UNDER DIFFERENT GRINDING CONDITIONS AND THEIR IMPACT ON OIL SHALE FLOTATION

By
Nesren Mohamed Khairy Abd El-Aziz Khalf

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
MINING ENGINEERING

Under the Supervision of

Prof. Dr. Ayman A. El-Midany
Professor of Mining Engineering
Mining, Petroleum and Metallurgy Dept.
Faculty of Engineering, Cairo University

Prof. Dr. Salah El-Din M.El-Mofty
Professor of Mining Engineering
Mining, Petroleum and Metallurgy
Dept. Faculty of Engineering, Cairo
University

Prof. Dr. Islam Hamza Abou El-Magd
Professor of Remote Sensing
Environmental Studies Dept.
National Authority for Remote Sensing and Space sciences

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2021

INVESTIGATING THE SURFACE CHANGES UNDER DIFFERENT GRINDING CONDITIONS AND THEIR IMPACT ON OIL SHALE FLOTATION

By
Nesren Mohamed Khairy Abd El-Aziz Khalf

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
MINING ENGINEERING

Approved by the
Examining Committee

Prof. Dr. Ayman A. El-Midany **Thesis Main Advisor**

Prof. Dr. Salah El-Din M. El-Mofty **Advisor**

Prof. Dr. Islam Hamza Abou El-Magd **Advisor**
Professor of Remote Sensing, NARSS.

Prof. Dr. Ahmad M. El-Mahdy **External Examiner**
Associate Professor, Central Metallurgical R&D Institute

Prof. Dr. Wael M. Fathy **External Examiner**
Associate Professor, Faculty of Engineering, Azhar University.

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2021

Engineer's Name: Nesren M. KhairyA.El-Aziz khalf
Date of Birth: 16/9/1984
Nationality: Egyptian
E-mail: Nesrenkhairy@yahoo.com
Phone: 01222916031
Address: 5 Sanan St. Hadayek El-Zayton
Registration Date: 1/10/2013
Awarding Date:/....../2021
Degree: Doctor of Philosophy
Department: Mining, Petroleum and Metallurgy Engineering



Supervisors:

Prof. Ayman A. El-Midany
Prof. Salah El-Din M. El-Mofty.
Prof. Islam Hamza Abou El-Magd
Professor of Remote Sensing, NARSS

Examiners:

Prof. Ayman A. El-Midany (Thesis main advisor)
Prof. Salah El-Din M. El-Mofty (Advisor)
Prof. Islam Hamza Abou El-Magd (advisor)
Professor of Remote Sensing, NARSS
Prof. Ahmad M. El-Mahdy (External examiner)
Associate Professor, CMRDI
Prof. Wael M. Fathy (External examiner)
**Associate Professor, Faculty of Engineering,
Al-Azhar University**

Title of Thesis:

INVESTIGATING THE SURFACE CHANGES UNDER DIFFERENT
GRINDING CONDITIONS AND THEIR IMPACT ON OIL SHALE
FLOTATION

Key Words:

Oil shale; Surface change; Grinding; Flotation; Heating.

Summary:

Oil shale surface sensitivity is one of the challenging problems. Therefore, the oil shale breakage, as well as its surface characteristics, was studied under different applied grinding loads in terms of the number of balls, ball diameter, grinding time, and density of balls (steel and ceramic) and fitted to first and second grinding kinetic laws. Although the d_{50} size decreases with increasing the applied load and time, the higher the load is the less the flotation performance. In addition, matching the FTIR spectra for heated oil shale samples surface with those for the ground product at different conditions indicated that the grinding zone temperature does not exceed 150 °C with high oil shale oxidation with finer grinding. Furthermore, FTIR and Zeta potential indicated that although there is no organics release, the fine particles coating leads to bad flotation results. Finally, grinding and flotation mechanisms were suggested.

Disclaimer

I hereby declare this thesis is my 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: Nesren Mohamed Khairy Abd El-Aziz Khalf

Date:../../2021

Signature:

Dedication

This thesis is dedicated to my beloved family who has meant and continues to mean so much for me. First to my mother, whose love, support, and encouragement have meant to me so much. She is my source of inspiration and always gives me strength when I am almost giving up. To my father who is no longer of this world, his memories continue to regulate my life. whose love for me knew no bounds and, who taught me the value of hard work. To my brother and sister, who shared their words of advice and encouragement during the challenges of study and life. I am truly thankful for having you in my life. my wonderful sister's kids as they are the joy to me.

