

๓ ๑๘๗

**THE KINETICS, GROWTH AND DEPOSITION OF SILICA
PARTICLES**



Ms. Chawiwat Jiraratchwaro

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma
and Case Western Reserve University

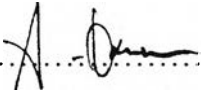
2000

ISBN 974-334-124-2


119296770


Thesis Title : The Kinetics, Growth, and Deposition of Silica Particles
By : Ms. Chawiwat Jiraratchwaro
Program : Petrochemical Technology
Thesis Advisors : Prof. H. Scott Fogler
Assoc. Prof. Sumeath Chavadej

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfillment of the requirements for the Degree of Master of Science.


..... College Director
(Prof. Somchai Osuwan)

Thesis Committee


.....
(Prof. H. Scott Fogler)


.....
(Assoc. Prof. Sumeath Chavadej)


.....
(Dr. Pomthong Malakul)

บทคัดย่อ

ฉวีวรรณ จิระราชวโร: จลนพลศาสตร์, การเติบโต, และการตกตะกอนของอนุภาคซิลิกา (The Kinetics, Growth, and Deposition of Silica Particles) อาจารย์ที่ปรึกษา: ศ. สก๊อต เอฟ ฟอกเลอร์ และ รศ. ดร. สุเมธ ชวเดช 49หน้า ISBN 974-334-124-2

การชะล้างโดยใช้น้ำ (Water flooding) เป็นวิธีการทั่วไปที่ใช้สำหรับเพิ่มการนำกลับคืนมาของน้ำมัน (Oil recovery) ครั้งที่สองและสาม บริเวณหินน้ำมันไม่เคยมีความสม่ำเสมอ ในความเป็นจริงแล้วบริเวณที่มีการแพร่ผ่านได้ง่ายมีมากมายหลายส่วน เปรียบเสมือนกับท่อส่งผ่านน้ำจากบริเวณบ่อสูบน้ำ (Injection well) ไปยังบ่อผลิต (Production well) ส่งผลให้เกิดอัตราส่วนที่ไม่เหมาะสมระหว่างน้ำและน้ำมัน วัตถุประสงค์หลักของงานวิจัยนี้ คือ ลดความสามารถในการแพร่ผ่านของตัวกลางที่มีรูพรุน โดยการสร้างอนุภาคซิลิกา (Silica particle) ขึ้นภายใน (in-situ) การสังเคราะห์อนุภาคซิลิกาทำได้โดยนำเตตระเอทิลออร์โทซิลิเกต (Tetraethyl orthosilicate, TEOS) มาทำปฏิกิริยากับน้ำโดยใช้สารละลายแอมโมเนียเป็นสารเร่งปฏิกิริยา ได้ทำการศึกษาระบบของไมโครอิมัลชันน้ำในน้ำมัน ซึ่งใช้สารลดแรงตึงผิวประเภทไร้ประจุ ว่าชนิดและความเข้มข้นของสารช่วยสารลดแรงตึงผิว รวมทั้งความเข้มข้นของแอมโมเนีย มีผลต่อจลนพลศาสตร์และอัตราเร็วของการเกิดอนุภาคซิลิกาในระบบไมโครอิมัลชัน การประยุกต์ข้อมูลการทดลองต่อการเกิดอนุภาคภายใน coreflood ได้รับการพิสูจน์ ผลของการทดลอง coreflood แสดงให้เห็นมีความเป็นไปได้ในการนำอนุภาคซิลิกาไปใช้ประโยชน์ในการลดความสามารถในการแพร่ผ่านของตัวกลางที่มีรูพรุน

ABSTRACT

4171010063: PETROCHEMICAL TECHNOLOGY PROGRAM

KEYWORD: Permeability Reduction/Silica Particles/Microemulsions/
Coreflood.

Chawiwat Jiraratchwaro: The Kinetics, Growth and Deposition
of Silica Particles.

