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Enhanced heavy oil recovery by alkali-surfactant in the Pennsylvania Warner sandstone

Rabia Mohamed Hunky

Department: Geosciences and Geological and Petroleum Engineering

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ENHANCED HEAVY OIL RECOVERY BY ALKALI- SURFACTANT IN THE PENNSYLVANIA WARNER SANDSTONE

by

RABIA MOHAMED HUNKY

A DISSERTATION

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

DOCTOR OF PHILOSOPHY

in

PETROLEUM ENGINEERING

2011

Approved
Shari Dunn-Norman
Baojun Bai
Parthasakha Neogi
Ralph Flori
Runar Nygaard

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ABSTRACT

In this research, a study of the non-thermal method of alkaline-surfactant (AS) flooding to enhance heavy oil recovery from the Pennsylvanian Warner sandstone reservoir in Western Missouri was conducted. This work includ testing approximately 30 commercial surfactants and using a heavy oil sample with an API of 17. It was found that a number of surfactants could create stable emulsions. The viscosity of heavy oil could be reduced from 18,518 cp to 2.5 cp at 25 °C through emulsification of certain surfactants. One of the major findings was that the emulsion created by the commercial surfactant, Igepal® CO-530 was stable at 25 °C, but the oil and brine could be readily separated at 40 °C. The addition of alkaline to Igepal® CO-530 produced a more stable emulsion of the heavy oil and formation brine. This emulsion separated automatically at 55 °C. Core flooding tests were performed by the use of Igepal® CO-530 and alkaline NaOH at 0.6 wt% in the synthetic brine. These tests were conducted under both oil-wet and water-wet reservoir conditions, but the highest oil recovery always obtained under water-wet condition. The wettability alteration was studied through the measurement of interfacial tension and the contact angle of water on the sandstone surface treated with a model of the heavy oil sample was measured using Goniometer. Results indicated that wettability of the sandstone surface pre-treated with heavy oil could be effectively changed to water-wet by the surfactants. Additionally, spontaneous imbibition tests were conducted and it was found that the oil recovery was between 40% and 60% by nonionic surfactants, 10% and 20% by anionic surfactants, and 0% by formation water only. These results were used to conduct a simulation. The simulation results matched the experimental work, suggesting that further testing of AS flooding should be conducted.

ACKNOWLEDGMENTS

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

NOMENCLATURE

Symbol	Description
σ_{ow}	Oil-Water Interfacial Tension
σ_{os}	Interfacial-free energy between solid and oil
σ_{ws}	Interfacial-free energy between solid and water
θ	Contact angle
τ	Shear stress
K	Consistency constant
γ	Shear rate, and n is the flow index
μ_{app}	Apparent viscosity
$\overline{v}_c$	Average velocity
d	Capillary diameter
$\overline{v}$	Average velocity
μ_{eff}	Effective viscosity
C_0	Initial concentrations of surfactant (mg/L)
C_e	Equilibrium concentrations of surfactant (mg/L)
V I	Volume of solution
W	Weight of the powder used (g)
q_e	Amount absorbed (mg/g) at equilibrium
b	Langmuir constant
q_{max}	Maximum adsorption capacity (mg/g).
ρh	Density of oil
ρd	Density of water
ω	Angular velocity
D	Drop minor axis semi diameter

1. INTRODUCTION

In the United States, heavy oil reserves are estimated to be more than eight times the amount of remaining conventional crude oil. Interest in producing this resource is increasing, as conventional oil production declines. Yet, economic production of heavy crude oil is difficult to achieve because of low gravity and high viscosity, which inhibits its ability to flow through reservoir rock. Historically a range of methods for producing heavy oil have been used, including steam flooding, cyclic steam stimulation, in-situ combustion, SAGD, as well as non-thermal methods (cold flow with sand production, cyclic solvent process, VAPEX and other chemical methods).

The production of heavy oil can be even more challenging from shallow reservoirs, particularly reservoirs found at depths significantly less than 1,000 ft. Such reservoirs typically have low formation fracture pressures. Low breakdown pressures can limit effectiveness of thermal EOR methods such as steam flooding, cyclic steam injection and miscible flooding.

Among the many shallow heavy oil deposits found throughout the United States, heavy oil is present in discontinuous Pennsylvanian Cherokee Warner and bluejacket sand in Western Missouri counties. Figure 1.1, in this area, the bluejacket sand occurs at approximately 130-135 feet with a net pay of 8-12 feet and the Warner sand occurs at approximately 160-170 feet with a net pay of 15-30 feet.

Recovery of the heavy oil from the Warner Sandstone has proven difficult due to the viscose nature of the oil (10-18° API, 1000+ cp) and low reservoir pressure due to shallow reservoir depth. Historically, industry has examined or attempted a number of development methods including steam injection, CO_2 flooding, and in-situ combustion, but the shallow nature of the reservoirs and an underlying water contact present unique challenges in applying these EOR methods (Dunn-Norman et al.,2002; VA1lEROY et al., 1967).

This dissertation investigates the feasibility of applying alkaline surfactant flooding as an alternate method of recovering heavy oil from the shallow Pennsylvanian sands in Western Missouri.

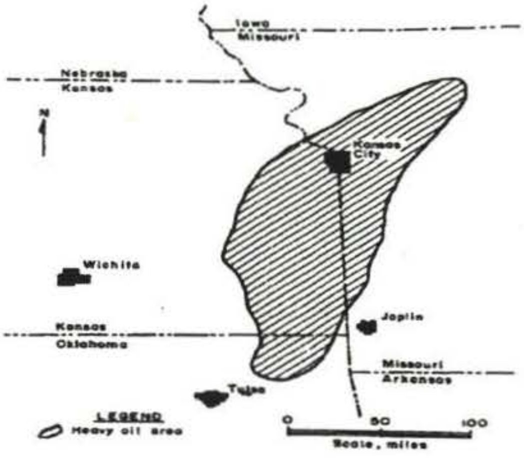


Figure 1.1 Areal Distribution of Heavy Oil in Western Missouri and Eastern Kansas

The research methodology employed includes (a) sampling relevant oil and water from the Warner formation and testing, (b) testing commercially available anionic, ionic, and cationic surfactants for their ability for maintain a stable emulsion at different temperatures, (C) sandpack flooding experiments to determine incremental recovery possible with alkaline surfactant flooding. (D) Investigating wettability alteration by different methods including the contact angle measurement and spontaneous imbibitions, and (E) applying reservoir simulation, to model the experimental alkaline surfactant flooding performance. Results of this work indicate that alkaline surfactant flooding may prove beneficial in heavy oil recovery in Western Missouri. Details of the experimental work and results are included in this dissertation.

2. BACKGROUND AND LITERATURE REVIEW

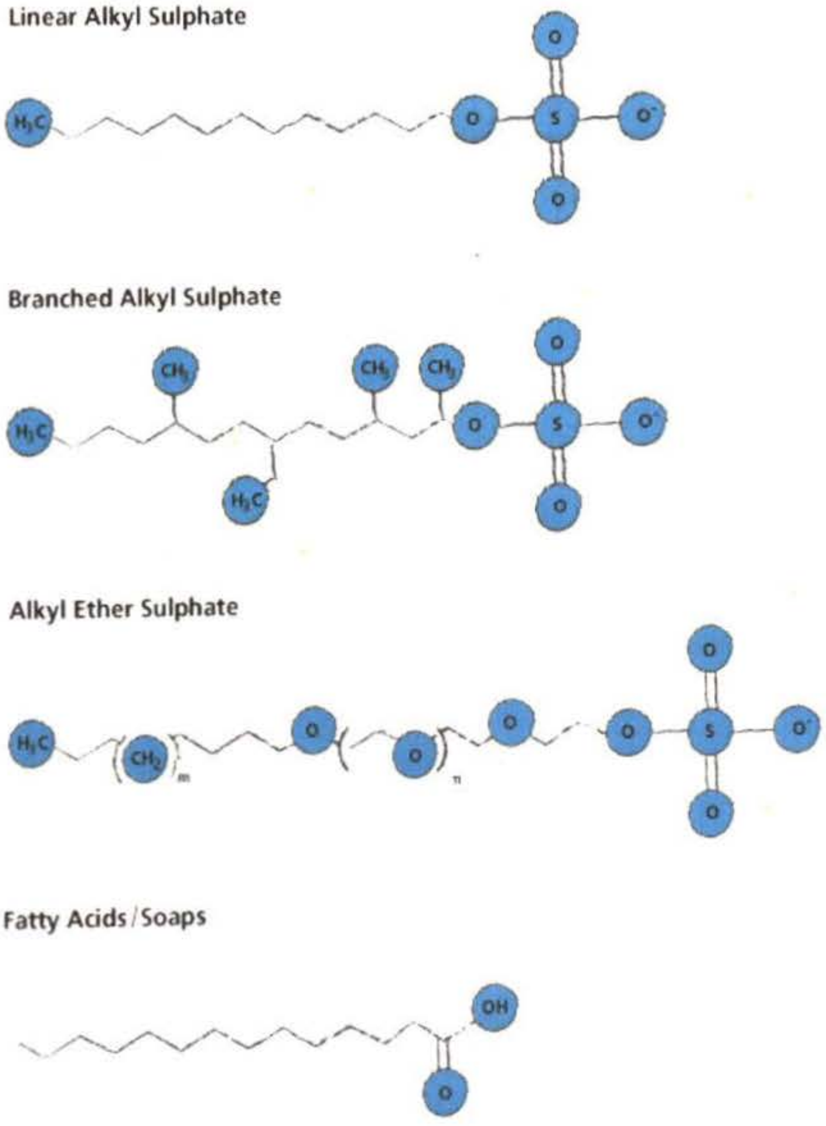
This chapter provides background information on alkaline surfactant flooding and historical work relevant to the current research. While there is an extensive body of literature related to alkaline surfactant flooding, only the literature related to experimental procedures and heavy oil applications is included here. In general, after primary and secondary recovery, it is noted that the remaining oil in the light and medium oil reservoirs is generally in the range of 50-60% of the original oil in place (OOIP) and the oil left in the heavy oil reservoirs is much higher.

The EOR chemical methods were most popular in the 1980's with most of the chemical floods developed between the 1960's and 1980's (Manrique et al., 2007). Active projects peaked in 1986 with polymer flooding considered the most significant chemical method of EOR. Chemical flooding has been shown to be sensitive to oil prices due to the chemical additive costs. There is still a great need for novel chemical additives for more efficient EOR processes in all types of reservoir applications. However, EOR chemical methods such as AS (Alkali-Surfactant) are proven technologies that may play a key role in the near future regarding mature and waterflooded sandstone reservoirs to help meet future energy demands. Alkaline surfactant flooding, also known as caustic flooding is an EOR technique wherein an alkaline chemical, such as sodium hydroxide, sodium orthosilicate, or sodium carbonate is injected into hydrocarbon reservoirs during the waterflooding stage (Lake, 1989). Alkaline surfactant was first applied in 1925 as a "soda" flood in the Bradford area in an east Texas oil field. Surfactant flooding in early laboratory core floods and selected small-scale tests in the 1960s, particularly in the

Robinson field in Illinois, indicated that the surfactant (or micellar-polymer) flooding technology was ready for wide-scale field use.

2.1 SURFACTANT

Surfactant is an organic compound that is amphiphilic and contains both a hydrophobic group (tail) and hydrophilic group (head). This compound lowers the surface tension between two liquids. There are four main types of surfactants used in oil industry. Depending on the type of the charge of the head, a surfactant belongs to the anionic, cationic, non-ionic or amphoteric/zwitterionic family. An anionic surfactant is negatively charged. The most commonly used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates and soaps as shown in the Figure 2.1. A cationic surfactant's head is positively charged. Non-ionic surfactants do not have an electrical charge, which makes them resistant to water hardness deactivation. Figure 2.2 show that example 1 of cationic surfactants is the esterquat. The cationic surfactant (positive charge) improves the packing of anionic surfactant molecules (negative charge) at the stain/water interface. Figure 2.3 illustrates an example 2 of a cationic surfactant used in this category that is a mono alkyl quaternary system. The most commonly used non-ionic surfactants are ethers of fatty alcohols, as shown in the Figure 2.4. Non-ionic surfactants contribute to making the surfactant system less sensitive to water hardness. Amphoteric/zwitterionic surfactants can be anionic (negatively charged), cationic (positively charged), or non-ionic (no charge), depending upon the acidity or pH of the water. Surfactants can work to lower the heavy oil/water interfacial tensions and emulsification and solubilization. An example of an amphoteric/zwitterionic surfactant is alkyl betaine as shown in the Figure 2.4.



Linear Alkyl Sulphate

Branched Alkyl Sulphate

Alkyl Ether Sulphate

Fatty Acids / Soaps

Figure 2.1 Anionic Surfactants

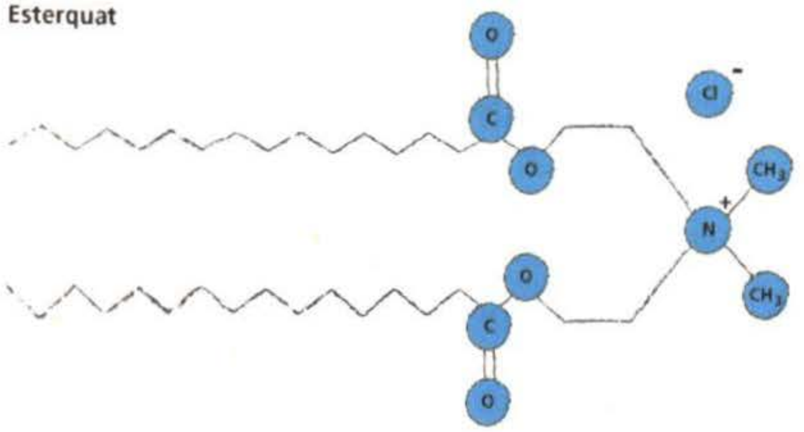


Figure 2.2 Cationic Surfactants Example 1

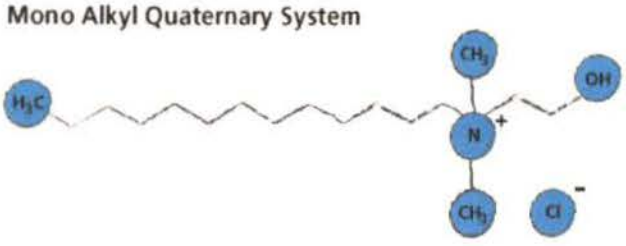


Figure 2.3 Cationic Surfactants Example 2

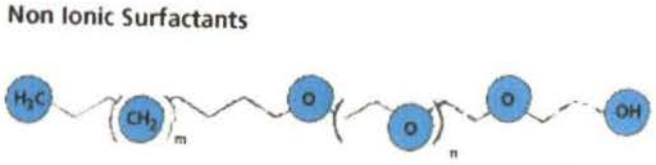


Figure 2.4 Non-ionic Surfactants are Ethers of Fatty Alcohols

Figure 2.5 Amphoteric/Zwitterionic Surfactants

2.2 EMULSION

An emulsion is created due to the dispersion of two mutually insoluble liquids (e.g., oil and water). Normally, one is referred to as the internal phase or dispersed phase, while the other is considered the external or dispersing phase. Emulsions are created with the help of a natural or artificial third party emulsifying agent or surfactant whose main objective is to reduce the interfacial tension at the interface of the two mutually insoluble phases. This is done to facilitate emulsion by inducing stability. Alkaline (NaOH), in combination with a natural surfactant, can be used to create caustic emulsion. Emulsions can also be classified into several types, from simple O/W to more multifaceted types such as water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O). In the oil and gas industry, the W/O and O/W emulsions are the commonly encountered forms of emulsions. As for the W/O emulsion, water is considered the dispersed phase (internal) and oil is the dispersing phase (external). Emulsion can also be classified on the basis of their droplet diameters. The emulsion is considered to be a macro emulsion, easily visible under a microscope if the droplet size is greater than 0.4 and as a nono-emulsion if the droplet size is less than 0.1. Micro-emulsion is another type with a droplet size between 0.1 and 0.4.

A stable emulsion forms when two immiscible liquids, such as oil and water, where one liquid becomes the dispersed phase, exists in the form of droplets suspended in the other the continuous phase. Emulsion stability, structure, and rheology depend on the composition, thickness, and viscoelasticity of the adsorbed stabilizing layer at the oil-water interface. (Qiang Liu et al., 2005) pointed out that the oil cannot be emulsified in brine by adding only alkali (Na_2CO_3) or only surfactant regardless of how high their concentrations are raised. Re-emulsification of the gravity separated oil is easier than the initial emulsification. The presence of fine water droplets trapped in the separated oil phase is believed to aid in the re-emulsification of the equilibrium oil into the equilibrium brine. Eric Dickinson (1992) introduced the concept that oil-in-water emulsions are stabilized by two main types of molecular emulsifying agents: small-molecule surfactants and water-soluble polymers. In complex emulsions of commercial or technological importance, there often exists a multicomponent mixture of small amphiphiles and surface-active polymers.

A Hydrophile-Lipophile balance (HLB) are emulsifiers which show that greater solubility in water would be better for oil in water emulsifications, and emulsifiers showing great solubility in oil would be better for water in oil emulsifications. The lower HLB valued emulsifiers are better in water in oil that is more lipophilic while the higher valued HLB emulsifiers are more hydrophilic. HLB is used to determine whether the surfactant is favorable to W/O or O/W emulsion. The HLB number is found to be less than 9 for the W/O emulsion and greater than 11 for the O/W emulsion, respectively.

2.3 WETTABILITY ALTERATION

Wettability alteration is one of the major factors that control the distribution and flow of fluids in the pores of a reservoir (Anderson, 1986). The mechanism of wettability alteration in a heavy oil/brine/solid system can be examined by analyzing the contact angle and imbibitions test. Additionally, the contribution of electrostatic forces to wettability alteration was investigated through IFT measurements.

The Interfacial Tension (IFT) between oil and surfactant solution could be reduced further by adding Na_2CO_3 or NaOH. The precipitation of Ca^{2+} by Na_2CO_3 or NaOH contributed to the lowering of IFT. When surfactant was added into the alkaline solution, the IFT became even lower and the heavy oil could be more easily dispersed in the formation brine. Also, the interaction of added surfactant and in situ surfactant from the reaction of alkali and organic acids in oil can significantly reduce the dynamic interfacial tension between oil and water and increase the surface charge density of emulsions. The synergistic enhancement between alkali and surfactant is the key mechanism of emulsifying heavy oils in brine under slight interfacial disturbance (Bryan, 2007).

Adsorptions of surfactant on sand and at oil-water interfaces in an alkaline/surfactant flooding for heavy oil recovery and the reaction between alkalis and the acidic compounds of the heavy oil resulted in the formation of oil-in-water emulsions. This greatly increased the oil-water interface area in water phase. The formation of emulsions dramatically reduced surfactant loss to sand surface. The adsorptions of surfactant on sand and at oil-water interface were determined under various alkaline concentration and Salinities (Zhou, 2005).

The arrangement of fluids in contact with a solid surface is governed by both the IFT of the liquids and the interfacial-free energy between the individual fluids and the solid equation (1):

$$\sigma_{ow} \cos\theta = \sigma_{os} - \sigma_{ws} \qquad (1)$$

Where σ_{ow} is oil-water interfacial tension (mN/m), σ_{os} is interfacial-free energy between the solid and the oil (mN/m). σ_{ws} is interfacial-free energy between the solid and the water (mN/m) and θ is the contact angle.

Equation (1), also known as Young's Equation, explains how fluids will distribute if both fluids are in contact with the solid surface. The interfacial-free energies between oil and water with the solid cannot be directly measured. Therefore, the tendency of the solid to be wetted by one phase or another is determined by measurements of the fluid IFT value and the contact angle. Wagner and Leach (1959) reported rock wettability was reversed from oil-wet to water-wet, which improved oil recovery by injecting water solutions with some added chemicals. This work was limited when applied to the oil-wet reservoirs where the wettability could be reversed from oil-wet to water-wet and consequently improve oil recovery.

The majority of the research work that focused on wettability alteration has been performed by the injection of chemicals into a core initially saturated. One of the main parameters in wettability and imbibition studies is the water composition that can affect the wettability. (Liu et al., 2006) pointed out that surfactants have been used to change the wettability, with the goal of increasing the oil recovery by increasing imbibition of the water into the rock matrix, although it has been suggested (Anderson, 1987) that when the reservoir wettability is favorably altered to a more water wet state, the residual oil saturation decreases and more oil is recovered.

2.4 THE PRINCIPLE OF ALKALINE SURFACTANT FLOODING FOR ENHANCED HEAVY OIL RECOVERY

Important principles that can be established to govern the alkaline surfactant flooding are W/O or O/W emulsion and wettability alteration. The W/O emulsion was formed as a result of the injection of the alkaline surfactant solution in an effort to block the highly permeable zones, which partially alter the pore walls from water-wet to oil-wet. This resulted in an increased pressure drop and consequently increased the tertiary oil recovery. Another important mechanism was the creation of the O/W emulsion, which was a result of the reaction of heavy oil with alkaline and surfactant solution. The O/W emulsion drops worked as a plugging factor to improve oil recovery. The interaction of added surfactant and alkali was due to the reaction with organic acids in oil which can significantly reduce the dynamic interfacial tension between oil and water and increase the surface charge density of emulsions. Furthermore, the addition of alkalis in water phase reduced surfactant adsorption on sand. Moreover, the reaction between alkaline and the acidic compounds of the heavy oil resulted in the formation of oil-in-water emulsions, which greatly increased the oil-water interface area in water phase. Experimental results showed that the synergistic enhancement between alkali and surfactant was the key mechanism of emulsifying heavy oils in brine under slight interfacial disturbance (Liu at el, 2005). Average incremental oil recovery in coreflood studies by alkali-surfactant flooding was 14.6% OOIP (Zahari Ibrahim et al., 2006).

Various methods are used to evaluate AS flooding efficiency and factors that impact AS flooding efficiency. Alkali-surfactant (AS) solutions are injected into the systems containing viscous heavy oil. AS solutions reduce the interfacial tension between oil and water to values that allow for emulsions to form under the shear from flow at normal reservoir rates. When these emulsions form, AS injection can lead to considerable improvements in the flooding response, even without the addition of polymers to stabilize the flood (Bryan et al., 2007).

(Liu et al., 2006) showed that Sandpack tests using AS flooding can recovered approximately 24% IOIP for the heavy oil with 14°API by injecting a chemical slug consisting of 0.30 wt. % Na_2CO_3, 0.30 wt. % NaOH, and 300 mg/L surfactant. Injecting 0.5 PV of chemical slug was economical. The combination of Na_2CO_3/NaOH/surfactant was necessary to obtain a high tertiary oil recovery in sandpack flood tests. The added Na_2CO_3 and surfactant have a synergistic effect in emulsifying the heavy oil in formation brine; NaOH could rapidly react with the organic acids in oil, leading to the formation of an oil bank. During injecting the Na_2CO_3/NaOH/surfactant in sandpack flood tests, the pressure drop responded significantly and the oil cut in effluent samples could reach 40–100%. Higher oil cut in effluent samples was obtained when a longer sandpack was used. Chiwetelu et al. (1994) performed core flooding tests by using an in-situ surfactant base and sandpacks at 25°C and 65°C, respectively. The viscosities of crude oil were 454 mPa·s at 25°C and 46 mPa·s at 65°C, respectively. The relationship between temperature and oil recovery was found to be inversely strong. For example, at a NaOH concentration of 0.05%, the oil recovery was measured to be 42.4% at 25°C compared to 7.3% at 65°C.

(Al-Bahar et al., 2004) explained that the characteristics of Alkaline and the absorbing of surface surfactant in reservoir rock are decreased by increasing the alkaline. (Ibrahim et al., 2006) explained that dilute surfactant processes without alkali recovered little incremental oil, and the incremental oil recovery in coreflood studies by alkali-surfactant flooding was 14.6% OOIP.

El-Abbas and Shedid (2001) investigated the potential of enhancing tertiary oil recovery of heavy crude oil using steam, caustic steam, surfactant steam, and caustic-surfactant steam flooding through horizontal wells. The results of the dynamic experiments indicated that steam flooding through a horizontal well substantially improved oil recovery. The addition of caustic (sodium hydroxide) or surfactant (X-Triton-100) to steam drive method recovered additional oil of 5.6 % OOIP.

(Wu et al., 2008) studied the five nonionic surfactants in spontaneous imbibitions tests, among them Tergitol 15-S-3, Tergitol 15-S-7, Tergitol 15-S-40, Neodol 25-7, and the ethoxylated nonyl phenol Igepal CO-530, which has the best performance of these nonionic surfactants, recovering as much as 50% from limestone core. This is comparable to the oil recovery by the cationic surfactants, C12TAB, ARQUAD C-50, and ARQUAD

T-50. An additional feature of the Igepal CO-530 is that it has almost the lowest IFT of tested surfactants.

The emulsification and entrainment of crude oil into displacing water is one of the mechanisms of alkaline flooding (Liu et al., 2005). When this mechanism is applied in heavy oil reservoirs, the flow of viscous oils and subsequently the oil recovery can be greatly improved. It was found that adding the surfactant reduced the equilibrium IFT to an ultralow value and widened the pH range for ultralow IFT and spontaneous emulsification. (Dong et al., 2006) evaluated IFT extensive emulsification tests and oil/water interfacial tension and conducted tests to screen alkaline and surfactants for the Brintnell oil/formation brine system. The results of emulsification tests and oil/water interfacial tension (IFT) measurements indicate that Brintnell oil/brine interfacial tension can be reduced to <0.1 dyn/cm by adding both Na2CO3 and NaOH to the brine.

