

**PRECIPITATION AND DISSOLUTION OF CALCIUM -
PHOSPHONATE ON INHIBITION OF SCALE FORMATION
IN POROUS MEDIA**

Mr. Pairat Rerkpattanapipat

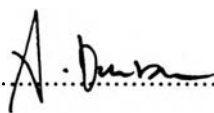
A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College
Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma
and Case Western Reserve University

1996

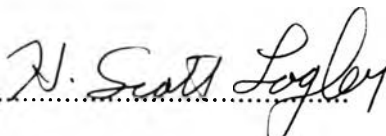
ISBN974-633-781-5

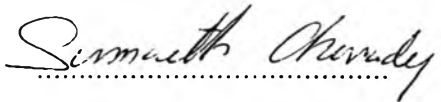
Thesis Title : Precipitation and Dissolution of Calcium-Phosphonate
on Inhibition of Scale Formation in Porous Media
By : Mr. Pairat Rerkpattanapipat
Program : Petrochemical Technology
Thesis Advisors : 1. Professor H.Scott Fogler, Ph.D.,
2. Dr. Sumaeth Chavadej

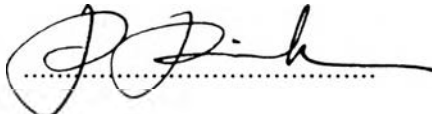
Accepted by the Petroleum and Petrochemical College, Chulalongkorn
University, in Partial Fulfillment of the Requirements for the Degree of Master
of Science.


..... Director of the College
(Prof. Somchai Osuwan, Ph.D.)

Thesis Committee


.....
(Prof. H. Scott Fogler, Ph.D.)


.....
(Dr. Sumaeth Chavadej)


.....
(Dr. Pornpote Piumsomboon)

ABSTRACT

- ## 941009 : Major Petrochemical Technology
- Key Words : Squeeze Treatment/ Scale Inhibitor/ Phosphonates/
Precipitation/ Dissolution

Pairat Rerkpattanapit : Precipitation and Dissolution of Calcium-Phosphonate on Inhibition of Scale Formation in Porous Media :
Thesis Advisors : Prof. H. Scott Fogler, Ph.D. and Dr. Sumaeth Chavadej, 62 pp., ISBN974-633-781-5

The scale inhibitor squeeze treatment is an effective means in inhibition of scale formation occurring in the oilfield. Calcium carbonate is one of the prominent scales often found in the production. The role of scale inhibitor is to form a sparingly soluble precipitate with a divalent cation and prevent scale from forming in the field for a long production period.

In this study, the phosphonate amino tri(methylene phosphonic acid) was used as scale inhibitor formed with calcium chloride anhydrous under temperature of 25 °C , molar product of 0.08 M² and a precipitating pH of 1.5-7.0. Three forms of precipitates (1:1, 2:1 and 3:1 Ca/ATMP molar ratio precipitates) were synthesized in batch experiments and their properties were then characterized. From SEM, the morphologies of 1:1 , 2:1 and 3:1 precipitates were sheet, spherical and spherical particles, respectively. The dissolution result showed that the 3:1 precipitate had the lowest solubility. The 3:1 precipitate thus gave the longest squeeze lifetime in the release of precipitate from both micromodel and coreflood experiments.

บทคัดย่อ

ไพรัตน์ ฤกษ์พัฒนาพิพัฒน์ : การตกตะกอนและการละลายของแคลเซียม - ฟอสฟอเนต เพื่อการยับยั้งการเกิดตะกรัน ในวัสดุพรุน [Precipitation and Dissolution of Calcium-Phosphonate on Inhibition of Scale Formation in Porous Media], อาจารย์ที่ปรึกษา : Prof. H. Scott Fogler และ ดร.สุเมธ ชวเดช, 62 หน้า, ISBN974-633-781-5

