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# An experimental study of surfactant enhanced waterflooding

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# **AN EXPERIMENTAL STUDY OF SURFACTANT ENHANCED WATERFLOODING**

A Thesis

Submitted to the Graduate Faculty of the  
Louisiana State University and  
Agricultural and Mechanical College  
in partial fulfillment of the  
requirements for the degree of  
Master of Science in Petroleum Engineering.

in

The Craft and Hawkins Department of Petroleum Engineering

By

Paulina Mwangi  
B.S. & B.A., University of Rochester, 2008  
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This work is dedicated to my dearest parents, Simon and Jane Mwangi, and to my wonderful brother Anthony Mwangi...

# TABLE OF CONTENTS

ACKNOWLEDGEMENTS .....	ii
LIST OF TABLES .....	v
LIST OF FIGURES .....	vi
NOMENCLATURE .....	ix
ABSTRACT .....	x
1. INTRODUCTION .....	1
1. 1    Background .....	1
1. 2    Objective .....	2
1. 3    Methodology .....	4
2. LITERATURE REVIEW .....	5
2. 1    Waterflooding .....	5
2. 2    Surfactant .....	7
2.2.1    Effect of surfactants on interfacial tension .....	9
2.2.2    Surfactant flooding .....	11
2. 3    Wettability .....	15
2.4.1    Effect of surfactants on wettability .....	17
2. 4    Core cleaning .....	18
3. EXPERIMENTAL APPARATUS AND PROCEDURE .....	22
3. 1    Experimental setup .....	22
3. 2    Experimental procedure .....	25
3. 3    Experimental design .....	35
3. 4    Coreflood simulator .....	38
4. RESULTS AND DISCUSSION .....	40
4. 1    Set 1: Ideal surfactant concentration determination .....	41
4.1.1    Reactive rock-fluid system (Yates crude oil) .....	41
4.1.2    Non-reactive rock-fluid system (Decane) .....	48
4. 2    Set 2: Ideal soaking period .....	52
4. 3    Set 3: Effect of varying surfactant slug size on incremental oil recovery .....	57
4. 4    Set 4: Comparison of the four improved waterflood methods with three baseline cases .....	60
4. 5    Economic consideration .....	64
5. CONCLUSIONS AND RECOMMENDATIONS .....	68
5.1 Summary of findings and conclusions .....	68
5.2 Recommendations for future work .....	69
REFERENCES .....	71
APPENDIX .....	74

VITA.....	77
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## LIST OF TABLES

Table 1: Surfactant properties .....	25
Table 2: Cleaning solvent properties .....	29
Table 3: Surfactant selection results .....	35
Table 4: Yates crude oil aging period .....	36
Table 5: Experimental design – 4 sets of experiments.....	37
Table 6: Craig’s rules of thumb used for wettability interpretation, adopted from Ayirala (2002) .....	40
Table 7: Experimental and simulation results for the reactive case at various surfactant concentrations ..	41
Table 8: Experimental and simulation results for the non-reactive case at various surfactant concentrations .....	48
Table 9: Recoveries of non-reactive and reactive system at various surfactant concentrations .....	51
Table 10: Experimental and simulation results for the soaking time experiments .....	52
Table 11: Experimental and simulation results for various surfactant slug sizes .....	57
Table 12: Experimental results for the seven EOR processes.....	61
Table 13: Cost analysis results for the seven IOR methods.....	65

## LIST OF FIGURES

Figure 1: Improved waterflood process: left figure has a surfactant soaked production zone and the right figure has a surfactant soaked injection zone - water alternating surfactant process (WASP) .....	3
Figure 2: Schematic definition of the critical micelle concentration adopted from (Lake, 1989) .....	8
Figure 3: The figure on the left shows when micelles form in water, and the figure on the right shows when micelles form in oil .....	8
Figure 4: Schematic representation of the: Type II (-) system (left), Type II (+) system (middle), and Type III system (right) (Lake, 1989).....	10
Figure 5: Idealized cross section of a typical micellar-polymer flood.....	12
Figure 6: Four region adsorption isotherms for a monoisomeric surfactant. Figure adopted from Schramm, 2000. ....	14
Figure 7: Schematic of mixed wettability (Salathiel, 1973) .....	17
Figure 8: Effectiveness of the solvents used in restoring wettability in a sandstone core samples. Figure adopted from Gant and Anderson (1988) .....	21
Figure 9: Effectiveness of the solvents used in restoring wettability in a limestone core samples. Figure adopted from Gant and Anderson (1988) .....	21
Figure 10: Schematic of coreflood experimental setup.....	22
Figure 11: Coreflood apparatus.....	23
Figure 12: Data acquisition system.....	23
Figure 13: Core cleaning system – flow through core cleaning method.....	24
Figure 14: Soxhlet extraction cleaning system .....	25
Figure 15: Schematic of an improved waterflood or improved LC surfactant flood in the core .....	27
Figure 16: Schematic of the water alternating surfactant process (WASP) in the core .....	28
Figure 17: Pressure drop profile of the core cleaning procedure using IPA as a dehydrant.....	33
Figure 18: Pressure drop profile of the core cleaning procedure using Acetone as a dehydrant .....	33
Figure 19: Relative permeability ratio curves for the Yates crude oil aging period .....	36
Figure 20: Experimental and simulation recovery curves of all surfactant concentrations in the reactive (Yates) system.....	42

Figure 21: Experimental and simulation pressure drop curves of all surfactant concentrations in the reactive (Yates) system. ....	43
Figure 22: Relative permeability ratio curves for various surfactant concentrations in the reactive (Yates) system. ....	44
Figure 23: Fractional water flow curves of various surfactant concentrations and viscosities in the reactive (Yates) system.....	45
Figure 24: Fractional water flow curves of all surfactant concentrations in the reactive (Yates) system...	45
Figure 25: Fractional water flow curves of various viscosities at 3000ppm surfactant flood in the reactive (Yates) system.....	47
Figure 26: Recovery curves for all surfactant concentrations in the non-reactive (decane) system. ....	49
Figure 27: Pressure drop curves for all surfactant concentrations in the non-reactive (decane) system. ...	49
Figure 28: Oil-water relative permeability ratios with increasing surfactant concentration in a non-reactive system .....	50
Figure 29: Fractional flow curves of all surfactant concentrations in the non-reactive (decane) system. ..	51
Figure 30: Schematic of an improved waterflood process in the core. ....	52
Figure 31: Recovery curves of all soaking period experiments. ....	54
Figure 32: Pressure drop curves of all soaking period experiments. ....	55
Figure 33: Oil-water relative permeability ratios of soaking period experiments. ....	55
Figure 34: Fractional water flow curves of all soaking period experiments.....	56
Figure 35: Recovery results at different soaking periods.....	56
Figure 36: Recovery curves for various surfactant slug sizes.....	57
Figure 37: Pressure drop curves for various surfactant slug sizes .....	58
Figure 38: Oil-water relative permeabilities ratios for various sizes of surfactant slug.....	59
Figure 39: Fractional flow curves for various surfactant slug sizes.....	59
Figure 40: Recovery results at different pore volume sizes.....	60
Figure 41: Recovery results for the six EOR processes .....	62
Figure 42: Calculated profits of the seven EOR methods.....	66
Figure 43: Incremental profit of each EOR method when compared to the waterflood profit .....	67



Figure 44: Experimental and simulation recovery curves of all surfactant concentrations in the non-reactive (decane) system. ....	74
Figure 45: Experimental and simulation pressure drop curves of all surfactant concentrations in the non-reactive (decane) system. ....	74
Figure 46: Experimental and simulation recovery curves of all soaking period experiments. ....	75
Figure 47: Experimental and simulation pressure drop curves of all soaking period experiments.....	75
Figure 48: Experimental and simulation recovery curves for various surfactant slug sizes .....	76
Figure 49: Experimental and simulation pressure drop curves for various surfactant slug sizes .....	76

## NOMENCLATURE

- $N_{ca}$  - capillary number
- $V$  - velocity
- $\mu$  - viscosity
- $\sigma$  - oil-water interfacial tension (IFT)
- $\theta$  - contact angle
- $\Delta P$  - pressure drop
- $q_o$  - rate of oil production
- $K$  - permeability
- $k_{ro}$  - oil relative permeability
- $k_{rw}$  - water relative permeability
- $S_{wi}$  - initial water saturation
- $S_{ro}$  - residual oil saturation
- $\mu_o$  - oil viscosity
- $A$  - area of reservoir
- $h$  - pay zone thickness
- $\phi$  - porosity
- $PV$  - pore volume
- $\overline{S_w}$  – saturation behind the front at breakthrough time
- $N_{pbt}$  – cumulative oil at breakthrough time

## ABSTRACT

Surfactants have a variety of applications in the petroleum industry due to their remarkable ability to lower the oil-water interfacial tension and alter wettability. However, surfactant adsorption on rock surfaces has severely crippled this means of improving oil recovery due to the high cost associated with the large quantities of surfactant needed. A previous experimental study by Ayirala (2002) reported the development of mixed wettability using a nonionic surfactant. At this mixed-wet state he was able to recover about 94% of the original oil in place. The underlying motivation of this study was to achieve such high recoveries without using large quantities of surfactants. A new surfactant enhanced waterflood method is proposed as the means to accomplish this task. This improved waterflood method consists of soaking the area around the production or injection well with an optimally concentrated surfactant slug prior to conducting a waterflood. Four variations of this novel process were investigated. The first two variations examined two surfactant slug sizes (0.2PV and 0.3PV) soaked around the production well prior to conducting a waterflood. The third variation explored the idea of soaking the area around the injection well instead of the production well prior to a waterflood. After soaking the area around the production well with a surfactant slug, the fourth variation used a low concentration (LC) surfactant solution to flood the reservoir instead of water.

The main objective of this study was to evaluate whether these proposed improved waterflood methods are technically feasible, and also determine their effectiveness when compared to a conventional waterflood. In addition, simple cost analysis calculations were carried out to show the economic feasibility of the proposed improved waterflood variations, especially when compared to a conventional waterflood. All the experiments utilized the same rock and fluid properties, as those used by Ayirala in his coreflood experiments. A surfactant (Tomadol™ 91-8) with similar properties and recovery to that used by Ayirala was used in this project. This project was divided in four sets of experiments.

This study found that all four improved waterflooding variations were technically feasible, and were more effective in improving oil recovery than a conventional waterflood. In addition, the proposed

improved waterflood variations accomplished the task of significantly improving oil recovery with small quantities of surfactant.

# 1. INTRODUCTION

## 1.1 Background

Since the beginning of the oil and gas industry, petroleum companies have tried to produce more oil by either maximizing oil recovery or by finding new reserves. With much of the easy oil already produced, petroleum companies have entered an era where they have to push the bounds of technology, and think outside the box on how to produce the large quantities of remaining oil in place (ROIP), unconventional resources, and from remote regions. To do so, fascinating and unconventional means of oil production are being developed, while the conventional methods are being optimized to increase their effectiveness. The technology gaps that exist in enhancing oil recovery provide exciting and fascinating research problems for the petroleum industry.

In recent years, the field of enhanced oil recovery has grown to become more popular due to a combination of the world's rising energy consumption, stagnant oil production, and low recoveries by conventional methods. On average, both the primary and secondary oil recovery phases account for about one-third of the original oil in place (OOIP). The rest of the oil is trapped in the rock due to high capillary forces that prevent oil from flowing through the rock and into the wellbore for production. The field of enhanced oil recovery focuses on overcoming these competing forces in order to recover large and economical quantities of the remaining oil in place. Any process that involves injection of fluid(s) to supplement natural reservoir energy by interacting with the rock-oil-brine system to create favorable conditions for maximum oil recovery is known as an enhanced oil recovery (EOR) process (Willhite et al., 1998). These favorable interactions to maximize oil recovery may be oil swelling, lowering the interfacial tension, rock wettability modification, oil viscosity reduction, and favorable phase behavior. In the U.S alone, out of the 536 billion barrels of original oil in place (OOIP) there still remains about 350 billion barrels of oil trapped in onshore producing reservoirs. In addition, the deepwater Gulf of Mexico region remaining oil in place is estimated to be in the 40 billion barrel range (KR, 2009). These large reserves of remaining oil in place illustrate the gigantic EOR target in the US alone. Therefore, there is a

need to develop more efficient, effective, and economical EOR techniques, as the conventional methods are being improved.

EOR processes offer prospects for ultimately producing 30-60% or more of the reservoir's OOIP (ARI, 2006). There are three major enhanced oil recovery applications: chemical flooding, gas flooding, and thermal recovery. Chemical flooding uses surfactants, alkali, and/or polymers to increase oil recovery. Surfactants are used to lower the oil-water interfacial tension (IFT) and modify the wettability of the reservoir rock. Surfactants can either be water based (chemically enhanced waterflooding) or gas based (foam). Polymers are used to increase and control the mobility of water. Alkaline chemicals are used to react with crude oil to generate soap and increase pH. Either of these chemicals can be combined to complement each other in various forms of recovery methods. Despite the high potential of chemical EOR in increasing recovery, it only accounts for less than 1% of the US EOR production (ARI, 2006). This limited use of chemical EOR is a reflection of the technology gaps in a number of failed projects.

## **1.2 Objective**

Waterflooding is the most widely used improved oil recovery method both in onshore as well as in offshore regions. However, when water saturation increases oil is trapped due to capillary forces that cause water to collect at pore throats, and thus blocking the movement of oil. As a result, production declines as more oil becomes trapped. On the other hand, surfactants are effective in decreasing these capillary forces by lowering interfacial tension and favorably altering the wettability. However, the major disadvantage faced by surfactant flooding is the cost associated with using large quantities of surfactants due to surfactant adsorption on the rock.

A previous experimental study by Ayirala (2002) reported the development of mixed wettability using a nonionic surfactant (NEODOL™), Yates oil, and Yates synthetic brine in a Berea core. At this mixed-wet state he was able to recover about 94% of the original oil in place (OOIP) after flooding the reservoir with 3500ppm surfactant solution for 2 pore volumes. This study explores how to achieve such high recoveries in the field without using large quantities of surfactants. Figure 1 illustrates the proposed

surfactant enhanced waterflood method. This proposed method consists of soaking the area around the production or injection well with optimally concentrated surfactant slug prior to conducting a waterflood. Four variations of this novel process were tested. The first two variations varied the size of the surfactant slug injected around the production well. The third variation explored the concept of soaking the area around the injection well instead of the production well. This process was named the water alternating surfactant process (WASP) and is illustrated in the right schematic in Figure 1. The fourth variation tested, explored the idea of soaking the area around the production well but instead of executing a conventional waterflood, a low concentration surfactant flood was conducted. This process was named as the improved low concentration surfactant flood.

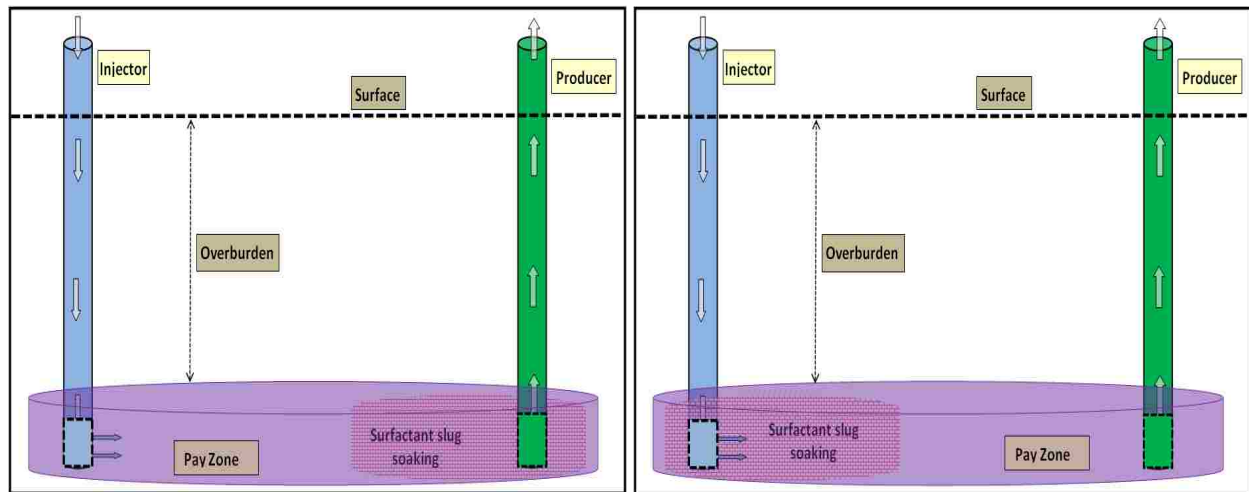


Figure 1: Improved waterflood process: left figure has a surfactant soaked production zone and the right figure has a surfactant soaked injection zone - water alternating surfactant process (WASP)

The main objective of this study was to evaluate whether these proposed improved waterflooding techniques are technically feasible, and also determine their effectiveness when compared to a conventional waterflood. The motivation behind the improved waterflood method is to get recoveries as high as those achieved in a mixed-wet state, but with using less surfactant.

### **1.3 Methodology**

This experimental study is divided into four sets of experiments where each set of experiments builds on the previous one. The first three sets were used to optimize different facets of the proposed improved waterflooding process. The first set determined the optimal surfactant concentration in two rock-fluid systems (reactive and non-reactive). The second set of experiments determined the ideal soaking period for 0.2PV of surfactant slug size. The third set of experiments evaluated the effects of varying the size of surfactant slug injected. Lastly, the fourth set tested the four improved waterflooding variations and compared them to a conventional waterflood, a low concentration surfactant flood (1000ppm), and an ideal surfactant (3000ppm) flood where mixed wettability was developed.

Since this project was based on Ayirala's findings, the same rock fluid systems were used, which included Berea sandstone, Yates oil, Yates synthetic brine, and decane (for non-reactive system). Every experiment was run under Yates reservoir conditions of 700psi and 82°F. Thereafter, the coreflood simulator was used to generate relative permeability curves and fractional flow curves, using the recovery and pressure data collected for the coreflood experiments. Each experiment was evaluated based on its recovery, pressure drop, fractional flow curves, saturations, and relative permeability.



## **2. LITERATURE REVIEW**

### **2.1 Waterflooding**

A predominant fraction of the world's oil reservoirs is produced by the solution gas drive mechanism (Gulick and William, 1998). This drive mechanism has low energy and thus leaves behind large quantities of oil when the production reaches its economic limit. In addition, all reservoirs are heterogeneous which contributes to the problem of leaving behind huge reserves of unproduced oil. One of the cheapest and most popular means of maintaining and restoring reservoir energy is waterflooding. Waterflooding is the most predominant improved recovery process in both onshore and offshore regions. This recovery method consists of injecting water through an injector well to push oil to the producing wellbore.

The history of waterflooding dates back to the 1860s, however, the use of waterflooding as a means of recovery was not widely accepted until the 1950's (Gulick and William, 1998). In the 1950's, there was a significant expansion of the oil and gas industry in West Texas due to the discovery of a number of gigantic reservoirs (i.e. Wasson, Slaughter, Levelland, North and South Cowden, Means, and Seminole). These reservoirs were found in highly heterogeneous shallow shelf carbonates and had a solution gas drive mechanism. As a result, the reservoir energy depleted within a few years and producing rates rapidly dropped. Consequently, it was crucial to find a way to restore and maintain the reservoir energy, hence the wide use of water injection.

Some of the lessons learned in industry on how to conduct a successful waterflood operation are described below.

1. Implementation of water injection early in the life of a reservoir has proved to be critical in the success of a waterflood. From the start of primary depletion, the reservoir energy drops to the bubble point where gas comes out of solution and creates a gas cap. The loss of solution gas from oil increases the crude oil viscosity, thereby lowering the flow rate of oil, and negatively impacting the

mobility ratio which in turn decreases the areal sweep efficiency. Therefore, the start of an early waterflood operation in a field's life, even in very large offshore fields, has been successful in the past (Gulick and William, 1998).

2. The understanding of the field's geology is fundamental to the success of a waterflood operation. A full suite of openhole logs, areal distribution of whole cores, bottom-hole sampling of produced fluids, bottom-hole pressure measurements, pressure drawdown tests, production history, and a multidisciplinary team of engineers and geologists, are all essential and necessary components in having a good and detailed understanding of a field's geology (Namba and Hiraoka, 1995).
3. Infill drilling to reduce lateral pay discontinuities also aides the success of water injection especially in highly heterogeneous reservoirs (Wu et al. 1989).
4. Water injection with a pattern waterflood is critical especially if there is a preferential permeability direction, natural fracturing, or a combination of in-situ stresses and rock properties that would cause the formation to fracture in a particular direction during stimulation or injection above parting pressure (Pande et al., 1994).
5. Both production and injection wells must be completed in the entire hydrocarbon productive zones (Gulick and William, 1998).
6. It is also imperative to keep the production wells pumped off in order to minimize the bottom-hole pressure and therefore maximizing the production. For injectors, it is important to inject below the formation parting pressure in order not to fracture the formation and introduce thief zones (Stiles, 1976).
7. Water quality is also crucial to the success of a waterflood operation. There are four main problems associated with water injection quality: dissolved solids in the injection water can precipitate and form scale, oil and suspended solids that can plug wellbores, oxygen in the water can cause corrosion, and lastly, bacteria in the system can cause corrosion and suspended solids. Injection water can be cleaned either mechanically or chemically (Bennion et al., 1998).
8. It is vital to have a strong surveillance program monitoring the waterflood (Talash, 1988).

All in all, water injection plays a significant role in restoring and maintaining reservoir pressure and therefore prolonging the economic limit of reservoir production. This process is dependable, well understood, and reliable. However, due to the capillary forces, the effectiveness of waterflooding is limited and thus the need to consider other processes such as the use of surfactants to combat the limiting capillary effects.

## **2.2 Surfactant**

The term surfactant finds its origin from the term “surface active agent”. Surfactants are organic compounds that have an amphipathic nature, meaning they contain both a hydrophobic group (their tail) and hydrophilic group (their head) (Schramm, 2000). Therefore, they are soluble in both organic solvents and water. Surfactants reduce the interfacial tension between water and oil by adsorbing at their interface. They can also change the wettability of rock surfaces by adsorbing to the liquid-rock interface and therefore making the rock surface have a strong affinity towards one of the immiscible fluids, preferably water. Surfactants also assemble into aggregates that are known as micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration (CMC). The relationship between surfactant monomer concentration and total surfactant concentration is shown in Figure 2. Above the CMC point, any further increase in surfactant concentration will cause an increase in the micelle concentration. Since CMCs are typically quite small (about  $10^{-5}$  to  $10^{-4}$  kg-mole/m<sup>3</sup>) at nearly all concentration practical for surfactant flooding, the surfactant is predominantly in the micelle form (Lake, 1989). Surfactants prefer the interface to the micelle, however, only a small fraction of the surfactant concentration is needed to saturate the interface.

When micelles form in water their tails form a core that is like an oil droplet as shown in Figure 3, and their ionic heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the opposite takes place, where the heads are in the core and the tails maintain favorable contact with oil.

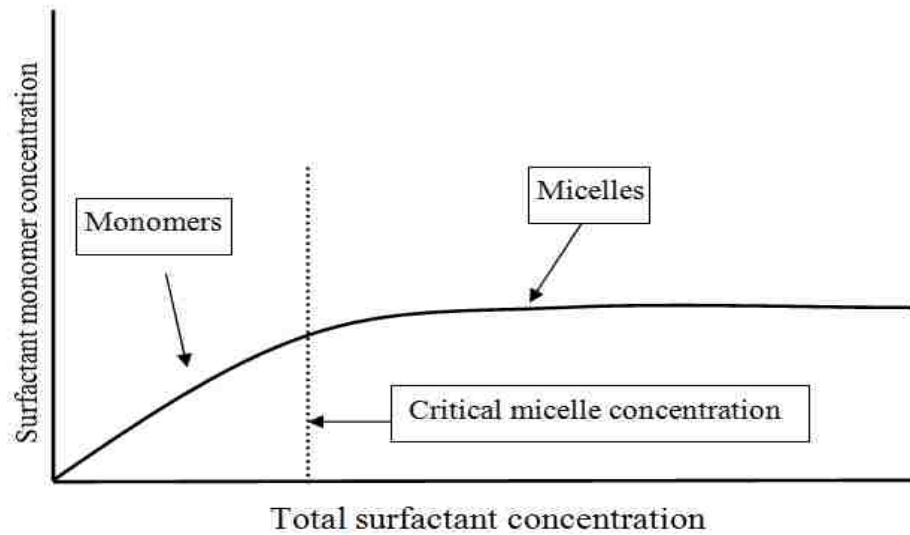


Figure 2: Schematic definition of the critical micelle concentration adopted from (Lake, 1989)

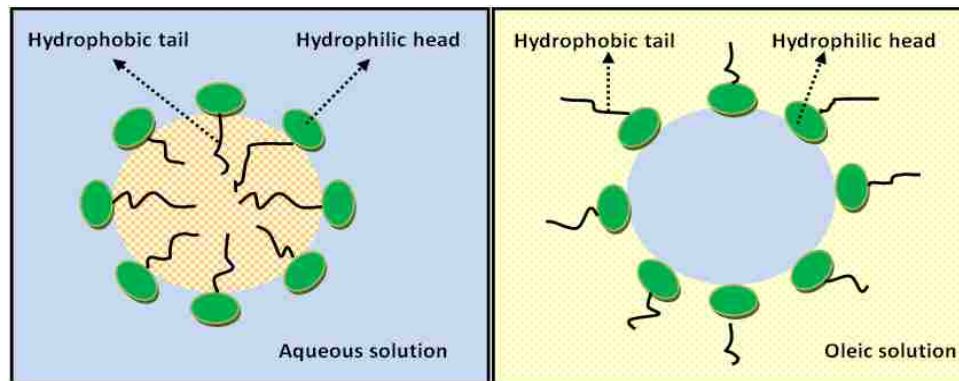


Figure 3: The figure on the left shows when micelles form in water, and the figure on the right shows when micelles form in oil

Surfactants are classified in four groups depending on the nature of their hydrophilic group (Lake, 1989 and Schramm, 2000).

