INVESTIGATION OF METHODS TO MAKE ROCKS MORE WATER WET

By

Nurul Bahiyah Binti Abdul Aziz

16894

Dissertation submitted in partial fulfilment of

the requirement for the

Bachelor of Engineering (Hons) Petroleum Engineering

MAY 2015

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

INVESTIGATION OF METHODS TO MAKE ROCKS MORE WATER WET

by

Nurul Bahiyah Abdul Aziz

A project dissertation submitted to the Petroleum Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the BACHELOR OF ENGINEERING (Hons) (PETROLEUM ENGINEERING)

Approved by,

Approved by,

(AP Dr Syed Mohammad Mahmood)

(Dr Muhammad Ayoub)

UNIVERSITI TEKNOLOGI PETRONAS TRONOH, PERAK MAY 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contain herein have not been undertaken or done by unspecified sources or persons.

NURUL BAHIYAH ABDUL AZIZ

ABSTRACT

Enhanced oil recovery (EOR) is an essential method to maximize the extraction of residual oil from reservoirs. EOR methods can be classified as gas flooding, hydrocarbon miscible injection, thermal and chemical injection. Wettability is one of the key parameters targeting the remaining oil-in-place. Few studies have focused on improving oil recovery in sandstone reservoirs by wettability alteration. The objective of this dissertation is to prove that altering the wettability of a sandstone rock to preferentially water-wet condition will reduce the remaining oil saturation and thus increase the percentage of recovered oil. One best commercial surfactant (AOS₁₄₋₁₆) was after analysing the interfacial properties of two surfactants. Best surfactant then was tested for their ability to alter the wettability of sandstone rocks. The ability of selected surfactants to increase the percentage of recovered oil then was examined using oil-treated cores by water and gas injections. AOS significantly improve oil recovery from sandstone through spontaneous imbibition.

ACKNOWLEDGEMENT

The writer of this report is a Petroleum Engineering student from Universiti Teknologi PETRONAS (UTP). This final year report title is 'Investigation of Methods to Make Rocks More Water Wet. First of all, the author like to express my gratitude to Allah the Almighty God because of His will; the author managed to complete final part of final year project on May 2015.

The author also would to express her sincere gratitude to main supervisor, Associate Professor Dr Syed Muhammad Mahmood and co-supervisor, Dr Muhammad Ayoub for their dedication, support and enthusiasm guiding author to complete her Final Year Project (FYP) on time. Not forgetting, the graduate assistance Mr Mudassar Mumtaz for serving as mentor to help the author in research development. The successful completion of this project would not have been possible without his guide and supports. The gratitude also extends to all Universiti Teknologi PETRONAS staffs especially laboratory technologist, Mr Saiful Nizam and Mr Shahrul for their commitment and supports.

Lastly, the author would like to thank her family and everyone who involve directly or indirectly throughout this research.

Thank you.

Contents

| CERT | IFICAT | ION OF APPROVALi | | |
|--------|---|--|--|--|
| CERT | IFICAT | ION OF ORIGINALITYii | | |
| ABST | RACT. | | | |
| ACKN | NOWLE | DGEMENTS iv | | |
| LIST (| OF FIG | URESvii | | |
| LIST (| OF TAE | BLES | | |
| CHAP | TER 1 - | INTRODUCTION | | |
| 1. | Backg | round of Study 1 | | |
| 2. | Proble | m Statement 2 | | |
| 3. | Project | t Significance | | |
| 4. | Object | ive | | |
| 5. | Scope | of Study | | |
| CHAF | TER 2 | – LITERATURE REVIEW | | |
| 1. | Wettal | bility and Its Effect on Oil Recovery | | |
| 2. | Wettal | bility Alteration | | |
| | 2.1 | Thermal Flooding | | |
| | 2.2 | Non-Thermal Flooding | | |
| 3. | Surfact | ants and Its Classification5,6 | | |
| | 3.1 | Anionic Surfactant | | |
| | 3.2 | Non-ionic Surfactant7 | | |
| | 3.3 | Cationic Surfactant | | |
| | 3.4 | Amphoteric Surfactant7 | | |
| 4. | Wettal | bility Measurement | | |
| | 4.1 | Quantitative Method | | |
| | 4.2 Qualitative Method | | | |
| CHAP | TER 3 – | METHODOLOGY | | |
| 1. | Screen | ing of Wettability Alteration Methods9 | | |
| 2. | Screening of Surfactants | | | |
| 3. | Theory of Surfactant Alternate Gas(SAG) Flooding 10 | | | |
| 4. | Prepar | ation10 | | |
| | 4.1 | Porous Media10 | | |
| | 4.2 | Materials11, 12 | | |

