Screening and Optimization of Chemicals to Alter Reservoir Wettability

By

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Dissertation report submitted in partial fulfilment of the requirements for the

Bachelor of Engineering (Hons) Petroleum Engineering

May 2011

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CERTIFICATION OF APPROVAL

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Petroleum Engineering Programme Universiti Teknologi PETRONAS

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(PETROLEUM ENGINEERING)

Approved By,

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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 concept as specified in the references and acknowledgement, and that the original work contained herein have not been undertaken or done by unspecified sources or persons

(MOHD SADRUDDIN BIN AWANG MOHAMED @ BUSU)

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ABSTRACT

Wettability is one of the main factors that affected the recovery of oil and gas in a reservoir. A reservoir need unique of wettability to produce optimum hydrocarbon. Alteration of wettability needed in some reservoir in order to get that unique feature of wettability for different type of reservoir. Chemicals can be used as the tools to help the process of the wettability alteration. There were few types of chemicals that commonly used in industry toward the alteration of the wettability. Hence, in order to find the best chemicals, the criteria and properties of different case study should be taken into account to produce a set of analysis. This procedure is called the screening process. After the analysis done by collecting the data, the best chemicals can be selected toward the suitable reservoir according to its properties.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Screening criteria is very important for all enhanced oil recovery method (J.J Taber, 1997). Data from few of carbonate reservoirs collected to be examined and produced the optimum chemicals that enhance the oil recovery by reversibility of the reservoir wettability. The preference of a solid to contact one liquid or gas, known as the wetting phase, rather than another. The wetting phase will tend to spread on the solid surface and a porous solid will tend to imbibe the wetting phase, in both cases displacing the nonwetting phase (Schlumberger Glossary, 2009). Rocks can be water-wet, oil-wet or intermediate-wet. Wettability alteration of the oil- wet rocks to water-wet is crucial to enhance oil recovery (E.Golabi , 1997). In order to reverse the reservoir wettability from oil-wet to water-wet in fractured carbonate reservoirs, two different methods have been reported in the literature including adding a certain amount of chemicals by using surfactants (Standnes and Austad T , 2000) and by increasing temperature (H.S. Blunt , 2000) . Three different types of surfactants commonly used in the process including anionic surfactants (Standnes and Austad T, 2000), non-ionic surfactans (Kenyon,D.E , 2000) and cationic surfactants (Schameborn , 1993).

1.2 Problem Statement

1.2.1 Problem Identification

The challenge to screen and optimize the chemicals that can alter the reservoir wettability. Different type of chemicals performance only reacts with unique type of reservoir. Nonionic surfactants more tolerant than anionic surfactant in high salinity environment. Meanwhile, anionic surfactant was not able to react in anionic organic carboxylates reservoir. It is important to identify which chemical will be used in different types of reservoirs.

1.2.2 Significant of the Project

This project very important in order to find the optimize chemicals for the different type of reservoir. The screening criteria are based on the previous project that has been done successfully.

1.3 Objectives

There were several objectives for this project which are:-

1) To identify type of chemicals that has ability to alter the reservoir wettability
2) To identify the mechanism of wettability alteration for the specific reservoir
3) To find the criteria that important for wettability alteration

1.4 Scope of Study

For this project, the scope of study covered about the criteria of the chemicals for the screening purposes in order to find the best and suitable chemicals that have the ability to alternate the wettability of a reservoir.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter will briefly covers few basic terms that need to be understood in order to complete this research. The term such as screening, chemicals that can alter the reservoir wettability and the wettability itself will be explained in throughout this chapter. Then, two case studies are stated in order to give clear picture regarding the effects of chemicals toward the reversibility of the reservoir wettability.

2.2 Screening

Screening criteria have been used in the Enhance Oil Recovery (EOR) method. The best known and most widely use, screening criteria appeared in the 1976 and 1984 Natl. Petroleum Council (NPC) report (Haynes, 1976 & Bailey 1984). In recent years, computer technology has improved the application of screening criteria through the use of artificial intelligence techniques but it depends on the accuracy of the data inserted (Parkinson, 1990 ; Elemo, 1993 ; Basnieva, 1994). Screening criteria manually based on the combination of the reservoir and oil characteristic of successful project has been done (J.J. Taber , 1997). There were few criteria in order to screen the chemicals (surfactant) such as CMC-value, hydrophobic property, IFT-value and steric effect (Dag C. Standness, 2000).