Heavy oil reservoirs produced a small amount of oil from water flooding. The introduction of surfactant into the brine phase can improve the oil production by lowering the oil-water interfacial tension (IFT) and by altering the wettability of the matrix block to water-wet (Adibhatla et al., 2005). In other hand the wettability can change to more water wetting at 100ºC from the presence of SO_4^{2-}, Ca^{2+} and Mg^{2+} ions and without surfactants in the system (Tweheyo et al., 2006) . The three divalent ions seem to have different effects in the two processes: wettability alteration and spontaneous imbibitions. Wei Xu et al. (2008) established that the anionic surfactant altered the weak water-wet behavior of live oil to strongly oil-wet (165°). It was also able to alter the strong oil-wet behavior of stock tank oil to less oil-wet (<135°). The nonionic surfactant was able to alter the water-wet live oil system to intermediate-wet (82°), while it did not affect the strongly oil-wet behavior of stock tank oil system. Yongfu Wu et al. (2008) conducted a spontaneous imbibition test of porous limestone cores. In general, the results show that there is some rough correlation between the observed oil recovery and the IFT. Surfactants with high oil recovery (>40%) generally show a low IFT (~0.5 mN/m). Tang and Morrow (1997) found that the salinity of the connate water and invading brines can have a major influence on wettability and oil recovery. Zhang and Austad (2006) verified that the ions Ca^{2+} and SO_4^{2-} could increase the water-wetting of chalk and thereby increase the water-oil capillary pressure of matrix blocks. Additionally, there is an abrupt change in the zeta potential when only small amounts of ions are added to the aqueous solution.

2.5 THE CURRENT STATUS OF AS FLOODING

Several authors have published work related to the current status of AS flooding for heavy oil recovery and many of these papers demonstrate an analytical method or testing of specific surfactants. Only a few papers discuss AS flooding in heavy oil reservoirs. Sandpack flood tests were conducted for a heavy oil sample with a viscosity of 1800 mPa s at 22 °C. The results showed that the tertiary oil recovery could reach 24% IOIP. The formation of an oil-in-water (O/W) emulsion and an oil bank was necessary to improve the heavy oil recovery in sandpack flood tests (Liu et al., 2006). This is viable by injecting a chemical slug containing Na2CO3, NaOH and a very dilute surfactant. Na_2CO3/surfactant had a synergistic enhancement in lowering interfacial tension, leading to the formation of the O/W emulsion. (Bryan and Kantzas, 2007) conformed that the addition of NaOH accelerated the neutralization of organic acids in oil in the sandpack flood tests so that the emulsified oil accumulated to produce an oil bank.

The response from the direct injection of AS systems is compared to the AS injection after waterflooding. Both oil-in-water and water-in-oil emulsions can lead to the recovery of additional oil. This synergistic effect has been reported (Liu et al., 2005). It is critically important to emulsify heavy oil in brine for improved mobility. Furthermore, the oil and water could be separated easily in a short period (Bryan et al., 2008). The AS floods indicate that emulsification is most efficient when used to block pre-formed water channels and improves the sweep efficiency of the flood. The O/W and W/O emulsions may both form in the same system, even under controlled salinity conditions. (Liu et al., 2005) explained that the oil cannot be emulsified in brine by adding either only an alkali (Na2CO3) or a surfactant regardless of how high their concentrations are raised. The synergistic enhancement between the added surfactant and the in situ surfactant from the reaction of alkali and the acidic oil results in ultralow dynamic interfacial tension and high potential.

Wang and Dong (2009) conducted alkaline/surfactant (A/S) flood tests and used sandpacks to demonstrate the effectiveness of the sweep efficiency improvement by the in-situ generated O/W emulsion. A properly designed alkaline flooding for heavy oil recovery could effectively improve sweep efficiency through in-situ generated O/W emulsion. (Zhao et al., 2008) presented results for high molecular weight internal olefin sulfonate (IOS) surfactants that show excellent performance when tested using several crude oils with characteristics such as high wax content and viscosity. These have made it very difficult to achieve high oil recovery with most surfactants used in the past. High carbon number internal olefin sulfonates, when used with appropriate co-surfactants, co-solvents, and alkaline show the type of phase behavior and ultra-low interfacial tension needed for almost 100% oil recovery in cores.

Laboratory results designed at the enhanced recovery of a crude oil from a "J" Sand reservoir in Nebraska indicated that the addition of a surfactant to the alkaline solution achieved ultralow interfacial tensions. The interaction tensions between alkaline solutions and the crude oil are not enough for efficient oil displacement (Martinat et al., 1985).

Vahid Khosravi (2010) pointed out that one of the most important productions of micro-organisms is the wettability of the surface. This surface has two parts which are water-wet and oil-wet, and by putting the surfactants in the surface between oil and water, they decrease the interfacial tension, and in this way oil flow is assisted in going toward the wells. Alkali was found to help decrease surfactant adsorption on the rock and improve surfactant consistency by increasing the pH level. It also improved the amount of recovery by reducing the hardness of water and increasing the sweep efficiency.

Bryan (2008) carried out experimental studies to examine whether wettability changes during AS flooding. The total relaxation rate is the summation of the bulk and surface terms, as shown in Equation (2). The bulk relaxation rate is proportional to the fluid viscosity. The higher viscosity fluids will relax at a faster rate than low viscosity fluids. Surface relaxation is proportional to the surface-to-volume ratio of the rock pores that contain the fluid being measured. Smaller pores have larger values of S/V, which will in turn lead to faster surface relaxation. In considering heavy oil and water in a porous media, there are two extremes.

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} \alpha \mu + \frac{S}{V} \tag{2}$$

Where $1/T_2$ = the measured relaxation rate, $1/T_{2B}$ = the bulk relaxation rate of a fluid $1/T_{2S}$ = the surface relaxation rate of the fluid, μ = the fluid viscosity S = the surface relaxivity of the rock, S/V = the surface-to-volume ratio of the rock.

Delshad et al. (2006) found that surfactants could change the wettability for increasing the oil recovery by increased imbibition of the water into the matrix rock. The effect of surfactant on wettability alteration was modeled and implemented in UTCHEM by changing relative permeability, capillary pressure, and capillary de-saturation curves. However, (Guoa et al., 2005) reported that the wettability alteration was a result of the presence of magnesium ion. The negative charges in both systems, the oil/alkaline and solution/sand interfaces, were reduced by a positive charge from the adsorption of magnesium ions. Since oil recovery was greatly affected by the wettability alteration of sand, the effect of the composition of the water phase on wettability alteration in the heavy oil/water/sand system was tested. The presence of either Na_2CO_3 or Mg^{2+} alone in the water phase could not induce wettability alteration. The reduction of repulsive electrostatic forces between oil drops and sand surfaces contributed to the wettability change of the sand from water-wet to more oil-wet (Liu et al., 2007).

Adibhatla (2005) developed a 3-D numerical simulator model with the process of the capillary pressure, relative permeability, and residual saturations of both phases. These are considered functions of IFT and wettability, which are correlated to the surfactant and salt concentrations based on the data obtained from laboratory experiments. The mass balance equations are solved with a fully implicit scheme. The numerical simulation was matched with the experimental data obtained for alkaline surfactant flooding and imbibitions test.

The simulation results indicate that both capillary and gravity forces assist in improving oil production, and in the early stage of the production the capillary is found to be the major driving force, while in the later stage, gravity dominates the production. The surfactant diffusion into the matrix block leads to IFT and wettability alterations which in turn lead to oil mobilization. By the time the surfactant is completely diffused into the matrix block, there is an approximately 30% increase in the oil production. The oil production rate decreases as a result of the following factors: the matrix block height increases, the wettability is altered to a lesser degree, and the permeability decreases.

Simulations showed promising results of chemical flooding for heavy oils. It was indicated that a certain length of waterflooding time would benefit the final oil recovery, and there existed an optimum chemical slug size (Wang and Dong, 2010), their laboratory results and the simulation technique are helpful in the simulation and design of field-scale projects of chemical flooding for enhanced heavy oil recovery. The gradient in soap-to-surfactant ratio develops with conditions shifting from over optimum near the rear of the oil bank to under optimum behind the main displacement front. The wide range of low tensions found for the surfactant blend used was found to be an important factor contributing to the high recovery predictions. (Liu et al., 2006) pointed out that reservoir simulation is required to scale up the process from laboratory to field conditions, as well as to understand and interpret reservoir data. As well as chemical-flooding simulator is adapted to model improved-oil-recovery processes involving wettability alteration using surfactants. Multiple relative permeability and capillary pressure curves corresponding to different wetting states should be used to model the wettability alteration.

Simulations were performed to better understand and predict enhanced oil recovery as a function of wettability alteration and to investigate the impact of initial water saturation and formation wettability. The wettability alteration model and its implementation were successfully validated against laboratory experiments. Upscaled simulations indicated the importance of matrix properties on the rate of imbibition. The oil recovery increases with an increase in matrix permeability and a decrease in matrix initial water saturation (Delshad et al., 2009).

In this study four different families of surfactants were screened and tested. The surfactant and alkaline ability to create emulsion and adsorption tests was conducted in addition to the alkaline/surfactant (A/S) flood tests that were performed in oil- wet and water-wet sandpacks to demonstrate the effectiveness of sweep efficiency improvement by the generated oil-in-water (O/W) emulsion and wettability alteration. Excellent tertiary oil recoveries were obtained in water- wet sandpack flood test. The simulation results and the experimental results were matched by including the mechanisms of emulsion as well as the chemical adsorption and the reduction of interfacial tension involved in the chemical flooding process and the simulation results was provided accurate and reliable estimates of relative permeability curve.

3. SURFACTANTS SCREENING AND CORE FLOODING TEST

3.1 METHODOLOGY

3.1.1. Analysis of Missouri Heavy Oil and Water Samples. The heavy oil sample provided by the MegaWest Company was from an oil field in Vernon County, west Missouri. The viscosity of the heavy oil sample was measured to be 18,815 cp (clean sample) at 25 °C. The original formation water was also provided by MegaWest Company from the oil field in Vernon County, west Missouri. Its composition was analyzed by Fluid System Technologies Company in St. Louis, MO. The brine composition is listed in Table 3.1. The synthetic brine used in this study was prepared based on the composition of the original formation water. The recipe of the synthetic brine is shown in Table 3.2. According to compositions of the original formation water, the recipe of the synthetic brine was designed. The salts were weighed out and then added to distilled water to total 3000 grams. The synthetic brine was stirred for one hour. Using a pH meter, the NaOH (0.200 M) solution was adjusted to create synthetic brine with a pH of 7.3. The synthetic brine was then ready to use.

Table 3.1 Compositions of Reservoir Formation Brine

Ions	PPM	A.W.	Total Charge
Potassium ion K+	49.1	39.1	1.256x(+1)
Sodium ion Na+	1950.0	23.0	84.783x(+1)
Calcium ion Ca2+	95.4	40.1	2.379x(+2)
Magnesium ion Mg2+	40.0	24.3	1.646x(+2)
Barium ion Ba2+	2.08	137.3	0.015x(+2)
Chloride ion Cl-	3000.0	35.5	84.507x(-1)
Sulfate ion SO42-	142.0	96.1	1.478x(-2)
Bicarbonate ion HCO3-	1060	100.0	10.60x(-1)
Check pH	Adjust pH to 7.0	TDS	6338 PPM

Table 3.2 Recipe for Synthetic Formation Brine

Salt	M.W	g/L	Ions	mg/L
NaCl	58.5	4.400	Total Na+	2041.1
NaHCO3	84.0	0.890	K+	49.1
KCl	74.6	0.094	Ca2+	95.4
Na2SO4	142.1	0.230	Mg2+	40.0
CaCl2·2H2O	147.0	0.351	Total Cl-	3000.0
MgCl2·6H2O	203.3	0.335	SO42-	142.0
			HCO3-	1060.0
Check pH	Adjust pH to 7.0		TDS	6427.6 PPM

3.1.2. Measurement of Heavy Oil Viscosity. The viscosity of the heavy oil was measured at different temperatures of 25°C, 50°C, 60°C ,70°C, and 80°C and 3 different shear rates using a Brookfield DV-II+Pro viscometer. Figure 3.1 shows the viscometer which is used for viscosity measurement.

Figure 3.1 Viscosity Measurement Instrument

3.1.2.1. Experimental procedures. Since sand and other material was found in the crude oil (e.g., formation), the centrifuge machine was used to clean it. The viscosity of the crude oil was then measured at different temperatures, e.g., RT, 25°C, 30°C, 35°C, 40°C, 45°C, 50°C, 60°C and 70°C. At the lower temperature, spindle #25 was used to get data at the various RPM (shear rate), and at the higher temperature, spindle #18 was used.

The centrifuge machine was used to clean the Missouri heavy oil as following:

1. Clean plastic tube and dry in the oven for 30 minutes.

2. Pour the crude oil into the tube; since the crude oil was very viscous at room temperature, it was heated to 60 °C for 30 minutes to ensure a better flow into and out of the tube.

3. The tubes were put in the centrifuge machine for 30 minutes and centrifuged at 3500 RPM for 30 minutes.

4. Steps 2 and 3 were repeated several times to obtain very clean oil.

5. After the above procedures, the sand and formation water contained in the heavy oil was separated and the clean heavy oil was measured for viscosity.

3.1.2.2. Viscosity measurement of the clean and unclean crude oil. The viscosity was measured for the Long Farm crude oil sample over varying temperatures and shear rates.

3.1.2.3. Experimental procedures. The laboratory measured of crude oil viscosity was as the following:

1. A volume of the crude oil sample was transferred into the cylinder. The sample was transferred into a jar first as it would have been difficult to take it from the 2 gallon container.

2. A suitable spindle was selected. Since the tested crude was very viscous, a small spindle #25 was chosen so that the viscosity measurement fell within the right torque percentage and was persistent enough to give a stable reading. These two criteria had to be met in order for the readings to be accurate. Since the viscosity decreased as the temperature increased, larger spindles, #18 and 25, were used.

3. The viscosity was measured at room temperature before heating the sample. The spindle was left to turn, depending upon the rotation speed, in order for the reading to stabilize. It was likely to stabilize after 20 rotations so if the measurement was at 0.5 rpm, the spindle needed to spin for about 40 minutes before a reading could be taken. About 5 different shear rates were used for each temperature depending on if the resulting torque fell between 10 to 90 percent.

4. Once readings for each shear rates were taken, the water bath circulating pump was turned on to heat the sample. A wait period of 30 minutes was taken once the desired temperature was reached. This allowed the sample temperature to be in equilibrium. Once the readings became consistent, the viscosity reading was taken again with varying shear rates.

3.1.2.4. Viscosity measurement at different shear rates. For different temperatures, the viscosity of the heavy oil didn't seem to change greatly with different shear rates. This is one of ideal characteristics of a Newtonian fluid where the ratio (viscosity) of shear over stress is constant. Hence the plot is a horizontal straight line.

There is a chance that water may be present in the sample. If the amount of water is significant and it is naturally emulsified, it will behave like a Newtonian fluid at low shear rates but becomes non-Newtonian at high shear rates. A reasonable explanation can be that at a high shear rate, the water droplets become smaller causing the viscosity to decrease. The Brookefield viscometer can only provide a shear rate of 100 RPM. The viscosity behavior beyond this shear rate value is unknown.

3.1.2.5. Viscosity at varying temperature. The viscosity of the crude sample decreases with higher temperature. Even though the crude oil is Newtonian, the viscosity measured was a little different for each shear rate value. It was most likely caused by practical or experimental errors, which caused a slight deviation. Hence, the average value was calculated and plotted for each temperature with error bars to distinguish the viscosity range at a certain temperature. It seems that at lower temperature, the error percentage was significantly larger compared to the ones at higher temperatures. Perhaps at a higher temperature, the crude oil was more consistent provided by the reduced viscosity. The viscometer was used to measure the viscosity of the Long Farm crude oil sample over varying temperatures and shear rates and the density and API of the crude oil for Missouri heavy oil was determined.

3.2 SURFACTANT TO BE USED.

30 surfactants were used to test in this study. These surfactants can be divided three types: anionic, cationic and nonionic surfactants. Their commercial name and chemical name are listed in Table 3.3.Each surfactant molecule has a hydrophilic (water-loving) head that is attracted to water molecules and a hydrophobic (water-hating) tail that repels water and simultaneously attaches itself to heavy oil. Surfactants are also referred to as alter wetting surface. Surfactants lower the surface tension of the medium in which it is dissolved, by lowering this interfacial tension between two media or interfaces. A surfactant consists of a hydrophobic (non-polar) hydrocarbon "tail" and a hydrophilic (polar) "head" group, as shown on the Figure 3.2. This appearance is the key to its behavior. The water loving or hydrophobic tail absorbs to the oil.

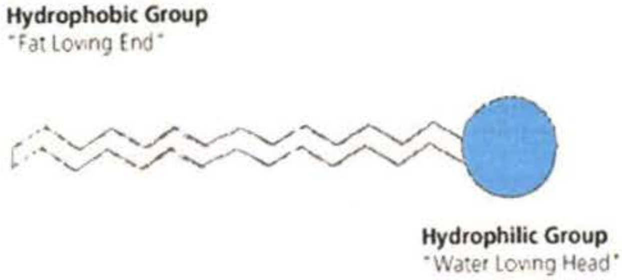


Figure 3.2 Surfactant Consists of a hydrophobic (non-polar) hydrocarbon "tail" and a hydrophilic (polar) "head" Group

Table 3.3 Chemical Name for the Surfactants Investigated

Surfactant Name	Chemical Description	HLB
Neodol® 1-5	Linear C11 primary alcohol with 5 moles of ethylene oxide(EO)	11.2
Neodol® 1-7	Linear C11 primary alcohol with 7 moles of ethylene oxide(EO)	12.8
Neodol® 1-9	Linear C11 primary alcohol with 9 moles of ethylene oxide(EO)	13.9
Neodol® 25-7	Linear C12-C15 primary alcohol with 7 moles of EO	12.3
Neodol® 25-9	Linear C12-C15 primary alcohol with 9 moles of EO	13.1
Tomadol® 25-12	Linear C12-C15 primary alcohol with 7 moles of EO	12.3
Tomadol® 45-7	Linear C12-C15 primary alcohol with 9 moles of EO	13.1
Tomadol® 45-13	Linear C12-C15 primary alcohol with 12 moles of EO	14.4
Tergitol® 15-S-3	Linear C14-C15 primary alcohol with 7 moles of EO	11.6
Tergitol® 15-S-9	Linear C14-C15 primary alcohol with 13 moles of EO	14.4
Tergitol® 15-S-12	C12-14 secondary alcohol ethoxylate with 3 moles of EO	8.3
Tergitol® 15-S-20	C12-14 secondary alcohol ethoxylate with 9 moles of EO	13.3
Tergitol® NP-10	C12-14 secondary alcohol ethoxylate with 12 moles of EO	14.7
Igepal® CO-530	C12-14 secondary alcohol ethoxylate with 20 moles of EO	
Triton® X-405	Ethoxylated nonylphenol with 10 moles of EO	
Calamide® CW-100	Ethoxylated nonylphenol with 5 moles of EO	
Calamide® CWT	Ethoxylated octylphenol with 40 moles of EO	
Calamide® F	Modified coconut diethanolamide	
Calsoft® LAS-99	Modified coconut amidesoap superamide	
Calimulse® EM-99	Vegetable oil diethanolamide	

Table 3.3 Chemical Name for the Surfactants Investigated (Continued)

Surfactant Name	Chemical Description	HLB
Calimulse® PRS	Benzensulfonic acid, C10-C16 alkyl derivitives	Acid
ARQUAD® T-50	Benzensulfonic acid, C10-C16 alkyl derivitives	Acid
Ethomeen® C/12	Benzensulfonic acid, dodecyl branched	Acid
Ethomeen® S/12	Block copolymers of propylene, ethylene oxides	
Aerosol® MA-80	Block copolymers of propylene, ethylene oxides	7.0
Alfoterra® 23	Ammonium nonylphenol ethoxylate sulfate, 4 EO	Anionic
Alfoterra® 48	Sodium lauryl ether sulfate, 30 EO	Anionic
Tomadol® 600	Sodium lauryl sulfate (S.D.S.)	Anionic
Tomadol® 901	C10-C16 ethoxylated alcohol	10.6
Tomadol® 91-6	C9-C11, C10-C16 ethoxylated alcohols	12.1
Tomadol® 91-8	C9-C11 ethoxylated alcohol	14.3

3.2.1. Emulsion Stability Measurement for Surfactant Screening. In this study, more than 30 commercial surfactants were selected for a screening test of their ability to create the emulsion of heavy oil and formation brine. All surfactant solutions were prepared at 1.00 wt. % with the synthetic brine. 2.0 grams of heavy oil and 18.0 grams of the surfactant solution were mixed in a transparent glass bottle. The bottles were shaken for 30 seconds by hand at room temperature to create an oil/water emulsion. The bottles were then placed in a rack to stand-by for an emulsion stability test. For the unstable emulsion systems, the oil and brine quickly separated automatically. The top layer of the oil turned black while the bottom layer of brine turned to a cloudy white or brown color. For very stable emulsion systems, the bottles remained a uniform black color and there was no dividing line between the oil and brine. To quantify the stability of the emulsions, the height of the brine layer in the bottle was measured every half hour during the first 24 hours, once an hour during the second 24 hours, and once every two hours for another 24 hours. In this way, a height of the brine phase indicated that the emulsion was easier to separate. The results showed that this emulsion system is not stable. However, if no brine is separated from the emulsion, it is considered a stable emulsion. To quantify stability for the emulsion systems, the percentage of the brine height to total height of brine and heavy oil in a bottle was calculated and used for quantitative evaluation of the emulsion stability. Stability results of the emulsions formed by the selected surfactants are shown in Figures 3.13 to 3.20. For very stable emulsion systems, the bottles remain uniformly black and there is no dividing line between the oil and brine. For unstable emulsion systems, the oil and brine very quickly separated automatically.

$$\text{Emulsion Stability} = \frac{(h_{max}) - (h_{brine}) * 100}{(h_{max})} \quad (3)$$

3.2.2. Sand Test with Formation Water and Surfactant. Silica and Kaolinite powder was purchased from the US Silica Company in Pacific, Missouri and the Kaolinite was purchased in Phelps County, Missouri. These powders were activated at 120°C for 2 hours before being used for experiments.

3.2.3. Oil recovery test with oil-wet and water-wet sand. Before the sand could be used for the experiment, it was washed with tap water several times until the water turned clear and was then rinsed three times with distilled water. The washed sand was put into an oven at 90 °C to dry for two days. Sieves were then used to separate the dried sand. The sand that was between 20 and 30 mesh size was collected for test.

Two water-wet sand samples were prepared. Each sample was made by mixing 10.00 grams of dry clean sand and 1.25 grams of formation water to make the sand water-wet. 2.0 grams of Missouri heavy oil was then added to each sample. These sand-oil mixtures were warmed at 40 °C for half an hour to ensure that the heavy oil mixed effectively with the sand. To compare the performance of the surfactant with and without alkaline in the enhanced heavy oil recovery from water-wet sand, 35.00 mL of surfactant solution (Igepal CO-530 at 2.00wt. %) was added to one sample to approximately the 40 ml mark on the bottle; meanwhile, 35.00 mL of surfactant and alkaline (Igepal CO-530 at 2.00wt. %, NaOH at 0.6 wt. %) solution was added to another water-wet sample. The samples were checked overnight at room temperature.

In order to compare the surfactant performance in the enhanced heavy oil recovery from oil-wet and water-wet sand, two oil-wet sand samples were also prepared in the same manner described above but without the addition of 1.25 grams of formation water. 35.00 mL of surfactant solutions with and without alkaline were added to the two samples separately. The samples were checked overnight at room temperature.

For these sand samples with different initial wettability, they exhibited very different recovery of the heavy oil. Generally, water-wet sand indicates a much higher oil recovery than oil-wet sand. The surfactant solutions with alkaline show higher oil recovery than that without alkaline for both water-wet and oil-wet sand. The photo taken after oil recovered is shown in Figure 3.24. The oil recovery data are listed in Table 3.6.

3.3 ALAKLINE- SURFACTANT FLOODING TEST

The alkaline surfactant flooding process, in the heavy oil reservoirs, has been studied extensively; however, few efforts have been made to study alkaline surfactant flooding in heavy oil reservoirs. In this chapter, experimental techniques have been developed to measure cumulative oil production associated with alkaline surfactant flooding for heavy oil reservoirs. Experimentally, both the oil-wet and water-wet sandpack were tested and oil recovery was measured in an alkaline surfactant flooding process, while the associated emulsification was also created. Theoretically, a simulation technique was developed based on the experimental results to match with the model.

3.3.1. Experimental

3.3.2. Materials. A sample of heavy oil and brine was provided by the MegaWest Company from an oil field in Vernon County in western Missouri, USA and used in the experiments. The brine was artificially prepared with the same ingredients of various salts as the reservoir brine (see Table 3.1, 3.2). The sand used in the experiment was from the US Silica Company in Pacific, MO with 20-30 mesh size. This sand powder was activated at 120°C for 2 hours before being used for experiments.

Prior to the experiments, the brine and surfactant/ alkaline solution were prepared with synthetic brine. The original formation water was also provided by Mega West Company. Its composition was analyzed by Fluid System Technologies Company in St. Louis, MO. The brine composition is listed in Table 3.1. The synthetic brine used in this study was prepared based on the composition of the original formation water. The recipe for the synthetic brine is shown in Table 3.2. The recipe of the synthetic brine was designed according to compositions of the original formation water. Salts were weighed and then added to the distilled water to total 3000 grams. The synthetic brine was stirred for one hour. The pH meter and NaOH (0.200 M) solution was used to adjust the synthetic brine to pH = 7.3 and the synthetic brine was ready to use.