| 5. | Metho | odology of Surfactant Alternate Gas (SAG) Flooding | 13 |
|------|--------|---|-----------|
| | 5.1 | Core Cleaning | 14 |
| | 5.2 | Drying | 14 |
| | 5.3 | Core Saturation | 14 |
| | 5.4 | Determination of OOIP | 15 |
| | 5.5 | Secondary Recovery (Water Flooding) | 15 |
| | 5.6 | Tertiary Recovery (SAG Flooding) | 15 |
| 6. | Step o | of Surfactant Flooding using BPS | 16 |
| 7. | Step o | of N2 Gas Flooding and SAG Flooding using RPS | 17 |
| CH | APTER | 4 – RESULT AND DISCUSSION | |
| 1. | Surfac | e Tension Measurement | |
| 2. | Surfac | tant Flooding using Mineral Oil | 20 |
| 3. | Gas F | looding Without Surfactants | 21 |
| 4. | Surfac | ctant Alternate Gas (SAG) Flooding using Dulang Oil | 22,23, 24 |
| CHAI | PTER 5 | - CONCLUSION AND RECOMMENDATION | |
| 1. | Concl | usion | 25 |
| 2. | Recor | nmendation | 25 |
| REFE | RENCE | | vii |
| APPE | NDIX | | ix |

LIST OF FIGURES

| Figure 1 | Contact Angles for Three Different Rocks | 4 |
|-----------|---|----|
| Figure 2 | Schematic of Surfactants behaviour in aqueous solution with oil emulsion called a micelle | 6 |
| Figure 3 | Surfactant classification according to the composition of their head: non-ionic, anionic, cationic and amphoteric | 6 |
| Figure 4 | Methodology | 9 |
| Figure 5 | Berea Sandstones | 11 |
| Figure 6 | Dulang Oil, AOS, and Mineral Oil | 12 |
| Figure 7 | Methodology of SAG Flooding | 13 |
| Figure 8 | Core Cleaning Process in Fume Hood | 14 |
| Figure 9 | Benchtop Permeability System (BPS) | 16 |
| Figure 10 | Relative Permeability System (RPS) and Sample Point | 17 |
| Figure 11 | IFT Measurement of AOS 1% | 18 |
| Figure 12 | Surface Tension of AOS | 18 |
| Figure 13 | IFT Measurement of IOS 1% | 19 |
| Figure 14 | Surface Tension of IOS | 19 |
| Figure 15 | Mineral Oil Displaced after Secondary Water flooding and Surfactant Flooding | 20 |
| Figure 16 | Oil and Brine Displaced by Secondary Water flooding | 21 |
| Figure 17 | Oil Recovery After Gas Flooding | 22 |
| Figure 18 | Oil Recovery by using SAG Flooding | 23 |
| Figure 19 | Comparison of Oil Recovery by using Three Different Methods | 23 |

LIST OF TABLES

| Table 1 | Advantageous and Disadvantageous of Surfactant and Steam Flooding | 9 |
|---------|---|----|
| Table 2 | Rock Properties of Berea Sandstone | 10 |
| Table 3 | Chemical Composition of Synthetic Sea Water Brine | 11 |
| Table 4 | Dulang Field Reservoir and Fluid Properties | 12 |
| Table 5 | Surface Tension of AOS | 18 |
| Table 6 | Surface Tension of IOS | 19 |
| Table 7 | Data Collected during Surfactant Flooding | 20 |
| Table 8 | Data Collected during Gas Flooding | 21 |
| Table 9 | Data Collected during SAG Flooding | 22 |

CHAPTER 1

INTRODUCTION

1. BACKGROUND OF STUDY

The ultimate goal for oil and gas companies is to achieve optimum production which leads to highest profitability. In order to achieve the goal, the company should think and plan thoroughly since the development of process will be costing. Both conventional and unconventional oil reservoir are mostly started to produce under primary recovery.

The oil recovery has been divided into three categories, primary, secondary and tertiary recovery. Primary recovery displaces 5-30% of the original oil in place (OOIP) by using natural energy such as natural water drive, solution gas drive and liquid gas expansion. Secondary recovery is implemented after primary production declines and produces up to 20-35 % of the OOIP. Water flooding and gas injection is carried out to sweep the oil trapped inside the reservoir towards surface. The water or gas is injected inside reservoir to maintain the pressure, hence push the oil to the surface. However, this secondary recovery does not respond positively and efficiently for certain reservoir. Tertiary recovery, or enhanced oil recovery (EOR), can increase the oil recovery up to 30-60% or more. EOR methods can be categorized into four types: thermal, gas, chemical and others. Chemical EOR can be classified into three categories, polymer, surfactants and alkaline agents; in addition, combinations of the three categories can be used, such as alkali-polymer (AP), surfactant-polymer (SP) and alkali-surfactant polymer (ASP). Surfactant-induced wettability alteration has been studied intensively for the past 50 years as a promising method by which to reduce the remaining oil saturation in reservoirs.

In conventional reservoir, there is a source rock dominantly by sedimentary rock; sandstone and carbonate. Some of rocks are found to be either oil-wet or water-wet. This rock properties is called wettability which generally known as the preferentially of solid phase towards liquid phase. Rock is defined to be water-wet if the rock has much more affinity for water than oil whereas the rocks which prefer to be contact with oil are called oil-wet rock. However, there is a case where the rocks are found to

be intermediate-wet, which some of the pores in the rocks are covered by water and oil. Since the rocks wettability influence the performance of oil recovery, therefore laboratory test should be carry out to find the effective method to make rocks more water wet.