I dedicate this work and give special thanks to my best friend Ghada for being there for me. I also dedicate this dissertation to my friends at the mining department, Ola, Tahany, Reham, Amr, and Raweya, whom have supported me throughout the study, especially Ola for her overall help and support. Also, I would like to thank my friends at NARSS Esraa, Mona, Rasha, Naglaa, Shaima, Hossam, and Khaled for all they have done to me.

Acknowledgments

First, I thank Almighty GOD for helping me finish my thesis. I would like to sincerely thank my supervisors, Prof. Ayman El-Midany, Head of Mining Division, Mining, Petroleum, and Metallurgy department, Prof. Salah El-Dien El-Mofty, Professor of Mineral processing, Faculty of Engineering, Cairo University and Prof. Islam Abou Elmagd Professor of remote sensing and environment, National Authority for Remote Sensing and Space Sciences, for supporting me throughout my thesis by providing me with knowledge, sharing ideas and encouraging me. Also, their guidance helped me in all time of research and writing of this thesis.

I offer my sincerest thanks to Prof. Enas El-Sheikh at Nuclear Materials Authority for her help and support. Also, I would like to thank the staff of mineral processing laboratories particular Mr. Abd El Aty, and friends and members of the mining department, Faculty of Engineering, Cairo University for all the help.

Last but not least, I want to thank my family for their unconditional support, both financially and emotionally throughout my degree, in particular, the patience and understanding shown by my mom.

Table of contents

LIST OF TABLES	V
LIST OF FIGURES	VI
ABSTRACT	X
CHAPTER 1: INTRODUCTION	1
1.1. OVERVIEW	1
1.2. OIL SHALE.....	2
1.2.1. Composition	2
1.2.2. Classification.....	3
1.2.3. Quality of Kerogen.....	3
1.2.4. Oil shale uses.....	4
1.2.5. Oil shale in world	4
1.3. OIL SHALE IN EGYPT	5
1.4. BENEFICIATION ROLE IN OIL SHALE DEVELOPMENT	7
CHAPTER 2: LITERATURE REVIEW.....	8
2.1. GRINDING	8
2.2. FLOTATION TECHNIQUES.....	9
2.2.1. Froth flotation.....	9
2.2.2. Column flotation	10
2.3. MAIN FACTORS AFFECTING OIL SHALE FLOTATION.....	11
2.3.1. Mineralogy	11
2.3.2. Grinding as flotation feed preparation step	12
2.3.3. Surface characteristics.....	13
CHAPTER 3: EXPERIMENTAL.....	14
3.1. OIL SHALE SAMPLES.....	14
3.2. PREPARATION.....	14
3.2.1. Crushing	15
3.2.2. Grinding	15
3.2.2.1. Grinding procedure	15
3.2.2.2. Intermittent and Elongated grinding	17
3.2.2.3. Grinding Kinetics.....	17
3.2.3. Screening.....	18
3.3. SAMPLE CHARACTERIZATION.....	18
3.3.1. Microscopic Analysis	18
3.3.2. Scanning Electron Microscope.....	18
3.3.3. Energy Dispersive X-Ray Analysis.....	18
3.3.4. Chemical analysis.....	18
3.3.5. Ore characteristics analysis.....	19
3.3.6. Screening analysis	19
3.3.7. Thermal analysis	19

3.3.8. Fourir Transform Infrared	20
3.3.8.1. Prediction of generated heat in grinding	20
3.3.9. Electro-Kinetic measurements	20
3.4. FLOTATION	21
CHAPTER 4: RESULTS AND DISCUSSION	23
4.1. CHARACTERIZATION OF OIL SHALE SAMPLES	23
4.1.1. Chemical analysis	23
4.1.2. Ore characteristics	23
4.1.3. Screening analysis	24
4.1.4. Energy Dispersive X-Ray Analysis.....	24
4.1.5. Microscopic analysis results.....	26
4.1.6. Scanning Electronic Microscope.....	28
4.1.7. Thermal analysis	29
4.1.8. Fourier Transform Infrared	32
4.2. OIL SHALE GRINDING	34
4.2.1. Effect of different parameters on oil shale grinding	34
4.2.1.1. Effect of oil shale composition	34
4.2.1.2. Effect of grinding media	35
4.2.1.3. Effect of ball size	35
4.2.1.4. Effect of balls filling	41
4.2.1.5. Effect of grinding time	45
4.2.2. Optimization of oil shale grinding process.....	49
4.2.2.1. El-Nakheil.....	49
4.2.2.2. El-Beda	56
4.2.3. Grinding kinetics	63
4.2.3.1. First-order law determination.....	63
4.2.3.2. Second-order law determination	69
4.2.3.3. Breakage rate determination	73
4.2.4. Prediction if there is any generated heat in grinding.....	74
4.2.4.1. Effect of different heating temperatures and time	74
4.2.4.2. Correlation of the heating results to grinding by different grinding media and time.....	77
4.2.4.3. Intermittent and Continuous grinding	81
4.2.5. Effect of grinding conditions on oil shale surface	83
4.2.5.1. Grinding time.....	83
4.2.5.2. Number of balls.....	86
4.3. OIL SHALE FLOTATION	89
4.3.1. Effect of grinding parameters on flotation	89
4.3.1.1. Effect of ball size	89
4.3.1.2. Effect of balls filling	92
4.3.1.3. Effect of grinding time	95
4.3.1.4. FTIR of ground Vs floated product.....	101
4.3.2. Optimization of oil shale flotation process.....	103
4.3.2.1. El-Nakheil.....	103
4.3.2.2. El-Beda	110
4.3.3. Zeta Potential	116
4.3.4. Illustration of grinding and flotation processes	118
4.4. FUTURE RECOMMENDATIONS	119
4.4.1. Technical recommendation.....	119
4.4.1. Economic recommendation.....	119

