# INHIBITION OF SILICATE PRECIPITATION DURING ANALCIME DISSOLUTION

Pornchai Sae-Lim

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,

Case Western Reserve University and Institut Français du Pétrole

2006
ISBN 974-9937-69-4

Thesis Title:

Inhibition of Silicate Precipitation during

Analcime Dissolution

By:

Pornchai Sae-Lim

Program:

Petrochemical Technology

Thesis Advisors:

Asst. Prof. Pomthong Malakul

Prof. H. Scott Fogler

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

Nantayo Yanumet . College Director

(Assoc. Prof. Nantaya Yanumet)

**Thesis Committee:** 

(Asst. Prof. Pomthong Malakul)

(Prof. H. Scott Fogler)

(Asst. Prof. Kitipat Siemanond)

(Dr. Thammanoon Sreethawong)

#### ABSTRACT

4771016063: Petrochemical Technology Program

Pornchai Sae-Lim: Inhibition of Silicate Precipitation during

Analcime Dissolution

Thesis Advisors: Asst. Prof. Pomthong Malakul, Prof. H. Scott

Fogler, 60 pp. ISBN 974-9937-69-4

Keywords : Analcime/ Dissolution/ Precipitation/ Inhibition/ Citric Acid

Acidization is a common technique for increasing well productivity by injecting acid into the formation at low pressure to achieve radial penetration into formation. However, the presence of zeolite could result in silicate precipitation and hence decrease the productivity. This study investigates the dissolution of analcime in HCl and in citric acid and subsequent silicate precipitation. The results showed that the dissolution of analcime in HCl was through aluminum selective removal from the framework and followed Michaelis-Menten model. The activation energy of the reaction was also calculated. Increasing the amount of analcime, citric acid concentration or temperature resulted in an increase of silicate precipitation rate. Citric acid was found to increase analcime dissolution rate compared to HCl at the same initial pH. The induction time of silicate precipitation in citric acid was found to be longer than in HCl at the same pH. A hypothesis for these phenomena also presented.

## บทคัดย่อ

พรชัย แซ่ลิ้ม: การชะลอการตกตะกอนของซิลิเกตระหว่างการละลายของอะนัลซีม (Inhibition of Silicate Precipitation during Analcime dissolution) อ. ที่ปรึกษา: ผศ. คร. ปมทอง มาลากุล ณ อยุธยา, ศ. เอช สกอตต์ ฟอกเลอร์ (Prof. H. Scott Fogler) เอกสารจำนวน 60 หนัว ISBN 974-9937-69-4

การบำบัคด้วยกรคเป็นวิธีการหนึ่งในการเพิ่มผลผลิตของหลุ่มน้ำมัน โดยการฉีดกรคลง ไปในหลุมผลิตด้วยความดันต่ำเพื่อเพิ่มการซึมซาบของน้ำมันในแนวรัศมี อย่างไรก็ตามในระหว่าง หากมีซีโอไลต์อยู่ในหลุ่มผลิตจะก่อให้เกิดการตกตะกอนของซิลิเกต การบำบัด ความสามารถในการผลิตลง งานวิจัยนี้ศึกษาการละลายของอะนัลซึมในกรดไฮโครคลอริกและ กรคซิตริกและการตกตะกอนของซิลิเกตภายหลังการละลายของอะนัลซึม การละลายของอะนัล ซึมเป็นผลมาจากปฏิกิริยาที่เฉพาะเจาะจงของการละลายอลูมิเนียม ออกจากโครงสร้างผลึกของ อะนัลซึม และเป็นไปตามโมเดลของ Michaelis-Menten ค่าพลังงานกระตุ้นของปฏิกิริยาการ ละลายของอะนัลซืนในกรคไฮโครคลอริกได้ถูกคำนวณไว้ หากเปรียบเทียบอัตราเร็วของปฏิกิริยา การละลายของอะนัลซึมในกรคไฮโครคลอริก และกรคซิตริกที่ความเข้มข้นเริ่มต้นของไฮโครเจน ไอออนเท่ากันพบว่า อัตราการละลายในกรคซิตริกสูงกว่าในกรคไฮโครคลอริก จากการศึกษาการ ตกตะกอนของซิลิเกตในกรคซิตริกพบว่า อัตราเร็วของปฏิกิริยาการตกตะกอนจะเพิ่มขึ้นเมื่อเพิ่ม อุณหภูมิ, ปริมาณของอะนัลซึม หรือความเข้มข้นของกรค เมื่อเปรียบเทียบระหว่างกรคซิตริกและ กรดไฮโดรคลอริกพบว่า กรดซิตริกใช้เวลาเหนี่ยวนำในการตกตะกอนของซิเกตนานกว่าที่ความ เป็นกรด-ค่างเคียวกัน สมมติฐานของปรากฏการณ์ ต่าง ๆ ที่ได้กล่าวมาได้ถูกแสดงไว้ในงานวิจัยนี้

### **ACKNOWLEDGEMENTS**

First and foremost, I would like to thank Professor H. Scott Fogler, my US advisor, for giving me the opportunity to complete this challenging work. I thank you for all of your kindness, guidance and encouragement during the thesis work. I wish to express my appreciation and sincere gratitude to Assistant Professor Pomthong Malakul, for their invaluable suggestions and time spent discussing on various aspects.