Most of the rock surface chemistry can be alter by adsorption and deposition of organic polar components in the crude oil. The charge of the rock surface is strongly affected by brine salinity and pH. The rock surface turns to positively charged when the pH is decreased and the rock surface becomes negatively charged when the pH is increased. The solubility of wettability altering compounds tends to increase when temperature and pressure are elevated. Studies have proved experimentally that the wettability can be alter by injecting of N₂ gas and lowering interfacial tension (IFT). Strong oil wet rocks results in low oil recovery because the wetting phase which is oil occupies the small pores, which leads to a high residual oil saturations. In contrast, the residual oil saturation in intermediate-wet rocks decreases if water shares those small pores. Therefore, it is theoretically plausible to speculate that the residual oil saturation will follow an exponential relationship with the rock wettability.

2. PROBLEM STATEMENT

Numerous studies have discussed that there is a correlation between the wettability and the efficiency of oil recovery which the wettability influence amounts of oil produced from the reservoir. Some of the source rocks in reservoir are founded to be preferentially intermediate-wet or oil-wet. Studies proved that increasing water wetness will increasing the oil recovery. Alongside with this statement, a research is required to determine the most effective method to make rocks more water-wet in order to gain optimum oil recovery.

3. PROJECT SIGNIFICANCE

Enhanced oil recovery implies a reduction of remaining oil saturation in reservoir[1]. It can be reduces by lowering interfacial tension (IFT) and wettability. Since the study is related on making rocks more water wet, therefore this EOR method can be apply.

4. OBJECTIVE

The objectives of this study is:

- a) To determine the most effective method to make rocks more water-wet
- b) To study the relationship between wettability and oil recovery

5. SCOPE OF STUDY

The scope of study includes:

- a) Selection of methods in making more water wet
- b) Experimental setup to determine surface tension using two types of anionic surfactants
- c) Experiment setup for oil recovery using three different methods of Enhanced Oil Recovery (EOR)

CHAPTER 2

LITERATURE REVIEW

1. WETTABILITY AND ITS EFFECT ON OIL RECOVERY

Wettability can be defined as the tendency of one fluid to spread on or stick to a solid surface in the existence of other fluid called immiscible fluids [2]. In other words, wettability is a parameter that showed the solid is prefer to be in contact with one fluid rather than another[3]. It also can be refers as the interaction between solid surface and fluid phases. Reservoir rocks can be either water-wet, oil-wet or intermediate-wet.



Figure 1: Contact angle for three different rocks

On Figure 1, it described the wettability of three different wetting rocks. From left, the oil is dropped onto the surface of the rock and the contact between the oil and surface is only 0° which indicated that the surface is water-wet. If the oil is spreading 180° onto the surface, it called oil-wet surface.

As per discussed earlier, one of the main factors that affect oil recovery is wettability[4]. In line with above statement, the wettability of porous rock is measured as a function of the displacement properties of the rock-water-oil system[5]. Over the past 50 years, most of the reservoir rocks presumably to be very strongly water-wet (VSWW) which the surface of rocks always prefer water compare to oil[6]. Some of the studies have been made which they believed that reservoir rocks which is preferentially water-wet more efficiently than oil-wet rocks during oil recovery stages [7]. Morrow has proved in his research that decreasing the water-wetness will decrease the oil recovery[6]. He also concluded that optimum oil recovery can be obtained when the rock is neutral-wet.

2. WETTABILITY ALTERATION

In order to enhance oil recovery in fractured media, wettability alteration to water-wet or intermediate-wet condition is really important in improving it[8].Surfactants[9] and thermal flooding[10] are two suggested EOR methods in altering wettability.

2.1 Thermal Flooding

Thermal flooding is another EOR methods that widely used in this field. Under this method, there are three categories of thermal flooding, which are cyclic steam injection, steam flooding and combustion. Usually, steam injection is not only used to achieve optimum oil recovery, it is also used to alter rock wettability. The implication of thermal recovery on the system are not only changing the fluid properties and fluid-fluid interaction, it is also changed the rock-fluid interactions[11]. Some of experiment has proved that the oil-wet nature of calcite surface at temperature of 22°C changed to water-wet when the temperature raised up to 60°C [12]. However, the temperature dependence of contact angles which initially water-wet can shift to oil-wet after undergo steam flooding injection[11]. In addition, steam injection flooding will be highly successful in altering wettability and oil recovery if the steam is injected together with chemicals[13]. Therefore, it is suggested to conduct steam injection with surfactants in this experiment.**2.2** Non-thermal Flooding

Chemical flooding is one of non-thermal methods that widely used in enhancing oil recovery (EOR). There are six types of chemical floods which normally known as surfactant, polymer, alkaline, emulsion, micelle flooding and combinations. Surfactants flooding is one of EOR method that most successfully in recovering oil production.