Thesis Advisors: Prof. H. Scott Fogler and Assoc. Prof.
Sumaeth Chavadej, 49 pp ISBN 974-334-124-2

Water flooding is a common procedure used to enhance the secondary and tertiary oil recovery. The porous rock matrix of a petroleum reservoir is never completely homogeneous. In fact, there are numerous zones of high permeability that act as conduits for almost direct transfer of water from the injection well to the production well resulting in an unfavorable ratio of the water and oil. The main objective of this work was to reduce the permeability of porous media by the in-situ formation of silica particles. Batch experiments were carried out to synthesize silica particles by the hydrolysis of tetraethyl orthosilicate (TEOS) via the aqueous ammonia based catalyst in nonionic surfactant W/O microemulsion system. The effects of the type and concentration of co-surfactant as well as the ammonia concentration on the kinetics and growth rate of silica particles formation in microemulsion were also investigated. The applicability of these batch data to the formation of particles within the coreflood experiment was elucidated. The results of coreflood experiment indicated a clearly promising prospect of the usage of the in-situ silica particles to reduce the permeability of porous media.

ACKNOWLEDGEMENTS

This work would not success without the assistance from the following individuals and organizations.

I would like to express my graceful thank to Prof. H. Scott Fogler, my advisor, for stimulating advice and giving me a precious time at the University of Michigan for eight months. I am grateful to Assoc. Prof. Sumaeth Chavadej, my Thai advisor, for useful discussions, creative suggestions and encouragement and I wish to thank Prof. Richard M. Laine for kindly help with Fourier Transform Infrared Spectrophotometer.

I am grateful to Dr. Pomthong Malakul for kindly advice and for being my thesis committee.

I would like to give my special thank to Arm Youyen for being my good friend, encouragement and cheerfulness throughout the course of my work at Michigan.

I would like to thank Rhone-Poulenc Inc. for kindly support the chemical used in this thesis

I would like to thank everyone in Porous Media Group for invaluable discussions and friendship.

I wish to give my special thank to Thai students at the Department of Chemical Engineering, University of Michigan for their assistance and unlimited suggestions.

I would like to express my deep appreciation to my family for understanding, endless love, encouragement and support.

I would like to thank the Petroleum and Petrochemical's staff for their help.

Special thank to all my friends for their assistance, friendship, encouragement and giving me enjoyable life.

CONTENTS

	PAGE	
Title Page	i	
Abstract (in English)	iii	
Abstract (in Thai)	iv	
Acknowledgments	v	
Table of Contents	vi	
List of Tables	ix	
List of Figures	xi	
CHAPTER		
I	INTRODUCTION	1
II	BACKGROUND AND LITERATURE SURVEY	3
	2.1 Blocking Agents	3
	2.2 Silica Particles Formation in W/O Microemulsions	5
	2.2.1 The Kinetics of Silica Particles Formation in W/O Microemulsions	5
	2.2.2 Control of Silica Particle Formation in W/O Microemulsions	9
III	EXPERIMENTAL SECTION	11
	3.1 Batch Experiment	11
	3.1.1 Sample Preparation	11
	3.1.2 UV-VIS Spectrophotometric Measurement	11
	3.1.3 Fourier Transform Infrared Spectroscopic Measurement	12

CHAPTER		PAGE
	3.1.4 Transmission Electron Microscopic Measurement	12
	3.2 Linear Coreflood Experiment	13
IV	RESULTS AND DISCUSSION	15
	4.1 Relative Particle Density of Reaction Mixtures	15
	4.1.1 The Effect of Ammonia Concentration	15
	4.1.2 The Effect of Surfactant Concentration	16
	4.1.3 The Effect of H ₂ O to TEOS Molar Ratio	17
	4.1.4 The Effect of Type and Concentration of Co- Surfactant	18
	4.2 The Kinetics of TEOS Hydrolysis in Microemulsion Solutions	20
	4.2.1 The Effect of Ammonia Concentration	22
	4.2.2 The Effect of Surfactant Concentration	24
	4.2.3 The Effect of H ₂ O to TEOS Molar ratio	26
	4.2.4 The Effect of Type and Concentration of Co- Surfactant	27
	4.3 Size and Morphology of Silica Particles	27
	4.4 The Deposition of Silica Particles	33
V	CONCLUSIONS AND RECOMMENDATIONS	36
	5.1.1 Batch Experiments	36
	5.1.2 The Deposition of Silica Particles in Porous Media	37