2.3 Types of Chemicals

Chemical flooding methods are targeted at recovering of residual oil left in the reservoir after water flooding. There were six major groups of chemicals which are polymer, surfactant, alkaline, combinations, micellar and emulsion (S.M Farouq Ali , 1996). Three different types of surfactants commonly were used in the wettability alteration process including anionic surfactants (Standnes and Austad T, 2000), non-ionic surfactans
(Kenyon,D.E , 2000) and cationic surfactants (Schameborn , 1993).

Data and physical properties of the surfactants

Surfactant	Producer	Pureness	Brine	CMC[a] (25°C) (wt.%; M)	Conc. range (wt.%)
C12TAB	Sigma	≈ 99%	1	0.43; $1.4 \cdot 10^{-2}$	0.1–5.0
C16TAB	Sigma	≈ 99%	1	0.03; $8 \cdot 10^{-4}$	1.0
n-C_8–Ph–$(EO)_2$–$N(CH_3)_2(CH_2$–Ph)Cl (Hyamine)	Fluka	> 99%	2	0.16; $3.6 \cdot 10^{-3}$	0.2
n-$(C_8$–$C_{18})$–$N(CH_3)_2(CH_2$–Ph)Cl (ADMBACl)	Aldrich	> 96.5%	1	0.19[b]; $6.8 \cdot 10^{-3}$	0.5
C10TAB	Fluka	> 98%	1	1.9; $6.8 \cdot 10^{-2}$	2.5
C8TAB	Fluka	≥ 98%	1	3.4; 0.14	4.5
$(n$-$C_8O_2CCH_2)(n$-$C_8O_2C)CH$–SO_3Na (Cropol)	Croda	≈ 70%	1		0.5
$R(EO)_8SO_3Na$ (B 1317)	Hoechst		1		0.5
n-C_9–Ph–$(EO)_x$–PO_3Na (Gafac)	R-P		1		0.5
$R(EO)_8OCH_2COOH$ (Akypo)	Chemy/Promol		1		0.5
SDS	Aldrich	> 99%	3	0.023; $8.1 \cdot 10^{-3}$	0.1
$R(EO)_3SO_3Na$ (S-74)			1		0.5
$R(PO)_4(EO)_2OSO_3Na$ (APES)	Synthesis[c]	≈ 40%	2		1.0
$R(EO)_{15}SO_3Na$ (S-150)			1		0.5

[a]CMC values in distilled water from Munkerjee and Mysels (1971).
[b]CMC value for Decylbenzyldimethylammonium chloride. Temperature unknown.
[c]Surfactant synthesised from the corresponding alcohol, $C_{12\text{-}15}(PO)_4(EO)_2OH$ (Kelland, 1994).

Figure 1: Several Types of Surfactants (Standness, 2000)

2.3.1 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.

*R symbolize hydrocarbon groups.

2.3.2 Non-ionic Surfactants

Non ionic surfactants produced from non ionic groups that have polarity. For instance, polyoxyethylene (POE or OCH2CH2O-) or R-polyol groups. They didn't form bonds, but can pull chemicals due to electronegativity effect when dissolve in water. Since, it is better to be used in high salinity water.

2.3.3 Cationic Surfactants

Cationic Surfactant is positively charged substance, such as ammonium halides (R4N+X-). The surfactant also carries inorganic anion to balance the charges. Cationic surfactants is suitable for clay application due to high absorbtion of anionic surfaces of clay.

There is also amphoterics groups, containing 2 or more classes to suit reservoir application

2.4 Wettability

Wettability is defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids (Craig, 1971) . The wettability of a rock is important because it controls the location, flow and distribution of fluids within reservoir rock (Anderson, 1986A). When a rock is oil-wet, the oleic phase will will occupy the center of larger pores and form globules that might extend over many pores. Then, if the rock is water-wet, the aqueous phase will be retained by capillary forces in the smaller pores and on the walls of the larger pores. A rock can have neutral wettability if there is no clear preference for one fluid or another. Fractional wettability can happen when many minerals have different surface chemistry and adsorption properties. A mixed-wet rock will have oleic phase completely occupying the oil-wet large pores and the aqueous phase occupying the water-wet small pores (Salathiel, 1973).