3. SURFACTANT AND ITS CLASSIFICATION

Surfactant is stand for "Surface Active Agent" in English term is a chemical substance that will adsorb into the surface or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces when present in low temperature[2]. Surfactants are amphiphilic molecules which consisting of a hydrophilic head group and a hydrophobic hydrocarbon chain of various length[9].



Figure 2: Schematic of Surfactants behaviour in aqueous solution with oil emulsion called a micelle

In general, hydrophilic head can be described "water-lover" which it attracts more to water while hydrophobic tend to be "water-repellent". During surfactant flooding into reservoir, the rocks tend to absorb water into the surface which it resulting the decreasing angle of between the oil and surface. This scenario happened due to surfactants head turn around (hydrophilic head) towards water while the hydrophobic tall is forming inverse bubble that shielding oil into a bubble form. This situation make the oil lost its attachment with the rock surface and it allows the imbibition process to be occur. The surfactant chemicals that will be used to alter wettability in this project and will pass through screening process of which surfactants cause the best mode of alteration, are chemical studied by Golabi [9] and other commercial surfactants.



Figure 3: Surfactant classification according to the composition of their head: nonionic, anionic, cationic and amphoteric

Figure 3 above showed the composition of surfactant head which known as hydrophilic head that can be classified into four types; non-ionic, anionic, cationic and amphoteric.

3.1 Anionic Surfactant

Anionic surfactant is chemical that utilize negatively charged group such as carboxyl (RCOO-M+) or phosphate (ROPO3-M+). This type of surfactant is good for its stability and resistance to retention. Anionic surfactants is cheaper compared to cationic surfactant. However, this type surfactant is widely used in altering wettability of rocks. Thus, we decided to use anionic surfactant in this research.

*R symbolize hydrocarbon groups

3.2 Non-ionic Surfactant

Non-ionic surfactants produced from non-ionic groups that have polarity. For instance, polyoxyethylene (POE or OCH2CH2O-) or R-polyol groups. They did not form bonds, but can pull chemicals due to electronegativity effect when dissolve in water. It is usually used for better performance in high salinity water.

3.3 Cationic Surfactant

Cationic surfactant is class of surfactant that contained positive charged substances, for example ammonium halides (R4N+X-). The surfactant also carries inorganic anion to balance charges. Cationic surfactants is suitable for clay application due to high absorption of anionic surfaces of clay. According to [14], they had proved in studies that wettability of carbonate formations can be alter from oil-wet to water-wet using cationic surfactants.

3.4 Amphoteric Surfactant

There is also amphoteric or zwiterionic group which contained both anionic and cationic charges in single molecule surfactant. It is normally used in synthetic products like betaines and natural substances aminoacids.

4. WETTABILITY MEASUREMENT

There are two categories of wettability measurement: quantitative and qualitative methods. Under these two types of categories; there are several methods that have been developed to measure the reservoir's wetting preferences.

4.1 Quantitative Methods

Example of quantitative methods in measuring wettability are contact angle, Amott test and USBM test[11]. Apart from that, The contact angles measures the wettability of a specific surface, while Amott and USBM test measures average wettability[15]. Among these three measurement methods, contact angle measurement is most widely used methods in measuring wettability of rock surface[1, 16]. Contact angle can be defined as the function of interfacial tension between the solid-liquid and liquid-liquid interfaces [17].

4.2 Qualitative Methods

Qualitative wettability measurement also can be determine by using relative permeability curves, capillary pressures curves, imbibition rates and so on[15].

CHAPTER 3

METHODOLOGY



Figure 4: Methodology

1. SCREENING OF WETTABILITY ALTERATION METHODS

| Method | Advantageous | Limitations |
|---------------------|--------------------------|----------------------------|
| Surfactant Flooding | Increase in sweep | High adsorption into solid |
| | efficiency and lower the | surfaces, thereby a lot of |
| | interfacial tension | surfactants needed and it |
| | | will be high cost[18] |
| Steam Flooding | High temperature | Since we used sandstone |
| | influence wettability | rocks in this study, |
| | characteristics of | therefore steam flooding |
| | carbonate rocks from oil | cannot be applied due to |
| | wet to water wet and | wettability of sandstone |
| | sandstones rocks from | rocks will changed into |
| | strongly water wet to | neutral wet at high |
| | neutral wet[11]. | temperature. |

Table 1: Advantageous and Disadvantageous of Surfactant and Steam Flooding

2. SCREENING OF SURFACTANTS TO ALTER WETTABILITY

Two anionic surfactants: Alpha Olefin Sulfonates (AOS) and Internal Olefin Sulfonates (IOS) are used for screening purpose in this experiment. Only one of anionic surfactants will be selected for core flooding experiment. The selection are made based on low interfacial tension (IFT) and low viscosity. Interfacial Tension (IFT) Meter was used in this experiment to measure the surface tension of surfactants.