CONCLUSION.....	121
REFERENCES.....	123

List of Tables

Table 1.1: Basic Kerogen types in sedimentary rocks.....	4
Table 3.1: Steel and Ceramic balls diameters and weight.....	16
Table 4.1: Chemical analysis of oil shale samples.....	23
Table 4.2: Ore characteristics of oil shale samples.....	23
Table 4.3: Loss-on-ignition (LOI) for different particles sizes.....	24
Table 4.4: FTIR peaks identification.....	32
Table 4.5: Oil shale characteristics effect on oversize wt. %.....	34
Table 4.6: Effect of grinding media on oversize wt. %.....	37
Table 4.7: Effect of ball size on oversize wt. %.....	40
Table 4.8: Effect of balls filling number on oversize wt. %.....	44
Table 4.9: Effect of grinding time on oversize wt. %.....	48
Table 4.10: Statistical design results of El-Nakheil in terms of d_{50}	49
Table 4.11: ANOVA for d_{50} steel balls response of El-Nakheil.....	50
Table 4.12: ANOVA for d_{50} ceramic balls response of El-Nakheil.....	50
Table 4.13: El-Nakheil Statistical data for d_{50} - steel and ceramic balls.....	51
Table 4.14: Statistical design results of El-Beda in terms of d_{50}	56
Table 4.15: ANOVA for d_{50} of El-Beda grinding by steel balls.....	57
Table 4.16: ANOVA for d_{50} of El-Beda grinding by ceramic balls.....	57
Table 4.17: El-Beda Statistical data for d_{50} - steel and ceramic balls.....	57
Table 4.18: El-Nakheil, Coefficient of determination R^2	70
Table 4.19: El-Beda, Coefficient of determination R^2	72
Table 4.20: El-Nakheil Specific breakage rate, S_i	73
Table 4.21: El-Beda Specific breakage rate, S_i	73
Table 4.22: Effect of grinding type on the passed % -0.3mm.....	82
Table 4.23 Statistical design results of El-Nakheil in terms of LOI%.....	103
Table 4.24: ANOVA for LOI % of El-Nakheil using steel balls	104
Table 4.25: ANOVA for LOI % of El-Nakheil using ceramic balls.....	104
Table 4.26: El-Nakheil Statistical data for LOI%- steel and ceramic balls.....	105
Table 4.27: Statistical design results of El-Beda in terms of LOI%.....	110
Table 4.28: ANOVA for LOI% steel balls response of El-Beda.....	110
Table 4.29: ANOVA for LOI% ceramic balls response of El-Beda.....	111
Table 4.30: Statistical data from LOI% - steel model.....	111