3.3.2.1. Experimental setup. Figure 3.3 is a schematic of the experimental setup used to conduct the alkaline surfactant flooding tests. It consists mainly of a tube pump (77120-52, Cole-Parmer, Vernon Hills, IL), a pressure transducer (PPT-2, Ashcroft, and Stratford, CT), a sandpack holder, and a sample cylinder as show in Figure 3.4.

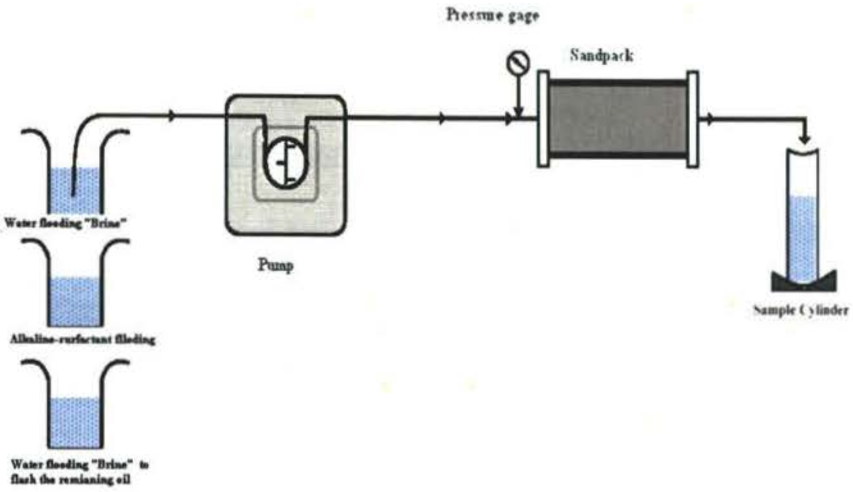


Figure 3.3 The Experimental Setup of Alkaline Surfactant Flooding Tests

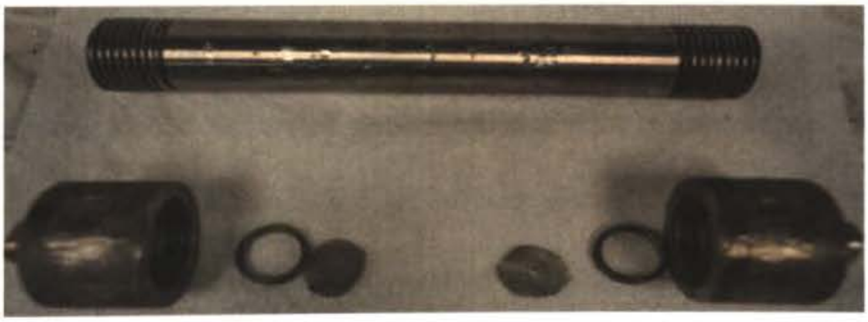


Figure 3.4 The Core Holder

3.3.2.2. Experimental Procedures.

3.3.2.2.1. Sandpack preparation. Fresh sand was used was in this experiment were maintained at an ambient temperature of 22°C. Two types of sandpacks were prepared: water-wet and oil-wet. Each sample was made by mixing 10.00 grams of dry clean sand and 1.25 grams of formation water to make the sand water-wet. 2.0 grams of

Missouri heavy oil was then added to each sample. The oil-sands was prepared in a similar manner of oil-sand but without the addition of 1.25 grams of formation water.

3.3.2.2.2. Alkaline surfactant flooding. Prior to surfactant alkaline flooding, the surfactant solution was prepared by diluting a known concentration of surfactant in the brine solution. The surfactant concentrations of 2 % and alkaline of 0.6 % were prepared for the alkaline surfactant flooding tests.

The experimental procedure for the alkaline surfactant flooding test is briefly described as follows: Prior to the alkaline surfactant flooding test, waterflooding was injected into the sand pack to displace the oil until no additional oil was produced. Additionally, an alkaline surfactant solution with the above concentration was injected into the sandpack with a slug size of 1 pore volume (PV). The injection of the waterflood was conducted after 48 hours of relaxation time of the alkaline surfactant solution slug. The waterflood injection continued until there was no oil production. Two alkaline surfactant flood tests were conducted for oil-wet and water-wet sandpack tests. The incremental oil recovery was obtained with a known alkaline surfactant concentration and was the same for each test.

To make a sandpack for AS flooding test, a core holder with a diameter 2.6 cm and the length of 24 cm was used. The cores were packed as follows: 40 grams of heavy oil was weighed and then warmed at 40 °C for 2 hours. Next, 200 grams of sand (30–20 mesh) was saturated completely with the formation brine for the water-wet sand. 65 grams of warm heavy oil was then added. The mixture was put in the oven for 2 hours. no brine was added for the oil-wet sandpack. The porosity of the sandpack was 45–58% and the absolute permeability to water was approximately 2.5–4.5 D. The displacement tests were conducted horizontally. Sandpack flood tests were conducted using the oil sample at ambient conditions. For each test, fresh sand was packed to ensure the same initial status of sand wettability. The core was waterflooded, using the pump (Perkin-Elmer series100). The injection rate was 0.5 ml /min and the synthetic formation brine was injected continiously until the oil production became negligible (oil cut <1%). 1.0 PV of preflush slug was then injected. The preflush slug was 2% surfactant and 0.6 wt. % alkaline NaOH in the formation brine. The precipitation of divalent ions in both preflush and chemical slugs was removed prior to the injection. In the stage of the tertiary chemical flood, a 1.0 PV chemical slug was injected. Chemical injection was followed by an extended waterflood until oil production became negligible. The oil production was determined on a volume basis.

3.4 ADSORPTION MEASUREMENT

3.4.1. Experimental

3.4.2. Materials. In this study, the adsorption of surfactant on silica and kaolinite powder surfaces was measured. The Igepal CO-53 surfactant was investigated because surfactant loss in reservoir due to adsorption on the rock surface poses a serious problem in the application of chemical flooding.

3.4.2.1. Set up. The spectrophotometer was used in this experiment. In brief, the sequence of events in a spectrophotometer is as follows: The spectrophotometer must be calibrated by a procedure known as "zeroing." The absorbency of a reference substance is set as a baseline value, so the absorbencies of all other substances are recorded relative to

the initial "zeroed" substance. The spectrophotometer then displays % absorbency (the amount of light absorbed relative to the initial substance). Figure 3.5 shows the spectrophotometer instrument, which was used in this study.

Figure 3.5 The Spectrophotometer Instrument

3.4.2.2. Experimental procedures. The adsorption for selected surfactants on silica and kaolinite clay was measured. In general, the less adsorption by the rock surface, the better quality of the surfactant. At the beginning of the experiment, a series of surfactant solutions of Igepal CO-530 was prepared at various concentrations from 20, 40, 60, 80, 100, 150, 200, 250, 300, 400, and 500 ppm. In this experiment, a UV-visible Spectrophotometer (UVmini-1240, Shimadzu) was used for analyzing surfactant Igepal CO-530 concentration. Using the prepared intitial solutions, UV absorbance (ABS) of Igepal CO-530 was measured at the wavelength of 265 nm (λ), where absorbance of Igepal CO-530 shows a peak, then the ABS for all the initial solution was measured at 265 nm. A calibration curve for this surfactant was obtained by plotting the ABS versus the initial concentrations and is shown in Figure 3.22.

To measure adsorption of the surfactant on silica and kaolinite clay, all the powder samples were dried in an oven at 100 °C for 48 hours to remove all moisture. For each surfactant solution, a clean test tube was used to weigh 10.00 grams of the surfactant solution. 0.5 grams of silica was then added to the test tube. All the tubes were shaken at room temperature for 24 hours to establish the adsorption equilibrium. After that, the test tubes were put in a centrifuge to separate the solution and the solid powder. For the surfactant concentration after adsorption, it was calculated through this calibration curve and it's ABS. Then the adsorption of the surfactant on powder surface was calculated by the equation (4) (Krumrine at el, 1982):

$$q_e = \frac{(C_0 - C_e) \cdot V}{W} \tag{4}$$

Where C_0 and C_e are the initial and equilibrium concentrations of surfactant respectively (mg/L), V is the volume of solution (L), and W is the weight of the powder used (g). The adsorption isotherms are shown in Figures 3.23.

3.5 RESULTS AND DISCUSSION

3.5.1. Temperature and Shear Rates Effect on Viscosity of the Heavy Oil. The viscosity of the crude oil decreases with the increase of temperature. Even though the crude oil is Newtonian, the viscosity measured was a little different for each shear rate value. It was most likely caused by practical or experimental errors which caused a slight deviation. Hence, the average value was calculated and plotted for each temperature with error bars to distinguish the viscosity range at a certain temperature. It appears that at lower temperatures, the error percentage was significantly larger compared to those at higher temperatures. Perhaps at a higher temperature, the crude oil is more consistent due to the reduced viscosity.

The viscometer was used to measure the crude oil sample viscosity of Long Farm over varying temperatures and shear rates. The density and API of the Crude oil for Missouri heavy oil was calculated. The viscosity was measured at different shear rates using a viscometer BROOKFIELD PV-II+Pro. At a low temperature range, e.g., below 40°C, the viscosity of the heavy oil decreased more significantly than at a higher temperature. The API gravity of the heavy oil in the Long Farm reservoir was 15°API. Figure 3.6 shows the viscosity at different temperatures (before and after cleaning).

At room temperature, 25°C, the viscosity of the clean heavy oil in the Long Farm reservoir was 18,518 cp. The viscosity of the heavy oil decreased rapidly with the increased temperature.

The viscosity was measured at shear rates ranging from 0.1 to 1000 using an RS150 viscometer. The viscosity changed at the different temperature ranges. It was found that at the low temperature range, e.g., below 40 °C, the viscosity of the heavy oil decreased more significantly than at a higher temperature.

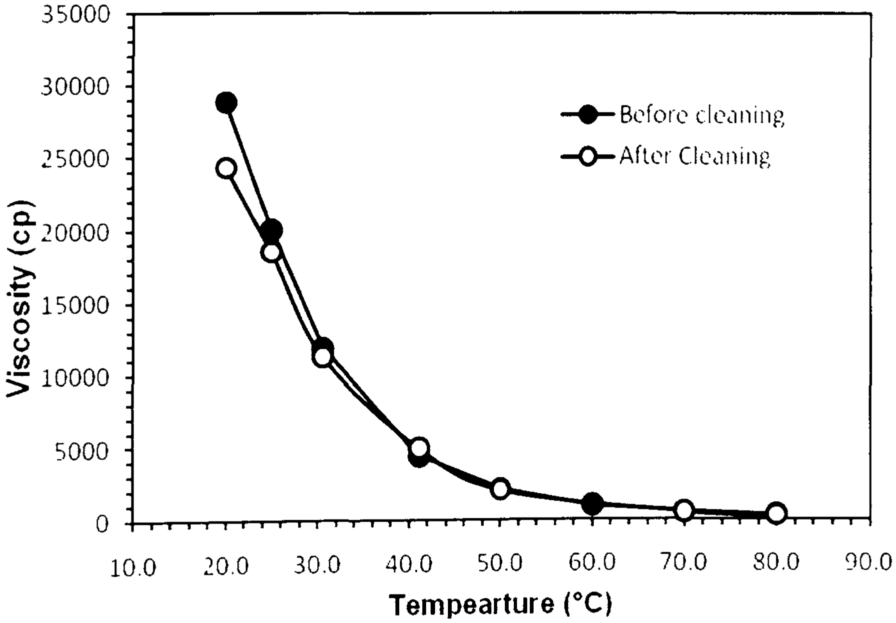


Figure 3.6 Viscosity of Heavy Oils before and after Cleaning at Different Temperatures

Figure 3.7 shows the relationship between shear stress S and shear rate R and the fluid's viscosity at a varying shear rate R. The typical heavy oil is Newtonian fluids. As a result, at a given temperature the viscosity of a Newtonian fluid remains constant regardless of which viscometer model, spindle, or speed was used to measure it. The behavior of Newtonian liquids in experiments conducted at constant temperature and pressure had the same features. The viscosity didn't vary with shear rate and it was constant with respect to the time of shearing. The stress in liquid fell to zero immediately after the shearing stopped.

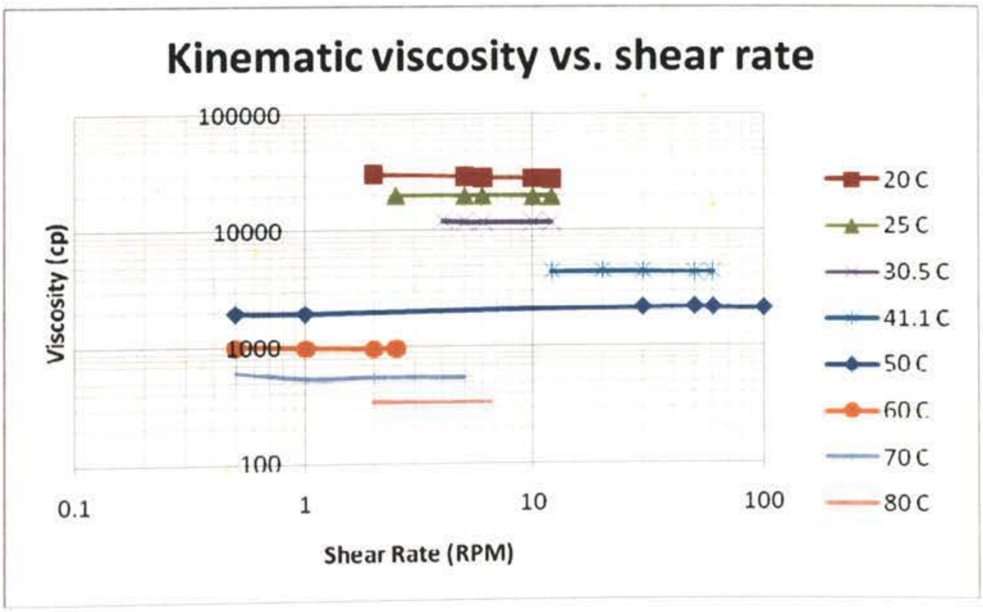


Figure 3.7 Viscosity of Heavy Oils at Different Shear Rate and Temperatures

3.5.2. Density and API of the Crude Oil Calculation. For future use, the density of the crude oil sample was determined. Due to the viscous nature and cohesiveness, it was impractical to measure the density using a hydrometer or specific gravity balance. Instead, the easiest way was to transfer an amount of oil into a small test bottle, measure its mass, and divide by its volume. Table 3.4 shows the crude oil calculation before and after cleaning.

Table 3.4 The Crude Oil Calculation

Heavy Oil viscosity	**Volume of the Crude Oil (cm^{3})**	**Mass of Crude Oil**	**Density of Crude Oil g/cc**	**API**
Before Cleaning	140	135.252	0.966	15.0
After Cleaning	140.68	133.956	0.9522	17.10

Since the crude oil was not clean, the density of the clean crude oil sample was re-measured, due to the viscous nature and cohesiveness. It was impractical to measure the density using a hydrometer or specific gravity balance. Instead, the easiest way was to transfer an amount of oil into a small test bottle, measure its mass, and divide by its volume.

Crude Oil Volume Determination

Mass of empty test bottle: 17.318 g

Mass of water filled bottle: 157.569 g

Mass of water: 140.251 g

Density of water at room temperature: 996.96 kg/m^3 (0.997 g/cm^3)

Bottle volume:

0.140251 / (996.95) = 140.68 cm^3

Crude Oil Mass Determination

Mass of crude oil filled bottle: 151.274 g

Mass of crude oil: 133.956 g

Density and API Gravity Determination

Density of crude oil:

(133.956) / (140.68) = 0.9522 Kg/ m ^{3}

API Gravity:

API= 141.5/density-131.5= (141.5/0.9522) -131.5= 17.10

3.5.3. Emulsion of the Heavy Oil by Surfactants and Stability of the Emulsion.

Figure 3.8 shows the emulsion stability of the heavy oil and synthetic brine emulsified by 11 anionic surfactants. These surfactants are ethoxylated primary alcohols. The emulsions were unstable and separated into two layers of heavy oil and aqueous solution automatically within 2 hours. In a few of them, e.g., Neodol 1-5 and Tomadol 91-6, the emulsion became stable after approximately 4 hours. Figure 3.9 shows the 10 samples of nonionic surfactants (secondary alcohols). For most of them, the emulsion was very unstable and broke quickly and the oil and surfactants solution divided into two layers except for the Igepal CO-530 surfactant, which was stabile for more than 72 hours. The emulsion stability resulted by anionic surfactants are shown in Figure 3.10. The emulsions created by the 6 anionic surfactants were very unstable. As a result, it was expected that the interfacial tension (IFT) between Missouri heavy oil and the formation brine could not be reduced by these anionic surfactants. Stability results of the emulsion by the 3 cationic surfactants are shown in Figure 3.11. All the samples of cationic surfactants were very unstable.

3.5.4. Temperature Effect. Emulsion stability at the elevated temperature of 40 °C was also studied. To compare the stability results at the different temperatures of 25 °C and 40 °C, the percentages of height/equilibrium height (h_{max}) for heavy oil/synthetic brine/surfactant emulsion at 40°C are shown in Figures 3.12, 3.13, 3.14 and 3.15. It could be found that most of the emulsions with nonionic surfactants were unstable after 1 hour, but all the samples with anionic and cationic surfactants became unstable immediately. It is worth noting that Igepal CO-530 shows a very different emulsion stability at 25 °C and 40 °C as shown in Figures 3.9 and 3.13. In Figure 3.19, it can be observed that the emulsion with Igepal CO-530 was very stable at 25 °C and there was no separation between heavy oil and brine for more than 72 hours. In Figure 3.13, the emulsion was stable for 2 hours at 40 °C. After that time, the emulsion became unstable and automatically separated into two layers, leaving a clear aqueous phase with oil on the top.

One photo showing the emulsion stability at 25°C and 40 °C is Figure 3.16. Consequently, this surfactant could be used to generate stable oil and water emulsion at 25°C, and the emulsion could be easily separated at 40 °C.

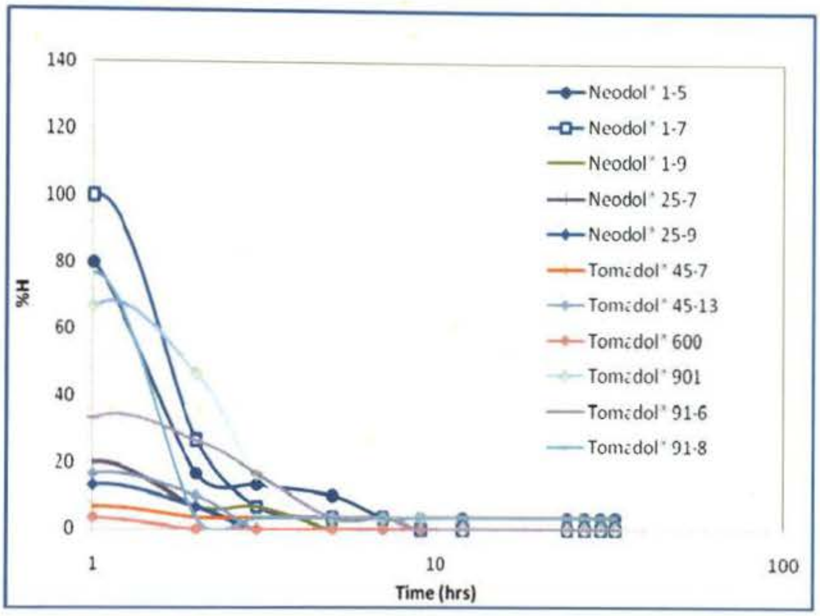


Figure 3.8 Nonionic Surfactants (primary alcohols) Percentage of Height / Height Equilibrium (H max) for Heavy Oil/Synthetic Brine / Surfactant Emulsion at 25°C

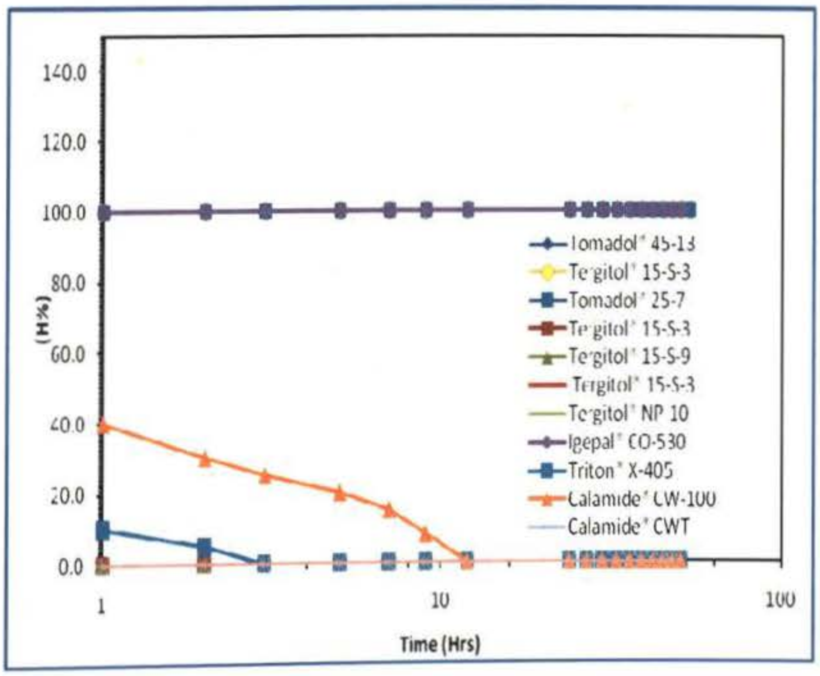


Figure 3.9 Nonionic Surfactants (secondary alcohols) Percentage of Height / Height Equilibrium (H max) for Heavy Oil/Synthetic Brine / Surfactant Emulsion at 25 °C

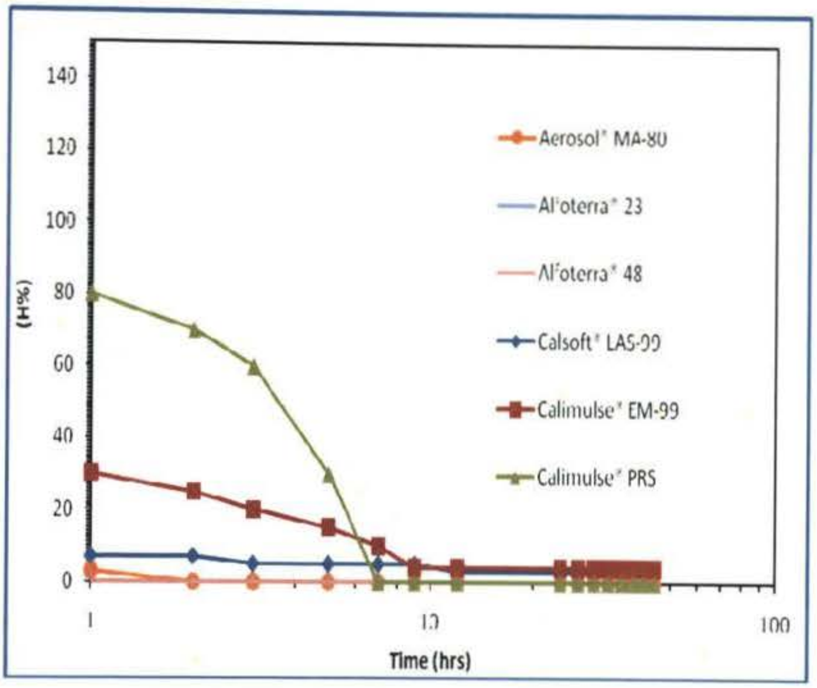


Figure 3.10 Anionic Surfactants Percentage of Height / Height Equilibrium (H max) for Heavy Oil/Synthetic Brine / Surfactant Emulsion at 25 °C

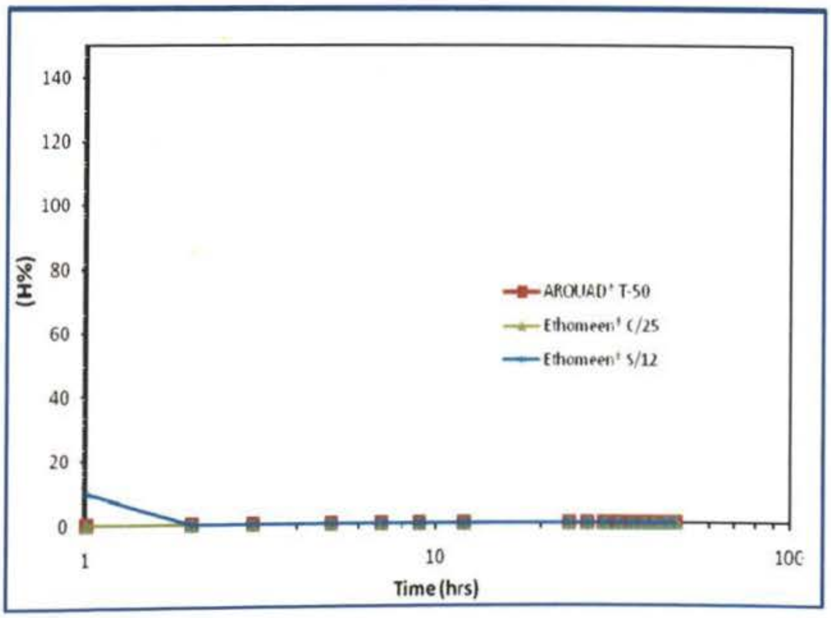


Figure 3.11 Cationic Surfactants Percentage of Height / Height Equilibrium (H max) for Heavy Oil/Synthetic Brine / Surfactant Emulsion at 25 °C