1. Anionics have a surface active portion that bears a negative charge. In an aqueous solution, the molecule ionizes in free cations and the anionic monomer. Anionic surfactants are the most common in surfactant-polymer flooding because they are relatively resistant to retention, stable, and can be made relatively cheaply. Anionics are more resistant to adsorption due to their negative charge that repels from the negative charges of the clays.

2. Cationics have a surface active portion that bears a positive charge. In this case, the surfactant molecule contains an inorganic anion to balance the charge. This group of surfactants is rarely used because they are highly adsorbed by the anionic surfaces of interstitial clays. Cationics are less resistant to adsorption due to their positive charge that attracted to the negative charges of the clays.
3. Nonionics have a surface active portion that bears no charge. This group of surfactants has been extensively used, mostly as a cosurfactant but increasingly as a primary surfactant. These surfactants do not form ionic bonds but when dissolved in aqueous solutions, they exhibit surfactant properties by electronegativity contrast between their constituents. Nonionics are much more tolerant of high salinities than anionics and historically have been considered as poorer surfactants.
4. Amphoteries also known as zwitterionic have a surface active portion that may contain both positive and negative charges.

### **2.2.1 Effect of surfactants on interfacial tension**

When a surfactant solution is injected to an oil water system, it mobilizes and banks the oil until the surfactant is diluted or otherwise lost due to adsorption by the rock. To achieve low residual oil saturations when neglecting wettability alteration by surfactants, the interfacial tension has to be reduced from oil-brine values of about 20-30 mN/m to 0.001-0.01 mN/m (Schramm, 2000). Research groups have found that ultra-low interfacial tension in the required range could be achieved by using petroleum sulfonate or alcohol surfactants (Hirasaki et al., 2008). It has been found that interfacial tension of an oil-brine-surfactant system is a function of salinity, oil composition, surfactant type and concentration, cosurfactant, electrolytes, and temperature. In addition, the interfacial tension of a system is directly correlated to its phase behavior (Lake, 1989).

The surfactant-brine-oil phase behavior is strongly affected by the salinity of the brine. This phase behavior is represented by a ternary diagram, where 1 = brine, 2 = oil, and 3 = surfactant as shown in Figure 4. For low brine salinities, a typical surfactant flood will exhibit good aqueous phase solubility and poor oil-phase solubility. As shown by the left schematic in Figure 4, the overall composition near the

brine-oil boundary of the ternary diagram will split in two phases: a pure oil phase and a microemulsion phase that contains brine, surfactant, and some solubilized oil (Lake, 1989). The solubilized oil occurs when globules of oil occupy the central core of the swollen micelles. This lower phase microemulsion system is known as the Winsor Type II (-) system where II means no more than two phases can form, and (-) means the tie lines have a negative slope. For high brine salinities, the surfactant solubility is decreased in the aqueous phase by electrostatic forces. As shown by the middle schematic in Figure 4, an overall composition within the two phase region will split in two: a pure aqueous phase, and a microemulsion phase that contains most of the surfactant and some solubilized aqueous phase. This upper phase microemulsion system is known as the Winsor Type II (+) system. Between the low and high salinities, there is a range of salinities where a third surfactant rich phase is formed. An overall composition within the three phase region separates into excess oil and brine phases, as in the type II (-) and II (+) environments, and into a microemulsion phase whose composition is represented by an invariant point. This middle phase microemulsion system is known as a Winsor type (III) system. As shown by the right schematic in Figure 4, the upper right and left of the three phase region are type II (-) and type II (+) where two phases will form. Below the three phase system, there is a third two phase region whose extent is usually very small that is considered negligible. In this three phase region, there are now two interfaces between the microemulsion and oil, and the microemulsion and brine.

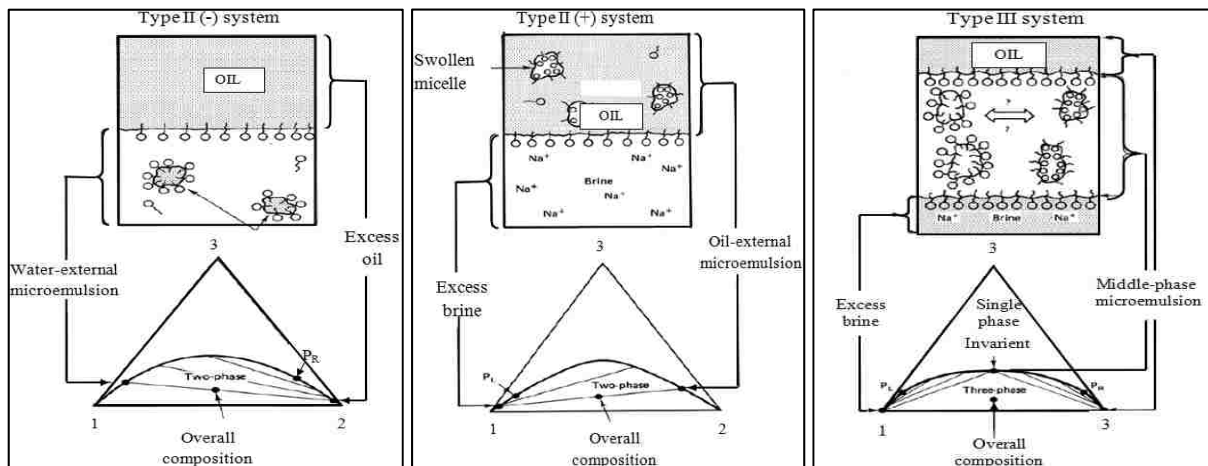


Figure 4: Schematic representation of the: Type II (-) system (left), Type II (+) system (middle), and Type III system (right) (Lake, 1989)

The structure of a surfactant also determines its solubility in either brine or oil. Increasing the importance of the nonpolar end of the surfactant will increase oil solubility. This can be accomplished by increasing the nonpolar molecular weight, decreasing the tail branching, decreasing the number of polar groups, and decreasing the strength of the polar part of the surfactant (Lake, 1989). Wellington and Richardson (1997) showed that branched alkyl chains with propylene oxide (PO) and ethylene oxide (EO) groups could yield ultra-low interfacial tension and high oil recovery at very low concentrations. Wu et al. (2005) studied the effect of PO and EO in sulfated surfactants for enhanced oil recovery. Levitt et al. (2006) investigated branched alcohol propoxy sulfates with hydrophobes ranging from  $C_{12}$  to  $C_{24}$  and with three to seven PO groups with a Texas crude oil and concluded they are promising EOR surfactants for reservoirs with low temperatures. Jayanti et al. (2002) reported that branched alcohol propoxylated sulfates were excellent surfactants for removing organic liquid contaminants from soil.

In addition, oil properties do affect the surfactant solubility to oil. High specific gravity crude oils tend to be rich in organic acids thus the surfactant-oil solubility is lower in high gravity oils. Some correlations have been found in the tendency for surfactant to dissolve in oil as the temperature increases. For most anionics higher temperatures mean better brine solubility. This trend is reversed for nonionics. On the other hand, surfactant solubility is not affected by pressure difference except for gassy crude oils. Lastly, cosurfactants can be used to modify solubility so that the transition from Type II (-) system to Type II (+) system can occur at different salinities.

### **2.2.2 Surfactant flooding**

Primary and secondary recovery techniques usually recover about one-third of the original oil in place (OOIP) due to high capillary forces that trap oil in the porous media. Capillary forces are a result of the interfacial tension between the oil and water phases that resist externally applied viscous forces such as water injection. Early efforts of enhanced oil recovery strove to displace this oil by decreasing the oil-water IFT. Though many techniques have been proposed and field tested, the predominant EOR technique for achieving low IFT is surfactant flooding (Zhang et al., 2007).

Surfactant flooding has appeared in literature under many names: detergent, low-tension, soluble oil, microemulsion, chemical, and micellar-polymer flood. Many variations of this method have been tried and the most successful one has been the surfactant-polymer combination. Figure 5 shows an idealized version of the surfactant-polymer flood sequence. The process is usually applied as a tertiary flood. The complete process consists of (Lake, 1989):

1. Preflush injection of brine whose purpose is to change the salinity of the formation brine so that mixing with the surfactant will not cause loss of interfacial activity.
2. Surfactant slug injection follows and its purpose is to lower the IFT and favorably modify wettability in order to increase oil recovery.
3. Mobility buffer injection follows in the form of a dilute polymer solution with the purpose of driving the surfactant slug and banked-up fluids to the production wells. This buffer is crucial to the recovery ability of the entire sequence. The target oil for the surfactant flood is the residual oil which is different from that of a polymer flood which is the movable oil.
4. Taper injection follows thereafter, as a volume of brine that contains polymer grading from that of the mobility buffer at the front end to zero concentration at the back end. The gradual decrease in concentration mitigates the effect of the adverse mobility ratio between the mobility buffer and the chase water.
5. Chase water injection completes the cycle and its purpose is to simply reduce the expense of continually injecting polymer.

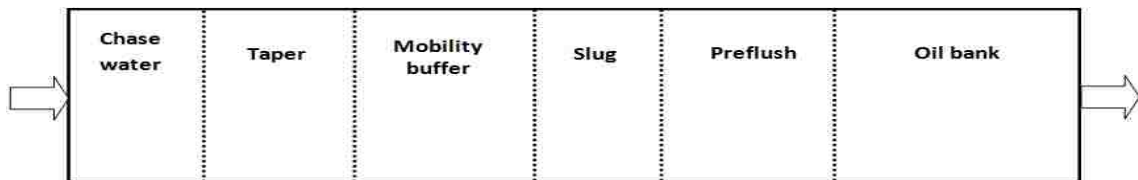


Figure 5: Idealized cross section of a typical micellar-polymer flood

The limitation of most surfactants is usually related to high adsorption and the formation of high viscosity emulsions or microemulsions. It is critical to select surfactants that do not have these problems.



Once a good surfactant is selected, then surfactant modeling is carried out with only a few well designed experiments to provide the most important process parameters. The remaining challenges are proper reservoir characterization, and optimization. In the surfactant selection (disregarding wettability modification), anionic surfactants are preferred because they have low adsorption at neutral to high pH on both sandstones and carbonates. They can also be tailored to a wide range of conditions, and they are widely available at low cost and special cases. However, when focusing on altering the wettability of the rock, adsorption is needed and thus nonionic surfactants are also favorable (Ayirala, 2002).

Surfactant selection is a crucial process that affects the success of this enhanced oil recovery process. Prior to implementation of the process, extensive laboratory studies are needed in order to assure the surfactant chosen is right for the reservoir of interest. Also, parameters such as optimal concentration, injection rate, and surfactant behavior at reservoir conditions, have to be tested and determined. This grants the operator knowledge of the surfactant's advantages and disadvantages with respect to the reservoir of interest, which can help in the oil recovery prediction. Some of the experiments that can be used in selecting a surfactant are: oil solubilization test, effect of electrolyte, microemulsion densities test, surfactant and microemulsion viscosity test, coalescence times test, identification of optimal surfactant-cosolvent formulations, and identification of optimal formulation for coreflood experiments (Lake, 1989). Some of the key surfactant selection criteria are: high solubilization, favorable wettability alteration, low to no retention on reservoir rock in the case of negation of wettability modification, economics, branching needed in order to form low viscosity micelles and microemulsions, and minimal propensity to form liquid crystals, gels, and macroemulsions.

A crucial and interesting subject in surfactant flooding is surfactant adsorption, since it can easily make or break a surfactant flood project. Surfactant adsorption or retention is highly considered in any application where surfactants come in contact with a solid surface. Many surfactants adsorb on the rock grains due to the electrostatic interactions between charged sites on the solid surface and those of a surfactant. In the case of nonionic surfactants, the interactions involve hydrogen bonding and hydrophobic bonding (Schramm, 2000). Factors affecting the surfactant adsorption in a reservoir include

temperature, pH, salinity, surfactant type, and rock type. Usually, the only factor that can be manipulated for enhanced oil recovery purposes is the surfactant type, the rest are governed by reservoir conditions.

The mechanism driving surfactant adsorption is generally discussed in terms of a four region isotherm as shown in Figure 6 (Schramm, 2000). At low surfactant concentrations designated as region 1, the adsorption behavior can be described as linear with a slope of one. In this region, adsorption is due to electrostatic attraction between the charged surfactant ion and the electric double layer of the solid. In the case of a nonionic surfactant it is due to the hydrogen bonding and hydrocarbon bonding. In region 2, the mechanism dominating adsorption is the association of the adsorbed surfactants into patches at the solid-liquid interface. In region 3 a decrease in slope compared to region 2 is observed. This has been attributed to the surfactant ions having filled all the surface sites by the end of region 2 with further adsorption being due to association between first and second layer hydrocarbon chains in region 3. In addition, it was also attributed to a reversal in surface charge due to the adsorbed surfactant ions. Region 4 beings at or near the CMC point and is characterized by little or no increase in adsorption with increasing surfactant concentration.

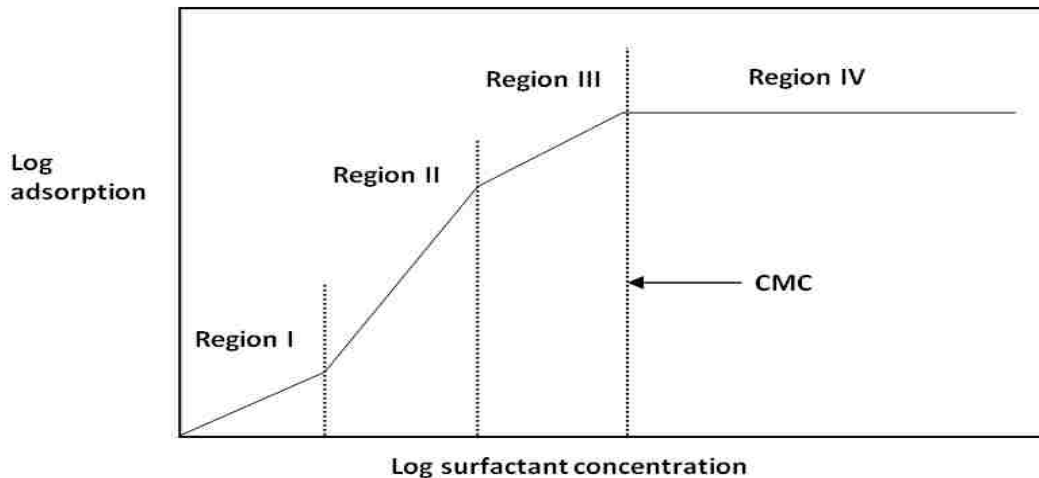


Figure 6: Four region adsorption isotherms for a monoisomeric surfactant. Figure adopted from Schramm, 2000.

Technical feasibility of surfactant flooding has already been established, however, the economic feasibility depends on complex factors such as oil prices, surfactant consumption, and surfactant cost.

Generally, the cost of the surfactant is the single most expensive item in the cost of a chemical flood. These costs include both the initial investment in purchasing the surfactant, as well as the cost of replacing surfactant which has been lost to adsorption. It is frequently found that the amount of surfactant adsorbed accounts for most of the cost of the surfactant. Since these surfactants are synthesized from petroleum, their cost will rise at least as fast as that of the oil they are used to produce. So simply waiting for oil prices to increase will not necessarily make surfactant flooding economically feasible. The revenue from the oil produced by surfactant flooding must at least pay for the cost of surfactant, additional engineering services, equipment, and operating costs during the several years the flood, in order to provide a reasonable return on investment. Producing more barrels of oil for each pound of surfactant injected into the reservoir is a technological problem that has direct bearing on the economics of this enhanced oil recovery process. Understanding and controlling the amount of surfactant adsorbed directly affects the economics

## **2.3 Wettability**

Wettability is the ability of one fluid to spread or adhere on a rock surface in the presence of another immiscible fluid. Subsequently, this parameter has a profound effect on multiphase rock fluid interactions. In porous media wettability affects: the efficiency of immiscible displacement, electrical properties, capillary pressure, relative permeability, saturation profiles, and determines the distribution of fluids in a reservoir. Spreading of a liquid on a solid surface depends on the solid surface properties as well as the liquid properties. Therefore, by manipulating the properties of the rock and/or liquid, one can optimize the function or performance of either to achieve the desired wetting condition. Generally, most reservoirs are oil wet. Treibel et al. (1972) studied the wettability of petroleum reservoirs where they tested fifty-five core samples. Of the fifty-five core samples 27% were water-wet, 66% were oil wet, and 7% were intermediate wet. Thirty of the fifty-five core samples were sandstone and 43% were water-wet, 50% were oil-wet, and 7% were intermediate wet. Twenty-five of the fifty-five core samples were carbonate, 8% were water wet, 84% were oil wet, and 8% were intermediate wet. A sandstone rock is

mostly made of quartz which is water wet. However, it changes its wettability to oil wet after being aged with oil at higher temperatures and pressures. Compounds are deposited on the surface of the rock changing its wettability to oil wet.

There are several methods of measuring the wettability of a system and each has its advantages and disadvantages (Anderson, 1986). The most common way of defining wettability is using the contact angle ( $\theta$ ) which is measured through the denser fluid. The three broad classification of homogenous wettability are: water-wet ( $\theta < 70^\circ$ ), intermediate-wet ( $70^\circ < \theta < 115^\circ$ ), and oil-wet ( $\theta > 115^\circ$ ). In addition, there exists heterogeneous state of wettability which is mixed-wet state. Wettability plays an important role in the production of oil and gas as it not only determines the initial fluid distributions, but also is the main factor in the flow processes in the reservoir rock. Wettability affects primary recovery, residual oil saturation left after waterflooding, and the shape of the relative permeability curves. Some of the parameters that affect the wettability of a porous medium are: surface roughness, brine composition, oil composition, the use of surfactants, etc.

In this study the concept of mixed wettability is one of great interest. The idea of mixed wettability was first proposed by Salathiel (1973) to explain the abnormally high oil recoveries in Woodbine floods in East Texas. In mixed wet conditions, the finer pores and grain contacts are water-wet and the surfaces of larger pores are strongly oil-wet. If these oil wet paths were continuous through the rock, water would displace oil from the larger pores so that the capillary forces would hold little or no oil in smaller pores or at grain contacts. Salathiel proposed the development of mixed wettability with the following explanation. As oil accumulates in a reservoir, water present in the initially water-wet rock is displaced from the larger pores while the capillary pressure retains water in smaller pores and at grain contacts. After extended periods of time, some organic materials from the oil may deposit on to those rock surfaces that are in direct contact with oil, making those surfaces strongly oil-wet. This phenomenon leads to the development of so called mixed wettability. The development of mixed wettability condition as proposed by Salathiel is shown in Figure 7. It is obvious from the literature that a steady increase in

initial water saturation, higher oil recoveries, lower residual oil saturations and shift to the right in relative permeability ratio curves are the clear indication for the development of mixed wettability.

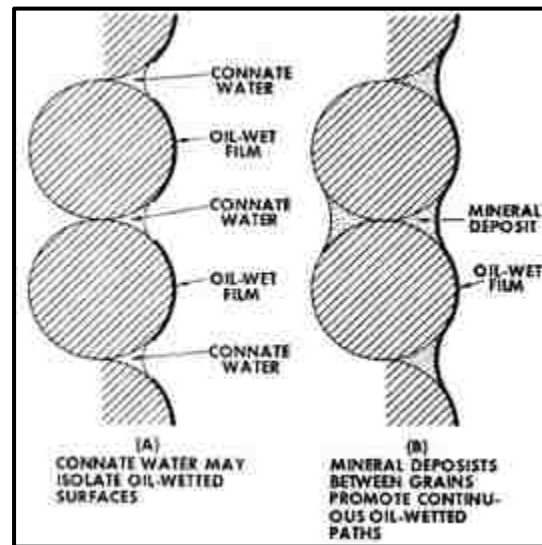


Figure 7: Schematic of mixed wettability (Salathiel, 1973)

#### 2.4.1 Effect of surfactants on wettability

Surfactant flooding schemes for recovering residual oil have been less satisfactory due to loss of surfactant by retention on reservoir rocks and precipitation. Adsorption and wettability changes are determined mainly by the surfactant structure, surface properties of the rock, composition of the oil and reservoir fluids, salinity, pH and temperature (Schramm, 2000). The mineralogical composition of reservoir rock and reservoir fluids properties, play an important role in determining surfactant interaction at their interface (Somasundaran and Zhang, 1997).

Wettability has been stated to be the most important factor in waterflood recovery after geology (Morrow, 1990). However, most of the previous work done in the area of surfactants focuses on its ability to lower IFT and has ignored wettability effects. Significant enhancements in oil recovery require several orders of magnitude reduction in IFT. The amount of surfactant capable of generating this large IFT reduction will be large and thus expensive. As a result, this could render a project uneconomical for field application. Wettability alteration can be induced by low cost surfactants at moderate concentrations.

Therefore, combining the effects of IFT reduction and favorable wetting conditions would make the use of surfactant more effective at lower concentrations.

Most importantly, the effect of surfactants on wettability depends not only on how much is adsorbed but also on how they adsorb on the rock. A water-wet rock surface that is beneficial for displacement of oil can be obtained by manipulating the orientation of the adsorbed layers (Somasundaran and Zhang, 1997).

## **2.4 Core cleaning**

There are two reasons for cleaning cores: the first is to remove all the liquids from the core so that porosity, permeability, and fluid saturations can be measured, and the second, is to clean the core in order to restore the wettability of the core to its initial state. Many special core analyses, including capillary pressure, relative permeability and saturation exponent are affected by the wettability of the core. The most accurate measurements are made on native state cores, where special precautions are taken to minimize the changes in the reservoir wettability. Native state refers only to core taken with suitable oil based drilling mud, while the term fresh state refers to a core with unaltered wettability (Gant and Anderson, 1988). Due to cost factors, cores will continue to be cut using oil based mud, however, this type of mud tends to contain surfactants that alter the wettability of the core and as a result the original reservoir wettability is not maintained.

Some of the several methods in core cleaning are: distillation/extraction (Dean-Stark and soxhlet), flow through core cleaning, centrifuge flushing, gas driven solvent extraction, and super critical fluid extraction and critical point drying (Gant and Anderson, 1988). So far, distillation/extraction and flow through core cleaning methods are usually the ones frequently used especially in wettability restoration.

Distillation/extraction methods are the most commonly used in the industry, and they are fairly slow and gentle on the core. In this method, a sample is placed in a soxhlet or Dean Stark apparatus and cleaned with hot, refluxing solvent. In the Dean Stark apparatus, the solvent is continuously distilled,

condensed, and then distributed over the top of the sample. In the soxhlet apparatus, the samples soak in the hot solvent, which is periodically siphoned off, distilled, condensed and distributed back to the extractors. The benefit of using this cleaning method is that the fluid saturation can be determined during core cleaning. A challenge associated with this method is that the solvent may not contact the entire core. Another challenge associated with this method is that it is possible to change an originally water wet rock to an oil wet one. This is attributed to the solvent (usually toluene) boiling away the water before extracting the crude oil (Gant and Anderson, 1988). In the absence of adsorbed water, crude oil components become strongly adsorbed on the mineral surfaces at sites that normally would be occupied by water. Subsequent contact of the surfaces with water may not displace adsorbed crude oil components to restore the wettability.

Flow through core cleaning methods place the sample in a core holder and solvents are injected under pressure into the core. The solvent injection can be continuous or maybe halted periodically to let the core soak in the solvent. This method of cleaning has been found to be more effective than the distillation/extraction method since the cleaning solvents are injected under pressure and thus are in contact with more of the core, especially when back pressure is applied (Cuiec, 1975).

The gas driven solvent extraction method cleans the core by repeated cycles of internally dissolved gas drive. A solvent (usually toluene) is saturated with CO<sub>2</sub> and injected into the core under pressure. The pressure is reduced rapidly, allowing the CO<sub>2</sub> to expand and flush the solvent through the pore spaces to remove the oil and water. The core may be heated to increase the cleaning efficiency. The recommended cycles are about 5–10 and the core should be essentially oil free, and the remaining solvents and water are removed by vaporization. This process is effective, however, it may separate or fracture unconsolidated or poorly consolidated cores (Cuiec, 1975). In addition, reaction of some crude oils with CO<sub>2</sub> can cause precipitation of asphaltenes and resins, rendering the core more oil-wet.

Super critical fluid extraction and critical point drying have been extensively used to clean sensitive clay and biological samples without causing structural damage from drying. In this method, the sample is flushed with a series of miscible fluids to remove fluids from the core. Because the fluids are

miscible, interfaces between the displacing and displaced phases are avoided, preventing surface tension effects and allowing all the fluids originally in the core to be removed (Gant and Anderson, 1988). The last step is drying the core without forming any liquid/vapor interfaces in the core by using a super critical liquid, typically supercritical CO<sub>2</sub>. The liquid CO<sub>2</sub> is injected into the core and then the temperature is raised above the critical point. Other cleaning methods include steam cleaning and firing the core in the presence of oxygen.