List of Figures

Figure 1.1:	Total world primary energy demand.....	1
Figure 1.2:	Van Krevelen diagram.....	3
Figure 1.3:	Top ten countries with recoverable oil shale deposit.....	5
Figure 1.4:	Oil shale in Egypt	6
Figure 3.1:	Experimental work flow sheet.....	14
Figure 3.2:	Gyratory crusher.....	15
Figure 3.3:	Mechanism of grinding in ball mill.....	16
Figure 3.4:	Different grinding media.....	16
Figure 3.5:	Zeta meter	21
Figure 3.6:	Hallimond tube.....	22
Figure 4.1:	EDX spectrum of El-Nakheil oil shale.....	25
Figure 4.2:	EDX spectrum of El-Beda oil shale.....	25
Figure 4.3:	Thin section of El-Nakheil oil shale (a, b, c).....	26
Figure 4.4:	Polished section of El-Nakheil oil shale.....	27
Figure 4.5:	Thin section of El-Beda oil shale (a, b, c).....	28
Figure 4.6:	SEM of El-Nakheil Raw Sample.....	29
Figure 4.7:	SEM of El-Beda Raw Sample.....	29
Figure 4.8:	TGA of El-Nakheil oil shale.....	30
Figure 4.9:	DTA and of El-Nakheil oil shale.....	30
Figure 4.10:	TGA of El-Beda oil shale.....	31
Figure 4.11:	DTA and of El-Beda oil shale.....	31
Figure 4.12:	The FTIR spectra of El-Nakheil oil shale.....	33
Figure 4.13:	The FTIR spectra of El-Beda oil shale.....	33
Figure 4.14:	Effect of oil shale composition on grinding results for 20 minutes using 10 balls of 3 cm diameter.....	34
Figure 4.15:	Effect of grinding media on oil shale grinding for 20 minutes using 10 balls of 4 cm diameter, a) El-Nakheil, and b) El-Beda.....	36
Figure 4.16:	Effect of grinding media on d ₅₀ particle size for 20 minutes using 10 balls of 4 cm diameter.....	37
Figure 4.17:	Effect of ball size on El-Nakheil grinding for 20 minutes using 10 balls a) Steel balls, and b) Ceramic balls.....	38
Figure 4.18:	Effect of ball size on El-Beda grinding for 20 minutes using 10 balls a) Steel balls, and b) Ceramic balls.....	39
Figure 4.19:	Effect of ball size on d ₅₀ particle size for 20 minutes using 10 balls a) El-Nakheil, and b) El-Beda.....	40
Figure 4.20:	Effect of ball filling El-Nakheil grinding for 30 minutes using 4 cm. diameter balls a) Steel balls, and b) Ceramic balls.....	42
Figure 4.21:	Effect of ball filling on El-Beda grinding for 30 minutes using 4 cm. diameter balls a) Steel balls, and b) Ceramic balls.....	43
Figure 4.22:	Ball filling effect on d ₅₀ particle size for 30 minutes using 4 cm. diameter balls a) El-Nakheil, and b) El-Beda.....	44
Figure 4.23:	Effect of grinding time on El-Nakheil grinding using 17 balls of 4 cm. diameter balls a) Steel balls, and b) Ceramic balls.....	46

Figure 4.24: Effect of grinding time El-Beda grinding using 17 balls of 4 cm. diameter balls a) Steel balls, and b) Ceramic balls.....	47
Figure 4.25: Effect of grinding time d_{50} particle size using 17 balls of 4 cm. diameter balls a) El-Nakheil, and b) El-Beda.....	48
Figure 4.26: d_{50} response of El-Nakheil using steel balls a)10 min., (b) 20 min., and (c) 30 min.....	52
Figure 4.27: Cube graph for El-Nakheil grinding using steel balls.....	53
Figure 4.28: d_{50} response of El-Nakheil using ceramic balls a)10 min., (b) 20 min., and (c) 30 min.....	53
Figure 4.29: Cube graph for El-Nakheil grinding using ceramic balls.....	54
Figure 4.30: Interaction graphs of El-Nakheil using steel balls a)10 min., (b) 20 min., and (c) 30 min.....	54
Figure 4.31: Interaction graphs of El-Nakheil using ceramic balls a)10 min., (b) 20 min., and (c) 30 min.....	55
Figure 4.32: d_{50} response of El-Beda using steel balls a)10 min., (b) 20 min., and (c) 30 min.....	59
Figure 4.33: Cube graph for El-Nakheil grinding using steel balls.....	60
Figure 4.34: d_{50} response of El-Beda using ceramic balls a)10 min., (b) 20 min., and (c) 30 min.....	60
Figure 4.35: Cube graph for El-Beda grinding using ceramic balls.....	61
Figure 4.36: Interaction graphs of El-Beda using steel balls a)10 min., (b) 20 min., and (c) 30 min.....	61
Figure 4.37: Interaction graphs of El-Beda using ceramic balls a)10 min., (b) 20 min., and (c) 30 min.....	62
Figure 4.38: Effect of balls size on first-order plots using 5 balls filling (a)steel balls, and (b) ceramic balls.....	64
Figure 4.39: Effect of balls size on first-order plots using 17 balls filling (a)steel balls, and (b) ceramic balls.....	65
Figure 4.40: Effect of balls size on first-order plots using 5 balls filling (a)steel balls, and (b) ceramic balls.....	67
Figure 4.41: Effect of balls size on first-order plots using 17 balls filling (a)steel balls, and (b) ceramic balls.....	68
Figure 4.42: Effect of balls size on second-order plots using 5 balls filling (a)steel balls, and (b) ceramic balls.....	69
Figure 4.43: Effect of balls size on second-order plots using 17 balls filling (a)steel balls, and (b) ceramic balls.....	70
Figure 4.44: Effect of balls size on second-order plots using 5 balls filling (a)steel balls, and (b) ceramic balls.....	71
Figure 4.45: Effect of balls size on second-order plots using 17 balls filling (a)steel balls, and (b) ceramic balls.....	72
Figure 4.46: El-Nakheil heating at 150°C at different times.....	75
Figure 4.47: El-Nakheil heating at 300°C at different times.....	75
Figure 4.48: El-Nakheil heating at 500°C at different times (a)FTIR spectrum, and b) Impact of heating time on oil shale.....	76
Figure 4.49: FTIR correlation of heating at 150°C at 20 min and ground products using different ceramic balls' numbers of 4 cm. diameter at 20 min.....	78
Figure 4.50: FTIR correlation of heating at 150°C at 20 min and ground products using different steel balls' numbers of 4 cm. diameter at 20 min.....	78