CHAPTER	PAGE
5.2 Recommendations	37
REFERENCES	39
APPENDIX	42
CURRICULUM VITAE	49

LIST OF TABLES

TABLE		PAGE
4.1	Composition of all reactants used to synthesize silica particles for coreflood experiment,	33
A-1	Absorbance value at different NH_3 concentration. Composition of microemulsions: 0.1901 M DP6, $\text{H}_2\text{O}:\text{TEOS}=7.67:1$ and 0.1494 M TEOS in heptane.	42
A-2	Absorbance value at different surfactant concentration. Composition of microemulsions: 0.0156 M NH_3 , $\text{H}_2\text{O}:\text{TEOS}=7.67:1$ and 0.1494 M TEOS in heptane.	43
A-3	Absorbance value at different $\text{H}_2\text{O}:\text{TEOS}$ molar Ratio. Composition of microemulsions: 0.1901 M DP6, 0.0156 M NH_3 and 0.1494 M TEOS in heptane.	43
A-4	Absorbance value at different butanol concentration. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, $\text{H}_2\text{O}:\text{TEOS}=7.67:1$, and 0.1494 M TEOS in heptane.	44
A-5	Absorbance value at different octanol concentration. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, $\text{H}_2\text{O}:\text{TEOS}=7.67:1$, and 0.1494 M TEOS in heptane.	45
A-6	Absorbance value at different dodecanol concentration. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, $\text{H}_2\text{O}:\text{TEOS}=7.67:1$, and 0.1494 M TEOS in heptane.	46

TABLE	PAGE
B-1 Apparent rate constant at different NH_3 concentration. Composition of microemulsions: 0.1901 M DP6, $\text{H}_2\text{O}:\text{TEOS} = 7.67:1$, and 0.1494 M TEOS in heptane.	47
B-2 Apparent rate constant at different DP6 concentration. Composition of microemulsion: 0.0156 M NH_3 , $\text{H}_2\text{O}:\text{TEOS}=7.67:1$, and 0.1494 M TEOS in heptane.	47
B-3 Apparent rate constant at different $\text{H}_2\text{O}:\text{TEOS}$ molar ratio. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, and 0.1494 M TEOS in heptane.	47
B-4 Apparent rate constant at different butanol concentration. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, 0.1494 M TEOS, and $\text{H}_2\text{O}:\text{TEOS}=7.67:1$ in heptane.	48
B-5 Apparent rate constant at different octanol concentration. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, 0.1494 M TEOS, and $\text{H}_2\text{O}:\text{TEOS}=7.67:1$ in heptane.	48
B-6 Apparent rate constant at different dodecanol concentration. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, 0.1494 M TEOS, and $\text{H}_2\text{O}:\text{TEOS}=7.67:1$ in heptane.	48

LIST OF FIGURES

FIGURE		PAGE
1.1	Schematic diagram of the effects of shallow and deep plugs on enhanced oil recovery.	2
2.1	Schematic of the coagulation of hydrolyzed polymeric silica species through the mass exchange among W/O microemulsion droplets.	7
3.1	Schematic of coreflood apparatus.	14
4.1	Turbidity of microemulsion solutions at different NH_3 concentration. Composition of microemulsions: 0.1901 M DP6, $\text{H}_2\text{O}:\text{TEOS}= 7.67:1$ and 0.1494 M TEOS in heptane.	16
4.2	Turbidity of microemulsion solutions at different surfactant concentration. Composition of microemulsions: 0.0156 M NH_3 , $\text{H}_2\text{O}:\text{TEOS}= 767:1$ and 0.1494 M TEOS in heptane.	17
4.3	Turbidity of microemulsion solutions at different $\text{H}_2\text{O}:\text{TEOS}$ molar Ratio. Composition of microemulsions: 0.1901 M DP6, 0.0156 M NH_3 and 0.1494 M TEOS in heptane.	18
4.4	Turbidity of microemulsion solutions at different co-surfactant concentration. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, $\text{H}_2\text{O}:\text{TEOS}=7.67:1$, and 0.1494 M TEOS in heptane.	19