ในปัจจุบัน ปัญหาการเกิดตะกรันในบ่อขุดเจาะน้ำมันสามารถบำบัดได้โดยการฉีดสารยับยั้งตะกรัน (Scale inhibitor squeeze treatment) หินปูน (แคลเซียมคาร์บอเนต) เป็นสารหลักที่พบในตะกรันที่เกิดขึ้นในกระบวนการผลิต น้ำที่ของสารยับยั้งตะกรัน คือการทำให้เกิดการรวมตัวกับไอออนประจุบวกสองเป็นตะกอนที่ละลายได้น้อย ซึ่งสามารถป้องกันการเกิดตะกรันในการผลิตได้ยาวนาน

ในการทดลองนี้ สารยับยั้งตะกรันเป็นสารกลุ่มฟอสฟอเนต คือ Aminotri (methylene phosphonic acid) ได้ทำปฏิกิริยากับแคลเซียมคลอไรด์ ภายใต้สภาวะอุณหภูมิ 25 องศาเซลเซียส ผลคูณของความเข้มข้น คือ 0.08 โมลาร์³ และ pH ในการไตเตรตคือ 1.5 - 7.0 และ อัตราส่วนความเข้มข้นระหว่างแคลเซียม ต่อฟอสฟอเนต คือ 1:1, 2:1 และ 3:1 จากผลการวิเคราะห์โดยวิธี SEM พบว่า ตะกอนที่เกิดขึ้นมี 3 รูป ตะกอนแบบ 1:1 มีลักษณะอนุภาคเป็นแผ่นบาง ส่วนตะกอนแบบ 2:1 และ 3:1 มีลักษณะเป็นอนุภาคเล็กกลม จากผลการทดลองการละลายของตะกอนที่สังเคราะห์ได้ พบว่าตะกอนแบบ 3:1 มีค่าการละลายต่ำสุด ดังนั้นการทดลองในแบบจำลองวัสดุพรุน ตะกอนแบบ 3:1 มีระยะเวลาการปล่อยสารยับยั้ง (Squeeze Treatment Lifetime) ที่ยาวนานที่สุด

ACKNOWLEDGMENTS

The author would like to express the deepest appreciation for the assistance of the following individuals and organizations in this research work :

Prof. H. Scott Fogler, The Vennema Distinguished Professor of Chemical Engineering, The University of Michigan, U.S.A., who acted as my advisor and guided me in accomplishing this thesis with his valuable suggestions.

Dr. Sumaeth Chavadej, my erudite advisor, who provided many beneficial comments and helped in the acquisition of the equipment needed in this thesis.

Special thanks are extended to Dr. F. Henry Browning for sharing his helpful suggestions and assisting in technical discussion.

The author would like to express gratefulness to Monsanto and Daika Companies for some special chemicals used in this study, to the National Research Council of Thailand for financial support, and to the University Development Linkage Program (UDLP) for giving the opportunity for the author to run this research at the University of Michigan, U.S.A.

TABLE OF CONTENTS

CHAPTER	PAGE
Title Page	i
Abstract	ii
Acknowledgments	iii
Table of Contents	v
List of Tables	vii
List of Figures	viii
I INTRODUCTION	
1.1 Squeeze Treatment	1
1.2 Scale Inhibitor	5
1.3 Objectives	5
II LITERATURE REVIEW	6
III METHODOLOGY	
3.1 Batch Synthesis Experiments	
3.1.1 Materials	12
3.1.2 Experimental System and Procedure	13
3.1.3 Characterization Techniques	14
3.2 Precipitate Performance in Porous Media	
3.2.1 Experimental System of Coreflood	17
3.2.2 Experimental System of Micromodel	19
IV RESULTS AND DISCUSSION	
4.1 Batch Synthesis and Characterization	
4.1.1 Morphologies of Ca-ATMP Precipitates	22