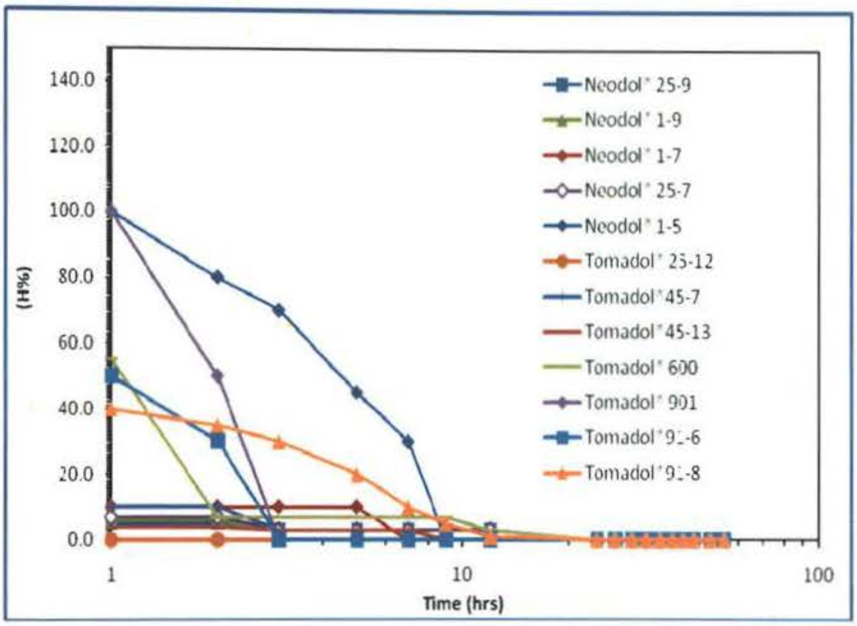


Figure 3.12 Nonionic Surfactants (primary alcohols) Percentage of Height / Height Equilibrium (H max) for Heavy Oil/Synthetic Brine / Surfactant Emulsion at 40 °C

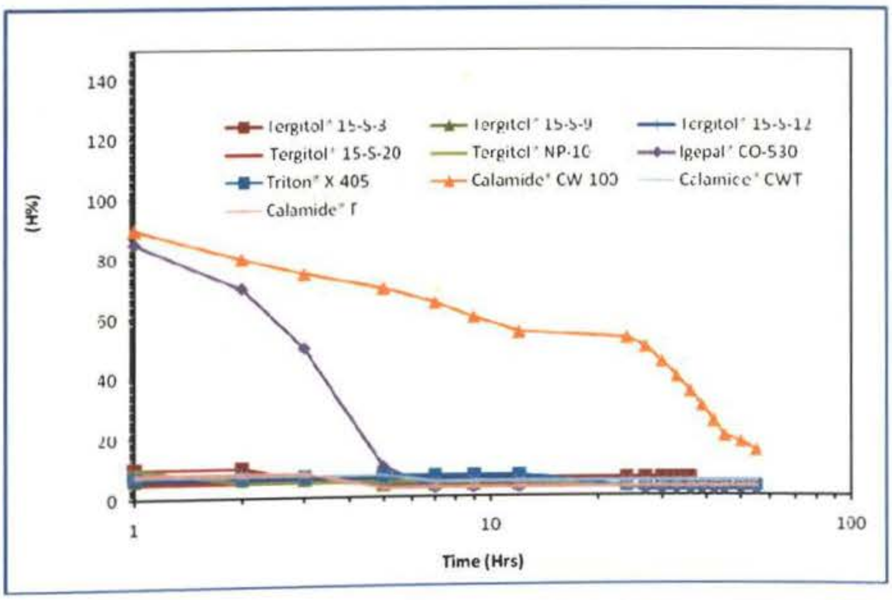


Figure 3.13 Nonionic Surfactants (secondary alcohols) Percentage of Height / Height Equilibrium (H max) for Heavy Oil/Synthetic Brine / Surfactant Emulsion at 40 °C

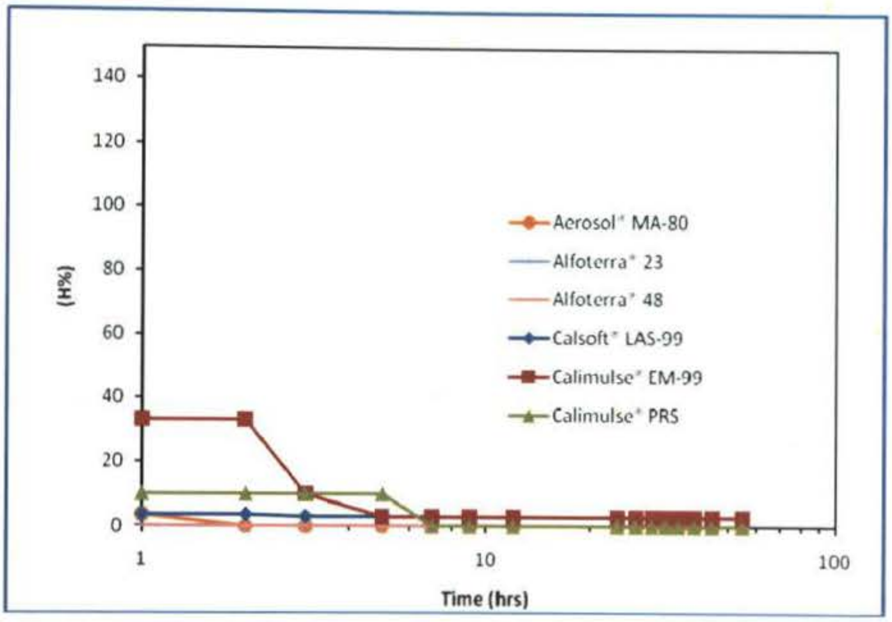


Figure 3.14 Anionic Surfactants Percentage of Height / Height Equilibrium (H max) for Heavy Oil/Synthetic Brine / Surfactant Emulsion at 40 °C

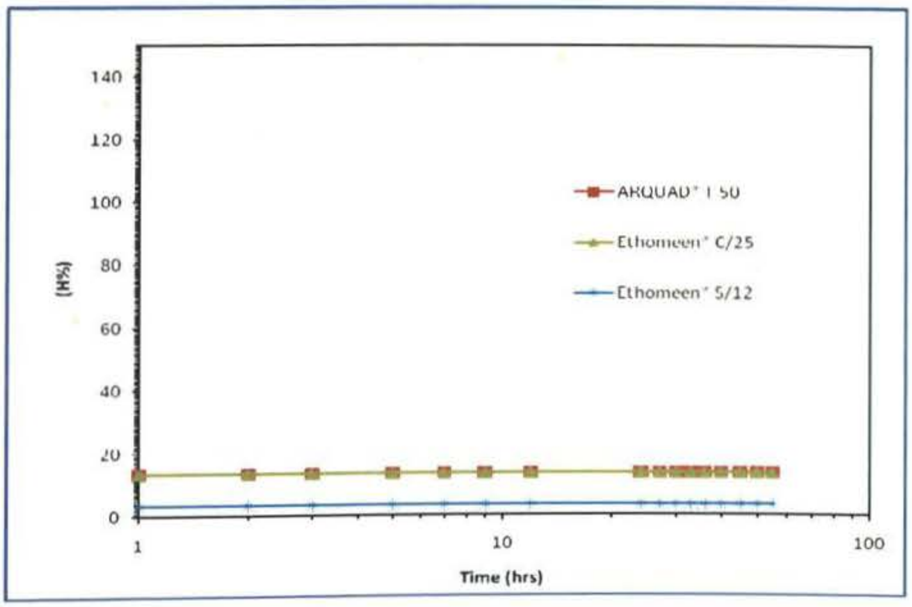


Figure 3.15 Cationic Surfactants Percentage of Height / Height Equilibrium (H max) for Heavy Oil/Synthetic Brine / Surfactant Emulsion at 40 °C

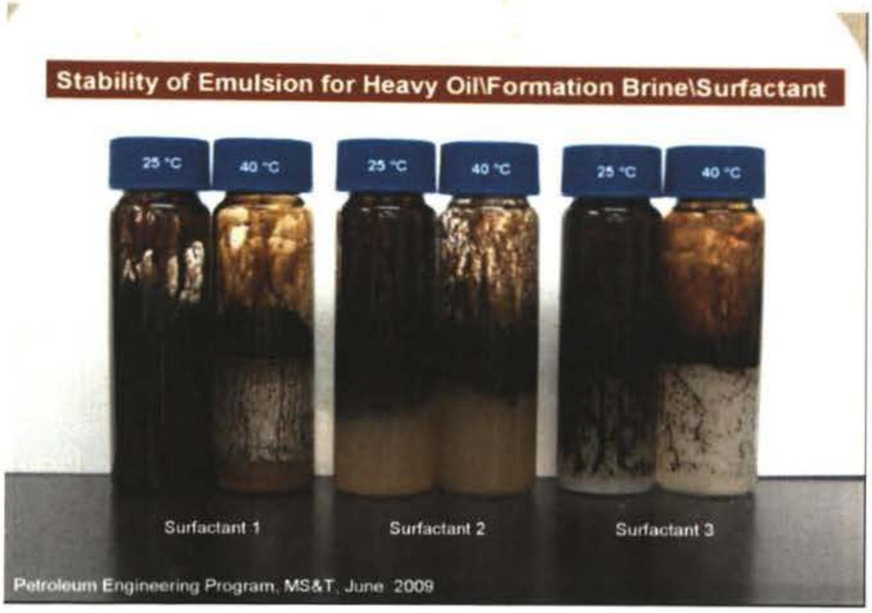


Figure 3.16 Stability of Emulsion for Heavy Oil /Synthetic Brine System at Different Temperatures

3.5.5. Surfactant Concentration Effect. Different concentrations of surfactant Igepal CO-530/ synthetic brine were tested at 25°C. 18.0 grams of surfactant-brine solutions with different concentrations of 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.%, 1.0 wt.%, and 2.0 wt.% were mixed with 2.0 grams of heavy oil, separately, and shaken by hand for 1 minute. Figure 3.17 shows that a higher concentration (above 1.0 wt. %) could create a stable emulsion which could reduce the interface tension between oil and brine, but concentrations lower than 1.0 wt. % could not create a stable emulsion; the lower concentration cannot reduce the interface tension between the heavy oil and surfactant-brine solution.

Figure 3.17 Effect of Surfactant Concentration on Emulsion Stability

3.5.6. Effect of Oil- Water Ratio. The influence of oil to Igepal CO-530 Surfactant/synthetic brine ratio was investigated; the four samples of Igepal CO-530 surfactant / brine solution at different ratio were prepared as follows:

Sample A: 4 g warm oil + 16 g surfactant / brine solution- 20% oil to 80% Igepal solution.

Sample B: 6 g warm oil + 14 g surfactant / brine solution- 30% oil to 70% Igepal solution.

Sample C: 8 g warm oil + 12 g surfactant / brine solution- 40% oil to 60% Igepal solution.

Sample D: 10 g warm oil + 10 g surfactant / brine solution- 50% oil to 50% Igepal solution.

The effect of the surfactant to oil ratio on the emulsion stability was evaluated. Figure 3.18 illustrates the results systematically changing the water–oil ratio. While keeping the other variables constant, the systems exhibited different stability behavior. The results revealed that the effect of the water–oil ratio on system behavior decreased the water/oil ratio which led the system to change from

Stable → partially stable → unstable.

This provided a useful tool for designing optimum formulations suitable for heavy oil recovery.

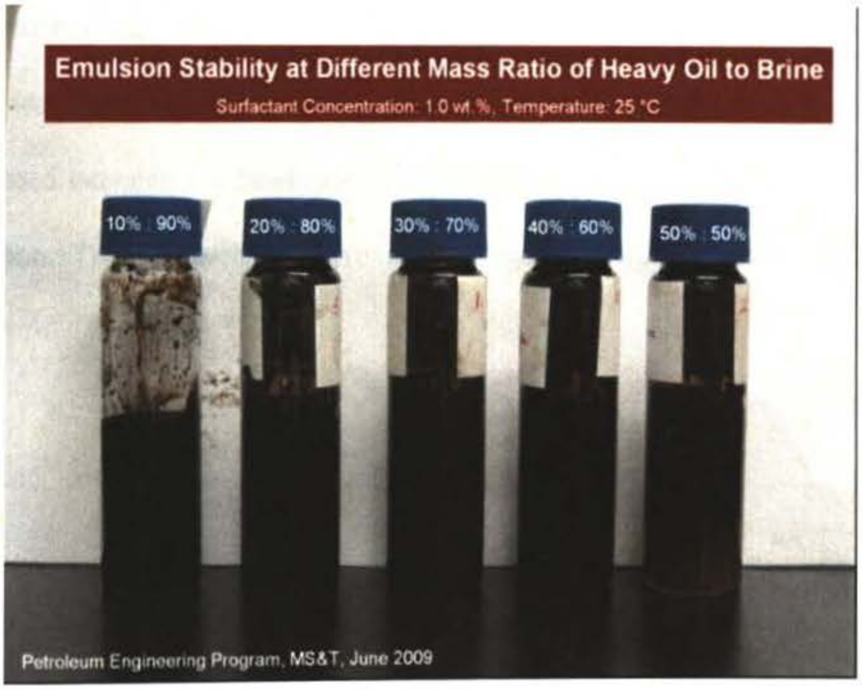


Figure 3.18 Effect of Surfactant to Oil Ratio on the Emulsion Stability

3.5.7. Effect of Alkaline NaOH / Igepal CO-530 Surfactants on Stability of the Emulsion. The influence of Alkine NaOH / Igepal CO-530 surfactant / brine solution was investigated; the four samples of Igepal CO-530 surfactant / brine solution at different ratios were prepared as follows: 2 g warm heavy oil with 0.6 % Wt. of alkaline

NaOH / and 1 % Wt. of Igepal surfactant / brine solution at the temperatures of 25 °C and 55 °C. Figure 3.19 revealed that the effect of the Alkali on the system behavior made the emulsion more stable at the room temperature of 25°C, but the stability decreased when the temperature was increased. For example, at 45 °C the sample was partially stable; however it automatically separated at 55°C. Hence, at the room temperature of 25°C, the emulsion was stable due to the AS solution. This solution was highly soluble in brine and reduced the interface tension between the heavy oil and brine, but at the temperature of 55°C it could not create a stable emulsion because the AS solution was less soluble in brine. This was based on the interface tension at the high temperature. The tension could not be reduced between the heavy oil and alkaline NaOH / Igepal CO-530 surfactant / brine solution. This research will provide the industry with a useful design for AS flooding.

Figure 3.19 Effects of Alkaline NaOH / Igepal CO-530 Surfactants on Stability of the Emulsion.

3.5.8. Effects of AS Solution on Wettability. The formation sand saturated with heavy oil was investigated in order to check the ability of surfactant and alkaline to change the wettability of the oil-wet sand to water wet. Two samples of the oil-wet sandpack were saturated with the heavy oil and mixed with the Igepal CO-350 synthetic brine and another two samples of the water-wet sand were mixed with the alkaline surfactant solution. These samples were shaken overnight. Figure 3.20 shows that the oil-wet sand changed to water-wet sand and that the oil could be recovered. When the surfactant combined with the alkaline, more oil was produced due to the alkaline reaction with the organic acid in the heavy oil and further reduced the interfacial tension. Table 3.5 illustrates oil recovery test with water-wet and oil-wet sandpack.

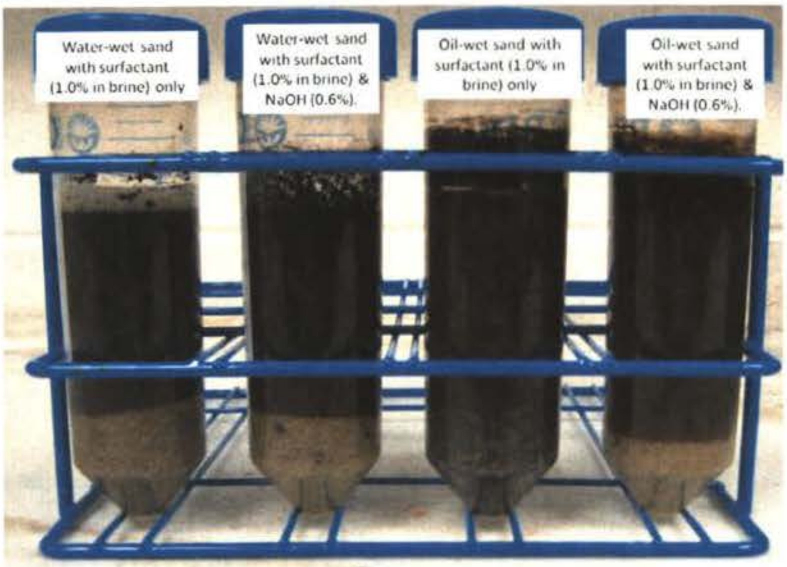


Figure 3.20 Effect of Igepal CO-530 and Alkaline NaOH on Wettability

Table 3.5 Oil Recovery Test with Water-wet and Oil-wet Sandpack

Wettability of sand-pack	**2.0 wt. % of Igepal CO-530 Surfactant**	**0.60 wt. % NaOH Alkalis / 2.0 wt. % of Igepal CO-530 Surfactant**
Water -wet	90% OOIP	96% OOIP
Oil -wet	50% OOIP	70% OOIP

3.5.9. Heavy Oil Recovery by AS Flooding. As described in the previous section, the injection of the alkaline NaOH and Igepal CO-530 surfactant increased the tertiary oil recovery. To further investigate the effect of the alkaline/ Igepal CO-530 surfactant on the EOR efficiency, the results for the sandpack flood tests with 2.0 wt. % of Igepal CO-530 surfactant and 0.60 wt. % NaOH were compared. In the two types of sandpack tests, the oil recovery curves are shown in the Figure 3.20. It is necessary to use as little NaOH as possible in the chemical formula so that by adding alkaline the surfactant loss is reduced. The incremental oil recovery was only about 5-11% OOIP with 1 PV injection of the chemical solution followed by an extended waterflood. These results indicate that the use of NaOH was necessary to obtain optimum enhanced oil recovery. NaOH and the surfactant had a synergistic effect in reducing IFT and forming O/W emulsions. The use of NaOH increased the reaction rate between the alkaline and the organic acids in oil, leading to a significant pressure drop response.

3.5.9.1. Oil-wet sandpack. To investigate the function of surfactant and alkaline in the EOR process, a sandpack flood test was conducted using a 2.0 wt. % of surfactant and alkaline (0.60 wt. % NaOH). Figure 3.21 shows that no incremental oil was recovered after the AS flood 5% OOIP compared to the water flooding test which was 11 % OOIP. This indicated that there may have been a water channel created after the water flooding. The results of the recoveries of the AS flooding are listed in Table 3.7. The volumetric sweep efficiency and displacement efficiency were all quite low, but resulted in the additional 5 % (v/v) recovery of original oil in place (OOIP).

3.5.9.2. Water-wet sandpack. In order to further study the displacement efficiency of the alkaline and surfactant fluid, flood tests were performed on a second type of water-wet sandpack. The results of the floods are listed in Table 3.6. It can be seen that the displacement efficiency was extremely good. The two sandpack tests do not have similar displacement efficiencies and the water-wet had a higher recovery of 11% OOIP.

Table 3.6 Oil Recovery for Water Flood & AS Flooding

Sandpack Type	**Water Flooding Test (V/V) %**	**AS Flooding Test (V/V) %**
Oil-wet	17	5 (2.1%AS+2.8%water)
Water-wet	15	11 (6 %AS+4.9%water)
	From OOIP	From Remaining OOIP

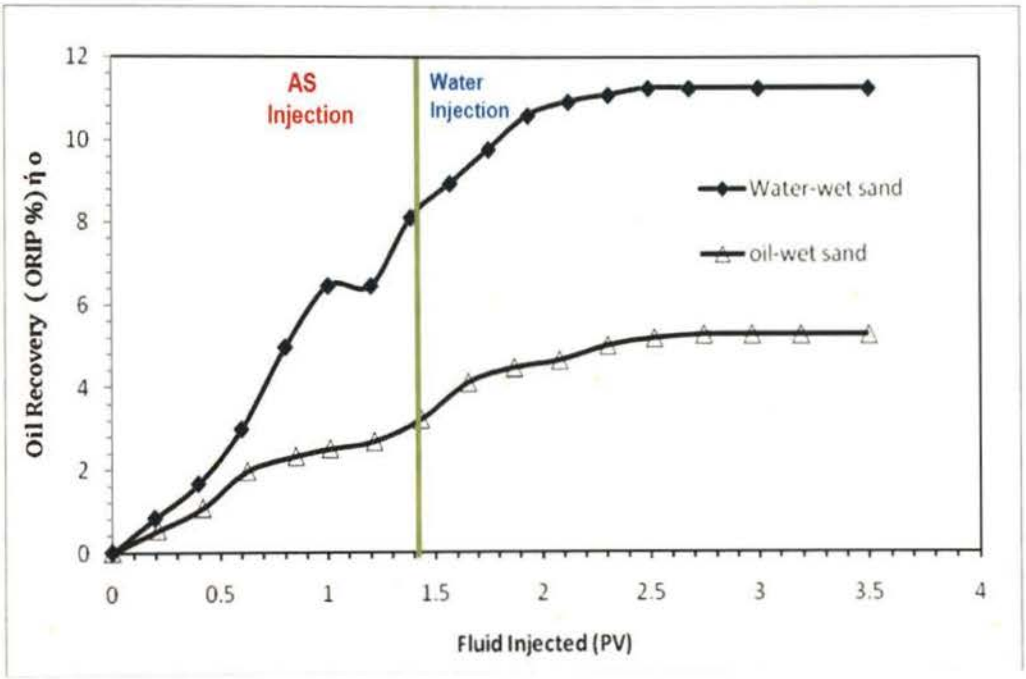


Figure 3.21 Oil Recovery of Water-wet and Oil-wet Sand (AS Flooding)

3.5.10. Adsorption of Surfactants on Silica and Kaolinite Clay. Adsorption of the surfactant Igepal CO-530 on silica and kaolinite clay was tested. Adsorption isotherms are shown in Figure 3.22. These procedures were repeated with 0.1 grams of kaolinite. The fact that the adsorption isotherms corresponded with the Langmuir type may be due to the mutual compensation of several factors which affect the shape of isotherm. When adsorption isotherms follow the Langmuir type the equilibrium data was processed by employing the Langmuir equation (5):

$$\frac{C_e}{q_e} = \frac{1}{q_{Max}} b + \frac{C_e}{q_{\max}} \tag{5}$$

where C_e and q_e are surfactant concentrations (mg/L) and the amount absorbed (mg/g) at equilibrium, respectively. b is the Langmuir constant, q_{max} is the maximum adsorption capacity (mg/g).

In Figure 3.23, it was found that Igepal CO-530 had a higher adsorption on kaolin clay than on Silica-30. The maximum adsorption of Igepal CO-530 on kaolin clay was 22.13 mg per gram of clay, while the maximum adsorption of Igepal CO-530 on Silica 30 was 6.9 mg per gram of silica. A similar type of isotherm has been found by several researchers for the adsorption of anionic or cationic surfactants on carbons. The explanation for this is primarily focused on two aspects: (1) with the increase of the surfactant concentration, the ionic strength was increased and the depth of the surface double layer was decreased, which resulted in the transformation of a surface micelle, and (2) the swelling of the solid materials in the surfactant solution caused the increase of available surface of adsorbent. Unfortunately, there was no definite conclusion that could be drawn. The lower adsorption capacity shown by Silica 30 with Igepal – CO-530 was due to the fact that the hydrophobic and hydrogen bond interactions between the surfactants and the adsorbent were weak.

The experimental results with kaolin clay show that the adsorption of Igepal CO-530 surfactant increased with its concentration and achieved a plateau, but then sharply decreased. The reason for this decrease is currently unknown.