FIGURE	PAGE
4.5 The evolution of FTIR spectrum of DP6/heptane microemulsions. Composition of microemulsions: H ₂ O:TEOS=7.67:1, 0.0781 M NH ₃ , 0.1901 M DP6 and 0.1494 M TEOS in heptane.	21
4.6 The time evolution of the concentration of TEOS hydrolyzed in W/O microemulsions. Composition of microemulsions: 0.1901 M DP6, H ₂ O:TEOS=7.67:1, and 0.1494 M TEOS in heptane.	21
4.7 Specific hydrolysis rate constant k_h vs. the initial aqueous ammonia concentration. Composition of microemulsions: 0.1901 M DP6 H ₂ O:TEOS=7.67:1, and 0.1494 M TEOS in heptane.	22
4.8 The delay time $t_{1/2}$ ($C/C_0 = 0.5$) vs. initial aqueous ammonia concentration. Composition of microemulsions: H ₂ O:TEOS=7.67:1, 0.0156 M NH ₃ , 0.1901 M DP6, and 0.1494 M TEOS in heptane.	23
4.9 Specific hydrolysis rate constant k_h vs. the initial DP6 surfactant concentration. Composition of microemulsion: 0.0156 M NH ₃ , H ₂ O:TEOS=7.67:1, and 0.1494 M TEOS in heptane.	24
4.10 Specific hydrolysis rate constant k_h vs. the initial H ₂ O:TEOS molar ratio. Composition of microemulsions: 0.0156 M NH ₃ , 0.1901 M DP6, and 0.1494 M TEOS in heptane.	25

FIGURE	PAGE
4.11 Specific hydrolysis rate constant k_h vs. the initial co-surfactant concentration. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, 0.1494 M TEOS, and $\text{H}_2\text{O}:\text{TEOS}=7.67:1$ in heptane.	26
4.12 The delay time $t_{1/2}$ vs. initial co-surfactant concentration. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, 0.1494 M TEOS, and $\text{H}_2\text{O}:\text{TEOS}=7.67:1$ in heptane.	27
4.13 TEM micrograph of silica particles synthesized in W/O microemulsions with different type and concentration of co-surfactant. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, 0.1494 M TEOS, and $\text{H}_2\text{O}:\text{TEOS}=7.67:1$ in heptane.	29
4.14 The effect of co-surfactant concentration on the size of silica particles synthesized in W/O microemulsions. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, 0.1494 M TEOS, and $\text{H}_2\text{O}:\text{TEOS}=7.67:1$ in heptane.	30
4.15 The size of silica particles synthesized in W/O microemulsions with and without 1-butanol at various time. Composition of microemulsions: 0.0156 M NH_3 , 0.1901 M DP6, 0.1494 M TEOS, and $\text{H}_2\text{O}:\text{TEOS}=7.67:1$ in heptane.	30

FIGURE		PAGE
4.16	TEM Micrographs of silica particles synthesized in W/O microemulsions with and without 1-butanol at various time. Composition of microemulsions: 0.0156 M NH ₃ , 0.1901 M DP6, 0.1494 M TEOS, and H ₂ O:TEOS=7.67:1 in heptane.	31
4.17	The size distribution of silica particles synthesized in W/O microemulsions with and without 1-butanol at various time. Composition of microemulsions: 0.0156 M NH ₃ , 0.1901 M DP6, 0.1494 M TEOS, and H ₂ O:TEOS=7.67:1 in heptane.	32
4.18	Permeability ratio, K/K ₀ , during microemulsion solutions with silica particles injection. Composition of microemulsions: heptane, 0.0156 M NH ₃ , 0.1901 M DP6, 0.1494 M TEOS, 1.1462 M H ₂ O, and 0.2550 M Butanol.	35