CHAPTER	PAGE
4.1.2 Parameters Concerning with the Precipitation	32
4.1.3 Factors Governing the Formation of Calcium-ATMP precipitates	35
4.2 Performance of Precipitate in Porous Media	40
4.2.1 Description of the 1:1 Calcium-ATMP Precipitate Released from Model	42
4.2.2 Description of the 2:1 Calcium-ATMP Precipitate Released from Model	44
4.2.3 Description of the 3:1 Calcium-ATMP Precipitate Released from Model	47
V CONCLUSIONS AND RECOMMENDATIONS	
5.1 Conclusions	50
5.2 Recommendations	51
APPENDICES	
APPENDIX A	53
APPENDIX B	54
APPENDIX C	55
REFERENCES	60

LIST OF TABLE

TABLE		PAGE
4.1	Summary of Batch Synthesis and Characterization Experiments	23

LIST OF FIGURES

FIGURE		PAGE
1.1	The Procedure of Squeeze Treatment Technique.	2
1.2	Comparison Between an Ideal Elution Curve and a Typical Elution Curve.	4
3.1	Properties of Aminotri(methylenephosphonic acid).	13
3.2	Schematic of Batch Synthesis Apparatus.	14
3.3	Flow Chart of the Characterization Procedures.	15
3.4	Schematic of Coreflood Experiment.	18
3.5	Schematic of Micromodel Experiment.	21
4.1	The Resulting Morphology of 1:1 Calcium/ATMP Precipitate at a pH Value of 1.5.	24
4.2	The Resulting Morphology of 2:1 Calcium/ATMP Precipitate at a pH of 4.0 and a Precipitating Molar Ratio of 1:1.	25
4.3	The Resulting Morphology of 2:1 Calcium/ATMP Precipitate at a pH of 4.0 and a Precipitating Molar Ratio of 10:1.	25
4.4	The Resulting Morphology of 2:1 Calcium/ATMP Precipitate at a pH of 6.0 and a Precipitating Molar Ratio of 1:1.	26
4.5	The Resulting Morphology of 3:1 Calcium/ATMP Precipitate at a pH of 6.0 and a Precipitating Molar Ratio of 10:1.	27
4.6	The Resulting Morphology of 3:1 Calcium/ATMP Precipitate at a pH of 7.0 and a Precipitating Molar Ratio of 5:1.	27

FIGURE		PAGE
4.7	The Resulting Morphology of 3:1 Calcium/ATMP Precipitate at a pH of 7.0 and a Precipitating Molar Ratio of 10:1.	28
4.8	The Morphology of 2.14 Calcium/ATMP Precipitate at a pH of 7-6.432 and a Precipitating Molar Ratio of 1:1.	29
4.9	The Morphology of 2.85 Calcium/ATMP Precipitate at a pH of 7-4.888 and a Precipitating Molar Ratio of 10:1.	29
4.10	XRD Patterns as a Function of Calcium/ATMP Molar Ratio.	31
4.11	The Effect of a Precipitating pH and Molar Ratio on the Precipitates.	33
4.12	The Effect of a Precipitating pH on the Resulting Ca-ATMP Dissolution.	34
4.13	The Effect of pH on the Deprotonation of ATMP and the Resulting Species Composition.	36
4.14	The Effect of Calcium in Solution on the Resulting Titration Curves of ATMP.	38
4.15	Precipitation of Ca-ATMP as Function of pH and Calcium Concentration.	39
4.16	Effect of Precipitate Types of the Release of ATMP from Micromodel Experiment.	41
4.17	Elution Curve Resulting from the Dissolution of a 1:1 Calcium-ATMP Precipitate in Porous Media.	42
4.18	Release Regimes of 1:1 Ca ⁺⁺ -ATMP Precipitate from a Micromodel.	43

FIGURE		PAGE
4.19	Elution Curve Resulting from the Dissolution of a 2:1 Calcium-ATMP Precipitate in Porous Media.	45
4.20	Release Regimes of 2:1 Ca ⁺⁺ -ATMP Precipitate from a Micromodel.	46
4.21	Elution Curve Resulting from the Dissolution of a 3:1 Calcium-ATMP Precipitate in Porous Media.	47
4.22	Release Regimes of 3:1 Ca ⁺⁺ -ATMP Precipitate from a Micromodel.	49