Gant and Anderson (1988) and Cuiec (1975) found that toluene was an ineffective solvent in restoring wettability. However, when combined with other solvents, such as methanol (CH<sub>3</sub>OH) or ethanol (CH<sub>3</sub>CH<sub>2</sub>OH), toluene proved to be very effective. Toluene is effective in removing the hydrocarbons, including asphaltenes and some of the weakly polar compounds while the more strongly polar methanol or ethanol removes the strongly adsorbed polar compounds that are often responsible for altering wettability. Some of the successful mixtures used to clean the core are: toluene/methanol, toluene/ethanol, chloroform/acetone, and chloroform/methanol. Therefore, when choosing cleaning solvents it is important to consider: (1) the best choice of solvents depends heavily on crude oil and the mineral surfaces, and (2) mixtures or series of solvents are generally more effective than a single solvent (Gant and Anderson, 1988). The crude oil and mineral surfaces in the core are important because they help determine the amount and type of wettability altering materials adsorbed. It is also important to note that solvents that may one for one type of core may not be ideal for another.

Gant and Anderson (1988) tested different solvents for cleaning Berea cores that were contaminated with drilling mud that contained surfactant. Figure 8 illustrates the effectiveness of the solvents used in restoring wettability in a sandstone core. The special solvent is a mixture of 49.5% toluene, 49.5% methanol, and 1% ammonium hydroxide proved to be the most effective. A 50/50 toluene/methanol mixture cleaned with essentially the same effectiveness. The three step process consisted of three successive Dean-Stark extractions, first with toluene, then with glacial acetic acid, and lastly ethanol. Each process lasted twelve hours each, but unfortunately the entire process was found to be poor. The least effective solvent used was toluene. Figure 9 illustrates the effectiveness of the solvents



used in restoring wettability in a limestone core. Similar to the sandstone case, the special solvent and the 50/50 toluene/methanol mixture are the most effective solvents, however, toluene proved to be more effective in cleaning limestones.

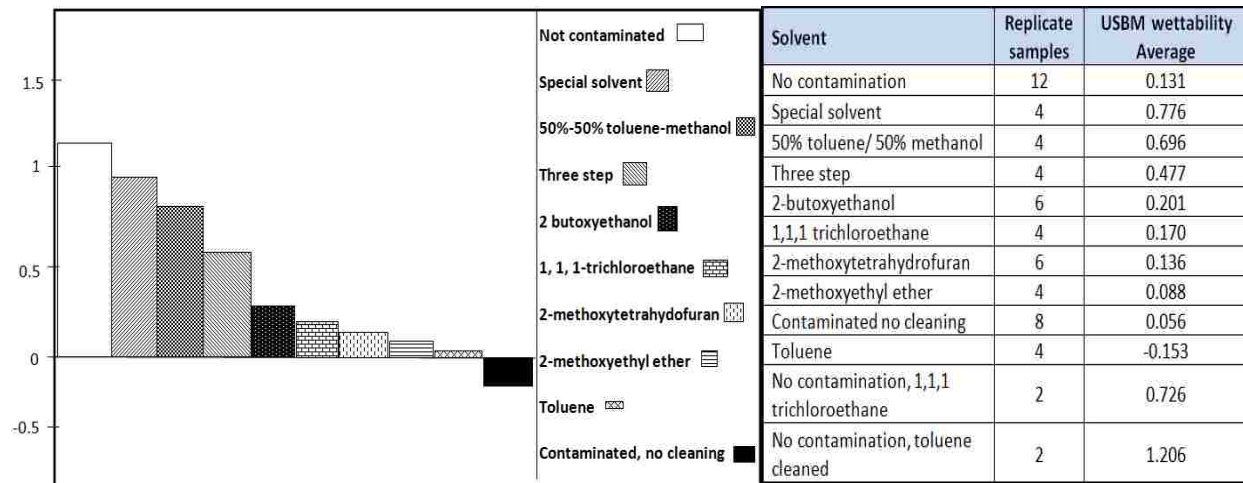


Figure 8: Effectiveness of the solvents used in restoring wettability in a sandstone core samples. Figure adopted from Gant and Anderson (1988)

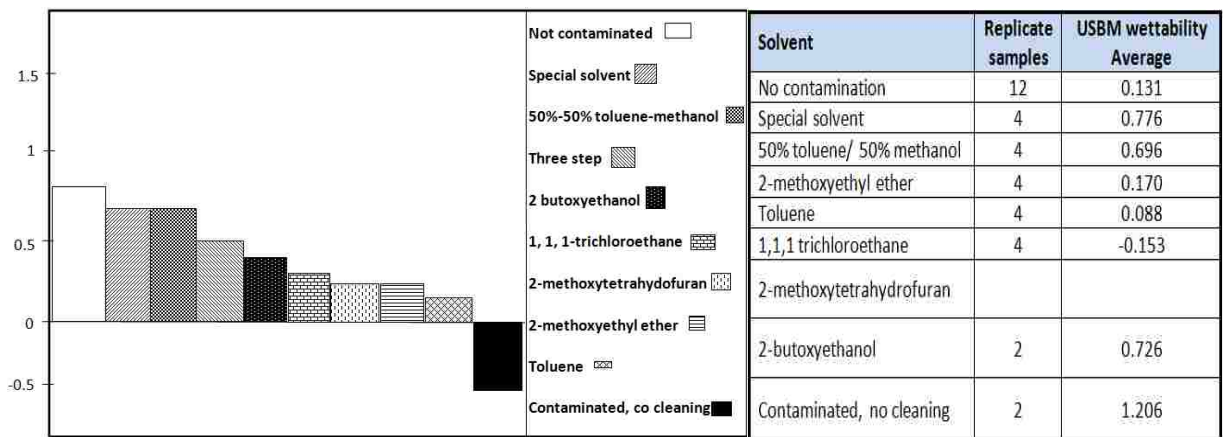


Figure 9: Effectiveness of the solvents used in restoring wettability in a limestone core samples. Figure adopted from Gant and Anderson (1988)

### 3. EXPERIMENTAL APPARATUS AND PROCEDURE

#### 3.1 Experimental setup

Figure 10 shows a schematic of the whole laboratory set up. There are three parts to this setup: the coreflood apparatus system, the data acquisition system, and the cleaning system.

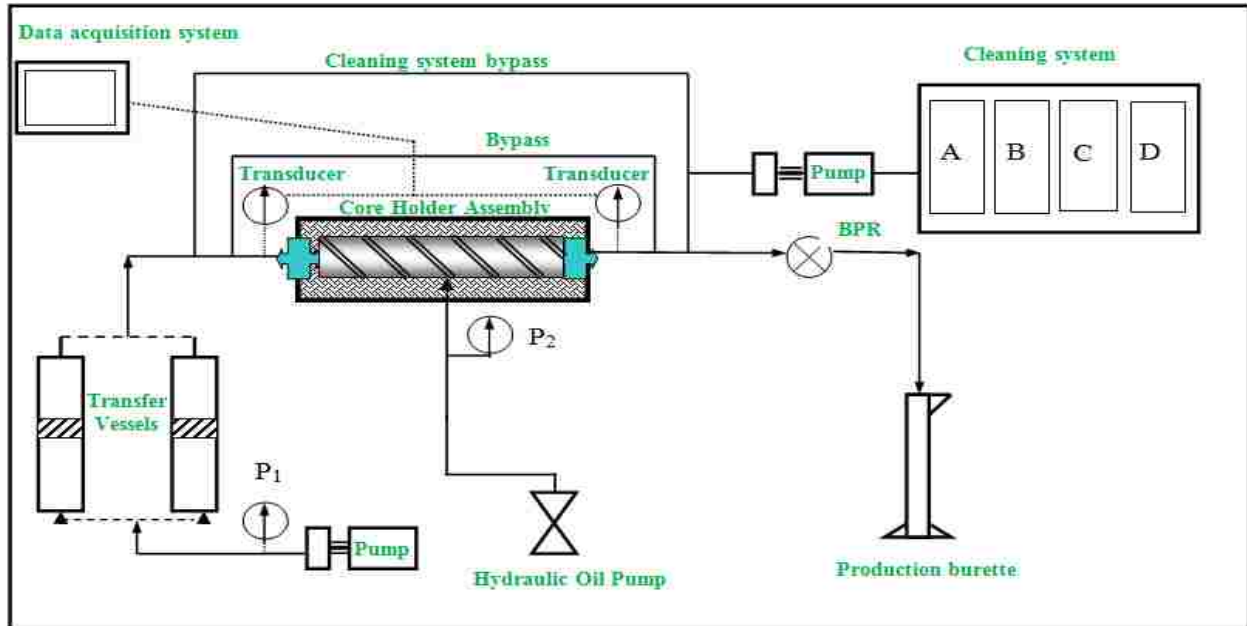


Figure 10: Schematic of coreflood experimental setup

**Coreflood Apparatus:** Figure 11 shows the actual coreflood setup built to run all the experiments in this project. The syringe pump in Figure 13 was used to inject fluids (oil, brine and surfactant) into the core. Two back pressure regulators were used to control and maintain the pressure at 700psi. A heater was used to control and maintain the temperature at 82°F. Two pressure transducers linked to the data acquisition system were placed at the inlet and outlet of the coreholder. This coreflood system is designed in such a way that either side of the coreholder can serve as an injector or producer. This is especially useful during the cleaning process, where chemicals are flushed in the forward and backward direction.

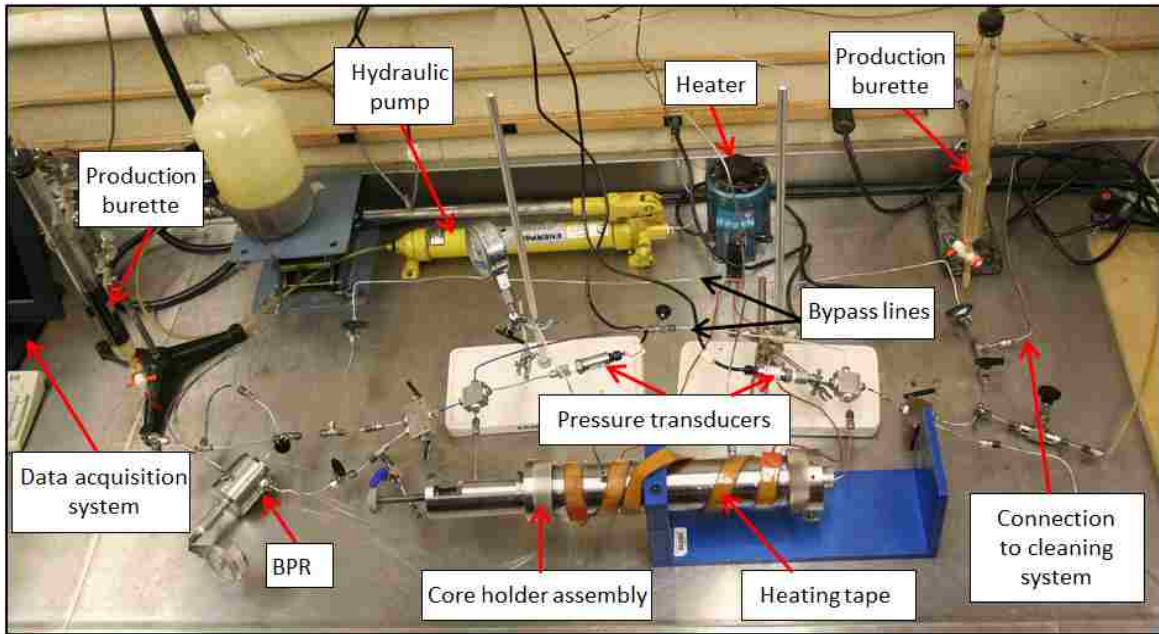


Figure 11: Coreflood apparatus

**Data acquisition system:** This system uses the output signals from the two pressure transducers placed at the inlet and outlet of the coreholder. The signals are converted to pressure values and recorded at the set time interval (every 5 seconds) in a Microsoft Excel® worksheet. Figure 12 presents the data acquisition system.

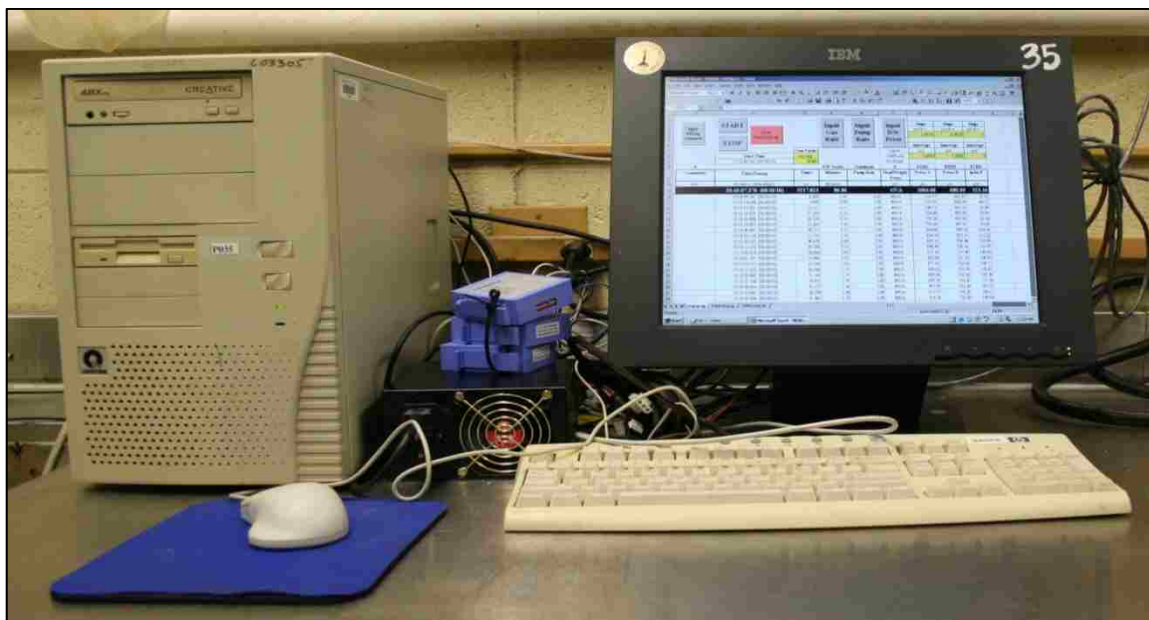


Figure 12: Data acquisition system

**Cleaning system:** Two methods are used to clean the core, and therefore, two systems were built. The first system is illustrated by Figure 13 and this consists of four cleaning fluids that are injected into the core by a pulsing pump. The type of cleaning system used is the flow through the core method. The cleaning solvents used in this system are: dilute brine, methylene chloride, isopropyl alcohol, toluene, and methanol. The second system illustrates the soxhlet extraction cleaning system. This system uses the soxhlet extraction core cleaning method. The solvent used in this system is toluene and methanol mixture.

**Core:** Berea sandstone cores from Cleveland Quarries were used in this study. The dimensions of the core were: one-foot long, one and a half inches in diameter, permeabilities ranged from 40 – 70mD, and porosity ranged from 16 -17%.

**Oil and brine:** The two types of oil used were decane and Yates crude oil. The Yates crude oil used in all the experiments was from the same batch that Ayirala (2002) used in his work. Additional Yates crude oil was provided by Kinder Morgan Inc. for future experiments. The Yates brine used was fashioned after the Yates brine composition provided by Marathon Oil Company.

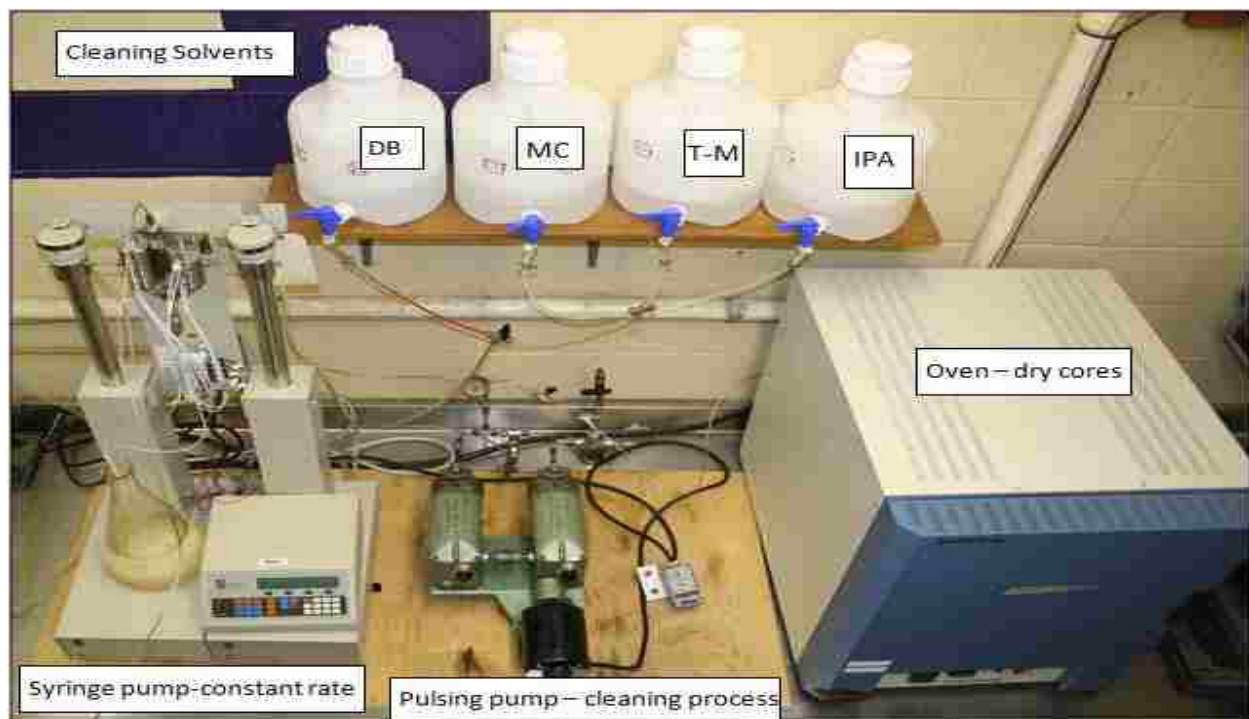


Figure 13: Core cleaning system – flow through core cleaning method

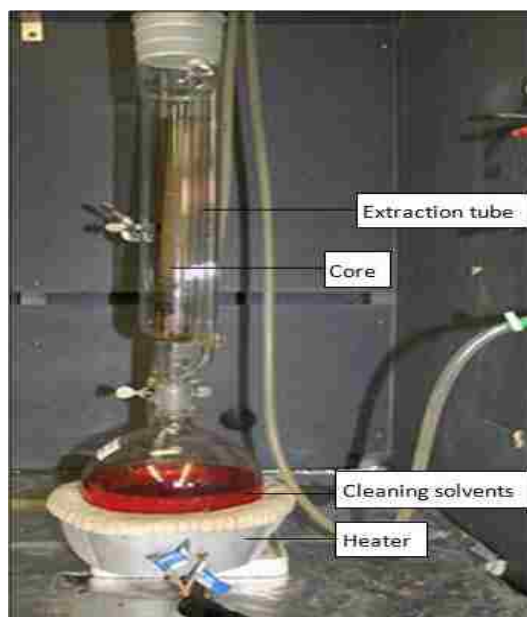


Figure 14: Soxhlet extraction cleaning system

**Surfactant:** Four nonionic surfactants were provided by Interstate Chemical Company and Sasol Chemical Company. The four nonionic surfactants were tested to find the surfactant that produced similar recoveries to that used by Ayirala (2002). Table 1 illustrates the four nonionic surfactants and their properties.

Table 1: Surfactant properties

Company	Surf. used by Ayirala	Interstate Chemical	Sasol Chemical		
Chemical Name	NEODOL	Tomadol™ 91-8	NOVEL® 23E7	NOVEL® 23E9	NOVEL® 23E30
EO Group/Avg	8.4	8.3	7	9	30
Molecular weight	527	524	501	589	1512
Carbon Chain	C <sub>9</sub> - C <sub>11</sub>	C <sub>9</sub> /C <sub>10</sub> /C <sub>11</sub>	C <sub>12</sub> - C <sub>13</sub>	C <sub>12</sub> - C <sub>13</sub>	C <sub>12</sub> - C <sub>13</sub>
Sp. Gravity	1	1.008	1	1	1

## 3.2 Experimental procedure

- 1. Pore volume and porosity determination:** The core was loaded into the coreholder and vacuum was applied using a vacuum pump. After vacuum was achieved the pump was shut off and the system was

left to sit for a few hours under vacuum. After several hours, the pressures were evaluated to check if vacuum had been maintained. If not, there was a leak in the system. The leak would be fixed and the previous step would be repeated until the vacuum was maintained. Brine was then injected at a very low rate 0.1cc/min and the injected volume was noted. When the core was completely filled with brine, the pressure would rapidly increase. At this point, the volume injected would be recorded and the following calculations were made.

- Pore volume = Volume injected – Dead volume
- Bulk volume = Area of core \* length of core

$$\text{Porosity} = \frac{\text{Pore Volume}}{\text{Bulk volume}} \quad \text{Equation 1}$$

**2. Absolute permeability determination:** Brine was injected through the core using 3 different rates (q) for 1 pore volume each. The stabilized pressure drops ( $\Delta P$ ) were averaged for each rate, which was then used to calculate the absolute permeability ( $K_{\text{abs}}$ ) using Darcy's law. The 3 rates and their pressure drops would all give the same permeability.

$$\text{Darcy's law} \rightarrow q = \frac{KA \Delta P}{\mu \Delta x} \rightarrow K_{\text{abs}} = \frac{q\mu \Delta x}{A \Delta P} \quad \text{Equation 2}$$

**3. Establishing initial condition:** After the completion of the absolute permeability test, the core was saturated with brine and was ready for oil saturation. Oil was injected at 2 cc/min for 3 pore volumes. At this point the core would be at connate water saturation, therefore, brine would not be observed in the effluent produced by the second to third pore volume of oil injection. In order to calculate the effective permeability ( $K_{\text{eff}}$ ), the rate was changed to 3 cc/min and 4 cc/min and injected for 1 pore volume each in order to get the stabilized pressure drop for each rate. The effective permeability was calculated using Darcy's equation. Having both the effective and absolute permeabilities, the endpoint oil relative permeability was then calculated. In addition, the brine produced was measured and used to calculate the connate water saturation. At this point, the oil was left to age prior to the coreflood experiments.



$$\text{End point relative permeability} \rightarrow K_{ro}^* = \frac{K_{eff}}{K_{abs}} \quad \text{Equation 3}$$

4. **Waterflood or surfactant flood:** After the initial conditions had been established, the core was ready for a waterflood or surfactant flood. Prior to the injection of brine or surfactant, all the lines were flushed with the fluid about to be injected. This avoided contamination and reduced the dead volume. After flushing all the lines, the valves, data acquisition system, back pressure regulators were double checked to make sure everything was at its proper position. Once everything was readied, brine or surfactant injection was began and likewise, the data acquisition system. Each brine flood or surfactant flood was conducted for 2 pore volumes at 2 cc/min. In order to calculate the effective permeability ( $K_{eff}$ ), the rate was changed to 3 cc/min and 4 cc/min and injected for 1 pore volume each in order to get the stabilized pressure drop for each rate. The effective permeability is calculated using Darcy's equation. Having both the effective and absolute permeabilities, the endpoint water relative permeability was calculated. In addition, the oil produced would be measured and used to calculate the total oil recovery and the residual oil saturation. At this point, the core was ready to be cleaned and restored to its initial state prior to the next coreflood experiment.

**Improved waterflood procedure:** After initial conditions were achieved, a slug of surfactant of a specified size was injected in the production end as shown in Figure 15. It was observed that the surfactant slug could not be injected without producing oil on the injector side due to the high pressure build up. The coreflood apparatus used in this project has a pressure limit of 5000psi. After the surfactant slug had been injected and some oil had been produced on the other end, a new initial water saturation and oil in place were calculated. Thereafter, the surfactant was left to soak for the required period of time.

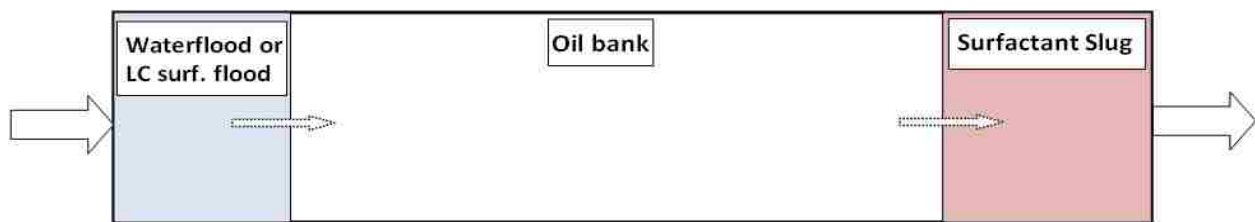


Figure 15: Schematic of an improved waterflood or improved LC surfactant flood in the core

At this point, waterflooding or LC surfactant flood would be executed for 2 pore volumes at 2 cc/min as shown in Figure 15. In the case of WASP, the surfactant slug was injected around the injection well instead of the production well as shown in Figure 16. The surfactant was left to soak for the required period of time. A waterflood was then carried out for 2 pore volumes at 2 cc/min.

