INVESTIGATION OF BARIUM SULFATE DEPOSITION BY CAPILLARY FLOW

AND

THERMAL EFFECT ON SILICA PRECIPITATION IN ACIDIC SOLUTION



Satinee Yindee

A Thesis Submitted in Partial Fulfillment 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,

Case Western Reserve University, and Institut Français du Pétrole.

2010

Thesis Title:

Investigation of Barium Sulfate Deposition by Capillary Flow

and Thermal Effect on Silica Precipitation in Acidic Solution

By:

Satinee Yindee

Program:

Petrochemical Technology

Thesis Advisors:

Prof. H. Scott Fogler

Asst. Prof. Pomthong Malakul

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

Dean

(Asst. Prof. Pomthong Malakul)

Thesis Committee:

(Prof. H. Scott Fogler)

(Asst. Prof. Pomthong Malakul)

(Asst. Prof. Thammanoon Sreethawong)

(Dr. Piyarat Wattana)

บทคัดย่อ

สาธิณี ขินคี: การศึกษากลไกการเกาะติดของแบเรียมซัลเฟตด้วยเทคนิคการไหลผ่านท่อ แคปปิลลารี (Investigation of Barium Sulfate Deposition by Capillary Flow) และ การศึกษา อิทธิพลของอุณหภูมิที่มีผลต่อการตกตะกอนซิลิกอนในสารละลายกรด (Thermal Effect on Silica Precipitation in Acidic Solution) อ. ที่ปรึกษา: ศ. เฮช สกอตต์ ฟอกเลอร์, ผศ.ดร. ปมทอง มาลากุล ณ อยุธยา 52 หน้า

ตะกรันที่ประกอบด้วยแบเรียมซัลเฟตเป็นปัญหาหนึ่งที่ยุ่งยาก รุนแรงและพบมากใน กระบวนการผลิตน้ำมัน เนื่องจากค่าการละลายของแบเรียมซัลเฟตที่ต่ำมาก ในงานวิจัยนี้มุ่งเน้น การพัฒนาเทคนิคเพื่อศึกษาการเกาะติดของแบเรียมซัลเฟตบนท่อแคปปิลลารี ซึ่งเทคนิคการใหล่ ผ่านท่อแคปปิลลารีได้รับการพัฒนาให้เป็นเทคนิคที่มีศักยภาพสำหรับทำการทดลองการเกาะติดของตะกรัน ดังนั้นการศึกษานี้จึงใช้เทคนิคนี้จึงถูกใช้ในการศึกษากลไกการเกาะติดของตะกรัน ด้วยการติดตามการเปลี่ยนแปลงของผลต่างความดัน ปริมาณตะกรันที่เกาะติดสามารถทราบได้ จากการละลายด้วยสารไดเอทิลีนไตรในตริลโลเพนตะ อะซิติคแอซิค ซึ่งสามารถละลายและสร้าง สารประกอบเชิงซ้อนกับแบเรียมไอออนได้อย่างมีประสิทธิภาพ จากผลการศึกษาแสดงให้เห็นว่า ตะกรันมีการเกาะติดแบบไม่สม่ำเสมอและส่วนมากเกาะอยู่ที่ผิวในช่วงหน้าของแคปปิลลารี

อีกปัญหาหลักที่เกิดขึ้นระหว่างกระบวนการแมทริกซ์แอซิไดเซชั่นคือ การตกตะก่อนของ ซิลิกอน งานวิจัยนี้จึงได้ศึกษาเกี่ยวกับอิทธิพลของอุณหภูมิที่มีผลต่อการตกตะกอนของซิลิกอนใน สภาวะกรดที่รุนแรงและที่อุณหภูมิ 50 องศาเซลเซียส จากผลการทดลองพบว่า การเติบโตของ อนุภาคซิลิกอนที่อุณหภูมิสูงเกิดขึ้นเร็วกว่าที่อุณหภูมิต่ำ (5 องศาเซลเซียส) และจากการทดลอง โดยใช้เครื่องยูวี-วิส พบว่ากลไกการสลายตัวของกรดโมโนซิลิซิคเป็นไปตามปฏิกิริยาอันดับสาม นอกจากนั้นยังได้ศึกษาพลังงานการกระตุ้นของปฏิกิริยานี้ และพบว่ามีค่าเป็น 7.2 กิโลแคลอรีต่อ โมล

ABSTRACT

5071020063: Petrochemical Technology Program

Satinee Yindee: Investigation of Barium Sulfate Deposition by

Capillary Flow and Thermal effect on silica precipitation in acidic

solution

Thesis Advisors: Prof. H. Scott Fogler, and Asst. Prof. Pomthong

Malakul, 52 pp.

