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Writer: Roberto Kenneth Ramos Loredo (Writer's signature)
Faculty supervisor: Ingebret Fjelde External supervisor(s):	
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SURFACTANT FLOODING IN CARBONATE ROCK

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To the people working in IRIS who always were eager to help.

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SUMMARY

Studies with surfactant flooding in sandstones have been done. These studies have reported that surfactants can alter the flow functions in mixed wet cores. Carbonate rocks are usually not water wet and have microfractures. If a surfactant with properties to alter wettability in the carbonates is injected, then an improvement in the oil production could be obtained. If the mechanism of changing wettability can enhance spontaneous imbibitions then it will improve and achieve an increase on oil recovery.

In this thesis two different surfactant processes were studied in chalk cores. In the core flooding experiments it was used a wettability alteration surfactant. This process was compared with water flooding. The result showed that the system with wettability alteration properties brings a later water breakthrough. The wettability alteration process was also compared in two different aging times, giving as a result a more efficient performance in the rock that was more oil wet. And the second process was the interfacial tension reduction surfactant system that showed on the experiments a lower saturation of oil in the cores than the wettability system.

Further work is recommended to perform surfactant flooding experiments in chalks: to vary wettability; and to study wettability alteration and reduction of interfacial tension by surfactant for other oil reservoirs with different oil, brine and rock composition.

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SYMBOLS

CDC	Capillary Desaturation Curve
CMC	Critical Micelle Concentration
EOR	Enhanced Oil Recovery
HLB	Hydrophilic/Lipophilic Balance
IFT	Interfacial Tension
k_{r1}^o	End Point Permeability 1
k_{r2}^o	End Point Permeability 2
K_r	Relative Permeability
k_{r1}	Relative Permeability Curve 1
k_{r2}	Relative Permeability Curve 2
k_{ro}	Relative Permeability for oil
k_{rw}	Relative Permeability for water
N_c	Capillary Number
N_{cc}	Critical Capillary Number
P_c	Capillary Pressure
SIFT2	Surfactant with Interfacial Tension Reduction Properties Hydrophilic
SIFT1	Surfactant with Interfacial Tension Reduction Properties Lipophilic
SIFT3	Surfactant with Interfacial Tension Reduction Properties
S_{or2}	Residual Oil Saturation
S_{oR2}	Remaining Oil Saturation
SWA1	Surfactant with Wettability Alteration Properties
S_{wr1}	Trapped Water Saturation
WBT	Water breakthrough

1. INTRODUCTION

1.1 OIL PRODUCTION AND EOR

As population and the need of energy grow, so the oil demand around the world. With this demand also the price of oil will rise, which allow the use of different recovery methods (Lake, 1989).

Water flooding as secondary oil recovery can improve oil recovery but it has its limitations especially when the rock wettability tends to be more oil-wet. Primary recovery can get to 15% by expansion processes (Ansari, 2012) Added up to water flooding can get to about 50% in the best cases. Water flooding has easy availability, inexpensive compared with other methods, easy injection and high efficiency for displacing oil. Now with the increase of oil price it is possible to think on the use of surfactants and increase that percentage of recovery for 15% with EOR (Lake, 1989)

More than 60% of the oil remaining in the world is in carbonate rock. (Mohan, 2009) (Wang & Mohanty, 2013). That makes the improvement of oil recovery in chalks an important matter now a days.

Mohan, (Mohan, 2009), says that the wettability alteration can be more important on the secondary recovery than in the third because the recovery from oil-wet reservoirs is improved by a change of wettability to more water-wet with the addition of surfactants and other components. This change can reduce the amount of macroscopic bypassing improving the overall recovery, which is something that easily happens in carbonate reservoir rocks since this type of rock usually contains micro fractures.

In general all EOR has three categories: thermal, chemical, and solvents (Lake, 1989). In this document the focus will be in chemical flooding, specifically water and surfactant flooding.

1.2 SURFACTANTS

There have been used 2 different types of surfactant solutions. A surfactant solution is a compound that can cause IFT to reduce (Lake, 1989). In this experiments it is used surfactant with ability to alter the wettability (the affinity or preference of the rock to oil or water, in this case alter from oil wet to water wet), and the other with the ability to reduce the interfacial tension (IFT). Approaches to observe an enhancement of recovery from two sides, the interfacial tension, if this force is reduce then it is easier for the surfactant to drag more oil; and from the side of wettability, if the rock become more hydrophilic, then the oil will be expelled from the rock, and the production will be increased. These effects will be compared and join to observe the best effect in oil recovery.

1.3 THESIS OBJECTIVES

The purpose of this work is to characterize the behavior of the oil flow with the presence of surfactants in chalk core plugs. As a base of comparison there has been a flooding with FW so in this case the production occurred with no chemical help but just physical movement to push the oil our of the rock. This base will be compared with the effect of the different surfactant products. They will interact differently with the rock-oil system and, in the best case, increase oil production when they are used in different cases of sequence.