Several methods can be used to determining the wettability of a rock. Three most common quantitative methods are contact angle measurement, the Amott method and USBM method. The contact angle method only measure wettability of single solid surface while Amott and USBM can measure average wettability of a core sample (Anderson, 1986B).

Amott method utilizes a sequence of imbibitions and forced displacement test. One problem with Amott method is its insensitivity near neutral wettability (Anderson, 1986B). USBM method was first introduced by Donaldson et al. 1969. The advantage of this method compare to Amott method is the sensitivity near neutral wettability while Amott mehthod is not. UBSM method utilizes the following equation to determine the wettability (W) :

$$W = Log\, A_1/A_2$$

Where A_1 and A_2 are the areas under the water and oil derived capillary pressure curves, respectively. UBSM just only can be conducted on plug-sized samples (Anderson, 1968B)

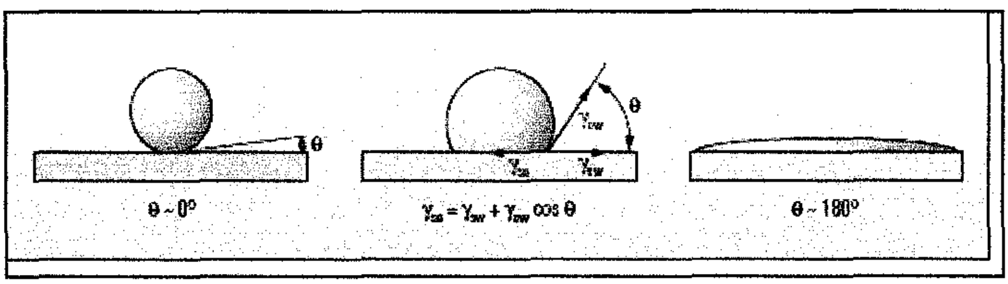


Figure 2: Type of Wettability (Fundamentals of Wettability,2007)

Contact angle. An oil drop (green) surrounded by water (blue) on a water-wet surface (left) forms a bead. The contact angle is approximately zero.On an oil-wet surface (right), the drop spreads, resulting in a contact angle of about 180°

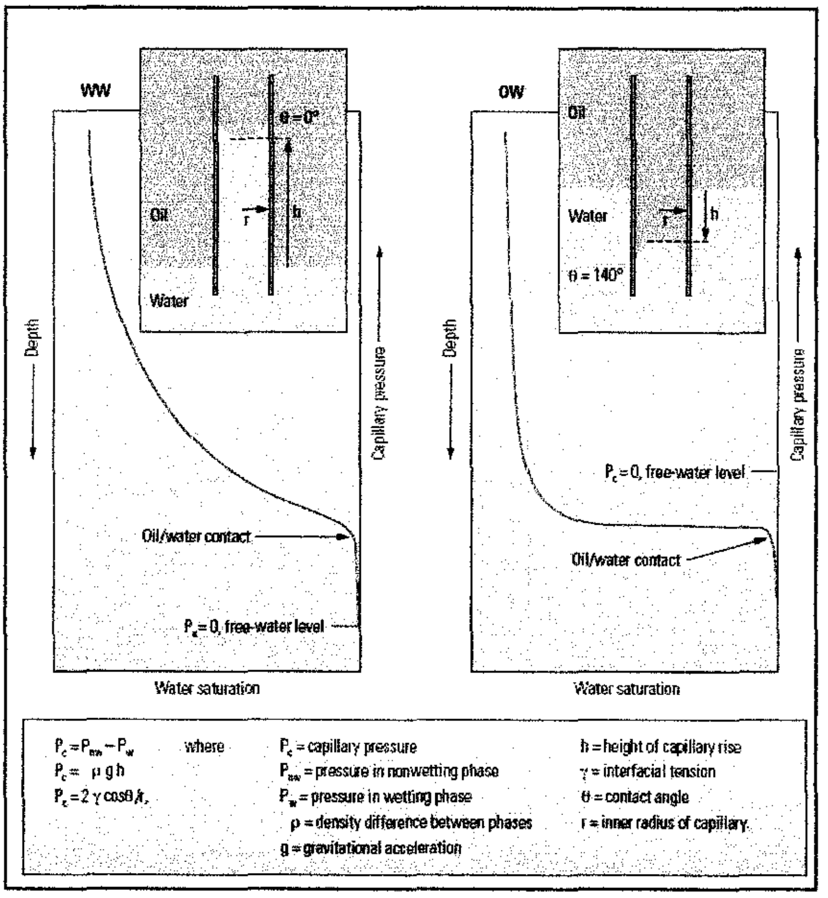


Figure 3: Properties of Wetting (Fundamentals of Wettability, 2007)

Forming a transition zone. A homogeneous formation exhibits a zone of transition from high oil saturation at the top to high water saturation at the bottom (blue curves). In capillary tube water-wetting surface forces cause water to rise, displacing oil but if in oil-wetting, the oil push down the water. In a water-wet formation, oil/water contact is above the FWL. In oil-wet formation, the contact is below the FWL.

