Effects of Reversibility of Surfactant Adsorption on Surfactant Flooding

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Petroleum Engineering
Department of Mining and Petroleum Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2015

ผลกระทบของการผันกลับได้ของการดูดซับสารลดแรงตึงผิวที่มีต่อกระบวนการฉีดอัดสารลดแรงตึงผิว

นายอิช ฮุย โง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมปิโตรเลียม ภาควิชาวิศวกรรมเหมืองแร่และปิโตรเลียม
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2558

Thesis Title	Effects of Reversibility of Surfactant Adsorption on Surfactant Flooding
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Field of Study	Petroleum Engineering
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อิช ฮุย โง : ผลกระทบของการผันกลับได้ของการดูดซับสารลดแรงตึงผิวที่มีต่อกระบวนการฉีดอัดสารลดแรงตึงผิว (Effects of Reversibility of Surfactant Adsorption on Surfactant Flooding) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร. ฟ้าลั่น ศรีสุริยชัย, 132 หน้า.

การฉีดอัดสารลดแรงตึงผิวมีวัตถุประสงค์หลักเพื่อลดแรงตึงระหว่างผิวของน้ำและน้ำมันให้เข้าสู่สภาวะแรงตึงผิวต่ำยิ่งยวด ที่สภาวะดังกล่าวน้ำมันจะหลุดออกและถูกผลิต ทำให้ผลิตน้ำมันได้ในปริมาณที่มากขึ้น อย่างไรก็ดีการดูดซับของสารลดแรงตึงผิวบนพื้นผิวตัวกลางที่มีรูพรุนส่งผลให้เกิดความไม่มีประสิทธิภาพในเชิงเศรษฐศาสตร์ การศึกษานี้จัดทำเพื่อค้นหากระบวนการดูดซับและกระบวนการคายตัวรวมไปถึงค่าการย้อนกลับของการดูดซับของสารลดแรงตึงผิวทั้งแบบคงที่และแบบพลวัตระหว่างโซเดียมโดเดคซิลเบนซีนซัลโฟเนตและหินทรายเบเรีย จากนั้นการศึกษาตัวแปรเชิงปฏิบัติการได้แก่ขนาดก้อนมวลของสารลดแรงตึงผิว ความเข้มข้นของสารลดแรงตึงผิวและค่าการดูดซับของสารลดแรงตึงผิวร่วมกับค่าการย้อนกลับของการดูดซับได้ถูกทำการศึกษาโดยใช้โปรแกรมแบบจำลองการไหลในแหล่งกักเก็บ STAR

ผลการทดลองการดูดซับแบบคงที่แสดงให้เห็นว่า การดูดซับของสารลดแรงตึงผิวบนหินทรายเบเรียเป็นไปตามการดูดซับของแลงเมียร์ไอโซเทอมโดยค่าการดูดซับและการคายตัวสูงสุดคือ 90 มิลลิกรัม และ 27 มิลลิกรัมต่อร้อยกรัมของหินตามลำดับที่ความเข้มข้นของสารลดแรงตึงผิว 1 เปอร์เซ็นต์โดยน้ำหนัก อย่างไรก็ตาม ความแตกต่างของค่าการดูดซับและค่าการคายตัวที่ได้จากวิธีแบบพลวัตด้วยการใช้ความเข้มข้นของสารลดแรงตึงผิวที่เดียวกันอยู่ที่ 54.65 มิลลิกรัม และ 47.86 ต่อร้อยกรัมของหินตามลำดับ

การศึกษาผลกระทบของค่าการย้อนกลับของการดูดซับสารลดแรงตึงผิวบนตัวแปรเชิงปฏิบัติการเปิดเผยให้เห็นว่าปริมาณน้ำมันที่ได้เพิ่มมากขึ้นได้มาจากการใช้ก้อนมวลสารลดแรงตึงผิวที่มีขนาดใหญ่และความเข้มข้นของสารลดแรงตึงผิวนอกเหนือไปจากความเข้มข้นที่เกิดค่าการดูดซับสูงสุด ในกรณีของการยึดปริมาณของสารลดแรงตึงผิวคงที่ ก้อนมวลสารขนาดใหญ่ที่ความเข้มข้นของสารลดแรงตึงผิวต่ำจะเหมาะกับการใช้สารลดแรงตึงผิวปริมาณต่ำในขณะที่การใช้ปริมาณสารลดแรงตึงผิวมากจะเหมาะกับก้อนมวลสารขนาดเล็กที่ความเข้มข้นสูง

การนำไปใช้จริงของการฉีดอัดสารลดแรงตึงผิวซึ่งพิจารณาผลกระทบของค่าการย้อนกลับร่วมด้วยควรกระทำที่ความเข้มของสารลดแรงตึงผิวนอกเหนือไปจากความเข้มข้นที่ทำให้เกิดค่าการดูดซับของสารลดแรงตึงผิวสูงสุดและใช้ก้อนมวลสารขนาดใหญ่ ยิ่งไปกว่านั้น ก้อนมวลสารขนาดเล็กเหมาะกับแหล่งกักเก็บที่มีค่าการดูดซับสูง ในขณะที่ก้อนมวลสารขนาดใหญ่จะเหมาะกับหินที่มีค่าการดูดซับต่ำ

ภาควิชา	วิศวกรรมเหมืองแร่และปิโตรเลียม	ลายมือชื่อนิสิต	....
สาขาวิชา	วิศวกรรมปิโตรเลียม	ลายมือชื่อ อ.ที่ปรึกษาหลัก	....
ปีการศึกษา	2558		

5771231321 : MAJOR PETROLEUM ENGINEERING
KEYWORDS: ADSORPTION REVERSIBILITY / SURFACTANT FLOODING / CHEMICAL ENHANCED OIL RECOVERY

ICH HUY NGO: Effects of Reversibility of Surfactant Adsorption on Surfactant Flooding. ADVISOR: FALAN SRISURIYACHAI, Ph.D., 132 pp.

The application of surfactant flooding is aimed to reduce interfacial tension (IFT) between aqueous and oil phases to achieve ultra-low condition. By this ultra-low condition, oil can be liberated and consecutively oil recovery is increased. However, surfactant adsorption in porous media as surfactant solution is in contact with reservoir rock surface results in a considerable economical ineffectiveness. This study is proposed to investigate adsorption and desorption mechanisms together with reversibility of surfactant adsorption in static and dynamic tests between Sodium Dodecyl Benzene Sulfonate (SDBS) and Berea sandstone. After that, study of operational parameters including surfactant slug size, surfactant concentration, and surfactant adsorption value is performed in STAR® commercial simulator. Furthermore, degrees of reversibility of surfactant adsorption on operational parameters are evaluated to investigate the effectiveness of this behavior on surfactant flooding.

Laboratory experiment results of static tests revealed that adsorption of SDBS onto Berea sandstone obeys Langmuir adsorption isotherm, and the maximum adsorption and desorption values are 90 mg/100g and 27 mg/100g respectively at surfactant concentration of 1.0 %wt. However, different adsorption-desorption values are observed in dynamic tests on 1.0 %wt. concentration, which are 57.65 mg/100g and 47.86 mg/100g respectively.

Study of the effects of reversibility of surfactant adsorption on interested operational parameters revealed that the best additional oil recovery is obtained from bigger injection slug with concentrations other than the maximum adsorption concentration. In case of fixed injection mass, larger slug size with less concentration for small surfactant amount, and smaller slug with higher concentration for large surfactant amount are preferred.

Implementation of surfactant flooding with consideration on effects of reversibility should be performed at concentrations other than the maximum surfactant adsorption concentration with bigger slug size. Moreover, small slug size is suitable for high adsorption reservoir, while larger slug is preferred in case of low adsorption rock surface.

Department:	Mining and Petroleum Engineering	Student's Signature	....
		Advisor's Signature	....
Field of Study:	Petroleum Engineering		
Academic Year:	2015		

ACKNOWLEDGEMENTS

First and the foremost, I would like to express my sincere gratitude to my thesis advisor, Dr. Falan Srisuriyachai, who conveys his precious guidance, support, patience, encouragement during my graduate studies. His sophistication and trustful knowledge has stimulated me a lot throughout this research.

My profound thanks to all professors and faculty members in the Department of Mining and Petroleum Engineering who contributed education of petroleum engineering and valuable suggestion. I wholeheartedly appreciate the opportunity to involve in field of petroleum engineering, and to be a part of the Department of Mining and Petroleum Engineering. I also would like to show courtesy to my thesis committees for their recommendations on my study.

I would like to express my gratefulness to Mr. Panupong Lohrattannarungrot for instructing me basic knowledge of CMG software, and also appreciate helpful discussion to solve for solution.

It is my privilege to acknowledge AUN/SEED-Net for financial support and the Department of Mining and Petroleum Engineering for laboratory equipment for all experiment performance of this study.

I am grateful to all my classmates during my graduate studies in Thailand, who always offer me sincere friendship and reinforcements.

Last but not least, my gratitude goes to my family for their encouragement, patience, assistance and understanding.

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List of Abbreviations

%wt.	Weight by percent
%RF	Recovery Factor by percent
^{o}API	American Petroleum Institute gravity
bbl	Barrel
bbl/day	Barrel per day
BHP	Bottomhole Pressure
^{o}C	Degree Celsius
Ca^{2+}	Calcium ion
CaCl$_2$	Calcium Chloride
CAC	Critical Admicelle Concentration
cm^3	Cubic meter
CMC	Critical Micelle Concentration
Cu.ft	Cubic feet
cP	CentiPoise
cSt	CentiStokes
Da	Dalton
DTWELL	First time step size after well change
DWOC	Water-Oil Contact Depth
dyne/cm	Dyne per centimeter
EO	Ethlylene oxide Oligomer
EOR	Enhanced Oil Recovery
^{o}F	Degree Fahrenheit
ft.	Foot/Feet
g	Gram
g/ml	Gram per milliliter
gm/cm^3	Gram per cubic meter
GOR	Gas Oil Ratio

IFT	Interfacial Tension
ISOTHERM	Isothermal option
ITERMAX	Linear solver iteration
KCl	Potassium Chloride
KRGCL	Relative permeability to gas at connate liquid saturation
KROCW	Relative permeability to oil at connate water saturation
KROGCG	Relative permeability to oil at connate gas saturation
KRWIRO	Relative permeability to water at irreducible oil saturation
lb/lbmole	Pound per mole
mD	MilliDarcy
Mg^{2+}	Magnesium ion
$MgCl_2$	Magnesium Chloride
mg/100g	Milligram per hundred grams
ml	Milliliter
MMbbl	Million barrel
MW	Molecular Weight
Na	Sodium
NaCl	Sodium Chloride
$NaHCO_3$	Sodium Hydrogen Carbonate
Na_2SO_4	Sodium Sulfate
OOIP	Original Oil In Place
pH	Potential of Hydrogen
ppm	Part per million
psia	Pound per square inch absolute
PV	Pore Volume
PVT	Pressure-Volume-Temperature
p.z.c.	Point of zero charge
REFDEPTH	Reference depth
REFPW	Reference pressure
SCF/STB	Standard Cubic Feet per Stock Tank Barrel
SDBS	Sodium Dodecyl Benzene Sulfonate

SGCON	Connate gas saturation
SGCRIT	Critical gas saturation
SOIRG	Irreducible oil saturation for Gas-Liquid table
SOIRW	Irreducible oil saturation for Water-Oil table
SORG	Residual oil saturation for Gas-Liquid table
SORW	Residual oil saturation for Water-Oil table
STL	Surface liquid rate
STO	Surface oil rate
STW	Surface water rate
SWCON	Connate water saturation
SWCRIT	Critical water saturation
TRES	Reservoir temperature
WCUT	Water-cut
WOC	Water-oil contact

Nomenclatures

γ_o/w	Interfacial tension between oil and water
ϕ	Porosity
ϕ_{eff}	Effective porosity
μ_g	Gas viscosity
μ_w	Water viscosity
μ_o	Oil viscosity
A	Area per surfactant molecule
Ad	Adsorption concentration
B_g	Gas formation volume factor
B_o	Oil formation volume factor
C_o	Surfactant initial concentration
C_e	Surfactant concentration after adsorption
k_h	Horizontal permeability
k_v	Vertical permeability
k_{rg}	Relative permeability to gas
k_{rog}	Relative permeability to oil for Gas-Liquid system
k_{row}	Relative permeability to oil for Water-Oil system
k_{rw}	Relative permeability to water for Water-Oil system
M	Molecular weight of the surfactant
Nc	Capillary number
p_b	Bubble point pressure
q	Flow rate per unit cross-sectional area
R_s	Solution gas-oil ratio
S_l	Liquid saturation
S_w	Water saturation
S_{wc}	Connate water saturation
S_{wi}	Initial water saturation

V	Surfactant solution volume

CHAPTER 1

INTRODUCTION

1.1 Background

In reservoir study, oil is conventionally produced by means of primary recovery that principally depends on driving energy of reservoir itself in early stage. Once reservoir is exploited for certain period, the subsurface driving force is no longer sufficient to lift oil up to surface. Secondary recovery methods such as water injection and gas injection are then applied to provide additional energy to reservoir. Generally, additional forces could help to produce up to 30-50 % of oil after primary and secondary techniques [1]. But remaining oil which is trapped by means of capillary pressure, unfavorable rock-fluid condition (oil-wettability) and inaccessible from reservoir heterogeneity will not be recovered by means of secondary methods. Therefore, tertiary recovery or Enhanced Oil Recovery (EOR) techniques can be selected to resolve these problems.

Enhanced oil recovery techniques are highly effective in terms of driving more oil from reservoir. Surfactant flooding is a technique that can potentially lower interfacial tension (IFT) between oil and aqueous phases. At ultra-low IFT, oil can be liberated by an aid of surfactant in a form of emulsion. Nevertheless, surfactant can be highly absorbed onto reservoir rock from both physical and chemical interactions. Depletion of surfactant causes severe impact in terms of quantity of surfactant required in the operation; this implies that extra expenses of surfactant consumption should be taken into consideration.

Several studies of surfactant adsorption suggested that surfactant will not be permanently absorbed onto or can desorb from rock surface [2]. At certain surfactant concentration and certain ratio of surfactant amount and specific rock surface, adsorption of surfactant can be reversible, partially reversible or permanently irreversible. This different degree of reversibility in surfactant adsorption will result in different selection of proper operating conditions as well as effects from reservoir parameters on surfactant flooding process. Therefore, if reversibility of surfactant adsorption can be determined and quantified, oil recovery can be maximized based on production scheme fit for different degrees.

Regarding to this problem, a study of reversibility of surfactant adsorption is investigated. In this study, both laboratory study and reservoir simulation are performed. First, a representative anionic surfactant is experimented to identify surfactant adsorption/desorption with Berea sandstone. Dynamic adsorption and degree of reversibility are determined for different surfactant concentrations at reservoir temperature. Obtained data are used in reservoir simulation study. A reservoir simulator called STAR® commercialized by Computer Modeling Group (CMG) is utilized in reservoir simulation section. Surfactant concentration, surfactant slug size surfactant adsorption will be taken into consideration. In the last step, important parameters of surfactant flooding including reversibility value and magnitude of surfactant adsorption are studied for their sensitivity by varying the values. Oil recovery factor, surfactant consumed per barrel of oil recovered, and water production are used for evaluating effectiveness of surfactant flooding. From this study, adsorption of surfactant can be well understood, and this would facilitate maximizing oil recovery.

1.2 Objectives

1. To quantify reversibility of static and dynamic surfactant adsorption of anionic surfactant on sandstone surface.
2. To study effects of reversibility of surfactant adsorption on operating parameters in surfactant flooding, including surfactant concentration, surfactant slug size, and surfactant adsorption.
3. To evaluate effects of interest properties including value of reversibility of surfactant adsorption and magnitude of surfactant adsorption on effectiveness of surfactant flooding.

1.3 Outline of Methodology

1. Perform laboratory experiment of interested rock sample and surfactant by stirring process and flowing through core sample to obtain adsorption value and reversibility degree.
2. Base case reservoir model is developed in reservoir simulator to perform waterflooding for attaining reference oil recovery and water production.
3. Simulate the reservoir simulation model to investigate the influence of internal parameters on the effectiveness of reversibility of surfactant adsorption on surfactant flooding which include
    - Interfacial tension value
    - Capillary number of wetting and non-wetting phases
4. Simulate the models to evaluate the effects of operational parameters which include
    - Surfactant concentration
    - Surfactant slug size
    - Surfactant adsorption values
    - Reversibility degree of surfactant adsorption
5. The sensitivity analysis of all cases will be performed with the consideration of oil recovery, surfactant consumption, and water production.

1.4 Outline of Thesis

There are six chapters in this thesis as shown in following outline.

Chapter I introduces background of surfactant flooding and indicates the objectives and abbreviated methodology of this study.

Chapter II introduces previous studies related to surfactant flooding and adsorption behaviors of surfactant onto reservoir rock, and petrophysical and reservoir properties which affect surfactant adsorption.

Chapter III demonstrates the relevant theories related to the mechanism of surfactant flooding, interaction of surfactant with rock surface, and surfactant loss mechanism.

Chapter IV describes the details of laboratory experiment and designs of tests. Then the structures and designs of reservoir model dimension and petrophysical properties, pressure-volume-temperature (PVT) properties of reservoir fluids, core analysis data, and well data are presented.

Chapter V provides the results and discussions for laboratory experiments and reservoir simulation studies. In laboratory experiment section, test results will be discussed to use as reference values for reservoir simulation. The results of reservoir simulation section are compared mainly on oil recovery factor together with amount of produced water and surfactant consumption. The final effectiveness of reversibility of surfactant adsorption on surfactant flooding is discussed in comparison of additional oil recovery to non-reversible surfactant adsorption.

Chapter VI presents the conclusion and recommendations of this study.

CHAPTER 2
LITERATURE REVIEW

2.1 The Study of Reversible and Irreversible Surfactant Adsorption

During surfactant flooding, reservoir rock is in direct contact with surfactant slug prior to chasing water. This creates an environment with high tendency of surfactant to adhere onto reservoir rock rather than staying in bulk solution. According to this, surfactant is adsorbed onto reservoir rock and fails to establish the ultra-low interfacial tension condition. Therefore, adsorption behavior of surfactant solution onto reservoir rock plays an important role in surfactant flooding. Reversibility and irreversibility of surfactant adsorption from reservoir rock have been studied and are reviewed in this section.

Somasundaran and Shafick Hann [3] studied adsorption and desorption of sulfonates on reservoir rock with various sulfonate concentrations. In this study, several sodium dodeclbenzenesulfonate (SDBS) concentrations were performed in the laboratory test on Na-kaolinite mineral. The term abstraction was used to describe adsorption of sulfonate and other precipitation reactions onto rock surface. The results of batchwise abstraction and stepwise de-abstraction showed that there was significant amount of sulfonates desorbed from rock surface with the dilution of surfactant concentration. Interestingly, de-abstraction isotherms indicated remarkable hysteresis occurrence when large different amount between pre-dilution surfactant concentration and the concentration which abstraction isotherms reached the maximum. This phenomena was explained to be caused by the bulk precipitates which can block pore space. Apart from surfactant concentration, pH value of the solution also showed noticeable adsorption results. At nearly neutral pH of 6.6, there was less hysteresis which means the de-abstraction isotherm was similar to the abstraction isotherm. As the experiment was performed at more acidic pH of 4.6, there was marked hysteresis; this indicated that there was higher problematic with acidic pH as more precipitation occurred. Moreover, the study also pointed out that higher adsorption of surfactant solution by rock surface occurs at lower pH value.

In 2000, Geffroy et al. [4] investigated the reversibility and kinetics of nonionic surfactant adsorption onto polystyrene. The research was conducted to use four types of nonionic surfactant consisting of alkyl group (C8, C12) and short ethylene oxide oligomer (EO). The experiment was performed by using C8E5, C12E5, C12E6 and C12E8 onto hydrophobic polystyrene surface. The study postulated that surfactant adsorption was reversible with evidences that it was matched residual surfactant concentration on surface between desorption test by flowing pure water and adsorption isotherms at very low concentration. In addition, the same re-adsorbed amount of surfactant with the initial surfactant concentration was found after desorption experiment. From the study, it is also interesting to note that there is a limit residual amount of surfactant which can be either not desorptable or it would take extremely long time to observe which is reported up to about 10^7 hours.

2.2 Reservoir and Petrophysical Properties Affecting Surfactant Adsorption

As easy or conventional oil era has almost come to the end, more challenging reservoirs must be taken into production with Enhanced Oil Recovery (EOR) methods. Surfactant flooding is one of the common chemical EOR which is believed to lower interfacial tension between immiscible fluids, alter wettability of rock surface, and improve oil recovery. Meanwhile, the application of surfactant is not proficient as there are still challenges of the method. One of which is the adsorption of surfactant onto reservoir rock that reduces its efficiency in terms of economic consideration. To respond to this matter, a lot of surfactant adsorption research have been performed to mitigate surfactant adsorption. The section below reviews the previous studies on several reservoir and petrophysical properties that affect the surfactant adsorption as well as caution to prevent further adsorption.

Ziegler et al. [5] studied the effects of temperature which can alter the adsorption of surfactants. In the study, two conventional types of surfactants, sodium dodecylbenzenesulfonate and nonylphenoxypolyethanol, were tested on Fired Berea sandstone in several selected temperature values. The observation of anionic surfactant showed that surfactant tends to adhere more onto rock surface in lower temperature (25°C) than the higher (95°C). This phenomenon is also true in the case of using nonionic surfactant and applicable as well with the condition that surfactant concentration is high. Moreover, the study also pointed out that adsorption behavior may also be affected from the degradation of surfactant at high temperature when using nonionic surfactant, because when shortening equilibration time there was only little decrease in adsorption when temperature increased.

Hamid and Onur [6] performed a study of surfactant adsorption behaviors with the consideration of effects of surfactant concentration, reservoir temperature and solution pH value. In the experiment, sodium dodecylsulfate, an anionic surfactant was tested on the Berea sandstone with variable concentrations, temperature and pH values. Focusing on changes in concentration, the adsorption rises with the increases in surfactant concentration. However, no more adsorption takes place when the isotherm curve reaches a plateau which indicates that there is no available space for surfactant molecule to adhere onto rock surface. This adsorption behavior of anionic surfactant goes along with the Langmuir theory. The result of temperature effect indicated that adsorption of surfactant onto rock surface drops substantially when increasing temperature of experiment. This is understood as a result of solubility of surfactant, it is enhanced as the temperature builds up. Therefore, surfactant prefers to accommodate in solution than to attach to rock surface. The outcome of pH effects showed that adsorption decreases as pH increases in the case of using anionic surfactant. This could be explained by electrostatic repulsion of same negative charges between rock surface and anionic surfactant polar molecules, because as pH is more basic, rock surface become more negatively charged.

Azam et al. [7] investigated the static adsorption of anionic surfactant onto crushed Berea sandstone. In the study, temperature, pH, and salinity were examined to determine their effects on adsorption of anionic surfactant. In the laboratory experiment, synthesized anionic surfactant (16 to 18 carbons chain with a sulfonate head group), sodium tetraborate, sodium metaborate, sodium hydroxide, hydrogen chloride, sodium chloride, methanol, sulfuric acid and sodium carbonate together with Berea sandstone core were utilized as testing materials. The analysis of point of zero charge of Berea sandstone was found to be pH 8.0; therefore, any pH of solution higher than this value will lead to lower adsorption of surfactant as the repulsion of same negative charge between anionic surfactant and rock surface and vice versa. The study also verified the effect salinity by adding NaCl into solution. As a result, the increase of anionic adsorption was found as salt concentration was increased. This is because of decrease of the function of electrostatic repulsion in adsorbed layer. The authors also reported that adsorption of anionic surfactant drops as temperature rises. This can be explained as there is weaker force interaction between Berea sandstone and surfactant at hotter environment.

El Mofty [8] studies the surfactant enhanced oil recovery by wettability alteration in sandstone reservoirs. There were two types of surfactants used to perform on Berea sandstone in order to analyze sensitivity of oil recovery in the study, Alfoterra 145-4S and Alfoterra 145-8S. Both surfactants are sodium salt of a monoalkyl C_{14}-C_{15} branched propoxysulphate, but differ in density, 1.01g/ml and 1.03g/ml, viscosity of 4,485 cSt and 1,600 cSt, respectively. For the wettability test, different surfactant concentrations were used to measure contact angle of water droplet on the oil-treated glass chips. The results showed continuous reduction of droplet contact angles to zero after surfactant was brought to the system. This indicated that wetting condition of glass has been altered from oil-wet to water-wet after mixing with surfactant solution. Moreover, with higher surfactant concentration, the duration of contact angle declines to zero was faster than that of lower concentration. In terms of oil recovery, the study showed that there was additional 26 to 27% of OOIP recovered from the effects of wettability. Resulting from the effects of wettability alteration, duration of achieving additional recovered oil decreases with an increase in surfactant solution concentration.

ShamsiJazeyi et al. [9] compared sacrificial agents for reducing adsorption of anionic surfactants on several reservoir minerals. In the study, two types of surfactant were used including NI-Blend (Neodol-67 and IOS15-18) and Petro-step S13B, to perform on purified calcite, industrial calcite, Carlpool dolomite, Indiana limestone, purified kaolinite, and powdered Berea sandstone. Varied molecular weights of sodium polyacrylate, and sodium carbonate as alkali were utilized as chemical additives and comparison was made. The results of performing batch adsorption test between blend anionic surfactants and different minerals with addition of sodium polyacrylate or sodium carbonate revealed that there was a significant reduction in adsorption with mixing of both sacrificial agents. Moreover, it was proven that using sodium polyacrylate reduced more adsorption of anionic surfactant onto dolomite, kaolinite, calcite and limestone compared to sodium carbonate. However, in case of anionic surfactant/Berea sandstone system, the decline adsorption values by both chemicals showed further drop of adsorption amount when using sodium carbonate. The experiment also discovered inefficacy of alkali where calcium sulfate minerals present (usually gypsum and anhydrite), so this gave an idea that alkali is not applicable when reservoir rock contains high amount of anhydrite or gypsum. When questioning how much sodium polyacrylate molecular weight was sufficient to reduce anionic surfactant adsorption, the answer was 4,500 Da, and adsorption decreased with increase in molecular weight. As the experimental data revealed, over this rate, the adsorption curves lay on the same path as which of 4,500 Da.

From literature reviews, surfactant adsorption and desorption onto reservoir rock surface have been studied in a certain degree. However, the effectiveness of reversibility of surfactant adsorption in surfactant flooding has not yet been performed. This study is then aimed to investigate the effects of reversibility of surfactant adsorption in surfactant flooding.

CHAPTER 3
RELEVENT THEORY

3.1 Surfactant Flooding

Surfactant flooding is an enhanced oil recovery technique that is used to lower the interfacial tension (IFT) between oil and aqueous phase by injecting mixture of surfactant and fluid. As a result, oil can be liberated from rock surface, turning into small droplets or emulsion form [10]. Surfactant flooding is one among the most popular EOR techniques; but because of the high cost of injectant, it cannot be economically performed. However, when the crude oil price increases, surfactant is considered to be a potential improved oil recovery agent. Thus, studying the adsorption behaviors of surfactant on rock surface and considering the criteria for reservoir and oil properties are very important for controlling surfactant loss into the formation. Surfactant flooding is not suitable for reservoir which its temperature and depth are higher than 200°F and 9,000 feet respectively. As temperature is elevated in deeper formation, surfactant is less resistive in this environment. Reservoir thickness and average permeability do not potentially affect the process. Sandstone reservoir is preferred as most surfactant used in the process is anionic type which reduces the problem of surfactant depletion. In addition, light to intermediate oil is recommended for surfactant flooding. Therefore, oil gravity and viscosity are generally limited for the range greater than 20°API and lower than 35cP, respectively. Some other criteria also affect the effectiveness of surfactant flooding such as presence of clay, formation water chlorides above 20,000 ppm, and divalent ions (Ca^{2+} and Mg^{2+}) higher than 500 ppm [11].

Surfactant is amphiphilic; a single surfactant molecule commonly contains hydrophobic non-polar part or tail portion which is soluble in hydrocarbon, and hydrophilic polar part or head portion which is soluble in water [2].

According to the ionic head portion of surfactant, it can be categorized into four groups as anionic, cationic, nonionic, and zwitterionic or amphoteric. As shown in Figure 3.1, anionic surfactant contains negative charge in polar part, making it to be less adsorbed onto sandstone surface; therefore, it is extensively applicable for chemical flooding of EOR processes. In contrary, positive charge of the polar portion of cationic surfactant makes it inapplicable for sandstone reservoir because of the high adsorption rate onto the rock surface; but cationic surfactants can be utilized for positively charged carbonate rock to alter the wettability from oil-wet to water-wet. Nonionic surfactant is not preferable in terms of IFT reduction, but it can tolerate high salinity environment; therefore, it is mostly used with anionic to cope with great salinity. Zwitterionic surfactants can be in forms of nonionic-anionic, nonionic-cationic, or anionic-cationic; they are applicable in high temperature and high salinity conditions, but they are costly [2].

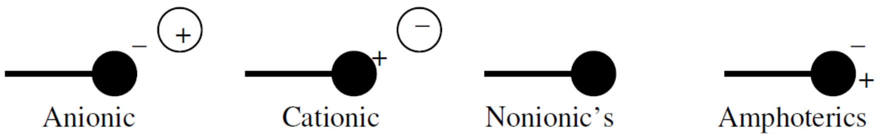


Figure 3.1 Classification of surfactants [10]

The objective of surfactant flooding is to decrease residual oil saturation, and this is related to capillary number. After performing waterflooding, typical value of capillary number ranges from 10^{-6} to 10^{-7}. Half of oil will be expelled from waterflooded reservoir if capillary number is raised to 10^{-3}, and all of oil will be depleted when increasing capillary number to the range of 10^{-2} to 10^{-1}, as demonstrated in Figure 3.2. There are several means to increase capillary number, by increasing the aqueous phase viscosity and flow rate, or by lowering IFT between oil and water phases. In order to increase capillary number to the mentioned range, corresponding IFT of 10^{-3} or 10^{-4} dynes/cm must be achieved by using right amount of surfactant [12]. Capillary number can be expressed in Equation 3.1:

$$N_C = \frac{\mu_w \emptyset q}{\gamma_o / w} \qquad \text{Equation 3.1}$$

where N_C is capillary number, μ_w is viscosity, q is flow rate per unit cross-sectional area of water and γ_o/w is interfacial tension between oil and water.

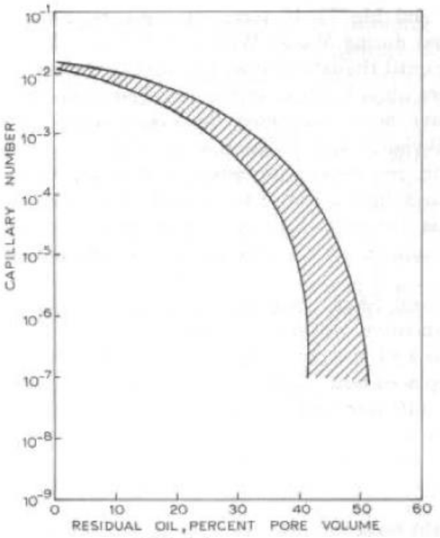


Figure 3.2 Correlation between capillary number and residual oil saturation [12]

Figure 3.3 Role of IFT in surfactant flooding [12]

Figure 3.3 shows the movement of oil through pore throat. An ultra-low IFT provides ease for residual oil to flow through narrow necks of pore channels, and this can be achieved by the use of appropriate amount of surfactant [12]. Initially, when surfactant is brought to the system, the molecule sticks at the interface of oil and aqueous phase, and it reduces interface energy and separates hydrophobic parts of the surfactant from contact with water. As surfactant reaches its Critical Micelle Concentration (CMC), monomers of surfactant start to form micelles, this will lower the contact area of hydrophobic parts of surfactant with water phase, thus IFT is effectively decreases [2]. As dedicated in Figure 3.4, after reaching CMC, any further addition of surfactant will just increase the number of micelles and monomers are pulled away from interface, thus IFT increases again. However, Figure 3.5 presents that adding surfactant to certain concentration, IFT starts to decline again and create a new film layer phase as a bridge between oil and water phase.

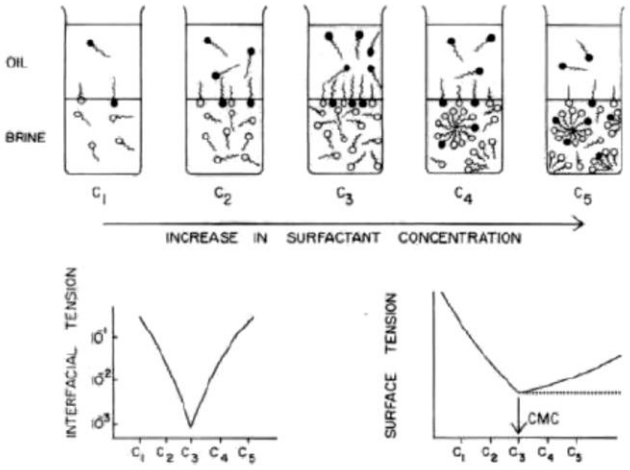


Figure 3.4 Molecular mechanism for the effect of surfactant concentration on interfacial surface tension [12]

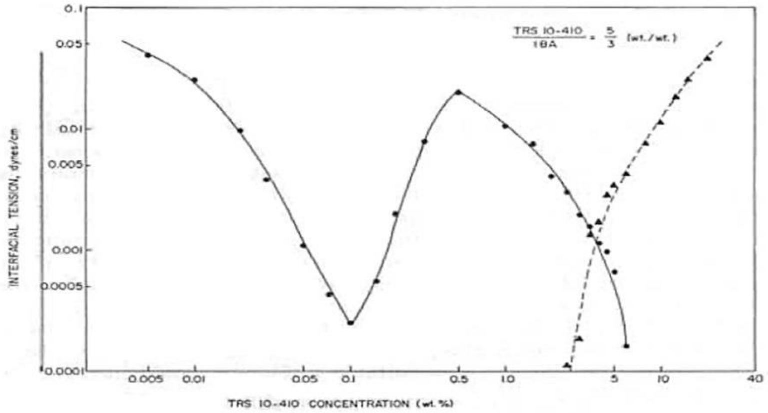


Figure 3.5 Effect of surfactant concentration on IFT [12]

Surfactant solution phase behavior is very sensitive to salinity of brine. As brine is increased in salinity, surfactant hence reduces its solubility in the brine. This kind of phase behavior is commonly dedicated on the ternary diagram as shown in Figure 3.6. At low salinity, surfactant is more soluble in aqueous phase; but there is surfactant free in oil phase. Therefore, the system generates two phases, an excess oil phase and a water-external micro-emulsion phase. This micro-emulsion is called Winsor type II(-), because there are two phases and the slopes of tie lines are negative. At high salinity, system develops an oil-external micro-emulsion phase and an excess water phase. This micro-emulsion is called Winsor type II(+) because tie line-slope is positive. At moderate range of salinity, system produces three phases, excess oil, micro-emulsion, and excess water. This micro-emulsion is called Winsor type III, and ultra-low IFT occur when brine change to this salinity [2].