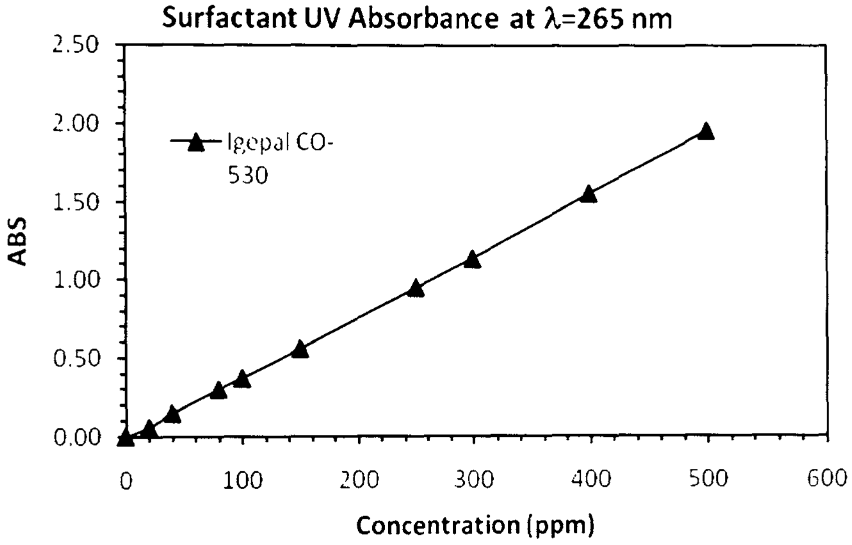


Figure 3.22 UV Calibration Curve for Igepal CO-530 Surfactant

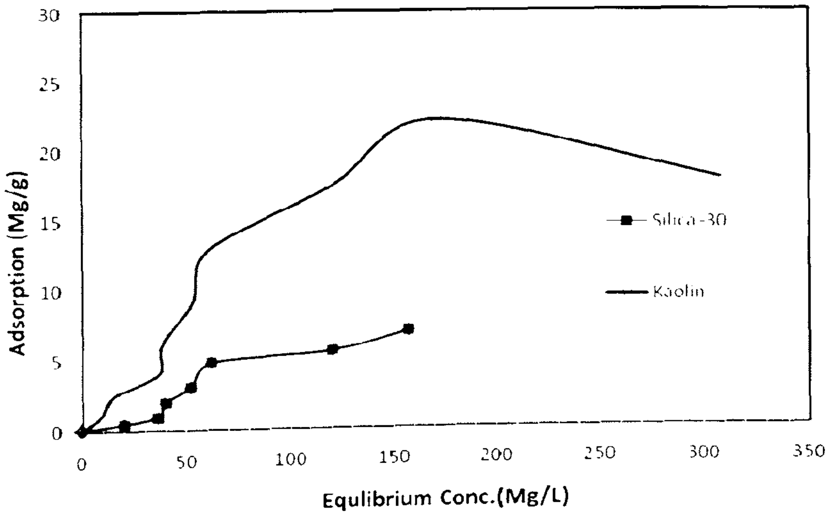


Figure 3.23 Adsorption Isotherms of Igepal CO-530 on Kaolin Clay and Silica at 25 °C

In summary, one of the purposes of this study was to identify the best surfactants that are capable of forming a stable emulsion for western Missouri heavy oil and the formation water. It was found that the nonionic surfactant Igepal® CO-530 could form a very stable emulsion for the heavy oil and synthetic brine. The viscosity of the heavy oil was reduced from 18,518 cp to 2.5 cp at 25 °C through the emulsion. Therefore, the mobility of the heavy oil improved significantly. Moreover, the emulsion created by Igepal® CO-530 became unstable at higher temperatures. At 40 °C, this emulsion separated automatically to two layers within 2 hours without any addition of the de-emulsion agent.

By adding the alkaline NaOH to the nonionic surfactant Igepal® CO-530, a very stabile emulsion was created. However, at 55 °C, this emulsion could easily be separated into two layers within 2 hours without any addition of the de-emulsion. This research provides a great advantage for the application of this technology to increase heavy oil recovery.

AS Flooding test results showed that a higher heavy oil recovery could be obtained by the combination of the alkaline and surfactant (AS). Adding 0.6 % Na OH to the surfactant Igapal® CO-530 solutions could change the wettability of sandstone from oil-wet sand to water-wet sand. For Missouri heavy oil, the water-wet sandpack indicated a higher oil recovery than the oil-wet sandpack. By AS flooding, the tertiary heavy oil recovery from the water-wet sandpack was enhanced to 12 % of original oil in place (OOIP).

4. WETTABILITY ALTERATION

Currently, several technologies have been developed to enhance heavy oil recovery. All the technologies involve either heating the reservoirs to liquefy the hydrocarbons or attack the deposits with diluents or solvents. Recent studies have found that a combination of alkali-surfactant flooding, when properly designed, can lead to significant improved heavy oil recovery and has considerable potential for non-thermal technology. However, a more challenging case is the heavy-oil fractured reservoirs where the recovery is limited only to the matrix oil drainage gravity due to the unfavorable wettability.

Wettability alteration is usually achieved through application of proper surfactants. In this study, research of the surfactant improved heavy oil recovery by wettability alteration was conducted. As a non-thermal recovery technology, its application will benefit the oil industry by identifying the best surfactants to enhance heavy oil recovery. For heavy oil production in the U.S., increasing the unlocked heavy oil by 1% means a gain of more than 1.5 billion barrels production. Studying the relation between wettability alteration and oil recovery, this research provides principles to design surfactant-based formulations for enhanced heavy oil production, through low IFT and wettability alteration. Surfactants have been used to change the wettability, with the goal of improving the oil recovery by increased imbibition and changing the contact angle of the water into the rock matrix.

This study considers the screening of different classes of surfactants and a series of branched alcohol propoxylate sulfate surfactants, as candidates for chemical EOR applications. The mechanisms for improved heavy oil recovery result in the combined effects of reduced interfacial tension (IFT), reduced mobility ratio, and wettability alteration with dilute 0.1 wt% surfactant solutions from Berea sandstone cores.

The wetting of solid substrates by liquids is a fundamental phenomenon with relevance to both the technological and natural worlds. The wettability of solid-fluid-fluid interfacial phenomena is often characterized by measuring the contact angle formed between a liquid drop and a solid surface. This measurement is considered to be a relatively simple, useful, and sensitive tool for assessing hydrophobicity or *hydrophilicity* of a surface, surface heterogeneity, surface roughness, solid surface energy, liquid surface tension, and line tension, although this is not uncomplicated but poses several questions to researchers.

In this study, spreading the water and surfactant on sandstone solid surfaces to measure the contact angle as an expression of wettability of the liquid on a solid surface is one method of finding contact angles. The contact angle provides more accurate indication to the wettability and the spreading of different liquids on different solid surfaces.

4.1. EXPERIMENTAL TO MEASUREMENT WETTABILITY ALTERATION

4.1.1. Materials. The heavy oil sample provided by the MegaWest Company was from an oil field in Vernon County in western Missouri. The viscosity was measured to be 18,815 cp at 25 °C.

The original formation water was also provided by MegaWest Company from the same oil field. Its composition was analyzed by Fluid System Technologies Company in St. Louis, MO.

The Brine Composition is provided in Table 3.1. The synthetic brine used in this study was prepared based on the composition of the original formation water. The recipe of the synthetic brine is shown in Table 3.2. Surfactant Samples: 20 commercial surfactants were tested in this study. These surfactants were divided into three types: anionic, cationic and nonionic surfactants. Their commercial and chemical names are listed in Table 3.4.

4.1.2. Experimental Procedures. The surfactant concentration solution was diluted to a 1000 ppm concentration. The surfactant solution was added to the synthetic brine and the surfactant solution and synthetic brine was mixed by shaking it thoroughly for 30 minutes.

The sandstone core was purchased from a company in Missouri. The homogeneous sandstone cores were cut to small chips with a thickness of 2 mm for the contact angle measurement as shown in Figure 4.1. The contact angles of water on the sandstone chips surface were measured by the advanced Goniometer rame-hart 500 in this lab as shown in Figure 4.2 For the imbibition test, the cores were 2.5 in (6.35 cm) length with a diameter of 1.25 in (3.18 cm) as shown in Figure 4.3. These sandstone cores were washed and dried. The clean core was put in an oven at 80 °C for 24 hours to remove all the water absorbed during the cutting and washing.

The sandstone cores were vacuumed and then saturated by diluted oil for 48 hours. The core was put in an oven at 60° C for 72 hours. The cores were then dried at the room temperature of 25°C for 2 hours. Figure 4.4 shows the vacuum system saturation of the model oil with the core samples.

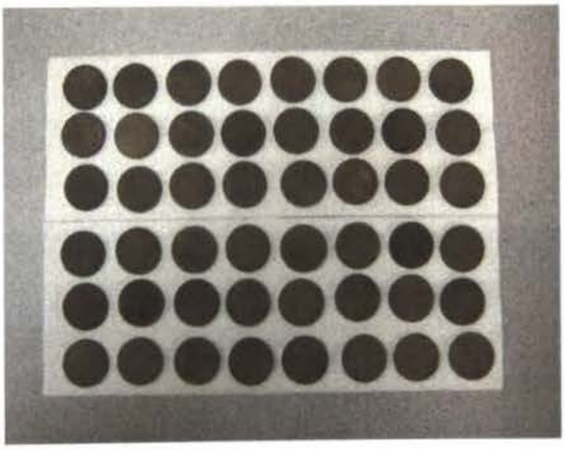


Figure 4.1 Sandstone Chips Saturated with Crude Oil

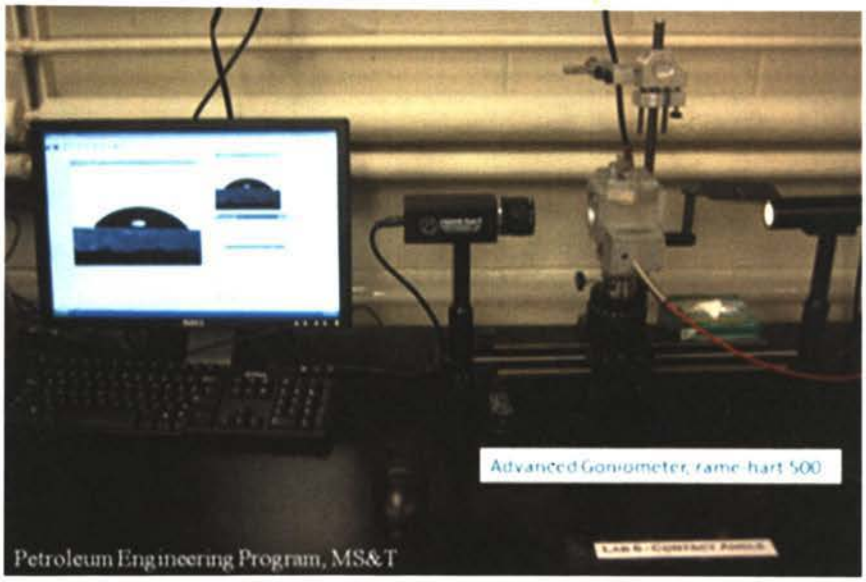


Figure 4.2 Goniometer to Measure Contact Angle of Water and Surfactant Solution

Figure 4.3 Imbibitions Cores (Bulk Volumes)

Figure 4.4 Vacuum Systems for Saturation of Model Oil
with the Core Samples

The heavy oil samples used in this test contain 5% of Missouri heavy oil and were diluted by 95 % of n-decane and shaken for 48 hours until the heavy oil was completely mixed and became homogenous. The Figure 4.5 shows the heavy oil was diluted.

Figure 4.5 Diluted Heavy Oil

4.2 SPONTANEOUS IMBIBITION TEST

Experimental Procedures: In this study an imbibition test was performed for vertically oriented Sandstone cores of the Missouri field. 20 surfactants were selected for a spontaneous imbibition test to evaluate their ability to recover oil from porous sandstone core. All the surfactant solutions were prepared with synthetic brine at 0.1 wt. % concentration and the test was conducted at 25 °C. The selected surfactants were ionic surfactants, anionic and cationic surfactant, and most of them were commercial products. The experimental procedures were as follows:

1. The cores were completely dried as shown in Figure 4.6 and cooled to room temperature. An ink marker was used to mark the cores as #1, #2, #3, were weighed on a balance, and the exact weight for each sandstone core was recorded. 6 to 8 cores were placed in a 1,000 ml Pyrex flask for the next vacuum process. Because air was trapped in the porous media of the dry sandstone cores, it was removed by the vacuum process to ensure a good oil recovery result.
2. An apparatus was set-up to vacuum the core. This consisted of a vacuum pump, pressure gauge, 1,000 ml Pyrex flask, etc.
3. The Pyrex flask was connected with the sandstone cores to the vacuum system. The model oil was used to screen the test for the best surfactant candidates. Nalgene PVC vacuum tubing (30 to 40 cm) was connected to a bottle with 600 ml of 98% n-decane and with the Pyrex® flask containing the core samples. The tubing was closed by the use of a tubing clip and the part on the n-decane side was filled with the model oil in order to remove the air in that part of tubing. The end of this part of tubing was carefully placed into the bottom of the bottle with

600 ml of model oil, preventing any air from entering the tubing again. The vacuum apparatus is shown in the Figure 4.4.

4. The vacuum pump was turned on. The reading on the pressure gauge quickly decreased from Zero MPa to -100 KPa (-1 atm). The vacuum pump remained running and the low pressure was maintained for 4 hours to remove the air trapped in the sandstone cores. After that, the vacuum tubing clip was opened very slowly because of the reduced pressure in the vacuum system and the n-decane was allowed to flow into the Pyrex flask and to be absorbed by the sandcores. When the n-decane covered all the sandstone cores in the flask, the vacuum pump was turned off. After 30 minutes, the tubing was disconnected from the Pyrex flask vacuum system and left there overnight. The sandstone sucked more model oil of n-decane under the regular air pressure.

5. The Amott cells were designed and made especially for the imbibition test as shown in the Figure 4.7. A label with the surfactant name was put on the outside of the container (lower part of the Amott cell) and were marked as #1, #2, #3... The container and cover (top part) were weighed separately for each cell and the data was recorded.

6. The n-decane was poured from the Pyrex flask. The sandstone cores sucked the model oil slowly out of the flask and the core was placed in the Amott cell container with the same number. The total mass of the container and sandstone core with the n-decane was determined. The mass (g) of the n-decane sucked in this core = Total mass – container mass – dry core mass. The initial volume of the n-decane sucked in a sandstone core was calculated by the mass divided by the

density of n-decane. (0.73 g/ml). The amount of the model oil in the core sample was the target of the oil recovery test by imbibition.

7. A very small amount of high vacuum grease (Dow Corning) was applied onto the unpolished surface of the top part of Amott cell and assembled into the two parts. The joint was slowly turned to ensure that the two parts connected tightly to ensure that there would be no leakage after the cell was filled with the surfactant solution. The rubber bands were put on each side of the cells.
8. The surfactant solution was slowly added to the Amott cell with and the correct label and number and placed on the buret. If air bubbles formed in the buret during the solution addition, the air bubbles were removed or de-foamed to ensure that the solution was added to exactly the 0 mark. After that, the total mass of each Amott cell containing the sandstone core and surfactant solution was weighed. The weight of the surfactant solution was calculated: Total weight - weight of empty Amott cell – sandstone core sucked with model oil.
9. The model oil in the sandstone cores were displaced by the surfactant solution through gravity and/or reduction of capillary force (interfacial tension, IFT). Because the model oil had less density than surfactant solution in brine, the displaced (or recovered) model oil moved up and floated on top of the buret. The volume of the float oil was measured by taking the reading on the buret. During the first week, the reading was taken every day. After that, the reading was taken every 2 or 3 days. After one month, the reading was taken once a week. This reading was continued until no more oil could be recovered or the oil recovery had stopped.

The results were recorded and the cumulative oil recovery was calculated. Figure 4.9 and 4.10 shows the oil recovery during imbibition test vs. time (number of days) and demonstrated the comparison between the surfactants and formation water.

Figure 4.6 Sandstone Cores

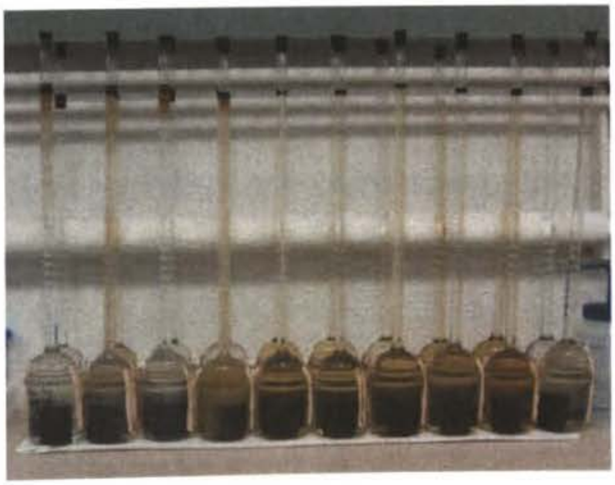


Figure 4.7 Amott Cells for Imbibition Test

4.3 CONTACT ANGLE MEASUREMENT

Experimental Procedures: For the contact angle measurement, 20 commercial surfactants and the formation water were selected for the contact angle measurement. All the surfactant solutions were prepared at 0.10 wt% with the synthetic brine. The advanced Goniometer was used to measure the contact angle of the formation water and surfactant solution (0.10 wt %) on the oily sandstone chip. One chip was used for 3 ~ 4 measurements. Each time, a droplet of liquid was applied to a different point of the chip and was conducted under the same conditions. Figure 4.2 illustrates the Goniometer which was used to measure the contact angle of the water and surfactant solution (0.1 wt %) on the oily sandstone chip in the Figure 4.7.

The method used for measuring the contact angle was the sessile drop method, which involved depositing a liquid drop on a smooth solid surface and measuring the angle between the solid surface and the tangent to the drop profile at the drop edge. If the drop stopped spreading some time after deposition, the final angle was easily measured through the contact angle goniometry principles. This angle is called the advancing static contact angle θ_S. During the spreading, the angle measured is called the advancing dynamic contact angle θ. It has been found experimentally that when the drop is spreading the contact angle is greater than θ_S and the drop keeps spreading until the angle decreases to θ_S.

4.4 MEASUREMENT OF INTERFACIAL TENSION (IFT)

Experimental Procedures: As a follow-up to contact angle measurement, the same 20 surfactants were selected for IFT test to evaluate their ability to reduce the IFT between the heavy oil and the surfactant solution. All the surfactant solutions were prepared with synthetic brine at 0.1, 0.5, 0.2 wt. % concentration and the test was conducted at 25 °C. Each sample was prepared with 10 ml of surfactants solution and 10 ml of Missouri heavy oil which was dilated as mentioned in the material section. Figure 4.8 shows these samples. The dynamic IFT values between Missouri heavy oil and surfactant solutions with different concentration were measured by the American Texas-500 spinning drop interfacial tension apparatus, with image acquisition and analysis software as shown in Figure 4.9.

Figure 4.8 Samples of IFT Measurement

Figure 4.9 Texas-500 Spinning Drop Interfacial Tension Apparatus

The principle used to measure interfacial tensions with the spinning drop method was that the oil (low density) could form a long oval drop in the water-phase (high density) under the effect of centrifugal force, gravity, and interfacial tensions. Its major axis is L and minor axis is D.

When L/D ≥4, the IFT obtained from equation (6).

$$\gamma = 3.42694\times 10^{-7}(\rho h - \rho d)\omega^2 D^3 \tag{6}$$

Where ρh and ρd are the density difference between oil and water, ω is angular velocity and D is drop minor axis semi diameter, respectively.

In fact, the spinning drop interfacial tension apparatus shows the parameter p which is reciprocal of speed. Thus the metrical drop diameter is not the actual size but an apparent diameter d. So equation (6) can be transformed into equation (7).

Where *d*, *p* and *n* are drop apparent diameter, reciprocal of speed and solution refractive index (measured by WZS-1 abbe's refractometer), respectively. When L/D <4, equation (7) should be modified as follows:

$$\gamma = 2.74156E - 3\frac{(\rho h - \rho d)\omega^2}{C} \tag{7}$$

Where *C* is the correction factor, it is related to L/D and obtained from the table. The first IFT was measured for all the surfactants type at 1 wt. % concentration as shown in Table 4.1. After, the lowest IFT value of 1wt. % was selected. The measurement at different and lesser concentrations of 0.2 and 0.5 wt. % was conducted and then compared with 1 wt % as illustrated in Figure 4.17. The molecular structure, critical micelle concentration, and HLB values were studied. The results of this analysis are illustrated in Figures 4.18 to 4.21, which shows the IFT in (myn/m) vs. HLB values, and the IFT in (mN/m) vs. the moles.

4.5 RESULTS AND DISCUSSION

4.5.1. Missouri Heavy Oil Recovery by the Surfactants. In general, the results show: (1) Oil recovery by the nonionic surfactants is between 40 and 60%, and the formation water has very low oil recovery; (2) Oil recovery by the use of ionic surfactants is between 10 and 25 %, except for some correlation between the observed oil recoveries. The contact angle is also relatively high, at 70 and 90, respectively. The high contact angle cases may include gravity effects in their oil recovery, whereas a situation with the contact angle likely has the oil recovery controlled by a uniform imbibition process. (3) There is obvious relationship between the oil recovery and contact angle. The oil recovery of these surfactants at 0.1 wt. % was calculated and plotted as shown in Figures 4.10 and 4.11, respectively. These plots use the time (days) as the x-axis as this way the data plot as a straight line where the diffusion processes are involved (Barenblatt et al., 2002). Among the 11 surfactants, during the initial period, the recovery rates were approximately the same. This indicated that early oil recovery was governed by imbibition of water near the surface and subsurface around the sandstone core. The six Tomadol® surfactants used in the spontaneous imbibition test are ethoxylated primary alcohols with a linear C12-C15 alkyl chain. The Neodol® surfactants are ethoxylated primary alcohols with a linear C11 alkyl chain. All of the Neodol® surfactants recovery had limited amounts of oil from the sandstone core, but it was still higher than the formation water recovery. Among the 20 surfactants studied, Igapel-C0-350, Tomadol® 25-12, and Tomadol® 45-13 surfactants showed the highest oil recovery. The final recovery at the end of 35 days was 50% recoverable oil as compared to the other surfactants which was only about 20% recoverable oil. These nonionic surfactants have by far the best performance as they recover as much as 50% from the sandstone core.

Note that this observation was consistent with the results of the wettability alteration that was discussed in the previous research. Yongfu et al. (2008) stated that compared with all of the oil recovery results, the surfactants changed wettability more effectively and showed a higher oil recovery, e.g. Igepal CO-530, Tomadol® 25-12, and Tomadol® 45-13.

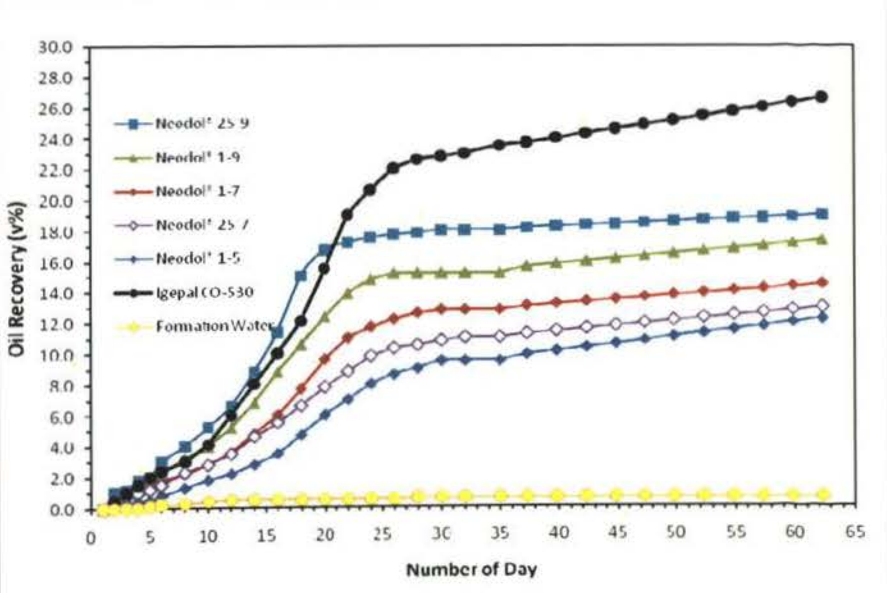


Figure 4.10 Cumulative Oil Recoveries by Imbibition Test

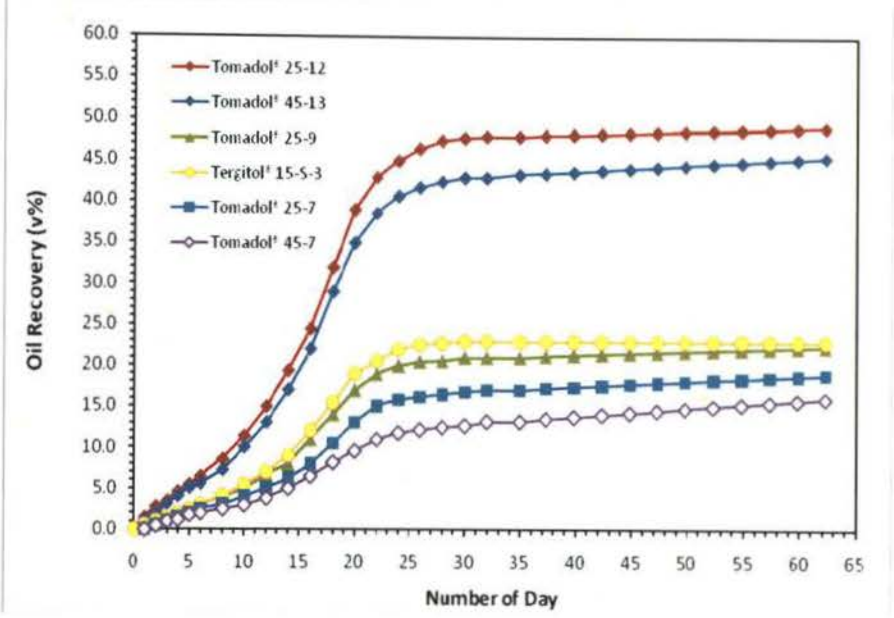


Figure 4.11 Cumulative Oil Recoveries by Imbibition Test

4.5.2. Contact Angle Measurement on Sandstone Surface. The surfactant can change wettability of the sandstone surface from oil-wet to water-wet, since the contact angle of water was initially as high as 150 ° as shown in Figure 4.12, but the contact angle decreased dramatically when a surfactant was applied in the solution. The wettability of the oily sandstone chips had been changed to the water-wet condition. Based on the experimental results shown in Figures 4.12 and 4.13, the effectiveness of the surfactant to change the wettability ranged in the order of Igepal CO-530> Tomadol® 25-12 > Tomadol® 45-13 > Tomadol® 25-9 ~ Neodol® 25-9 > Tergitol®15-S-3 > Tomadol® 25-7 > Tomadol® 45-7 > Neodol® 1-9 > Neodol® 1-7 > Neodol® 25-7 > Neodol® 1-5. Due to the porous structure of the sandstone chips, the first drop of the brine solution usually was not stable on the surface but was quickly absorbed into the porous structure. Therefore, the 2nd or 3rd drop of the solution was applied to the surface to ensure a reproducible result of the contact angle It typically takes a much longer time for stabilization on the surface.