2.5 Wettability Alteration

Rock wettability is highly dependent upon the surface chemistry and adsorption properties of the grains. Most of the geologic formations are strongly water-wet initially because the formations are completely saturated with water during deposition. When the hydrocarbon migrate into water-saturated formation, the rock can be remain as water-wet or change due to the migration of the hydrocarbon. The reason of the formation has stability natural wetting state and wettability alteration briefly explained by Buckley in 1989. If the water film coating the grain surfaces remains stable, the formation wettability can remain strongly water-wet. Besides, the formation can remain strongly water-wet if the oil does not contain water-soluble components such as soaps or asphaltenes than can alter the chemical charge of the fluid-fluid or fluid-solid interfaces. When the water film become unstable, it can allow the oil to contact the rock surface and allow water-insoluble components to adsorb onto the grain surface and cause altering its charge and wettabilty. Several factors that cause the stability of water film are pH, brine composition and capillary pressure.

Natural wettability alteration can happen over geologic time (Buckley,1989). But, the alteration of the formation's wettability can also be happen by inducing thermally and chemically. The mechanism by which the wettability was altered during steam or hot water injection is desorption of asphaltenes from the rock surface.

Few studies carried to see the effect of chemical injection on wettability alteration. Primary chemicals used for wettability alteration are surfactants and alkali. Surfactants are anionic, cationic, non-ionic or amphoteric. The surfactant will adsorb on rock surface and preferentially attract a particular phase under the right condition. This phenomenon may change the wettability of the rock. For example, a positively charged rock will strongly attract an anionic surfactant and negatively charged rock will strongly attract a cationic surfactant. Non-ionic surfactants are attracted to mineral surfaces by hydrogen bonding and van de Waal forces.

2.6 Case Study

Wettability alteration of outcrop obtained from Asmari formation was investigated using surfactant. Three different surfactants including a cationic surfactant: dodecyltrimethylammonium bromide (DTAB), an ionic surfactant: sodium dodecylbenzenesulfonate (SDBS) and non-ionic surfactact that was Tritton X-100 were used. (E.Golabi, 2009)

Wettability alterations in the presence of each surfactant for three surfactant concentrations from 0.1 to 0.3 wt% in brine and at four different temperatures, from 25 °C to 80°C were examined. Surfactant solution droplets were placed on the rock surfaces after being saturated with brine and placed in crude oil. The potential of surfactants to alter the wettability was determined by estimating the contact angle between surfactant droplet and surface of the rock. (E.Golabi, 2009)

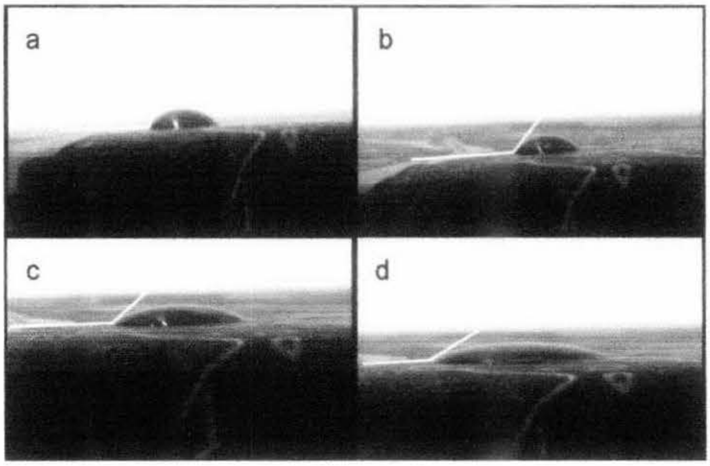


Figure 5: Contact angels for 0.1 wt% DTAB solution and Aghajari oil reservoir rock at different temperature (a) 25, (b) 30 , (c) 50 and (d) 80° C (E.Golabi, 2009)