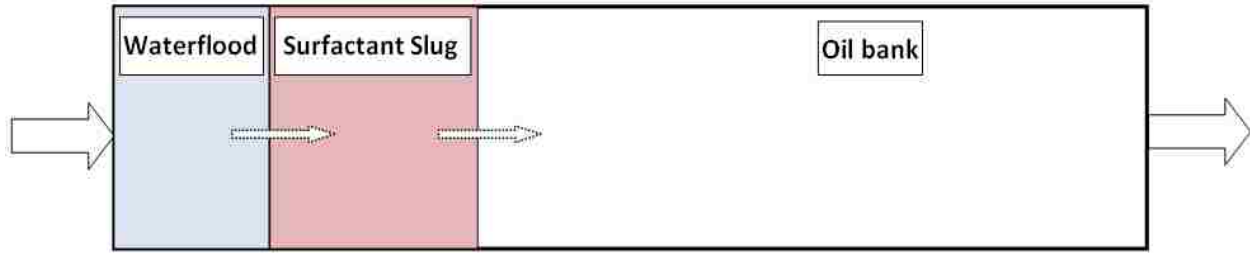


Figure 16: Schematic of the water alternating surfactant process (WASP) in the core

After the waterflood or LC surfactant flood, the effective permeability ( $K_{eff}$ ) was calculated. Having both the effective and absolute permeabilities, the endpoint water relative permeability was then calculated. In addition, the oil produced was measured and used to calculate the total oil recovery and the residual oil saturation. The new initial water saturation and oil in place calculated after the injection of surfactant slug, accounted for the new initial condition where water saturation had been increased and oil saturation decreased. Therefore, the recovery measured after the waterflood or LC surfactant flood only accounted for the effectiveness of the waterflood after surfactant slug injection. At this point, the core was ready to be cleaned and restored to its initial state prior to the next coreflood experiment.

5. **Core cleaning procedure:** Establishing a core cleaning procedure that was both effective and efficient proved to be a challenging and significant part of this project. Table 2 lists the cleaning solvent properties used in the following procedures. The following sections will describe the three cleaning procedures used in this project.



### **Fresh core procedure – flow through core method**

Fresh cores were cleaned since there was no previous knowledge of what fluids the core had been exposed to. Prior to cleaning a fresh core the pore volume would first be measured using brine. The procedure that was found to be most efficient and effective is described below:

Table 2: Cleaning solvent properties

<b>Cleaning solvent</b>	<b>Density (g/cm<sup>3</sup>)</b>	<b>Viscosity (cP) @ 20°C</b>	<b>Boiling point (°F)</b>	<b>Solubility in water</b>
Methylene Chloride	1.327	0.437	104.0	13 g/L at 20 °C
Toluene	0.867	0.590	231.1	0.47 g/l (20–25°C)
Methanol	0.791	0.590	148.4	Miscible
Isopropyl alcohol	0.786	2.410	181.0	Miscible
Acetone	0.792	0.307	134.0	Miscible

- 1. Methylene chloride** – was injected for about 1.5PV in each direction in order to displace the brine and dissolve impurities in the core. At this point only methylene chloride would be left in the core.
- 2. Dilute brine** –was flushed for about 2 – 3 pore volumes in each direction to displace methylene chloride. If methylene chloride was observed in the effluent produced, injection of dilute brine would be continued until the effluent is free of methylene chloride. With injection of dilute brine, the pressure drop would increase gradually and stabilize at a higher pressure drop than the previous step. This is due to the less dense fluid (dilute brine) displacing a denser fluid, coupled with the rock-fluid interactions.
- 3. Vacuum** – the core was vacuumed for a minimum of 2 hours. This step was most effective when the core was vacuumed for longer periods of time (about 6 hours). This step is significant because it decreased the pressure drop of the core, meaning that the permeabilities were being improved. This may be because vacuuming dislodges whatever may be blocking the fluid pathways. Also, traces of methylene chloride left in system would be drawn out by the vacuum pump.
- 4. Brine** – was flushed for about 2-3 pore volumes in order to saturate the core with brine. The pressure drops at this point would be lower than the ones observed during the dilute brine step.

## 5. Absolute permeability test – see section 3.2.2

### **Oil and surfactant exposed core – flow through core method**

At the end of each surfactant flood, oil and brine containing surfactant were left in the core. Prior to starting a new coreflood, the core needs to be thoroughly cleaned and restored to its initial state. It was observed that the absolute permeability would inevitably decrease with each cleaning cycle. The objective was to find an efficient and effective procedure that would minimize this drop in permeability. At the end of the coreflood, the pressure drop in the core was typically high especially if emulsions were formed in the system. This high pressure drop indicates that the permeability had been severely affected. Therefore, by cleaning the core the pressure drop is decreased indicating that the permeability is being restored to its initial state. After testing different combinations of chemicals at different sequences, the most effective and efficient core cleaning procedure is described below.

1. **Brine** – inject about 1.5 pore volumes in both the forward and backward direction. The purpose of this step is to dilute the surfactant concentration present in the core. At this step the pressure drop was observed to remain high.
2. **Dilute brine** - inject 2 pore volumes in the forward direction to dilute the concentration of brine. If the brine concentration is low, this process was found to be unnecessary. Instead, the volume of brine injected in the previous step can be increased from 1.5PV to 2PV. The pressure drop still remains high at this stage as observed in Figure 17.
3. **Methylene chloride** – inject this solvent in the forward direction until the effluent clearer in color. Same applies for the backward direction. Methylene chloride is used as a buffer between the brine and the cleaning fluids in order to avoid precipitation of salts. Methylene chloride is an organic solvent that dissolves oil and therefore creates an emulsive state. As a result, when methylene chloride is injected in the core, the pressure drop gradually increases because this emulsive state is being formed in the core. After this emulsive mixture breaks through, the pressure drop rapidly decreases. This can be observed in Figure 17 and Figure 18. The drastic decrease in pressure drop by

the end of this step is a result of brine and a large fraction remaining oil being displaced. At the end of this step, methylene chloride, connate water, and a small percentage of oil are left in the core.

4. **Isopropyl alcohol (IPA)** – inject this solvent in the forward direction until connate water is produced and effluent is clear. IPA is used as a dehydrating agent and it also displaces some of the left over oil in the core as evidenced by the coloring of the effluent. When IPA is first injected, it displaces methylene chloride, then connate water, followed by IPA tinted with left over oil. At the end of this step only IPA and a very small fraction of oil are left in the core. IPA is a less dense fluid compared to methylene chloride, thus it is important to apply backpressure for effective cleaning. As IPA is injected into the core, the pressure drop gradually increases as observed in Figure 17. The reason is still unknown but it is hypothesized to be the interaction between IPA and the rock grains that causes this phenomenon to happen. As a result, only enough IPA should be injected to get rid of connate water. The better dehydrating solvent was observed to be acetone. However, it could not be used in this project because it was not compatible with the Viton core sleeve. To solve this problem, teflon heat shrink tubing was used to isolate the core from the Viton core sleeve. This worked very well for two cleaning runs until the core sleeve failed. This was because there was a slight section in the core sleeve that was exposed to acetone. Even though acetone proved to be more effective, it does pose the danger of causing failure to the Viton sleeve. To use acetone effectively, a teflon core sleeve should be used. Figure 18 illustrates the pressure profile when acetone was used instead of IPA which is shown in Figure 17.
5. **Methylene chloride** – inject about 1PV in each direction in order to displace the IPA in the core. As methylene chloride is displacing IPA the pressure drop does decrease. At the end of this step, only methylene chloride and a small fraction of oil is left in the core.
6. **50% toluene and 50% methanol** – flush this solvent until clear effluent is produced. For this project, about 3-4 pore volumes were used in each direction especially when cleaning Yates crude oil. This mixture of chemicals is used to dissolve residual oleic phase in the core. Toluene used alone was found to be the least effective solvent when the core is cleaned for wettability restoration (Gant and

Anderson, 1988). However, when combined with other solvents such as methanol, it was found to be very effective. This is because toluene is effective in removing the hydrocarbons, including asphaltenes and some of the weakly polar compounds. However, methanol effectively removes the strongly adsorbed polar compounds that are often responsible for altering wettability. At the end of this step, only toluene/methanol solvent should be left in the core.

7. **Methylene chloride** – inject about 2PV in each direction in order to displace the toluene/methanol solvent in the core. At this point only methylene chloride should be left in the core and the pressure drop should be low.
8. **Dilute brine** – flush about 2 – 3 pore volumes in each direction to displace methylene chloride. If methylene chloride can still be observed in the effluent produced, continue flushing the core with dilute brine until the effluent is free of methylene chloride. At this point, the pressure drop gradually increases. This is due to the lighter fluid (dilute brine) displacing a denser fluid. With injection of dilute brine, the pressure drop does increase gradually and stabilizes at a higher pressure drop than the previous step.
9. **Vacuum** – vacuum the core for a minimum of 2 hours. This step is most effective when the core is vacuumed for longer periods of time (about 6 hours). This step is effective in that it decreases the pressure drop of the core, meaning that the permeabilities are being improved. This may be because vacuuming dislodges whatever may be blocking the fluid pathways. Also, traces of methylene chloride left in the system should be drawn out by the vacuum pump.
10. **Brine** – flush about 2-3 pore volumes in order to saturate the core with brine. The pressure drop during this step should be lower than the ones observed during the dilute brine step.
11. **Absolute permeability test** - see section 3.2.2

Prior to any of these steps being executed, the incoming solvent needs to be flushed through the bypass lines in order to avoid contamination or precipitation of salts. For effective cleaning, the back

pressure needs to be applied at all times, especially when a less dense fluid is displacing denser fluid (methylene chloride) in order to avoid fingering when cleaning.

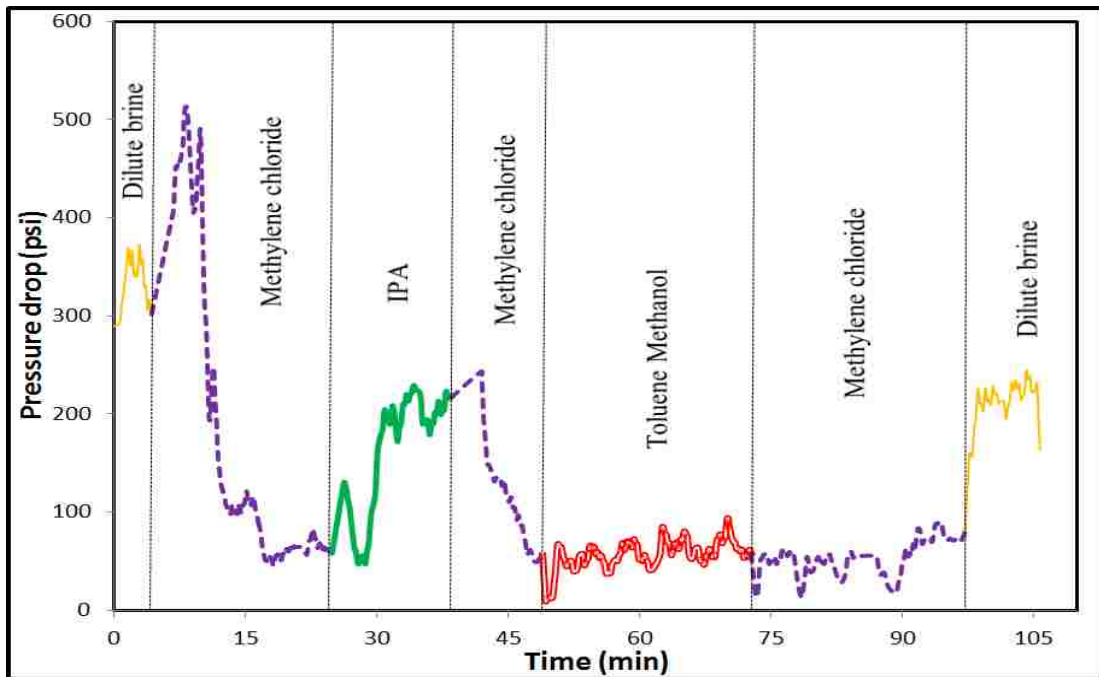


Figure 17: Pressure drop profile of the core cleaning procedure using IPA as a dehydrant

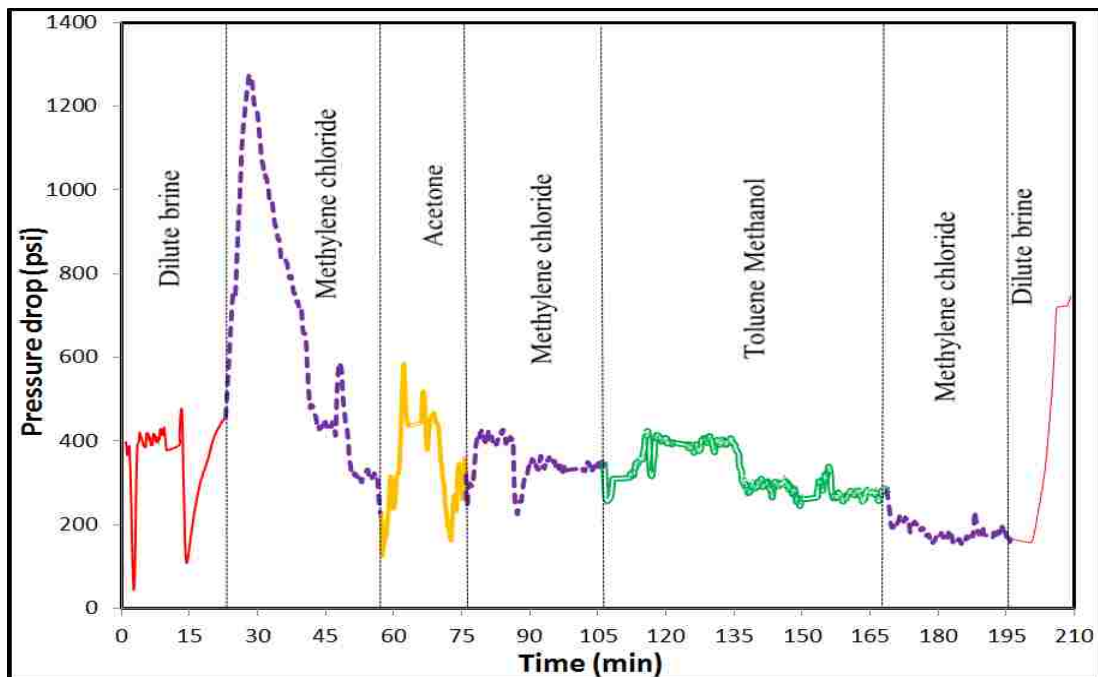


Figure 18: Pressure drop profile of the core cleaning procedure using Acetone as a dehydrant

### **Oil and surfactant exposed core – Soxhlet extraction method**

The soxhlet extraction method is relatively slow and gentle on the core. In this method, the contaminated core is placed in the soxhlet apparatus as shown in Figure 14 and is cleaned with hot, refluxing toluene and methanol mixture. The core is soaked in the hot toluene and methanol mixture, which is periodically siphoned off, distilled, condensed, and distributed back to the extractors. This method of cleaning would gently clean the core and restore the permeabilities to their initial state. It was observed that after using this method of cleaning the core was usually less water wet. Gant and Anderson (1988) attributed this phenomenon to the solvent (usually toluene) boiling away the water before extracting the crude oil. In the absence of adsorbed water, crude oil components become strongly adsorbed on the mineral surfaces at sites that normally would be occupied by water. Subsequent contact of the surfaces with water may not displace adsorbed crude oil components to restore the wettability. At the end of this soxhlet extraction cleaning process, the core is dried in the oven shown in Figure 13. The soxhlet system is especially useful when the core is contaminated with strong emulsions which cause very high pressure drops. Using the flow through core system can cause fractures in the core due to the high pressure drops.

All in all, three cores (A, B, and C) were used to run all the experiments in this project. Each core would be used for three to four experiments. After each experiment the flow through cleaning method would be used. Afterwards, the core would be taken out of the core-holder and placed in the soxhlet system where it would be cleaned for about one week. Then the core would be placed in the oven to slowly dry for about a week. Therefore, when core A was in the coreholder, core B would be in the soxhlet system getting cleaned, as core C would be in the oven drying. All three cores were rotated in this manner for the entire project.

### 3.3 Experimental design

The coreflood experiments in this project were used to evaluate the technical feasibility and effectiveness of the improved waterflooding process. All the experiments were conducted at reservoir conditions of 82°F and 700psi.

Prior to running the main sets of experiments three key components had to be established. The first component was to establish the surfactant that exhibited similar characteristics to those observed in Ayirala's work. Three of the four nonionic surfactants were tested. NOVEL<sup>®</sup>23E7 was not tested because it is very similar to NOVEL<sup>®</sup>23E9. On the other hand, NOVEL<sup>®</sup>23E30 had very different properties to the other three surfactants and so it was tested to observe its behavior. As shown in Table 3, Tomadol<sup>™</sup> 91-8 had the same recovery as the surfactant used by Ayirala, however, emulsions were formed. The other two NOVEL<sup>®</sup> surfactants had lower recoveries and formed strong emulsions. From this test, Tomadol<sup>™</sup> 91-8 was determined to be the most suitable surfactant for this project.

Table 3: Surfactant selection results

Surfactant type	3000ppm surfactant flood	Other differences
Surf. used by Ayirala	94%	No emulsions formed
Tomadol <sup>™</sup> 91-8	94%	Emulsions formed
NOVEL <sup>®</sup> 23E09	74%	Strong emulsions formed
NOVEL <sup>®</sup> 23E30	50%	Very strong emulsions formed – white solid at room temperature

The next parameter determined was the aging time for Yates oil. The core was brought to initial conditions using Yates crude oil, and was aged for 24 hours and 2 weeks. A waterflood was then carried out and the recoveries were measured. As shown by Table 4 the recoveries of both Yates oil aging times are similar. The relative permeability ratio curves in Figure 19 show that the wettability of the system is more or less the same. Therefore, the minimum Yates oil aging period was established to be 24 hours.

Table 4: Yates crude oil aging period

Aging time period	Experimental					Simulator				
	Recovery (%OOIP)	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	X-over Point
2 weeks	57.14%	0.471	0.226	0.531	0.104	0.47	0.209	0.98	0.13	0.650
24 hours	56.41%	0.413	0.251	0.502	0.079	0.41	0.195	0.98	0.13	0.693

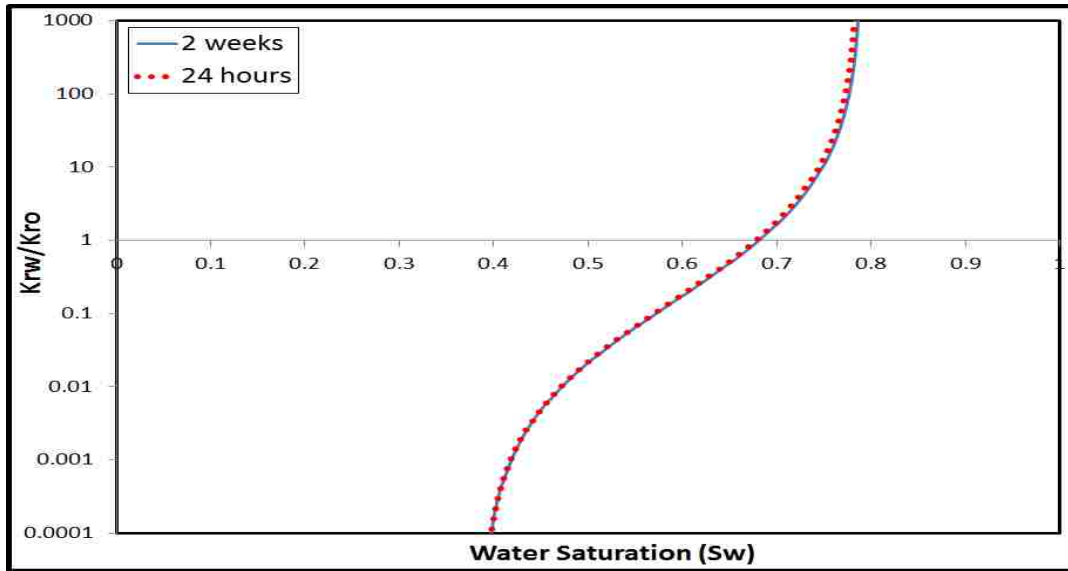


Figure 19: Relative permeability ratio curves for the Yates crude oil aging period

The last and most time consuming parameter to achieve was a suitable core cleaning procedure. The three core cleaning procedures developed and used in this project are described in section 3.2.

All the experiments are divided in four sets as illustrated by Table 5. **Set 1** was used to determine the ideal surfactant concentration in two rock fluid systems: reactive and non-reactive. Three concentrations (0, 1000, 3000ppm) were tested in both rock fluid systems. The concentration yielding the highest recovery was considered the ideal concentration. Surfactants improve recovery by lowering interfacial tension and changing the wettability. However, wettability is governed by factors such as brine, oil, surfactant, rock properties etc. All these variables are kept constant in both rock fluid systems except the type of oil used. In the non-reactive case, decane oil used which is considered non-reactive, and therefore it does not influence wettability. Hence, the increase in recovery due to wettability change is



strictly due to the use of surfactants. On the other hand, Yates crude oil is used since it influences wettability and therefore creating a reactive system. Thus, the increase in recovery observed is due to wettability change is a result of the combination of Yates crude oil and surfactant used.

Table 5: Experimental design – 4 sets of experiments

<b>Set 1</b>	Reactive (Yates) rock fluid system	0ppm
		1000ppm
		3000ppm
	Non-Reactive (decane) rock fluid system	0ppm
		1000ppm
		3000ppm
<b>Set 2</b>	Fixed surfactant slug size, varying soaking period	1 hour
		12 hours
		24 hours
<b>Set 3</b>	Fixed soaking period, varying surfactant slug size	0.1PV
		0.2PV
		0.3PV
<b>Set 4</b>	Seven IOR methods	Conventional waterflood – 2PV
		Improved waterflood - 0.2PV surfactant slug soak around the production well
		Improved waterflood - 0.3PV surfactant slug soak around the production well
		LC (1000ppm) surfactant flood – 2PV
		Improved LC surfactant flood - 0.2PV surfactant slug soak around the production well
		Water alternating surfactant process (WASP) - 0.2PV surfactant slug soak around the production well
		Ideal (3000ppm) surfactant flood – 2PV

**Set 2** was used to determine the ideal surfactant slug soaking period prior to a waterflood. After the initial conditions were achieved in the core, a 0.2PV surfactant slug was injected around the producing

well and soaked for 1 hour, 12 hours, and 24 hours in separate experiments. After the soaking period was completed, a waterflood was performed.

**Set 3** investigated the effects of varying the surfactant slug size injected around the production well. After the initial condition was achieved in the core, the surfactant slug was injected, soaked for 12 hours, then a waterflood was carried out. Three surfactant slug sizes were tested: 0.1PV, 0.2PV, and 0.3PV in separate experiments.

**Set 4** used the established conditions from the three previous sets, and applied them to the four improved waterflood variations. The first and second improved waterflood variations used a 0.2PV and 0.3PV surfactant slug, respectively, to soak the area around the production well prior to a waterflood. The third variation used a low concentration (LC) surfactant solution to flood the core after soaking the area around the production well with a 0.2PV surfactant slug. This method was named as the improved LC surfactant method. The fourth variation used a 0.2PV surfactant slug to soak the area around the injection well instead of production well prior to the waterflood. This method was named water alternating surfactant process (WASP). Each waterflood or LC surfactant flood was carried out for 2PV after the surfactant slug soaking period. The three baseline methods consisted of: a conventional waterflood, a LC (1000ppm) surfactant flood, and an ideal (3000ppm) surfactant flood. All baseline methods were also carried out for 2PV.

### **3.4 Coreflood simulator**

Obtaining accurate relative permeability curves from coreflood experiments is imperative for characterizing a reservoir and for estimating its production capability. This project is concerned with the unsteady state relative permeabilities that are obtained from waterflood and surfactant flood experiments conducted in a water wet medium. For each of the above experiments, recovery and pressure drop data were collected and used in a coreflood simulator. The coreflood simulator used is the academic version of CYDAR® (2010). Input parameters for the coreflood simulator were: rock and fluid properties, recovery data, pressure drop data, end point phase permeabilities, absolute permeability, injection rate, and the

breakthrough time of each run. The coreflood simulator was used to calculate the oil-water relative permeabilities, fractional flow, and relative permeability ratios curves. This user friendly simulator calculates Corey type oil and water relative permeabilities that best fit the production and pressure data using the JBN method. The data must be smooth and continuous in its overall trend because the JBN method requires differential of either the total flow rate or the pressure drop. The JBN method uses an explicit numerical method of calculating relative permeability values using the effluent history. A disadvantage of explicit methods is that derivatives of measured data must be estimated. It is well known that the effect of small measurement errors become amplified when derivatives of measured data are to be estimated (Tao and Watson, 1983). Due to the idealized nature of the JBN method, the relative permeability ratio curves will be used qualitatively in this project to describe the change in wettability.