Keywords: Barium Sulfate/ Scale/ Deposition/ Capillary/ Pressure Drop/ Silica

Precipitation/ Thermal Effect/ Reaction-Limited Aggregation/

Monosilicic Acid Disappearance

In the oil industry, scale composed of barium sulfate (BaSO₄) is one of the most troublesome and expensive problems found in the oil production process due to its relative low solubility compared with other typical scale minerals. This research is focused on developing a technique for investigating barium sulfate deposition - in particular. Capillary technique has been developed as a potential technique for scale deposition experiments. Subsequently, this technique is used to investigate the deposition mechanism by the change in pressure drop. Moreover, the mass of the deposit formed was determined by dissolution with DTPA (Diethylenetrinitrilopenta acetic acid) which effectively dissolve and form complex with barium ions. The results show that the deposit is non-uniform and preferentially located near the beginning of the capillary.

Another major problem mainly found in the oil industry is silica precipitation during matrix acidization. This research has observed the influence of thermal effect on silica precipitation in acidic circumstance at 50°C. The results show that the silica particle growth at high temperature is greater than that at low temperature (5°C). From UV-Vis experiments, it was found that the monosilicic acid disappearance rate is third order with respect to the molar concentration of monosilicic acid. The activation energy of monosilicic acid disappearance was determined and found to be 7.2 kcal/mole.

ACKNOWLEDGEMENTS

My master thesis could not have been possible without the direct support of several distinguished people. First and foremost, I am heartily thankful to my sincere gratitude to Professor H. Scott Fogler who not only served as my supervisor but also encouraged and challenged me throughout my stay at the University of Michigan. His invaluable advice and profound insights have been instrumental in shaping the direction of my research.

I would also like to thank the members of the Flow and Reaction in Porous Media Research Group at UM Ann Arbor: Michael Senra, Tabish Maqbool, Jason Huang, Nasim Balou, Shanpeng Han, and especially Michael Hoepfner for their continued interest, helpful advices, and thoughtful discussion as the work in this thesis matured. In addition, many thanks also go to ConocoPhillips for offering the equipment support, Professor Nicholas Kotov for Light Scattering measurement and Tom Yavaraski for ICP/MS measurement. I would also like to acknowledge and thank those who provided the technical support that carried this project through to completion: above all, to Shelley Fellers, Claire O'Connor, Susan Hamlin, Laura Bracken, Pablo Lavalle, and Michael Africa for departmental and visiting-scholar business.

In Thailand, the author is grateful for the scholarship provided by the Petroleum and Petrochemical College, and the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials. I would also like to express my gratitude to Assistant Professor Pomthong Malakul who served as my Thai advisor; Assistant Professor Thammanoon Sreethawong, and Dr.Piyarat Wattana, who served as my thesis committee and provided questions whose answers shaped my report into the finalized form as presented. Million thanks also go to Robert Wright, all the lecturers and my fellow classmates in PPC, especially Perapat Srikiratiwong, who came with me and did research work in the same laboratory, for his moral support.

Finally, I want to give a personal thank to my family for their financial and motivational support and to all the others who provided encouragement, advice, and sympathetic ears over the part two year of my Master at Chulalongkorn University. I thank and love them all.

TABLE OF CONTENTS

	P.	AGE
Title	Page	i
	ract (in English)	iii
	ract (in Thai)	iv
	nowledgements	v
	e of Contents	vi
	e of Tables	ix
	e of Figures	x
		Α.
СНАРТЕ	R	
I	INVESTIGATION OF BARIUM SULFATE	1
	DEPOSITION BY CAPILLARY FLOW	
	1.1 Abstract	1
	1.2 Introduction	1
	1.3 Literature Review	3
	1.3.1 Scale Formation	3
	1.3.2 Barium Sulfate	4
	1.3.3 Barium Sulfate Scale Tendency	5
	1.3.4 Barium Sulfate Deposition/Precipitation	5
	1.3.5 Technique for Investigating Barium Sulfate Deposition	on 6
	1.3.6 Dissolution of Barium Sulfate Scale Deposit	. 7
	1.4 Experimental	8
	1.4.1 Materials	8
	1.4.2 Equipments	8
	1.4.3 Software	9
	1.4.4 Experimental Apparatus	9
	1.5 Results and Discussion	11
	1.5.1 Equipment Design and Testing for Scale Deposition	11