Table 4.1 shows the contact angle for the time of each surfactant. The table includes the surfactant name, contact angle for the 1st round water drop, the time needed to stabilize the drop, the contact angle for the 1st round surfactant, and the data for the 2nd and 3rd round measurements. The water contact angle was low and was absorbed very slowly by the sandstone chip and indicated after application of the surfactant that the brine had spread on the surface completely. This process indicated a change in the wettability of the sandstone from an oil-wet to a water-wet condition. Without the addition of the surfactant, the formation water itself had the highest contact angle on the oily sandstone surface as shown in Table 4.1. The results indicated that from a 0 ° contact angle, the brine drop spread completely on the surface.

In addition to this, Figures 4.14, 4.15, and 4.16 show the image of the contact angle for the 1st round water drop, until the time required for the drop to stabilize, the second image shows the contact angle for the Igapel-C0-350 surfactant, and the last image shows the 2nd round water drop, until time required for it to stabilize. The water contact angle was high and was absorbed very slowly by the sandstone sample, but after the surfactant the spreading had high adsorption, and could change the wettability of the sandstone from oil wet to water because the contact angle for the 2nd round water drop was decreased. Therefore, the surfactant could change the wettability of the surface from oil wet to water wet, since the first drop of the water angle was high and changed from CA >100 to CA< 10, especially after the surface was wet by the Igapel-C0-350. The contact angle for the 2nd round water was very low and approximately zero degrees with a short stabilization time.

These results show that the surfactants selected could effectively change the oil-wet surface to water-wet, compared with the oil recovery results. For example, the surfactants changed wettability more effectively, showed a higher oil recovery, were Igapel-C0-350, Tomadol® 25-12, and Tomadol® 45-13. Those surfactants had the highest oil recovery during the imbibition test, a very low contact angle, and a short stabilization time with the sandstone core. The formation water had the highest contact angle and lowest oil recovery on the oily sandstone surface as shown in Figures 4.12 and 4.13. The anionic surfactants were found to alter the wettability at dilute concentrations and reduce the IFT to very small values, without requiring an alkaline agent or co-surfactant. Wagner and Leach (1959) reported that the rock wettability was reversed from oil-wet to water-wet, which improved the oil recovery by injecting water solutions with some added chemicals. The contact angle indicated an excellent wettability change. The surfactants which had the low contact angle was good for the sandstone core to alter the wettability. The wettability of the original water-wet reservoir rock or sand could be altered by the adsorption of polar compounds and the deposition of asphaltenes that were originally in the crude oil (Croker and Marchin, 1988, Dubey and Waxman, 1991, Liu et al., 2003).

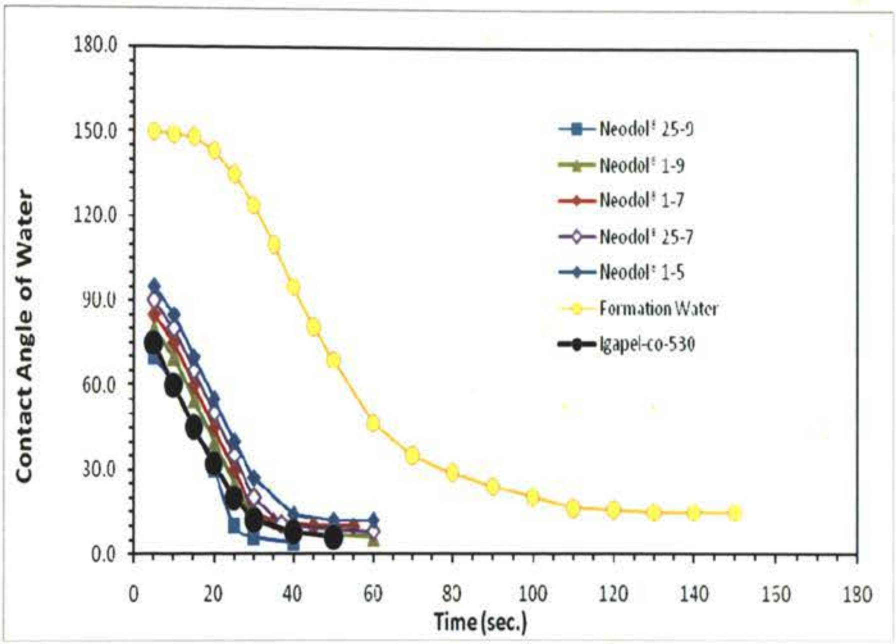


Figure 4.12 Contact Angle of Water and Surfactant on the Oily Sandstone Surface

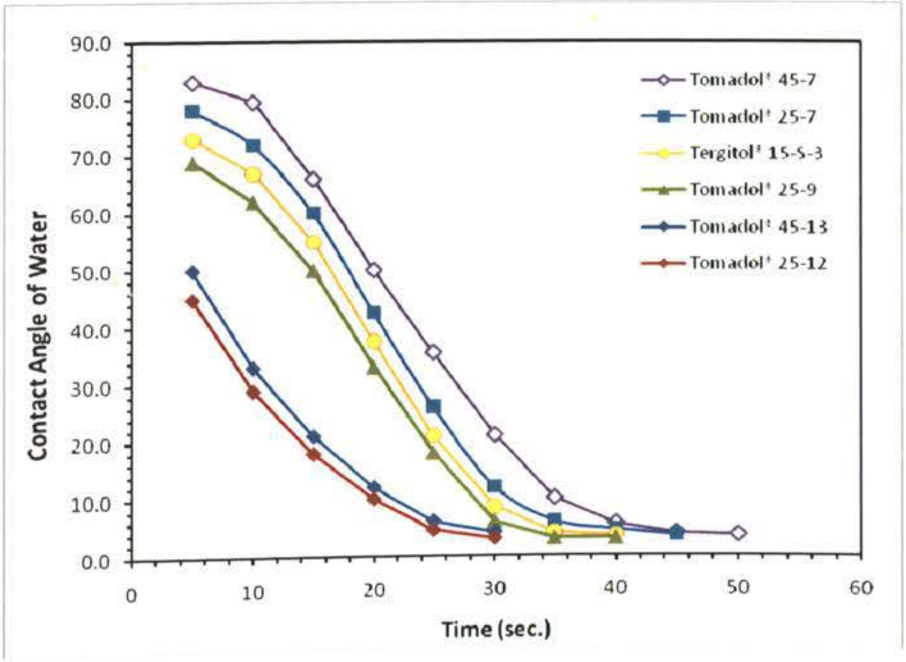


Figure 4.13 Contact Angle of Surfactants on the Oily Sandstone Surface

Figure 4.14 First Drop of Water

Figure 4.15 Image of Surfactant Igapal -CO-350

Figure 4.16 Second Drop of Water after Surfactant

Table 4.1. Contact Angle of Brine Drop at Different Time for Different Surfactants

Surfactant Name	**Contact Angle for 1st drop water**	**Time to Stabilize (Sec.)**	**Contact Angle for 2nd drop of water**	**Time to Stabilize (Sec.)**	**Contact Angle for 3rd drop of water**	**Time to Stabilize**
Aerosol® MA-80	95°	100	25°	30	24°	25
Calamide® CW-100	100°	80	35°	25	25°	19
Tomadol® 25-12	98°	60	10°	5	6°	1
Tomadol® 45-7	99°	60	18°	15	15°	10
Tomadol® 45-13	98°	60	5°	1	0°	0
Tomadol® 25-9	92°	60	21°	0	0°	5
Igepal CO-530	90°	60	15°	0	0°	0

4.5.3. Effect of Surfactant on Interfacial Tension. In order to determine a chemical formula that could effectively disperse the heavy oil in aqueous solutions, numerous surfactant and combination screening tests were performed. The interfacial tension behavior of the heavy oil / brine surfactant at 1 wt. % is shown in Table 4.2. The IFT measurement results indicated that the heavy oil and surfactant had the dynamic IFT values that were between 0.01 to 0.001mN/m with 1 wt. % compound surfactant solution. Figure 4.17 explains the measurement of the dynamic IFT at different concentrations of 10,000, 5,000, and 2,000 PPM, respectively vs. the IFT measurement that was demonstrated in Table 4.2. The minimum of the IFT was chosen as the representative for the next IFT measurement at different concentrations. When these surfactant concentrations were observed, the IFT decreased as the surfactant concentration increased as shown in Figure 4.17.

The IFT measurement was 0.06 dyne/cm for the Igabel – CO-530, 1 wt% concentration; the low IFT was achieved due to a decrease in the acid number of the crude oil sample (J. Li, et al., 2003). The IFT values shown in Figure 4.17 indicate the optimum surfactant concentration at which the lowest IFT was obtained. The relationship between the IFT and the Moloucer structure was investigated. Table 4.3 compares the surfactant names with the Hydrophillic-Lipophillic Balance (HLB), which is a concept for choosing emulsifiers. When the value of HLB ranges from 1-20, the low HLB emulsifiers are soluble in oil while the high HLB emulsifiers are soluble in water.

According to Bancroft's Rule, the type of emulsion (e.g., oil in water or water in oil) is dictated by the emulsifier and that the emulsifier should be soluble in the continuous phase. The low HLB emulsifiers are soluble in oil and give rise to water in the oil emulsions. HLB method : the HLB is indicative of emulsification behavior, when the HLB is 3-6, the w/o emulsion is created and when the HLB is 8-18, the o/w emulsion is produced. Figures 4.18 to 4.21 show the IFT vs. Moles and confirm similar results because it illustrates the same shape. As the moles increased the IFT increased; however, the relationship between the HLB and IFT show that it was reduced at 12 to 15 HLB, but before range of 12 and after the range of 15 the IFT increased.

Table 4.2 Measurement of Dynamic IFT

Surfactant Name	L (mm)	D (mm)	L/D	r_h (g/ml)	r_d (g/ml)	RPM	IFT (mN/m)
Nodel® 1-7	0.760	0.430	1.77	1.000	0.732	3000	0.085
Nodel® 1-9	0.185	0.165	1.12	1.000	0.732	3000	0.017
Nodel® 25-7	1.200	0.240	>4	1.000	0.732	3000	0.019
Nodel® 25-9		0.126	>4	1.000	0.732	3000	0.003
Tomadol® 25-12		0.280	>4	1.000	0.732	3000	0.031
Tomadol® 45-7		0.246	>4	1.000	0.732	3000	0.021
Tomadol® 45-13		0.109	>4	1.000	0.732	3000	0.002
Tergital® 15-S-3		0.170	>4	1.000	0.732	3000	0.007
Tergital® 15-S-9		0.139	>4	1.000	0.732	3000	0.004
Tergital® 15-S-12	0.550	0.150	3.67	1.000	0.732	3000	0.003
Tergital® 15-S-20	2.140	0.840	2.55	1.000	0.732	3000	0.849
Calamide® CW-100	1.070	0.620	1.73	1.000	0.732	3000	0.341
Calamide® CWT-99		0.620	>4	1.000	0.732	3000	0.341
Calamide® F		0.137	>4	1.000	0.732	3000	0.004
Ethomeen® S/12		0.690	>4	1.000	0.732	3000	0.470
Aerosol® MA-80		0.670	>4	1.000	0.732	3000	0.431
Alfoterra® 23		0.530	>4	1.000	0.732	3000	0.213
Alfoterra® 48		0.268	>4	1.000	0.732	3000	0.028
Tomadol® 901		0.308	>4	1.000	0.732	3000	0.042
Calsoft® LAS-99		0.380	>4	1.000	0.732	3000	0.079
Igapal® CO-630		0.160	>4	1.000	0.732	3000	0.006
Trition® X-405		0.278	>4	1.000	0.732	3000	0.031
AROUAD® T-50		0.280	>4	1.000	0.732	3000	0.031

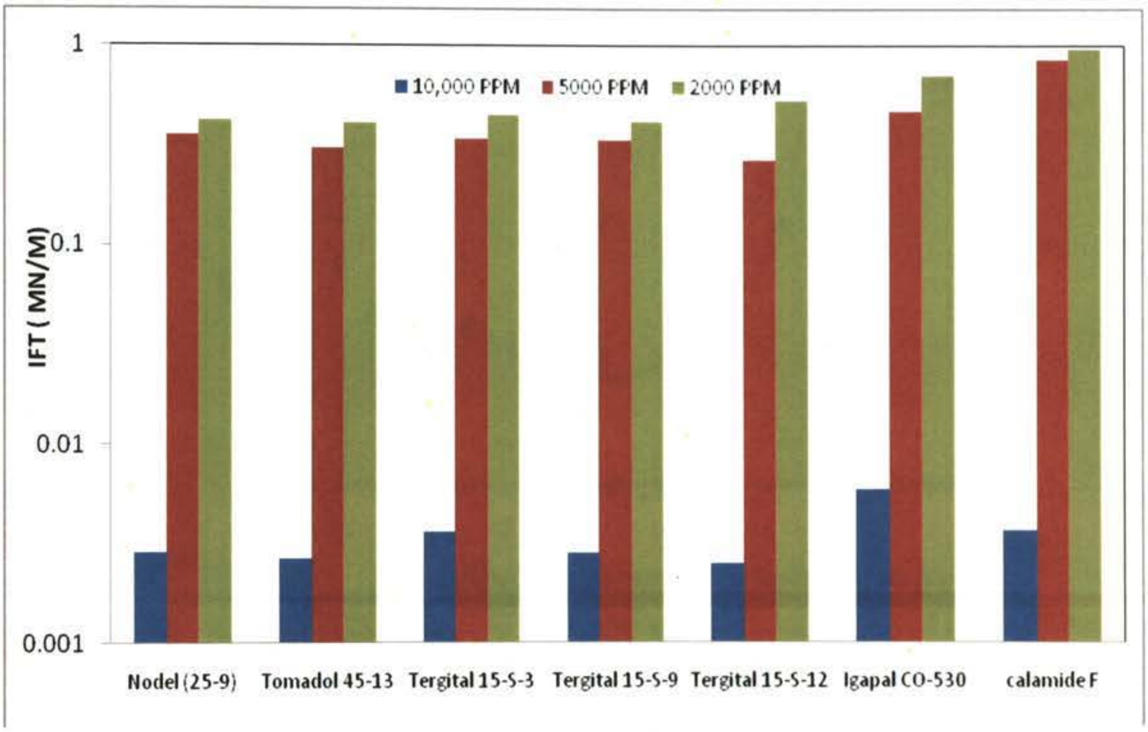


Figure 4.17 Measurement of Dynamic IFT

Table 4.3 Surfactant Name and Moloucer Structure

Name	HLB	moles
Nodel (25-9)	13.1	9
Tomadol 45-13	14.4	7
Tergital 15-S-3	11.6	13
Tergital 15-S-9	14.4	7
Tergital 15-S-12	13.3	3
Igapal CO-530	15.5	20

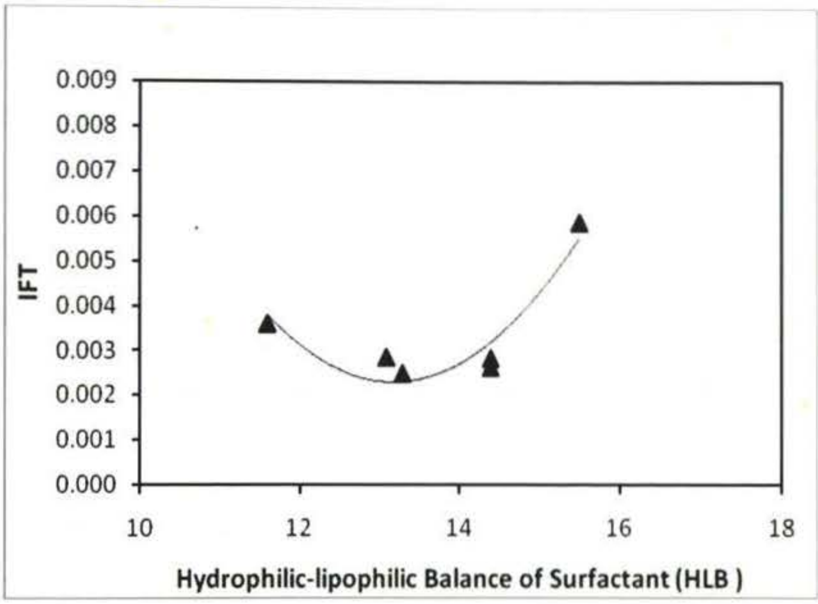


Figure 4.18 IFT and the Hydrophillic-Lipophillic Balance (HLB)

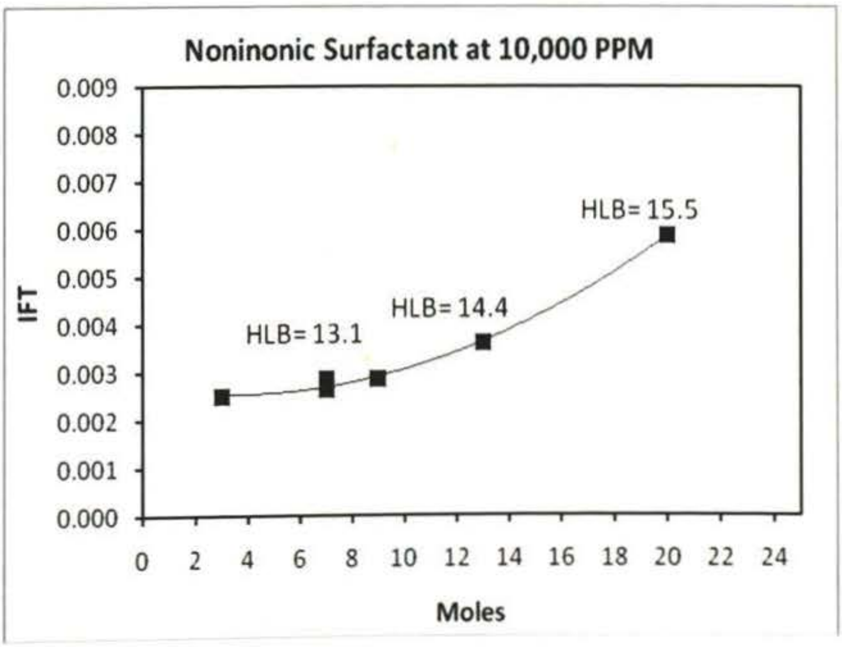


Figure 4.19 IFT and Moles at 10,000PPM

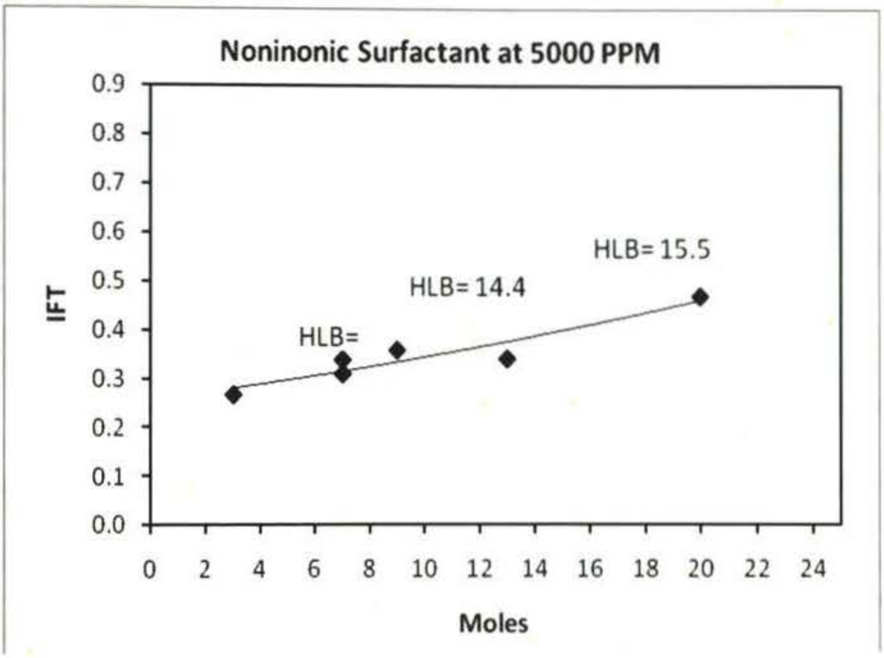


Figure 4.20 IFT and Moles at 5,000PPM

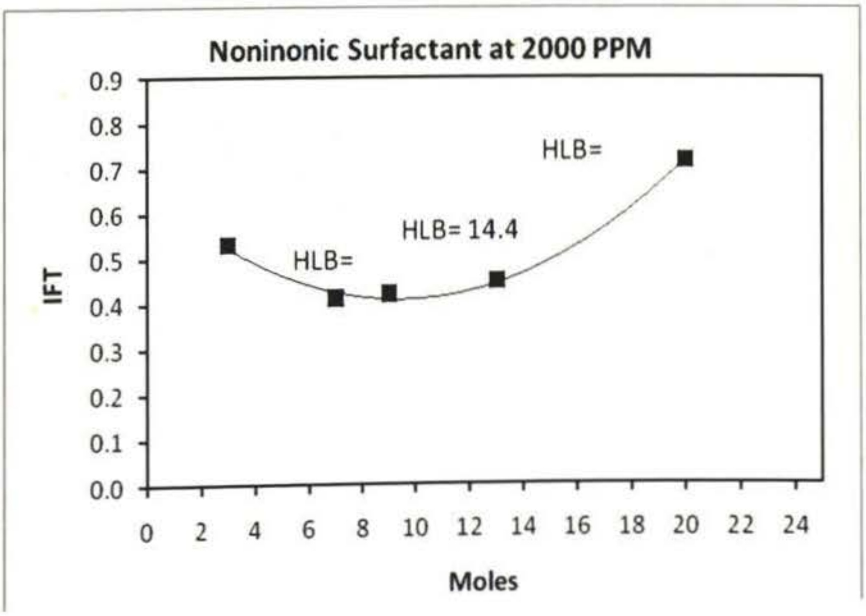


Figure 4.21 IFT and Moles at 2,000PPM

Summary: The purpose of this study was to elucidate wettability results with the mechanisms for oil recovery. Based on the chemical processes and surfactants leading to wettability alteration in sandstone surfaces, it was found that there were similar results between the wettability and oil recovery as described previously. Therefore, the contact angle measurement and imbibitions could be used as rapid screening tools to identify better EOR surfactants for increased recovery in sandstone reservoirs. In this research, nonionic surfactants have been found to be more efficient in recovering crude oil from sandstone core than the others. The results of this experiment were summarized as follows:

1. Formation water had the highest contact angle on the oily sandstone surface. An initial contact angle of 150 ° indicated that the oily sandstone surface was highly oil-wet.
2. Because of the absorption of the liquid by the porous structure of the dry chips, the contact angle decreased gradually with time.
3. The surfactant significantly reduced the contact angle of the water on the oily sandstone surface. The surfactants selected effectively changed the wettability from the oil-wet surface to water-wet and showed a higher oil recovery, e.g. Igepal CO-530, Tomadol® 25-12, and Tomadol® 45-13.

5. NUMERICAL SIMULATION

5.1 MODEL DESCRIPTION

Heavy oil reservoirs can produce a small amount of oil by water flooding. Adding alkaline surfactant into the brine phase can improve the oil production by lowering the oil-water interfacial tension (IFT) and by altering the wettability of the matrix block from oil-wet to water-wet (Adibhatla at el, 2005). Simulations were performed to understand and predict the enhanced heavy oil recovery as a function of wettability alteration (oil-wet and water-wet sandpack.)

An existing simulator (CMG STARS, Version 2008.10) was used to model the alkaline surfactant flooding performance for heavy oil recovery with the incorporation of relative permeability, interfacial tension, chemical adsorption, and viscosity of O/W emulsion. A three-dimensional (3D) numerical simulation model was developed to match the alkaline surfactant flooding performance in the lab sandpack models and in the history matching. The estimates of the relative permeability curves obtained accurate and reliable estimates of the relative permeability curve. There is no reliable theoretical model to describe relative-permeability curves. The sandpack of 24 cm in length and 2.6 cm in diameter was divided into 25 grids in I and 5 grids in both J and K direction, respectively. The reservoir was assumed to be homogenous. Figure 5.1 illustrates the 3D view of the numerical model.

Five components were used in the simulation: water, chemical (alkali/surfactant) and O/W emulsion in the aqueous phase, dead oil in oil phase, and trapped oil in solid phase. The concentration of each component in each grid was calculated from the conservation equation of the component.

The production of O/W emulsion was re-presented by a reaction of water, oil, and alkaline surfactant (J. Wang, 2010). The following equation was used in the simulation: Water + Chemical + Dead Oil → O / W Emulsion.