The rock chalk has in general very low permeability and is usually fractured (Seethepalli, et al., 2004), so the flushing forced used with water flooding is not enough to produce a large percentage of the oil, because the flow will prefer the fractures and avoid the small pores. Here is where the chemical help is useful; the reduction of interfacial tension will allow the flooding to get into the small pores meanwhile the change of wettability will allow the oil to escape from the rock because it will be exchanged with the water that will take place of the oil in the surface of the pore wall rock when the wettability changes from oil wet to water wet.

Carbonate reservoirs have still an important amount of residual hydrocarbons even though most of the reservoir have been depleted or have had different EOR processes

applied. In this document we observe the potential of surfactants that have been reported to alter the wettability and observe if exist an improvement on the flow function, which would mean potential improvement in the oil recovery.

This document is divided into 7 chapters and an appendix. After the introduction a literature study is provided that helps to understand the concepts used in the flooding experiments on general. Some of them: EOR, wettability, change of wettability, surfactants different types, water flooding, surfactant flooding and capillary pressure among others. The procedure to carried out this experiments is described in chapter 4 including the selection of surfactants by phase behavior. In the results section plots for the evolution of oil saturation through the flooding experiments is given along with the table of data from the 5 cores used. In the discussion chapter we compare some of the curves to analyze the most suitable flooding sequence. And the conclusions where this results are summarized.

2. LITERATURE STUDY

The literature study was carried out to review some basic concepts in order to understand the fluid-rock interaction. There will be defined some basic concepts: permeability, porosity, capillary pressure among others. Then the focus will be on the Enhanced Oil Recovery, since the analysis of the oil production improved by a surfactant is the aim of this study. More specific information will be reviewed in the surfactant flooding subject also explaining some important concepts involved such as: wettability, surfactant, surfactant flooding, phase behavior and others.

2.1 GENERAL CONCEPTS

2.1.1 POROSITY

There is a void between the grains that composed a rock (Tiab & Donaldson, 2004). These grains will never fit together due to the irregularity in their shape. The void space created is called pore space or interstice. The pore space is occupied by a fluid, (gas, water or oil). The porosity is then a relationship between the pore space and the bulk volume (Ahmed, 2001).

$$\phi = \frac{PV}{V_b}$$

$\phi = \text{Bulk Volume (fraction)}$

$PV = \text{Pore Volume}$

$V_b = \text{Bulk Volume}$

The rock or solid phase volume is the bulk volume minus the pore volume (Lake, 1989). For most naturally occurring reservoir rocks, the porosity is between 0.1 and 0.4 although, on occasion, values outside this range have been observed.

The porosity is a strong function of the variance of the local pore or grain size distribution and a weak function of the average pore size itself (Lake, 1989). For limestone formations, the porosity is mainly the result of changes that took place after deposition.

Porosity can be divided into an interconnected or effective porosity available to fluid flow and a disconnected porosity unavailable to fluid flow (Lake, 1989). In this case porosity will mean effective porosity.

2.1.1.1 EFFECTIVE POROSITY

Effective porosity is defined as “The ratio of the volume of interconnected pores and the dead end or cul-de-sac pores to the total or bulk volume” (Dandekar, 2006; Ahmed, 2001).

$$\phi_{effective} = \frac{\text{Vol. of interconnected pores}}{V_b}$$

In this work, we talk about the “effective porosity” as simply “porosity” since it is the only porosity obtained in these experiments.

2.1.2 FLUID SATURATION

The porosity is a measure of the amount of fluids that rocks can storage (Tiab & Donaldson, 2004). So it is important to know the amount of each fluid stored in the rock. The fluid saturation is a fraction of the pore volume occupied by the oil, gas or water. Then the oil saturation S_o , is expressed as:

$$S_o = \frac{\text{Volume of oil in the rock, } V_o}{\text{Total pore volume of the rock, } PV}$$

The same expressions can be written for water and gas. If we add all saturations of fluids content in the rock:

$$S_o + S_w + S_g = 1$$

2.1.3 WETTABILITY

Wettability is the tendency of a surface to prefer the contact of a particular fluid when there are other fluids presents (Agbalaka, et al., 2008). “The tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids” (Anderson, 1986; Ahmed, 2001).