3. THEORY OF SURFACTANTS ALTERNATE GAS (SAG) FLOODING

Historically, surfactant alternate gas (SAG) flooding have been successfully applied in enhancing oil recovery for many years. In Malaysia, almost of the reservoir are suitable for gas injection[19]. However, gas injection always tends to breakthrough earlier in heterogeneous formation such as sandstones due to fingering, channelling and overriding[20]. In order to solve this problem, Surfactant Alternate Gas (SAG) flooding is suggested to be applied in the reservoir. Alongside with this study, surfactant is used to alter the wettability of rocks. Nitrogen is used for the gas injection in this experiment.

4. PREPARATION

4.1 Porous Media

Experiments were conducted using of Berea sandstone rock. This type of rocks are commonly used for standard testing material as it have excellent and uniform material properties[21]. The Berea sandstone core plugs were sampled from a well drilled in a reservoir. There are three cores of Berea sandstone rocks, two with 6 inches and another one is 3 inch.

| Core | D(cm) | Length(cm) | K(mD) | ф(%) | Vp(cc) |
|------|-------|------------|--------|-------------|--------|
| Α | 3.32 | 14.80 | - | 20.10 | 33.2 |
| В | 3.74 | 14.98 | - | 14.87 | 25.0 |
| С | 3.68 | 7.17 | 79.269 | 18.26 | 13.92 |

Table 2: Rock Properties of Berea Sandstone



Figure 5: Berea Sandstones

4.2 Materials

The anionic surfactants used in this experiment are Alpha Olefin Sulfonate (AOS) and Internal Olefin Sulfonates (IOS). Dulang crude oil, mineral oil and synthetic Dulang Brine were also being used in this experiment. The chemical composition of synthetic sea water brine is given in Table 3.

| Chemical Compound | Total (%) |
|---|-----------|
| Sodium Chloride NaCl | 2.5 |
| Pottasium Chloride KCl | 0.65 |
| Sodium Sulphate Na ₂ SO ₄ | 0.406 |
| Magnesium Chloride MgCl ₂ | 1.108 |
| Calcium Chloride CaCl ₂ | 0.168 |

Table 3: Chemical Composition of Synthetic Sea Water Brine

| DULANG FIELD RESERVOIR AND FLUID | | | |
|----------------------------------|--------------|--|--|
| PROPERTIES [22] | | | |
| Oil Viscosity (at 95°C) | 0.625 cp | | |
| Oil Pour Point | 40°C | | |
| Oil Stock Tank Density | 0.8347 gm/cc | | |
| API | 37.4° API | | |
| Oil Formation Volume Factor | 1.279 rb/stb | | |

Table 4: Dulang Field Reservoir and Fluid Properties



Figure 6: Dulang Oil, AOS Surfactant and Mineral Oil

5. METHODOLOGY OF SURFACTANT ALTERNATE GAS (SAG) FLOODING EXPERIMENT

Below is flow chart of Surfactant Alternate Gas (SAG) flooding experiment using Relative Permeability System (RPS) to be carried out.



Figure 7: Methodology of SAG Flooding

5.1 Core Cleaning

Firstly, the cores were cleaned using soxhlet extractor. The cores were placed into the flask and toluene was poured into 500cc flask. The cores were then left heated in fume hood for 3 days. After that, the cores were dried in oven for one day. Each of cores were labelled as A, B and C and they were placed in PoroPerm machine for permeability and porosity calculation. Helium gas is used in this machine with pressure of 400psi.



Figure 8: Core Cleaning Process in Fume Hood

5.2 Drying

The clean core is placed inside the oven for drying purpose at temperature 70°C for one day. This is to ensure that there is no fluid present inside the pores.

5.3 Core Saturation

The Berea core is saturated with brine inside the desiccator. The desiccator is used to suck all the trapped air inside the pores and let the brine to fill in the pores. In this experiment, we were used synthetic sea water brine to saturate the cores. The cores was saturated in brine for one day in glass desiccators. The desiccator was connected with vacuum pump to pump out all trapped bubbles inside the cores and the brine can smoothly absorbed into the pores.

5.4 Determination of Original Oil in Place (OOIP)

Relative Permeability System (RPS) is used for Gas Flooding and Surfactant Alternate Gas (SAG) experiment. An amount of Dulang oil is injected inside the core and the displace oil will be collected at the outlet of RPS. Original oil in place (OOIP) can be determine by the deduction of total oil injected with the total of oil collected at the outlet.

OOIP = Volume of oil injected, V_1 – Volume of oil collected at outlet, V_2

5.5 Secondary Recovery (Water flooding)

Brine is injected to displace crude oil from the core. Brine is injected continuously and stop once there is no oil comes out from the outlet. The percentage of recovery can be calculated using the formula below.

Percentage of recovery,
$$\% = \frac{\text{Volume of oil recovered,V3}}{\text{OOIP}} \ge 100\%$$

5.6 Tertiary Recovery (N2 Flooding and SAG Flooding)

 N_2 gas is transfer from N_2 gas cylinder into accumulator 1. The gas will be compressed to pressure around 1900 psi to ensure the existence of liquid N2. The pressure to core compartment will be adjusted to 1900 psi which is equal to compressed gas N_2 pressure. This will ensure the liquid N_2 is injected into the core sample to recover the remaining oil inside the core. The oil recovered during tertiary recovery will be collected at sample point.