Figure 4.51: FTIR correlation of heating at 150°C for 40 min and ground products using different ceramic balls' numbers of 4 cm. diameter at 30 min	79
Figure 4.52: FTIR correlation of heating at 150°C for 40 min. and ground products using different steel balls' numbers of 4 cm. diameter at 30 min	79
Figure 4.53: FTIR correlation of different heating temperatures at 80 minutes and different impact loads using 17 balls of 4 cm. diameter at 30 min.....	80
Figure 4.54: FTIR correlation of heating at 200°C for 80 min. and ground products using 17 steel balls of 4 cm. diameter at different grinding times.....	80
Figure 4.55: FTIR correlation of heating at 200°C for 80 min and different grinding types using 17 steel balls of 4 cm. diameter at 2 hr. grinding time	81
Figure 4.56: Effect of grinding type a) cumulative passed wt.%, and b) d ₅₀ particle size	82
Figure 4.57: Effect of grinding type on oil shale surface.....	83
Figure 4.58: FTIR spectra of the El-Nakheil products at different grinding times using 5 steel balls of 4 cm diameter.....	84
Figure 4.59: FTIR spectra of El-Nakheil products at different grinding times using 5 ceramic balls of 4 cm diameter.....	84
Figure 4.60: FTIR spectra of El-Beda products at different grinding times using 5 steel balls of 4 cm diameter.....	85
Figure 4.61: FTIR spectra of El-Beda products at different grinding times using 5 ceramic balls of 4 cm diameter.....	85
Figure 4.62: FTIR spectra of El-Nakheil products at a different grinding time using 17 steel balls of 4 cm diameter.....	86
Figure 4.63: FTIR spectra of El-Nakheil products at a different grinding time using 17 ceramic balls of 4 cm diameter.....	87
Figure 4.64: FTIR spectra El-Beda products at a different grinding time using 17 steel balls of 4 cm diameter.....	88
Figure 4.65: FTIR spectra of El-Beda products at a different grinding time using 17 ceramic balls of 4 cm diameter.....	88
Figure 4.66: Effect of ball size on (a) LOI %, and (b) Recovery% in the float fraction.....	90
Figure 4.67: Effect of ball size on a) LOI %, and b) Recovery% in the float fraction.....	91
Figure 4.68: Effect of balls filling number on a) LOI %, and b) Recovery% in the float fraction.....	92
Figure 4.69: Effect of balls filling number on a) LOI %, and b) Recovery% in the float fraction.....	94
Figure 4.70: Effect of grinding time using the 5-balls filling number on (a) LOI %, and (b) Recovery% in the float fraction.....	95
Figure 4.71: Effect of grinding time using 10-balls filling number on (a)LOI %, and (b) Recovery% in the float fraction.....	96
Figure 4.72: Effect of grinding time using 17-balls filling number on (a)LOI %, and (b) Recovery% in the float fraction.....	97
Figure 4.73: Effect of grinding time using the 5-balls filling number on (a)LOI %, and (b) Recovery% in the float fraction.....	98
Figure 4.74: Effect of grinding time using 10-balls filling number on (a)LOI %, and b) Recovery% in the float fraction.....	99