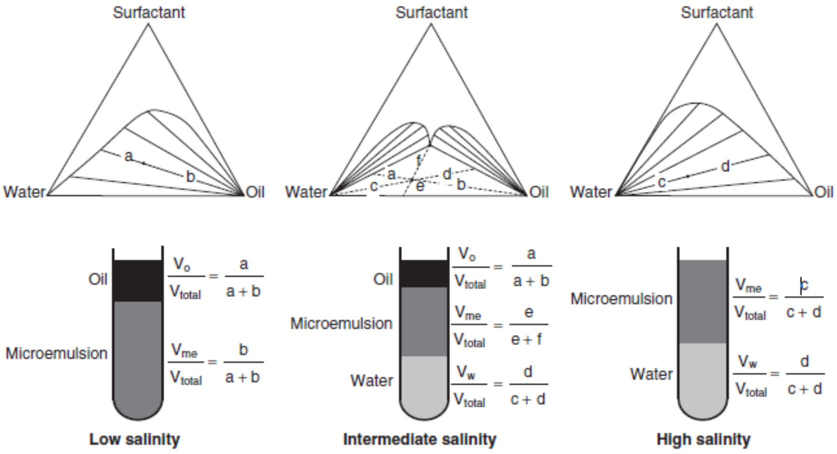
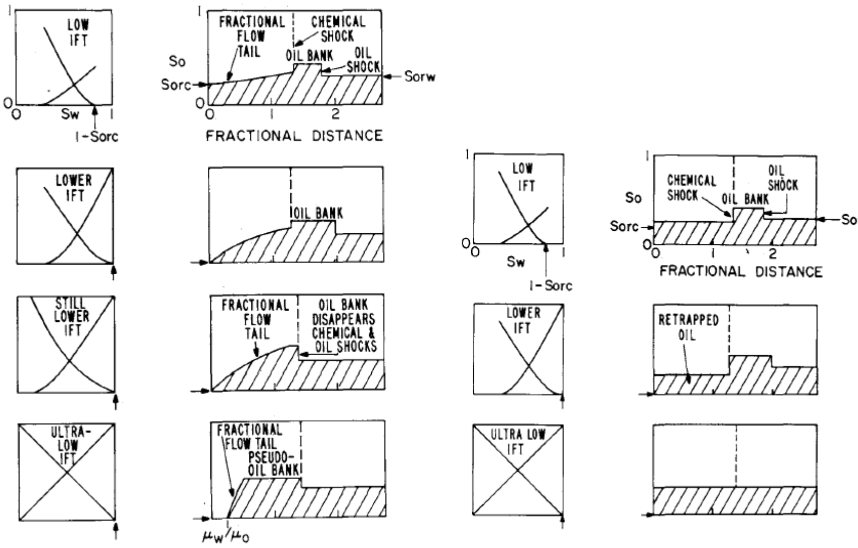


Figure 3.6 Three types of micro-emulsions and effects of salinity on the phase behavior [2]

Oil displacement mechanism mainly depends on emulsification entrainment and entrapment in terms of microscopic and macroscopic respectively. And these directly related to IFT and relative permeability curve. For emulsification and entrainment mechanism, when surfactant is increased reaching the concentration at which ultra-low IFT is generated, fine emulsion is formed and flow with water flow line through pore neck. As can be seen in Figure 3.7 (a), at low IFT condition, liberated oil increases to form an oil bank and fractional flow tail decreases. At the same time, water flows better at higher IFT because of rising of relative permeability to water. As the relative permeability to water increases, it stimulates the chemical shock front to flow at the same velocity as oil shock front by displacing irreducible water saturation in reservoir. The relative permeability curves to both oil and water will eventually become linear function with saturation when surfactant concentration reach ultra-low IFT. At this condition, injected chemical displaces all fluids and create pseudo oil bank.

In the emulsification and entrapment, the oil droplet is trapped in the small pore throats. This forces the injection water to drive into un-displaced pores. This results in increasing the displacement efficiency which turn the relative permeability curve into linear function again that can be found in Figure 3.7 (b).



(a) (b)

Figure 3.7 (a) Oil recovery by reduction of interfacial tension with no viscosity alteration (b) Oil recovery by reduction of interfacial tension upon dilution of chemical with water [13]

3.2 Interaction of Surfactant and Rock Surface

The process of adsorption involves with the concentration of any chemical species sticking at an interface between two phases. And the mechanism of transporting adsorbing species to the interface is depending on diffusion. The adsorption behavior can be either physical or chemical in nature. There are many different ways to distinguish physical and chemical adsorption such as lower heat generation of physical adsorption comparing to chemical adsorption, reversibility of physical adsorption-desorption, typical lower rate of chemical to physical adsorption. However, the most frequently criterion used to differentiate the adsorption type is the charge transfer. It is considered as physical adsorption if there is no sharing electron while adsorption taking place; in contrast, chemical adsorption occurs when electrons are transferred [14].

The adsorption of surfactant from aqueous solution is based on two factors, energy to alter the surface-water contact to surface-surfactant contact, and the removal of surfactant hydrocarbon moiety from the aqueous environment. Generally, surfactant adsorption occurs between a surface phase and the bulk solution phase as shown in Figure 3.8. The adsorption mechanism is according to the concentration of surfactant added into the system. Before approaching CMC, there is a slope that illustrates the adsorption energy with its steepness, the steeper the slope, the higher the adsorption energy. However, above CMC, the surfactant activity becomes constant and the adsorption turns to be more stable as illustrated in log-log plot in Figure 3.9. The adsorption can be expressed as in the relationship in Equation 3.2 [15].

$$A = \frac{M}{\Gamma_{max} \times 6.02} \qquad \text{Equation 3.2}$$

where:
A: Area per surfactant molecule ($\text{Å}^2/molecule$),
M: Molecular weight of the surfactant.

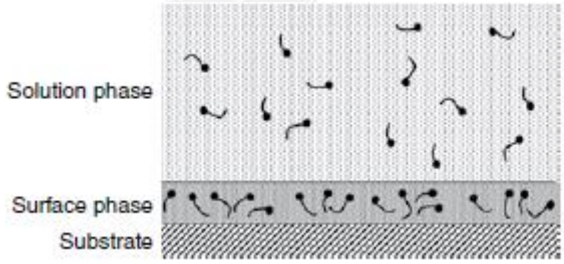


Figure 3.8 Adsorption onto the surface is regarded as a separate phase in equilibrium with the solution [15]

The adsorption of surfactant is commonly discribed in four-region isotherms. In the region I, low concentration of surfactant is introduced to the sytem, leading to individual adsorption of surfactant monomers as ions and there is no interaction between the adsorbed molecules. In region II, adsorbed surfactants are strengthened with increasing in concentration. As can be seen in Figure 3.9, at the changing slope point between region I and II, the first surfactant aggregates form on the rock surface; this corresponding concentration is called Critical Admicelle Concentration (CAC). The changing of slope in region III can be explained as that surfactant molecules are filled all the rock surface and surfactant further form another layer onto the existing one so-called bilayer formation of surfactant. This also indicates that the adsorbed surfactant ions causes reversal in surface charge of the rock. In region IV, the slope becomes horizontal meaning that there is very little or no increase in adsorption with any incremental of surfactant concentration. This phenomenon occurs when surfactant reaches CMC, and it is also the point where surfactant aggregates have a bilayer structure [16].

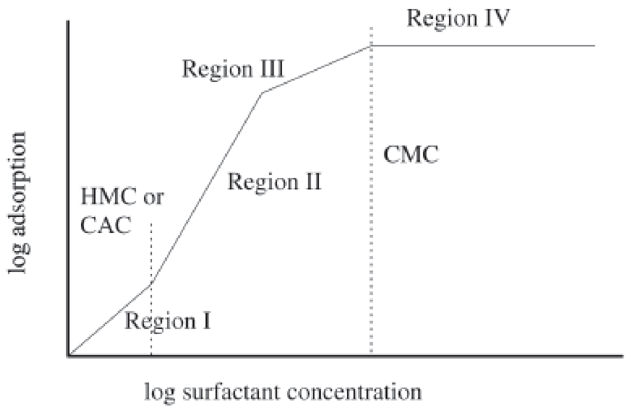


Figure 3.9 Typical four-region adsorption isotherm for a mono-isomeric surfactant [16]

The surfactant adsorption behaves differently when the surface is hydrophobic or hydrophilic. Figure 3.10 indicates that, surfactants stick their hydrocarbon chain at the surface when the concentration is low, but as the concentration increases higher, monolayer is formed on the hydrophobic surface. Driving force of the surfactant adsorption depends on the surfactant hydrocarbon moiety to desorb from aqueous environment. On the adsorbing at a hydrophobic surface some of the unfavorable water-hydrocarbon contacts are lost and this is the main driving force for adsorption. The mechanism of surfactant adsorbing to the hydrophilic surfaces is very different from which at hydrophobic surfaces. As illustrated in Figure 3.11, there is a weak adsorption at very low surfactant concentration, surfactants are individually adsorbed onto rock surface without interacting among each other; at critical concentration, a strong adsorption occurs which can be seen as the CMC in the surface phase, and it is ten times lower than CMC; meanwhile, adsorption will hit its limit at higher concentration, and there is no further adsorption.

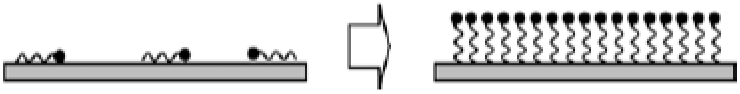


Figure 3.10 Illustration of the adsorption of surfactant at a hydrophobic surface [15]

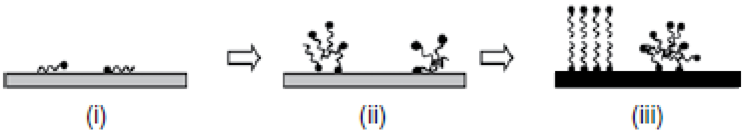


Figure 3.11 Illustration of the adsorption of surfactant at a hydrophilic surface [15]

However, surfactant can be desorbed from rock surface at salinity and pH at reservoir conditions. In 2011, Sheng illustrated that salinity can lower adsorption of surfactant with less saline water; this phenomenon is explained in Figure 3.12. pH value alters the charge of rock surface from negative to positive or vice versa which can be explained by the principle of Point of Zero Charge (p.z.c.) [10]. Sandstone generally possesses p.z.c. about 2.5 and carbonate rock has the value of 9.0. Therefore, at reservoir condition where pH value is in between 6 and 8, sandstone is negatively charged and carbonate rock is positively charged. This implies that, by increasing pH value of reservoir to above 9, anionic surfactant can be desorbed from carbonate rock surface because of the repulsion of same charged surface and surfactant polar portion.

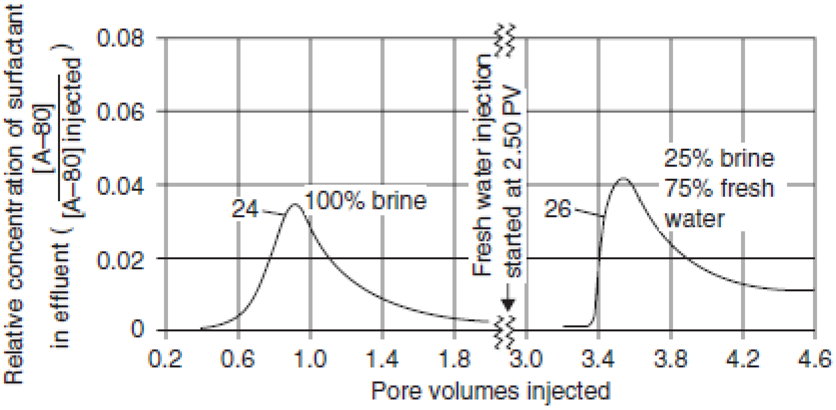


Figure 3.12 Produced surfactant concentration versus pore volume [2]

3.3 Other Surfactant Loss Mechanism

The efficiency of surfactant flooding is highly associated with the stability of injected surfactant during the oil displacement process. Several factors such as surfactant adsorption, surfactant precipitation, surfactant degradation, and phase trapping greatly control surfactant loss in the flooding process.

In the surfactant flooding, loss of surfactant usually happens when it contacts rock surface and reservoir brine. This indicates that only part of injected surfactant is available for oil recovery mechanism. Adsorption of surfactant is also related to other parameters [12]. In terms of wettability, petroleum sulfonate is adsorbed on oil-wet surface with higher degree compared to water-wet surface. In addition, increasing salt concentration will increase the adsorption, and the adsorption will reduce with a presence of low-molecular-weight alcohols (co-surfactant).

After waterflooding process, there are residual oil, formation water, and injected water remained in the reservoir. When the ionic content of injected water and formation water is different, during surfactant flooding, the surfactant slug may contact with both connate water and injected water. Therefore, precipitation occurs when surfactant is in contact with divalent cations in formation. As precipitation occurs, it will alter oil-surfactant IFT due to different ionic content of formation water and injected water, and it also decreases displacement efficiency due to high concentration of divalent ions.

The degradation of surfactant is strongly interrelated with thermal stability of surfactant and this greatly affects effectiveness of displacement mechanism. Most of surfactants are stable in the normal reservoir temperature, and some better heat tolerant surfactants can cope with higher temperature and can be stabilized at around 200°F.

Oil phase trapping happens when unequal of partitioning of surfactant in aqueous and oil phase, so ultra-low IFT fails to reach. Oil phase trapping will eventually cause surfactant loss due to its partitioning in oil.

CHAPTER 4

LABORATORY EXPERIMENT AND RESERVOIR SIMULATION MODEL

The details of laboratory experiment and reservoir model construction with explanation of each component of this research are dedicated in this chapter. Firstly, laboratory experiment on Berea sandstone to investigate adsorption/desorption behaviors and reversibility degree is performed. Thereafter, numerical reservoir simulator is used to determine the effects of these behaviors based on the results of laboratory experiment. In the reservoir simulation part, a reservoir simulator called STAR® commercialized by Computer Modelling Group Ltd. (CMG) is chosen to study effects of reversibility of surfactant adsorption onto sandstone reservoir. In this chapter, four main categories will be discussed which including laboratory experiments, reservoir physical properties, chemical properties, and detailed methodology of reservoir simulation part.

4.1 Laboratory Experiments

One of the major concerns about surfactant flooding is the adsorption of surfactant onto rock surface. In terms of economic viability, the consumption of surfactant controls cost of surfactant flooding techniques and also its efficiency. In this section, static and dynamic adsorption experiments are taken place to determine the adsorption value of surfactant onto sandstone surface. In static test, the experiment is carried out by stirring surfactant solution with grinded rock sample. For dynamic test, surfactant solution and soft brine are flowed sequentially through core sample.

4.1.1 Rock Sample Preparation

In this study, Berea sandstone is chosen as adsorbent to perform adsorption tests in both static and dynamic experiments. In static adsorption test, rock sample is grinded into grained size by mortar and pestle as shown in Figure 4.1. After that, the grinded Berea sandstone is dried in oven to prevent moisture content which can interfere sample weight. For dynamic adsorption experiment, the core sample is first cut into suitable length for ease of experiment procedures. Then the core is cleaned in Soxhlet using toluene to remove small particle as well as humidity remained inside the pores which can interfere the measurement of porosity and permeability. Moreover, this process can restore the wettability of the core sample back to water-wet condition. Properties and specification of core sample are shown in Table 4.1.

Table 4.1 Properties of core sample

Parameters	**Values**	**Unit**
Diameter	37.80	mm
Length	40.95	mm
Porosity	0.20	fraction

Figure 4.1 Grinded rock sample by the use of ceramic mortar and pestle

4.1.2 Fluid Sample Preparation

As Berea sandstone is selected as adsorbent, anionic surfactant is a better candidate to perform on sandstone because this leads to reduction in severe adsorption of surfactant molecules in porous media. Sodium Dodecyl Benzene Sulfonate (SDBS) is utilized in this study. Surfactant solution is then prepared for both static and dynamic adsorption tests. In static experiment, the concentration is varied from 0.1 to 1.0%wt. However, for the dynamic adsorption test, the concentrations used are 0.2%wt., 0.5%wt., and 1.0%wt. which are the representatives of adsorption regions in static adsorption test. After that, Hyamine solution is used for titration against SDBS solution to determine the concentration of remaining SDBS. Methylene blue in chloroform is used as indicator in two phase titration method. The preparation process of methylene blue solution is demonstrated in Appendix A.

4.1.3 Static Adsorption-Desorption Test

Static adsorption is determined by mixing grinded Berea sandstone with anionic surfactant solution. The mixture is then placed in the stirring process for 6 hours to attain adsorption equilibrium stage at desired suggested reservoir temperature. After that, the mixed solution is filtered with 45 µm membrane paper and left over night, so that supernatant can be easily separated as solid particles are precipitated. Supernatant liquid is then collected from the upper layer to prevent the contamination of solid particle. At this stage, filtered supernatant can be used to determine residual surfactant concentration by titration method together with the Equation 4.1. The procedures of two-phase titration are illustrated in Appendix A. The schematic explanation of the procedures is shown in the Figure 4.2. By knowing amount of surfactant adsorbed from static process, proper concentration of surfactant solution can be prepared for the dynamic adsorption test which will be more realistic value for implementation of surfactant flooding.

$$Ad = V/m\,(C_o - C_e) \qquad \text{Equation 4.1}$$

where Ad is adsorption concentration, V is surfactant solution volume (ml), m is mass of rock (g), C_o is surfactant initial concentration, C_e is surfactant concentration after adsorption.

In desorption test, separated grinded rock sample is collected again and put into drying process at 70°C to prevent moisture content which can dilute surfactant concentration. After rock sample is decreased back to ambient temperature, it is mixed and stirred with distilled water to carry out desorption test. The temperature of the process is controlled to be the same in adsorption test at designed reservoir temperature. Next, the desorption test follows the procedures of adsorption test which left the solution to stir for 6 hours, and determine the surfactant concentration in supernatant developed by desorbed surfactant by titration method and Equation 4.1.

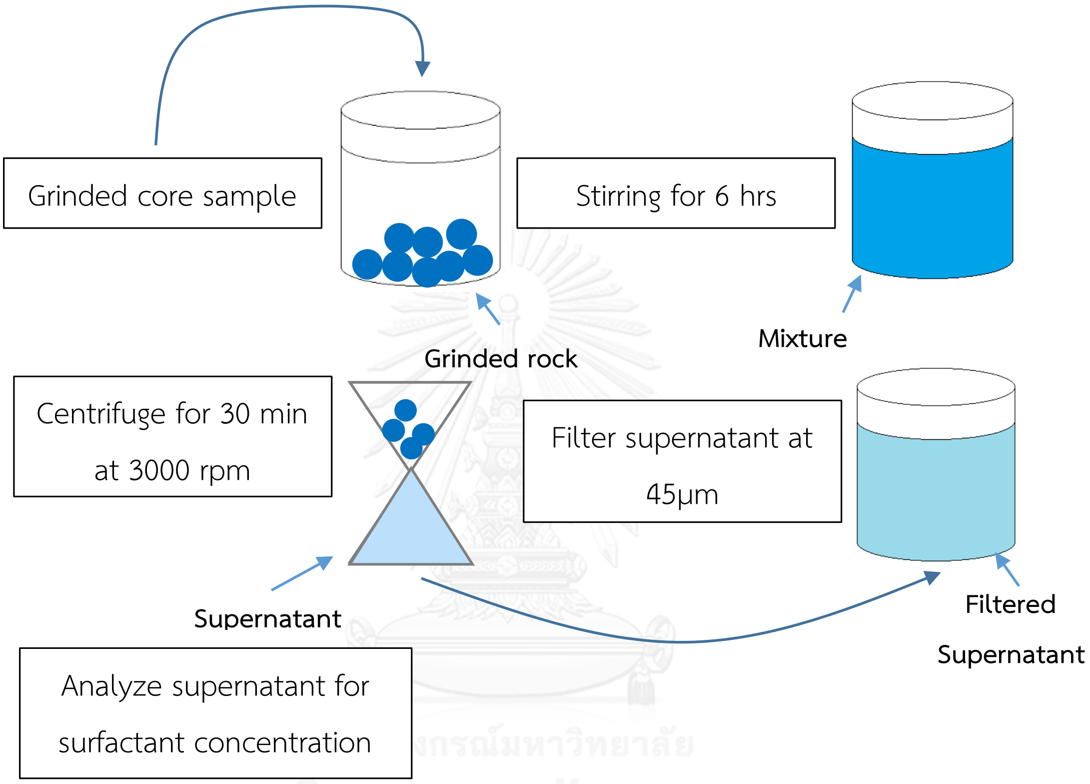


Figure 4.2 Schematic illustration of static adsorption experiment procedures

4.1.3 Dynamic Adsorption-Desorption Test

Dynamic adsorption is achieved by the use of coreflooding apparatus. Core sample is cut into the dimension of 3.78 cm in diameter and 4.095 cm in length and placed inside core holder. Confining system around core sample will prevent by-passing problem. As sandstone is usually water-wet in nature, dynamic adsorption test is performed on core saturated with only brine. This will ensure the adsorption value occurred through liquid-solid phase and loss of surfactant in oil phase due to oil soluble portion of surfactant is neglected. Soft brine is used in this study to avoid effects of divalent cations. Soft brine of 10,000 ppm is prepared from certain chemicals as illustrated in Table 4.2. Surfactant is injected into core sample until reaching the adsorption plateau by detecting surfactant concentration from effluent. The collected solution in effluent is determined for surfactant concentration by two phase titration method. The dynamic adsorption-desorption apparatus is shown in Figure 4.3.

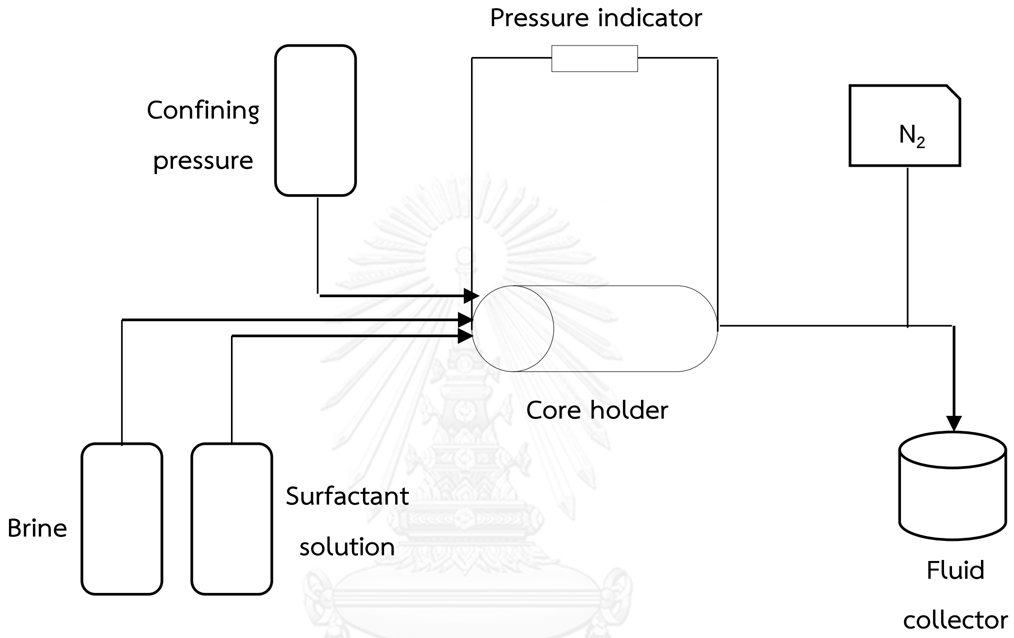


Figure 4.3 Schematic illustration of dynamic surfactant adsorption with coreflooding apparatus

After reaching adsorption plateau, the injecting fluid is changed to soft brine to commence dynamic desorption test. The fluid in effluent is then collected again while continuous injection of soft brine to titrate for desorbed surfactant concentration. The injection of soft brine is continuous until lowest surfactant concentration is detected in effluent. Therefore, the ratio of desorbed surfactant concentration over adsorbed surfactant concentration is the degree of reversibility of surfactant adsorption which can be used to study in reservoir simulation section.

Table 4.2 Chemicals used to prepare soft brine

Chemical	Mass (g)
Magnesium Chloride ($MgCl_2$)	1.3087
Calcium Chloride ($CaCl_2$)	0.2923
Potassium Chloride (KCl)	0.1658
Sodium Chloride (NaCl)	6.1359
Sodium Sulfate (Na_2SO_4)	2.0471
Sodium Hydrogen Carbonate ($NaHCO_3$)	0.0501

4.2 Reservoir Properties

Reservoir properties are contributed of rock and fluid properties which are basic reservoir physical properties, Pressure-Volume-Temperature (PVT) properties, rock-fluid properties and well & recurrent.

4.2.1 Reservoir Properties and Initial Conditions

Reservoir model is established base on experimental data from core sample and screening criteria of EOR projects as well as previous simulation study of surfactant flooding. The model is constructed as a rectangular shape in the Cartesian coordinates. The size of the reservoir model is 660 × 660 × 108 cu.ft and divided into 33 × 33 × 9 grids. The well spacing for this model is 933 ft. This is the optimum well spacing for both homogeneous and heterogeneous reservoirs and five-spot pattern [17]. The designed number of grids is 9,801 blocks, according to the limitation of 10,000 grid block of academic license of CMG simulator and the designed size of reservoir model referring to the optimum case of reservoir well spacing.

The reservoir physical properties are outlined in Table 4.3. The total bulk volume of the whole reservoir is 8.38 MMbbl with 1.68 MMbbl pore volume calculated from the 20% effective porosity. The value of porosity is determined from Berea sandstone in laboratory experiment. This indicates that the reservoir is presented as water-wet reservoir in reservoir simulation. Base on the 20% initial water saturation, the Original Oil In Place of the reservoir is 1.34 MMbbl. The datum depth of the reservoir is chosen at 2,600 ft., so that the corresponding reservoir temperature is determined from the typical oilfield geothermal gradient as shown in Figure 4.4. This temperature concern is to prevent the degradation of surfactant due to the elevated reservoir temperature of over 200^{o}F [12]. From the reference depth of the reservoir, the reservoir pressure can be determined from the relationship between typical hydrostatic pressures as a function of depth as shown in Figure 4.5. The corresponding pressure to the reservoir datum depth of 2,600 ft is about 1,225 psia. As this study focuses mainly on the effects of reversibility of surfactant adsorption, the location of water-oil contact (WOC) is set at 2,708 ft. which is the bottom of the reservoir. This is to prevent to water coning development around wellbore area.

The base case of reservoir model is plotted in Figure 4.6. The reservoir is designed to be homogeneous as it is a sandstone reservoir. The horizontal absolute permeability is 100 mD with the ten times less permeable vertical absolute permeability comparing to which of horizontal one.

Table 4.3 Basic reservoir properties for base case model

Parameters	**Values**	**Unit**
Grid dimension	33×33×9	Block
Grid size	20×20×12	ft
Top of reservoir	2,600	ft
Effective porosity (ϕ_{eff})	20	%
Horizontal permeability (k_h)	100	mD
Vertical permeability (k_v)	0.1 k_H	mD
Initial water saturation (S_{wi})	20	%
Reference pressure at datum depth	1,225	psia
Reservoir temperature	118	^{o}F
Total production time	30	years

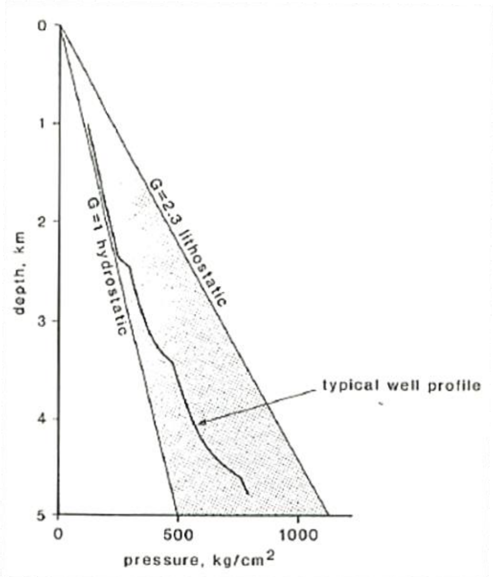


Figure 4.4 Reservoir pressure gradients as a function of depth [18]

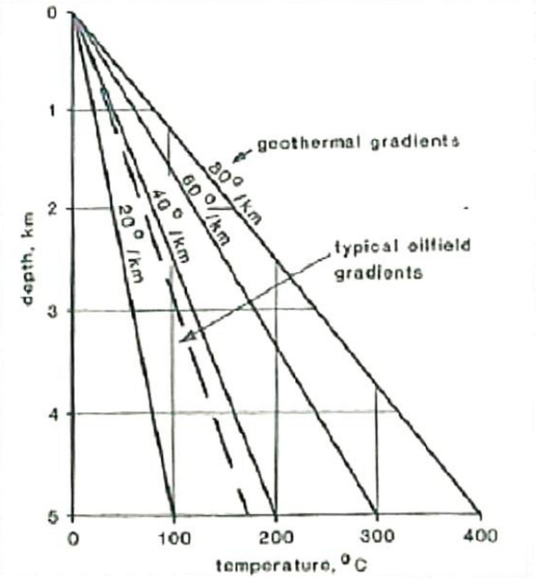


Figure 4.5 Geothermal gradients as a function of depth [18]

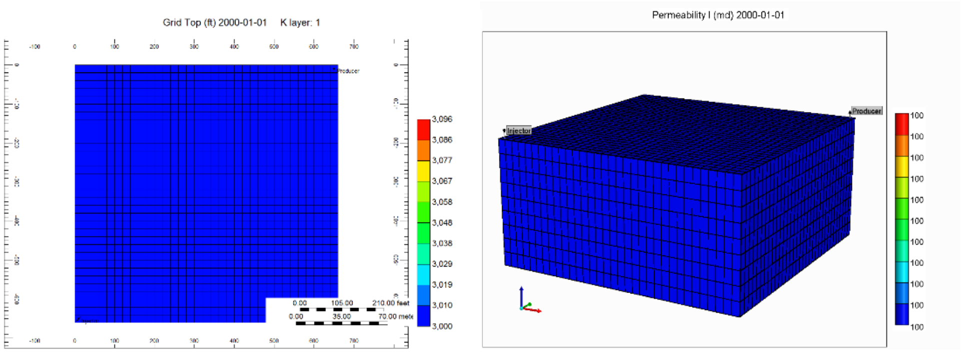


Figure 4.6 Top and 3D views base case reservoir model

4.2.2 Pressure-Volume-Temperature (PVT) Properties

In this section, the properties of reservoir fluids are presented, including solution gas, oil, and water. The PVT data of reservoir fluids are generated using the correlations and they are shown in Appendix B. The important data which are utilized to generate PVT data are illustrated in Table 4.4. Then, the generated oil and gas properties such as gas formation volume factor (B_g), gas viscosity (μ_g), oil formation volume factor (B_o), oil viscosity (μ_o) and solution gas-oil ratio (R_s) are illustrated from Figure 4.7 to Figure 4.11, respectively. There are two lines generated in oil and gas properties which are represented in blue and red colors that are carried out by Standing Katz and McCain correlations respectively. The value of solution gas-oil ratio and bubble point pressure (P_b) are accomplished from the correlation chart as shown in Figure 4.12. From the chart, the bubble point pressure and solution gas-oil ratio are 1,266 psia and 250, respectively.

Table 4.4 Important properties for PVT data

Parameters	Values	Unit
Oil gravity	30	^{o}API
Gas gravity	0.7	Fraction
Solution Gas-Oil Ratio (R_s)	250	SCF/STB
Reservoir temperature	118	^{o}F