Percentage of recovery,
$$\% = \frac{\text{Volume of oil recovered, V4}}{\text{ROIP}} \times 100\%$$

6. Step of Surfactant Flooding using Benchtop Permeability System (BPS)

- 1. Temperature and pressure was set up at ambient condition.
- 2. 25ml of brine is injected into the core with flowrate of 0.5cc/min.
- 3. 25ml of mineral oil is injected with 1.5cc/min until steady state condition.
- 4. Water flooding is carried out at flowrate of 1cc/min with 30ml of brine.
- 5. 10ml of surfactant is injected inside the core at flowrate of 0.5cc/min.
- 6. Water flooding is repeated at flowrate of 1cc/min.
- 7. Final injection of surfactant is conducted at flowrate of 0.5cc/min.
- 8. Last stage of brine flooding is performed at flowrate of 2.0 cc/min.



Figure 9: Benchtop Permeability System (BPS)

7. Step of N₂ gas and Surfactant Alternate Gas (SAG) Flooding using Relative Permeability System (RPS)

- 1. Temperature and pressure was set up at 80°C and 1900 psi significant to reservoir condition. Core is placed inside the accumulator 4.
- 2. N₂ gas is filled in into accumulator 1, brine into accumulator 2 and Dulang Oil is filled into accumulator 3.
- 3. N_2 gas is then compressed up to 1900 psi to convert the gas into liquid phase.
- 4. Brine is injected into the core at flowrate of 1cc/min until steady state conditions are achieved.
- 5. Crude oil is injected until steady state conditions.
- 6. Secondary water flooding is carried out at flowrate of 0.25cc/min.
- 7. Brine is replaced with surfactants in accumulator 4. Distilled water is used to displace remaining brine left inside the accumulator.
- 8. Gas is injected at flowrate of 0.25cc/min until no oil comes out. (Gas Flooding will stop until this step and continue with water flooding)
- 9. Surfactant flooding is conducted at flowrate of 0.25cc/min with 0.5PV.
- 10. SAG flooding is repeated until three cycles with 0.75PV of gas and 0.5PV of surfactants at flowrate of 0.4 and 0.8cc/min.
- 11. Water flooding will be conducted at 1.0cc/min until steady state conditions are achieved.



Figure 10: Relative Permeability System (RPS) and Sample Point

CHAPTER 4

RESULTS & DISCUSSION

1. SURFACE TENSION MEASUREMENT

| Table 5 : Surface Tension of Alpha Olefin | | | | |
|---|--------------|----------|--|--|
| Sulfonates (AOS) | | | | |
| Time | IFT, σ (N/m) | Contact | | |
| (s) | | Angle, θ | | |
| 0.0 | 33.71 | 104.57 | | |
| 0.1 | 33.78 | 104.78 | | |
| 0.2 | 33.79 | 104.93 | | |
| 0.3 | 33.79 | 104.94 | | |
| 0.4 | 33.79 | 104.92 | | |
| 0.5 | 33.79 | 104.90 | | |
| 0.6 | 33.78 | 104.87 | | |
| 0.7 | 33.78 | 104.86 | | |
| 0.8 | 33.78 | 104.87 | | |
| 0.9 | 33.77 | 104.83 | | |



Figure 11: IFT Measurement of AOS 1%



Figure 12: Surface Tension Of Alpha Olefin Sulfonates (AOS)

| | Internal Olefin | 6: Surface Tension O | Table |
|-----------------------------|-----------------|----------------------|-------|
| | S) | Sulfonates (IC | |
| | Contact | IFT, σ (N/m) | Time |
| | Angle , θ | | (s) |
| | 103.00 | 30.80 | 0.0 |
| | 103.10 | 30.74 | 0.1 |
| | 103.25 | 30.76 | 0.2 |
| Figure 13: IFT Me | 103.34 | 30.75 | 0.3 |
| Of Internal Olefin (IOS) | 103.57 | 30.77 | 0.4 |
| | 103.66 | 30.76 | 0.5 |
| | 103.69 | 30.74 | 0.6 |
| | 103.77 | 30.72 | 0.7 |
| | 103.77 | 30.74 | 0.8 |
| | 103.90 | 30.75 | 0.9 |



asurement Sulfonates



Figure 14: Surface Tension of Internal Olefin Sulfonates (IOS)

From the result above, IOS surfactant showed the lowest IFT value (30N/m) compare to AOS. However, AOS is selected to alter wettability since it is low viscosity than IOS. It can justified that AOS is easily attract to water-wet rock rather than oil-wet rock. Since we are using sandstone rock which is originally water-wet rock, thus AOS is selected as the best surfactant to alter wettability.

| Oil Injected,V1 | 20ml |
|----------------------------------|-------|
| Oil Collected,V2 | 8ml |
| Oil Recovered, V3 | 2.5ml |
| OOIP | 12ml |
| Percentage of Secondary Recovery | 21% |
| Residual Oil In Place (ROIP) | 9.5ml |
| Oil Recovered, V4 | 3.5ml |
| Percentage of Tertiary Recovery | 36.8% |
| Cumulative Recovery | 57.8% |