5.2 NUMERICAL PROCEDURES

Based on the experimental studies and results, the laboratory scale numerical simulations were conducted to match the production histories of the sandpack flood tests. The in-situ formation of O/W emulsion was represented by a reaction of oil, water and chemicals. The Filtration theory was used to simulate the emulsion capture in porous media. Five components were used in the simulation: water, chemical (alkaline/surfactant), and O/W emulsion in the aqueous phase, dead oil in the oil phase, and trapped oil in the solid phase. The concentration of each component in each grid was calculated from the conservation equation of the component in the model.

There was an adsorption term in the conservation equation for the chemical component. Before the injection of the alkaline surfactant slug, the concentrations of the three components, chemical, emulsion and trapped oil, were zero in each grid. During alkaline surfactant slug injection, the chemical concentration gradually increased in each grid. The production of O/W emulsion was presented by a reaction of water, oil and alkaline surfactant.

In the grids with a higher alkaline surfactant concentration, more emulsion was produced. The trapped oil was generated when the in-situ formed O/W emulsion drops were trapped, and the local water phase permeability was decreased by adding a resistance factor (> 1.0). Trapping oil is more likely to happen in a lower permeability region according to Wang et al., (2010). Phase permeability was decreased by adding a resistance factor (>1.0). (Permeability reduction of the porous medium is due to flow restriction caused with two major droplet-capture mechanisms).

The numerical simulation was done to match the sandpack coreflooding experiment results shown in chapter 3. The alkaline surfactant solution of 2% Igabel-CO-350 and 0.6%NaOH was used in the flooding process. The fluid and rock reservoir properties are exposed in Table 5.1. The IFT lab measurement vs. concentration shown in Table 5.2 was inputted into the model. The model includes one injection well (water flooding first, and then alkaline surfactant flooding) and one producer well. The water flooding was applied until water was 97%, which was produced in about 10 hours. The alkaline surfactant flooding was injected for 1 PV, after which the water flooding was injected again until the oil production was negligible. The Langmuir Isotherm Curve was used to fit the lab data of surfactant adsorption on silica. The fitting equation is:

$$\frac{C_e}{q_e} = \frac{1}{q_{Max}} b + \frac{C_e}{q_{\max}} \qquad (8)$$

where C_e and q_e are surfactant concentration (mg/L) and amount absorbed (mg/g) at equilibrium, respectively. b is the Langmuir constant and q_{max} is the maximum adsorption capacity (mg/g). From the fitting equation, the maximum adsorption capacity (mg/g) value is 0.980 mg/g as shown in Figure 5.2.

Figure 5.1 The 3D view of the numerical model

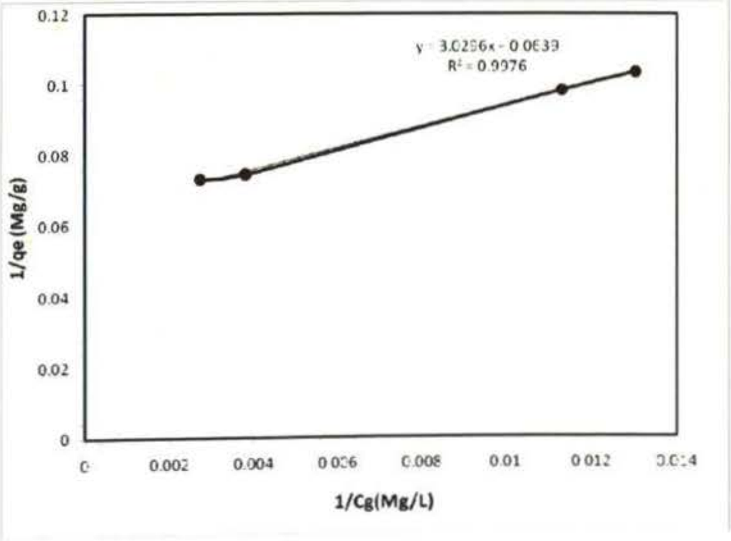


Figure 5.2 Langmuir Isotherm Curve

Table 5.1 Sandpack Properties

Sandpack Type	**D (cm)**	**L (cm)**	**K (D)**	**Φ (%)**	**WF Rate(mL/min)**	**AS Rate(mL/min)**
Oil-wet	2.6	24	5.0	45–58	0.5	0.5
Water wet	2.6	24	5.0	45–58	0.5	0.5

Table 5.2 IFT Lab Measurement for (Igapel-co-530)

Conc (%)	**IFT** (mN/m)
1	0.0058
0.5	0.096
0.25	0.51
0.2	0.64

5.3 RESULTS AND DISCUSSION

5.3.1. History Matching for Oil-Wet Sandpack. In the case of the oil-wet sandpack, the water saturation of 11% and oil saturation of 89% were inputted during the first water flooding. After water flooding, new water saturation distribution was obtained from the end of water flooding as shown in the Figure 5.3.

Two sets of relative permeability curves were used, corresponding to high IFT during water flooding and low during alkaline surfactant flooding IFT cases. Figure 5.4 illustrated the relative permeability curves for the oil-wet sandpack during water flooding. Figure 5.5 shows the relative permeability curve used for matching the alkaline surfactant flood test. Both the oil-phase and water-phase relative permeability increased during chemical flooding. The water-phase permeability in the grids where emulsion drops were trapped was decreased by including a water phase resistance factor.

The simulation results are appropriately matched with the experimental results as shown in Figure 5.6. The result of water production is illustrated in Figure 5.7, which depicts the cumulative water production vs. pore volume injected in comparison with the experimental results. In general, the simulated oil production and water production were very close to the test values.

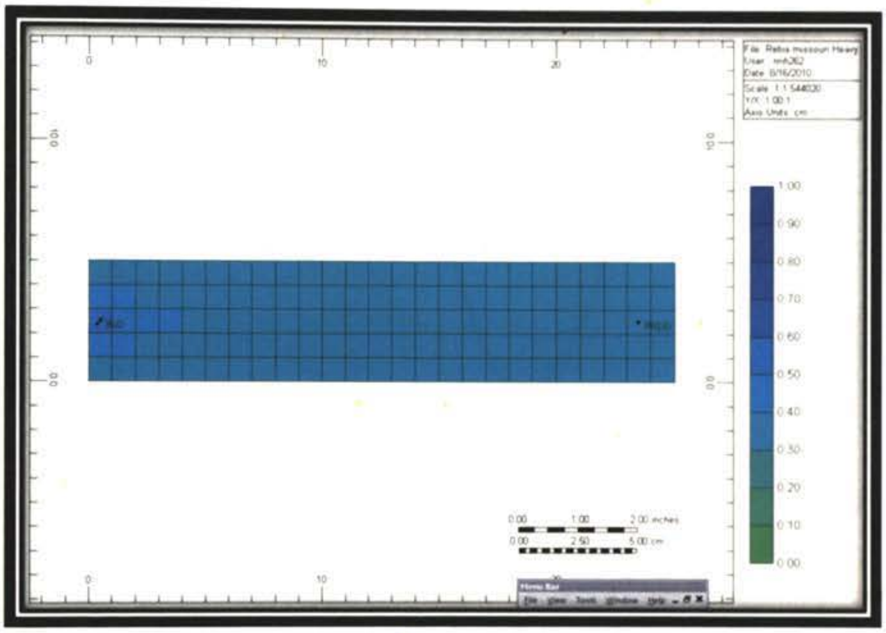


Figure 5.3 Model Water Saturation Distributions after Water Flooding

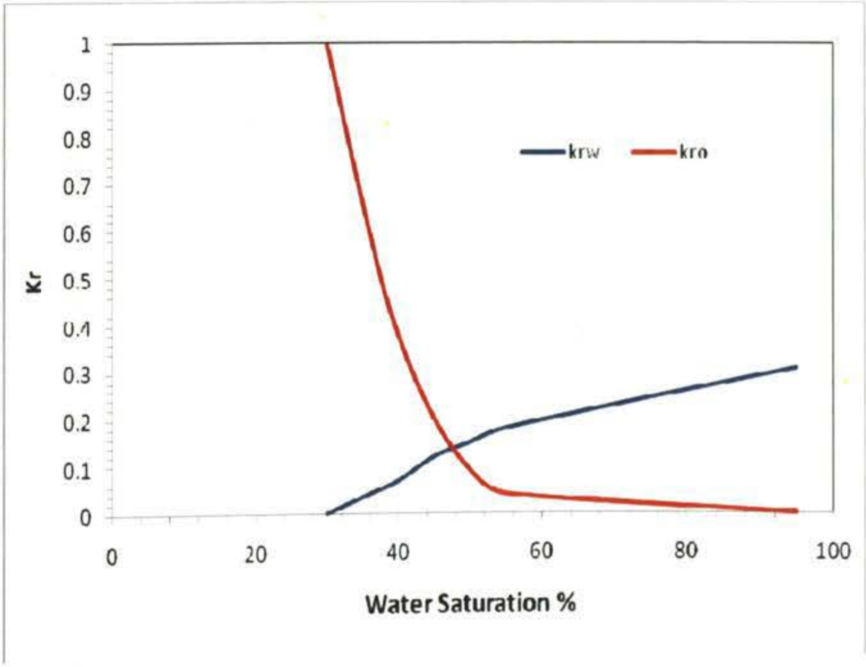


Figure 5.4 Simulation of Oil-Wet Relative Permeability Curves During Water Flooding.

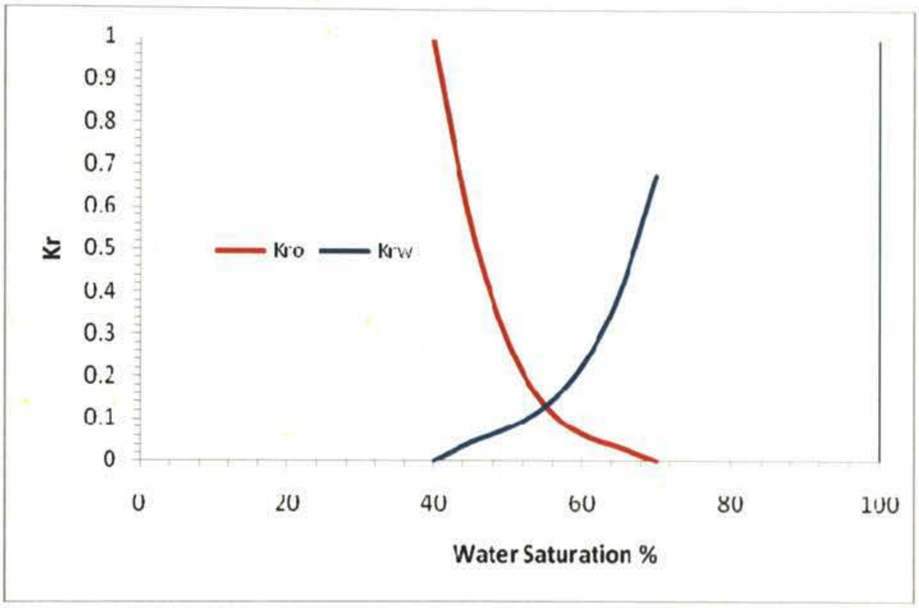


Figure 5.5 Simulation of Oil-Wet Relative Permeability Curves for Test of A/S Flooding.

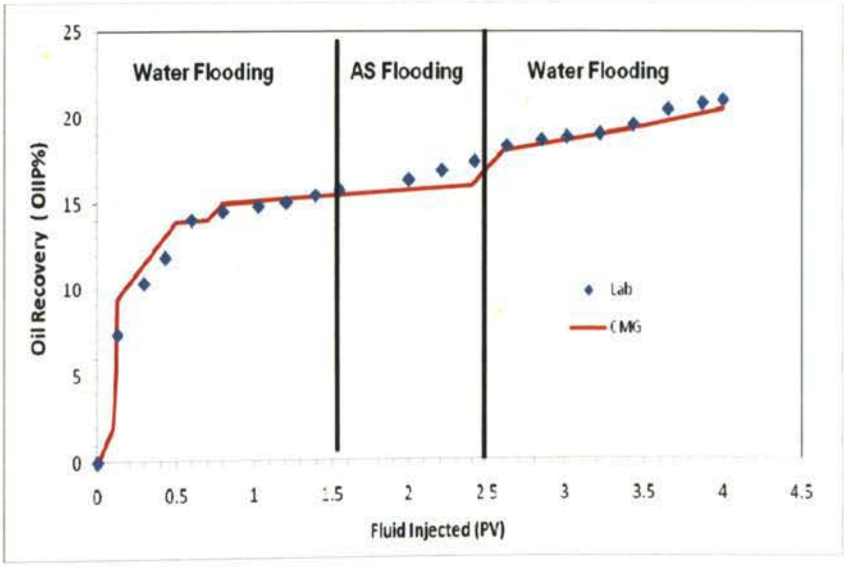


Figure 5.6 Oil Recovery of AS Flooding (lab and CMG modeling results)

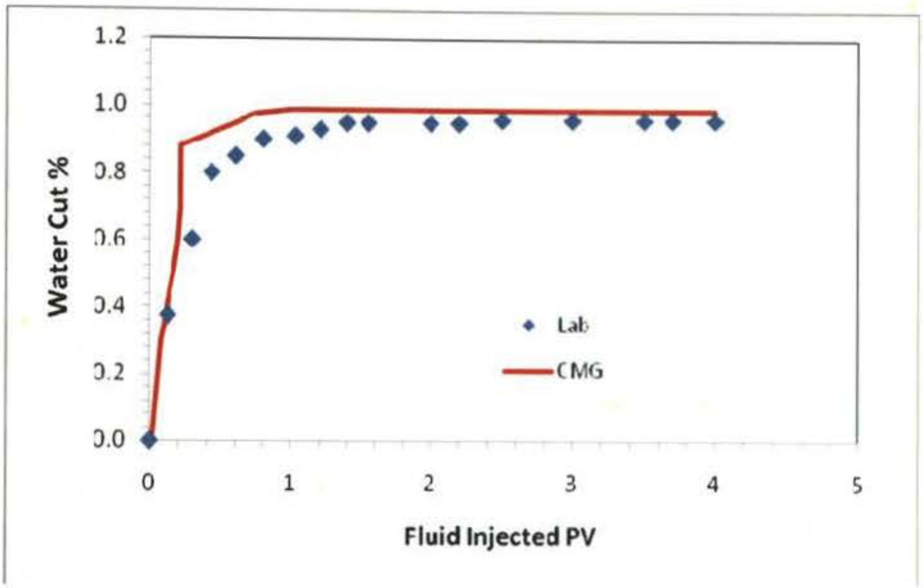


Figure 5.7 Water Cut (Lab and CMG Modeling Results)

5.3.2. History Matching for Water-Wet Sandpack. The input data of the water-wet sandpack was similar to that of the oil-wet sand pack except for the water and oil saturation. The water saturation was 50% during water flooding and then increased to 60 % in the following alkaline surfactant flooding. The new water distribution at the end of water flooding was exposed in Figure 5.8.

The relative permeability data was adjusted until the simulation results matched the experimental results. The relative permeability data has a significant influence on oil recovery. Oil recovery increases when k_{ro} increases and k_{rw} decreases. The water-wet sandpack relative permeability curves used for matching water flood test is shown in Figure 5.9. In Figure 5.10, the relative permeability curves during alkaline surfactant flooding is shown.

The matching of the experimental and model results is exposed in the Figure 5.11 cumulative oil recovery vs. pore volume injected. Furthermore, the water production of experimental and simulation results in Figure 5.12 shows the cumulative water production vs. pore volume injected in comparison with experimental results. The experimental results match well with the simulation results.

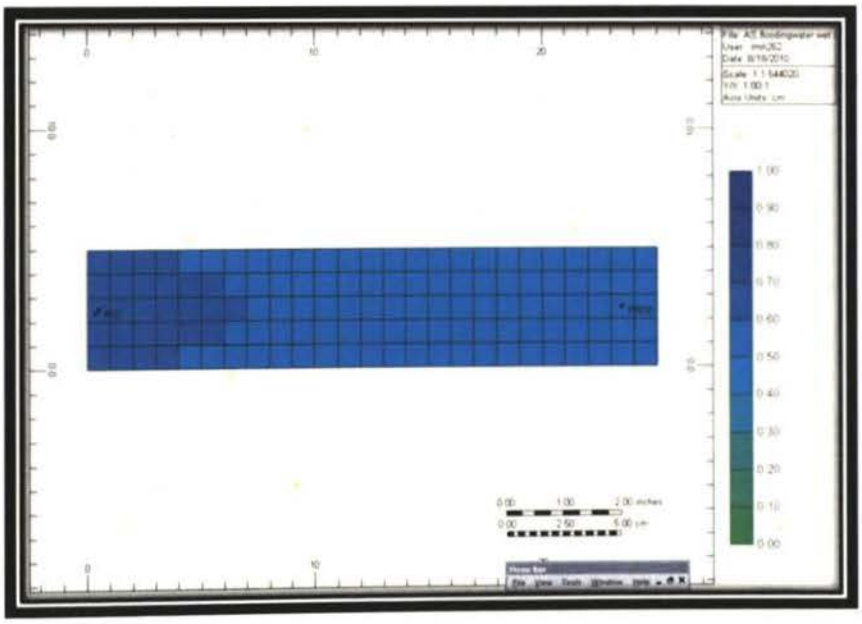


Figure 5.8 Model Water Saturation Distributions after Water Flooding

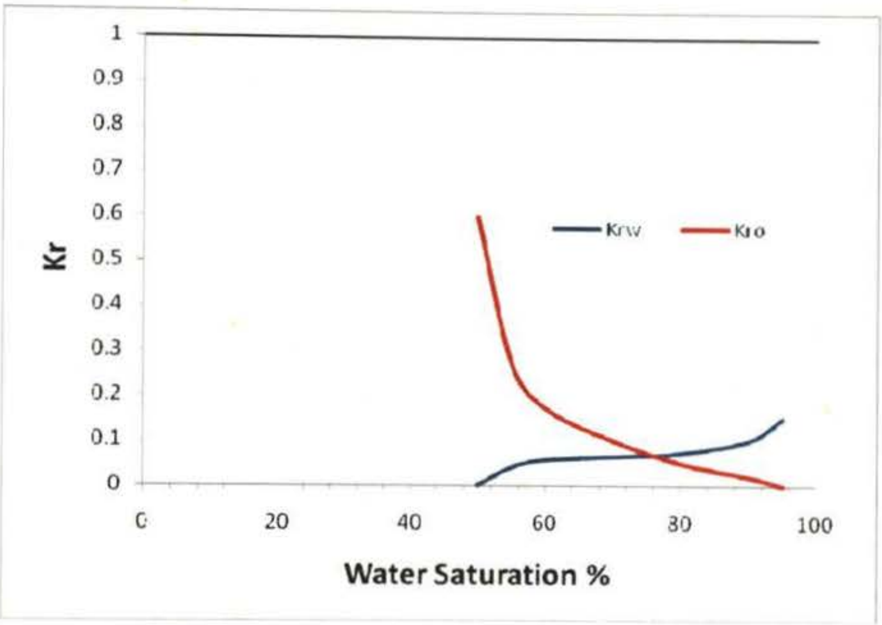


Figure 5.9 Simulation used Oil-Wet Relative Permeability Curves During Water Flooding.

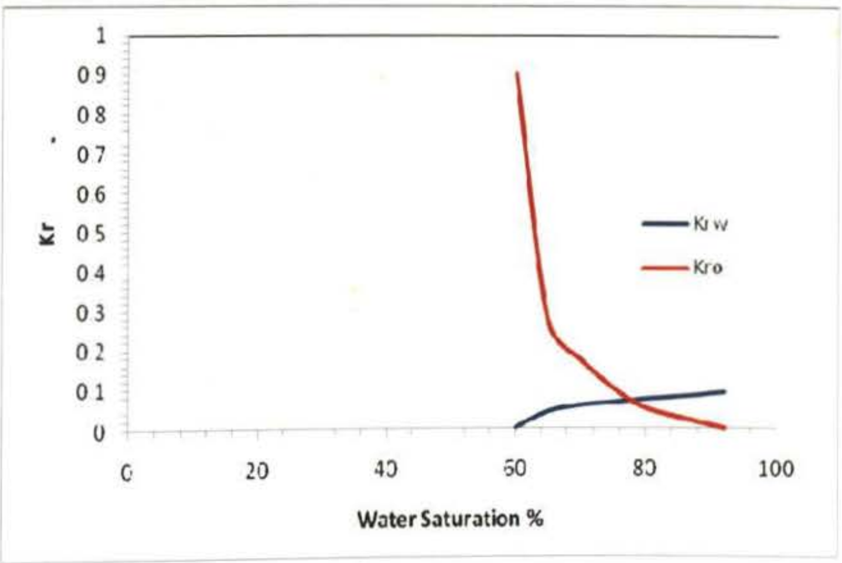


Figure 5.10 Simulation used Water-Wet Relative Permeability Curves for Test of A/S Flooding.

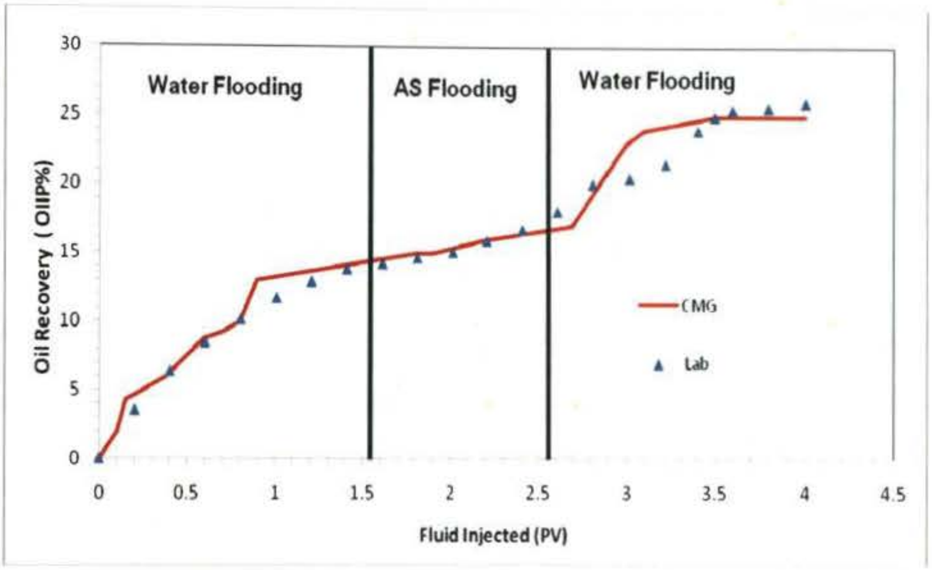


Figure 5.11 Oil Recovery of AS Flooding (lab and CMG Modeling Results)

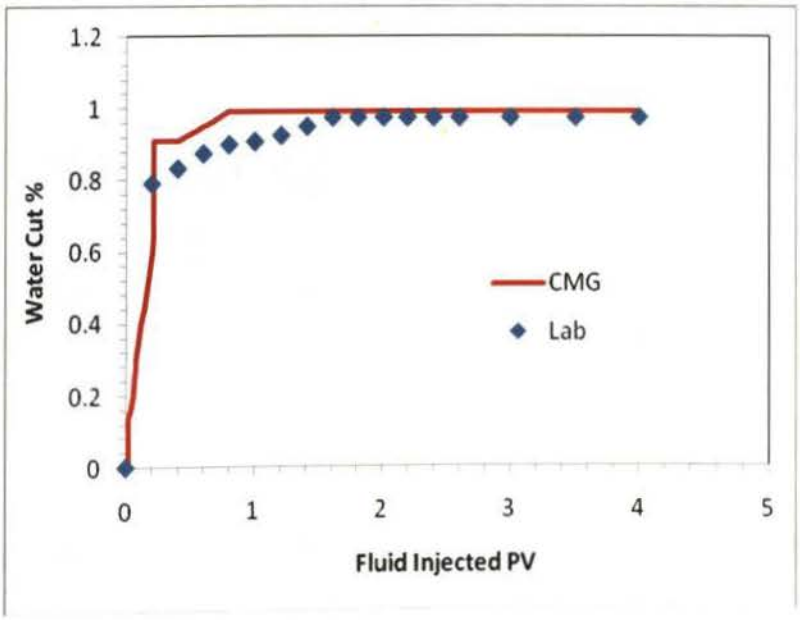


Figure 5.12 Water Cut (Lab and CMG Modeling Results)

In addition, during the alkaline surfactant flooding, the pressure drop, as shown in Figure 5.14, was increased compared to the pressure drop during the water flooding, as shown in Figure 5.13. The local water permeability decrease resulted from the entrapment of emulsion droplets. The oil recovery was increased mainly due to the improvement in the sweep efficiency. In addition, Figure 5.14 shows that the pressure around the injection well and the pressure gradient in the displacement front increased during the AS flooding process, even though the pressure drop increase became stable as indicated by the emulsion qualities at the inlet and outlet which reached equality.