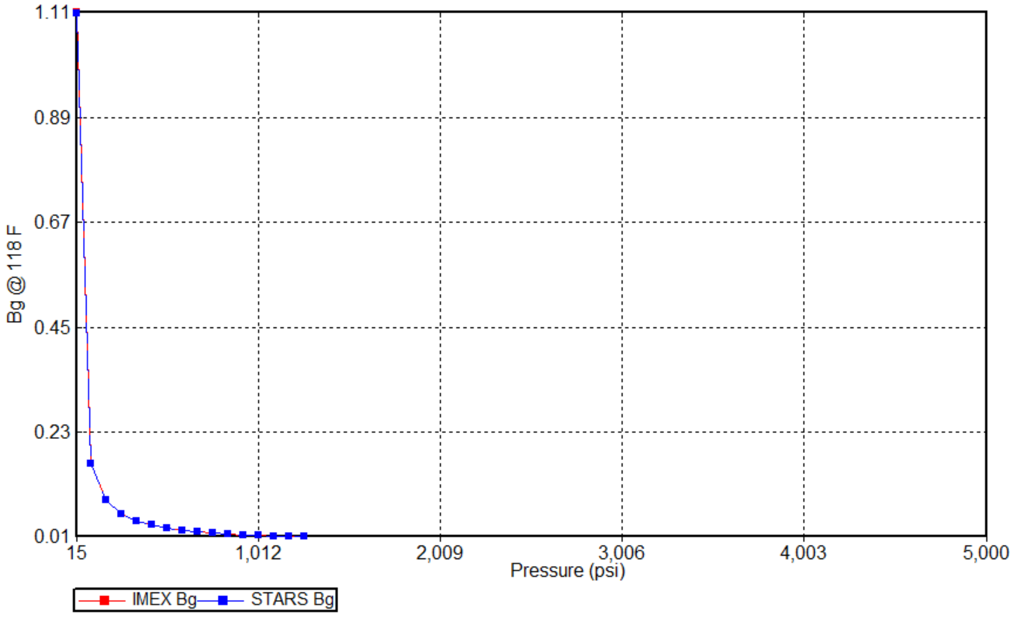


Figure 4.7 Dry gas formation volume factor (B_g) as a function of pressure

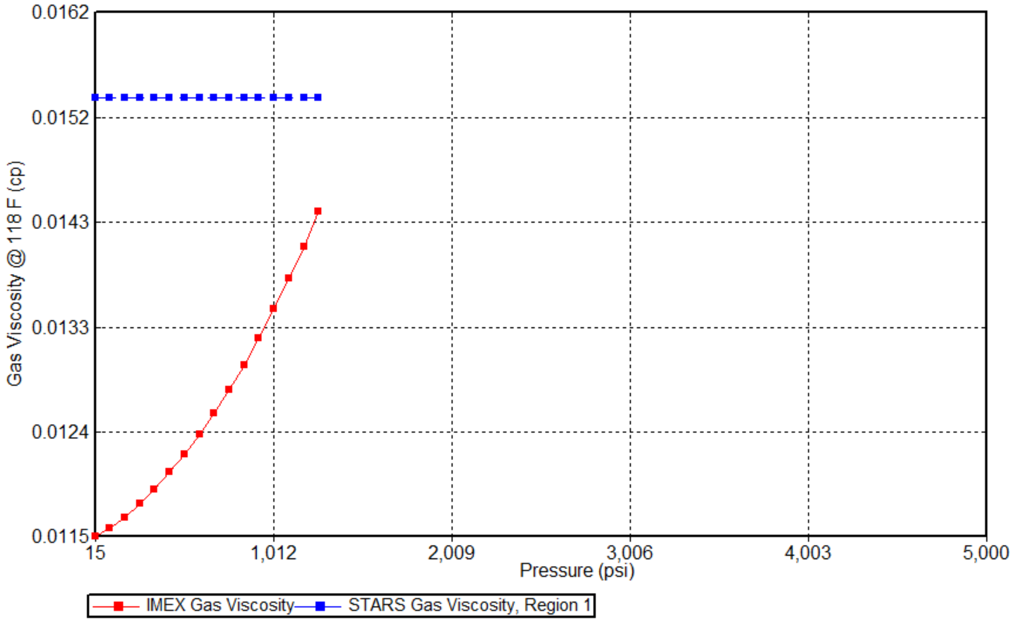


Figure 4.8 Dry gas viscosity (μ_g) as a function of pressure

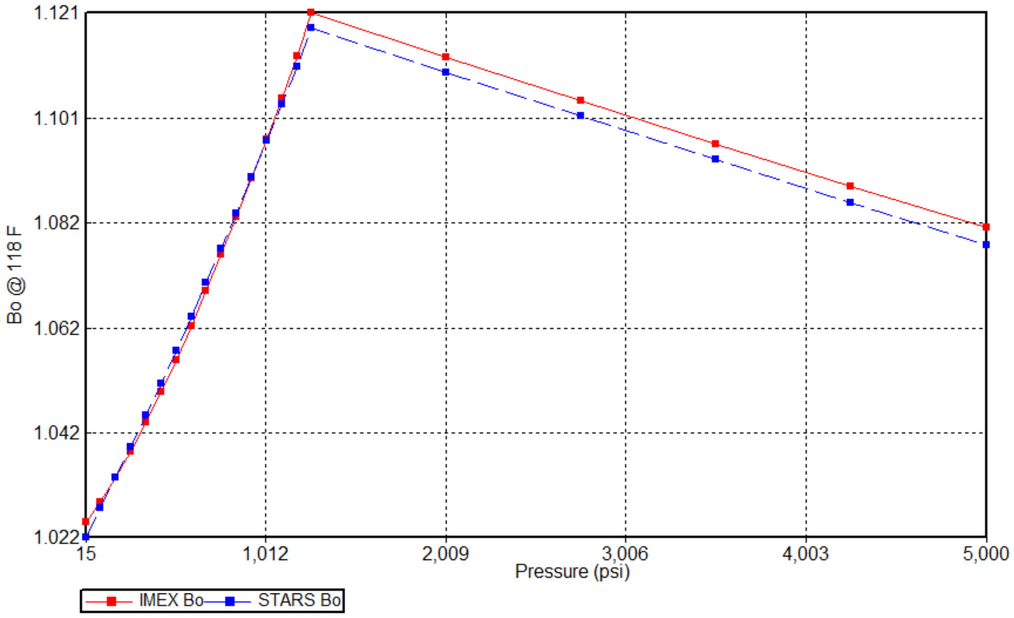


Figure 4.9 Oil formation volume factor (B_o) as a function of pressure

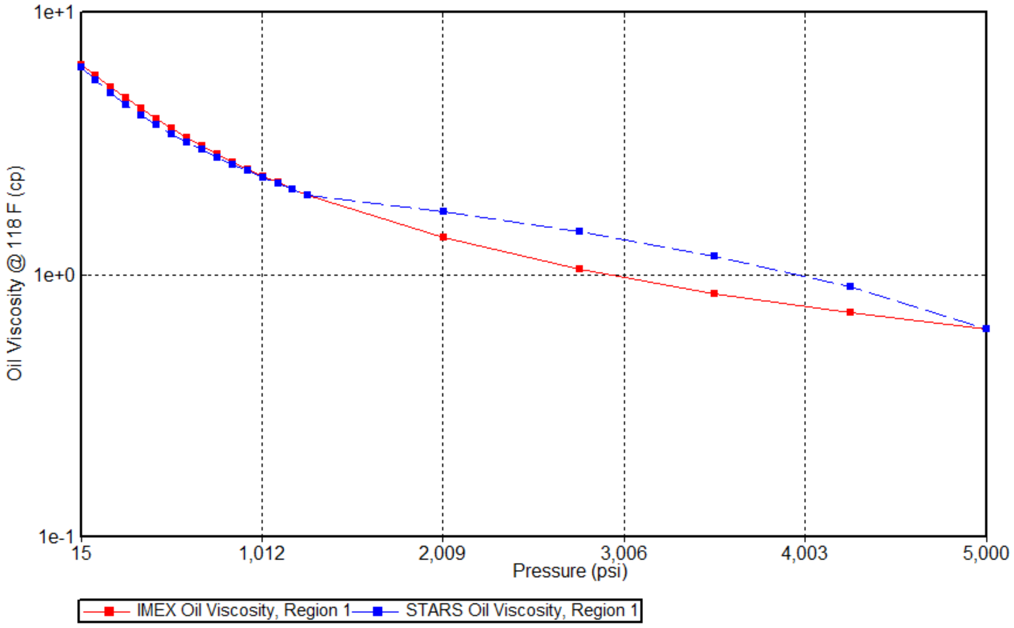


Figure 4.10 Oil viscosity (μ_o) as a function of pressure

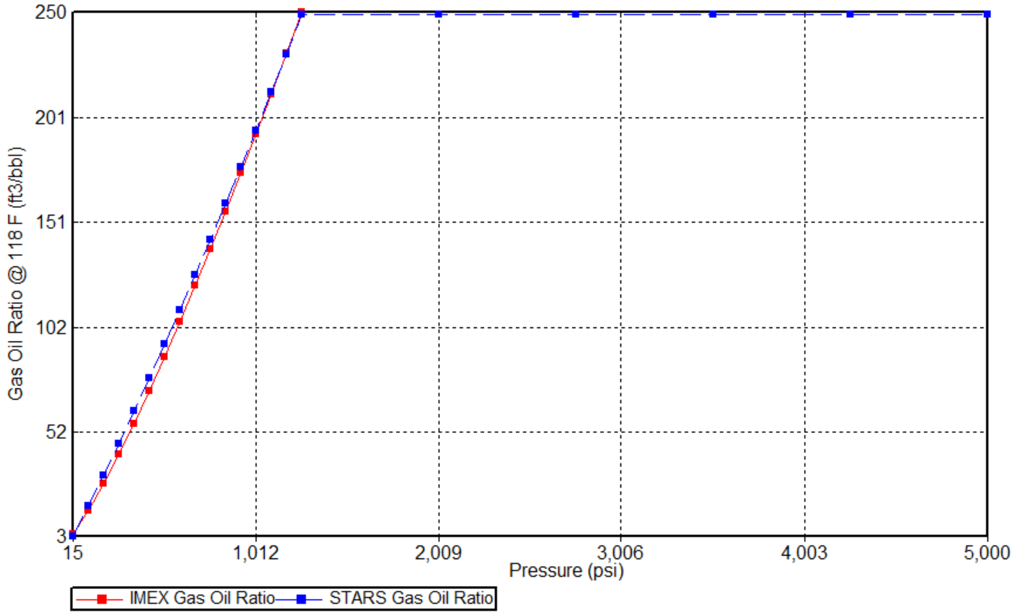
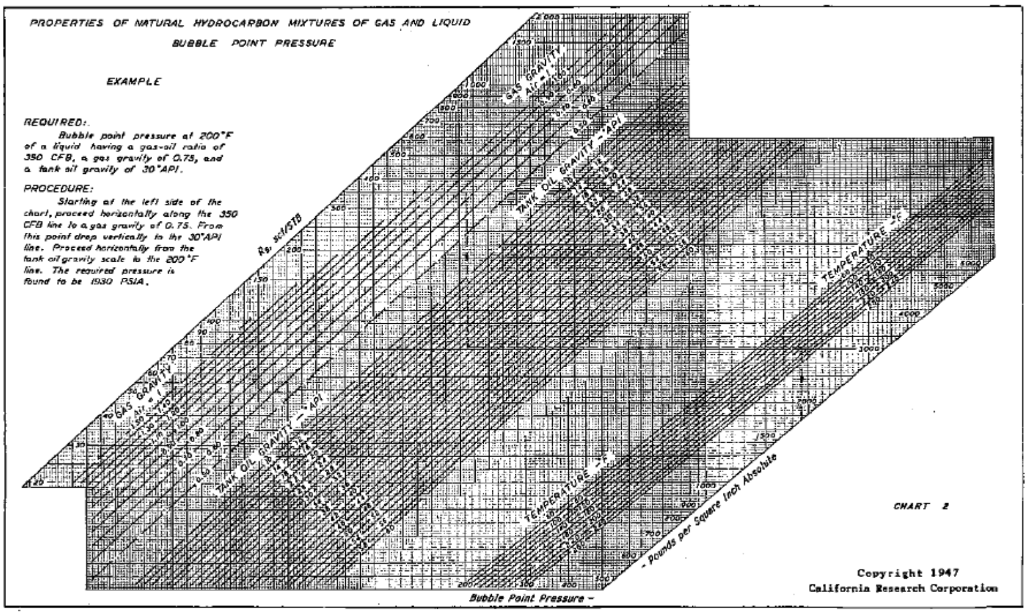


Figure 4.11 Solution gas-oil ratio (R_s) as a function of pressure



EXAMPLE

REQUIRED:

Bubble point pressure at 200°F of a liquid having a gas-oil ratio of 350 CFB, a gas gravity of 0.75, and a tank oil gravity of 30°API.

PROCEDURE:

Starting at the left side of the chart, proceed horizontally along the 350 CFB line to a gas gravity of 0.75. From this point drop vertically to the 30°API line. Proceed horizontally from the tank oil gravity scale to the 200°F line. The required pressure is found to be 1930 PSIA.

Fig. 11–1. Bubble-point pressure—solution gas-oil ratio correlation. (Copyright 1947 Chevron Oil Field Research Co., with permission.)

Figure 4.12 Relationship between solution gas-oil ratio and bubble point pressure [19]

4.2.3 Rock-Fluid Properties

In rock-fluid properties section, the most accentuated topics are the relative permeability curves and adsorption function of each component onto rock surface. As the wettability of the reservoir rock in this study is water-wet, the relationships between relative permeability curve and wettability also have to be emphasized and followed the rule of thumb which can be seen in Table 4.5. In order to generate relative permeability curves in relationship with water-wet rock, Corey's correlation together with validation in STAR program is utilized. The required parameters to develop the relative permeability curves are dedicated in Table 4.6. The connate water saturation, crossover saturation and relative permeability to water at residual oil saturation are according to the rule of thumb for water-wet condition. The results generated from Corey's correlation are illustrated in Appendix B. Corresponding relative permeability curves are plotted in Figure 4.13 and Figure 4.14 with water-wet rock surface as initial condition.

Table 4.5 Relative permeability rule of thumb for identifying wetting condition [20]

Properties	**Water wet**	**Oil wet**
Connate water saturation (S_{wc})	Greater than 20-25%	Frequently less than 10%
Crossover saturation	Greater than 50%	Less than 50%
k_{rw} at residual oil saturation	Generally less than 30%	Greater than 50%

Table 4.6 Required parameters for constructing relative permeability curve for base case model

Parameters	Values	Unit
Connate water saturation (SWCON)	0.2	fraction
Critical water saturation (SWCRIT)	0.2	fraction
Irreducible oil saturation for Water-Oil table (SOIRW)	0.3	fraction
Residual oil saturation for Water-Oil table (SORW)	0.3	fraction
Irreducible oil saturation for Gas-Liquid table (SOIRG)	0	fraction
Residual oil saturation for Gas-Liquid table (SORG)	0.2	fraction
Connate gas saturation (SGCON)	0	fraction
Critical gas saturation (SGCRIT)	0.05	fraction
Relative permeability to oil at connate water saturation (KROCW)	0.7	fraction
Relative permeability to water at irreducible oil saturation (KRWIRO)	0.15	fraction
Relative permeability to gas at connate liquid saturation (KRGCL)	0.7	fraction
Relative permeability to oil at connate gas saturation (KROGCG)	1	fraction
Exponent of k_{rw} from KRWIRO	3	
Exponent of k_{row} from KROCW	3	
Exponent of k_{rg} from KROGCG	3	
Exponent of k_{rog} from KRGCL	3	

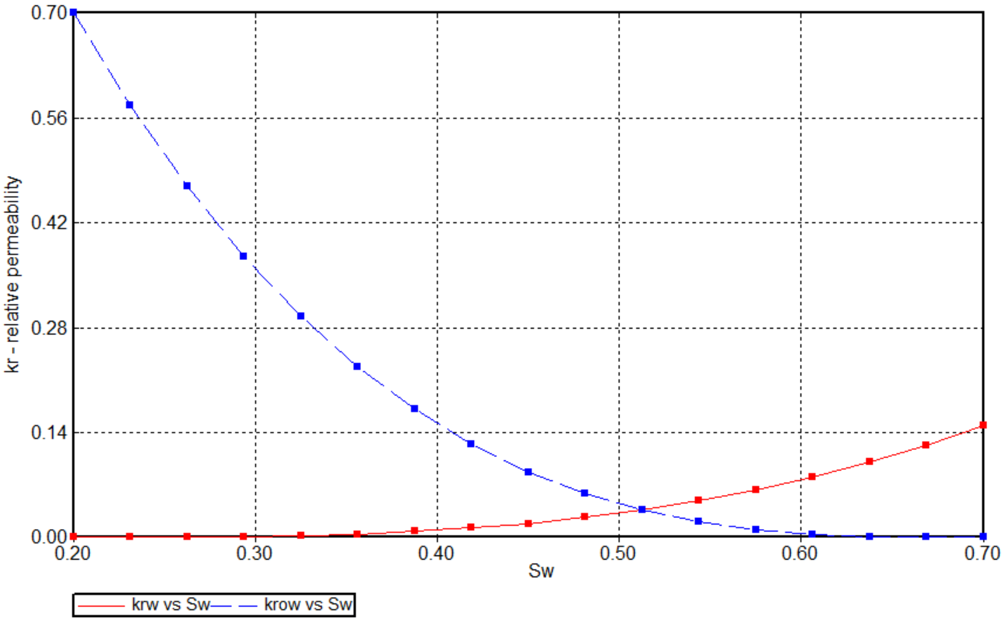


Figure 4.13 Relative permeability curves of oil and water as a function of water saturation

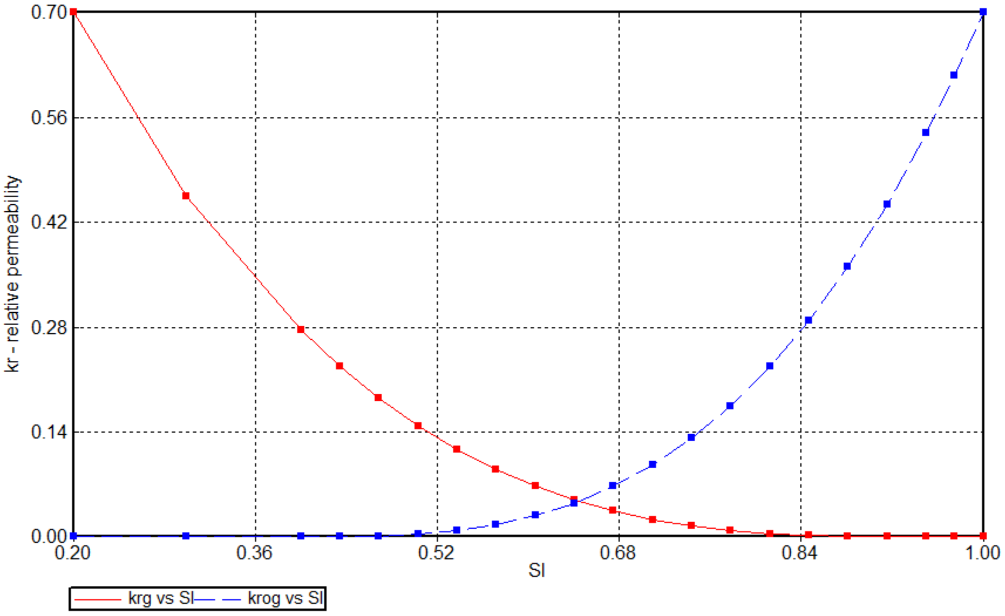


Figure 4.14 Relative permeability curves of liquid and gas as a function of liquid saturation

4.2.4 Well and Recurrent

In this study, quarter five-spot well pattern is selected, and there are two wells, injection well and production well, located diagonally at both edges of the model. For simplicity of the model, some assumptions are made; radius of both wells is 0.5 ft, and no skin effect around wellbore. Both wells are perforated all layers throughout the well located. In addition, constraints and economic limits for injection well and production well are specified in Table 4.7 and Table 4.8, respectively. The maximum bottomhole pressure for injection well is controlled to be lower than the fracture pressure which can be calculated from typical fracture gradient of consolidated sandstone of 0.7 psi per foot. As surfactant flooding is the modification of waterflooding; therefore, the injected fluid is determined by mole fraction between water and surfactant concentration. The total production period is fixed at 30 years as the maximum production duration. However, production process can be terminated in case of approach of one of the constraint.

Table 4.7 Injection well constraints

Parameters	Values	Unit
Maximum bottomhole pressure (BHP)	1,800	psi
Surface injection rate (STW)	500	bbl/day

Table 4.8 Production well constraints and economic limits

Parameters	Values	Unit
Minimum bottom-hole pressure (BHP)	200	psi
Surface production rate (STW)	500	bbl/day
Water-cut (WCUT)	0.95	Fraction
Minimum surface oil rate (STO)	25	bbl/day

4.3 Chemical Properties

In chemical properties section, the relationship between surfactant concentration to interfacial tension (IFT) and surfactant adsorption onto rock surface will be presented.

4.3.1 Surfactant Process

In STAR program, surfactant flooding can be set up by processing the wizard and input the required data and specify the necessary parameters. In this research, Sodium Dodecyl Benzene Sulfonate (SDBS) is selected as the anionic surfactant and study its effects of reversibility on oil recovery. Important parameters required for developing surfactant flooding model are summarized in Table 4.9.

Table 4.9 Fundamental parameters for surfactant flooding model

Parameters	Values	Unit
Use reversible partitioning of surfactant into oil	Yes	
Number of relative permeability sets for interpolation	3	Sets
Use adsorption for surfactant	Yes	
Rock type for conversion of adsorption values	Sandstone	
Rock Density	2.65	gm/cm^3
Interfacial tension is also dependent on surfactant weight %	Yes	

The main mechanism of surfactant flooding is to reduce the IFT between aqueous and oil phases to ultra-low condition. According to Equation 3.1, as IFT is decreased to ultra-low condition, then the capillary number is raised to a more favorable condition. In theory, all residual oil can be depleted from reservoir. However, Donaldson et al. [12] pointed out that ultra-low IFT value can be achieved when concentration of surfactant of the system reaches CMC. Moreover, from the static adsorption test of surfactant solution with grinded sandstone, the results showed that CMC of the system when increasing surfactant concentration to 1%wt. Function of IFT reduction is simulated and presented in Table 4.10 to generate a representative range that sensitivity of reversible adsorption can be evaluated.

Table 4.10 IFT value as a function of surfactant concentration for surfactant flooding

Surfactant concentration	IFT (Dyne/cm)
0	20
0.5	0.001
1.0	0.0001

One of the most crucial factor that effect the efficiency of surfactant flooding technique is the adsorption of surfactant particles onto reservoir rock surface. The maximum adsorption value together with reservoir porosity is required to input into reservoir simulation model. From the dynamic adsorption experiment in coreflooding, maximum surfactant adsorptions with various concentrations are discovered and provided into reservoir simulation.

After all necessary data are put into reservoir simulation, the model generation two additional sets of relative permeability curve by interpolation, which are labelled as set2 and set3 respectively. The generated relative permeability curves for set2 and set3 are plotted in Figure 4.15 and Figure 4.16. Furthermore, the capillary number is affected by the surfactant solution introducing into the system. Involving of surfactant takes control on IFT of the liquid interface, so that the function between capillary number and interpolation sets also receives the effect. This provides the idea that flow ability of oil and water phases are improved when the concentration of surfactant in the system reaches the value which IFT can be reduced to ultra-low condition. The capillary number of all interpolation sets are summarized in Table 4.11.

Table 4.11 Log Capillary number for interpolation set 1 to 3

Interpolation set	Phase	Values
Set 1	Wetting phase	-4
	Non-Wetting phase	-4
Set 2	Wetting phase	-3.5
	Non-Wetting phase	-3.7
Set 3	Wetting phase	-3
	Non-Wetting phase	-3

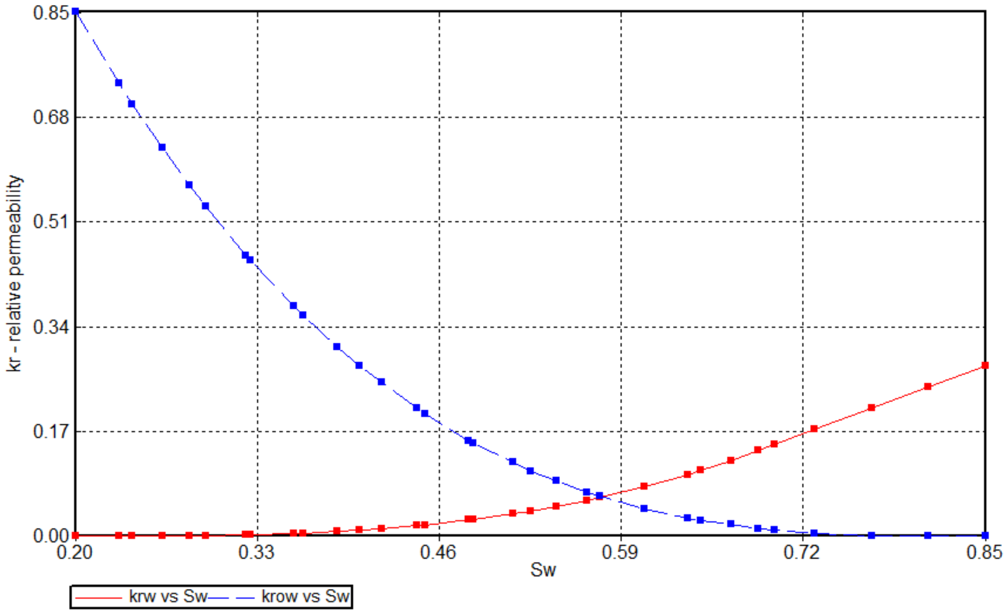


Figure 4.15 Relative permeability curves of oil and water of interpolation set2 as a function of water saturation

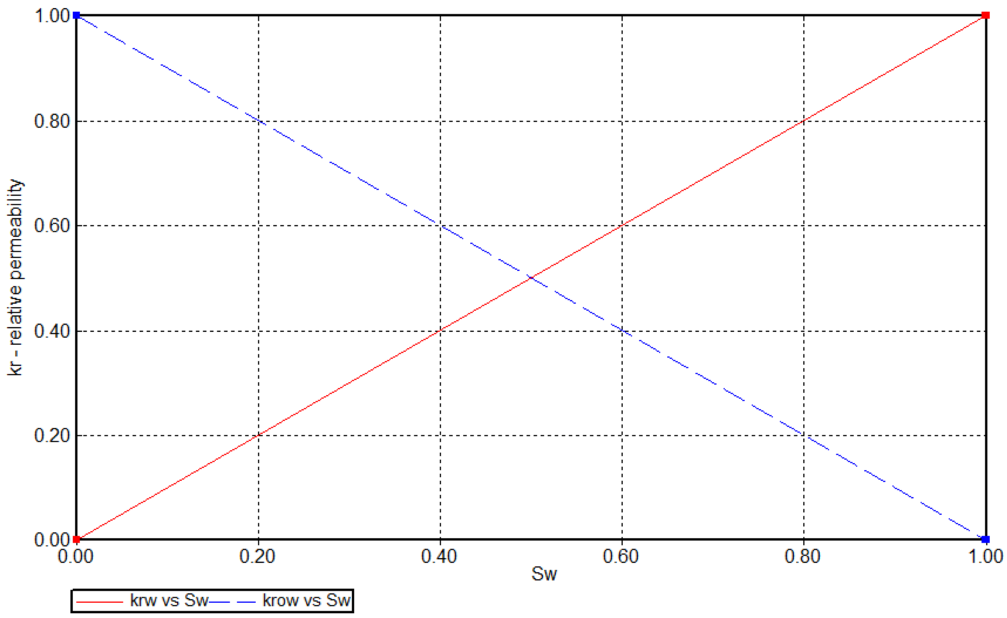


Figure 4.16 Relative permeability curves of oil and water of interpolation set3 as a function of water saturation

4.4 Thesis Methodology

This study is divided into two main sections. Laboratory experiment part is aimed to identify the adsorption values of surfactant and degree of its reversibility. Simulation is then taken place to obtain proper operational parameters, and thus effects of variation of adsorption values, and reversibility values can be studied and made comparison.

Step 1 Laboratory experiments are performed with anionic surfactants, Sodium Dodecyl Benzene Sulfonate on Berea sandstone.

- Static adsorption test: surfactant solution prepared by distilled water is mixed with grinded sandstone until it reaches equilibrium stage in static condition, and the mixture is then filtered and collected the supernatant. Collected supernatant is going under two-phase titration process to determine concentration of surfactant of the solution. As a result, adsorption can be calculated from differences between initial concentration and surfactant concentration in supernatant. The chosen surfactant concentrations are 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 %wt.

- For desorption test, distill water is utilized as dilute solution to blend with previous grinded rock sample. Observation is made to check how much surfactant is dissociated back from the system. Thus, residual surfactant concentration is obtained, and ratio of detached surfactant over previously attached surfactant is indicated as percentage of reversibility of surfactant adsorption.
- Dynamic adsorption test: after saturated with soft brine, core sample is placed in core holder and soft brine is injected through to ensure that core sample is fully saturated. After that, injection of surfactant slug is injected until the adsorption plateau is reached by means of detecting concentration of surfactant from effluents. From this point, soft brine is introduced into the system back again, thus desorption test is taken place. The representative surfactant concentrations are 0.2, 0.5, 1.0 %wt.

Step 2 Data received from step 1 are used to determine adsorption value as a function of surfactant concentration and degree of reversibility of surfactant.

Step 3 Base case reservoir model is developed in reservoir simulator to perform waterflooding for attaining reference oil recovery and water production.

Step 4 Reservoir simulation is run on base case model to select proper values of operational parameters including size of surfactant slug, and surfactant concentration. Ranges of each values are shown as follow:

- Slug size of surfactant: 0.15, 0.2, 0.25, 0.3,
- Surfactant concentration: 0.5, 1.0, 1.5 %wt.

Step 5 After selection of operating parameter, execute surfactant flooding by varying magnitudes of adsorption and degrees of adsorption reversibility to examine effects of interest parameters. Degree of reversible surfactant adsorption are shown:

- Degree of reversibility of surfactant adsorption: 0, 41, 83 percent.

Step 6 The simulation outcomes including oil recovery, surfactant consumption, and water production are collected for comparing and discussion for all cases.

Step 7 Summarize and identify the studied parameters which are sensitive on effectiveness of anionic surfactant flooding in sandstone reservoir.

Flow chart summarizing the whole study is illustrated in Figure 4.17.

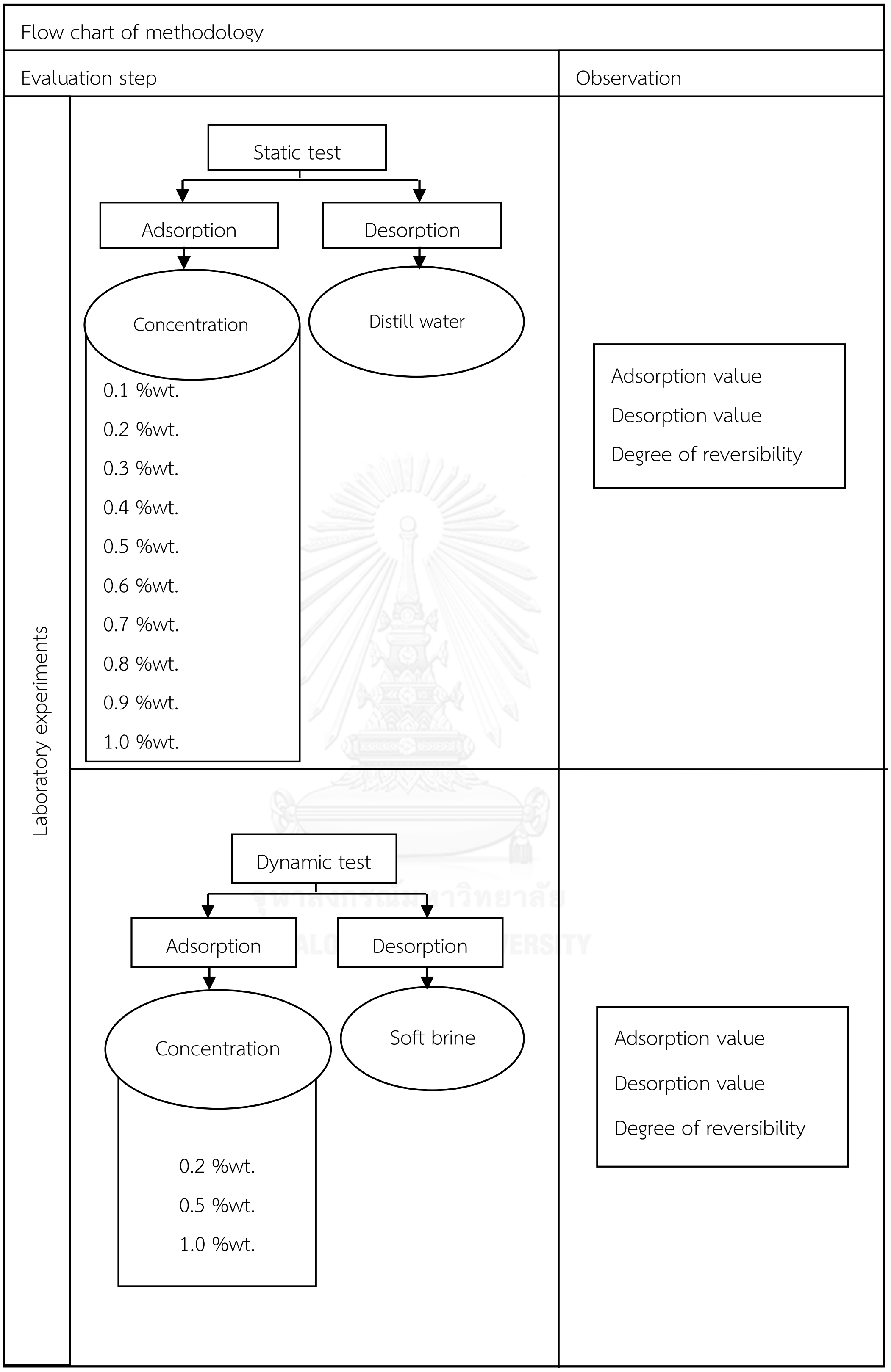


Figure 4.17 Summary of methodology of the whole study

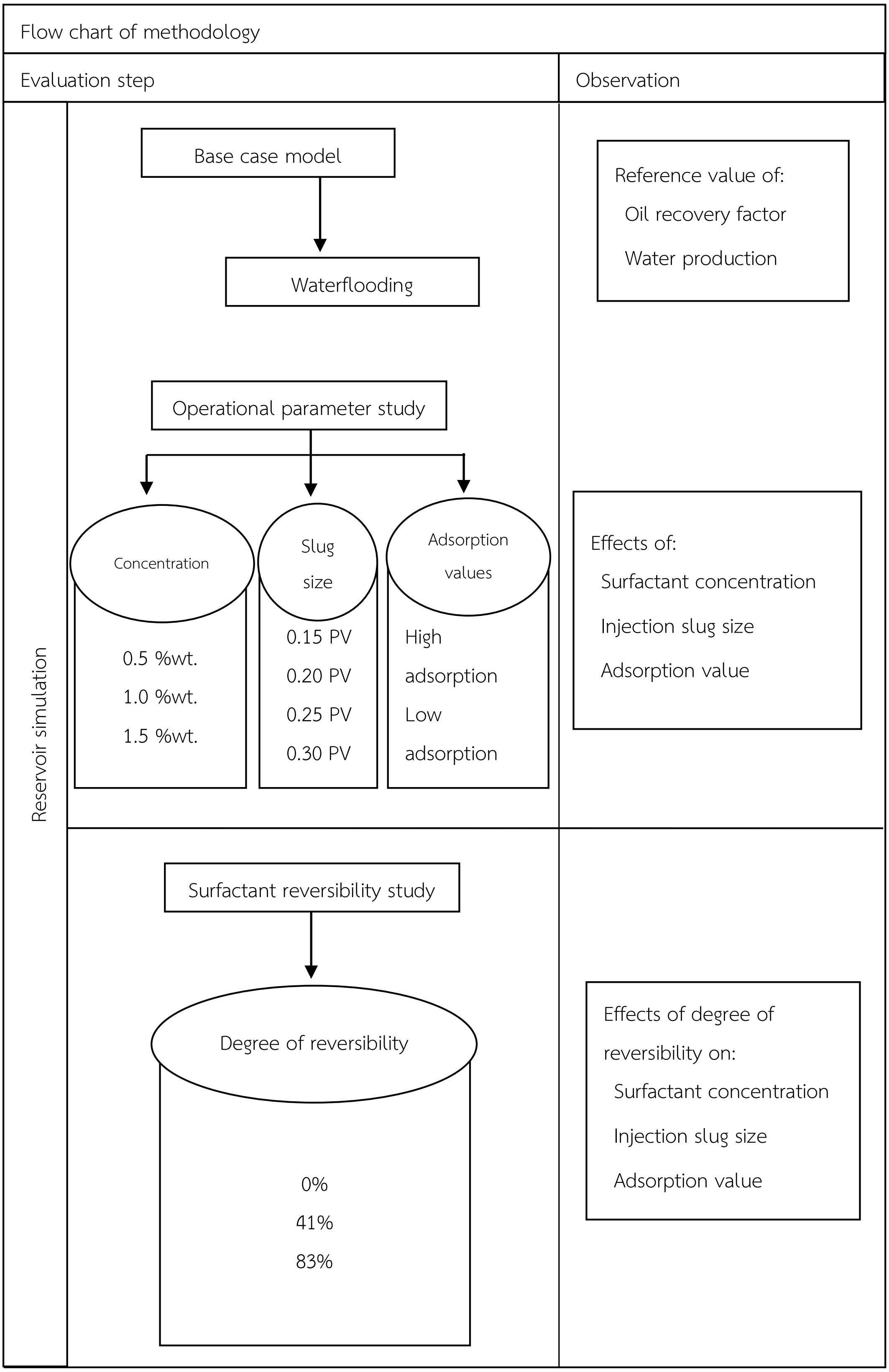


Figure 4.17 Summary of methodology of the whole study (continued)

CHAPTER 5

RESULTS AND DISCUSSION

In this study, as the main objective is to simulate the effectiveness of reversible surfactant adsorption from sandstone reservoir rock surface in surfactant flooding; therefore, the representative adsorption values and degrees of reversibility are performed first in laboratory scale. After reservoir model is constructed, surfactant flooding is implemented with several interested parameters in order to investigate the sensitivities on the effects of reversibility of surfactant adsorption in surfactant flooding. Waterflooding on reservoir model is initiated to obtain reference base case results. After that, surfactant flooding is performed on study parameters together with determined adsorption values and degrees of reversibility. The additional oil recovery factor is mainly utilized to evaluate and compare with waterflooding base case as well as adsorption value and degree of reversibility. To summarize, this chapter will focus on:

5.1 Static adsorption-desorption experiments,

5.2 Dynamic adsorption-desorption experiments,

5.3 Waterflooding base case,

5.4 Surfactant flooding base case,

5.5 Effect of surfactant injection slug size,

5.6 Effect of surfactant concentration,

5.7 Effect of adsorption value,

5.8 Effect of reversibility of surfactant adsorption.

5.1 Static Adsorption-Desorption Experiments

Static adsorption-desorption test is performed to discover reference surfactant concentrations for dynamic adsorption-desorption test. Therefore, static adsorption test is carried out with various surfactant concentrations ranging from 0.1 to 1.0% by wt. Distilled water is used to mix with grinded rock which includes adsorbed surfactant to identify desorption value of surfactant concentration. Therefore, the reversibility of adsorbed surfactant can be evaluated from the ratio of desorbed value over the adsorbed value. The results of static adsorption-desorption experiments together with degree of reversibility of surfactant adsorption in static mode are demonstrated in Table 5.1, Figure 5.1 and Figure 5.2.

Table 5.1 Results of static adsorption and desorption tests and their degree of reversibility

Concentration (%wt.)	**Adsorption (mg/g)**	**Desorption (mg/g)**	**Reversibility (%)**
0.1	0.06	0.054	90.00
0.2	0.12	0.054	45.00
0.3	0.18	0.081	45.00
0.4	0.28	0.108	38.57
0.5	0.45	0.135	30.00
0.6	0.64	0.162	25.23
0.7	0.77	0.189	24.55
0.8	0.88	0.216	24.55
0.9	0.90	0.243	27.00
1.0	0.90	0.27	30.00

A plot between surfactant concentrations and adsorption values is shown in Figure 5.1 gives similar trend to which of Langmuir adsorption isotherm which typically consists of four regions. In region I, as surfactant concentration is still low, the adsorption of surfactant onto rock surface is not very significant but it increases linearly. The adsorption behavior in region I is the electrostatic attraction between surfactant and rock surface charge. As surfactant concentration increases, the rate of adsorption in region II results in a sharp rise, this is due to the forming of aggregates on the rock surface so called Critical Admicelle Concentration (CAC). Then, when further increasing surfactant concentration of the solution, the adsorption trend changes the slope again and it moves to region III, this indicates the formation of bi-layer surfactant as the space in first layer are filled with surfactant monomers. When the surfactant concentration increases to Critical Micelle Concentration (CMC), the trend forwards to region IV, so there is very less incremental of surfactant adsorption occurred. From the plot in Figure 5.1, the adsorption trend is almost constant and no further incremental surfactant adsorption takes place, so the maximum adsorption of surfactant in batch experiment is 0.9 mg/g or rock or 90 mg/100g of rock.