## 4. RESULTS AND DISCUSSION

The objective of this project is to investigate the technical feasibility of the proposed improved waterflood variations and examine their effectiveness when compared to a conventional waterflood. In order to achieve this goal, a few parameters had to be established. **Set 1** determined the ideal surfactant concentration in two rock fluid systems. **Set 2** determined the ideal soaking period of a 0.2PV surfactant slug soak around the production well. **Set 3** examined the effect of varying the injected surfactant slug size around the production well. After these three parameters were optimized, the four improved waterflood variations and the three baseline methods were tested in **set 4**. The experimental results of each set are presented and discussed in this section. The rules of thumb used to interpret the wettability alterations are presented in Table 6. These rules of thumb only apply to oil wet, water wet, and intermediate wet conditions. For each set of experiments, four key components were analyzed to show the effectiveness of the experiment. These key components are recovery, pressure drop, relative permeability ratios, and fractional flow trends. Recovery trends are straightforward to interpret since the higher the recovery the more effective the process at improving oil recovery. Pressure drop trends can be used to confirm whether emulsions were formed during the coreflood. Relative permeability ratio curves are used to interpret the effect of lowering interfacial tension and modifying wettability. Lastly, fractional flow curves, which are calculated from relative permeability and viscosity values, are used to describe the immiscible fluid displacement process and interpret wettability alterations. Yates oil viscosity of 12.8cp and a water viscosity of 1cp were used to calculate relative permeability and fractional flow values.

Table 6: Craig's rules of thumb used for wettability interpretation, adopted from Ayirala (2002)

Criterion	Water-wet	Oil-wet
Initial water saturation ( $S_{wi}$ ), fraction	$> 0.25$	$< 0.15$
Water saturation at cross-over point, fraction	$> 0.5$	$< 0.5$
End-point relative permeability to water at $S_{or}$ , fraction	$< 0.3$	$> 0.5$
End-point relative permeability to oil at $S_{wi}$ , fraction	$> 0.95$	$< 0.7 - 0.8$

Lastly, the recovery and pressure drop figures showing the history match between the simulated and experimental data are presented in the Appendix section.

#### 4.1 Set 1: Ideal surfactant concentration determination

The objective of this set of experiments was to find the ideal surfactant concentration. This was achieved in two rock-fluid systems: non-reactive and reactive. The difference in these rock fluid systems is the oil used and its effect on wettability. Therefore, in the non-reactive case decane oil is considered non-reactive and therefore does not affect wettability. On the other hand, Yates crude oil is reactive meaning its interaction with the rock surface affects the wettability of the system. Any increase in recovery due to the use of surfactant can be attributed to lowering of the interfacial tension and wettability modification. However, in the reactive case, the observed wettability change is due to the combination of Yates crude oil and surfactant used. On the other hand, in the non-reactive case the change in wettability is strictly the result of using surfactant.

##### 4.1.1 Reactive rock-fluid system (Yates crude oil)

In the reactive rock fluid system, stable oil-water emulsions were formed when surfactant was introduced in the system. The higher the surfactant concentration injected the stronger (more viscous) the emulsions formed. These emulsions were observed after 12 hours, 24 hours, and 2 weeks and they did not show signs of breaking up, therefore, indicating they are stable emulsions.

Table 7: Experimental and simulation results for the reactive case at various surfactant concentrations

Reactive case (Yates oil)	Experimental					Simulator				
	Recovery (%OOIP)	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	X-over Point
0ppm	47%	0.175	0.431	0.943	0.097	0.175	0.430	0.980	0.091	0.414
1000ppm	52%	0.175	0.395	0.734	0.033	0.175	0.394	0.987	0.102	0.427
3000ppm	94%	0.480	0.027	0.980	0.088	0.480	0.095	0.980	0.050	0.819

**Recovery:** Figure 20 shows the relationship between recovery and injected pore volumes. The oil recovery significantly increases from 47% to 94% as the surfactant concentration is increased from 0ppm to 3000ppm. In the 0ppm flood, oil was not produced after breakthrough, while in the 1000ppm flood very little oil was produced after breakthrough. This behavior is indicative of water wet conditions. However, in the 3000ppm flood a significant amount of oil was produced after breakthrough leading to very high oil recovery of 94%. This indicates oil wet characteristics in the large pores where from oil is still produced after breakthrough. This positive oil recovery trend in the 3000ppm case indicates that 100% recovery is possible if the reservoir is continuously flooded by water or surfactant solution. The 3000ppm coreflood was repeated to confirm the high recovery phenomenon observed, and the same result was observed again in the repeated run. These high recoveries, significant oil production after breakthrough, and low residual oil saturations, indicate a system that is neither oil wet nor water wet but rather mixed wet as postulated by Salathiel (Salathiel, 1973).

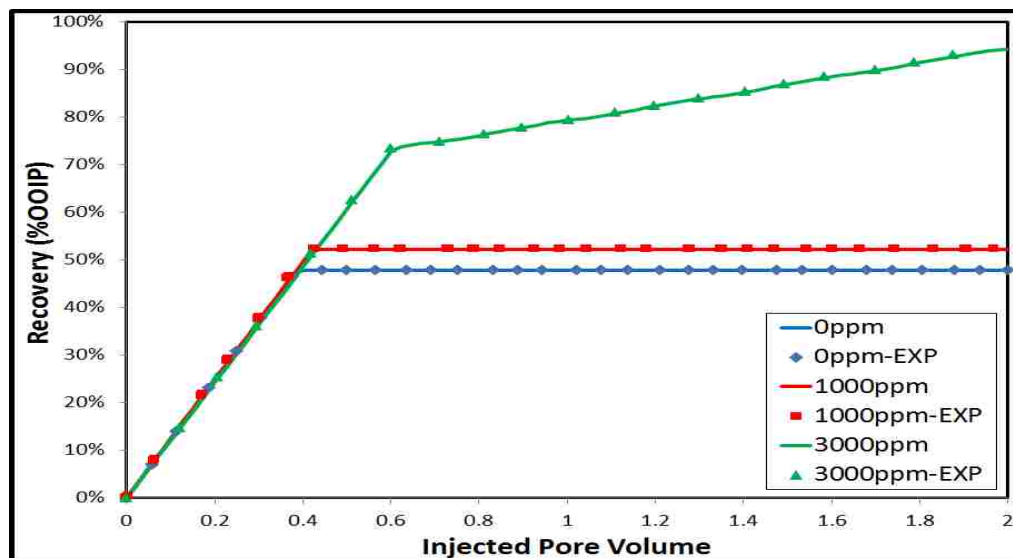


Figure 20: Experimental and simulation recovery curves of all surfactant concentrations in the reactive (Yates) system.

At initial conditions (when the core is at initial water saturation and surfactant is not present) the core is water wet. Hence, the rock surface is covered with a film of water and oil exists in the form of globules in the middle of the larger pores. In the presence of surfactant, this film could become unstable due to the

extent of adsorption of surfactant molecules at the rock-water interface compared to that at the oil-water interface. Also, the orientation of surfactant molecules at these interfaces does add to the instability of the water film. This instability of liquid film at the interface, results in oil-water-rock interactions forming a continuous oil-wet path for favorable displacement of oil. This indicates the mixed wet state first proposed by Salathiel (Salathiel, 1973).

**Pressure drop:** Figure 21 shows the relationship between pressure drop and injected pore volume. As observed, the pressure drop increases considerably as the surfactant concentration is increased. This is due to the formation of strong emulsions as the surfactant concentration is increased. In the 0ppm flood, emulsions were not formed hence the plateaued curve indicating that pressure drop had stabilized. However, as surfactant is introduced in the system, emulsions are formed resulting in increase of pressure drop with increasing injected pore volumes. Therefore, the steeper the pressure drop curve the stronger the emulsions formed.

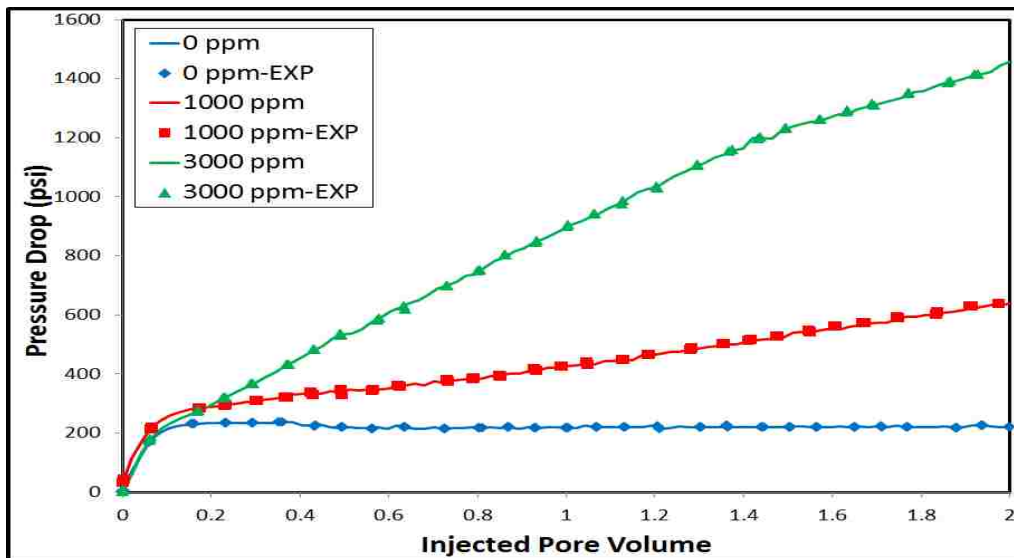


Figure 21: Experimental and simulation pressure drop curves of all surfactant concentrations in the reactive (Yates) system.

**Relative permeability:** Figure 22 illustrates relative permeability ratio curves of the three surfactant floods. It is observed that the relative permeability ratio curves are gradually shifting to the right as the surfactant concentration is increased. Considering the initial water wet nature of Berea sandstone cores,

this type of shift in the relative permeability ratio curves usually indicates the core is becoming more water wet, if only homogenous wettability is considered. However, considering the very high oil recovery values and the continual increase in recovery after breakthrough, this shift indicates the development of mixed wettability condition by use of surfactant (Anderson, 1971 and Rao, 1992).

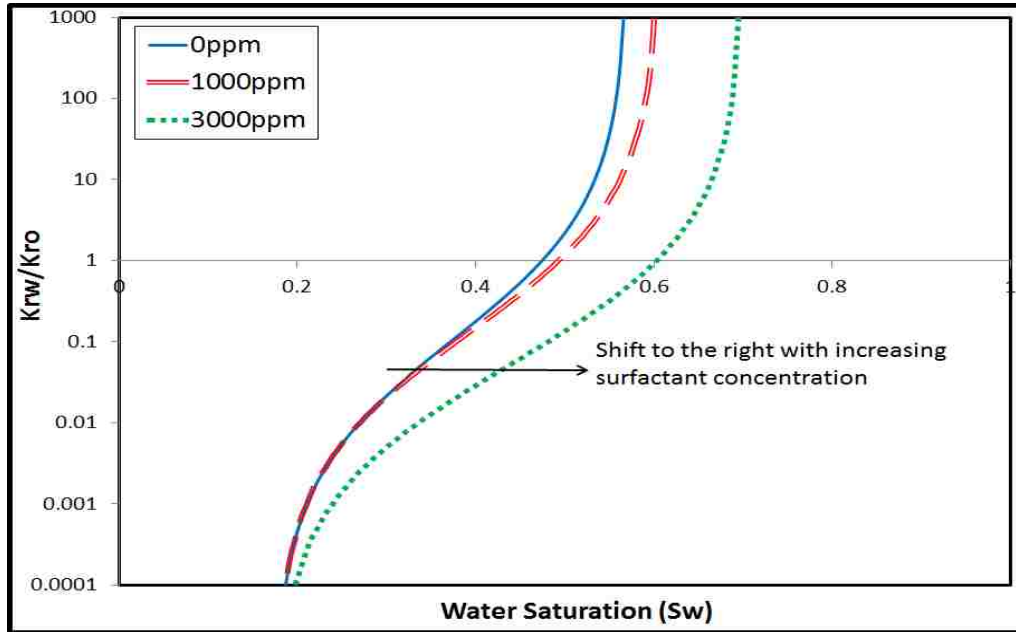


Figure 22: Relative permeability ratio curves for various surfactant concentrations in the reactive (Yates) system.

**Fractional flow:** Another practical approach to the assessment of the displacement efficiency of a coreflood is through fractional flow analysis. While the idealized nature of the fractional flow equation is recognized, it does provide insight into saturation distributions and wetting state of the core through the shape and position of the curve. Gravity and capillary effects are neglected in the fractional flow equation (equation 4) that is used to calculate the values used to plot Figure 23, Figure 24, and Figure 25. Figure 23 illustrates the effect of increasing surfactant concentration and assumed water viscosity on the fractional water flow curves.

$$F_w = \frac{1}{1 + \left(\frac{k_o}{k_w}\right)\left(\frac{\mu_w}{\mu_o}\right)} \quad \text{Equation 4}$$



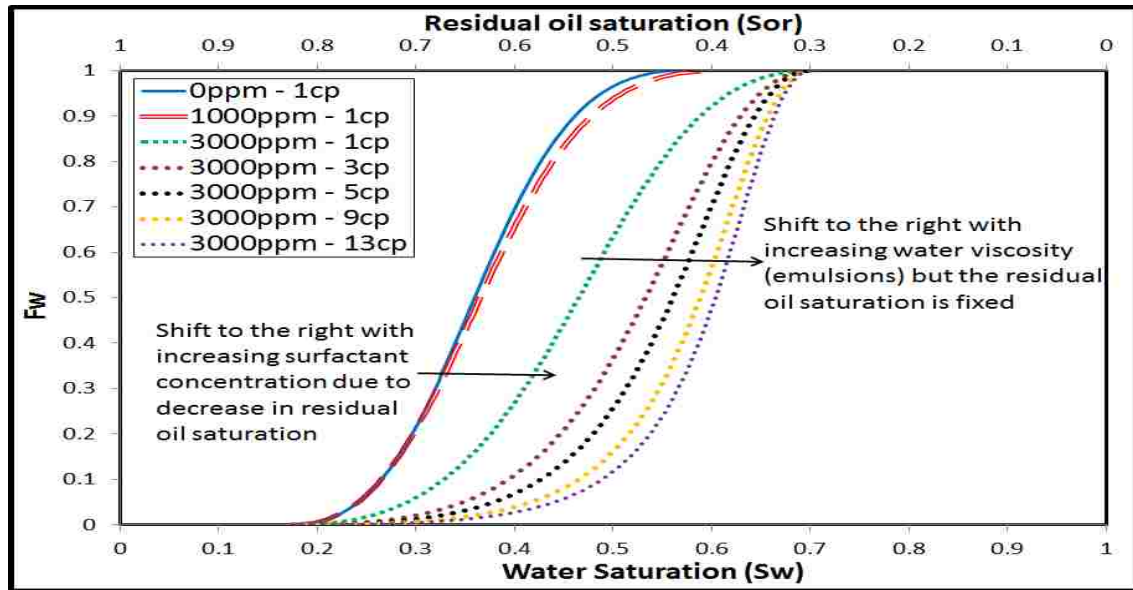


Figure 23: Fractional water flow curves of various surfactant concentrations and viscosities in the reactive (Yates) system.

Fractional flow analysis is used in this set of experiments to evaluate the effect of increasing surfactant concentration and formation of emulsion on recovery. As observed in Figure 24, the increase in surfactant concentration causes residual oil saturation to decrease and thus shifting the fractional flow curve to the right.

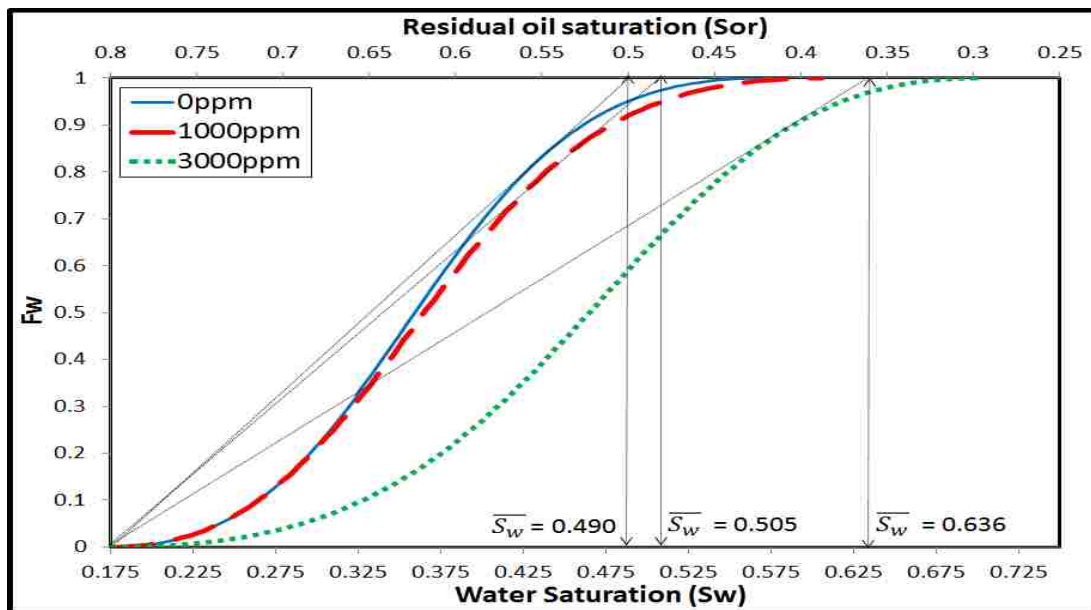


Figure 24: Fractional water flow curves of all surfactant concentrations in the reactive (Yates) system.

The decrease in residual oil saturation with increasing surfactant concentration is an indication of increasing oil recovery. The shift to the right in fractional flow curves indicates that wettability is changing with increasing surfactant concentration. All the above fractional flow curves start at the initial water saturation of 17.5%. However, as the surfactant concentration is increased the residual oil saturation decreases and therefore shifts the curve to the right. If homogeneous wettability is strictly considered, then this type of shift indicates that the rock fluid system is becoming more water wet. In a water wet system the  $K_{ro}$  values are larger while the  $K_{rw}$  values are lower than in an oil wet system, therefore larger fractional flow values are calculated which makes the shape of the curve less steep than in an oil wet case. In addition, a system that is shifting to more water wet conditions, the oil will be displaced from the smaller pores completely followed by the displacement of the larger pores. This renders the reservoir to have with less residual oil saturation than in an oil wet case. Due to this, the fractional flow curve for the oil wet case is much steeper than the water wet case. Consequently, the average saturation at the front (breakthrough saturation) is much higher for the strongly water wet system than the slightly water wet system as shown by Figure 24. Equation 5 calculates the cumulative oil produced at breakthrough time.

$$N_{pbt} = PV(\overline{S_w} - S_{wi}) \quad \text{Equation 5}$$

The cumulative oil produced at breakthrough time is calculated to be: 0.31PV at 0ppm, 0.33PV at 1000ppm, and 0.46PV at 3000ppm. The calculated breakthrough volumes compare well to the measured breakthrough volume, which validates the accuracy of the fractional flow curves. The implication of this is that more oil was produced at the breakthrough time in a strongly water wet system than a slightly water wet system. However, in a water wet system, there is no further (significant) oil recovery after breakthrough. This was only observed in the 0ppm and 1000ppm case. However, in the 3000ppm case, small slugs of oil were still being produced which ultimately lead to very high recovery of 94%. Strongly water wet and strongly oil wet rocks can be flooded by water to unusually low oil saturations. However, if mixed wettability is developed by the use of surfactants, recoveries such as those observed in the 3000ppm case can be achieved. In this condition the fine pores and grain contacts would be preferentially

water wet and the surfaces of the larger pores would be strongly oil wet. If oil wet paths were continuous through the rock, water could displace oil from the large pores and little or no oil would be held by capillary forces in the small pores or at grain contacts. This type of mixed wettability condition could account for the very low residual oil saturations observed in the 3000ppm case. Therefore, the shift in fractional curves due to the increase in surfactant concentration is due to the gradual shift in wettability from less water wet to mixed wet.

Another factor that influences the shape of the fractional flow curves is formation of emulsions which changes the viscosity of the displacing fluid, water. The coreflood simulator used to generate the fractional flow curves, does not have a way to account for the change in viscosity in the displacement fluid (water) due to the formation of emulsions. In order to illustrate the effect of emulsion formation, the viscosity of water was manually varied to 1cp, 3cp, 5cp, 9cp, and 13cp. As observed in Figure 25 with increasing water viscosity and a fixed residual oil saturation the shape of the fractional flow curve shifts to the right. As observed, with increasing water viscosity the average water saturation at breakthrough is higher which implies higher oil production. Using equation 5, the cumulative oil at breakthrough is calculated to be 0.405PV at 3000ppm (1cp) and 0.51PV at 3000ppm (13cp).

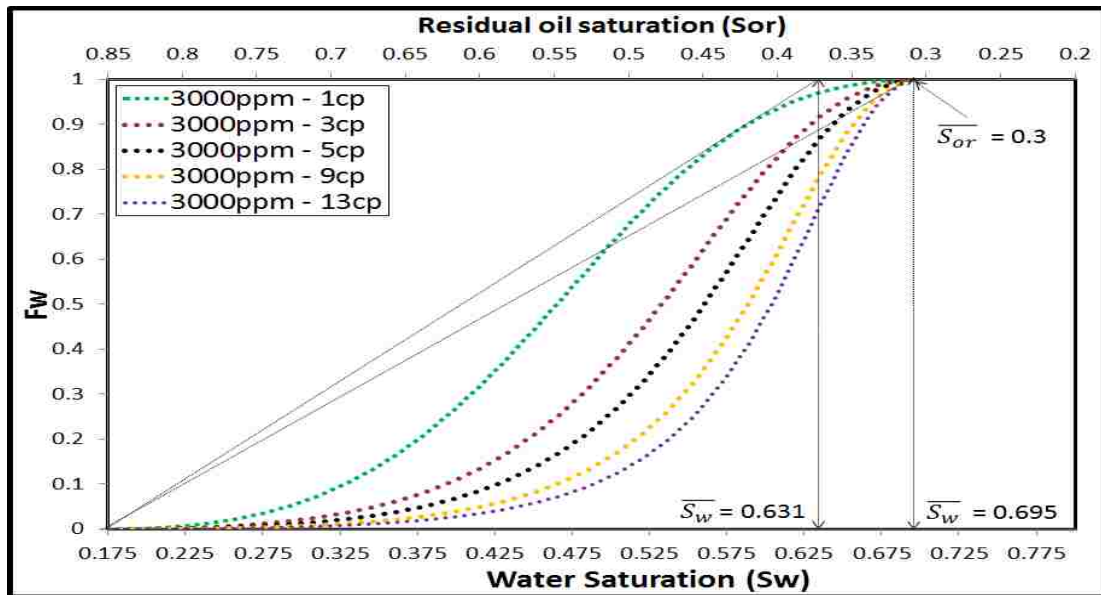


Figure 25: Fractional water flow curves of various viscosities at 3000ppm surfactant flood in the reactive (Yates) system.

The calculated cumulative oil at 3cp viscosity compared well to the measured breakthrough volume of the 3000ppm coreflood. It is important to note that viscosity of the emulsions increased as more surfactant solution was injected. A more representative fractional flow curve of the 3000ppm coreflood would be one that factors in the increase in displacing fluid viscosity with increasing pore volume injected.

#### 4.1.2 Non-reactive rock-fluid system (Decane)

The non-reactive rock fluid system consisted of Berea core, Yates synthetic brine, and decane oil. Emulsions were not formed in the 0ppm and 1000ppm surfactant floods, but weak emulsions were observed in the 3000ppm flood. Note that each flood was carried out for 2 pore volumes. Below are the results and discussions for the non-reactive experiments.

Table 8: Experimental and simulation results for the non-reactive case at various surfactant concentrations

Non-Reactive (Decane)	Experimental					Simulation				
	Recovery (%OOIP)	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	X-over point
0ppm	40%	0.283	0.428	0.764	0.101	0.283	0.429	0.981	0.101	0.439
1000ppm	46%	0.283	0.381	0.778	0.118	0.283	0.382	0.981	0.115	0.452
3000ppm	80%	0.580	0.083	1.000	0.006	0.580	0.085	0.981	0.130	0.751

**Recovery:** Figure 26 shows the relationship between recovery and injected pore volumes. The oil recovery gradually increases from 40% to 80% as the surfactant concentration is increased from 0ppm to 3000ppm. In the 0ppm flood there was a clean break in oil production after water breakthrough, and in the 1000ppm flood there was a very slight increase in recovery after breakthrough. However, in the 3000ppm case there was a significant increase in oil recovery even after water breakthrough. As discussed in the reactive rock fluid system, this is an indication of the development of mixed wettability due to use of surfactants. The increase in recovery due to the use of surfactants is attributed to reduction in interfacial tension and wettability modification. The change in wettability in this rock fluid system is strictly due to

the use of surfactant. The decane oil used is non-reactive, and therefore does not play a role in changing wettability.