A reservoir called water-wet will prefer contact with water; an oil-wet will prefer the contact with oil. When the rock is water-wet then the water, when present, occupies the small pores and exist in contact with the rock surface, while the oil stays in the center of the big pores surrounded by water (Anderson, 1986). Similarly in an oil-wet system the rock will prefer the contact with the oil. The “preference” of the rock does not necessarily indicate the content of it. In other words, the rock might be water-wet but it is saturated by oil, in this case when the rock gets in contact with water, the oil will be expelled to let the water in (the water would be imbibing the rock) (Milter, 1996). When the rock has no strong preference for either oil or water the system is said to be neutral or intermediate wettability (Anderson, 1986)

If we use these definitions of wettability into the reservoir rock, the situation complicates (Agbalaka, et al., 2008), it is then seen that reservoirs are not generally homogeneous, so the wettability is heterogeneous normally. This then led to the definition of mixed-wet state It means there are zones with different preference for oil and water inside the same rock. It is also known as fractional wettability, where different areas of the rock have different wetting preferences. If there is no preference for oil or for water then it is called neutral-wet.

We can summarize wettabilities into:

- Water-wet
- Oil-wet
- Neutral-wet
- Mixed-wet / Fractional wettability

The degree of natural water wetness or oil wetness depends much on:

- Adsorption or desorption of the components in the oil phase
- Rock mineralogy
- Deposition and spreading capability of the oil phase.

Polar components (like asphaltenes) can help in the adsorption process on the solid surface leaving a film over the rock pore, which might alter the reservoir rock surface wettability.

There have been observations that the variation in wettability can be related to the size of the water film between the oil and the rock surface (Agbalaka, et al., 2008). So the wettability is determined by the stability of these films. Some factors that can alter the wettability: Polar compounds, film forming components, high molecular weight paraffins, porphyrins, etc. Other factors that can have some influence: The type and distribution of minerals present, the type of rock, water salinity, etc.

The usual way to measure the wettability of a rock is by contact angle measurement (Agbalaka, et al., 2008). The contact angle is measured between the water-solid interface. So the possible wettabilities from contact angles can be:

- $\Phi < 90$ the rock is water-wet.
- $\Phi > 90$ the rock is oil-wet.
- $\Phi = 90$ or approximate, then is neutral-wet

It also can be described more specific as strongly water wet, weakly-oil-wet (Agbalaka, et al., 2008). There are some limitations of the contact angle method, which can bring the measurement as arbitrary and subjective. This can cause some wrong classification of wettability and reproducibility issues.

Wettability has a dominant effect on the microscopic distribution of phases and can cause important changes in the displacement mechanisms (Donaldson, 1985). Although contact angle method to measure wettability is universally accepted the real application is limited since it is not possible to see the contact angle inside the rock pores. Besides, this angle can vary from point to point in the rock as it has been said before, and also if there is adsorption involved, it also can be important the contact time or rate. For this reason, the most practiced method of wettability measurement

effects is through relative permeability measurements using reservoir fluids at reservoir conditions of temperature and pressure.

Wetting properties are mainly determined by the outermost layer of molecules and their orientation on the rock surface. Contact angles can be very sensitive to contamination by trace amounts of copper (for example) and nickel ions and products formed by oxidation of crude oil (Donaldson, 2008).

Recovery factor for water flooding of naturally fractured carbonate reservoirs depends on the matrix permeability, wettability, fracture intensity and fluid properties. Water flooding is an effective technique for fractured reservoir IF the formation is water-wet. In general carbonate reservoirs are mixed wet or oil wet that is why is so important to achieve a wettability alteration to water-wet or intermediate-wet conditions. (Seethepalli, et al., 2004).

The wetting phase that has the highest oil recovery has been in debate (Agbalaka, et al., 2008; Zhu, et al., 2013). The possible reasons for this divergence in conclusions are: Difficult reproductivity of wetting state, Lack of a unified standard, procedure for coring, the wetting state characterization method adopted; etc.

2.1.3.1 CHANGE OF WETTABILITY

Wettability alteration can take place during oil production and also with changes across the reservoir (Milter, 1996). When the reservoir is producing oil, redistribution of capillary forces may take place and normally water-wet sandstone can alter its wettability and become mixed or oil-wet. (Karimov, 2011)

Naturally fractured chalk oil reservoirs with low initial water saturation usually have mixed wet behavior (Milter, 1996). The saturation history of the material may influence surface wetting, the zones in contact with oil become oil-wet while the zones without it remain water-wet. This is an explanation for the reason of existence of mixed wet. Milter, (Milter, 1996), shows that it is possible to modify the wettability of

low permeability, chalk material by incubating the core material in the oil. This is used to prepare cores with to be more oil-wet.