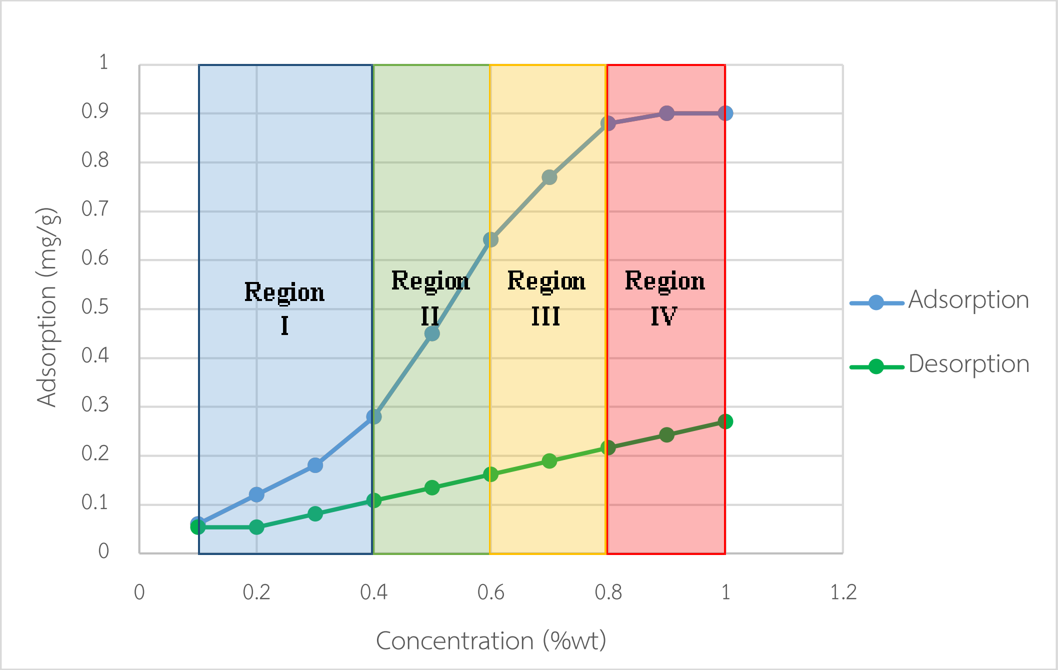


Figure 5.1 Adsorption-desorption results of static tests

The static desorption test is carried out by introducing the previously surfactant adsorbed grinded rock to mix with distilled water and analyzing for the desorbed surfactant concentration back in the solution. As illustrated in Figure 5.1, at low surfactant concentration, there is less in adsorption; however, the ratio of desorbed concentration to the adsorbed concentration is very significant. Desorption of surfactant increases linearly until the maximum batch desorption value (0.27 mg/g) reaches which is corresponding to the maximum batch adsorption concentration. On the contrary, the reversibility degree results in lower percentage at higher surfactant concentration, this is because of the re-adsorption behavior of surfactant takes place as there is available space for surfactant monomers to stick onto rock surface.

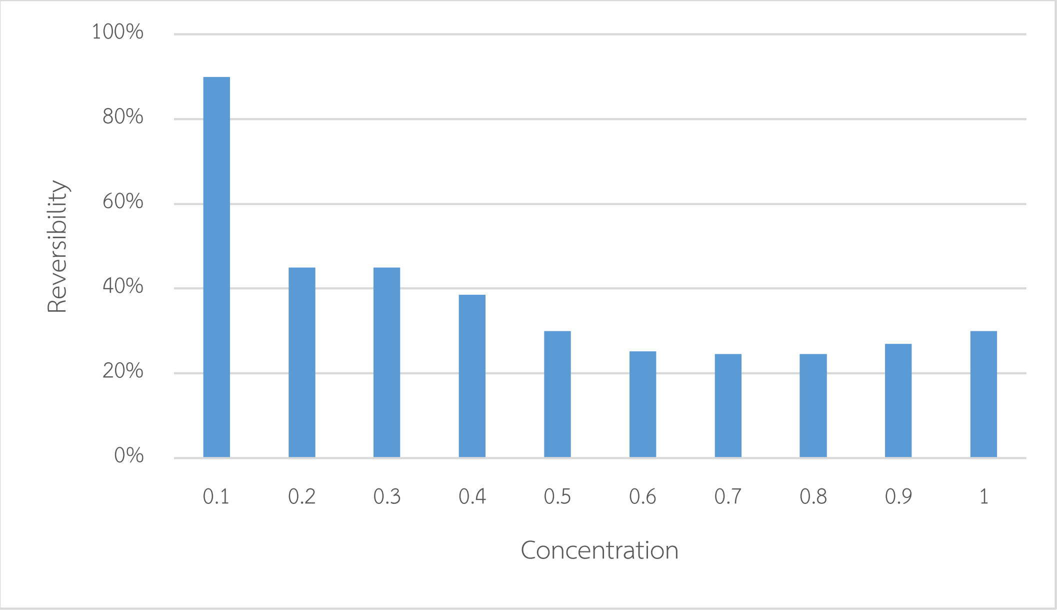


Figure 5.2 Reversibility degree of static test

5.2 Dynamic Adsorption-Desorption Experiments

Observation of results from static adsorption-desorption test gives an idea that surfactant concentrations in adsorption-desorption experiments can be categorized into four regions. Meanwhile, there are three major adsorption behaviors of surfactant to reservoir rock surface reflected. Surfactant concentration between 0.1 to 0.4 %wt. so called region I, surfactant adsorption occurs due to the electrostatic attraction between rock surface charge and surfactant polar head charge. In region II where concentration falls between 0.4 and 0.6 %wt., there is a sharp increase in adsorption as it is CAC. Another significant behavior which occurs from 0.8 to 1.0 %wt. is CMC where there is no more incremental of surfactant adsorption discovered. Due to these reasons, the design of surfactant concentrations used in dynamic adsorption-desorption test is fallen into these three major regions. Therefore, 0.2, 0.5, and 1.0 %wt. of surfactant concentrations are chosen to study. In terms of injection rate, it is designed to be related to surfactant injection rate in reservoir simulation which 500 bbl/day. By consideration with surfactant flood front and core diameter of tested Berea sandstone, the corresponding surfactant injection rate used in coreflooding experiment is 0.02 cm^3/sec. The summary of results of the dynamic adsorption-desorption test is illustrated in Table 5.2 and Figure 5.3.

Table 5.2 Results of dynamic adsorption and desorption tests and their degree of reversibility

Concentration (%wt.)	**Adsorption (mg/g)**	**Desorption (mg/g)**	**Reversibility (%)**
0.2	0.0415	0.040	97
0.5	0.3581	0.146	41
1.0	0.5765	0.479	83

In Figure 5.3, surfactant adsorption values of chosen surfactant concentration cases are plotted against the amount of surfactant volume injected through core sample. As can be seen from the figure, the maximum adsorption of surfactant from the injection shows different behaviors as surfactant concentration varies. As the dynamic adsorption-desorption test initiates with 0.2 %wt., the maximum adsorption occurs at 17.4 cm^3 of injected volume, and the maximum desorption finishes at 34.8 cm^3 of surfactant solution injected. Core sample is then flooded with increasing surfactant concentration to 0.5 %wt. The equilibrium adsorption appears at 13.92 cm^3 of surfactant volume injection while the desorption value become stable at 31.32 cm^3 of flooding volume. Lastly, the concentration increases to 1.0 %wt., the maximum adsorption occurs at 10.44 cm^3 of injected volume, and the maximum desorbed volume shows at 26.1 cm^3 of surfactant injection.

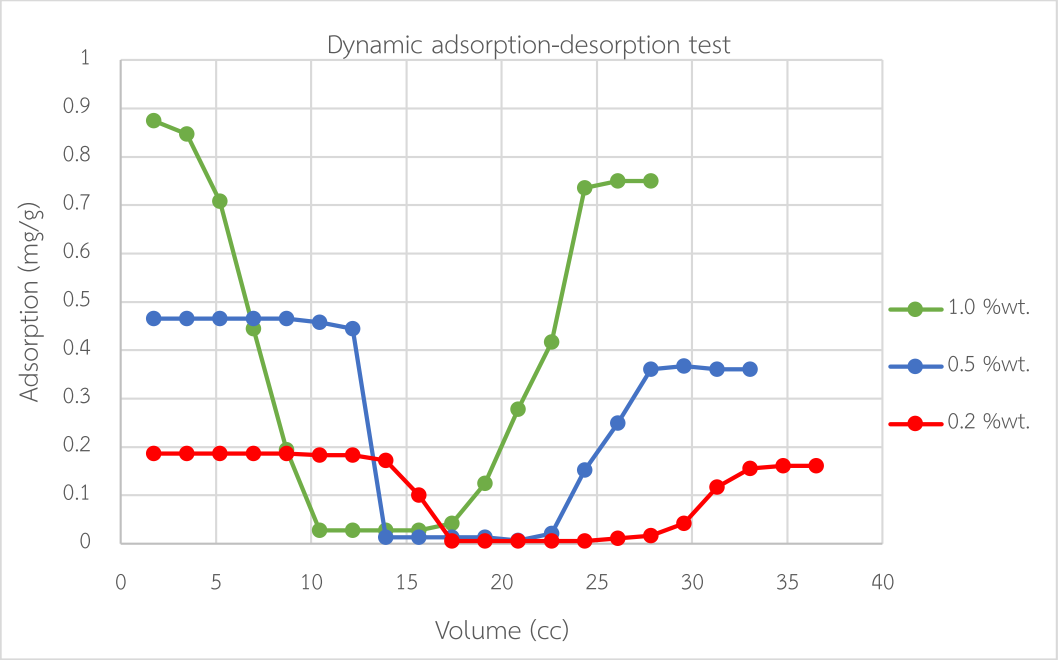


Figure 5.3 Adsorption-desorption results of dynamic tests

Observation on maximum adsorption and desorption duration with their corresponding volumes of surfactant injection explains the mechanism that maximum adsorption and desorption develop faster when concentration of injected surfactant solution increases. This shows the same trend of surfactant adsorption behaviors in static adsorption experiment. As concentration of surfactant solution is raised, the maximum adsorption value of 0.2, 0.5, and 1.0 %wt. cases are 0.042, 0.358, and 0.577 mg/g, respectively as dedicated in Table 5.1. After maximum adsorption takes place which can be observed from plateau adsorption values on Figure 5.3, injection solution is changed to soft brine to carry out desorption test. Desorption test is performed until desorption value reaches again to a plateau value. The maximum desorption value of 0.2, 0.5, and 1.0 %wt. are 0.04, 0.146, and 0.479 mg/g, respectively.

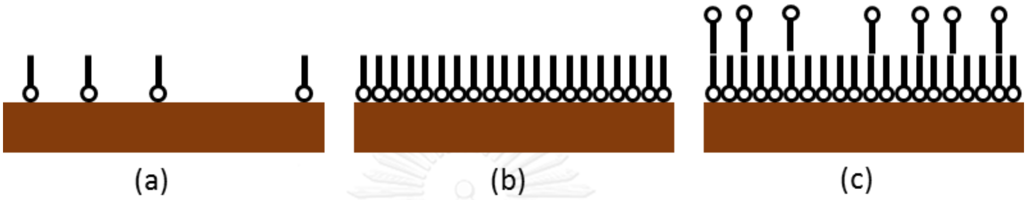


Figure 5.4 Adsorption behaviors of surfactant monomers due to different concentrations

Referring to Table 5.2, the degree of reversibility of each surfactant concentration case are not the same due to different mechanism behind the adsorption-desorption behaviors onto and from rock surface. As low concentration of surfactant (0.2 %wt.) is performed on core sample, the degree of reversibility is up to 97%. In using low surfactant concentration, only small numbers of monomers of surfactant are attached to rock surface as shown in Figure 5.4 (a), and their electrostatic attraction is not high enough to withstand with removing force causing by injected soft brine. This indicates that almost all of previously attached surfactant concentration onto pore surface is detached back into solution when chasing by soft brine. However, when surfactant concentration is increased to 0.5 %wt., the maximum adsorption value rise sharply from 0.042 mg/g to 0.357 mg/g, while only 41% of adsorbed surfactant concentration reverses back into the system. This adsorption-desorption behavior occurs in the case when surfactant concentration increases to CAC, where first adsorption layer is fully packed with surfactant monomers as demonstrated in Figure 5.4 (b). Therefore, the removing force brought by soft brine injection is not enough to recover most of adsorbed surfactant concentration. The last experiment with 1.0 %wt. of surfactant solution reveals that the incremental of surfactant adsorption is not very obvious as approaching to CMC. The dynamic adsorption value of the case of 1.0 %wt. is 0.577 mg/g, and the degree of reversibility gains again to 83%. The degree of reversibility of the case of 1.0 %wt. is higher than which of 0.5 %wt. is due to the combination mechanism of loosely packed of monomers in second layer and fully packed monomers in first layer as dedicated in Figure 5.4 (c). The loosely packed monomers on second layer are easy to remove as they link together by tail portion of the monomer which is considerably weaker than head portion. In contrary, the fully pack monomers in first layer is more difficult to remove by injecting soft brine as the attraction energy by rock surface and head portion of surfactant is stronger than second layer.

5.3 Waterflooding Base Case

Waterflooding is performed first to observe effectiveness of surfactant flooding. Waterflooding is executed from the first day of simulation until one of constraints of maximum water cut of 95% or minimum oil production rate of 25 bbl/day is attained. Since liquid production rate is fixed at 500 bbl/day, both constraints may be attained at the same time. As the reservoir model is constructed to simulate a quarter five-spot pattern, both injection and production wells are placed at each corner of the reservoir model. Table 5.3 and Figure 5.5 outline the reservoir base case results from waterflooding.

Table 5.3 Summary of interested parameters obtained from waterflooding base case

Parameters	Value	Unit
Oil recovery factor	49.99	%
Cumulative water production	284,666	bbl
Production period	2,100	Days
Initial water production	1,253	Days

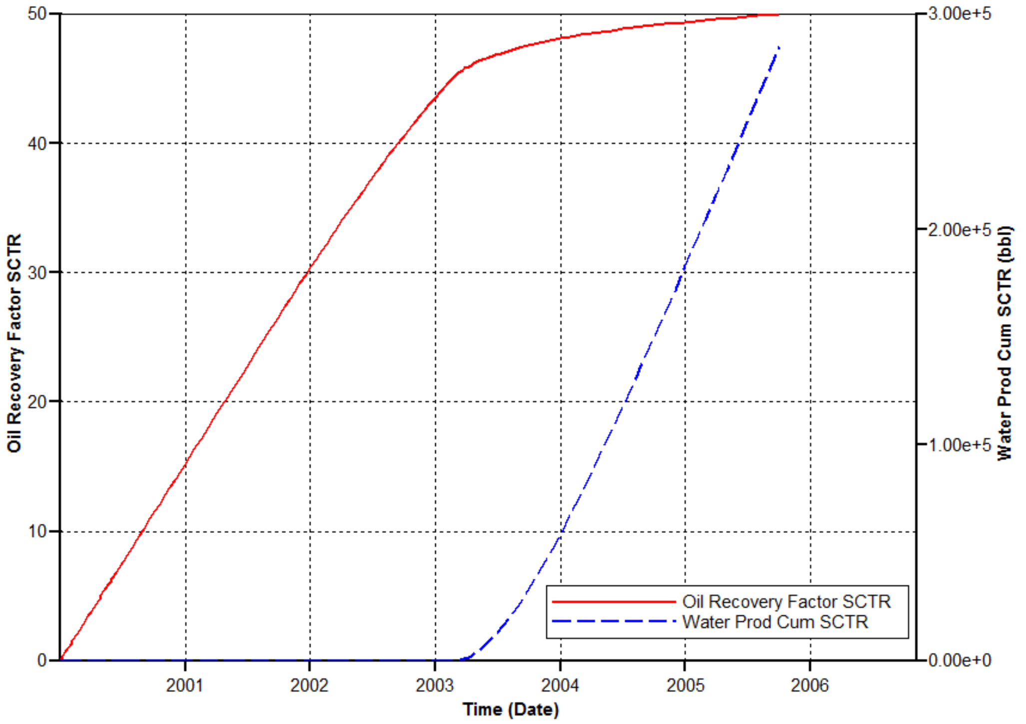


Figure 5.5 Oil recovery factor and cumulative water production of waterflooding base case as a function of time

Referring to Table 5.3 and Figure 5.5, after performing waterflooding from the first day of production, the total oil recovery factor for waterflooding base case which is kept as a reference result is 49.99%. Moreover, observation from Figure 5.6 in both 3D and areal views of oil saturation profile indicates that there is around 40% of oil saturation remained in the reservoir. Therefore, the implementation of surfactant flooding should provide viability to recover more remaining oil. However, in surfactant flooding process, the surfactant flooding condition should not perform in reservoir containing high water saturation, because as injected surfactant solution is flooded through reservoir, the solution will be diluted by high amount formation water. Therefore, from Figure 5.5, the first water production observed is at 1,253 days of waterflooding production, and this date will be used as the starting date of surfactant flooding as high water saturated front has already approached production well.

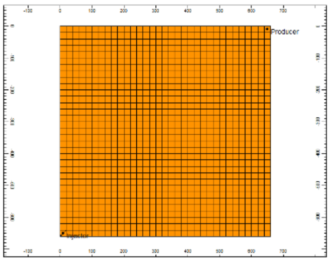
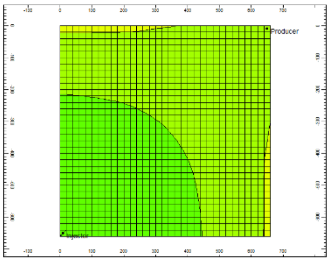
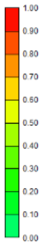
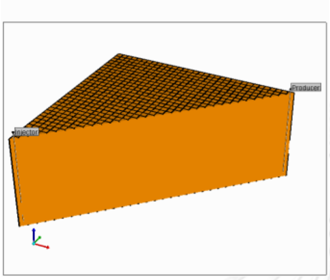
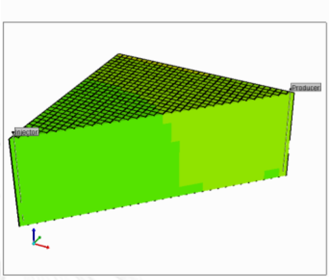
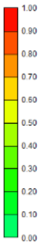
Production start	Production end	Scale
		
		

Figure 5.6 Oil saturation profile of waterflooding base case in 3D and areal views

5.4 Surfactant Flooding Base Case

In this study, the effect of reversibility of surfactant adsorption on surfactant injection slug sizes, surfactant concentrations, and surfactant adsorption are of the interested parameters to evaluate. However, prior to investigate the effects of reversibility to these parameters in this study, a reservoir model which is able to evaluate effects developed from degree of reversibility is constructed.

In evaluation of effects of each interested parameter, oil recovery factor, total production, amount of oil recovered per surfactant mass, and total production time are taken into consideration. Nevertheless, in this study, as the reservoir simulation model is constructed to mainly focus on the effects of reversibility of surfactant adsorption onto studied parameters, the capillary numbers used in the study are in the range of -4 to -3.5 to -3 corresponding to interpolation set1 to set3 for wetting phase, and -4 to -3.7 to -3 for non-wetting phase. However, in this capillary number range, the watercut at the producer fluctuates at the later stage of production, and this leads the reservoir simulation model to attain production constraints unexpectedly while reservoir is still able to produce. Therefore, the total production period is evaluated at 20 years of operation to investigate the effectiveness of the study.

Table 5.4 Summary of parameters used in study of range of capillary numbers

Parameters		**Value**
Concentration		1.0 %wt.
Slug size		0.15 PV
Interpolation Set 1	Wetting phase	-4
	Non-Wetting phase	-4
Interpolation Set 2	Wetting phase	-3.5
	Non-Wetting phase	-3.7
Interpolation Set 3	Wetting phase	-3
	Non-Wetting phase	-3

Fluctuation of watercut at production in late stage which is affected from range of capillary number range used in the study is observed. The summary of parameters used in surfactant flooding base case is illustrated in Table 5.4. As Figure 5.7 suggested, at the early period of production, production of water cut shows smooth curve; but while production approaches later stage, the watercut for model is fluctuated. This can be explained from 3D profiles of each model. At later stage of production, the concentration of surfactant inside reservoir is relatively lower than the point when surfactant is first introduced into the system as demonstrated in Figure 5.8 (a). As long as surfactant concentration in the reservoir is minimal, this leads the simulator to select a value between Set 1 and Set 2 to interpolate and simulate the results. From Figure 5.8 (b), the local capillary number for the model falls in both regions between Set 1 and Set 2, and region in the middle of Set 2 and Set 3. Therefore, the relative permeability curve which is working in concordance with capillary number of each interpolation sets alters the ability of water to flow inside reservoir as dedicated in Figure 5.8 (c). Therefore, simulator tends to use both Set 1 and Set 2 of relative permeability curves during interpolation. This behavior leads the flow ability of water in the model of this study to fluctuate a lot during production; therefore, the watercut at later stage varies through the end of production, and this makes simulator to meet a stop constraint before it should be, so evaluation of all cases is taken into consideration at 20 years of production.

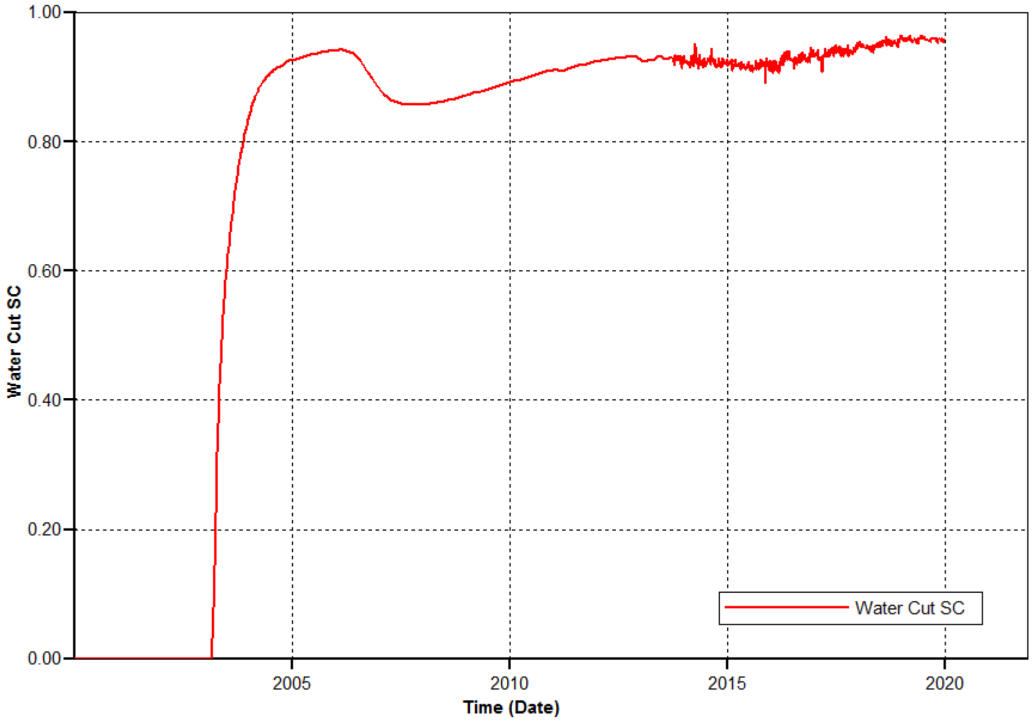
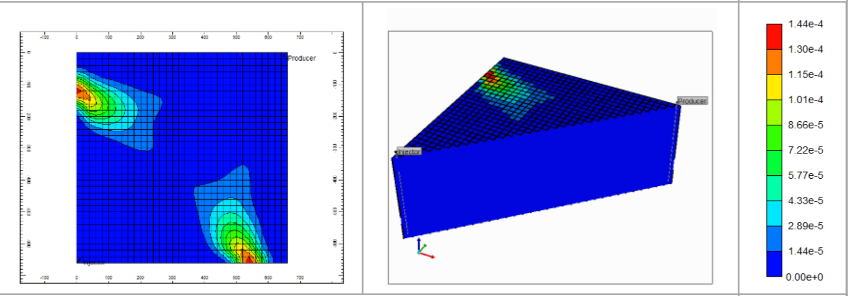


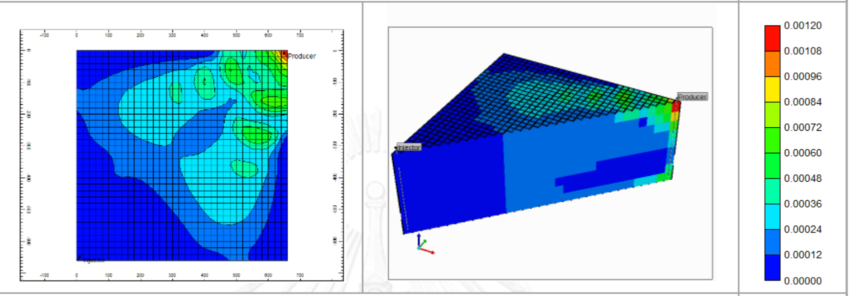
Figure 5.7 Comparison of watercut between study models and model with wider range of capillary numbers

Therefore, all cases performed in this study are compared at 20 years of production. This provides an unbiased comparison of all cases as watercut in the model is highly fluctuated at later stage of production as explained above.

(a) Surfactant concentration Scale



(b) Local capillary number Scale



(c) Water relative permeability Scale

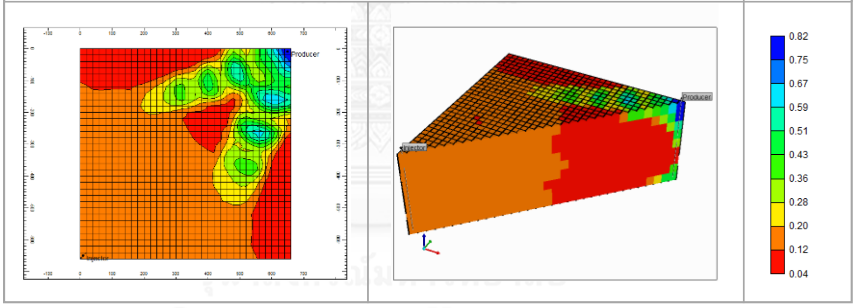


Figure 5.8 Effects of range of capillary numbers shown in areal and 3D profiles

Observing in Figure 5.9 (a), when surfactant is initially introduced to the reservoir, because of the relatively high water saturation for the injection path in diagonal direction, surfactant solution tends to advance to both sides of the reservoir. This behavior continues until the end of surfactant injection and the end of operation. This can be understood that surfactant concentration is diluted once it is flooded through the reservoir, and more severed dilution occurs at later stage while chasing with water. Therefore, surfactant concentration of each grid block of reservoir is varied, making capillary number profiles in Figure 5.9 (b) show non-symmetrical effects in later period of operation. The non-symmetrical effects is therefore caused by the variation of surfactant concentration and very sensitive of capillary number of each grid block to the changing in surfactant concentration. As illustrated in Figure 5.9, when surfactant concentration is relatively high in each grid block in the beginning and the end of surfactant injection periods, there is no non-symmetrical effects observed in both molecules of surfactant and capillary number profiles.

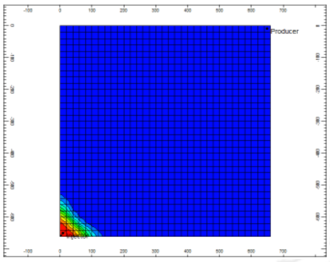
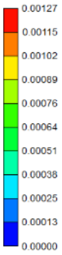
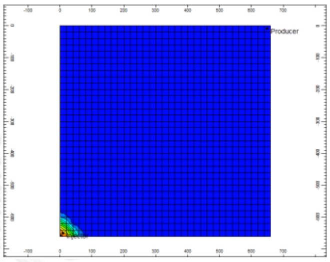
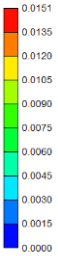
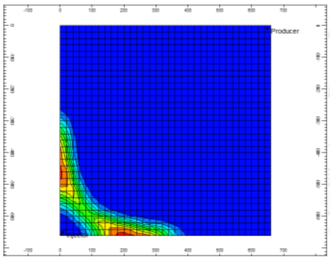
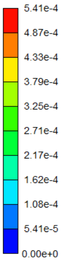
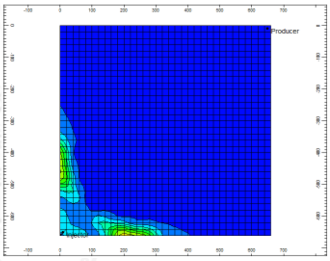
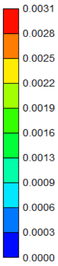
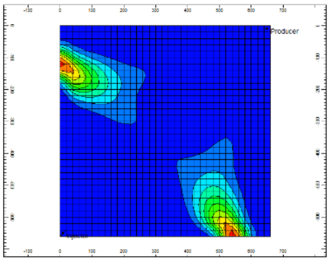
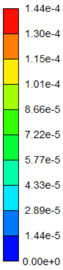
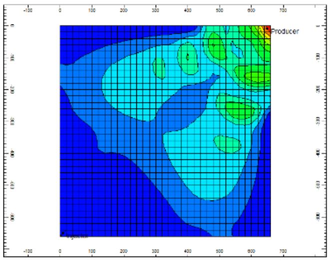
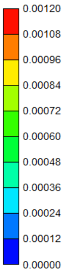
(a) Starting of surfactant	Scale	(b) Starting of surfactant	Scale
	 0.00127 0.00115 0.00102 0.00089 0.00076 0.00064 0.00051 0.00038 0.00025 0.00013 0.00000		 0.0151 0.0135 0.0120 0.0105 0.0090 0.0075 0.0060 0.0045 0.0030 0.0015 0.0000
(a) End of surfactant	Scale	(b) End of surfactant	Scale
	 5.41e-4 4.87e-4 4.33e-4 3.79e-4 3.25e-4 2.71e-4 2.17e-4 1.62e-4 1.08e-4 5.41e-5 0.00e+0		 0.0031 0.0028 0.0025 0.0022 0.0019 0.0016 0.0013 0.0009 0.0006 0.0003 0.0000
(a) End of production	Scale	(b) End of production	Scale
	 1.44e-4 1.30e-4 1.15e-4 1.01e-4 8.66e-5 7.22e-5 5.77e-5 4.33e-5 2.89e-5 1.44e-5 0.00e+0		 0.00120 0.00108 0.00096 0.00084 0.00072 0.00060 0.00048 0.00036 0.00024 0.00012 0.00000

Figure 5.9 Sequential profiles of (a) Surfactant molecule (b) local capillary number

5.4.1 Improved Oil Recovery by Surfactant Flooding

The cost of chemical flooding is generally high because of chemical consumption. Therefore, in this study, only certain pore volume of surfactant solution is flooded through reservoir. This is to prevent over consumption of surfactant which is inapplicable and unviable in terms of economic evaluation of surfactant flooding. Surfactant flooding is then designed with three schedules of flooding processes which are illustrated in Figure 5.10. Waterflooding is performed from the starting point of production, then the injection fluid is switched to surfactant solution when first water production observed at production well which is at 1,253 days of production. According to surfactant slug size used in various cases, following slug size of surfactant solution, the flooding process is altered to waterflooding again so called chasing water.

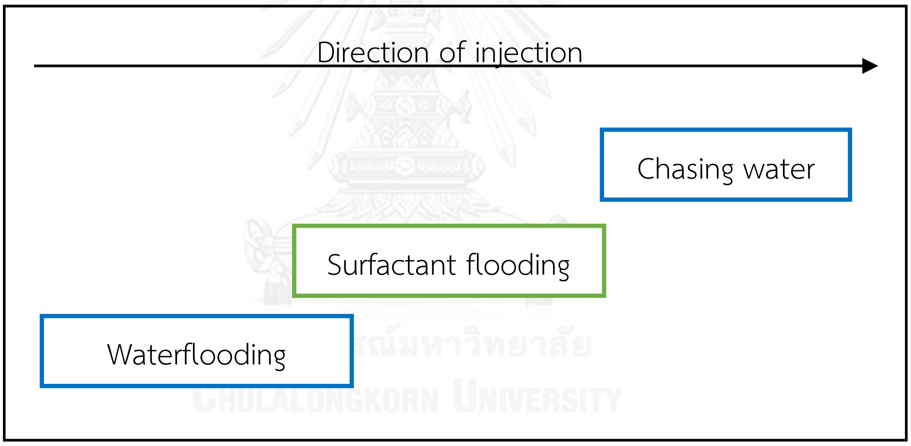


Figure 5.10 Sequences of surfactant flooding

In this section, the comparison between conventional waterflooding base case and surfactant flooding base case is emphasized. The main objective is to determine the improved oil recovery from waterflooding technique by base case of surfactant flooding. The summary of the results of both cases are shown in Table 5.5.

Table 5.5 Results of waterflooding in comparing with surfactant flooding

Parameters	**Waterflooding**	**Surfactant flooding**
Oil recovery factor	49.99%	65.72%
Additional oil recovery factor	-	15.73%
Cumulative water production	0.28×10^{6}bbl	2.41×10^{6}bbl

In comparison between waterflooding and surfactant flooding on the same model, the oil recovery factor is increased from 49.99% to 65.72% corresponding to waterflooding and surfactant flooding cases respectively. Therefore, the additional oil recovery factor is 15.73% which is brought by removal of trapped oil thereafter the mechanism of surfactant in water-oil and rock system. Observing at the starting point of surfactant flooding shown in Figure 5.11, oil recovery factor curve of surfactant flooding shifts up from which of waterflooding and proceeds further to 65.72% until 20 years of operation attained. The additional oil recovered from surfactant flooding is aimed from IFT reduction between aqueous and oil phases, and this facilitates in incremental of capillary number to a more favorable condition. From Figure 5.12, water saturation profiles from waterflooding and surfactant flooding are compared in both areal and vertical planes. It can be seen that dark blue color appears in certain regions in case of surfactant flooding. This color corresponds to extremely high water saturation which can sometimes arrive to 1.0. That means, surfactant can lower IFT value and it can liberate all the residual oil. Due to replacement of water and liberation of oil, water production is reduced at certain period and oil production starts to build up again as oil bank is formed as can be observed in Figure 5.13. Total production period from surfactant flooding is therefore extended due to delay of watercut and increment of oil production rate. This also causes higher amount of cumulative water production in case of surfactant flooding compared to waterflooding as summarized in Table 5.5.