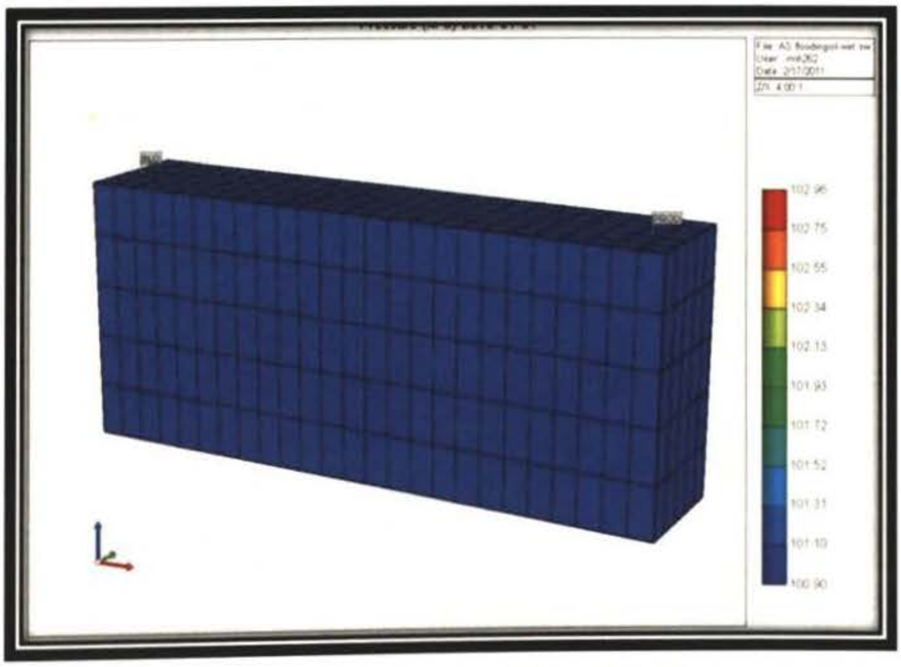


Figure 5.13 Pressures at the Water Flooding

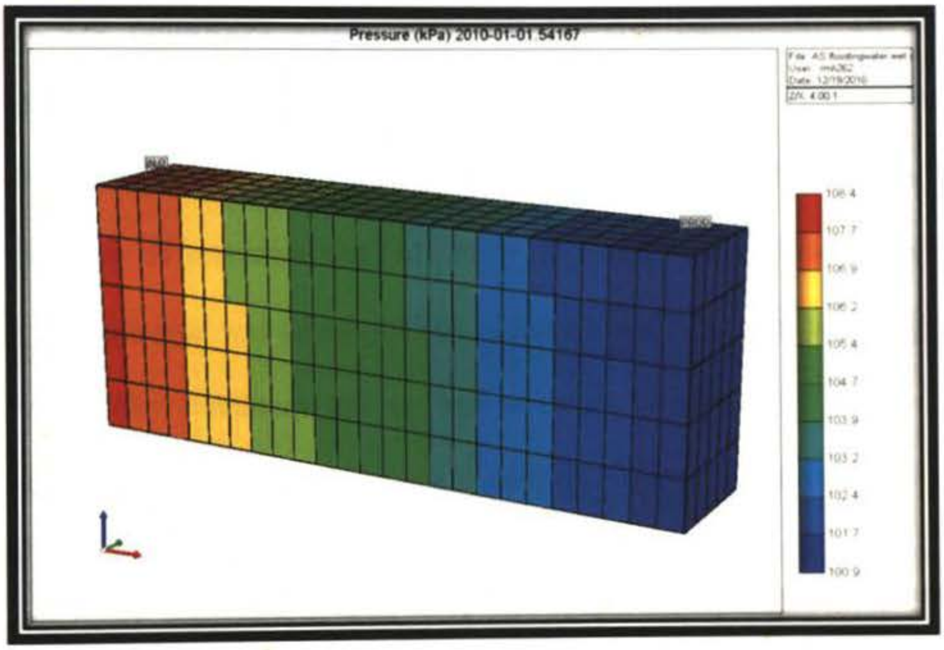


Figure 5.14 Pressure at the AS Flooding

5.3.3. Oil Saturation (Water-Wet and Oil-Wet Sandpack). Oil-saturation distributions of water-wet and oil-wet sandpack at the end of water flooding and at the end of the alkaline surfactant flooding are shown in Figures 5.15 through 5.18, respectively. The oil saturation was reduced in the middle matrix block in which the surfactant concentration was increased. The cumulative oil recoveries are compared for different wettability conditions (oil-wet and water-wet sandpack) in Table 5.3. The alkaline surfactant flooding shows that the highest recovery is the case of the water-wet condition with the recovery of approximately twice the oil wet condition oil recovery.

Figure 5.15 and 5.16 compares the oil saturation distribution in case of the oil-wet sandpack at the middle layer of the reservoir at the time prior to the chemical injection (or at the end of waterflooding) and at one point of time extended the waterflood after chemical injection. It shows that an oil bank was formed in the displacement front after the chemical injection.

Figures 5.17 and 5.18 illustrate the model oil saturation before and after alkaline surfactant flooding, respectively, showing more reduction in the oil saturation of the water wet sandpack than in the oil–wet sandpack. This reduction is due to the preference of the sand that is in contact with a water phase rather than an oil or gas phase; the alkaline surfactant can easily contact with the oil and reduce the interfacial tension. The water-wet rocks preferentially were imbibed by water; however, it is easy for the alkaline surfactant to diffuse and reduce interfacial tension between the oil and water. IFT between the oil and water can be reduced effectually by the alkaline surfactant and the oil can flow effortlessly without adsorption by sand which is not similar to the oil-wet sandpack condition.

Table 5.3 Oil Recovery for Water Flood & AS Flooding

Sandpack Type	Water Flooding Test (V/V) %	Increment by AS Flooding Test (V/V) %
Oil-wet	17	6
Water-wet	15	12

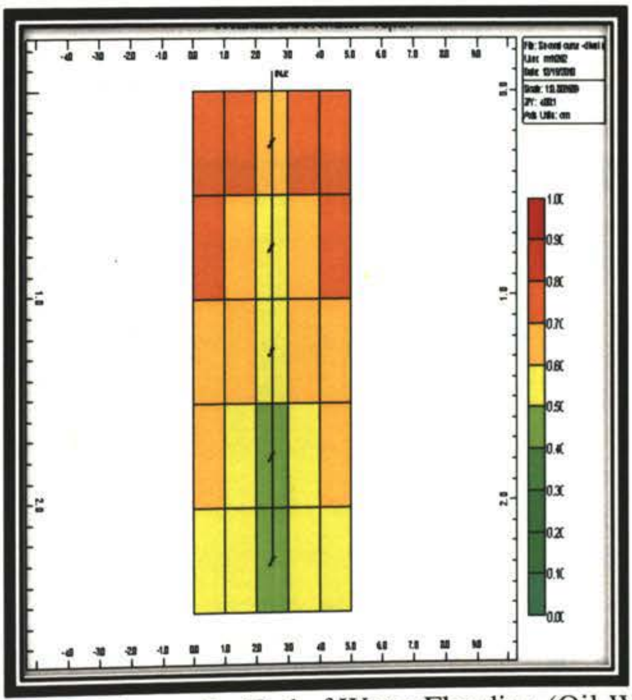


Figure 5.15 Oil Saturation at the End of Water Flooding (Oil-Wet Sandpack)

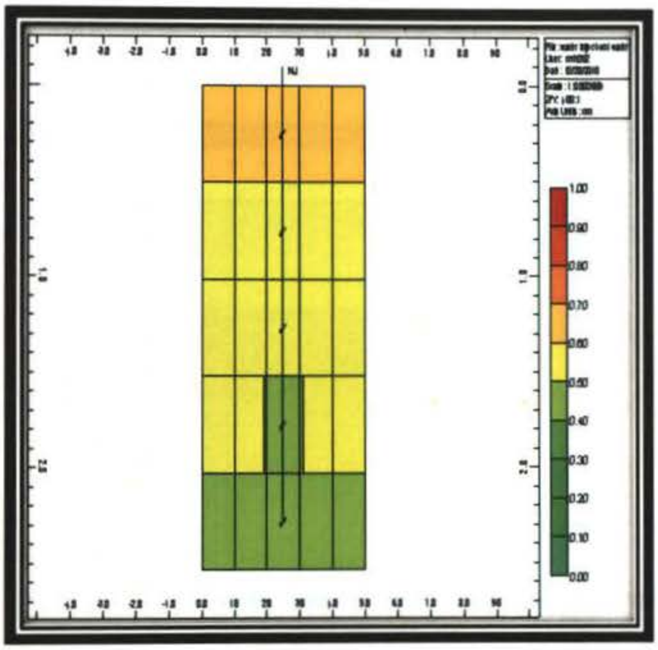


Figure 5.16 Oil Saturation at the End of AS Flooding (Oil-Wet Sandpack)

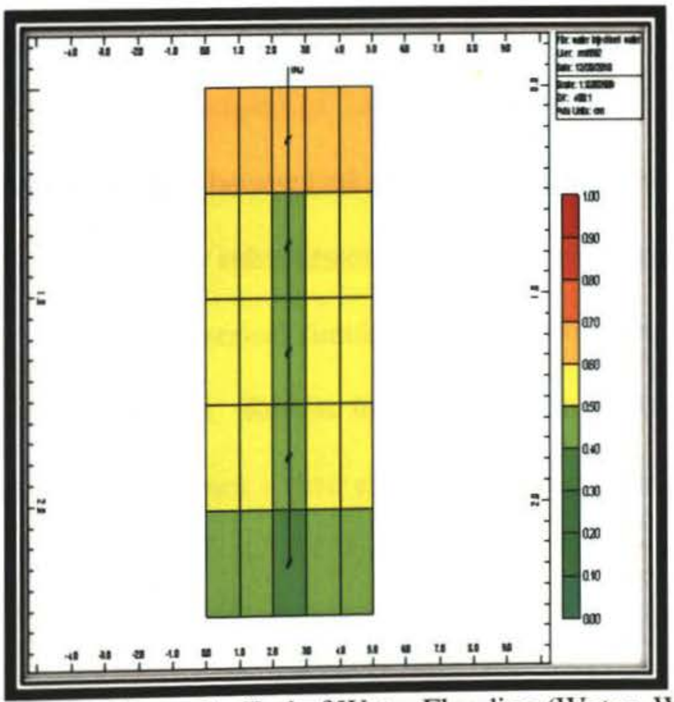


Figure 5.17 Oil Saturation at the End of Water Flooding (Water -Wet Sandpack)

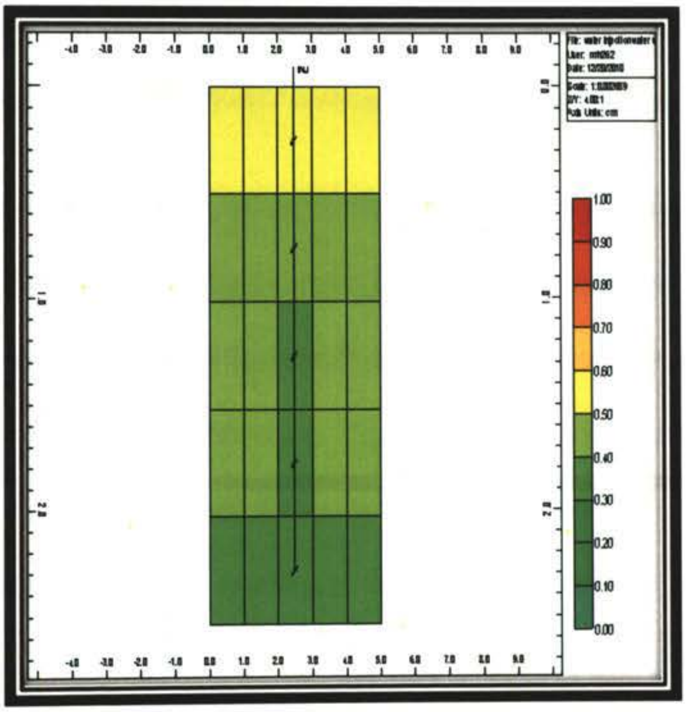


Figure 5.18 Oil Saturation at the End of AS Flooding (Water -Wet Sandpack)

Summary: The major mechanisms of alkaline surfactant flooding, including lowering of the interfacial tension between oil and water, emulsification of oil and water, wettability alteration, and mobility enhancement, have been considered to model alkaline surfactant flooding. The 3-D numerical simulator showed promising results of alkaline surfactant flooding for heavy oils. Results indicated that the water-wet sandpack had higher recovery than oil wet-sandpack if their chemical slug sizes were the same.

6. CONCLUSIONS AND RECOMMENDATIONS

1. A new screening method has been established to measure and calculate emulsion stability for heavy oil / syntheses brine and surfactant.

2. The screening tests of the surfactants for the enhanced western Missouri heavy oil were conducted by measuring the emulsion stability. It was been found that the nonionic surfactant Igepal CO-530 could form a very stable emulsion for the heavy oil and synthetic brine. Through the emulsion, the viscosity of the heavy oil could be reduced from 18,518 to 2.5 cp at 25 °C. This emulsion separated automatically to two layers within 2 hours without any addition of the de-emulsion agent at 40 °C. This provides great advantages for application of this technology.

3. The addition of the alkaline to the nonionic surfactant Igepal^{R} CO-530 will create a more stable emulsion of the heavy oil and formation brine. This emulsion separated automatically at a higher temperature 55 ^{0}C

4. Alkaline and Igepal CO-530 surfactants for enhanced western Missouri heavy oil were also conducted by measuring the emulsion stability. It has been found that the alkaline and nonionic surfactant Igepal CO-530 formed a very stable emulsion for the heavy oil and synthetic brine at 25° C and an unstable emulsion at 55° C, without adding any de-emulsion solution to separate.

5. The flooding test results show that a higher heavy oil recovery could be obtained by the combination of an alkaline and surfactant; the water-wet sandpack showed a higher recovery than the oil-wet sandpack.

6. A new method to evaluate the surfactant effect on oil recovery was established by using formation sand.

7. The sandstone core had a high water contact angle > 100 °, thus showing that the sandstone core was oil-wet. The surfactants significantly reduced the contact angle as low as 10°. This means that the surfactant selected effectively changed the surface from oil-wet to water-wet. The contact angle provided a good indication for the wettability and the surfactants which had the low contact angle and was good for the sandstone core to in order to alter the wettability.

8. The cumulative heavy oil recovery for the imbibition test results by the selected surfactants at the time of 35 days were as high as 55%. Igepal CO-530, Tomadol® 25-12, and Tomadol® 45-13 exhibited the highest oil recovery during the imbibtion test and had a very low contact angle and short stabilization time with the sandstone core.

9. A chemical flooding model was constructed to simulate improved oil recovery processes involving wettability alteration using alkaline surfactants. Multiple relative permeability curves corresponding to different wetting states were used to match the experimental results. The model matched well with the experimental results which were validated by the comparison with the published surfactant experiments.

10. More laboratory and model validations are needed to better understand the mechanisms responsible for the oil recovery under the different conditions in order to design the field trials effectively; this is required to design the field applications and implementing the studies from the laboratory to the field scale.

11. During the emulsion evaluation, the viscosity of the heavy oil was reduced from 18518 cp to 2.5 cp at 25 °C. Adding the polymer had better conformance because of the increase of the emulsified viscosity.

12. The emulsion stability evaluation for the alkaline surfactant, the emulsion mathematical model, and the emulsion rheological behaviors need to be studied further in detail.

13. Tomadol® 25-12 and Tomadol® 45-13 can be considered for improving the heavy oil recovery using AS flooding, because these surfactants have a partially stable emulsion and can change the wettability more effectively, showing a higher oil recovery.

APPENDIX

CMG DATA FILE (OIL-WET)

```
RESULTS SIMULATOR STARS 200800

**
************************************************************************
*************
** FILE :  Rabia Hunky **
**
************************************************************************
*************
** ==============  INPUT/OUTPUT CONTROL  ======================
** 2008-10-20,  rmh262
TITLE1 'MIssouri Heavy Oil, 20-30 mesh uniform sandpack'
TITLE2 'Water in Oil Emulsion 2% Igabel 0.6%NaOH'

*INUNIT *LAB
*OUTUNIT *LAB
OUTPRN GRID PRES RFW SO VOL SOLCONC SW VOLFR VISCCMP W
OUTSRF WELL COMPONENT ALL
WRST 100
WPRN GRID 100
WPRN ITER 1
OUTPRN WELL WELLCOMP
OUTPRN ITER NEWTON
OUTSRF GRID CAPN CMPVISG CMPVISO CMPVISW IFT KRO KRW PRES RFW SG SO
            VOL SOLCONC SW TEMP VISO VISOCOM VISW VISWCOM W X

**  ==============  GRID AND RESERVOIR DEFINITION  =================

*GRID *CART 25 5  5 ** Two-dimensional grid

*DI *CON 1
*DJ *CON 1
*DK *CON .508
**$ Property: NULL Blocks Max: 1 Min: 1
**$  0 = null block, 1 = active block
NULL CON            1

*POR *CON 0.356

**Varied Permeability, ranging 1000-5000 md; Kavg = 5000 md
*PERMI *CON   792286
PERMJ EQUALSI
PERMK EQUALSI
**$ Property: Pinchout Array Max: 1 Min: 1
**$ 0 = pinched block, 1 = active block
PINCHOUTARRAY CON            1

*END-GRID

ROCKTYPE 1
```

```
*PRPOR 101.1
**  =============  FLUID DEFINITIONS  ====================
**$ Model and number of components
MODEL 4 4 4 2
COMPNAME 'WATER' 'ALKALI' 'DEAD OIL' 'EMULSION'
CMM
0.018 0.04 0.38 0.35
PCRIT
300 2000 2000 2000
TCRIT
300 300 300 300

PRSR 101.1
TSURF 22
MASSDEN
0.001019 0.001020 0.000966 0.001

AVISC
0.9 0.9 18518 3600

**$ Reaction specification
STOREAC
8.0533 0.001 1 0
STOPROD
0 0 0 1.5
RPHASE
1 1 2 0
RORDER
0 1 0.7 0
FREQFAC 15000
O2CONC 'WATER'
O2CONC 'ALKALI'
RXCRITCON 'DEAD OIL' 1e-5
O2CONC 'EMULSION'
RXCMPFAC 'ALKALI' W 10000 8
** eff. perm     scale factor
PERMSCALE
5000    0.1
6000    0.2
7000    0.5
8000    1
9000    2
10000    4
11000    6
12000    8
13000    10
14000    15
15000 20
16000 25
17000 30
19000 50
20000    100
25000    200
*ROCKFLUID
RPT 1 WATWET
INTCOMP 'ALKALI' 'WATER'
IFTTABLE
```

```
**$ Composition of component/phase Interfacial tension
0    20
0.000225    5
0.0058    1
0.096    0.5
0.614    0.25
0.691    0.2


KRINTRP 1
DTRAPW -4.5
**  ==============  ROCK-FLUID PROPERTIES  ======================
**  Water-oil relative permeabilities
**   Sw          Krw        Krow
SWT
**$         Sw         krw       krow

            30            0            1
            36       0.0406          0.6
             4       0.0681         0.38
           4.5      0.09419        0.199
            50       0.1246         0.09
            55          0.2      0.04003
             1       0.3084            0

        **  Liquid-gas relative permeabilities
**   Sl          Krg        Krog
**  ----       -------    ------
SLT
**$         Sl        krg        krog
        0.54          1         0.
          0.6   0.37121        0.362
         0.95         0.          1.

**KRINTRP 2
**DTRAPW -2.5
**SWT
****$          Sw        krw        krow
**          0.08          0           1
**         0.231     0.0004        0.85
**         0.271     0.0008        0.78
**         0.341      0.001         0.6
**         0.391      0.002        0.45
**         0.431      0.004        0.30
**          0.50      0.007           0
**SLT
****$          Sl        krg        krog
**         0.194          1          0.
**           0.6    0.37121       0.362
**          0.95         0.          1.

**  Adsorption Data
```

```
**  ---------------

*ADSCOMP 'ALKALI' WATER       ** Data for reversible aqueous NaOH
adsorption
*ADMAXT 1.0E-6              ** no mobility effect
*ADSLANG 6.4E-2 0 10000       ** Langmuir concentration coefficients

*INITIAL
VERTICAL OFF

INITREGION 1
REFPRES 101.1

** ============== INITIAL CONDITIONS =====================


*PRES *CON 101.1
*SW *CON .30    ** So by difference
*TEMP *CON 22

SO CON        0.70
**$ Property: Water Mole Fraction(WATER)  Max: 1  Min: 1
MFRAC_WAT 'WATER' CON           1
**$ Property: Oil Mole Fraction(DEAD OIL)  Max: 1  Min: 1
MFRAC_OIL 'DEAD OIL' CON           1


*NUMERICAL

**  ==============  NUMERICAL CONTROL  =====================

*NUMERICAL                 ** All these can be defaulted.  The
definitions
** here match the previous data.
TFORM ZT
DTMAX 30
ISOTHERMAL
NORM PRESS 100 SATUR 0.1
CONVERGE PRESS 1 ZO 0.0001 ZAQ 0.0001

*RUN
DATE 2010 1 1
**  ==============  RECURRENT DATA  =====================
**TIME 0
DTWELL 0.1
**$
WELL  'INJ'
*INJECTOR 'INJ'
*INCOMP  *WATER  1.  0 0 0
TINJW  70.
**PINJW  138.
OPERATE MAX  STW  0.5  CONT
**OPERATE  MAX  BHP  1500 CONT
**$           rad  geofac  wfrac  skin
GEOMETRY  I  0.18  0.249  1.  0.
PERF  GEOA  'INJ'
**$ UBA     ff  Status  Connection
```

```
    1 3 1  1.  OPEN    FLOW-FROM  'SURFACE'  REFLAYER
    1 3 2  1.  OPEN    FLOW-FROM  1
    1 3 3  1.  OPEN    FLOW-FROM  2
    1 3 4  1.  OPEN    FLOW-FROM  3
    1 3 5  1.  OPEN    FLOW-FROM  4
**$
WELL  'PROD'
*PRODUCER 'PROD'
*OPERATE *BHP 101.1
**PRODUCER 'PROD'
**OPERATE  MAX  STO  0.15  CONT
**MONITOR    WCUT  1.  SHUTIN CONT
**$          rad  geofac  wfrac  skin
GEOMETRY  I  0.18  0.249  1.  0.
PERF  GEOA  'PROD'
**$ UBA     ff  Status  Connection
    24 3 1  1.  OPEN    FLOW-TO  'SURFACE'  REFLAYER
    24 3 2  1.  OPEN    FLOW-TO  1
    24 3 3  1.  OPEN    FLOW-TO  2
    24 3 4  1.  OPEN    FLOW-TO  3
    24 3 5  1.  OPEN    FLOW-TO  4
**$
WELL  'INJ2'
INJECTOR UNWEIGHT 'INJ2'
*INCOMP  *WATER  0.99  0.  0.01 0
TINJW  70.
**PINJW  20.
OPERATE  MAX  STW  0.5  CONT
**OPERATE  MAX  BHP  1500  CONT
**$          rad  geofac  wfrac  skin
GEOMETRY  J  0.18  0.249  1.  0.
PERF  GEOA  'INJ2'
**$ UBA     ff  Status  Connection
    1 3 1  1.  OPEN    FLOW-FROM  'SURFACE'  REFLAYER
    1 3 2  1.  OPEN    FLOW-FROM  1
    1 3 3  1.  OPEN    FLOW-FROM  2
    1 3 4  1.  OPEN    FLOW-FROM  3
    1 3 5  1.  OPEN    FLOW-FROM  4
**OPEN 'INJ2'
WLISTSHUT 'INJ2'
OUTSRF GRID PRES SG TEMP
DATE 2010 1  1.04167
DATE 2010 1  1.08333
DATE 2010 1  1.12500
DATE 2010 1  1.16667
DATE 2010 1  1.20833
DATE 2010 1  1.25000
DATE 2010 1  1.29167
DATE 2010 1  1.33333
DATE 2010 1  1.37500
DATE 2010 1  1.41667
WLISTSHUT 'INJ'
DATE 2010 1  1.5000
WLISTOPEN 'INJ2'
DATE 2010 1  1.54167
DATE 2010 1  1.58333
DATE 2010 1  1.62500
```

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VITA

Rabia Mohamed A. Hunky was born August 7, 1974 in Tripoli, Libya. She received her secondary education from AL-Najam Alsata in Tripoli, Libya and her Bachelor's in Petroleum Engineering from Al-Fatah University in 1998.

She has been working for the National Oil Corporation of Libya (NOC) for more than five years in the Reservoir and Production Engineering Department. She has been enrolled as a graduate school at the University of Missouri Science and Technology, Rolla (MS&T) since January 2006 and obtained her Master's degree in December 2007 from the Petroleum Engineering Department. Her thesis title is A Comparative Study of Hydraulic Fracturing Alternatives in the Lower Cretaceous Sandstone, Libya.

In 2008 she was awarded the Schlumberger Faculty for the Future Fund to begin her PhD study at the University of Missouri Science and Technology, Rolla (MS&T). Currently she is seeking a Doctor of Philosophy degree in Petroleum Engineering at the University of Missouri Science and Technology, Rolla (MS&T). Dissertation title is (ENHANCED HEAVY OIL RECOVERY BY ALKALI- SURFACTANT IN THE PENNSYLVANINA WARNER SANDSTONE)

SPE Paper:

1. **A New Technology Using Surfactant to Reduce Viscosity and Change Wettability for Enhanced Heavy Oil Reservoir in Ultra Shallow Reservoirs (SPE 142370)** Rabia Mohamed Hunky, SPE; Yongfu Wu, SPE; Shari Dunn-Norman, SPE, Department of Geological Science and Engineering, Missouri University of Science and Technology. This paper was

prepared for presentation at the Production and Operations Symposium held in Oklahoma City, Oklahoma, USA, March 27-29, 2011.

2. **An Experimental Study of Alkaline Surfactant Flooding in Ultra Shallow Heavy Oil Reservoirs (SPE 132537).** Rabia Mohamed Hunky, SPE; Yongfu Wu, SPE; Baojun Bai, SPE; Shari Dunn-Norman, SPE, Missouri University of Science and Technology (MS&T). This paper was prepared for presentation at Anaheim, California, Western Regional 2010, SPE, USA, and May 27-29, 2010.