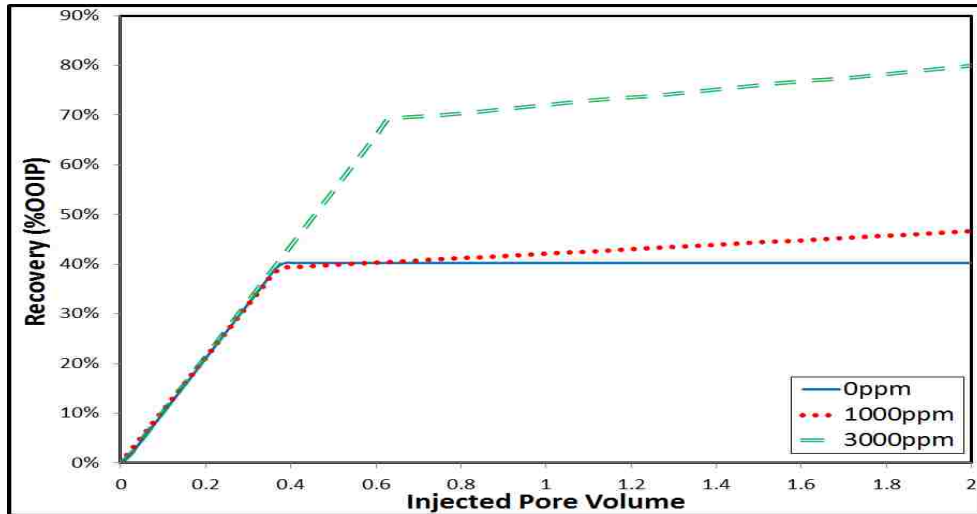


Figure 26: Recovery curves for all surfactant concentrations in the non-reactive (decane) system.

**Pressure drop:** Figure 27 shows the relationship between pressure drop and injected pore volume. As observed, the pressure drop decreases as the surfactant concentration is increased from 0ppm to 1000ppm indicating that no emulsions were formed. Thereafter, the pressure drop significantly increases as the surfactant concentration is increased from 1000ppm to 3000ppm indicating the formation of weak (lower viscosity) emulsions.

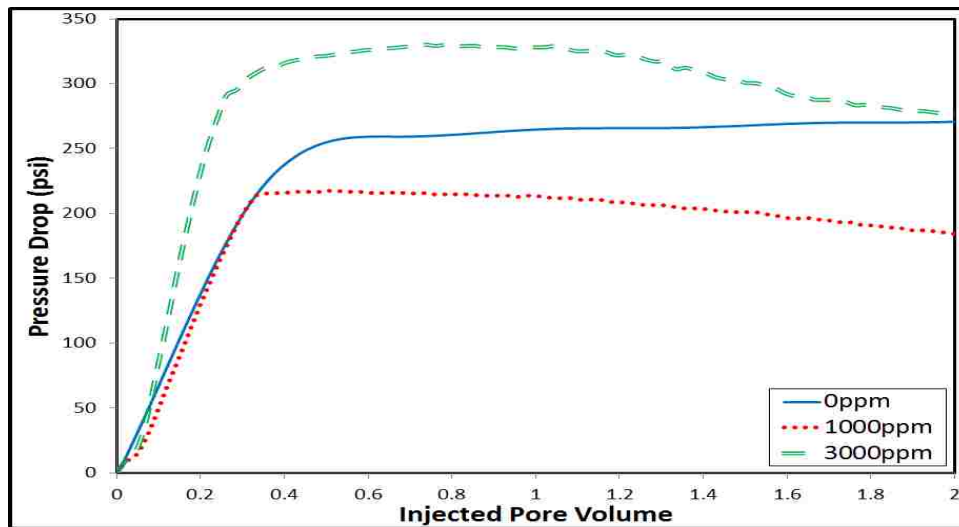


Figure 27: Pressure drop curves for all surfactant concentrations in the non-reactive (decane) system.

**Relative permeability:** The oil-water relative permeability ratio curves of these experiments are presented in Figure 28. A gradual shift to the right as the surfactant concentration is increased is observed. Considering the initial water-wet nature of Berea sandstone cores, this usually indicates a shift to more water wet conditions, but this is only when considering homogeneous wettability. But when one considers the high oil recoveries, with the significant increase in oil production after water breakthrough, this shift indicates the development of mixed wettability. To fully substantiate the development of mixed wettability, a higher concentration (5000ppm) flood needs to be conducted. In addition, the interfacial tension and contact angle measurements need to be carried out.

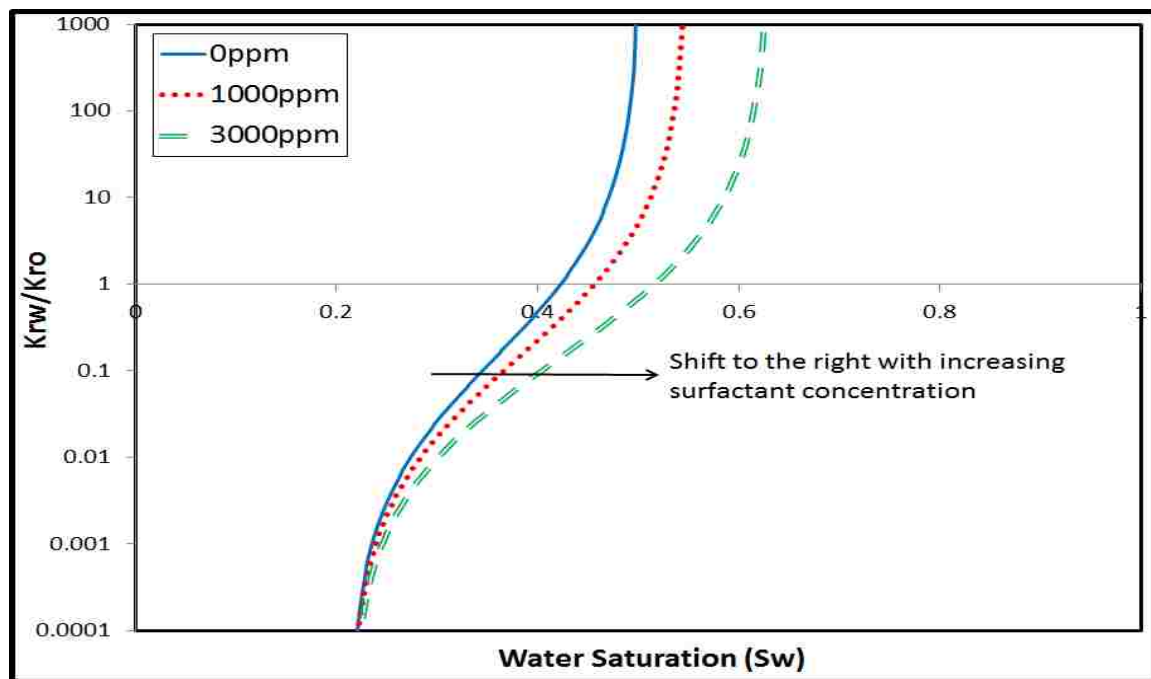


Figure 28: Oil-water relative permeability ratios with increasing surfactant concentration in a non-reactive system

**Fractional flow:** Figure 29 illustrates the relationship between fractional flow and water saturation. With increasing surfactant concentration the curves shift to the right. The wettability effect observed in this case is strictly due to the use of surfactant. Fractional flow analysis supports the observations made on the recovery section where oil recovery increased with increasing surfactant concentration.

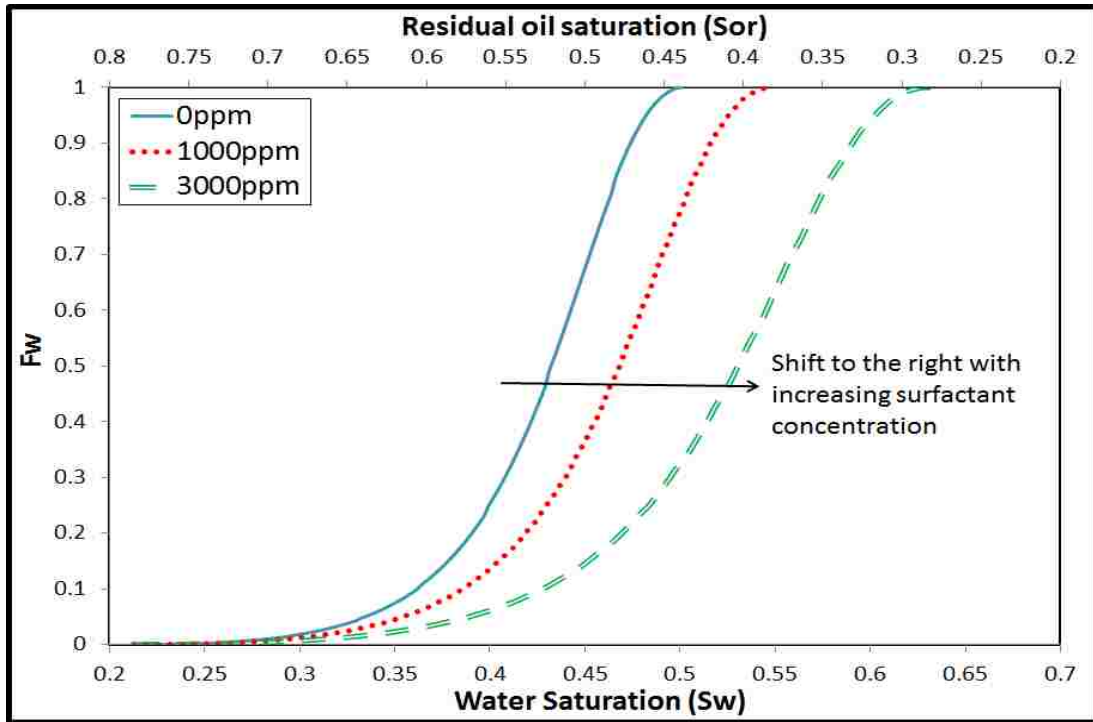


Figure 29: Fractional flow curves of all surfactant concentrations in the non-reactive (decane) system.

**Summary:** The recoveries in the reactive system are significantly higher than those in the non-reactive system as shown by Table 9. The difference in both rock fluid systems is the oil used and its influence on wettability. Therefore, in the non-reactive case decane oil is considered non-reactive and therefore does not affect wettability. On the other hand, Yates crude oil is reactive meaning its interaction with the rock affects the wettability of the system. Therefore, the additional recovery between the non-reactive and reactive rock fluid system can be attributed to the influence of oil on wettability.

Table 9: Recoveries of non-reactive and reactive system at various surfactant concentrations

Surfactant Flood	Non-reactive system recovery (% OOIP)	Reactive system recovery (%OOIP)	Additional recovery (non-reactive – reactive) %OOIP
0ppm	40%	47%	7%
1000ppm	46%	52%	6%
3000ppm	80%	94%	14%

## 4.2 Set 2: Ideal soaking period

The experiments in **set 1** have established the optimal surfactant concentration to be 3000ppm. The second parameter investigated was the ideal soaking period for a 0.2PV surfactant slug injected around the producing well prior to a waterflood. The three soaking times tested were 1 hour, 12 hours and 24 hours in separate experiments. These soaking times were compared to a conventional waterflood where there is no surfactant slug injection and therefore no soaking time needed. The results are discussed below.

Table 10: Experimental and simulation results for the soaking time experiments

Soaking period	Experimental					Simulation				
	Recovery (%OOIP)	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	X-over point
No soaking	47%	0.175	0.431	0.943	0.097	0.175	0.430	0.980	0.090	0.470
1 hour	47%	0.307	0.363	0.990	0.009	0.307	0.352	0.989	0.051	0.586
12 hours	55%	0.463	0.242	0.980	0.060	0.463	0.232	0.980	0.085	0.682
24 hours	56%	0.534	0.233	0.952	0.060	0.534	0.233	0.987	0.128	0.701

**Recovery:** Figure 31 shows the relationship between recovery and injected pore volume. The oil recovery increases from 47% to 56% with increasing soaking time. The increase in oil recovery is proposed to be due to the surfactant slug changing the wettability of the soaked area around the production well. As observed in the reactive rock fluid system in **set 1**, when the core was injected with ideal surfactant concentration (3000ppm) solution, mixed wettability was developed. Therefore, wettability around the surfactant soaked area would have also changed from its initial water wet state to a mixed wet state.

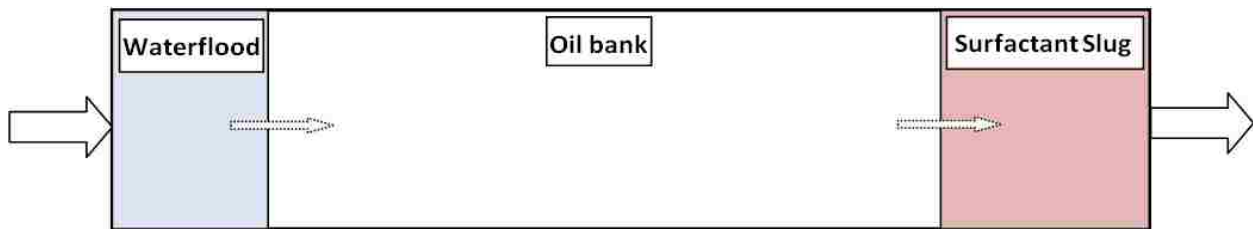


Figure 30: Schematic of an improved waterflood process in the core.



Therefore, when the waterflood is started, the injected water will displace the oil bank which will displace the surfactant slug as shown in Figure 30. Since the soaked area around the production well is mixed wet, when oil reaches this area it will travel by the continuous oil wet paths in the larger pores. However, if the wettability of the soaked area changed to oil wet conditions, then when the displaced oil bank arrives at that area it will travel through the small pores. If the wettability of the soaked area changed to more water wet conditions, the displaced oil bank will travel through the larger pores. An addition process that may aid the increase in recovery is the lowering of the interfacial tension and wettability alteration throughout the rest of the core due to surfactants diffusing from the surfactant slug to the rest of the core through the water film. This process can be verified by testing the water around the injector well prior to a waterflood and after the soaking period for the presence of surfactant. This would officially validate that the diffusion of surfactant from the surfactant slug to the rest of the core is taking place.

As observed in Figure 31, there was no increment in recovery between the no surfactant flood (conventional waterflood) and the 1 hour soaking time coreflood. This lack of incremental recovery is expected since the surfactant slug injected had not had enough time to change the wettability around the soaked area (and/or diffuse to the rest of the core). Due to this, the effect of recovery by the water injection following the surfactant slug soak was similar to that of a conventional waterflood. A 12 hour soaking period has an incremental recovery of about 8% when compared to the no surfactant coreflood case. This increment in recovery is a product of the wettability change around the production well and the presence of surfactant throughout most of core. A 24 hour soaking period resulted in an incremental recovery of about 9% from a waterflood. Since the increase in incremental recovery from 12 hours to 24 hours is only 1%, it indicates that the ideal soaking time is 12 hours for a 0.2PV surfactant slug. Another crucial observation made by analyzing the recovery trends is that the longer the soaking period is the more time is available for the fluids to redistribute in the core, and therefore the smaller the volume of surfactant slug is produced prior to oil production.

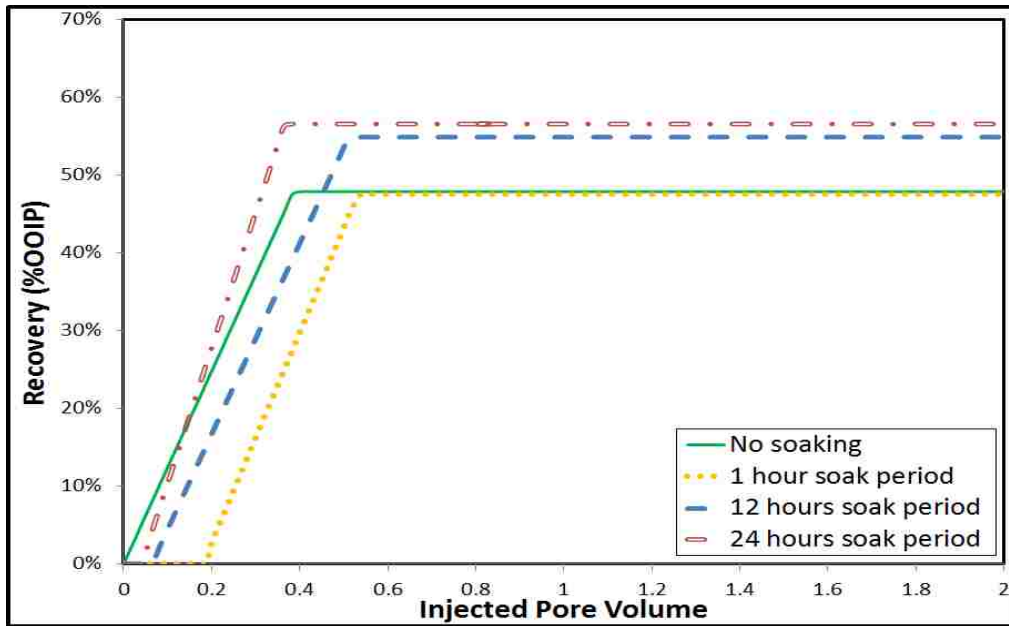


Figure 31: Recovery curves of all soaking period experiments.

**Pressure drop:** Figure 32 shows the relationship between pressure drop and injected pore volume. As observed, the pressure drop decreases with the soaking period. From the no surfactant case to the 1 hour soaking time case, the pressure drop significantly increases. The high pressure drop in the 1 hour soaking time is a result of the resistance in fluid flow due to the existence of two flood fronts created during the waterflood as duplicated in Figure 30. The first flood front is due to water displacing the oil bank, and the second flood front is the oil bank displacing the surfactant slug. In the 1 hour soaking coreflood, the surfactants have not had enough time to change the wettability and allow for the fluids to redistribute. Therefore, when the waterflood was started the entire volume of surfactant slug injected was first produced before the oil. This is clearly shown in the delay in oil production in the recovery trends. The longer the soaking period, the more time the fluids have to redistribute in the core, and therefore, the more the second front interface between the oil bank and surfactant slug fades and allows for less resistant flow to the wellbore. In the case of 12 and 24 hour soaking periods, the surfactants have had time to alter the wettability of the area around the production well (and surfactant has had time to diffuse to most of the core through the water wet film coating the rock grains). In addition, the fluids have had time to

redistribute which is indicated by less surfactant being produced prior to the oil bank therefore indicating a diffuse front between the oil bank and surfactant slug.

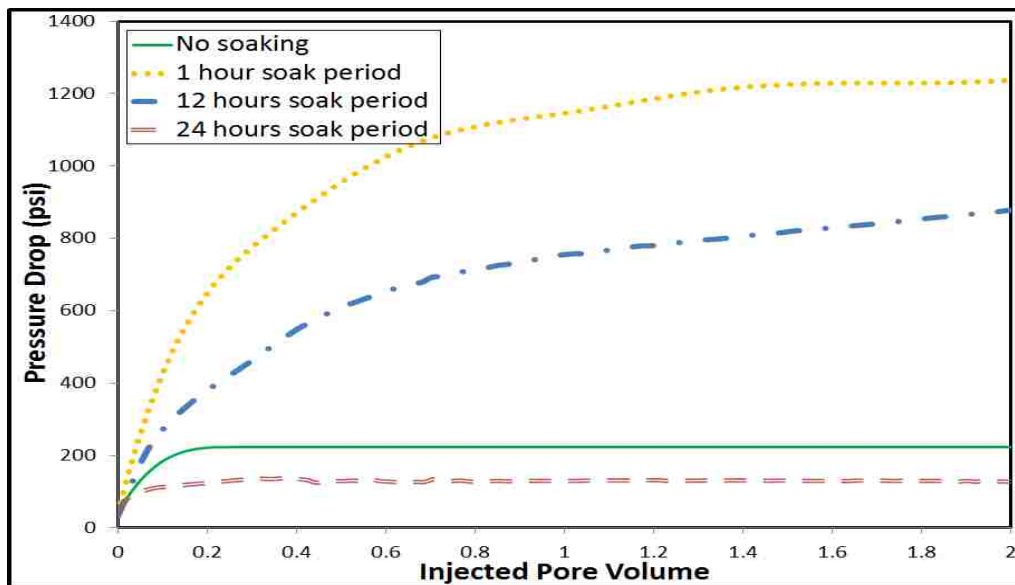


Figure 32: Pressure drop curves of all soaking period experiments.

**Relative permeability:** The oil water relative permeability ratio curves are presented in Figure 33. A shift to the right with increased soaking period is observed indicating a shift in wettability to more water wet conditions.

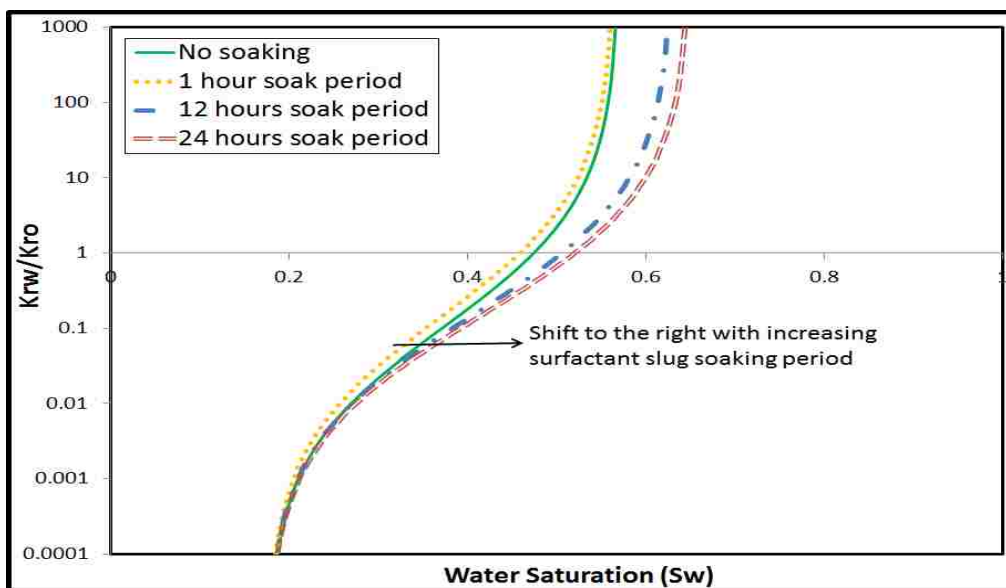


Figure 33: Oil-water relative permeability ratios of soaking period experiments.

**Fractional flow:** Figure 34 shows the relationship between fractional flow and water saturation. As observed, the curves shift to the right with increasing soaking time. This shift indicates a change in wettability to more water wet conditions.

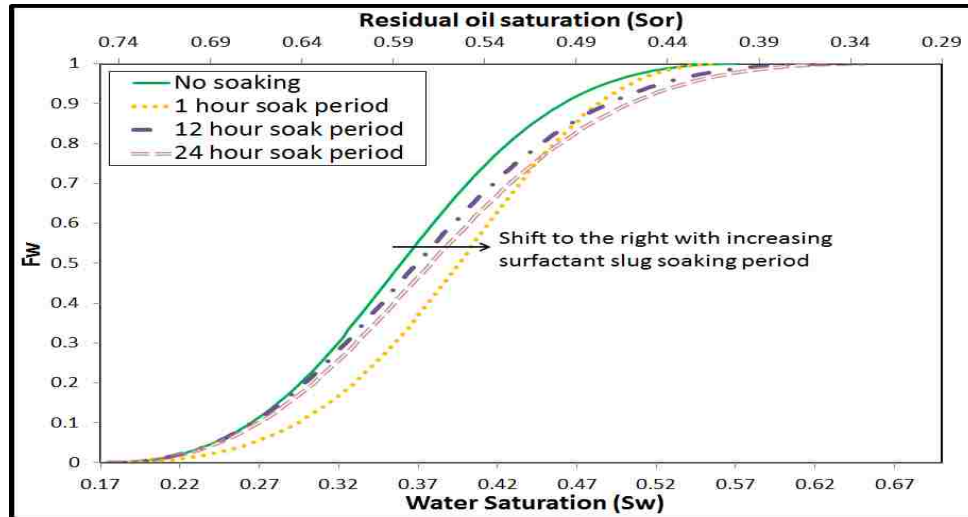


Figure 34: Fractional water flow curves of all soaking period experiments.

**Summary:** As indicated by the above results, soaking time has a significant impact on recovery, pressure drops, relative permeabilities and fractional flow. The longer the soaking time the higher the recoveries as shown in Figure 35 and the lower the pressure drops. The ideal soaking time was determined to be 12 hours for a 0.2PV surfactant slug injected around the production well.

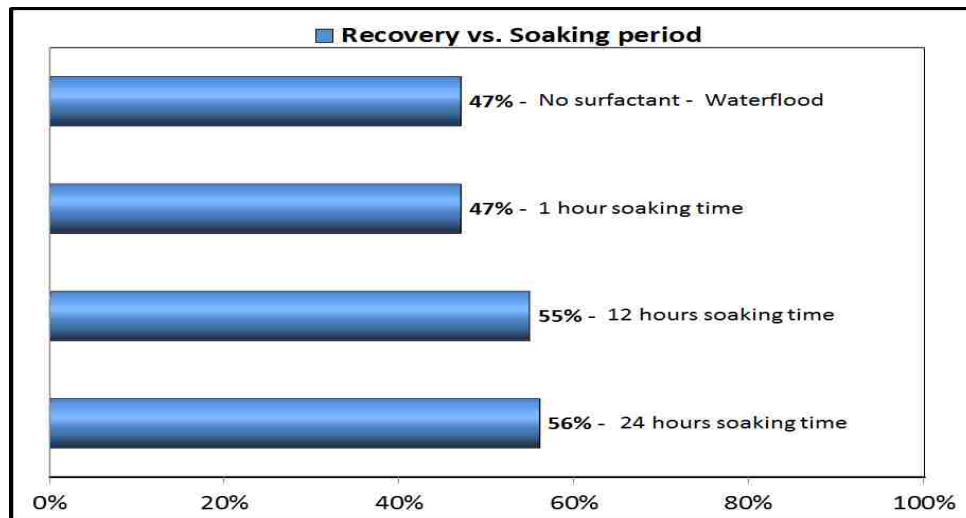


Figure 35: Recovery results at different soaking periods.