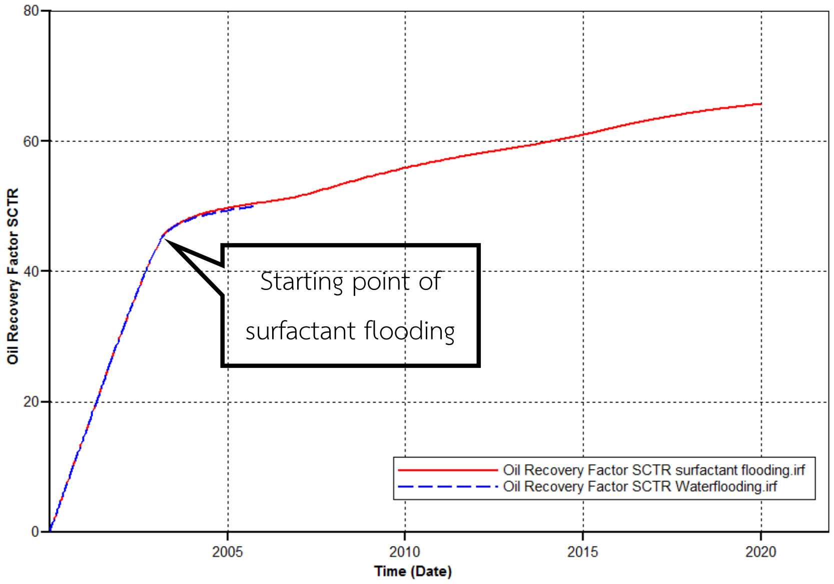
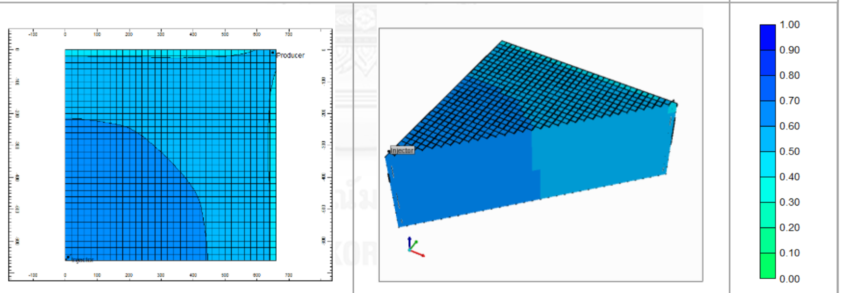


Figure 5.11 Comparison of oil recovery factor obtained from waterflooding and surfactant flooding as a function of time

(a) Waterflooding



(b) Surfactant flooding

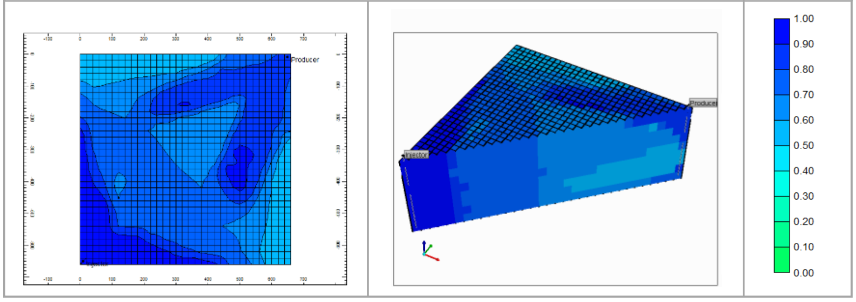


Figure 5.12 Water saturation profile in areal and 3D views

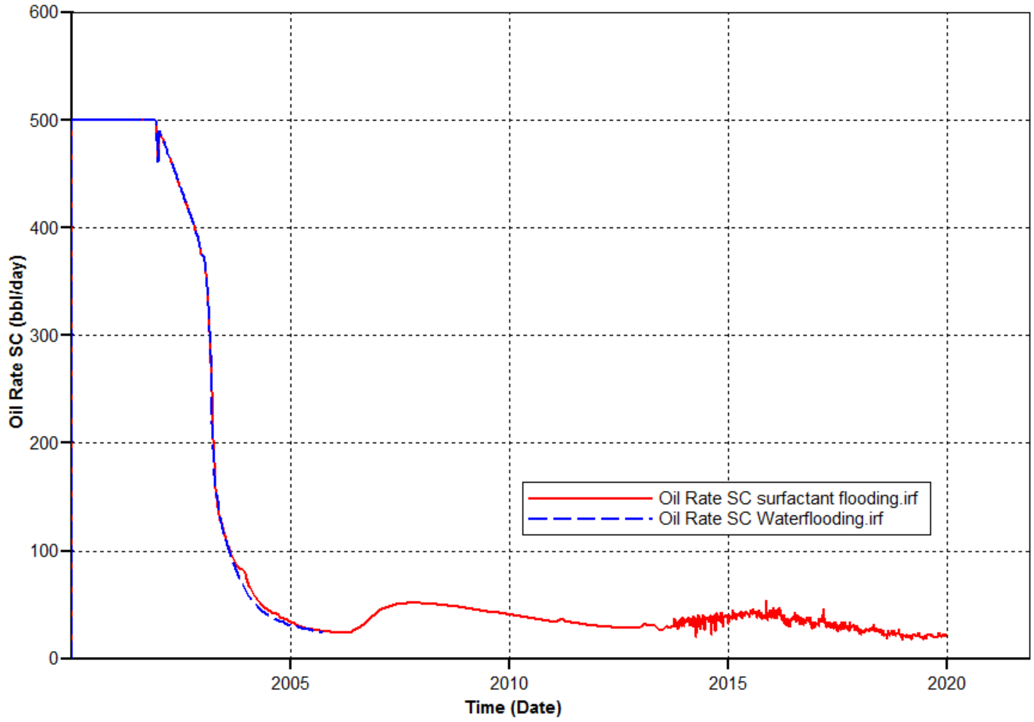


Figure 5.13 Comparison of oil production rates obtained from waterflooding and surfactant flooding as a function of time

5.5 Effects of surfactant Injection Slug Size

In this section, effects of slug size of surfactant are evaluated without taking account of effects of reversibility of surfactant adsorption. After waterflooding, slug of surfactant solution is varied from 0.15 PV to 0.30 PV while surfactant concentration remains constant. Due to different concentrations are performed in this section, corresponding adsorption values which are obtained from dynamic adsorption experiments are used. For surfactant concentration 0.5 %wt., the adsorption value of 35.81 mg/100g is used, while 57.65 mg/100g is used for 1.0 %wt. and 1.5 %wt. concentration cases. After that, chasing water is performed for every case until 20 years of production which is selected from reasons provided in Section 5.4. The sequence of injection in this section is summarized in Figure 5.14. Oil recovery factor and amount of oil recovered per mass of surfactant injected are used to discuss and to indicate favorable slug size for surfactant flooding. Oil recovery factor is extracted from CMG program, while additional oil recovered per mass of surfactant used is calculated from the ratio of additional oil produced compared to waterflooding over mass of surfactant used.

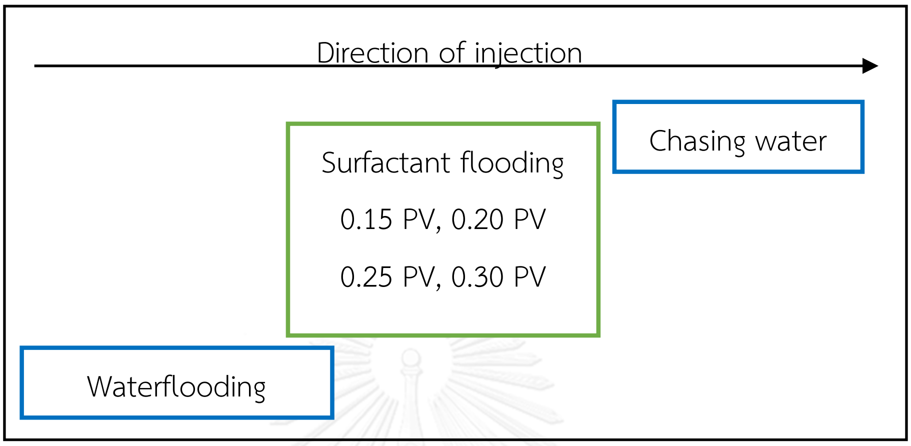


Figure 5.14 Sequence of surfactant flooding with various slug sizes

Oil recovery factor and amount of additional oil recovered per mass of surfactant used of various slug sizes are summarized and illustrated in Figure 5.15 and Figure 5.16. Oil recovery factors from CMG program are plotted as a function of time in Figure 5.17.

From the results of 0.5 %wt. and 1.0 %wt. concentration cases, as slug sizes of surfactant injection increases, corresponding oil recovery factor rises with the same trend as demonstrated in Table 5.6. However, the case of 1.5 %wt. concentration, the most favorable case in terms of oil recovery factor is observed at 0.25 PV slug size rather than the largest slug size used. Therefore, this case is used to explain the mechanism of surfactant flooding in variation of injection slug size. However, focusing on the amount of additional oil production by mass of surfactant used, the best result of every surfactant concentration case fall into in case where 0.15 PV surfactant slug size used. This is because of the difference in oil recovery factor of various cases are insignificant.

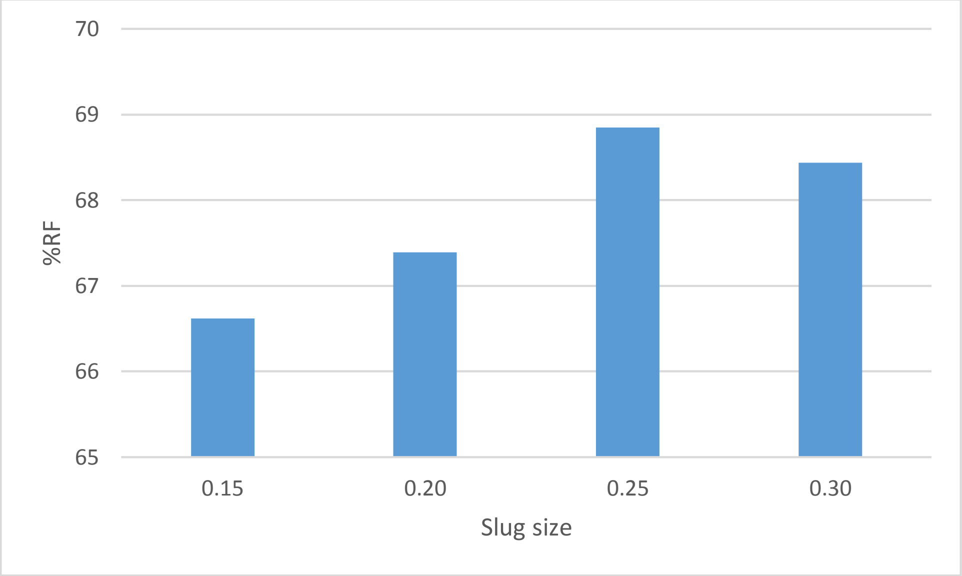


Figure 5.15 Comparison of oil recovery factor as a function of surfactant injection slug size, 1.5 %wt. surfactant concentration case

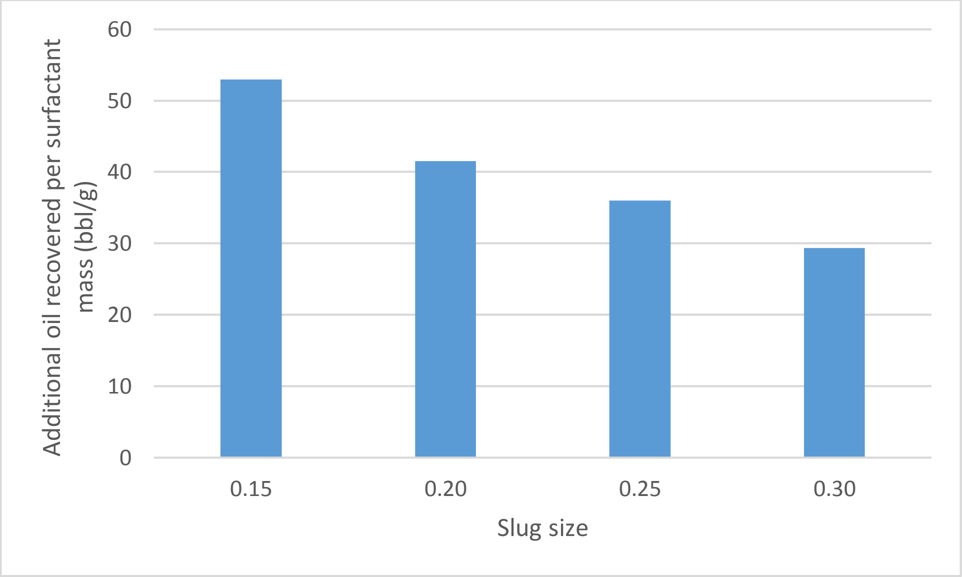


Figure 5.16 Comparison of additional oil recovered per surfactant mass as a function of surfactant injection slug size, 1.5 %wt. surfactant concentration case

Table 5.6 Results of all surfactant concentrations with variation in slug size

Parameters		**0.5 %wt.**	**1.0 %wt.**	**1.5 %wt.**
Oil recovery factor	0.15 PV	63.02%	65.71%	66.62%
	0.20 PV	64.00%	66.39%	67.39%
	0.25 PV	64.72%	67.18%	68.85%
	0.30 PV	65.27%	68.68%	68.44%
Additional oil recovery factor from waterflooding	0.15 PV	13.03%	15.73%	16.63%
	0.20 PV	14.01%	16.41%	17.40%
	0.25 PV	14.73%	17.19%	18.86%
	0.30 PV	15.28%	18.69%	18.45%
Additional oil recovery per mass of surfactant used (bbl/g)	0.15 PV	124.39	75.09	52.93
	0.20 PV	100.33	58.74	41.54
	0.25 PV	84.39	49.23	36.02
	0.30 PV	72.94	44.62	29.36

One of the main objectives of chemical flooding is to ensure injected fluid to sweep and be in contact with reservoir fluids as much as possible. As contact and interaction between injected fluid and reservoir fluids increases, chance of recovery mechanism of injected chemical to react with reservoir increases. Increasing in surfactant injection slug size is aimed to evaluate this behavior in surfactant flooding. The effects of surfactant injection slug size are described in areal and 3D profiles from Figure 5.18 to Figure 5.20. In Figure 5.18, illustration of the adsorption profiles of surfactant onto reservoir rock surface, the sweep efficiency of injected surfactant rises as surfactant slug size increases. With the same surfactant concentration used, the incremental of surfactant slug size provides surfactant solution to contact more area of the reservoir even surfactant concentration in solution is depleted from adsorption onto rock pore surface. However, when surfactant mass increases higher which can overcome dilution of formation water, adding more slug size will cause the accumulation of surfactant mass in certain distance from injector. In case of too big slug size is utilized, the accumulation of surfactant mass will add up to maximum adsorption concentration, this leads to high consumption of surfactant onto rock surface, thus IFT of the reservoir proceeds to unfavorable condition, and corresponding capillary number reduces which can be visually seen in Figure 5.19. Hence, residual oil saturation can be increasingly liberated when capillary number of the reservoir is increased from 0.15 to 0.25 PV as dedicated in Figure 5.20.

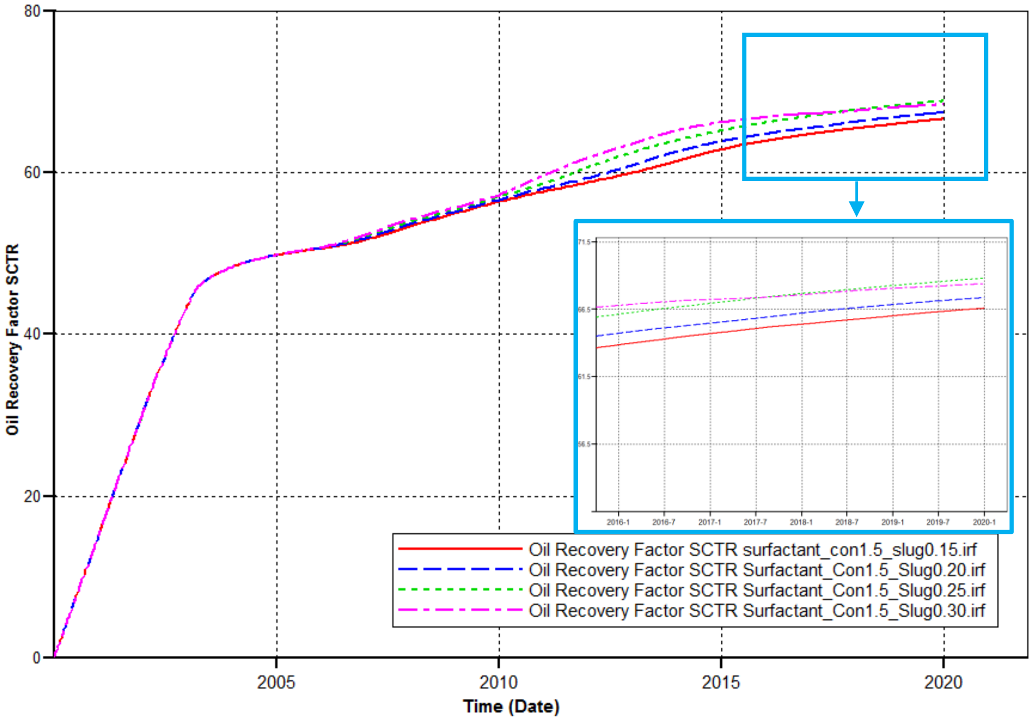


Figure 5.17 Oil recovery factor of 1.5 %wt. surfactant concentration case with variation in slug size as a function of time

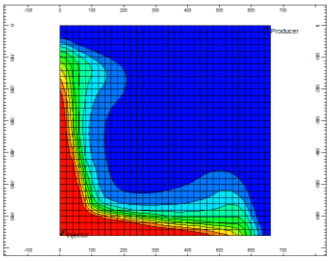
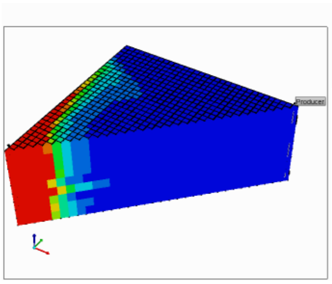
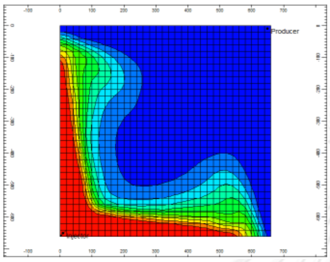
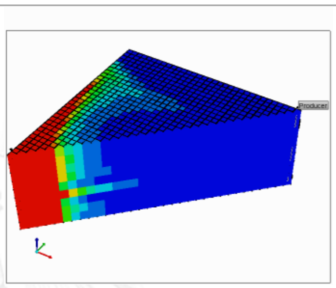
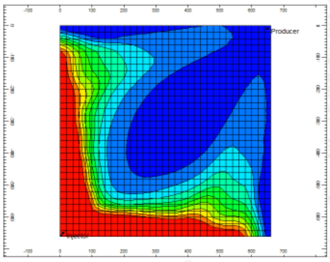
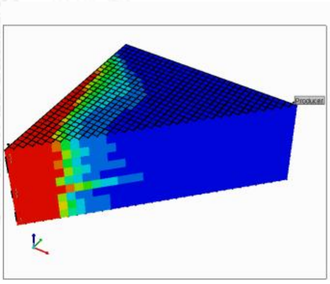
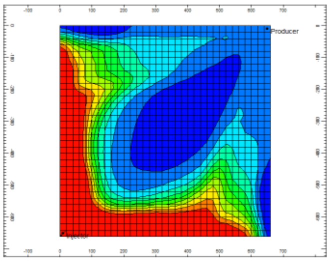
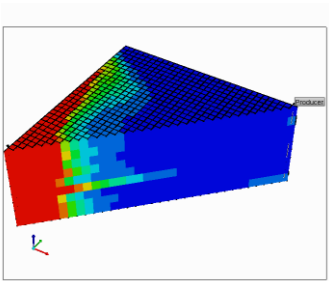
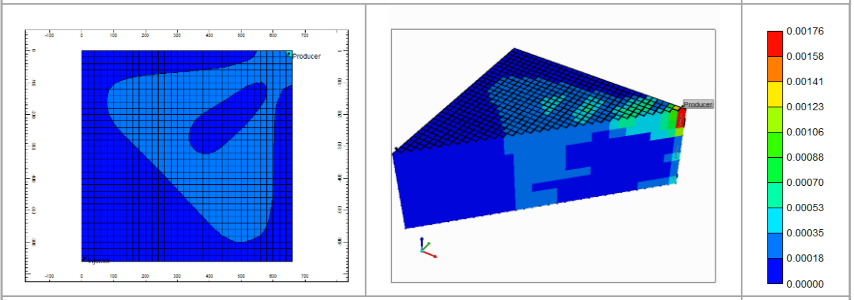
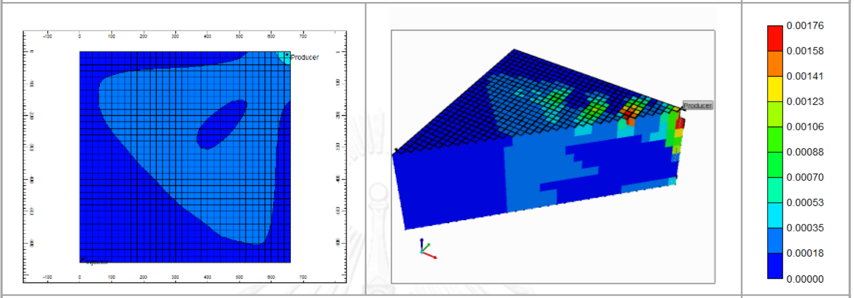
(a) 0.15 PV		Scale
		0.00127 0.00115 0.00102 0.00089 0.00076 0.00064 0.00051 0.00038 0.00025 0.00013 0.00000
(b) 0.20 PV		Scale
		0.00127 0.00115 0.00102 0.00089 0.00076 0.00064 0.00051 0.00038 0.00025 0.00013 0.00000
(c) 0.25 PV		Scale
		0.00127 0.00115 0.00102 0.00089 0.00076 0.00064 0.00051 0.00038 0.00025 0.00013 0.00000
(d) 0.30 PV		Scale
		0.00127 0.00115 0.00102 0.00089 0.00076 0.00064 0.00051 0.00038 0.00025 0.00013 0.00000

Figure 5.18 Surfactant adsorption profile in areal and 3D views of 1.5 %wt. case

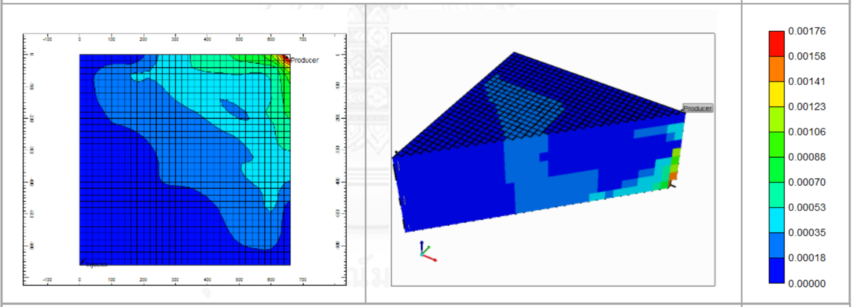
(a) 0.15 PV Scale



(b) 0.20 PV Scale



(c) 0.25 PV Scale



(d) 0.30 PV Scale

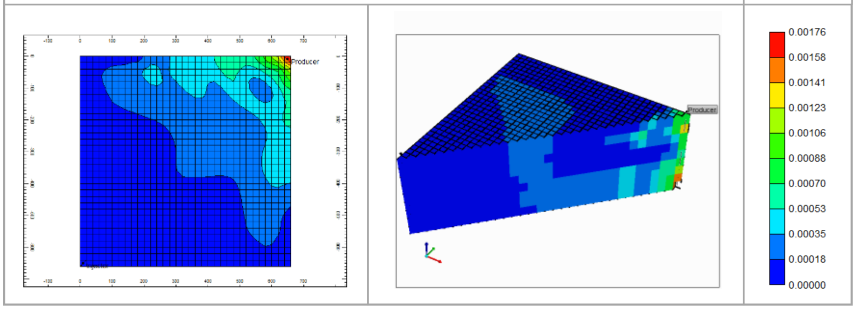
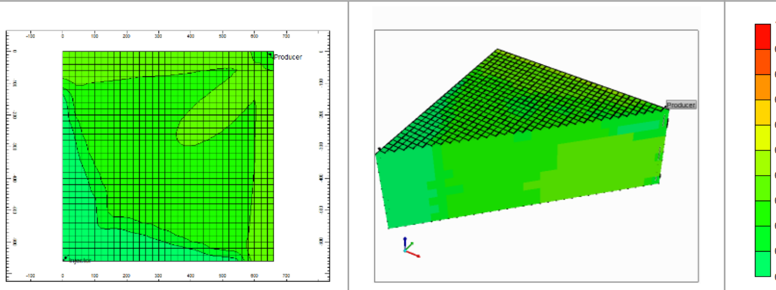


Figure 5.19 Local capillary number profile in areal and 3D views of 1.5 %wt. case

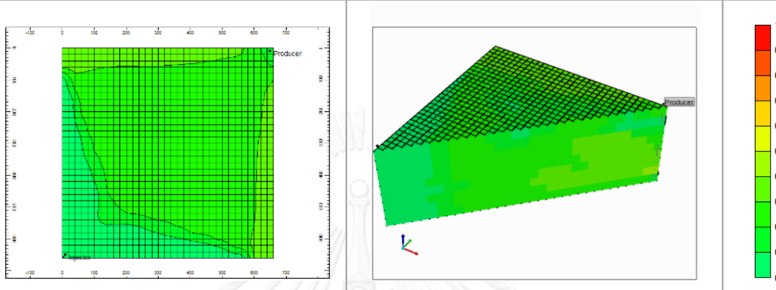
(a) 0.15 PV

Scale



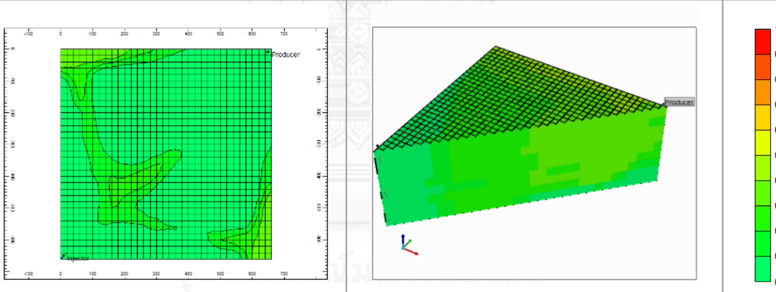
(b) 0.20 PV

Scale



(c) 0.25 PV

Scale



(d) 0.30 PV

Scale

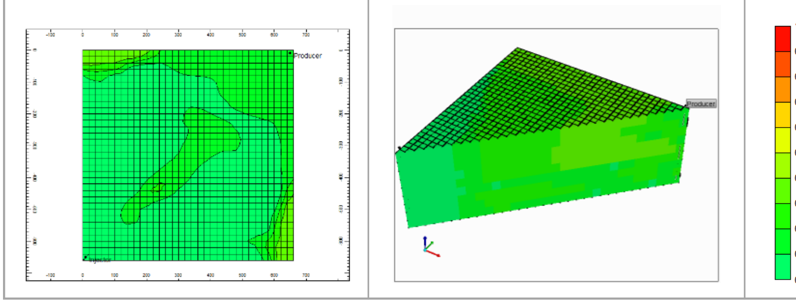


Figure 5.20 Oil saturation profile in areal and 3D views of 1.5 %wt. case

From result in this section, it can be seen that increasing amount of surfactant to the optimum mass yields the benefit on oil recovery factor as oil can be liberated more from rock surface as contact between surfactant solution and reservoir fluid is increased, but when too high amount of surfactant is used, there is accumulation of excess surfactant concentration adding up to maximum adsorption concentration which will then increase again IFT, and thus lower corresponding capillary number, so it is less favorable condition to recover residual oil. Nevertheless, increment of oil recovery factor does not go proportionally with amount of surfactant used. As residual oil is captured by certain conditions, higher amount of oil recovery factor may require more sacrificial of surfactant. Smaller surfactant slug therefore yields the highest oil recovered per fixed mass of surfactant. However, this does not indicate that surfactant flooding should be performed at the smallest slug size but economic consideration should be taken into account to judge the best slug size.

5.6 Effects of Surfactant Concentration

In previous section, effects of surfactant slug size on several surfactant concentrations are evaluated. The results show additional oil recovery improved as more pore volume of surfactant slug size used in the operation. In this section, another interest parameter which is surfactant concentration is taken into study as it is one of the main operational parameters that control the effectiveness on surfactant flooding that aims to lower IFT to ultra-low condition. Concentration of injected surfactant is varied as 0.5 %wt., 1.0 %wt., and 1.5 %wt. Meanwhile, adsorption value of each case is not the same as it is obtained from laboratory experiment as shown in Table 5.7. In addition, from static adsorption experiment, the maximum surfactant adsorption is found at 1.0 %wt.; therefore, the adsorption value of the case with surfactant concentration of 1.5 %wt. is assumed to be the same as which of 1.0 %wt. The sequence of injection of this section is illustrated in Figure 5.21.

Table 5.7 Adsorption values at different surfactant concentrations

Concentration (%wt.)	Adsorption (mg/100g)
0.5	35.81
1.0	57.65
1.5	57.65

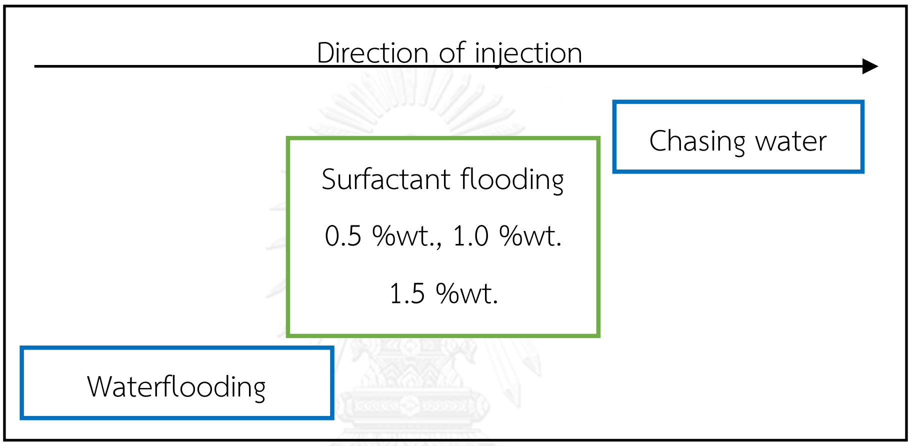


Figure 5.21 Sequence of surfactant flooding in variation of surfactant concentrations

Oil recovery factors obtained from various cases are summarized to Table 5.6 together with additional oil recovery, and additional oil produced per mass of surfactant used compared to waterflooding. In comparison with increasing of surfactant slug size, the rise in surfactant concentration shows relatively more significant improvement in terms of oil recovery factor. However, with larger slug of surfactant in case of 0.30 PV, more favorable oil recovery is found at 1.0 %wt. case. Case of surfactant slug size of 0.25 PV with increasing concentration is used as reference case to explain the mechanism. Plots of oil recovery factors obtained from various slug sizes with increasing surfactant concentration are demonstrated in Figure 5.22 and Figure 5.23. Referring to amount of oil produced by mass of surfactant used, the results show similar trend as that of varying slug size. The best result is obtained when the lowest concentration of surfactant is used as dedicated in Figure 5.24.

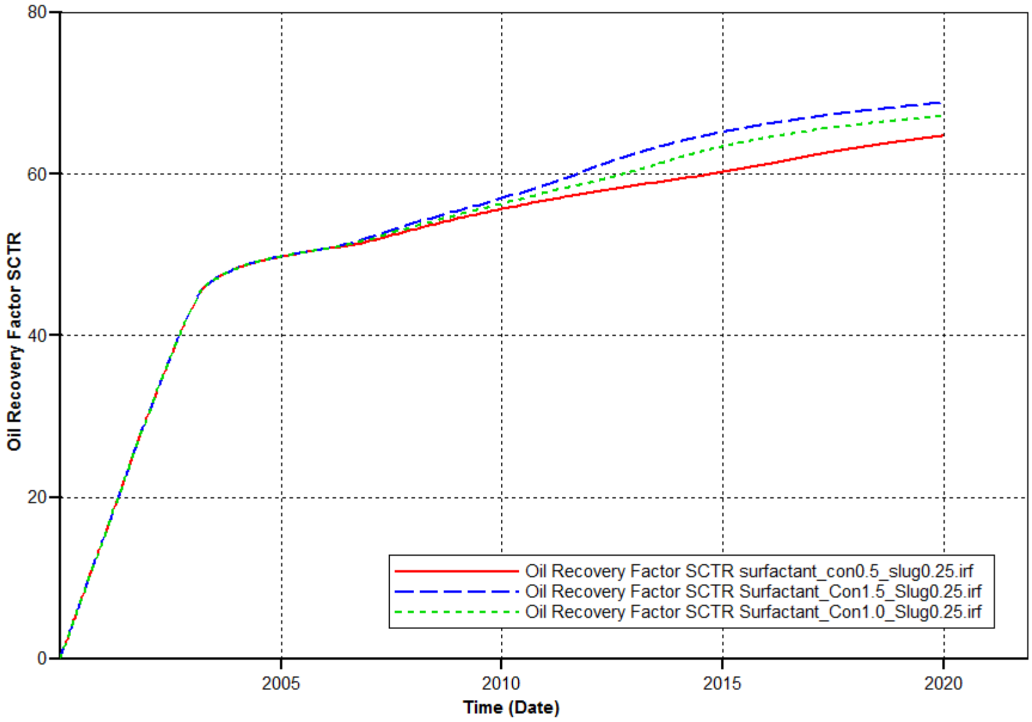


Figure 5.22 Oil recovery factors of 0.25 PV slug size case with variation in concentration as a function of time

As surfactant solution flows through the reservoir, the concentration of the solution is diluted from by mixing with formation water. Besides, the reservoir rock surface also accounts for parts of reduction of concentration, and the rest of surfactant solution is interacted with reservoir fluids which enables to reduce the IFT between oil and aqueous phases. Therefore, when surfactant concentration is increased in the system, it helps to sustain surfactant solution to flow further in the reservoir, and hence helps recovering more residual oil. According to Figure 5.25, incremental of oil recovered by increasing surfactant concentration is obtained from more trapped oil produced and accumulated in oil bank. From 6th year until 13th year of operation, oil production rate increases as more surfactant concentration is utilized. As surfactant concentration is increased, ultra-low IFT condition can be attained in larger extent of the reservoir. Higher reduction of residual oil saturation occurs. Change of relative permeability to oil is clearly observed from both areal and 3D profiles from Figure 5.26. Moreover, additional oil recovery from the expected effects from increasing surfactant concentration is increasing in local capillary number of the system as corresponding IFT is reduced to lower range. The areal and 3D profiles of local capillary number of each case are illustrated in Figure 5.27.