2. SURFACTANT FLOODING WITH MINERAL OIL

Table 7: Data Collected during Surfactant Flooding



Figure 15: Mineral Oil Displaced after Secondary Water flooding and Surfactant Flooding

Figure 15 showed the displaced mineral oil after Secondary and tertiary recovery. The volume of mineral oil is differentiate by the present of two phase in the cylinder. The below one should be brine since brine is more dense compare to mineral oil. The volume of mineral oil can be accurately differentiate if the liquid displaced is left for one day. The colour of mineral oil will turn to be a little dark than brine. The mineral oil is recovered around 2.5ml by secondary water flooding which the recovery is

around 21%. After surfactant flooding, the oil collected is 3.5ml which the recovery is increased by 36.8%. The cumulative recovery by using this method is around 57.8%.

| Effective Core Porosity | 20.10% |
|---------------------------------|---------|
| Average Absolute Permeability | 52.88mD |
| Pore Volume | 32.2 ml |
| Dead Volume | 5.2ml |
| Volume of Oil Injected, V1 | 40ml |
| Volume of Oil Collected, V2 | 17ml |
| Volume of Oil Recovered,V3 | 6ml |
| Original Oil in Place (OOIP) | 17.8ml |
| Percentage of Recovery | 35.3% |
| Residual oil in place (ROIP) | 12.8ml |
| Volume of Oil Recovered, V4 | 2ml |
| Percentage of Tertiary Recovery | 15.63% |
| Cumulative Recovery | 50.93% |

3. GAS FLOODING WITHOUT SURFACTANT

Table 8: Data Collected during Gas Flooding



Figure 16: Oil and Brine Displaced by Secondary Water flooding

Figure 15 above shown the volume of fluid displaced during core flooding experiment. The original oil in place (OOIP) inside core B was estimated around 17.8ml. The secondary water flooding successfully sweep the oil around 6ml and the recovery is 35.3%.



Figure 17: Oil Recovery after Gas Flooding

Figure 16 above showed the oil recovered after N_2 gas flooding and water flooding. The amount of oil displaced was around 2ml and the percentage of tertiary recovery is 15.63%. Total of recovery using Gas Flooding method is 50.93%.

4. SURFACTANT ALTERNATE GAS (SAG) FLOODING WITH OIL

| Oil Injected,V1 | 38.7ml |
|--|--------|
| Oil Collected, V2 | 13ml |
| Oil Recovered, V3 (Secondary Water Flooding) | 7ml |
| OOIP | 20.5ml |
| Percentage of Secondary Recovery | 34.15% |
| Residual Oil In Place (ROIP) | 13.5ml |
| Oil Recovered, V4 (Post SAG Flooding) | 4.5ml |
| Percentage of Tertiary Recovery | 33.33% |
| Cumulative Recovery | 67.5% |

 Table 9: Data Collected during SAG Flooding



Figure 18: Oil Recovery by using SAG Flooding

From left : Oil Flooding, Secondary Water Flooding, SAG 1, SAG 2, SAG 3, SAG 4 and Water Flooding after SAG

Figure 18 showed the oil collected by using Surfactant Alternate Gas (SAG) Flooding. The secondary recovery by using brine injection successfully displaced the oil by 34.15% which is 7ml. During tertiary recovery which is SAG flooding, the oil is recovered about 33.33% which is 4.5ml of residual oil is displaced from the core. The total recovery by using SAG flooding is 67.5%.



Figure 19: Comparison of Oil Recovery by using Three Different Methods

From figure 19 above, it showed the percentage of recovery by three different methods: Surfactant flooding, N₂ gas flooding without surfactant and Surfactant Alternate Gas Flooding. It can be concluded that injection of gas without surfactants will resulting the lowest recovery of oil compare to addition of surfactants in core flooding. It proved that N₂ gas flooding will breakthrough earlier in cores since it has low viscosity and easily mobile inside the cores. Surfactant flooding without gas injection resulted the second highest of oil recovery. It can be said that addition of surfactants inside the cores will cause the oil to leave the rock surface. This phenomena is called wettability alteration which surfactant will alter the wettability from oil-wet rock to water-wet rock. In contrast, SAG flooding showed the highest recovery compare to gas flooding and surfactant flooding. It is because the surfactant will stop the gas from early breakthrough. This retention will let the gas to channel and sweep the oil at the low permeable zone which is tight zone. Therefore, SAG flooding by using AOS surfactant is proved as the best method in altering the wettability of sandstone rock, hereby resulting in highest oil recovery.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

1. CONCLUSION

Based on the result from the experiment, it shown that Surfactant Alternate Gas (SAG) Flooding is the most effective method to alter the wettability of Berea sandstone rock, hereby increasing the oil recovery. Apart from that, the contact angles and surface tension for the surfactant were recorded and shown here in this report, which assisted in justifying the best surfactant in altering the wettability of the oil droplet.

Experimental core flooding, gave satisfactory results for the improvement of a secondary recovery method – water flooding, showing that the use of AOS surfactant did improve the effectiveness of the recovery and in this case by 67.5% in total.