I would like to express my special thanks to all of my teachers who guided me through their courses, establishing the knowledge needed for this thesis. I also would like to thank Assistant Professor Kitipat Siemanond and Dr.Thammanoon Sreethawong for serving on my thesis committee.

My gratefulness is absolutely extended to all members in the Porous Media Research Group, Dr. Ryan Hartman, Dr. Kristofer Paso, Dr. Yongzhong Liu, Elizabeth Wang, Michael Senra, Hyun Su Lee, Prashant Singh, Kriang and Tabish Maqbool for their help and valuable comments.

My thankfulness is also offered to Thai students at the University of Michigan, for generously providing my great welcome and warm-heartedness during one year of my stay there.

Furthermore, I would like to take this important opportunity to thank all of my graduate friends for their unforgeitable friendship and hospitality.

Finally, very special thanks are forwarded to my beloved family whose endless love, support, motivation, and understanding play the greatest role in my success.

This thesis work is also partially funded by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT consortium).

# TABLE OF CONTENTS

			PAGE
	Title	Page	i
	Abst	ract (in English)	iii
	Abst	ract (in Thai)	iv
	Ackr	nowledge nents	v
	Tabl	e of Contents	vi
	List	of Tables	ix
	List	of Figures	x
	Abb	reviations	xii
	List	of Symbols	xiii
C	HAPT	ER	
	I	INTRODUCTION .	1
	п	BACKGROUND AND LITERATURE SURVEY	3
		2.1 Problems in Oil Production (Pore Reduction Causes)	3
		2.1.1 Fines Migration	3
		2.1.2 Clay Swelling Due to Ion Exchange	3
		2.1.3 Gel Formation	3
		- 2.1.4 Minerals Precipitation	3
		2.2 Oil Well Stimulation	4
		2.2.1 Hydraulic Fracturing	4
		2.2.2 Acid Fracturing	5
		2.2.3 Matrix Acidizing	5
		2.3 Matrix Acidizing of Sandstone	5
		2.3.1 Preflush	6
		2.3.2 Main Acid Stage	6
		2.3.3 Postflush	6

CHA	APTER	PAGE
	2.4 Dissolution of Alumino-Silicates in Acid Solution	7
	2.5 Silicate Precipitation	10
	2.6 Chelating Agent	12
Ш	EXPERIMENTAL METHODS	16
	3.1 Materials	16
	3.2 Analcime Characterization	16
	3.3 Dissolution and Precipitation Experiments	18
IV	RESULTS AND DISCUSSION	19
	4.1 Analcime Dissolution in HCl	19
	4.1.1 Dissolution Rate of Analcime in HCl	19
	4.1.2 Activation Energy of Reaction	25
	4.2 Analcime Dissolution in Citric acid	26
	4.2.1 Dissolution Rate of Analcime in Citric Acid	26
	4.2.2 The Chang of Surface Morphology and	
	Composition during Dissolution	28
	4.3 Comparison Initial Dissolution of Analcime	
	in HCl and Citric Acid	30
	4.3.1 Dissolution Rate of Analcime in Mixture of	
	Citric acid and Hydrochloric Acid	30
	4.3.2 Citric acid - Analcime Interactions	35
	4.4 Silicate Precipitation	38
	4.4.1 Silicate Precipitation in HCl	38
	4.4.2 Silicate Precipitation in Citric Acid	39
	4.4.3 Possible Inhibition Mechanism by Citric acid	43

CH	APTE	R	PAGE
	v	CONCLUSIONS AND RECOMMENDATIONS	44
		5.1 Conclusions	44
		5.2 Recommendations	44
		REFERENCES	46
		APPENDICES	50
		Appendix A Calculation Method for Deprotination Curve	
		of Polyprotic Acid	50
		Appendix B Order of Magnitude Mass Transfer Calculation	52
		Appendix C Experimental Data	58
		CURRICULUM VITAE	60

# LIST OF TABLES

TABL	Æ	PAGE
4.1	The dissolution rate of aluminum and silicon of analcime in	
	hydrochloric at 5 °C, 10 °C and 25 °C	21
4.2	Evaluation of the kinetic parameters	22