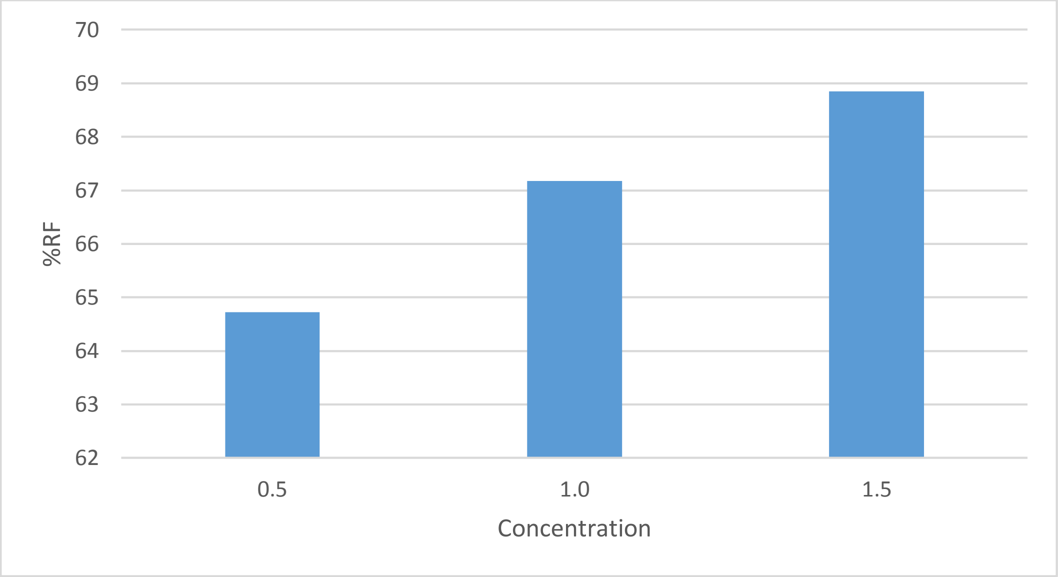


Figure 5.23 Comparison of oil recovery factor as a function of surfactant concentration, 0.25 PV case

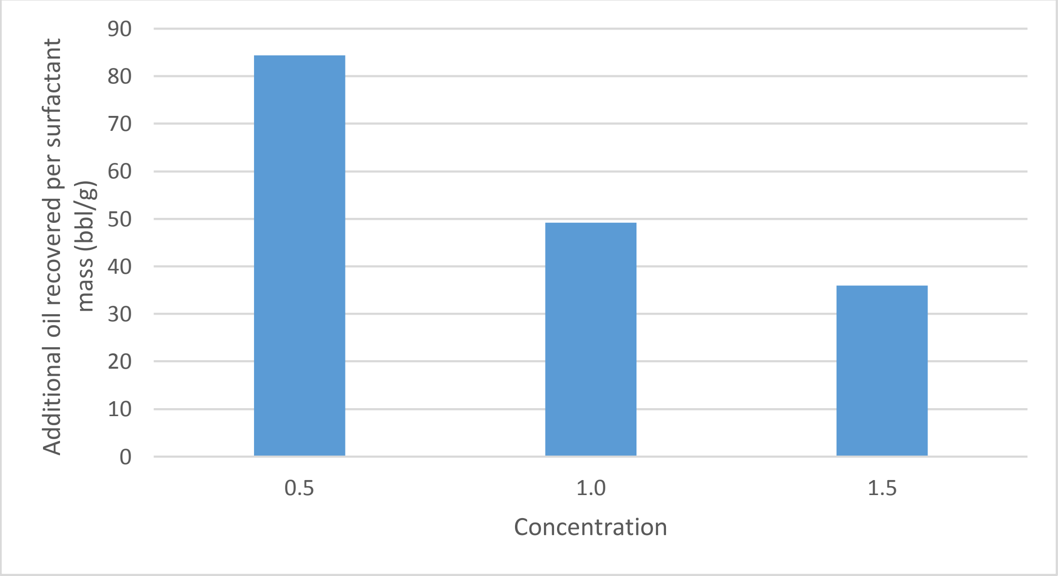


Figure 5.24 Comparison of additional oil recovered per surfactant mass as a function of surfactant concentration, 0.25 PV case

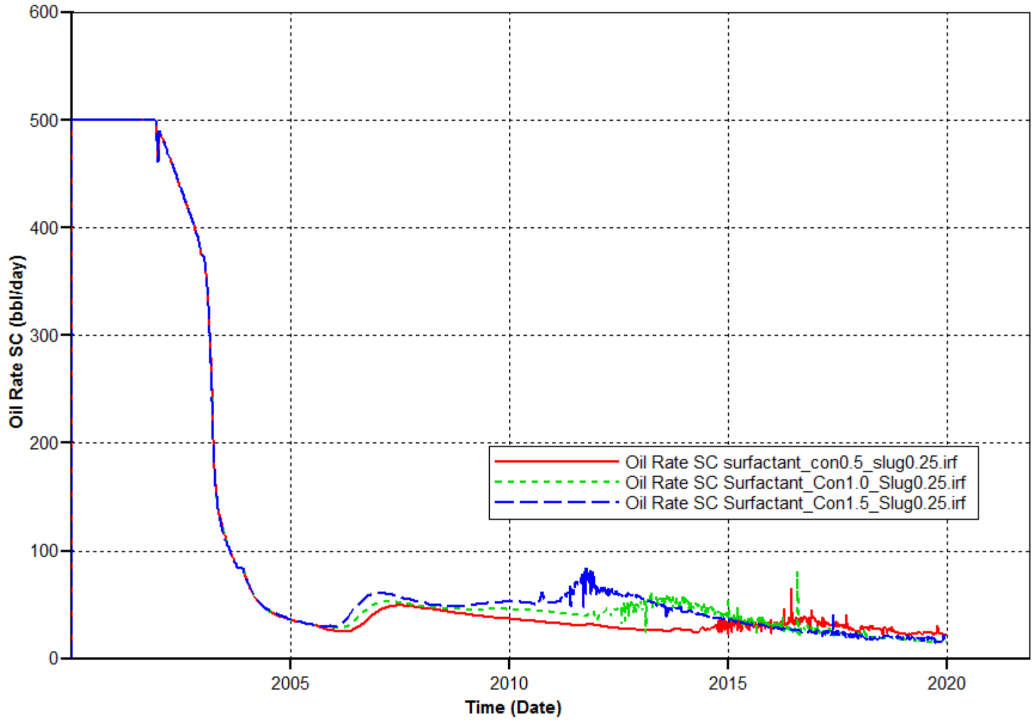


Figure 5.25 Oil production rates of 0.25 PV slug size case with variation in concentration as a function of time

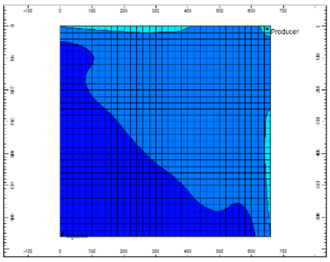
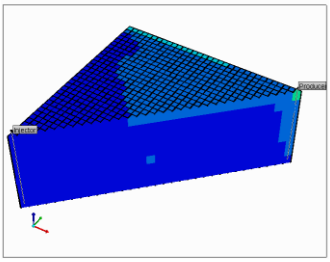
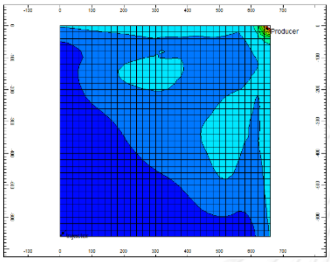
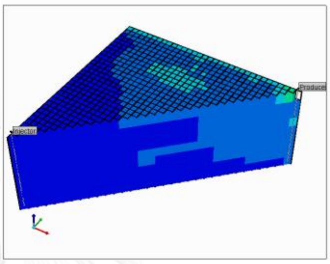
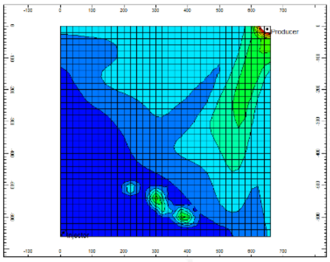
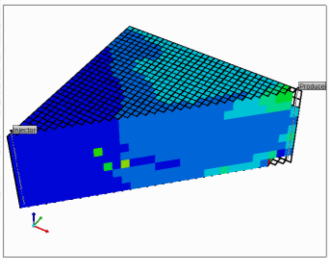
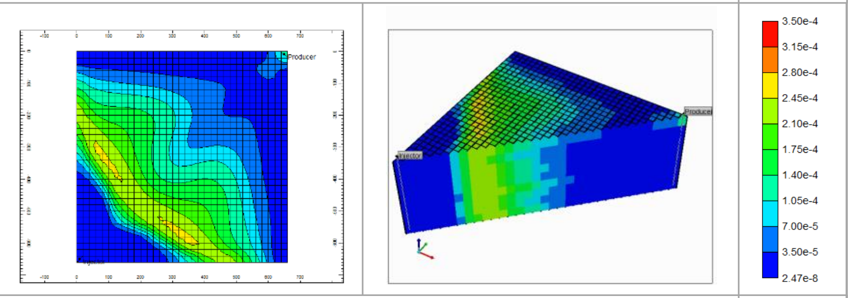
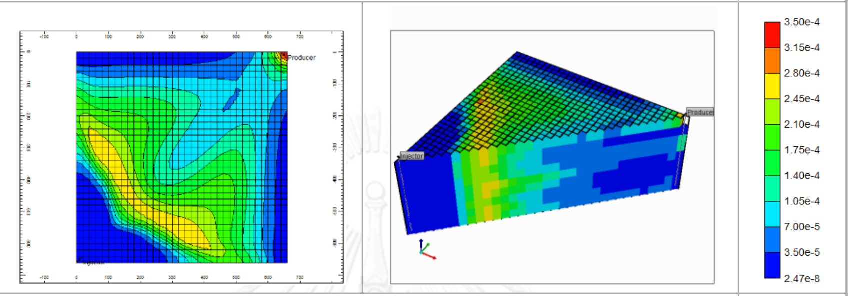
(a) 0.5 %wt.		Scale
		0.140 0.126 0.112 0.098 0.084 0.070 0.056 0.042 0.028 0.014 0.000
(b) 1.0 %wt.		Scale
		0.140 0.126 0.112 0.098 0.084 0.070 0.056 0.042 0.028 0.014 0.000
(c) 1.5 %wt.		Scale
		0.140 0.126 0.112 0.098 0.084 0.070 0.056 0.042 0.028 0.014 0.000

Figure 5.26 Relative permeability to oil profiles in areal and 3D views at 11th year of production, 0.25 PV case

(a) 0.5 %wt. Scale



(b) 1.0 %wt. Scale



(c) 1.5 %wt. Scale

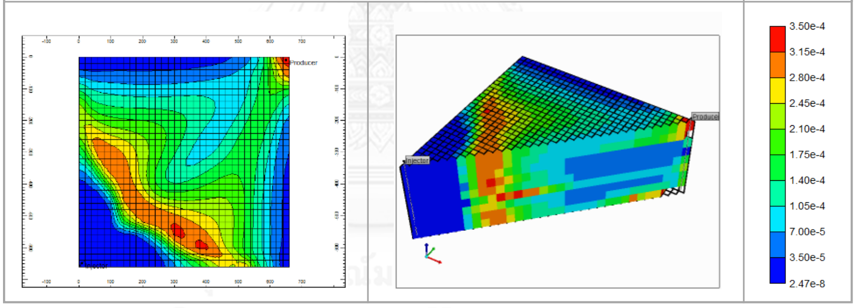


Figure 5.27 Local capillary number profiles in areal and 3D views at 11th year of production, 0.25 PV case

From these figures, it can be observed that relative permeability to oil is zero around the injection well. This indicates that there is no more oil remained in this region due to IFT reduction as surfactant concentration is still high prior to surfactant depletion from adsorption. A change in color with non-grading shade indicates forming of oil bank. As water is pre-injected into reservoir, oil saturation is reduced to residual oil saturation due to waterflooding and this corresponds to relative permeability to oil in range of 0.014 – 0.028 (medium blue color). Once surfactant solution is injected, oil saturation is suddenly reduced to zero and no oil flows in this region. Oil bank is pushed ahead this area and the relative permeability to oil increases up to 0.028 – 0.042 (light blue). In case that high surfactant amount is used such as in case of 1.5 %wt. with surfactant slug size of 0.25 (Figure 5.26c), oil bank is formed at relatively higher oil saturation as can be observed from light blue to green colors which correspond to relative permeability to oil around 0.042 to 0.084. As higher amount of surfactant remained, surfactant can remove more residual oil saturation and form oil bank with high oil saturation. Together with observation of relative permeability to oil, local capillary number shows concordances. High accumulation of oil in oil bank is a result from great reduction in residual oil saturation which is a function of changing in capillary number. Higher surfactant amount results in lower IFT value which yields higher capillary number. Orange to red colored region is therefore observed in larger area in Figure 5.27.

Surfactant concentration is very important parameter as it controls degree of reduction of residual oil saturation through IFT reduction and increasing of capillary number. Higher surfactant concentration yields better oil recovery factor as more oil is liberated from reservoir. Surfactant concentration should be high enough to maintain good adequately low IFT value from surfactant adsorption. In reservoir with high surfactant depletion from adsorption, surfactant concentration should be high or certain chemicals should be co-injected to prevent adsorption or to promote desorption. Nevertheless, similar to effect of slug size, very high oil recovery factor will be obtained with high sacrificing amount of surfactant due to more difficulty to remove this residual oil with much lower IFT value. Therefore, oil recovered per constant mass of surfactant consumed is higher at lower amount of surfactant used and it is reduced with higher amount of surfactant.

5.7 Effects of Surfactant Adsorption Values

Surfactant adsorption onto reservoir rock surface has always been one of the drawbacks of surfactant flooding technique. Therefore, it is very important to simulate the effects of surfactant adsorption. In this section, surfactant adsorption value alone will be studied without accounting for reversibility. The effects of surfactant adsorption values are determined by using different adsorption values which are obtained from static and dynamic adsorption experiments. Variation of adsorption values are simulated on surfactant flooding base case, which uses surfactant concentration of 1.0 %wt. and increasing slug size from 0.15 to 0.30 PV. The summary of sequence of this section is demonstrated in Figure 5.28.

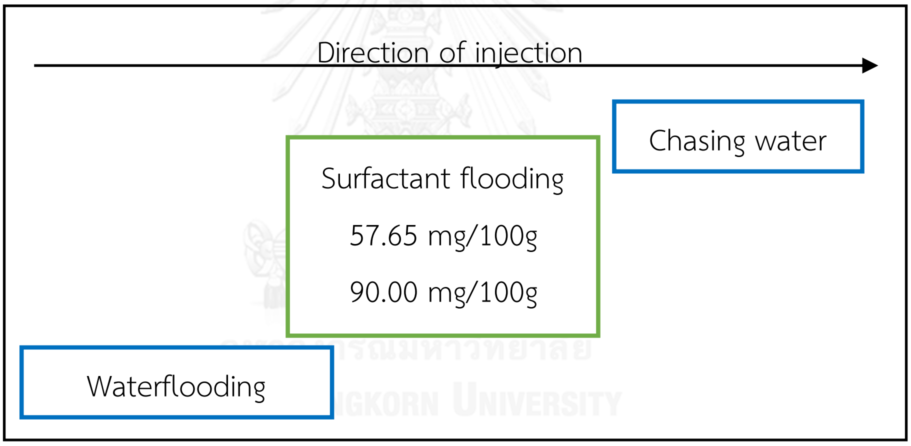


Figure 5.28 Sequence of surfactant flooding in variation of surfactant adsorption values

The recorded results are at after 20 years of production. Oil recovery factor and additional oil recovered per mass of surfactant used are the important parameters to evaluate the effectiveness in terms of surfactant adsorption on surfactant flooding. The numerical results of different adsorption values utilized in this section are summarized in Table 5.8. As the results from different adsorption values on varying in slug size are on the same trend, the case of 0.30 slug is used as reference to explain mechanism. In addition, results of oil recovery factor from CMG program are plotted in Figure 5.29. Comparison of oil recovery factor in Figure 5.30 together with additional oil production per surfactant mass used is determined and demonstrated in Figure 5.31.

According to oil recovery factor, as high surfactant adsorption value is used in the model, the results show lower oil recovery factor as expected in various cases of surfactant slug size used. Besides, this also causes lower additional oil that can be recovered from the same mass of surfactant used in each pore volume cases.

Table 5.8 Results of each surfactant adsorption case

Case	**RF (%)**		**Additional oil produced per surfactant mass**	
	Adsorption (57.65 mg/100g)	**Adsorption (90.00 mg/100g)**	**Adsorption (57.65 mg/100g)**	**Adsorption (90.00 mg/100g)**
Slug 0.15 PV	65.72	64.80	75.09	70.70
Slug 0.20 PV	66.39	65.96	58.74	57.19
Slug 0.25 PV	67.18	66.70	49.23	47.87
Slug 0.30 PV	68.68	67.52	44.62	41.84

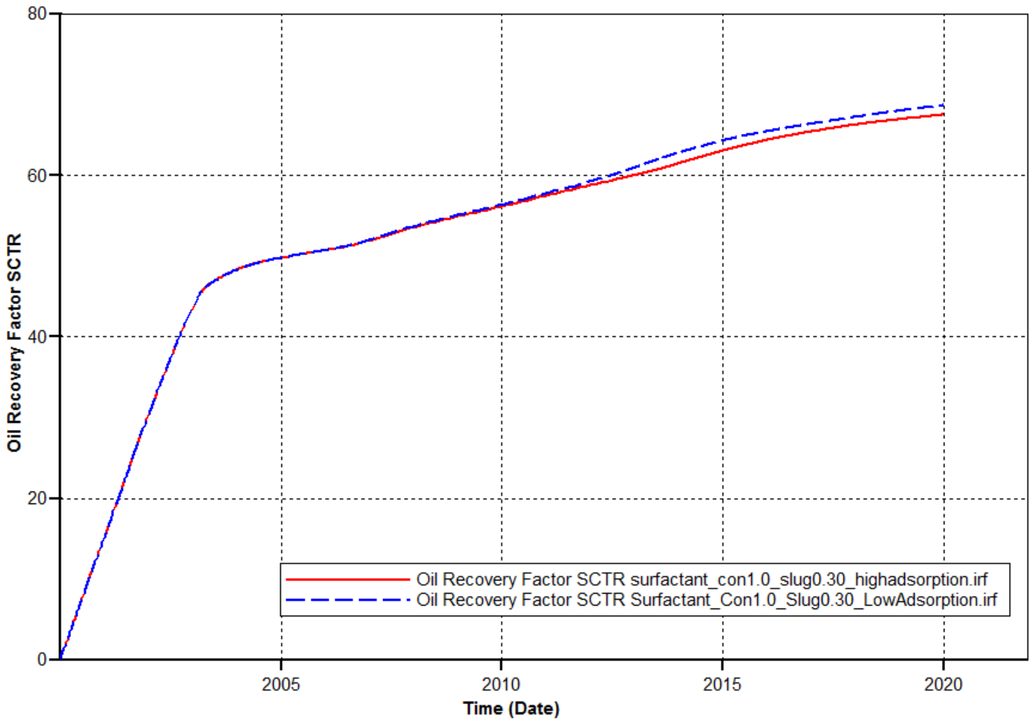


Figure 5.29 Oil recovery factor of 0.30 PV slug size case with variation in adsorption value as a function of time

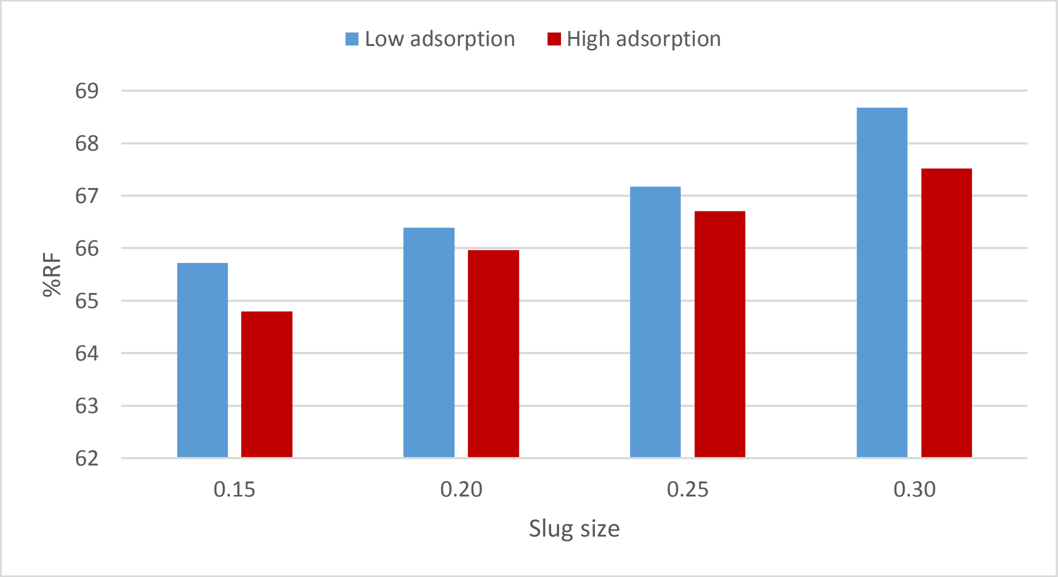


Figure 5.30 Comparison of oil recovery factor of low and high adsorption values as a function of surfactant injection slug size

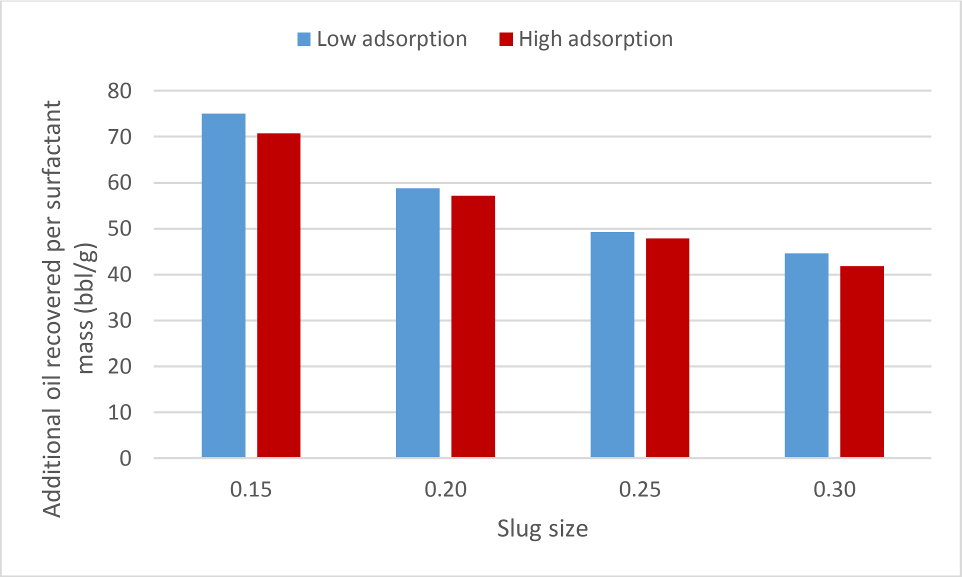


Figure 5.31 Comparison of additional oil recovered per surfactant mass of low and high adsorption values as a function of surfactant injection slug size

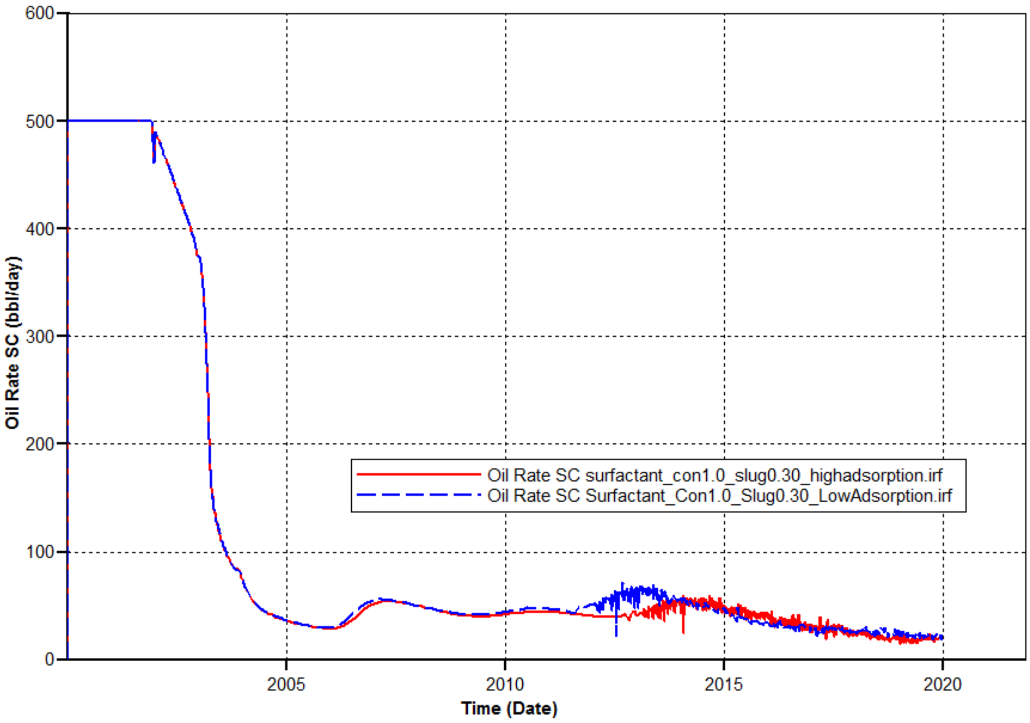


Figure 5.32 Comparison of oil production rates from low and high adsorption cases with 0.30 PV as a function of time

From Figure 5.32, it can be observed that increasing of surfactant adsorption results in delaying of oil bank. Even though the surfactant adsorption is much different, oil recovery factor as well as rate of oil production does not change much. This can be explained that after adsorption process, the remaining surfactant concentration in liquid phase of both cases is still adequate to reduce IFT to low condition.

As adsorption value is high, slightly lower oil recovery factor is obtained. Referring to Figure 5.33, the areal and 3D adsorption profiles, as adsorption of surfactant is high, more concentration of surfactant in the solution is consumed by reservoir rock surface. Another effect observed from this behavior is that with the same amount of surfactant concentration at flood front, the case with higher adsorption value, the chemical flood front can travel shorter distance than that of lower adsorption case. Therefore, when adsorption value is high, the ability to lower IFT becomes weaker which results in more difficulty to form oil bank, and thus less oil production rate is detected. Due to these effects, observation of local capillary number and oil saturation profiles after 20 years of operation is also taken into consideration. As illustrated in Figure 5.34 of lower adsorption occurs throughout the reservoir, surfactant solution can lower IFT in larger area, and thus corresponding capillary number rises in flooded locations indicating in green color. Therefore, oil saturation of lower adsorption case falls into lower range which indicates less trapped oil existed in reservoir as dedicated in more green and dark green colors in Figure 5.35.

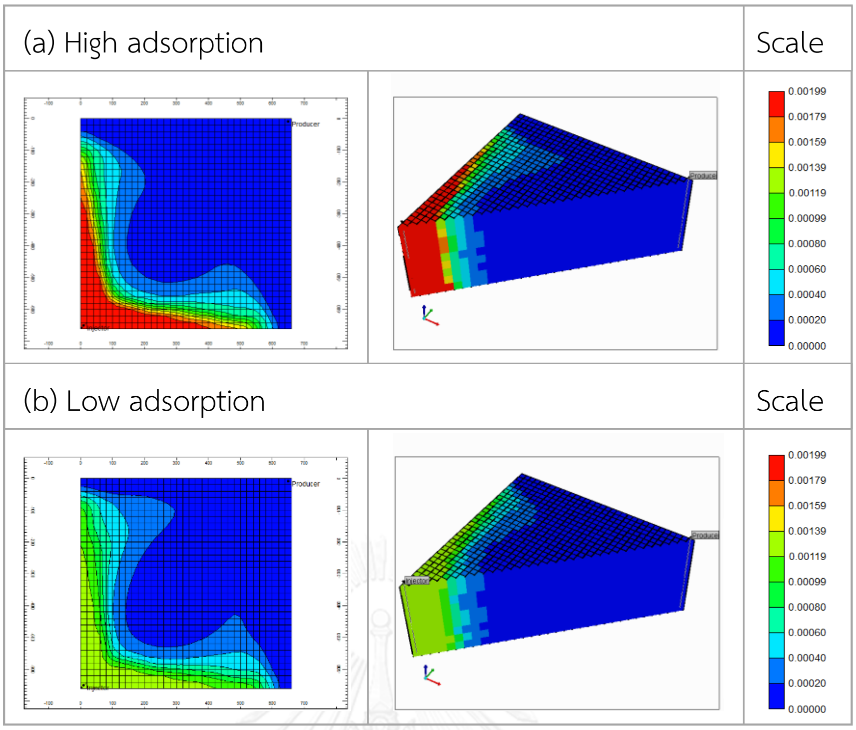


Figure 5.33 Surfactant adsorption profiles in areal and 3D views for 0.30 PV case

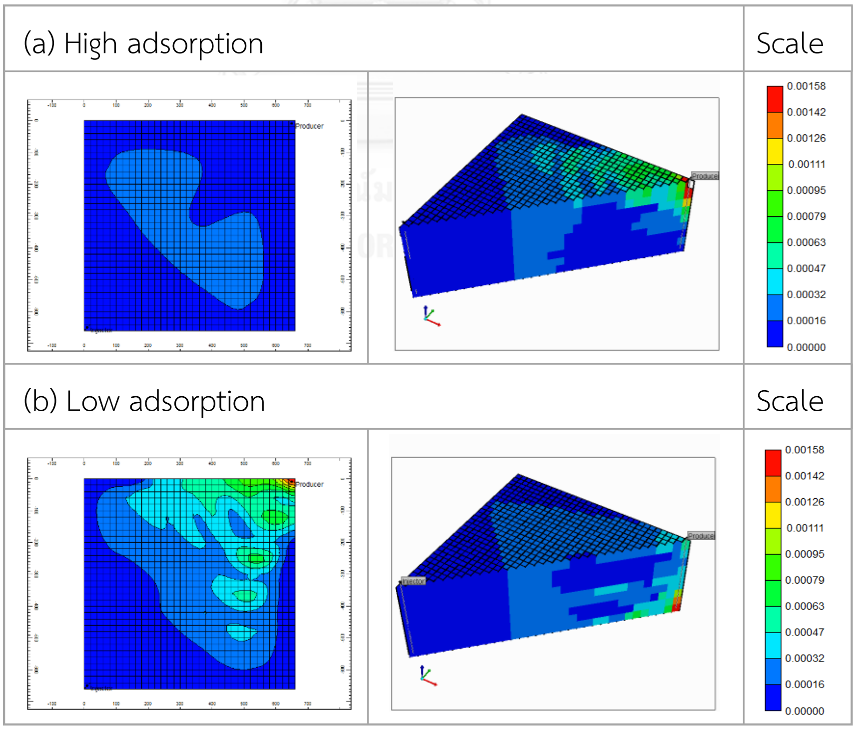
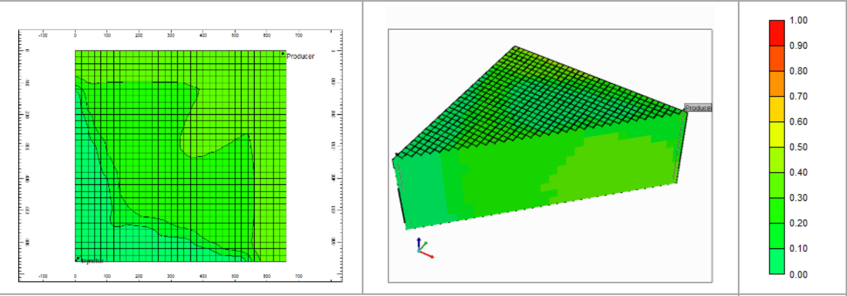


Figure 5.34 Local capillary number profiles in areal and 3D views for 0.30 PV case

(a) High adsorption

Scale



(b) Low adsorption

Scale

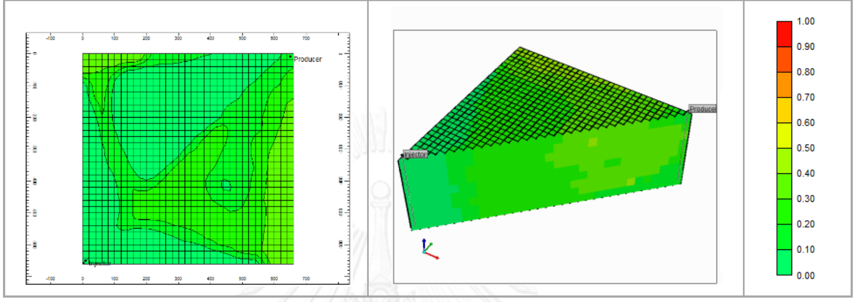


Figure 5.35 Oil saturation profiles in areal and 3D views for 0.30 PV case

As oil recovery mechanism by means of surfactant depends on amount of surfactant monomer in liquid phase, high degree of surfactant adsorption results in less surfactant concentration, resulting in more difficulty to form an oil bank due to higher IFT and lower capillary number. As a consequence, arrival of oil bank is delayed and oil recovery factor is slightly lower for case with high surfactant adsorption.

5.8 Effects of Reversibility of Surfactant Adsorption

The effects of surfactant injection slug size, surfactant concentration, and surfactant adsorption values have been revealed in sections 5.5, 5.6, and 5.7 respectively. However, as the objectives of this study points out, the effects of reversibility of surfactant adsorption on operational parameters have to be taken into account. In this section, evaluation of the effects of adsorption reversibility on interested operational parameters is divided into five sub-sections. Degrees of reversibility of surfactant adsorption which are obtained from laboratory experiments are utilized to apply in reservoir simulation. As dynamic adsorption and desorption tests suggested, the degree of reversibility of adsorption between SDBS and Berea sandstone is determined to be at 41% and 87% for 0.5 %wt. and 1.0 %wt. respectively. According to the explanation of fluctuation of water cut in section 5.2 due to range of capillary number range used in this study, all following studying cases are taken into comparison and evaluation at 20 years of production.

5.8.1 Effects of Reversibility of Surfactant Adsorption on Injection Slug Size

In section 5.5, evaluation of surfactant injection slug size is studied without taking account of reversibility of surfactant adsorption. In another word, reversibility of surfactant adsorption is zero. Results of the study reveal that oil recovery factor of each case increases when more pore volume of surfactant solution is injected into reservoir prior to reaching the optimum surfactant mass. However, the laboratory studies of adsorption and desorption of surfactant onto Berea sandstone suggest that adsorbed concentration of surfactant can be reversible in certain degrees when different injection concentrations are applied. Therefore, in reservoir simulation study, while remaining injection slug size to be constant, the effects of various degrees of reversibility are determined as illustrated in Table 5.9.

Observing from the results, the trend of oil recovery goes in the same direction, the case of 1.0 %wt. concentration and 0.25 PV slug with various degrees of reversibility is used as reference in explaining of the mechanism. The summary of results of oil recovery factor and additional oil recovered per surfactant mass consumed of all cases is plotted in Figure 5.36, Figure 5.37, and Figure 5.38 respectively.

Table 5.9 Summary of the results of each case of slug size and concentration variation

Parameter	**Oil recovery factor**	
Reversibility	**0%**	**41%**
Concentration	**0.5 %wt.**	
Slug 0.15 PV	63.02	63.66
Slug 0.20 PV	64.00	64.82
Slug 0.25 PV	64.72	65.44
Slug 0.30 PV	65.27	66.19
Reversibility	**0%**	**83%**
Concentration	**1.0 %wt.**	
Slug 0.15 PV	65.72	66.34
Slug 0.20 PV	66.39	67.22
Slug 0.25 PV	67.18	67.69
Slug 0.30 PV	68.68	69.31
Concentration	**1.5 %wt.**	
Slug 0.15 PV	66.62	67.71
Slug 0.20 PV	67.39	68.45
Slug 0.25 PV	68.85	70.18
Slug 0.30 PV	68.44	69.97

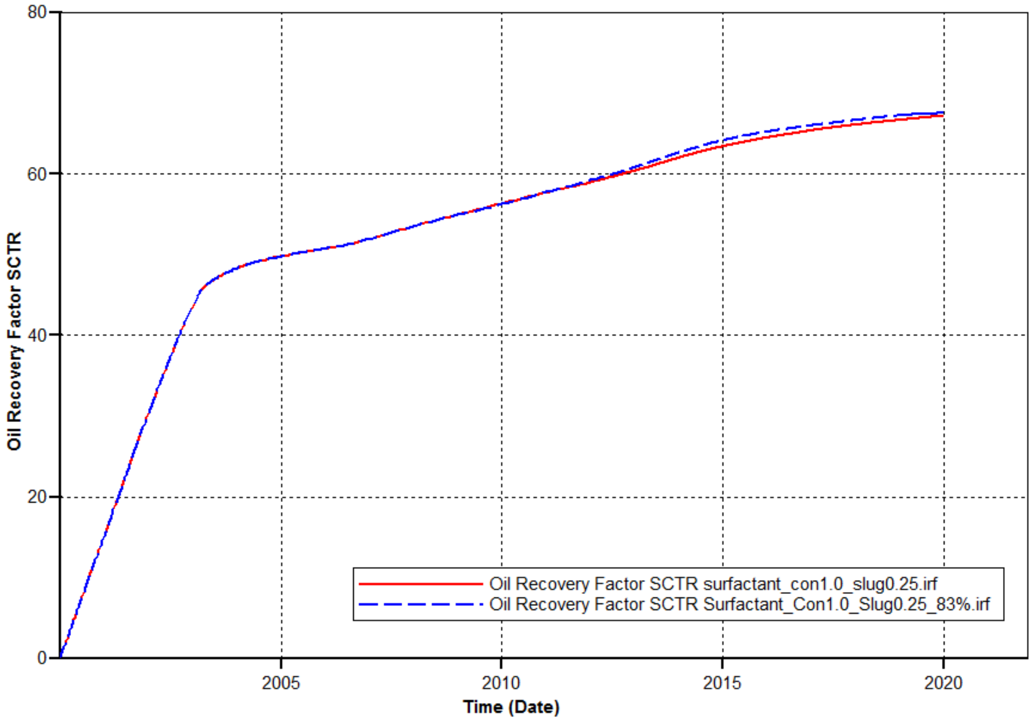


Figure 5.36 Oil recover factor of 0.25 PV slug size with various degrees of reversibility as a function of time

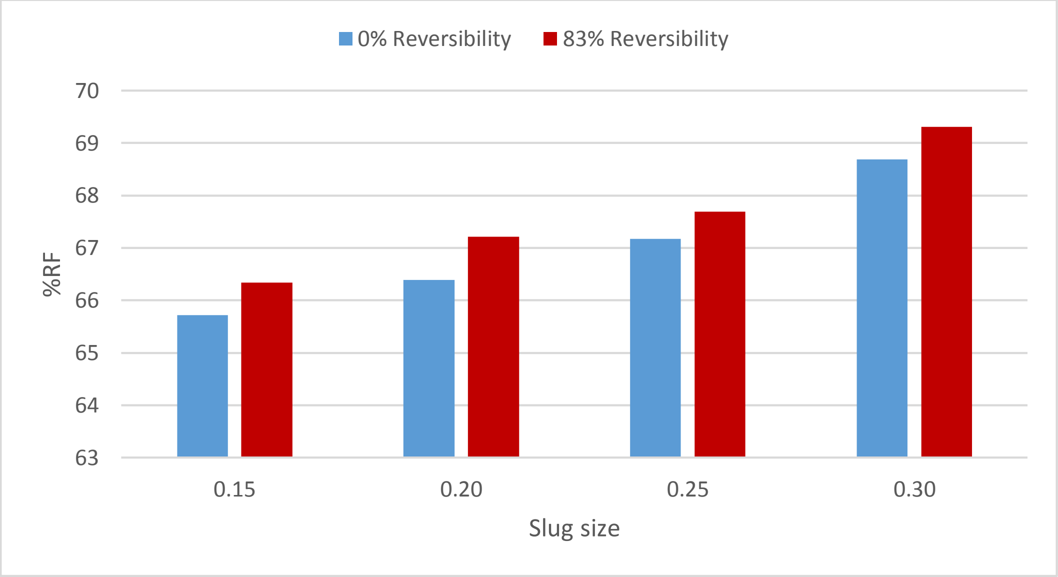


Figure 5.37 Comparison of oil recovery factor on various degrees of reversibility as a function of surfactant injection slug size, 1.0 %wt. case

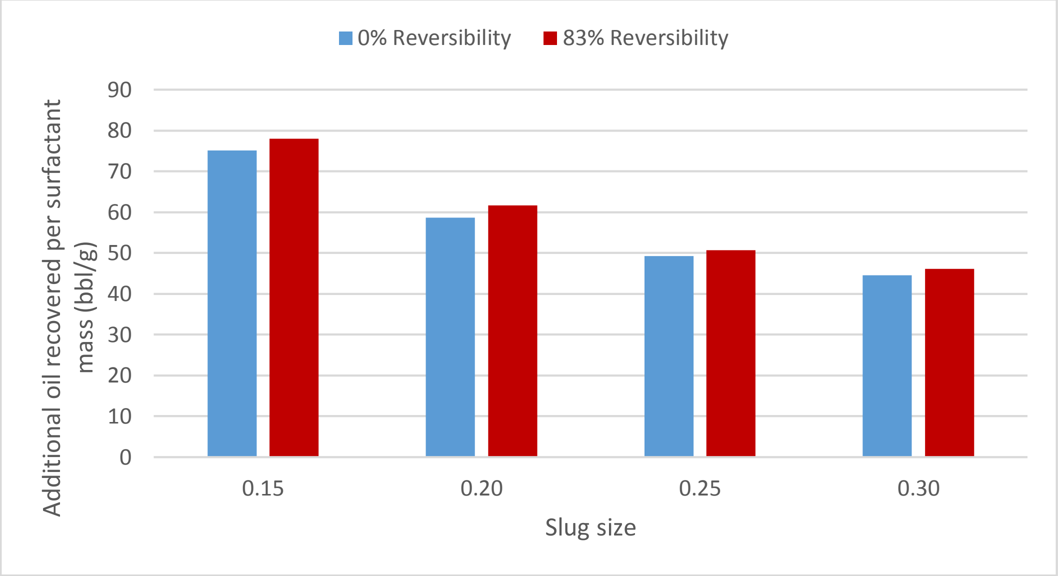


Figure 5.38 Comparison of additional oil recovered per surfactant mass of surfactant consumed on various degrees of reversibility as a function of surfactant injection slug size, 1.0 %wt. case

From the results, in addition to the incremental of oil recovery by increasing surfactant slug size, oil recovery is further increased when effects of reversibility are applied. From Figure 5.39 oil production rate from case with 0% and 83% degree of reversibility are compared. It can be observed that oil production rates mostly overlay throughout the production life but they tend to deviate from each other before the end of detection. With reversibility degree, even desorbed surfactant could be adsorbed onto rock surface again, but this result in more dissipation of mass of surfactant into larger volume of reservoir especially further away from injection well. This causes higher oil production rate at late production time.