2. **RECOMMENDATION**

- i. Fabrication of heating oven or box at the outlet of RPS equipment is suggested to collect all the displace liquid. This recommendation is made up based on the properties of Dulang oil which trapped inside the tube due to surface condition that lead the oil to become waxy. Due to that, the inlet and outlet pressure were rising above the pressure set up and will cause the failure of equipment.
- ii. Quantitative method to measure the wettability such as sessile drop is suggested to be install in laboratory. It easier for student to measure the contact angle using the equipment and the data gaining from the experiment can be compare with data from qualitative method.
- iii. The Surfactant Alternate Gas (SAG) using CO₂ gas injection should be further studies in order to determine the sweep efficiency of CO₂ in oil recovery.
- iv. Studies using various surfactant in altering wettability of rocks should also take into consideration.

REFERENCES

- [1] O. Elmofty, "Surfactants Enhanced Oil Recovery by Wettability Alteration in Sandstone Reservoirs," 2012.
- [2] M. J. Rosen and J. T. Kunjappu, *Surfactans and Interfacial Phenomena*: John Wiley & Sons, 2012.
- [3] W. Abdallah, J. S. Buckley, A. Carnegie, J. Edwards, B. Herold, E. Fordham, *et al.*, "Fundamental Of Wettability."
- [4] E. C. Donaldson, R. D. Thomas, and P. B. Lorenz, "Wettability Determination and Its Effect on Recovery Efficiency," 1969/3/1/.
- [5] E. Amott, "Observations Relating to the Wettability of Porous Rock," vol. 216, ed: Society of Petroleum Engineers, 1959.
- [6] N. R. Morrow, "Wettability and Its Effect on Oil Recovery," *Society of Petroleum Engineers*, 1990.
- [7] J. E. Bobek, C. C. Mattax, and M. O. Denekas, "Reservoir Rock Wettability -Its Significance and Evaluation," ed: Society of Petroleum Engineers.
- [8] A. Seethepalli, B. Adibhatla, and K. K. Mohanty, "Wettability Alteration During Surfactant Flooding of Carbonate Reservoirs."
- [9] E. Golabi, F. S. Azad, and O. Branch, "Experimental study of wettability alteration of limestone rock from oil-wet to water-wet using various surfactants," in *Paper SPE157801 presented at the SPE Heavy Oil Conference, Calgary, Alberta, Canada*, 2012, pp. 12-14.
- [10] H. S. Al-Hadhrami and M. J. Blunt, "Thermally induced wettability alteration to improve oil recovery in fractured reservoirs," SPE Reservoir Evaluation & Engineering, vol. 4, pp. 179-186, 2001.
- [11] D. N. Rao, "Wettability Effects in Thermal Recovery Operations," vol. 2, 1999/10/1/1999.
- [12] O. S. Hjelmeland and L. E. Larrondo, "Experimental Investigation of the Effects of Temperature, Pressure, and Crude Oil Composition on Interfacial Properties," 1986/7/1/.
- [13] S. M. F. Ali and S. Thomas, "A Realistic Look at Enhanced Oil Recovery," *Scientia Iranica*, vol. 1, 1994.
- [14] D. C. Standnes, L. A. Nogaret, H.-L. Chen, and T. Austad, "An evaluation of spontaneous imbibition of water into oil-wet carbonate reservoir cores using a nonionic and a cationic surfactant," *Energy & Fuels*, vol. 16, pp. 1557-1564, 2002.
- [15] W. Anderson, "Wettability Literature Survey- Part 2: Wettability Measurement," 1986/11/1/.
- [16] N. R. Morrow, "Wettability and its effect on oil recovery," *Journal of Petroleum Technology*, vol. 42, pp. 1476-1484, 1990.
- [17] M. B. Alotaibi, R. Azmy, and H. A. Nasr-El-Din, "Wettability Challenges in Carbonate Reservoirs."
- [18] P. Mwangi, "AN EXPERIMENTAL STUDY OF SURFACTANTS ENHANCED WATERFLOODING," 2010.
- [19] G. Nadeson, N. A. B. Anua, A. Singhal, and R. B. Ibrahim, "Water-Alternating-Gas (WAG) Pilot Implementation, A First EOR Development Project in Dulang Field, Offshore Peninsular Malaysia."

- [20] M. M. Salehi, M. A. Safarzadeh, E. Sahraei, and S. A. T. Nejad, "Comparison of oil removal in surfactant alternating gas with water alternating gas, water flooding and gas flooding in secondary oil recovery process," *Journal of Petroleum Science and Engineering*, vol. 120, pp. 86-93, 8// 2014.
- [21] J. C. Shaw, P. L. Churcher, and B. F. Hawkins, "The Effect of Firing on Berea Sandstone," 1991/3/1/.
- [22] A. Hussain, E. O. Egbogah, and W. R. Hovdestad, "Reservoir Management of the Dulang Oil Field, Offshore Peninsular Malaysia: The Heuristic Approach," 1992.