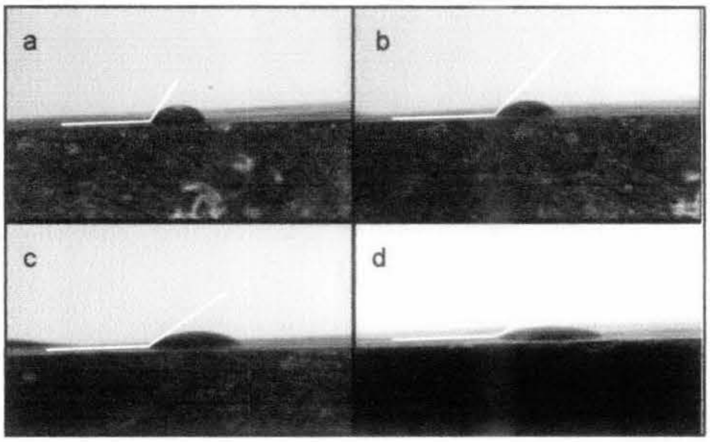


Figure 6: Contact angels for 0.1 wt% SDBS solution and Aghajari oil reservoir rock at different temperature (a) 25, (b) 30 , (c) 50 and (d) 80^{0} C
(E.Golabi, 2009)

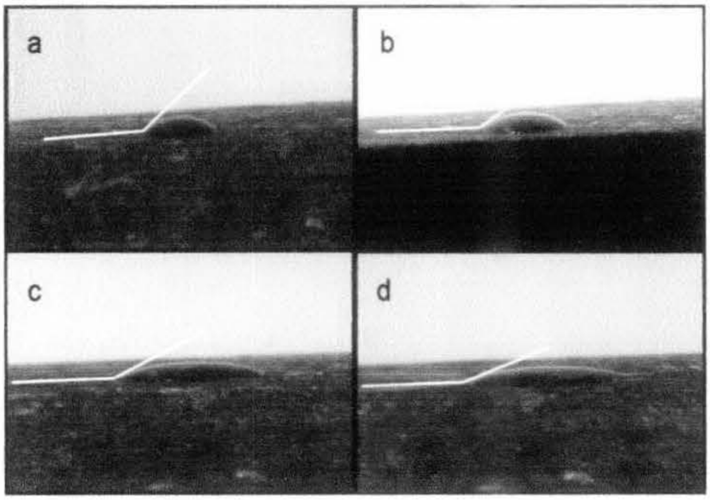


Figure 7: Contact angels for 0.1 wt% Triton X-100 solution and Aghajari oil reservoir rock at different temperature (a) 25, (b) 30 , (c) 50 and (d) 80^{0} C
(E.Golabi, 2009)

The results show that by increasing the surfactant concentration and temperature, more wettability alteration of the rock toward water-wer will be obtained. Triton X-100 as a non-ionic surfactant has higher potential for wettability alteration of the reservoir rock towards the water-wet condition compared to DTAB and SDBS. (E.Golabi, 2009)

CHAPTER 3
METHODOLOGY

Project methodology is one of the important aspects in this project to make sure the project is done smoothly and successfully. The methodology includes:

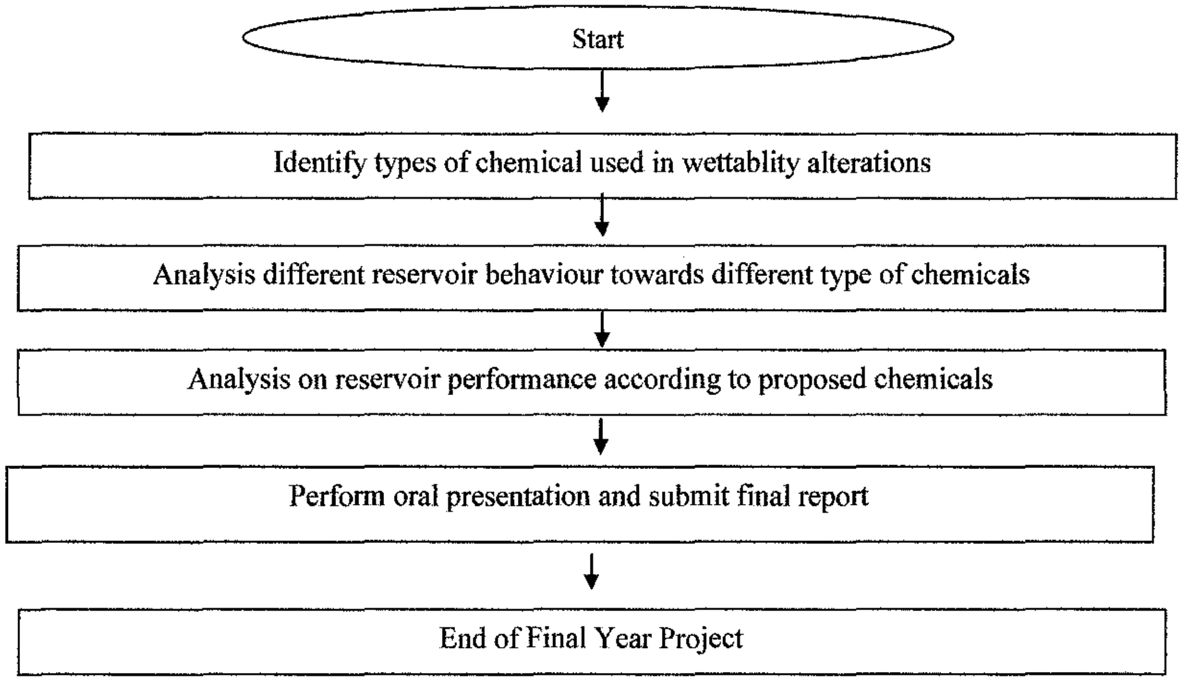
3.1 Research Methodology

For better understanding with this topic, the project research is conducted. From the research, lots of knowledge gained to help finish this project. Firstly, the research about the chemicals that have ability to alter the reservoir wettability. In the chemical flooding phase, not all chemicals play role to alter reservoir wettability. Few of them function to lower the interfacial tension (IFT) between the hydrocarbon and the surface. This will enhance the oil or gas recovery. The research is very important in order to run the screening process. After finished the screening process, a set of data regarding the criteria of the chemicals will be obtained. From that data, analysis will be run to find the suitable chemicals for the different types of reservoir.

The information gathered in the research is from any SPE papers and books that related to this topic.

3.2 Project Activities

PROJECT ACTIVITIES



3.3 Key Milestone

The key milestone and propose planning throughout this semester activities are as follow:

No	*Activities*	*Week*
1	**Progress Report Submission**	**Week 8**
2	**Pre - EDX**	**Week 11**
3	**Draft Dissertation Submission**	**Week 12**
4	**Dissertation Submission (Softbound)**	**Week 13**
5	**Technical Paper Submission**	**Week 13**
6	**Oral Presentation**	**Week 14**
7	**Dissertation Submission (Hardbound)**	**Week 14**

3.4 Gantt Chart

FYP

No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Analysis of The Journal														
2	Progress Report Submission														
3	Pre- EDX														
4	Draft Report Submission														
5	Dissertation Submission (Softbound)														
6	Technical Paper Submission														
7	Oral Presentation														
8	Dissertation Submission (Hardbound)														

CHAPTER 4
RESULTS AND DISCUSSIONS

Based on the screening process through few of previous papers, I found out that there were several chemicals that have the ability to alter the reservoir wettability. Usually, the using of the chemicals widely use in the fracture carbonate conditions. This is due to the highly percentage of residual oil in the formation. During first or second recovery, the formation use water flooding as the recovery process to get hydrocarbon. But, the process still not effective and it need chemicals instead of just water to enhance the oil recovery (EOR).

4.1 Dodecyltrimethylammonium bromide (C12TAB)

C12TAB is one the surfactant that has ability to alter the reservoir wettability. C12TAB is the cationic surfactant that widely used in the carbonate formation. In one of the experiment, chalk cores were used to represent the reservoir conditions. The cores were first aged in a crude oil in order to have oil-wet properties. During the process, the adsorption of negatively charged carboxylate groups from crude oil on the positively charge chalk surface changed the rock wettability toward oil-wet. By forming ion pairs between cationic head groups and the negatively charged carboxylate groups adsorbed on the rock surface, it will alter the oil-wet chalk surface toward a more water-wet surface (Mehdi and Johnson , 2008).