### 4.3 Set 3: Effect of varying surfactant slug size on incremental oil recovery

Set 1 and set 2 established the ideal surfactant concentration and the ideal surfactant slug soaking period to be 3000ppm and 12 hours, respectively. Set 3 examined the effects of varying the surfactant slug size. The surfactant slug injected around the producer well is at the ideal surfactant concentration of 3000ppm and is soaked for 12 hours. The three surfactant slug sizes tested were 0.1PV, 0.2PV, and 0.3PV. The results are presented below.

Table 11: Experimental and simulation results for various surfactant slug sizes

Surfactant slug size	Experimental					Simulation				
	Recovery (%OOIP)	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	X-over point
0 PV	47%	0.175	0.569	0.943	0.097	0.175	0.570	0.980	0.090	0.470
0.1 PV	47%	0.372	0.341	0.700	0.068	0.372	0.341	0.980	0.052	0.581
0.2 PV	55%	0.463	0.242	0.980	0.060	0.463	0.232	0.980	0.085	0.758
0.3 PV	62%	0.775	0.087	0.987	0.040	0.775	0.081	0.987	0.044	0.873

**Recovery:** Figure 36 shows the relationship between recovery and injected pore volume. The oil recovery increases from 47% to 62% with increasing pore volume size of 0PV to 0.3PV.

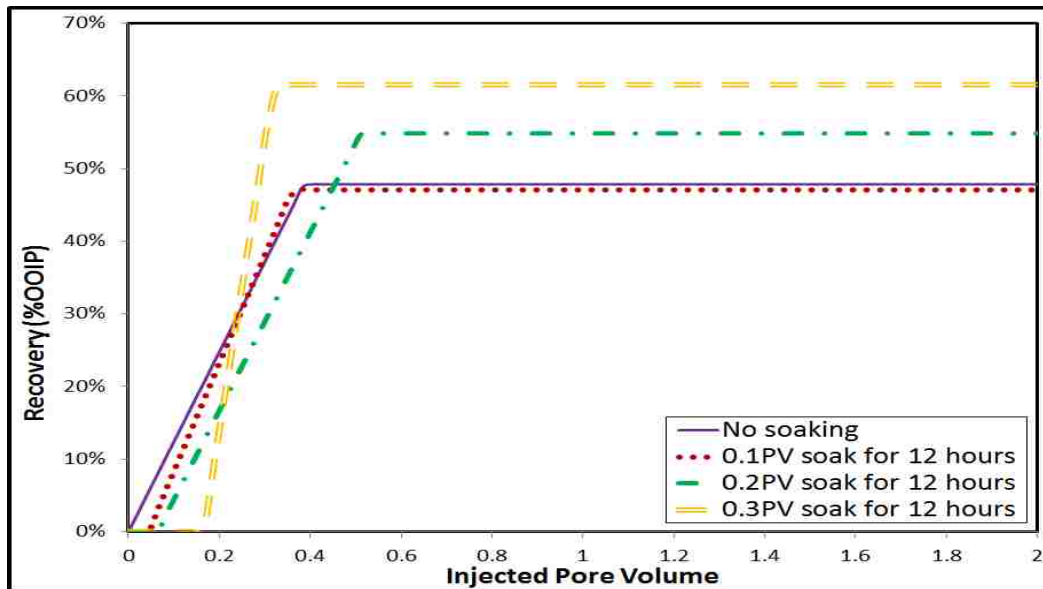


Figure 36: Recovery curves for various surfactant slug sizes.

As observed, there was no increment in recovery when 0.1PV of the core was soaked in surfactant. This is due to the small quantity of surfactant present in the core, meaning that a very small portion of the area around the production well has its wettability altered. The effect of this alteration is too small to increase the recovery. The 0.2PV and 0.3PV slug had an incremental recovery of 8% and 15%, respectively. The larger the surfactant slug size, the larger the area whose wettability is altered.

**Pressure drop:** Figure 37 shows the relationship between pressure drop and injected pore volume. As observed, the pressure drop increases with increasing size of surfactant slug injected. In the case of 0.1PV, the pressure drop is lower than a conventional waterflood. This is because the core used in the 0.1PV coreflood had a permeability of about 30mD higher, thus decreasing the pressure drop. If the experiment had been conducted using the same core, it would probably have given a similar pressure drop to that of a conventional waterflood. In the case of 0.2PV the pressure drop increases due to the presence of two flood fronts and also due to the slight decrease in absolute permeability by about 10mD from core cleaning. In the 0.3PV coreflood experiment, the increase in pressure drop was due to the presence of two flood fronts, decrease in permeability from core cleaning by about 10mD, and lastly, the formation of emulsions. Emulsions were formed in the 0.3PV case due to large quantities of surfactants introduced to the core.

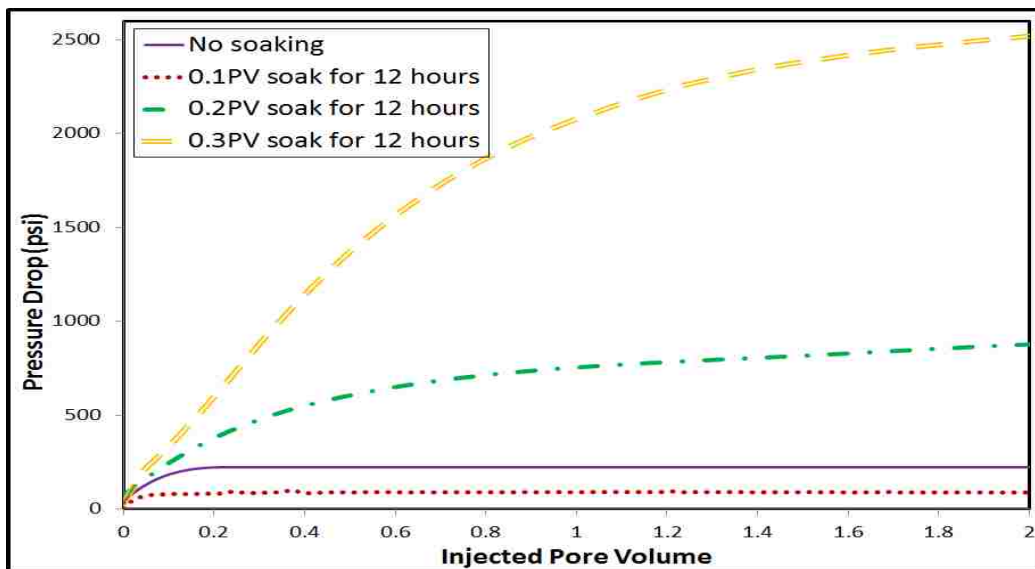


Figure 37: Pressure drop curves for various surfactant slug sizes

**Relative permeability:** The oil water relative permeability ratio curves are presented in Figure 38. The shift to the right with increasing surfactant slug size indicates wettability change to more water wet conditions.

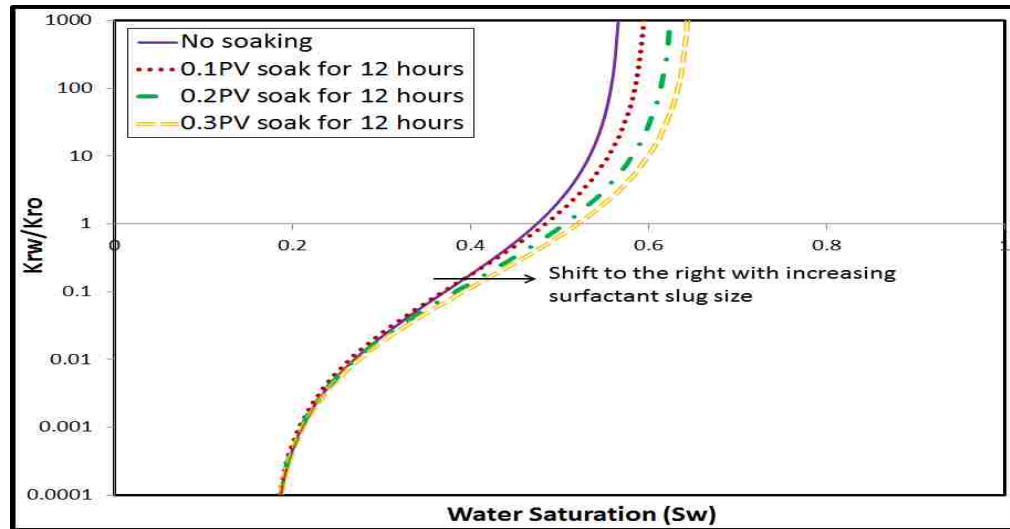


Figure 38: Oil-water relative permeabilities ratios for various sizes of surfactant slug.

**Fractional flow:** Figure 39 shows the relationship between fractional flow and water saturation. As observed, the curves shift to the right with increasing surfactant slug size. This indicates a shift in wettability to more water wet conditions.

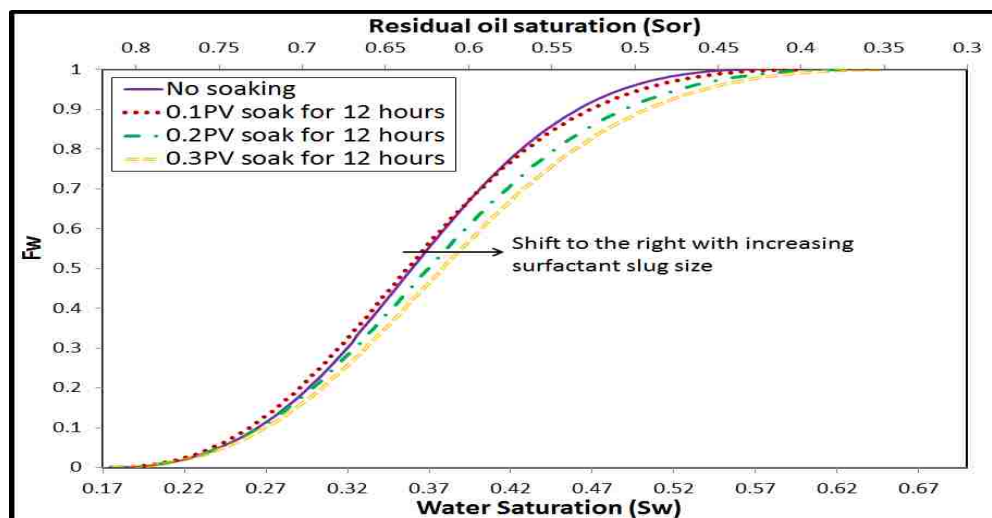


Figure 39: Fractional flow curves for various surfactant slug sizes.

**Summary:** As indicated by the above results, the size of surfactant slug soaked has a significant effect on the recovery. A conventional waterflood resulted in a recovery of 47% while the whole core treated with an ideal surfactant flood (3000ppm injected for 2PV) gave a recovery of 94%. Thus, if the core is treated with pore volumes between 0 and 2PV, the recoveries are expected to fall between 47% and 94%. The observed results in this section followed this hypothesis well. In addition, the size of pore volume soaked and the soaking time are also related. The larger the soaked pore volume the shorter the ideal soaking time. As observed, the ideal soaking time for 0.2PV was measured to be 12 hours, meaning that 0.1PV would need a longer soaking time as 0.3PV would need a shorter soaking time.

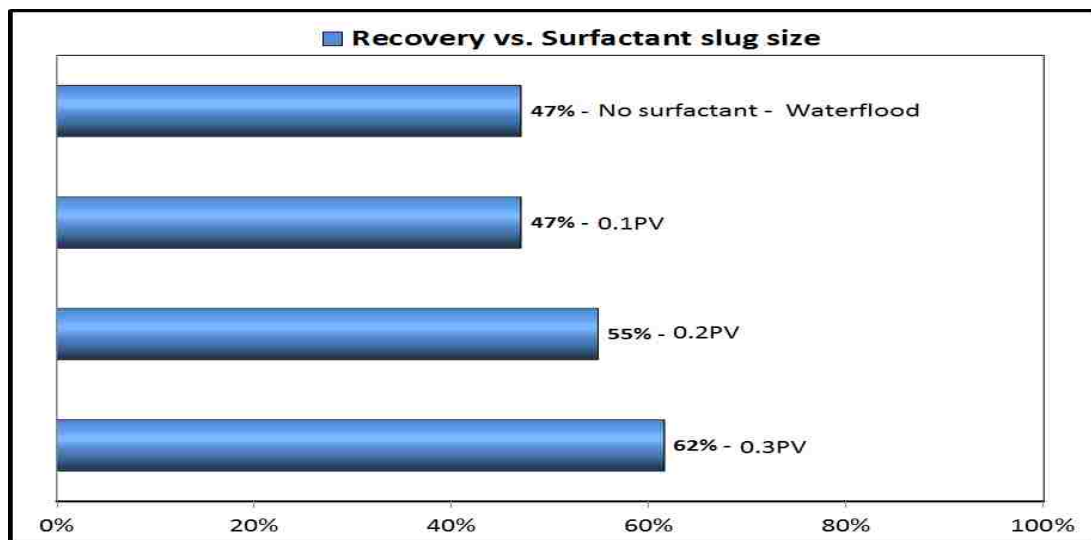


Figure 40: Recovery results at different pore volume sizes

#### 4.4 Set 4: Comparison of the four improved waterflood methods with three baseline cases

The previous three sets of experiments have determined the ideal surfactant concentration to be 3000ppm and soaking time to be 12 hours for a 0.2PV surfactant slug. It was also determined that increasing the surfactant slug size increases the recovery. **Set 4** used the parameters established in the previous sections to investigate the four proposed improved waterflood variations relative to three baseline cases. The first and second improved waterflood variations used a 0.2PV and 0.3PV surfactant



slug, respectively, to soak the area around the production well prior to a waterflood. The third variation used a low concentration (LC) surfactant solution to flood the core after soaking the area around the production well with a 0.2PV surfactant slug. This method was named as the improved LC surfactant method. The fourth variation used a 0.2PV surfactant slug to soak the area around the injection well instead of production well prior to the waterflood. This method was named water alternating surfactant process (WASP). Each waterflood or LC surfactant flood was carried out for 2PV after the surfactant slug soaking period. The three baseline methods consisted of: a conventional waterflood, a LC (1000ppm) surfactant flood, and an ideal concentration surfactant flood (3000ppm). All baseline methods were also carried out for 2PV.

Table 12 presents the experimental results of all the seven improved oil recovery processes. In this set of experiments, recovery is the only variable evaluated to show the effectiveness of each process.

Table 12: Experimental results for the seven EOR processes

EOR methods	Experimental					Simulator				
	Recovery (%OOIP)	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	$S_{wi}$	$S_{or}$	$K_{ro}$	$K_{rw}$	X-over point
Waterflood	47%	0.175	0.569	0.943	0.097	0.175	0.570	0.980	0.090	0.470
Improved Waterflood (0.2PV)	55%	0.463	0.242	0.980	0.060	0.463	0.232	0.980	0.085	0.758
Improved Waterflood (0.3PV)	62%	0.775	0.087	0.987	0.040	0.775	0.081	0.987	0.044	0.913
LC surfactant flood	52%	0.175	0.605	0.734	0.033	0.175	0.606	0.987	0.202	0.490
Improved LC surfactant flood	58%	0.688	0.13	0.990	0.014	0.688	0.13	0.998	0.170	0.791
WASP	67%	0.654	0.113	0.980	0.017	0.654	0.898	0.999	0.170	0.800
Ideal surfactant flood	94%	0.48	0.027	0.980	0.088	0.480	0.095	0.999	0.050	0.819

**Waterfloods:** A conventional waterflood was conducted as a base case that can be used to evaluate the effectiveness of the proposed improved waterflood variations. The recovery of the conventional

waterflood was 47%. The improved waterflood variation with a soaked volume of 0.2PV gave a recovery of 55% and therefore has an incremental recovery of 8%. The improved waterflood variation with a larger soaked volume of 0.3PV gave a recovery of 62% and therefore has an incremental recovery of 15%. The water alternating surfactant slug process (WASP) gave a recovery of 67% and therefore has an increment of 20%.

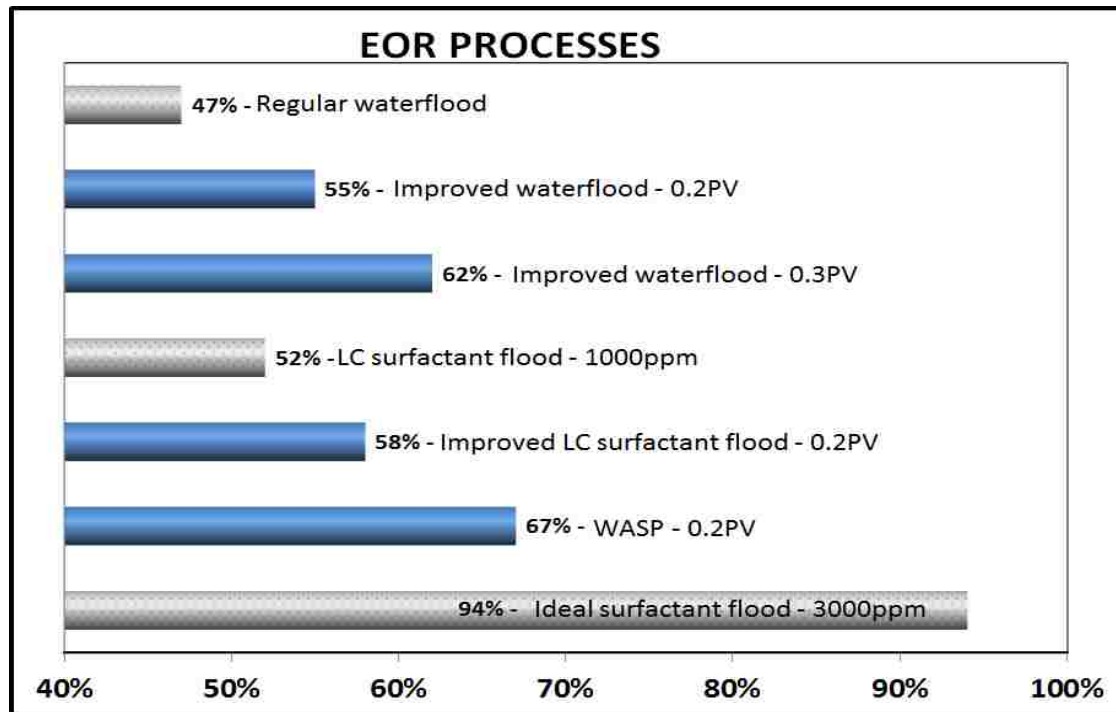


Figure 41: Recovery results for the six EOR processes

The WASP method is similar to the first improved waterflood variation using a 0.2PV surfactant slug around the production well. The only difference between the two variations is that the surfactant slug in the WASP method is injected around the injection well instead of the production well. However, with this minor difference between the two improved waterflood variations, there is a 12% recovery increase in recovery from soaking the production zone to soaking the injection zone. This indicates that treating the injection zone is more effective than treating the production zone prior to a waterflood. When the surfactant slug is injected around the production well it displaces the oil away from the production well. In addition, the only means to improve recovery is by the surfactant altering the wettability of the soaked

area and also by allowing time for the surfactants to diffuse to the rest of the core. The surfactant diffuses from the production side to the injector side (backwards), therefore, requiring a longer soaking period for the surfactant to be dispersed throughout the entire reservoir. On the other hand, when the surfactant slug is injected from the injector side the oil is displaced towards the production well. The injected surfactant slug alters the wettability of the soaked zone. Unlike the first two variations, the WASP method has two ways of dispersing surfactant to the rest of the reservoir. The first is by soaking the surfactant slug and letting surfactant diffuse to the rest of the reservoir. The second and most effective way is when the waterflood displaces the surfactant slug from the injection zone to the production well, and therefore exposing the whole reservoir to surfactant. In summary, the improved waterflood variations are more effective in displacing oil than a conventional waterflood. However the WASP method is the most effective of the improved waterflood variations.

**Surfactant floods:** A LC surfactant flood of 1000ppm was performed as a base case that can be used to evaluate the effectiveness of the improved LC surfactant flood. The recovery of the LC surfactant flood was 52%. The recovery from the improved LC surfactant flood was 58%, and therefore, has an incremental recovery of 6% when compared to the LC surfactant flood. When compared to a conventional waterflood, the improved LC surfactant flood had an increment of 11%. This indicates that the improved surfactant flood process is more effective in improving the recovery than a conventional waterflood and a LC surfactant flood.

**Overall:** The above results indicate that all four improved waterflood variations are technically feasible and are more effective in improving oil recovery than a conventional waterflood. Of the four variations, the most effective is the WASP method, followed by the 0.3PV surfactant soak improved waterflood, the 0.2PV surfactant soak improved waterflood, and finally, the improved LC surfactant flood. Lastly, the ideal surfactant (3000ppm) flood was conducted to set the target at which the improved waterflood variations can strive to achieve. This coreflood gave a recovery of 94% (47% increment) due to the development of mixed wettability. The underlying motivation of this study was to achieve such high recoveries without using large quantities of surfactants. The 94% recovery was achieved by flooding the

core with 2PV of 3000ppm surfactant solution. The WASP method gave a 67% recovery (20% increment) with using 0.2PV of 3000ppm surfactant solution. This indicates that it is possible to achieve high recoveries without using large quantizes of surfactant.

#### 4.5 Economic consideration

The following material balance calculations were performed for the four improved waterflood variations and the three baseline methods. This simple cost analysis provides yet another tool to evaluate the effectiveness of these improved waterflood methods. The capital (CAPEX) and operation (OPEX) expenses are assumed to be the same for all seven improved oil recovery methods. It is also assumed that the recoveries achieved in the coreflood experiments would also be achieved in the assumed reservoir. The objective of this exercise is to investigate the profitability of all seven IOR methods after surfactant cost is accounted for, when all things are equal. Let us consider the application of these seven EOR methods in a sandstone reservoir with the following properties:

- Reservoir area =  $A = 5$  acres
- Pay zone thickness =  $h = 20$  ft
- Porosity =  $\phi = 20\%$
- Initial water saturation =  $S_{wi} = 55\%$
- Oil price = \$60/bbl. The low end oil price from 2008 to 2010 was chosen as the conservative oil price for these calculations.
- Surfactant cost = \$1.75/lb. This price quote was provided by Pride Solvents and Chemicals Co (Pride, 2010).
- Pore volume (PV) =  $A * h * \phi = 20 \text{ acre} * \frac{43560 \text{ ft}^2}{\text{acre}} * 20 \text{ ft} * 20\% * \frac{0.17809 \text{ bbl}}{\text{ft}^3} = 155,152 \text{ bbl}$
- OOIP = Pore volume \*  $(1 - S_{wi}) = 155,152 \text{ bbl} * (1 - 0.55) = 69,818 \text{ bbl}$
- Oil produced (bbl) = Pore volume(bbl) \* Recovery(%)
- Gross income (\$) = Oil produced (bbl) \* Oil price ( $\frac{\$}{\text{bbl}}$ )

- Surfactant used (bbl) = PV (bbl) \* PV of surfactant injected \* Surfactant Concentration (ppm) \*

$$\frac{159\text{liters}}{\text{bbl}} * \frac{1*10^{-6}\text{kg}}{\text{mg}} * \frac{2.2046\text{lb}}{\text{kg}}$$

- Surfactant cost (\$) = Surfactant used (bbl) \* Surfactant price ( $\frac{\$}{\text{bbl}}$ )
- Profit (\$) = Gross income(\$) – Surfactant cost(\$)
- Increment profit compared to the waterflood method (\$) = Profit (\$) – waterflood's profit (\$)

Table 13 presents the cost analysis of the seven improved oil recovery processes. The rows containing the three baseline cases are shaded.

Table 13: Cost analysis results for the seven IOR methods

EOE methods	Recovery (%OOIP)	Oil-Prod (bbl)	Gross income (\$)	Surf. Conc. (ppm)	Surf. used (bbl)	Surf. cost (\$)	Profit (\$)	Increment profit (\$)
Waterflood	47%	32,221	1,933,272	0	0	0	1,933,272	0
Improved Waterflood (0.2PV)	55%	38,288	2,297,305	3,000	32,631	57,105	2,240,200	306,928
Improved Waterflood (0.3PV)	62%	42,966	2,577,975	3,000	48,947	85,657	2,492,317	559,046
LC surfactant flood	52%	36,424	2,185,456	1,000	108,771	190,350	1,995,106	61,834
Improved LC surfactant flood	58%	40,725	2,443,504	1,000	141,403	247,455	2,196,050	262,778
WASP	68%	47,127	2,827,645	3,000	32,631	57,105	2,770,540	837,269
Ideal surfactant flood	95%	65,978	3,958,703	3,000	326,314	571,049	3,387,654	1,454,383

As observed in Table 13, Figure 42, and Figure 43, the preliminary cost analysis indicates all seven IOR methods are profitable. The conventional waterflood method nets the lowest profit due to its low recovery. On the other hand, the ideal surfactant flood consumes the largest quantities of surfactant

therefore increasing the cost of surfactant, however, due to the very high recovery (94%) the cost of surfactant is easily upset and therefore this method of oil recovery nets the highest profit of all IOR methods considered. The underlying motivation of this study was achieving such high recoveries and thereby profits without using large quantities of surfactants. As observed in Figure 42 the four improved waterflood variations do accomplish this task. Even when the cost of surfactants is factored in, the WASP process nets the highest profit of all the improved waterflood variations. Another way to evaluate the effectiveness of these improved methods is by evaluating the incremental profit made over the waterflood profit. Likewise, of the improved waterflood variations the WASP method nets the highest incremental profit, followed by the 0.3PV improved waterflood, and lastly, the 0.2PV improved waterflood. Of the four improved waterflood variations, the improved LC surfactant flood nets the lowest profit due to the large quantities of surfactant used. The LC surfactant flood nets the smallest increment in profit. For this IOR method to be more profitable than a waterflood, the price of oil has to be greater than \$46/barrel.