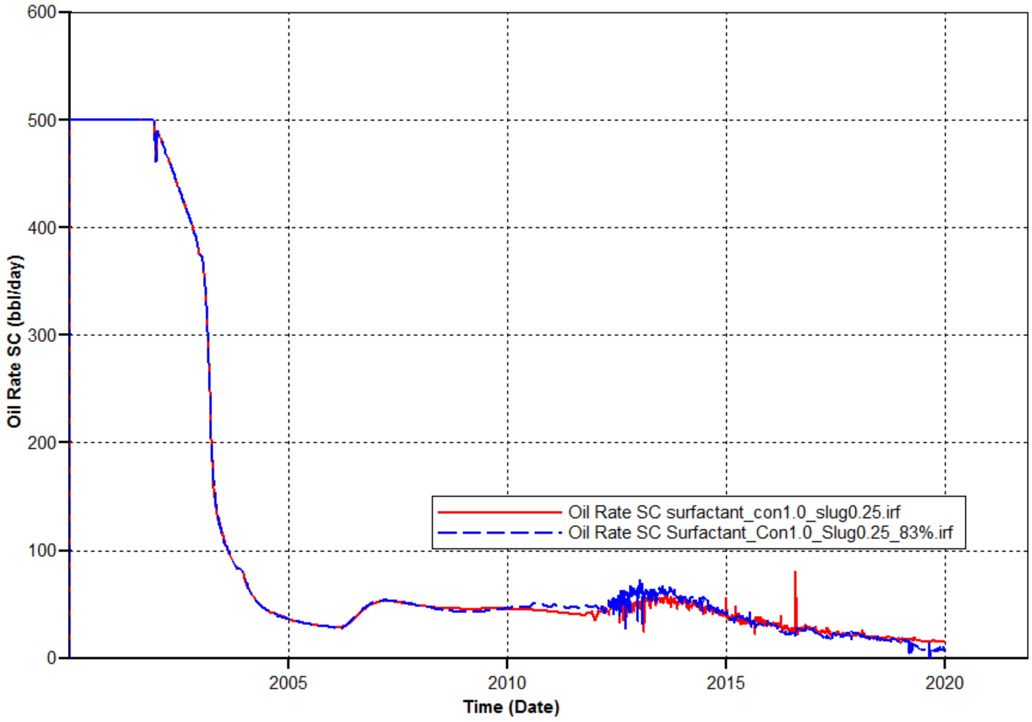
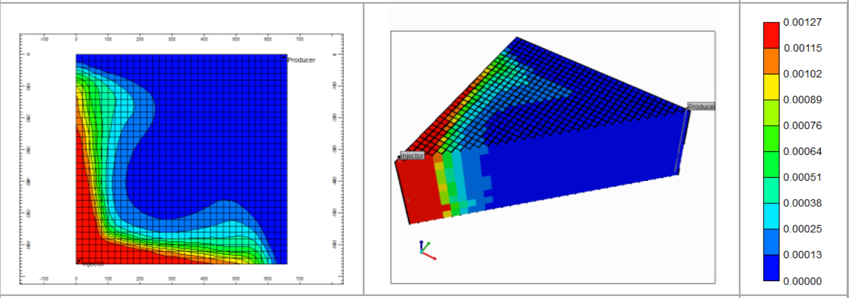


Figure 5.39 Comparison of oil and water production rate from various degrees of reversibility with 0.25 PV as a function time

The explanation of effects of degrees of reversibility on injection slug size is described from Figure 5.40 to Figure 5.42. As explained in section 5.5, effects of increasing surfactant injected pore volume is aimed to improve oil recovery from larger area of reservoir. The observation of reversible adsorbed surfactant concentration in Figure 5.40 points out that when adsorption is reversible, the previously adsorbed surfactant is detached back to solution when chasing water is flooded through reservoir. This favors detached surfactant solution to travel further into un-flooded region, thus the areal sweep efficiency is further increased. This leads trapped oil to be pushed out and accumulated in oil bank, which can increase oil production rate as shown from Figure 5.39. As sweep efficiency is enlarged by the effects of reversibility, local capillary number of each case is increased further due to lowering IFT in liquid phases corresponding to reversibility of surfactant adsorption as dedicated in larger green and red percentage in Figure 5.41. Therefore, lower oil saturation area which is in dark green color is observed as illustrated in Figure 5.42.

(a) 0% Reversibility

Scale



(b) 83% Reversibility

Scale

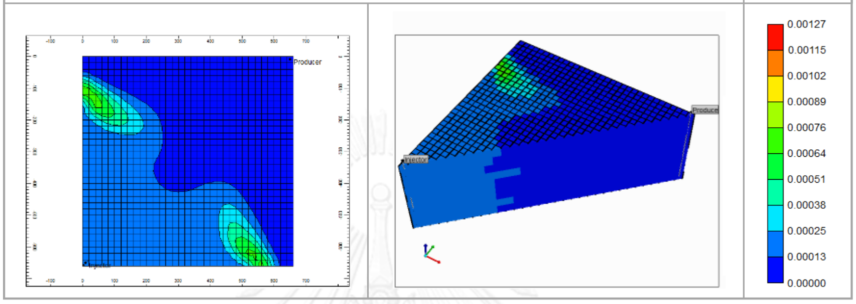
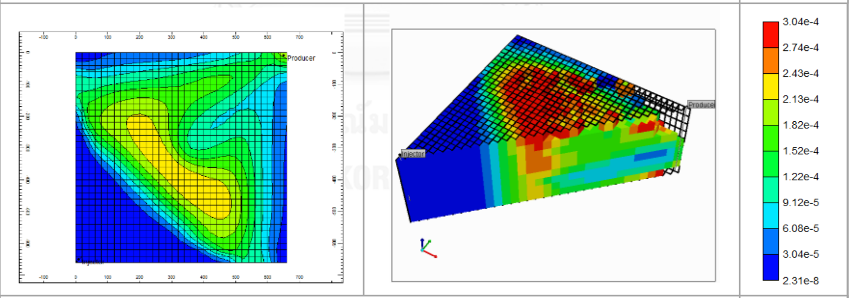


Figure 5.40 Surfactant adsorption profile in areal and 3D views for 0.25 PV case

(a) 0% Reversibility

Scale



(b) 83% Reversibility

Scale

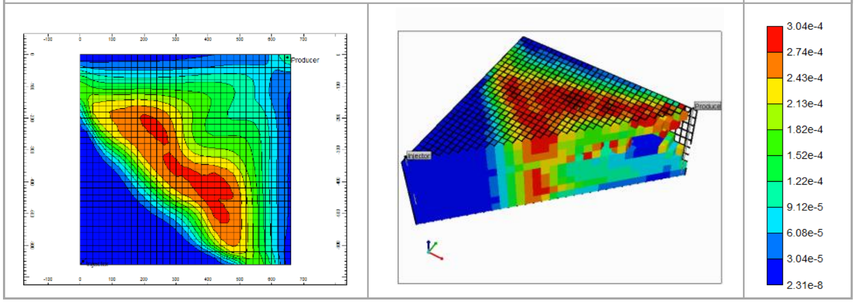


Figure 5.41 Local capillary number profile in areal and 3D views for 0.25 PV case

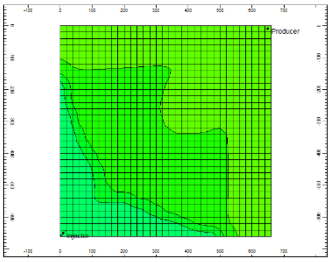
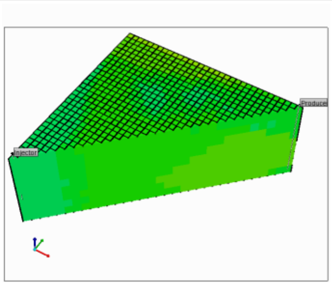
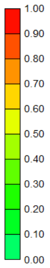
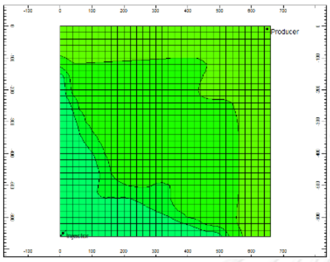
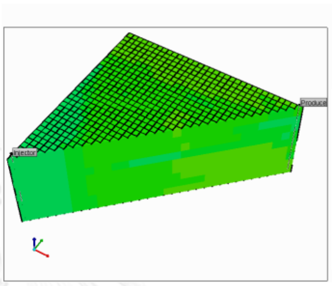
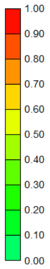
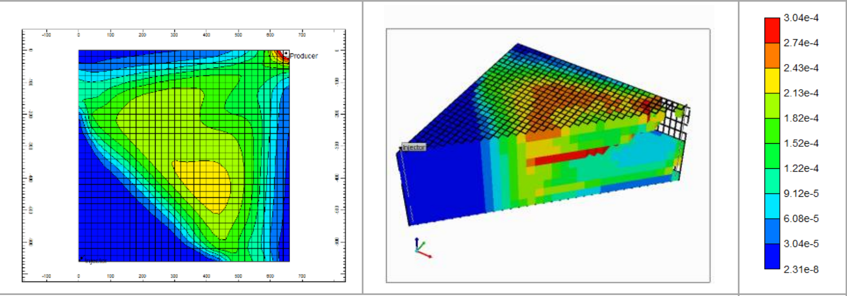
(a) 0% Reversibility		Scale
		
(b) 83% Reversibility		Scale
		

Figure 5.42 Oil saturation profile in areal and 3D views for 0.25 PV case

When changing the slug size of surfactant slug, injected mass of surfactant is different however, as concentration of surfactant is the same, degree of reversibility is also the same at certain location. Longer injection of surfactant solution therefore extends the area where desorbed surfactant can go and this results in different local capillary number profiles comparing between cases with different surfactant slug size as illustrated in Figure 5.43.

(a) 0.15 PV

Scale



(b) 0.25 PV

Scale

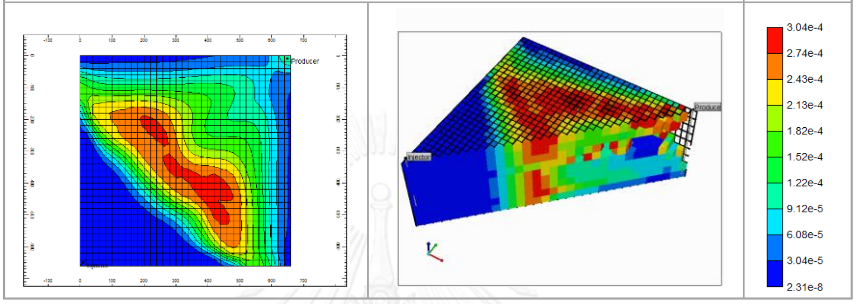


Figure 5.43 Comparison of local capillary number of different slug sizes on 83% reversibility

5.8.2 Effects of Reversibility of Surfactant Adsorption on Surfactant Concentration

In the study of surfactant concentration on surfactant flooding in section 5.6, as surfactant concentration is increased, the amount of surfactant adsorbed on rock surface rises. However, in case of using higher surfactant concentration, the corresponding IFT can be decreased to lower range. However, this higher adsorption is also compensated with higher amount of desorbed surfactant. The oil recovery factor and comparison of oil recovery factor and additional oil recovered per surfactant mass are demonstrated in Figure 5.44 and Figure 5.45. From the figure, increasing of oil recovery comes with higher amount of surfactant in the system.

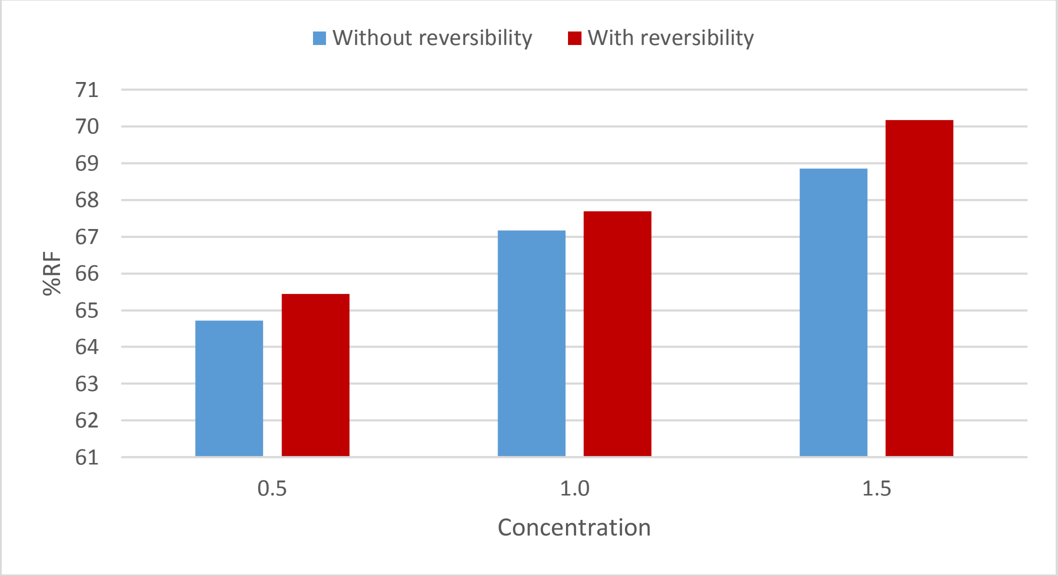


Figure 5.44 Comparison of oil recovery factor on various degrees of reversibility as a function of surfactant concentration, 0.25 PV case

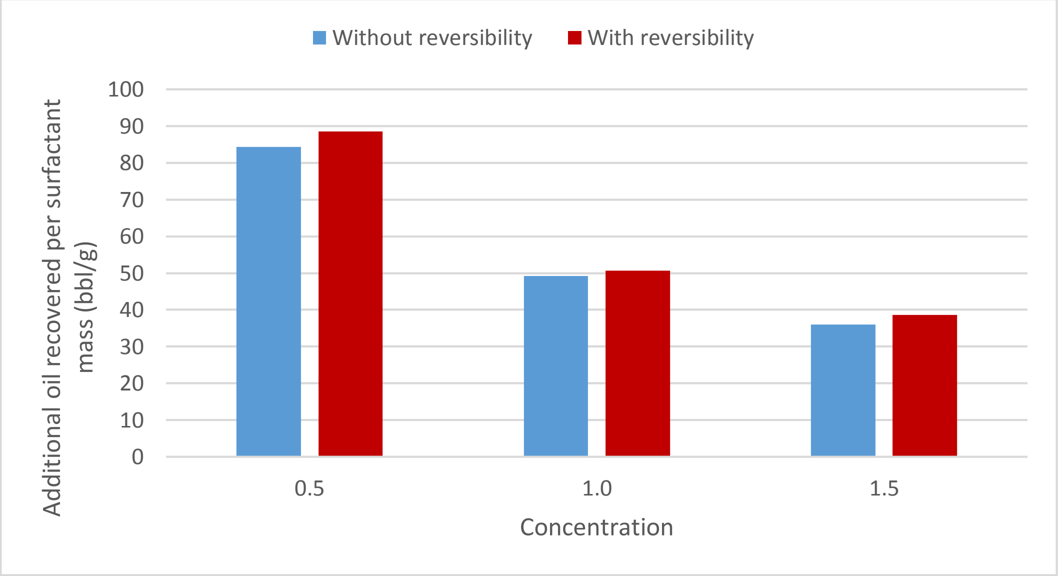


Figure 5.45 Comparison of additional oil recovered per mass of surfactant consumed on various degrees of reversibility as a function of surfactant concentration, 0.25 PV case

When concentration of surfactant is varied while slug size is maintained constant, oil production rates observed are mostly the same as for cases of changing slug size. Higher concentration which also comes with high adsorption and at the same time higher effects of degree of surfactant adsorption reversibility on surfactant concentration are demonstrated from Figure 5.40 to Figure 5.42. Referring to Figure 5.40, the areal and 3D profiles of surfactant adsorption reveal that, taking account of reversible behavior of surfactant adsorption tends to push surfactant concentration further into the reservoir while adsorption is reversible. However, due to the adsorption of surfactant onto rock surface increases when rise in surfactant concentration in the system; the more surfactant desorbs from rock surface, the more it is adsorbed back onto untouched rock surface, yet the more distance it can flood through the reservoir even parts of surfactant concentration still have to be consumed by reservoir rock surface. Therefore, incremental of oil production rate is observed because of more trapped oil is recovered and accumulated in oil bank. This behaviors of adsorption, desorption, re-adsorption, and re-desorption lead the difference in oil recovery factors is not significant. Nevertheless, if observing in Figure 5.41, the local capillary number shows more favorable condition in reversibility case which is indicated in green colors, this is also an evidence to prove more oil recovery factor observed when there is reversible surfactant adsorption. Therefore, the oil saturation profiles in Figure 5.42 show more dark green and green area on the reversibility case which means more oil has been depleted from reservoir than that of cases without reversibility.

When changing concentration while slug size is maintained, injected mass of surfactant is different however, as slug size is the same, degree of reversibility is different at any location based on surfactant concentration which affects adsorption amount and consecutively amount of desorbed surfactant. Difference in local capillary number profiles comparing between cases with different surfactant concentration is illustrated in Figure 5.46 which reveals difference in oil recovery factor when reversibility of surfactant is taken into account.

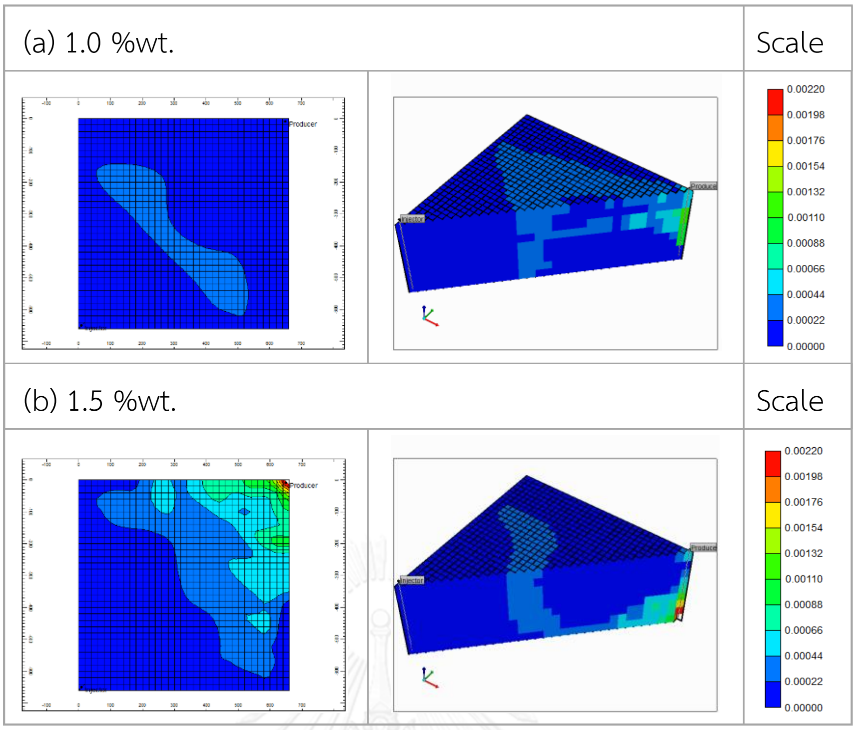


Figure 5.46 Comparison of local capillary number of different concentration on 83% reversibility

5.8.3 Sensitivity Analysis of Reversibility of Surfactant Adsorption on Surfactant Slug Size and Surfactant Concentration

In this section, the study of sensitivity of reversibility of surfactant adsorption on surfactant slug size and surfactant concentration is taken into consideration. The difference between reversibility and no reversible cases are evaluated. In addition, the difference in oil recovery factor of all cases on concentration and slug size is used to observe the most favorable additional oil recovery for operational parameters when considering degree of reversibility. The difference in oil recovery value of all cases on variation of surfactant concentration and surfactant slug size are demonstrated in Table 5.10.

Table 5.10 Comparison of oil additional oil recovery factor for all cases with and without reversibility effects

Parameter	Surfactant Mass (g)	Additional oil recovery
Reversibility	**41%**	
Concentration	**0.5 %wt.**	
Slug 0.15 PV	1256.76	0.648
Slug 0.20 PV	1675.68	0.823
Slug 0.25 PV	2094.60	0.723
Slug 0.30 PV	2513.52	0.924
Reversibility	**83%**	
Concentration	**1.0 %wt.**	
Slug 0.15 PV	2513.52	0.620
Slug 0.20 PV	3351.37	0.821
Slug 0.25 PV	4189.21	0.514
Slug 0.30 PV	5027.05	0.625
Reversibility	**83%**	
Concentration	**1.5 %wt.**	
Slug 0.15 PV	3770.29	1.088
Slug 0.20 PV	5027.05	1.054
Slug 0.25 PV	6283.81	1.335
Slug 0.30 PV	7540.57	1.532

Observing from Table 5.10, at 1.0 %wt. concentration which is the maximum adsorption concentration, the benefits by effects of reversibility of surfactant adsorption result in the least oil recovery improvement for all cases of surfactant injection slug size. The case of performing surfactant flooding at maximum adsorption concentration, the corresponding degree of reversibility is high (83%) after chasing with water. As higher amount of surfactant is desorbed back into flood front, this leads to more severe impact of the higher re-adsorption behavior onto rock surface. In return, surfactant left from re-adsorption is not adequate in lowering IFT. Comparing to the case with 1.5 %wt., as the ability of reversible surfactant is the same as which of 1.0 %wt., so the relatively higher amount desorbed surfactant is able to cope with re-adsorption of surfactant. In addition, with 0.5 %wt. case, the lower degree (41%) of reversibility, making it less amount of desorbed surfactant. As surfactant adsorption is a function of surfactant concentration, so the relatively less concentration of surfactant, making the re-adsorption behavior is less significant than that of 1.0 %wt. concentration. Therefore, as Figure 5.47 points out, local capillary number of 0.25 PV slug size with different concentrations are plotted to evaluate the effects of reversibility. The average local capillary number between with and without reversibility case are, 0.000214 and 0.000238, 0.000272 and 0.000285, 0.000264 and 0.000704, corresponding to 0.5, 1.0, and1.5 %wt. case respectively. Therefore, the difference in average capillary number is 0.000024, 0.000013, and 0.00044, this makes the oil recovery improvement for 1.0 %wt. results in less benefit comparing to other concentrations.

At 0.5 %wt. and 1.5 %wt. or concentration other than maximum adsorption concentration, larger injection slug size (0.30 PV) gives the most favorable improvement of oil recovery. Because when larger slug size of surfactant solution used in the operation, there are several benefits gaining from the process such as more contacted area between injectant and reservoir fluids, higher ability to cope with re-adsorption relationship between surfactant and rock surface. Therefore, there is excess surfactant solution to help to reduce IFT. However, in order to gain benefits from effects of reversibility of surfactant adsorption in case of performing surfactant flooding at maximum adsorption concentration (1.0 %wt.), injected slug size is needed to measure carefully to obtain better oil recovery improvement. Because at maximum adsorption concentration, re-adsorption behavior is severe throughout the reservoir, so the accumulation of desorbed surfactant will result in more surfactant consumes again onto rock surface.

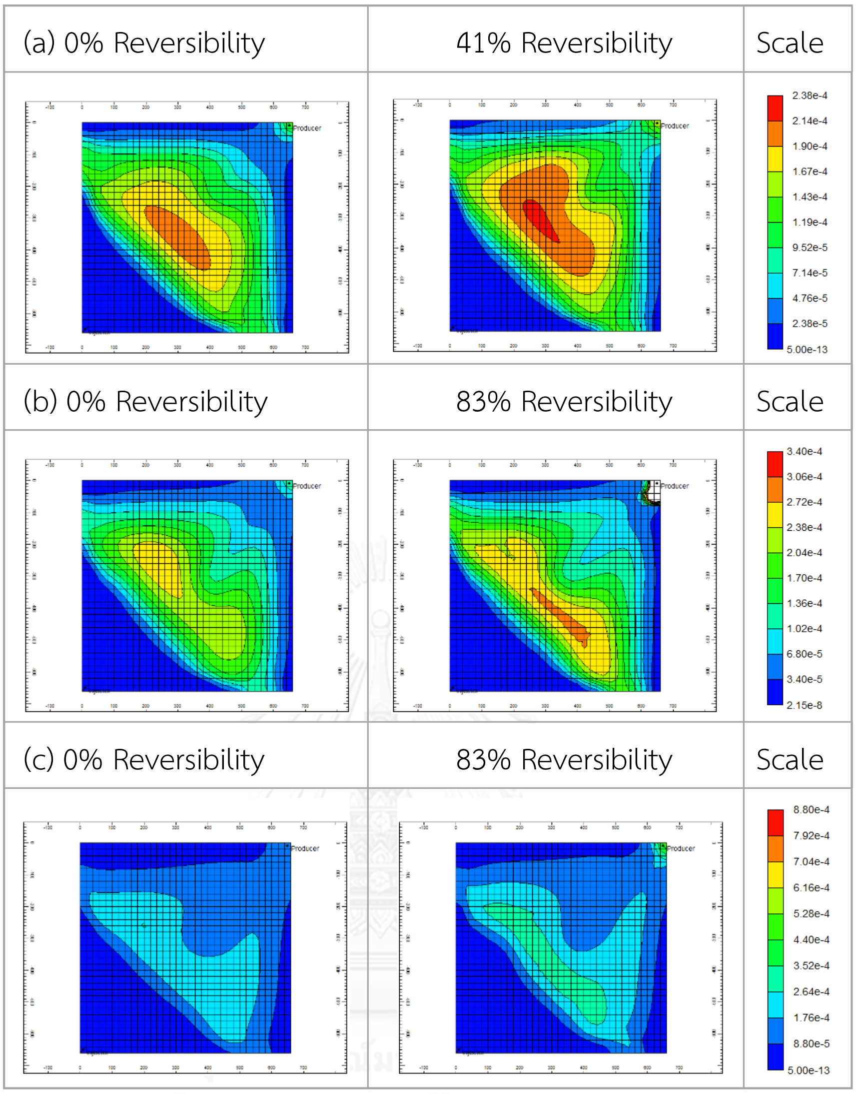


Figure 5.47 Local capillary number of different concentrations with and without reversibility effects (a) 0.5 %wt. (b) 1.0 %wt. (c) 1.5 %wt.

In terms of surfactant mass consumed in this study, there are two groups can be categorized which are mass of 2513.52 in light blue and mass of 5027.05 (which is two times of the previous case) in light orange as dedicated in Table 5.10. For low surfactant mass group, larger slug of injection and less concentration is more favorable in term of oil recovery improvement when concerning with the effects of reversibility. As relationship between surfactant concentration and surfactant adsorption points out, the higher concentration, higher adsorption will take place prior to CMC. In flooding surfactant solution with lower concentration, there is less adsorption occurring; after that, chasing water brings back desorbed surfactant in smaller amount, making it less significant in re-adsorption of surfactant onto rock surface. Furthermore, with low mass of surfactant available, preparing injectant with low concentration together with larger slug size also provides another benefit in terms of dilution prevention, hence larger regions of reservoir is possible to be in contact. Therefore, better improvement of oil recovery is observed because of less adsorption for both original surfactant and detached surfactant in the system, and larger contacted areas of surfactant to reservoir fluids leads to lower IFT of the reservoir in bigger region. However, with the same mass of surfactant, flooding surfactant solution with smaller slug size at maximum adsorption concentration (1.0 %wt.), there will be very significant adsorption due to higher concentration. After chasing with water, the higher reversible surfactant will then re-adsorb again onto rock surface in higher rate, making it less available amount of surfactant to interact with reservoir fluids. At later stage of water chasing, when re-adsorption behavior is not severe, but dilution effects causing from injected water results in difficulty to bring IFT of oil and water phases to achieve ultra-low condition. Therefore, in terms of gaining benefits form effects of reversibility where low surfactant mass is available, larger slug size and lower concentration of surfactant solution should be performed in order to cope with high adsorption and re-adsorption as well as dilution at later stage of operation.

For high mass group, surfactant solution is categorized into two cases, higher concentration with smaller slug, and maximum adsorption concentration with larger slug. Better improvement of oil recovery from effects of reversibility is determined in the case of higher concentration (1.5 %wt.) case. In injecting surfactant solution with higher concentration, there is more available surfactant to withstand with high adsorption of rock surface comparing to perform surfactant flooding at maximum adsorption concentration. After that, while chasing flooding front with water, the desorbed surfactant and excess surfactant concentration in solution can help to maintain IFT in more favorable condition as the ability of adsorption reversibility is the same for both 1.0 %wt. and 1.5 %wt. Nevertheless, to perform surfactant flooding with 1.0 %wt. which is the maximum adsorption concentration, the severe adsorption and re-adsorption behaviors lead to insufficient surfactant to maintain IFT to be at ultra-low condition. Therefore, in case of high surfactant mass, surfactant solution should be controlled in higher than maximum adsorption concentration with sacrificing benefits from larger injection slug size in order to obtain benefits from effects of surfactant adsorption reversibility.

To conclude, better improvement of oil recovery from surfactant adsorption reversibility should be performed at concentrations other than maximum adsorption concentration, then additional improvement could be obtained from incremental of larger surfactant slug size. Besides, with fix amount of surfactant mass available, in case of small mass, concentration should be controlled at lower than maximum adsorption concentration and bigger slug size. On the other hand, when higher surfactant mass is available, concentration should be raised up above maximum adsorption concentration with sacrifice of more contacted areas.

5.8.4 Effects of Reversibility of Surfactant Adsorption on Surfactant Adsorption Value

In section 5.7, the study of the effects of surfactant adsorption on surfactant flooding shows that as adsorption value increases, oil recovery factor decreases because of high surfactant concentration is consumed by rock surface. Hence, less surfactant concentration is able to interact with reservoir fluids to lower IFT in liquid phases. However, in this section, the study focuses on the reversible behavior of surfactant adsorption between low and high adsorption values applied, which are 57.65 mg/100g of rock and 90 mg/100g of rock, respectively. Oil recovery factor and additional oil produced per surfactant mass are used to evaluate the effects of degree of reversibility when surfactant adsorption value increases. Plots of comparison of oil recovery factor and additional oil produced per surfactant mass between surfactant adsorption values with effects of degree of reversibility is illustrated in Figure 5.48 and Figure 5.49. Oil recovery factor generated from CMG program is demonstrated in Figure 5.50.

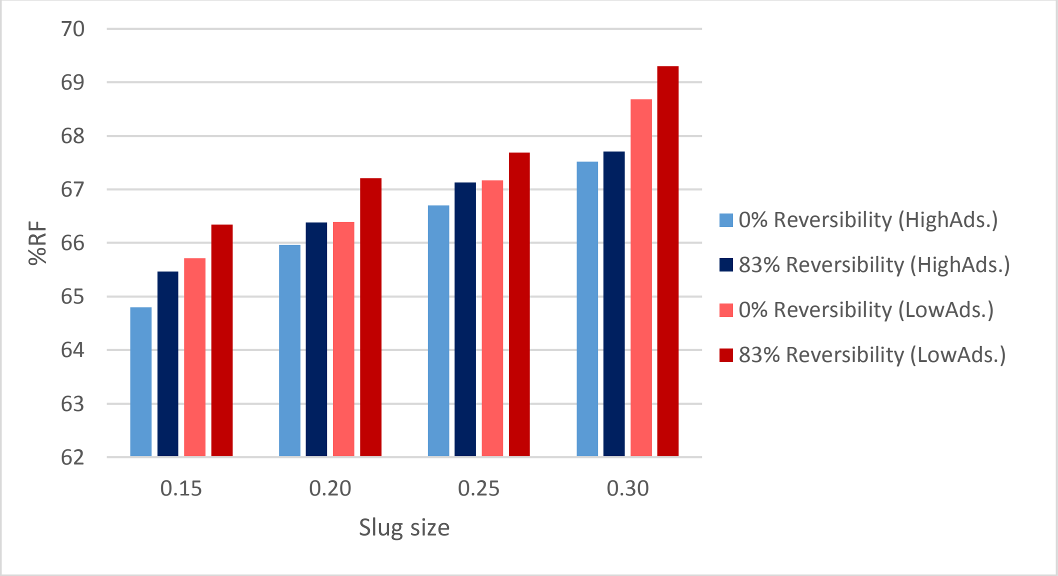


Figure 5.48 Comparison of oil recovery factor as a function of slug size used between high and low adsorption values

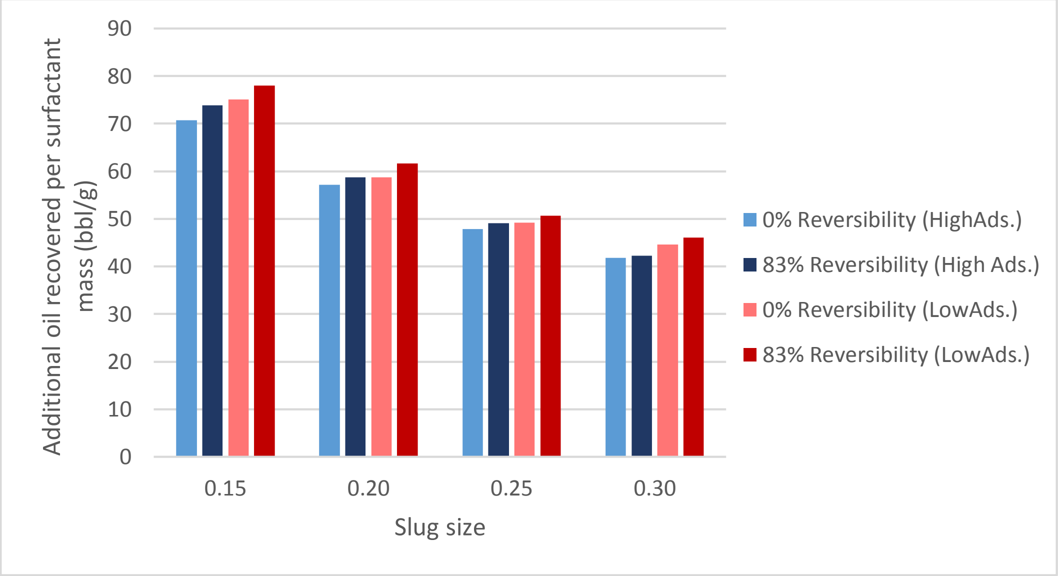


Figure 5.49 Comparison of additional oil recovered per surfactant mass as a function of slug size used between high and low adsorption values

As the comparison of oil recovery factor of various cases suggests, higher oil recovery factor is obtained in all surfactant slug sizes used for lower surfactant adsorption value cases. Therefore, the explanation of effects of reversible adsorption behaviors on different adsorption values can be made on any slug size. In this section, slug size of 0.20 PV will be used as reference with 83% reversibility to describe these mechanisms. In addition, the incremental of oil production rate is observed in certain periods because of the previously adsorbed surfactant concentration desorbs into the system to improve trapped oil to accumulate in oil bank in cases of increase in degree of reversibility as shown Figure 5.51.