CHAPTER		PAGE
	1.5.2 Initial Results	15
	1.5.3 Deposition Analysis	18
	1.5.4 Different Operation time	21
	1.6 Conclusions and Recommendations	23
	1.7 References	24
Ш	THERMAL EFFECT ON SILICA PRECIPITATION	27
	IN ACIDIC SOLUTION	
	2.1 Abstract	27
	2.2 Introduction	27
	2.3 Literature Review	28
	2.3.1 Matrix Acidization	28
	2.3.2 Analcime Dissolution	29
	2.3.3 Silica Polymerization/Precipitation	30
	2.3.4 Aggregation Modeling	31
	2.3.5 Thermal Effect on Silica Precipitation	34
	2.4 Experimental	36
	2.4.1 Materials	36
	2.4.2 Equipments	36
	2.4.3 Software	36
	2.4.4 Experimental Apparatus	36
	2.4.5 Characterization Techniques	37
	2.5 Results and Discussion	38
	2.5.1 Silica Precipitation	38
	2.5.2 Particle Growth Predictions Using Geometric	
	Population Balance Equations	42
	2.5.3 Thermal Effect on Monosilicic Acid Disappearance	43
	2.6 Conclusions and Recommendations	46
	2.7 References	47

CHAPTER	PAGE
APPENDICES	49
A. Capillary Length Experiment	50
CURRICULUM VITAE	52

LIST OF TABLES

TABLE		PAGE
1.1	Comparison of ΔP and radius for a section of 2 batches	
	of capillaries	14
1.2	Comparison of capillary radius before deposition,	
	after deposition, and after dissolution	17
1.3	The collected mass of 3 capillary sections	21
1.4	Comparison of the measured pressure drop of each section	
	after deposition for different operation time	22
1.5	Comparison of the calculated uniform deposit mass and	
	the collected mass of each section after deposition	22
2.1	Parameter values of the linear relationship	44

LIST OF FIGURES

FIGURES	S	PAGE
1.1	Schematic of mixing of injected seawater and formation wat	er
	in a reservoir which causes precipitation of barium sulfate.	4
1.2	Barium sulfate scale deposited on the pipe wall	
	and surface facilities.	4
1.3	Schematic diagrams of the structures of EDTA and DTPA	7
1.4	Schematic of the experimental apparatus for barium sulfate	
	deposition studies.	9
1.5	Theoretical and experimental values of pressure drop	
	across the capillary for different flow rates.	12
1.6	Error between theoretical and experimental values of	
	pressure drop for different flow rates.	13
1.7	Theoretical and experimental values of pressure drop across	
	the capillary for different flow rates, using measured radius	for
	the calculations.	13
1.8	Error between theoretical and experimental values of	
	pressure drop for different flow rates, using measured radius	
	for the calculations.	14
1.9	An increase in the pressure drop vs. time for 3 ft length capil	lary.15
1.10	Pressure drop due to deposition vs. time for 3 ft length capill	ary. 16
1.11	Percentage of barium sulfate dissolution as a function of	
	DTPA volume.	17
1.12	Mass of removed deposit as a function of time.	18
1.13	Schematic of uniform deposit analysis.	18
1.14	Schematic of non-uniform deposit analysis.	19
1.15	Schematic of capillary sections.	20
2.1	Schematic of hydrogen ion adsorption mechanism.	30
2.2	Schematic of surface reaction mechanism.	30

FIGURE	S	PAGE
2.3	A schematic outline of the polymer growth from	
	monomer to tetramer.	31
2.4	Representative particle growth profiles in accord with	
	(a) DLA and (b) RLA.	33
2.5	Mean particle diameter versus time for pure monosilicic aci	id
	in 2M, 4M, and 8M HCl solution with exponential fitting co	urves.35
2.6	Experimental Setup.	37
2.7	Concentration – time trajectory in 170mM monosilicic acid	
	+ 4M HCl solution at 50 °C measured by ICP/MS.	39
2.8	Mean silica particle diameter versus time in 170mM	
	monosilicic acid + 4M HCl solution at 50 °C	
	measured using DLS.	40
2.9	Concentration-time trajectories in 170 mM monosilicic acid	i
	+ 4MHCl solution at 5 and 50 °C measured by ICP/MS.	41
2.10	Mean silica particle diameter versus time in 170 mM	
	monosilicic acid + 4MHCl solution at 5 and 50 °C	
	measured using DLS.	41
2.11	Comparison of the silica particle growth between experimen	ntal
	data at 50 °C and simulation using RLA model.	43
2.12	The molybdate-reactive silica data: initial Si(OH) ₄ concentr	ration
	of 170 mM with 4MHCl at different temperature.	44
2.13	The Arrhenius plot, -ln k _D versus 1/T.	45
A.1	The pressure drop vs. time plot comparing an experiment	
	conducted with the long capillary to the one conducted	
	with the short capillary.	50
A.2	Proposed deposition mechanism only at first 3 ft section.	51