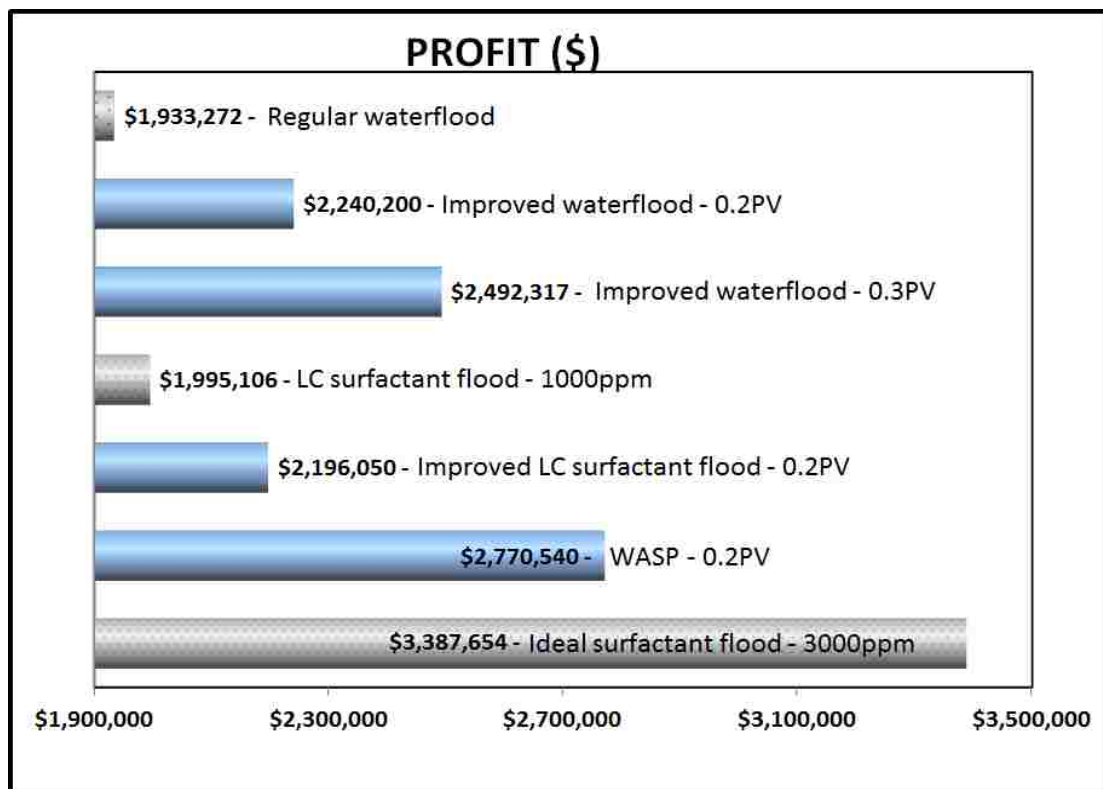


Figure 42: Calculated profits of the seven EOR methods

**Overall:** In this section, all the improved waterflood variations are economically feasible and more profitable than a conventional waterflood, under the assumed conditions. Of the four improved waterflood variations, the most profitable method is the WASP method, followed by the 0.3PV improved waterflood, then by the 0.2PV improved waterflood, and lastly the improved LC surfactant flood.

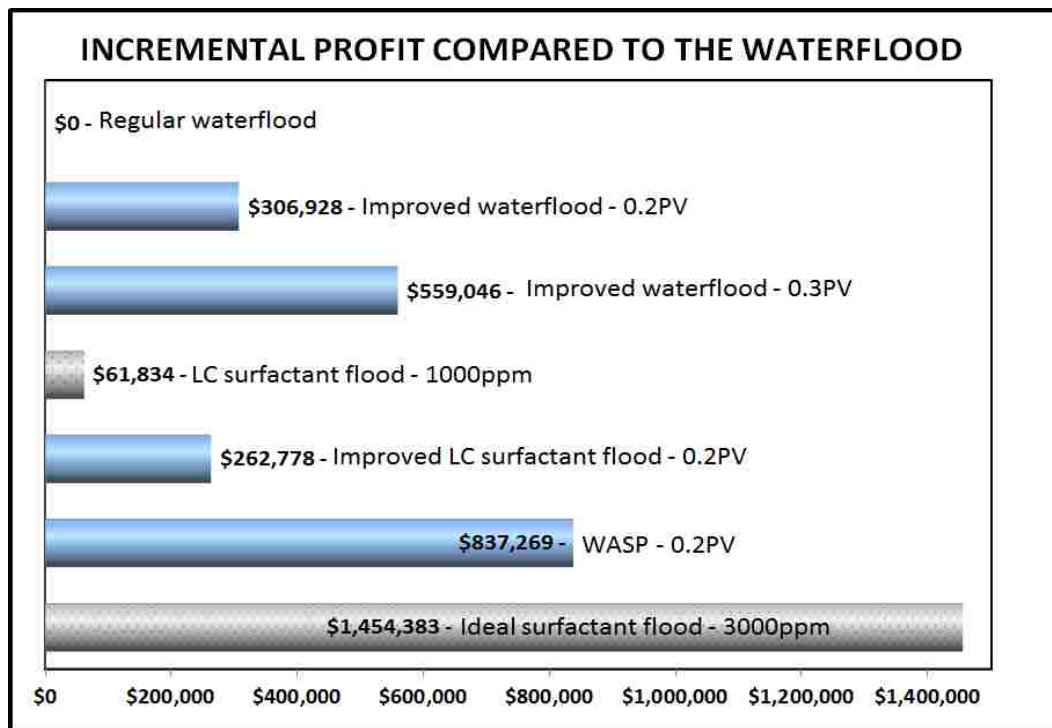


Figure 43: Incremental profit of each EOR method when compared to the waterflood profit

## **5. CONCLUSIONS AND RECOMMENDATIONS**

### **5.1 Summary of findings and conclusions**

The objective of this study was to evaluate whether the proposed improved waterflooding variations are technically feasible, and also to determine their effectiveness when compared to a conventional waterflood. This task was accomplished by conducting four sets of coreflood experiments. The first three sets of experiments were used to optimize the improved waterflood process. The fourth set tested the four improved waterflood variations and compared them to three baseline improved oil recovery methods. The significant findings in this study are presented below.

1. An effective and efficient core cleaning procedure for fresh and contaminated cores was developed.
2. Tomadol™ 91-8 was used throughout the project and its optimal concentration was found to be 3000ppm in two rock fluid systems, non-reactive (decane) and reactive (Yates). At this surfactant concentration mixed wettability was developed. In the first set of experiments, it was observed that the recoveries in the reactive rock-fluid system were significantly larger than those in the non-reactive rock-fluid system. The increment in recovery from the non-reactive to the reactive rock fluid system was attributed to the wettability alteration due to the oil used.
3. In the second set of experiments, it was observed that the longer the soaking period the higher the oil recovery. The increase in recovery by soaking the production zone with a surfactant slug was primarily attributed to the wettability change in the soaked area. Secondly, diffusion of surfactant from the surfactant slug to the rest of the core through the water films may have also played a role in increasing recovery. The soaking period was examined for a 0.2PV surfactant slug and the ideal soaking period was found to be 12 hours.
4. The third set of experiments, investigated the effect of varying the size of the surfactant slug soaked around the production zone. It was observed that the larger the surfactant slug size the higher the oil



recovery. This was attributed to the change in wettability of a larger area around the production well, which therefore creates an area that is more conducive to oil flow towards the production well.

5. The fourth set of experiments evaluated the four improved waterflood variations and the three baseline processes. All four improved waterflood variations were found to be technically feasible and more effective than a conventional waterflood. Of the four improved waterflood methods, the WASP method was the most effective oil recovery method while the improved low concentrated surfactant flood was found to be the least effective. The same result was observed in the cost analysis results.

In summary, this project has accomplished its objective in testing the feasibility of the proposed improved waterflood method, and also in determining its effectiveness when compared to a conventional waterflood. The experimental results clearly established that the improved waterflood variations are feasible and are more effective than a conventional waterflood.

## **5.2 Recommendations for future work**

Further testing is imperative in order to fully understand the reservoir mechanics of the improved waterflood variations and fully optimize them with respect to the field. The following are suggested recommendations for future work.

1. Contact angle and interfacial tension measurements are needed in order to quantify the effect of Tomadol™ 91-8 on wettability and lowering of interfacial tension. These measurements are to be carried out using both stock tank and live oil.
2. The four improved waterflood methods need to be carried out using live oil and larger cores.
3. The surfactant slug size and ideal soaking time needs to be further investigated. This would help develop a correlation between surfactant slug size and ideal soaking time. As a result, the soaking time for each surfactant slug can be properly upscaled to field conditions.
4. Two experiments are needed to validate the hypothesis that surfactant diffuse from the surfactant slug to the rest of the core and thereby increasing oil recovery by changing wettability and lowering

interfacial tension. In addition, the effect of varying surfactant slug concentration on recovery needs to be investigated.

5. Full reservoir scale simulations are needed to help understand the effectiveness of these improved waterflooding methods on a large scale.
6. Other variations of this improved waterflood concept need to be explored, for example, soaking both the production and injection zone.

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## APPENDIX

History matched oil recovery and pressure drop data.

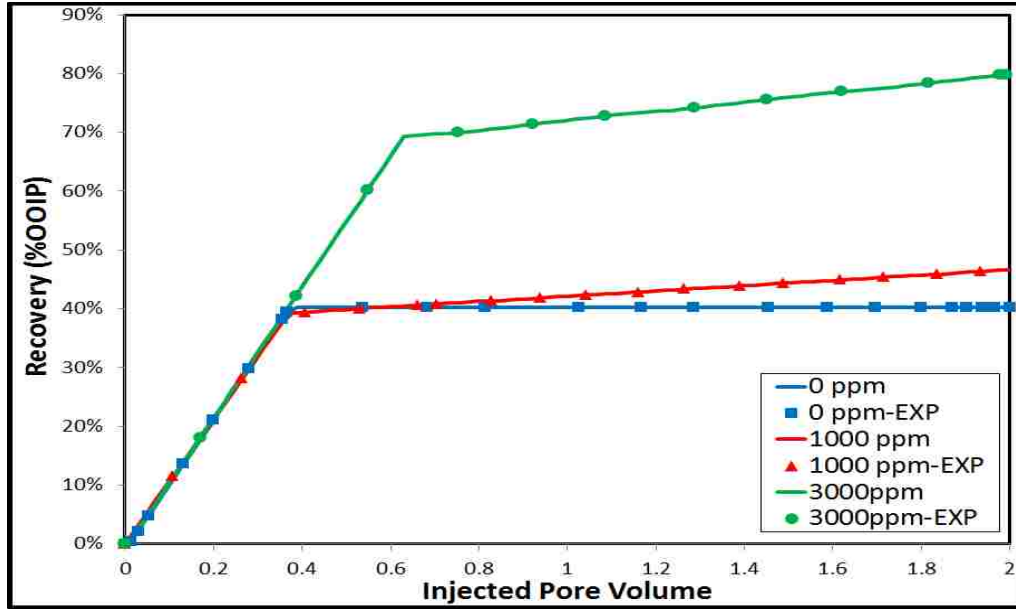


Figure 44: Experimental and simulation recovery curves of all surfactant concentrations in the non-reactive (decane) system.

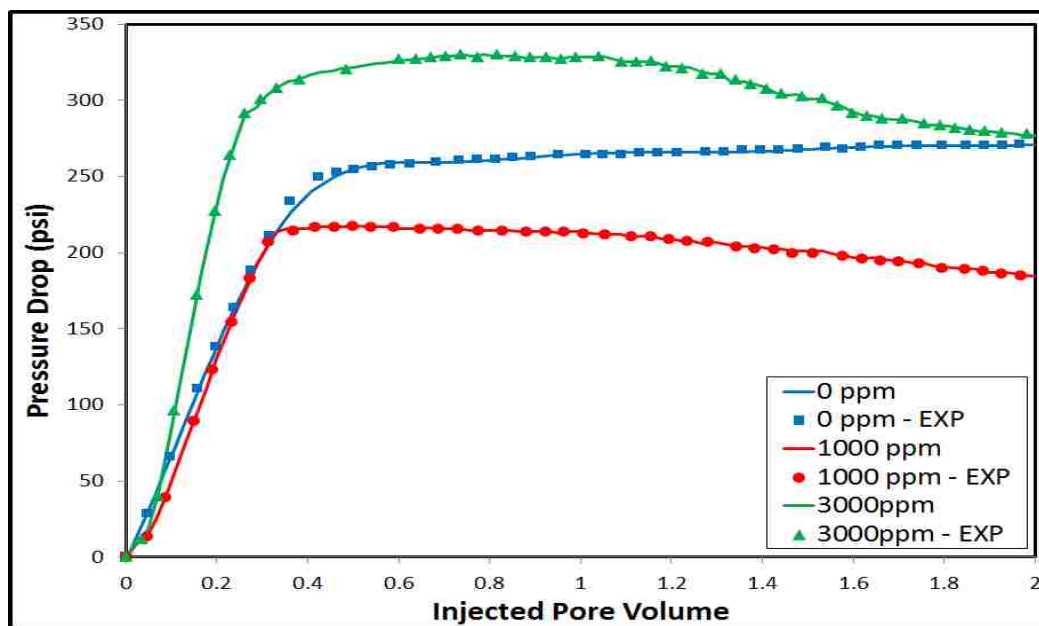


Figure 45: Experimental and simulation pressure drop curves of all surfactant concentrations in the non-reactive (decane) system.

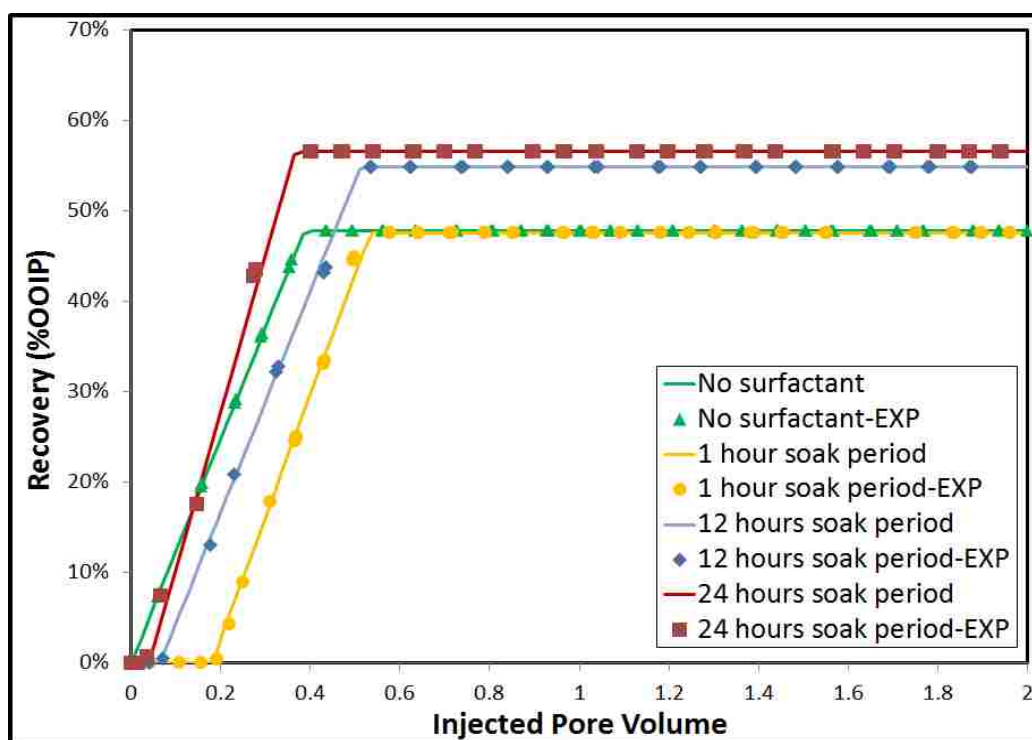


Figure 46: Experimental and simulation recovery curves of all soaking period experiments.

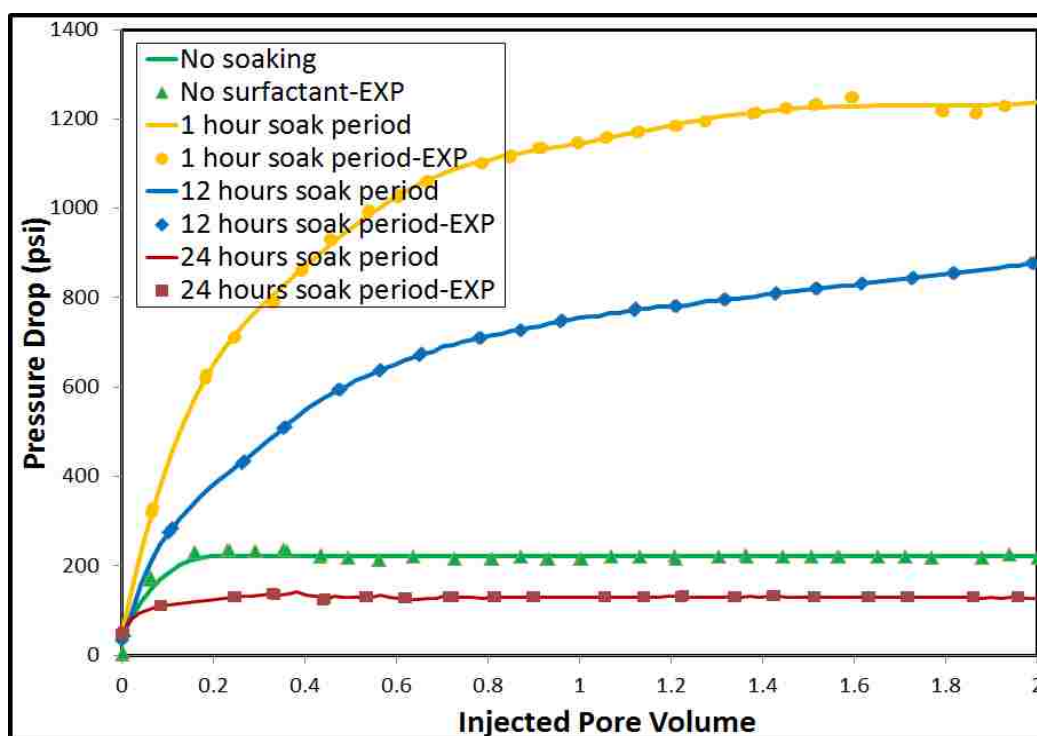


Figure 47: Experimental and simulation pressure drop curves of all soaking period experiments.

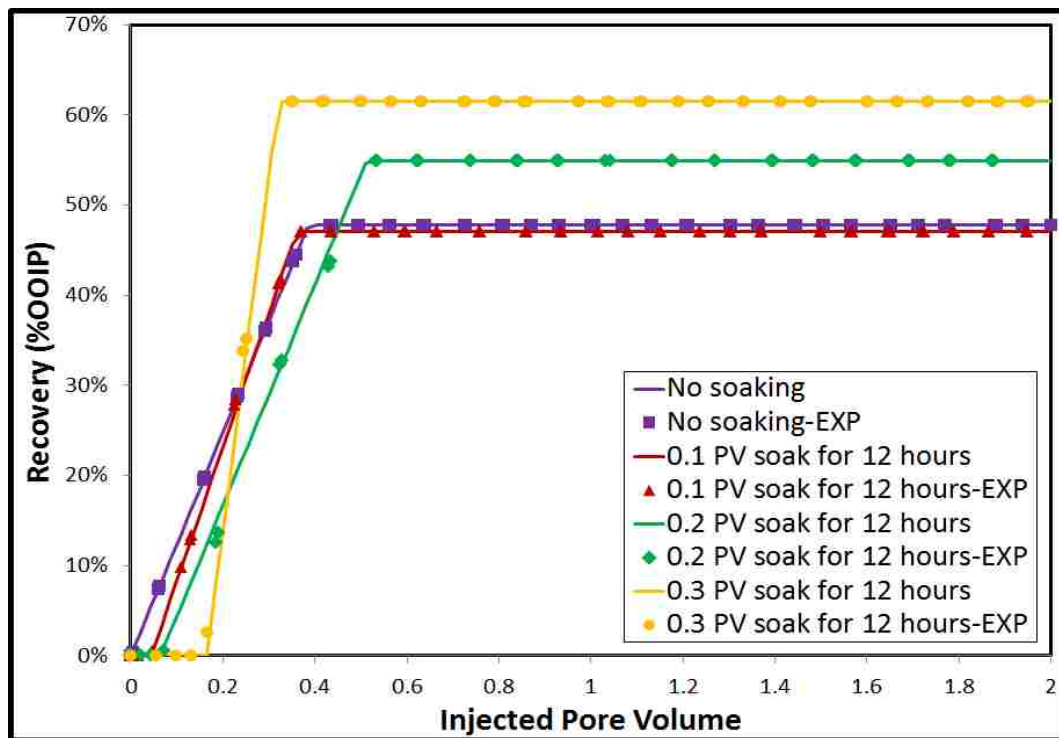


Figure 48: Experimental and simulation recovery curves for various surfactant slug sizes

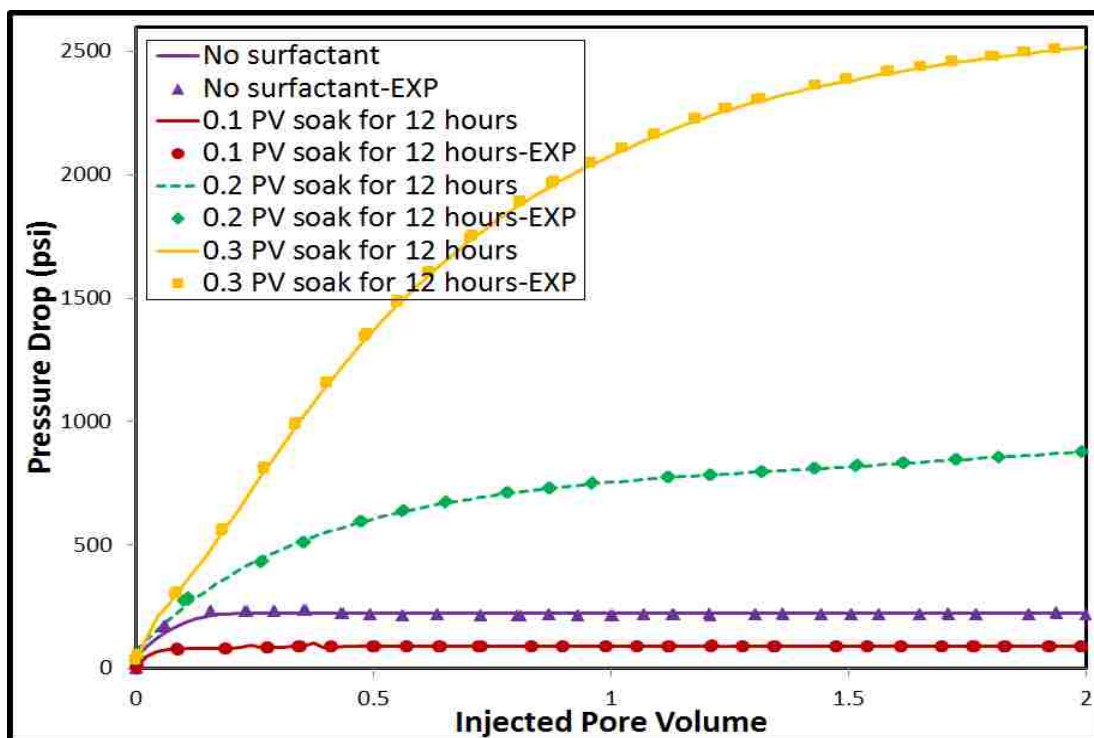


Figure 49: Experimental and simulation pressure drop curves for various surfactant slug sizes



## **VITA**

Paulina Mwangi, the daughter of Simon and Jane Mwangi, was born and raised in Lynn, Massachusetts, by way of Kenya. She attended and completed high school in Lynn Classical High School in June 2004. She later enrolled in the University of Rochester where she graduated with a Bachelor of Science in chemical engineering and Bachelor of Art in geology in May 2008. She also completed minors in environmental engineering and American sign language. In August 2008 she joined the Craft and Hawkins Petroleum Engineering Department, Baton Rouge, Louisiana. The degree of Master of Science in Petroleum Engineering will be conferred in December 2010.