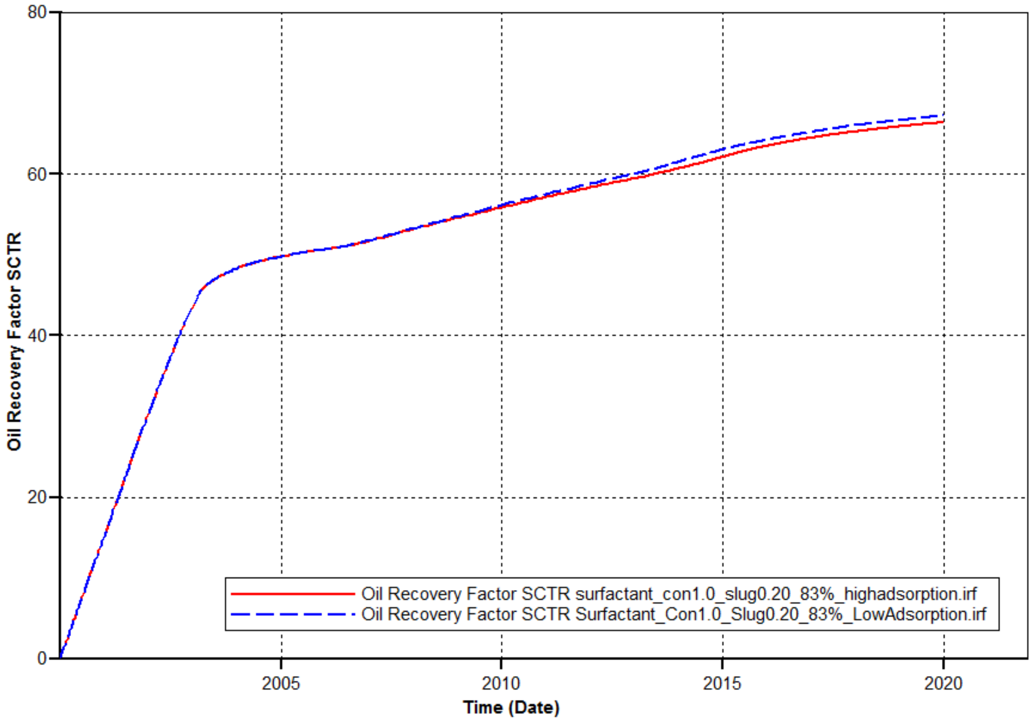


Figure 5.50 Comparison of oil recover factor of 83% degrees of reversibility between high and low adsorption cases as a function of time

Mechanisms behind the effects of reversibility of surfactant adsorption on different adsorption values are described from Figure 5.52 to Figure 5.54. From the adsorption profiles in areal and 3D views in Figure 5.52 for 83% respectively, with different adsorption values and the same degree of reversibility, the higher adsorption of rock surface consumes higher amount of surfactant from the solution. After chasing with water, even relatively the same ratio of surfactant concentration desorbs back into the system for both cases, but the higher adsorption behavior of higher surfactant adsorption case causes surfactant solution to deplete in shorter distance comparing to the case of lower surfactant adsorption. This gives a basic idea that even reversibility of surfactant adsorption is applicable to both high and low adsorption value cases, the ability of recovery of trapped oil is more favorable in lower surfactant adsorption cases. The confirmation of this behavior can be proved by local capillary number in various degrees of reversibility cases shown in Figure 5.53, there are relatively more green to red color regions in lower adsorption value; this indicates that local capillary number in more regions of reservoir is increased which is more favorable condition to push trapped oil out from porous media. Therefore, the corresponding oil saturation profiles of lower adsorption value with the same degree of reversibility reveal larger area of green and dark green color regions which means lower trapped oil remained inside the reservoir as dedicated in Figure 5.54.

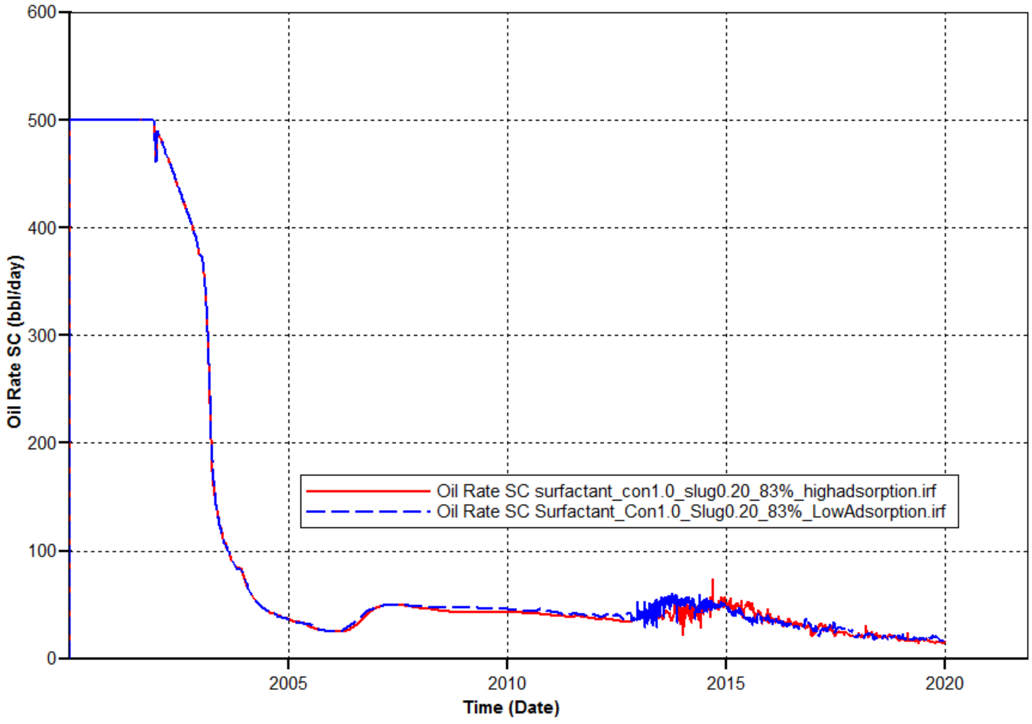


Figure 5.51 Comparison of oil and water production rate from 83% degrees of reversibility between high and low adsorption values as a function time

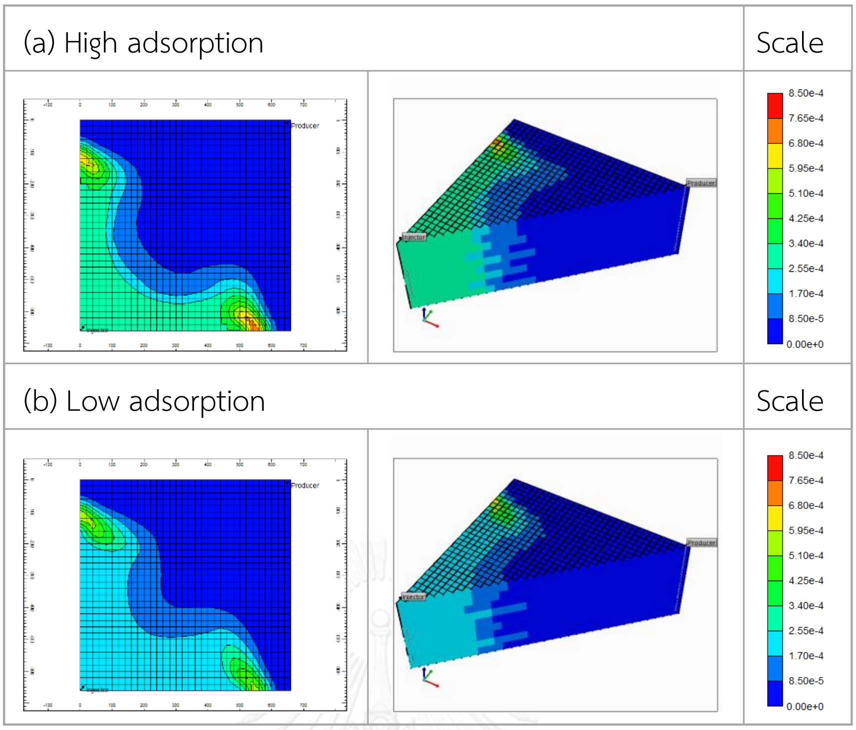


Figure 5.52 Surfactant adsorption profiles in areal and 3D views for 83% degree of reversibility

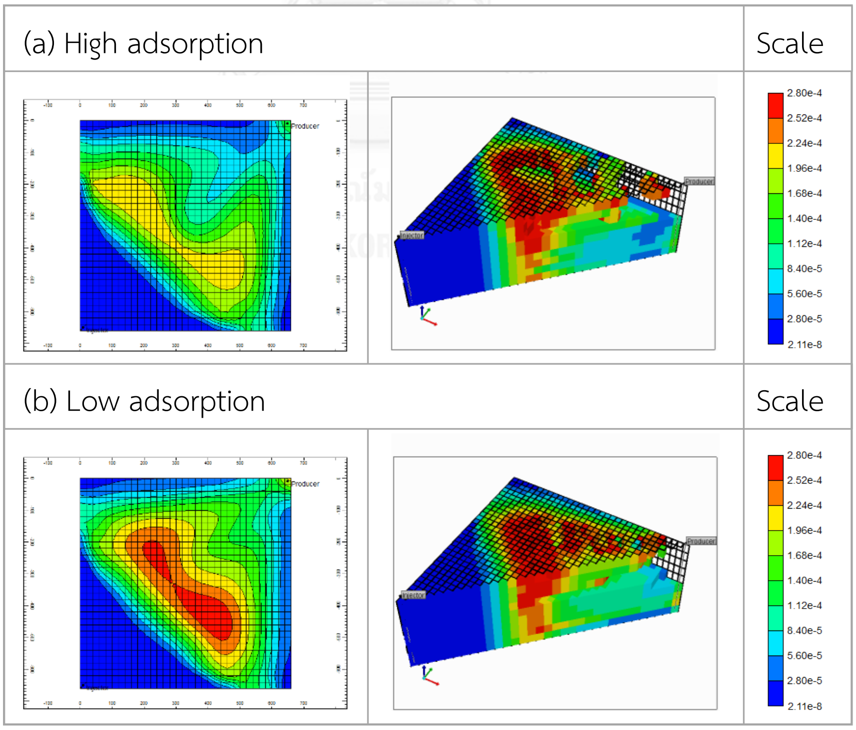
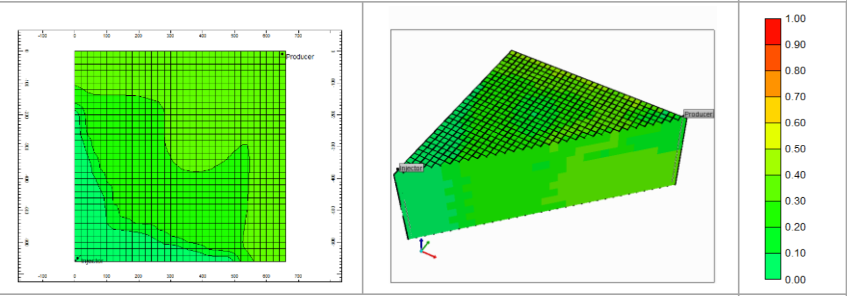


Figure 5.53 Local capillary number profiles in areal and 3D views for 83% degree of reversibility

(a) High adsorption

Scale



(b) Low adsorption

Scale

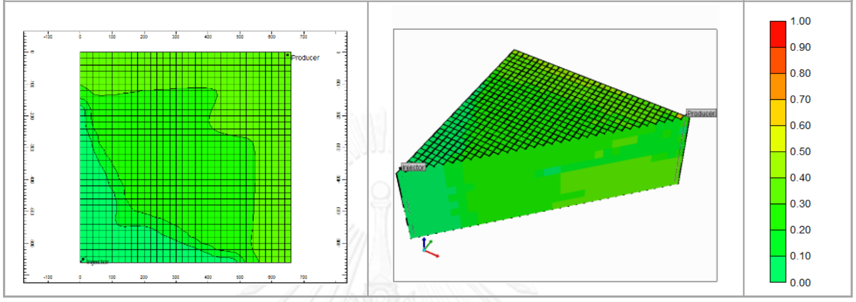


Figure 5.54 Oil saturation profiles in areal and 3D views for 83% degree of reversibility

5.8.5 Sensitivity Analysis of Effects of Reversibility on Surfactant Adsorption

In this section, the effects of reversibility are studied on different maximum adsorption values in various slug sizes. The summary of percent difference and its average value is demonstrated in Table 5.11.

Table 5.11 Comparison of additional oil recovery of different adsorption degree under effects of adsorption reversibility

Parameter	Additional oil recovery	
Reversibility	83%	
Concentration1.0 %wt.	Low Adsorption	High Adsorption
Slug 0.15 PV	0.620	0.669
Slug 0.20 PV	0.821	0.427
Slug 0.25 PV	0.514	0.432
Slug 0.30 PV	0.625	0.187

In performing surfactant flooding with the same concentration and degree of adsorption reversibility, the difference in adsorption magnitude takes effects of improvement of oil recovery in different behavior in terms of surfactant injection slug size. Referring to Table 5.11, with smaller slug of surfactant injection (0.15 PV), higher adsorption of rock surface is able to recover more residual oil from the effects of reversibility. Injection of surfactant solution in smaller slug size, making it is difficult to withstand with dilution causing by chasing water. For low adsorption case, as relatively less amount of surfactant that is previously attached to rock surface, so the amount of desorbed surfactant from chasing water is less and is inadequate to cope with dilution effect; this effect is therefore resulted in less capable to lower IFT to favorable condition. However, the case of strong surface adsorption, from the beginning of surfactant flooding, the adsorption of surfactant concentration is relatively higher than low adsorption case. After that, as the reversible behavior is the same after chasing with water; therefore, the desorbed surfactant is higher to withstand with dilution, and dilution also turns desorbed surfactant to be less re-adsorbed again to un-touched rock surface. As a result, the desorption of surfactant in higher adsorption case in performing smaller slug size is able to further improve more residual oil by the effects of reversibility due to better ability of detached surfactant to lower IFT between water and oil phases.

When increasing surfactant to larger slug size, the additional oil recovery from the effects of surfactant adsorption reversibility is more favorable for low adsorption behaviors of reservoir rock surface. In flooding surfactant with bigger slug size, the dilution effect causing by chasing water is minimal, because there is more surfactant mass in the system due to longer time of surfactant injection. As the dilution effect is not severe in larger surfactant slug size cases, the relatively higher desorbed amount of surfactant from previously adsorbed concentration of high adsorption case, making it higher re-adsorption at the same time. The relationship between surfactant concentration and surfactant adsorption points out, higher concentration, and higher adsorption will take place. Therefore, when dilution is minimal, the re-adsorption is very significant. On the other hand, with the case of low adsorption, even the same ratio of surfactant is desorbed, but there is less adsorption behavior of rock surface in nature. Therefore, it leads to gain more benefits from reversible surfactant by chasing water compared to higher adsorption case as there is more surfactant available to bring IFT to more favorable condition prior to rock surface consumption.

To conclude, in order to gain more benefits from effect of reversibility when adsorption of rock surface is varied, amount of surfactant injection should be carefully measured. For low adsorption behavior of reservoir rock surface, injectant should be controlled at larger slug in order to withstand with dilution by chasing water, hence adequate amount of surfactant is able to reduce IFT to ultra-low condition. On the contrary, as reservoir rock surface is strongly attached by surfactant, surfactant injection slug size which can better improve residual oil should be smaller. The dilution by water chasing is then turning desorbed surfactant to be less adsorbed onto rock surfactant, but at the range which can lower IFT.

CHAPTER 6

CONCLUSION AND RECOMMENDATION

This chapter presents the summaries of the study including the effects of interested operational parameters on surfactant flooding and the effects of reversibility of surfactant adsorption on surfactant flooding techniques. Parts of the results can be used as consideration for implementation of surfactant flooding in case that reversibility of surfactant adsorption is applicable with reservoir rock. In addition, recommendations are also provided for further study.

6.1 Conclusion

From results and discussion in Chapter 5, some summaries of the study can be concluded as:

1. The static adsorption-desorption experiments suggest that concentration of surfactant in solution affects the adsorption and desorption behaviors of the test. Adsorption behaviors between surfactant and rock surface follows Langmuir adsorption isotherm which is divided into four regions with different slopes, while desorption increases linearly when concentration increases. There is an incremental of adsorption and desorption of surfactant concentration onto and from reservoir rock surface. The maximum adsorption and desorption value in static test are 90 mg/100g and 27 mg/100g respectively.
2. The dynamic adsorption-desorption experiments confirm that surfactant adsorption increases when high concentration of chemical used in flooding solution. At the same time, surfactant molecules that can be desorbed from rock surface increase while higher concentration of surfactant used which is caused from more adsorption in previous step. However, degree of reversibility depends on the strength of attachment between rock surface and adsorbed surfactant monomers of different regions of Langmuir adsorption isotherm. By

performing 0.2 %wt., 0.5 %wt. 1.0 %wt. of concentration, adsorption value is found to be at 4.2 mg/100g, 35.81 mg/100g, and 57.65 mg/100g respectively.

3. Study of operational parameters of surfactant injection slug size, surfactant concentration, and surfactant adsorption values reveals similar trend of additional oil recovery. Gains in additional oil recovery is found when increasing in injectant slug size and concentration prior to CMC, because large slug size provides more contact areas between surfactant solution and reservoir fluids, and higher surfactant concentration is aimed to reduce oil saturation by IFT reduction and thus, increase capillary number. However, in case of injection of adsorption value, with low adsorption value, less surfactant is consumed onto rock surface, which results in high surfactant concentration that is more favorable to form oil bank due to lower IFT and higher capillary number. On the other hand, when considering on oil recovered per fixed mass of surfactant, smaller slug size and concentration yield better results. However, this does not indicate that small slug size and low concentration should be implemented in surfactant flooding, economic viability should be evaluated to investigate the best slug size and concentration.
4. Effects of reversibility of surfactant adsorption on injection slug size shows that flooding surfactant solution other than maximum adsorption concentration, more benefits are obtained from larger slug size (0.30 PV). Nevertheless, if implementation of surfactant flooding is at maximum adsorption concentration, injection slug size must be measured carefully to gain benefits from desorbed surfactant.
5. Accounting for effects of reversibility on surfactant concentration reveals that better improvement of oil recovery is determined at concentration differed from maximum adsorption concentration. At maximum adsorption concentration, the reversibility is higher, but the re-adsorption of desorbed surfactant leads to less amount of surfactant to interact with reservoir fluids. In terms of surfactant mass, lower amount of surfactant than maximum adsorption concentration and larger slug size is preferred, because of less severe of adsorption and re-adsorption behavior as well as toleration to

dilution from chasing water. However, in case of high surfactant mass, increasing concentration to be above maximum adsorption concentration but sacrifice benefits from larger slug gains more improvement because excess amount of surfactant from rock consumption can maintain IFT to more favorable condition.

6. The effect of reversibility of surfactant adsorption on surfactant adsorption shows more additional oil recovery in lower adsorption values case. When taking account effects of surfactant adsorption on effects of reversibility, better additional oil recovery is found in higher adsorption value when injection slug size is small (0.15 PV) due to more capability to withstand with dilution effect. On the contrary, the cases of larger slug size, more favorable of additional oil recovery is determined at low adsorption value case, this is because dilution effect is minimal, and so the less adsorption of rock surface case is more favorable.
7. Sensitivity of reversibility effects on improvement of oil recovery is more significant on variation in surfactant concentration than injection slug size. The most favorable condition to obtain benefits from reversibility, surfactant flooding should be performed with concentration other than maximum adsorption concentration, together with larger injection slug size (0.30 PV). Moreover, in case of adsorption of reservoir rock is high, smaller injection slug size yields better benefit. However, with less severe adsorption behavior reservoir rock, larger slug of surfactant solution is more favorable.

6.2 Recommendation

The recommendation provided in following parts are for future surfactant flooding technique in both laboratory experiments and simulation.

1. Laboratory experiments of IFT reduction in oil and aqueous phases by using interested surfactant in the study should be performed. As IFT is one of the most important parameters to achieve in surfactant flooding; therefore, laboratory test results of IFT provide more reliable values for reservoir simulation to generate more accurate findings, and hence reduce the degree of uncertainty in the study.
2. Clay content and divalent ions effects should be taken into consideration in reservoir simulation model in surfactant flooding. The presence of clay and divalent ions yields drawback on effectiveness of chemical flooding which obviously affects surfactant flooding.

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APPENDIX

APPENDIX A
LABORATORY EXPERIMENTS

The determination of surfactant concentration in surfactant solution is relied on two-phase titration technique by using various chemicals. The important chemicals and test procedures will be provided in follow section.

1. Equipment and chemicals

Titrant: Hyamine 1622, standard 0.004 M solution.

Standard Anionic Surfactant: Sodium Dodecyl Benzene Sulfonate

Reagents:

- Chloroform
- Methylene Blue powder and solution
- Sulfuric acid
- Phenolphthalein indicator solution
- Anhydrous sodium sulfate
- Sodium Hydroxide solution

Equipment:

- 30 ml burette
- 500-1000 ml beakers
- Glass stirrer
- 500-1000 ml volumetric flask
- Pipettes
- 100 ml graduated cylinder

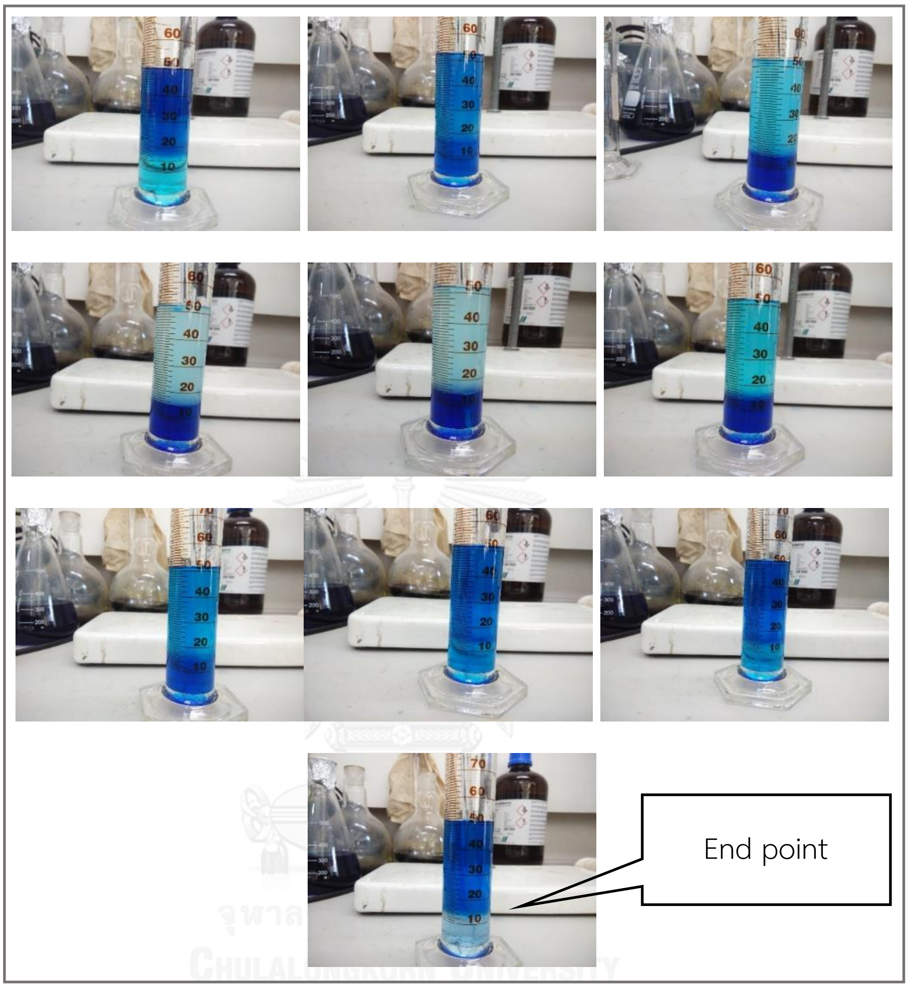
Preparation of Methylene Blue solution: dissolve 30 mg of methylene blue and 50 g of anhydrous sodium sulfate in 500 ml of distill water. The mixture is then transferred to 1000 ml volumetric flask. Slowly add 6.5 ml of sulfuric acid and dilute to 1000 ml with distill water.

Preparation of standardize Surfactant solution: accurately weigh surfactant solution sample into a beaker according to surfactant concentration used in solution. Dilute solution sample to 150 ml with distill water, add 2-3 drops of phenolphthalein solution, and then add drop of NaOH solution drop wisely until pink color is achieved.

Two-phase titration procedures:

- Transfer standardize surfactant solution to 500 ml volumetric flask and dilute to that volume with distill water.
- Pipette 10 ml of the solution to a 100 ml graduated cylinder
- Add 25 ml of methylene blue solution
- Finish with 15 ml of chloroform
- Titrate against with hyamine solution by adding drop by drop
- Stir the solution vigorously during titration
- The end point of two phase titration is reached when two layers have equal color intensity.

Graphical indication of titration method:



APPENDIX B
RESERVOIR MODEL CONSTRUCTION BY CMG SIMULATOR

In this study, CMG Builder program is utilized with specific selection of STARS simulator. There are six sections are required for input of reservoir specification including reservoir properties, pressure-volume-temperature (PVT) properties, rock-fluid properties, and well & recurrent.

Simulator Setting

Parameter	**Value**
Simulator	STARS
Working Units	Field
Porosity	Single porosity
Simulation start date	2000/01/01

1. Reservoir

1.1 Create Cartesian Grid

The reservoir is modeled by selecting “Create Cartesian Grid” wizard. The information input for creating grid is dedicated bellow.

Parameter	**Value**
Grid Type	Cartesian
K Direction	Down
Number of Grid Blocks	33, 33, 9 (I, J, K, direction respectively)
Block widths (I direction)	33×20
Block widths (J direction)	33×20

1.2 Array Properties

Parameter	Whole grid
Grid Top (ft) at Layer 1	2,600
Thickness (ft)	12
Porosity	0.2
Permeability I (mD)	100
Permeability J (mD)	100
Permeability k (mD)	10
Water Mole Fraction	1

2. Component

2.1 PVT Using correlation

Parameter	Option	Value
Reservoir temperature (^{o}F)		118
Generate data up to max. pressure of		5,000 psi
Bubble point pressure calculation	Generate from GOR value	250
Oil density af STC (14.7 psia 60^{o}F)	Stock tank oil gravity (API)	30
Gas density af STC (14.7 psia 60^{o}F)	Gas gravity (Air = 1)	0.7
Oil properties (Bubble point, Rs, Bo) correlation	Standing*	
Oil compressibility correlation	Glaso*	
Dead oil viscosity correlation	Ng and Egbogah*	
Live oil viscosity correlation	Beggs and Robinson*	
Gas critical properties correlation	Standing*	
Set/Update Value of Reservoir Temperature, Fluid Densities in Dataset		Available

*Refers to default of simulator

2.2 Water Properties Using Correlation

Parameter	**Value**
Reservoir temperature (TRES)	118 °F
Reference pressure (REFPW)	1,225 psi
Water bubble point pressure	
Water salinity	10,000 ppm
Set/Update Value of Reservoir Temperature, Fluid Densities in Dataset	Available

Water bubble point pressure is left to be blank for the default value of water.

3. Rock-fluid

Parameter input in this section is for preliminary data before using Process Wizard for chemical flooding in Appendix C.

3.1 Rock Type Properties

Parameter	**Value**
Rock wettability	Water wet
Method for evaluating 3-phase KRO	Stone's second model

3.2 Relative Permeability Table

Water-oil relative permeability table and liquid-gas table are included in rock-fluid properties.

S_w	K_{rw}	K_{row}
0.2	0	0.7
0.228125	0.000037	0.576782
0.25625	0.000293	0.468945

0.284375	0.0009888	0.375464
0.3125	0.0023438	0.295312
0.340625	0.0045776	0.227466
0.36875	0.0079102	0.170898
0.396875	0.012561	0.124585
0.425	0.01875	0.0875
0.453125	0.0266968	0.058618
0.48125	0.0366211	0.036914
0.509375	0.0487427	0.021362
0.5375	0.0632813	0.010938
0.565625	0.0804565	0.004614
0.59375	0.100488	0.001367
0.621875	0.123596	0.000171
0.65	0.15	0

S_l	K_{rg}	K_{rog}
0.2	0.7	0
0.3	0.455674	0
0.4	0.276059	0
0.434375	0.227466	0.000132
0.46875	0.184938	0.001053
0.503125	0.148072	0.003554
0.5375	0.116463	0.008425
0.571875	0.0897058	0.016454
0.60625	0.0673973	0.028433
0.640625	0.0491326	0.045151
0.675	0.0345074	0.067397
0.709375	0.0231173	0.095962
0.74375	0.0145578	0.131635

0.778125	0.00842466	0.175207
0.8125	0.00431343	0.227466
0.846875	0.00181973	0.289203
0.88125	0.00053918	0.361207
0.915625	0.0000674	0.444269
0.95	0	0.539178
0.975	0	0.616095
1	0	0.7

4. Initialization

Parameter	Value
Vertical Equilibrium Calculation Methods	Depth-Average Capillary-Gravity Method
Reference pressure (REFPW)	1,225 psi
Reference Depth (REFDEPTH)	2,600 ft
Water-Oil Contact Depth (DWOC)	2,708 ft

5. Numerical

Parameter	Value
First Time Step Size after Well Change (DTWELL)	0.001
Isothermal Option (ISOTHERM)	ON
Linear Solver Iteration (ITERMAX)	200

6. Wells and Recurrent

6.1 Injection Well

6.1.1 Perforations

Parameter	Value
Radius (ft)	0.5
Perforation start	1, 33, 1
Perforation end	1, 33, 9

6.1.2 Well Events

ID & Type

Name: INJECTOR

Type: INJECTOR MOBWEIGHT IMPLICIT

Constraint:

Constraint	Parameter	Limit/Mode	Value	Action
OPERATE	STW surface liquid rate	MAX	500 bbl/day	CONT
OPERATE	BHP bottom hole pressure	MIN	1,800 psi	CONT

6.2 Production Well

6.2.1 Perforations

Parameter	Value
Radius (ft)	0.5
Perforation start	33, 1, 1
Perforation end	33, 1, 9

6.2.2 Well Events

ID & Type

Name: INJECTOR

Type: INJECTOR MOBWEIGHT IMPLICIT

Constraint:

Constraint	**Parameter**	**Limit/Mode**	**Value**	**Action**
OPERATE	STL surface liquid rate	MAX	500 bbl/day	CONT
OPERATE	BHP bottom hole pressure	MIN	200 psi	CONT
MONITOR	WCUT water-cut (fraction)		0.95	STOP
MONITOR	STO surface oil rate	MIN	25 bbl/day	STOP

6.3 Dates

Add a range of dates: 360 months (not include the first month).

APPENDIX C
CHEMICAL MODEL CONSTRUCTION BY CMG SIMULATOR

The demonstration of input data below is utilized to construct chemical model of surfactant flooding in Process Wizard in Components.

1. Process Wizard Setting

Parameter	Value
Process	Alkaline, surfactant, foam, and/or polymer model
Model	Surfactant flood (add 1 component)

2. Detail of Surfactant Setting

Parameter	Value
Use reversible partitioning of surfactant into oil	Yes
Use irreversible partitioning of surfactant into oil	No
Number of relative perm. Sets for interpolation	3
Use adsorption for surfactant	Yes
Rock type for conversion of adsorption values (gm rock to PV)	Sandstone
Rock Density, gm/cm3	2.65

3. Interfacial Tension Setting

Surfactant wt. %	IFT
0	20
0.5	0.001
1.0	0.0001

4. Adsorption Setting

Surfactant wt. %	Surfactant adsorption (mg/100g rock)
0	0
0.5	35.81
1.0	57.65

Surfactant adsorption (mg/100g rock)	Degree of reversibility	Maximum adsorption capacity (ADMAXT)	Residual adsorption level (ADRT)
35.81	0%	0.000680004	0.000680004
	41%	0.000680004	0.000401202
57.65	0%	0.00109473	0.00109473
	83%	0.00109473	0.000186104

5. Component and Phase Properties

Chemical	MW (lb/lbmole)
Water	18
Surfactant	348.48

6. Component adsorption

Parameter	Value
Adsorption table dependency Enter/Edit Table Concentration	0
Composition dependence	Independent of temperature

7. Rock-Fluid Interpolation set2

S_w	K_{rw}	K_{row}
0.2	0	0.85
0.228125	0.000037	0.742272
0.239063	0.0001363	0.700378
0.25625	0.000293	0.642762
0.278125	0.0008341	0.569433
0.284375	0.0009888	0.551271
0.3125	0.0023438	0.469542
0.317188	0.0027161	0.45592
0.340625	0.0045776	0.397524
0.35625	0.006429	0.358593
0.36875	0.0079102	0.33223
0.395313	0.0123026	0.276208
0.396875	0.012561	0.273461

0.425	0.01875	0.224004
0.434375	0.0213989	0.207519
0.453125	0.0266968	0.180525
0.473438	0.0338644	0.151282
0.48125	0.0366211	0.142276
0.509375	0.0487426	0.109853
0.5125	0.050358	0.10625
0.5375	0.0632812	0.083805
0.551562	0.0718689	0.071179
0.565625	0.0804566	0.061691
0.590625	0.0982623	0.044824
0.59375	0.100488	0.043314
0.621875	0.123596	0.029717
0.629687	0.13093	0.02594
0.65	0.15	0.019357
0.66875	0.1676026	0.013281
0.707812	0.2042743	0.005603
0.746875	0.240947	0.00166
0.785937	0.2776187	0.000208
0.825	0.3142913	0

S_l	K_{rg}	K_{rog}
0.2	0.7	0
0.242969	0.595016	0
0.281667	0.500466	0
0.285937	0.490032	0.0000166
0.3	0.455674	0.0000712
0.328906	0.403754	0.000325282

0.363975	0.340765	0.00127874
0.377444	0.316573	0.00227267
0.4	0.276059	0.00393719
0.414844	0.255076	0.00571161
0.434375	0.227466	0.00851839
0.457813	0.19847	0.0129611
0.473222	0.180141	0.0166121
0.487439	0.164895	0.0199804
0.506146	0.145294	0.026592
0.528594	0.124653	0.0345261
0.54375	0.111598	0.042002
0.571993	0.0896288	0.0562996
0.586719	0.0800723	0.0659653
0.610903	0.0649254	0.0818396
0.63784	0.0506124	0.104543
0.652057	0.0442686	0.116526
0.675	0.0345074	0.140673
0.703688	0.0250019	0.17331
0.715625	0.021561	0.188657
0.74375	0.0145578	0.227221
0.758594	0.0119094	0.250108
0.778125	0.00842464	0.280952
0.802458	0.00551438	0.325278
0.816676	0.00401053	0.351175
0.846875	0.00181973	0.415335
0.868306	0.00102137	0.464282
0.8875	0.0004534	0.511324
0.901229	0.00026498	0.545756
0.91875	0.0000613	0.59482

0.934153	0.0000311	0.637953
0.95	0	0.685487
0.970069	0	0.748116
1	0	0.85

8. Rock-Fluid Interpolation set3

S_w	K_{rw}	K_{row}
0	0	1
0.999	1	0
1	1	0

S_l	K_{rg}	K_{rog}
0	1	0
0.999	0	1
1	0	1

9. Log Capillary Number for Interpolation set

Interpolation set	Phase	Values
Set 1	Wetting phase	-4
	Non-Wetting phase	-4
Set 2	Wetting phase	-3.5
	Non-Wetting phase	-3.7
Set 3	Wetting phase	-3
	Non-Wetting phase	-3

10. Injected Fluid at INJECTOR

Injected surfactant	**0.5 %wt.**	**1.0 %wt.**	**1.5 %wt.**
Component	Mole fraction	Mole fraction	Mole fraction
Water	0.999741	0.999479	0.999214
Surfactant	0.000259	0.000521	0.000786

VITA

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