# LIST OF FIGURES

FIGURE		PAGE
2.1	The zeolite framework constructed from silicon and	
	aluminum tetrahedron (zeolite type 4A)	8
2.2	Polymerization behavior ef silica. In basic solution (B)	
	particles in sol grow in size with decrease in number; in acid	
	solution or in presence of flucculating salts (A), particles	11
	aggregate into three-dimensional networks and form gels	
2.3	Deprotonation of citric acid	15
3.1	Crystalline structure of analcime analyzed by XRD	17
3.2	Experimental batch apparatus for analcime dissolution	
	experiments	17
3.3	Experimental batch apparatus for precipitation experiments	18
4.1	Rate data for typical dissolution experiment (a) dissolution	
	curve of analcime in 8 M HCl at 5°C (b) initial dissolution	
	rate method	20
4.2	Analcime dissolution rate as a function of hydrogen ion	
	concentration at 5°C, 10°C and 25°C (a) Silicon (b)	
	Aluminum	23
4.3	Hanes-Woolf plot for analcime dissolution at 5°C, 10°C and	
	25°C (a) Silicon (b) Aluminum	24
4.4	Plot of 1/T vs ln(V <sub>max</sub> ) for finding activation energy	26
4.5	The dissolution curves of silicon, aluminum and sodium	
	from analcime in 3.00 M citric acid	27
4.6	The dissolution rate of analcime as a function of citric acid	
	concentration at 5 °C	27
4.7	Scanning electron micrographs of dissolving analcime	
	particles at different reaction time	29

# LIST OF FIGURES

FIGUI	RE	PAGE
4.8	Silicon to Aluminum ratio of the un-dissolve particles	30
4.9	Analcime dissolution in 1.5 M citric acid and in 1.5 M	
4	sodium citrate at 5 °C (Silicon)	31
4.10	Analcime dissolution in 1.5 M citric acid and in 1.5 M	
	sodium citrate at 5 °C (Aluminum)	32
4.11	Degree of catalysis of citric of citric acid in 0.5 M	
	hydrochloric acid	34
4.12	Plot of 1/D <sub>AC</sub> as a function of 1/[CA]	34
4.13	dissolution rate of analcime compared between in HCl and	
	in citric acid at the same [H+] (a) dissolution rate	
	(b) rCitric acid/rHCl	37
4.14	Concentration profiles of aluminum and silicon from	
	analcime dissolution in 8 M HCl at 25 °C	38
4.15	Effect of citric acid concentration on silicate precipitation	41
4.16	Effect of amount of analcime on silicate precipitation in 3 M	
	citric acid	41
4.17	Effect of temperature on silicate precipitation in 3 M citric	
	acid	42
4.18	Comparison silicate precipitation in HCl with in citric acid at	
	25 °C; pH 1.44	42
4.19	Possible complex form between citric acid and monosilicic	
	acid (a) bideiate form (b) tridentate form	43

### ABBREVIATIONS

EDTA Ethylene Diamine Tetra Acetic acid

EDX Energy Dispersive X-ray Analysis

HCl Hydrochloric acid
HF Hydrofluoric acid

ICP Inductive Couple plasma\*

KCl Potassium Chloride

RLS Rate Limiting Step

SEM Secondary Electron Microscope

XRD X-ray Diffraction

### LIST OF SYMBOLS

A frequency factor or pre-exponential factor

CA molecular citric acid

C<sub>H+oS</sub> the concentration of the sites occupied by adsorbed hydrogen

ion

C<sub>T</sub> the total concentration of sites that can be occupied

Cwp The Weisz-Prater Criterion

D diffusivity

D<sub>AC</sub> degree of acid catalysis

D<sub>p</sub> particle diameter
E<sub>a</sub> activation energy

 $\Delta G$  active free energy

ΔG\* critical active free energy

H<sup>+</sup> bulk concentration of hydrogen ion

J nucleation rate for homogeneous nucleation

K<sub>0</sub> kinetic coefficient

K<sub>A</sub> equilibrium adsorption constant for hydrogen ion

K<sub>a</sub> equilibrium dissociation constant

K<sub>B</sub> equilibrium adsorption constant for citric acid

K<sub>m</sub> Michaelis-Menten constant

k specific reaction rate constant

k<sub>b</sub> Boltzmann constant

k<sub>c</sub> mass transfer coefficient

N<sub>H+</sub> molar flux of hydrogen ion

R gas constant

Re The Reynolds number

-r overall rate of dissolution

-r<sub>0</sub> un-catalyzed reference rate

### LIST OF SYMBOLS

r*	initial dissolution rate
Sc	The Schmidt number
Sh	The Sherwood number
$S_T$	total site
$V_{\text{max}}$	maximum rate of dissolution .
ρο	particle density
β	supersaturation ratio
Ω	volume of a molecule inside the crystal
γ	interfacial free energy between nucleus and solution
α	fraction of ionic species
η	effectiveness factor
ф	Thiele modulus