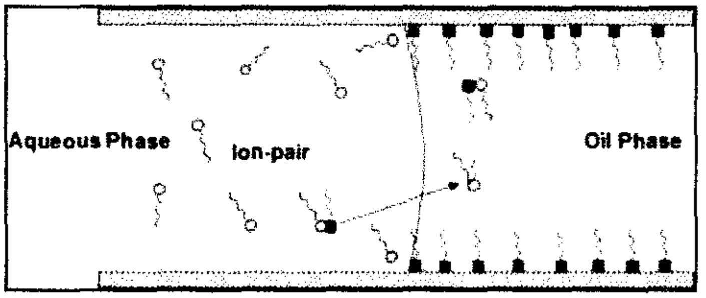


Figure 8

Model of alteration mechanism by C12TAB. Circles are cationic surfactant while squares are anionic material of crude oil (Standness, 2001)

In figure 8, the formation of ions pairs could strip the adsorbed layer of crude oil components from the rock surface. This phenomenon will expose the rock surface to water-wet as it original condition. The ion pairs formed during the process would no longer be water soluble and will leave the surfactant molecules in water phase to associate with adsorbed crude oil component. So, the surfactant will change the wettability from oil-wet toward water-wet state (Mehdi and Johnson , 2008).

4.2 STEOL CS-330 (SLS – Sodium Laureth Sulfate)

This chemical categorize in the anionic surfactant. Anionic surfactant also can play role as the agent to alter the reservoir wettability. The molecules of anionic can form a monolayer on the rock surface through hydrophobic interactions with the adsorbed crude oil components (Mehdi and Johnson , 2008). The layer of adsorbed surfactant with the hydrophilic head groups that covering the originally oil-wet surface could then change the wetting state of the rock surface toward water-wet state (Mehdi and Johnson , 2008).

4.3 Arquad MC-50

This chemical was evaluated by measuring the static contact angle on calcite surfaces. Static contact angle measurement is regarded to be a fast and easy method to evaluate the potential of surface-active agent to alter the wettability. In the previous studies, the concentration of the surfactant must be above critical micelle concentration,wt%, molar (CMC) so that the desorbed carboxylic matter could be solubilised into the micelles (Rao, 1999). Arquad has shown it has concentration above CMC and the value of the angel decrease to 46^{0}. So, it is proved that arquad MC-50 has the ability to alter the reservoir wettability. Beside, Arquad also tested by using imbibitions into low-permeable chalk. The result shows that the oil recovery was about 70% of OOIP. During reservoir dolomite cores test, the imbibitions rates increased as the permeability of the increased.

4.4 Dodigen

This chemical was tested with aruquad to see the comparison between two of it. In the static angel test, the angle decrease from 70^{0} C to 32^{0} C after exposing oil-treated calcite crystals. The fluid flow also showed that there was a tendency to be influence by gravity forces. The imbibitions rate was about 25% initial water compared with a 100% oil saturated system. Somehow, dodigen also can be used as the agent to alter the reservoir wettability (Standes and Austad , 2002).

4.5 Nontoxic low-cost amines

It is found that C_{10}-amine was compatible with high salinity brine at ph < 7. It was dissolve in brine at ph=6.5 and imbibed spontaneously into oil-wet reservoir dolomite. The mechanism of wettability alteration is similar to the C12TAB mechanism (Standes and Austad , 2002)

CHAPTER 5
CONCLUSIONS AND RECOMMENDATION

As the conclusion of my project, it found that there were just few of the chemicals have the ability to alter the reservoir wettability. Most of the chemical are came from the cationic surfactant group. Usually, this technique was wide widely used in the carbonate formation.

As the improvement based on the chemicals discussed above, the use of dimeric surfactants which have two charged head groups and two hydrophobic tails is highly recommended. Gemini surfactants where the molecules are joined at the head end are likely to be effective when ion-pair formation is the wettability alteration mechanism. For, Bolaform surfactant, in which molecules are joined by the hydrophobic tails, should more effective in the case of surfactant monolayer adsorption (Mehdi and Johnson , 2008).

Comparing between Arquad and Dodigen, it was conclude that Arquad is better that Dodigen. In term of static contact angle measurement, Arquad decrease angle to 46 degree compare to Dodigen just 32 degree. For the imbibitions into low-permeable chalk test, Arquad imbibed spontaneously by means of a counter-current flow mechanism. Dodigen seem that the fluid flow showed that it has tendency to be influenced by gravity forces (Standes and Austad , 2002).

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