Oil composition is the key to change the wettability of a naturally water-wet surface (Abdallah, et al., 2007). The polar components in resins and asphaltenes, with hydrophilic and hydrophobic characteristics determine the solubility. "A crude oil that is poor solvent for its own surfactants will have a greater propensity to change wettability than one that is a good solvent"

The rate of adsorption of surfactant material in the chalk surface is highest for the oil containing the largest volume fraction of surfactant (Abdallah, et al., 2007). In this case, the change in wettability is not related to precipitation of asphaltenes, but to surfactant adsorption onto the solid surface. If precipitation was the responsible for the change in wettability, then oil containing the largest fraction of n-heptane should respond with the greatest change in wettability (since the heptanes make the asphaltenes to precipitate and to change the wettability).

Hirasaki and Zhang (Seethepalli, 2004) have evaluated several sulfates in the presence of a low concentration alkali. They found that IFT can be lowered to ultralow levels (10⁻³ mN/m), wettability can be changed and imbibition improved by more than 35% OOIP using very dilute anionic surfactant/alkali solutions. (Seethepalli, et al., 2004)

2.1.4 INTERFACIAL TENSION

Surfaces of liquids or contacts between two immiscible liquids are usually acting as if a thin film was covering them (Ahmed, 2001). Although this "film" is very weak, it acts like a membrane and it resists to be broken. This is due to the attractions on each fluid system (water, oil or gas). The molecules that are inside the liquid have a balance between them, they have the same type of molecules around, but the molecules in the outside part have not that balance. That lack of balance makes them to obtain certain measurable tension, i. e. surface tension.

There is relationship between the interfacial tension and the oil recovery. The lower IFT the higher increment on oil recovery by the flooding can be obtained (Zhu, et al., 2013). i.e. if the IFT gets to 5×10^{-3} mN/m then is possible to get the highest increment in oil recovery for sandstone at least.

2.1.5 CAPILLARY PRESSURE

The capillary forces are in function of the effects of the interfacial tension between the fluids, the pore size and geometry, and the wetting characteristics of the system (Tiab & Donaldson, 2004). When two fluids that are immiscible exist in contact, a discontinuity in pressure exists between them. This pressure difference depends on the curvature between the fluids. Capillary Pressure P_c is that pressure difference:

$$\text{Capillary pressure} = \text{Nonwetting phase pressure} - \text{wetting phase pressure}$$

Capillary Pressure is a basic characteristic in the multiphase flow, just as porosity and permeability are the most basic properties in single phase flow (Christoffersen, 1995). It is caused by interfacial tension between oil, water, gas, and rock. The classical theory of capillarity in porous media says that the effect of IFT on capillary pressure is given for the Young-Laplace equation. This equation for a capillary tube or a circular pore with a small radius, considering the interface as a hemisphere then the equation can be reduce to:

$$P_c = \frac{2\sigma \cos\theta}{r}$$

θ = contact angle between liquid an the solid.

σ = Interfacial tension

r = radius of capillary tube

This is the definition of capillary pressure. This equation relates the capillary pressure across an interface to the curvature of the interface, IFT and the contact angle. If either the IFT is zero or the interface is perpendicular to the tube wall, the capillary pressure will be zero (Lake, 1989). Capillary pressure must be determined experimentally. Chalk

samples have pores that are much smaller than other reservoir rocks. The largest can be about 1µm in diameter (smallest pores in sandstone).

Karimov (Karimov, 2011) compared capillary pressure that comes from saturation measurements in the lab from water-wet samples, and saturations derived from the total porosity resistivity model with cementation and saturation exponent at the same condition. The discrepancy between the two is then used as part of identification of potential wettability alteration.

2.1.6 PERMEABILITY

Permeability is a rock property that is as important for oil recovery as porosity. Permeability is a tensorial property, a function of position and pressure (Lake, 1989). The permeability is a strong function of the local pore size and a weak function of the grain size distribution.

Permeability is the ability to allow petroleum fluids to flow through its interconnected pores (Tiab & Donaldson, 2004). It is a property of the rock (Ahmed, 2001). “It measures the capacity of the formation to transmit fluids”. This property was first defined by Darcy in 1856. He developed an equation for a linear flow of an incompressible fluid through a core. If we integrate that relationship, and rearranged it, we get:

$$k = \frac{q\mu L}{\Delta PA}$$

k = Permeability

q = Rate

μ = Viscosity

L = Core length

$$\Delta P$$

= *Differential pressure between the core outlet and inlet*

A = Transversal Area

So to get the value of k we need to pass a fluid of known viscosity through a core plug, with known dimensions, and then measure the pressure drop and the flow rate.

This equation is valid when:

- The rock is saturated 100% by only one fluid
- Laminar (viscous) flow
- Fluid is incompressible
- There is no reaction between fluid and rock

When the rock is saturated by only one fluid is called Absolute Permeability, when there are more fluids then it becomes effective permeability for that fluid. This effective permeability is “a relative measure of the conductance of the porous medium for one fluid when the medium is saturated with more than one fluid. ... is an associated property with each reservoir fluid” (Ahmed, 2001)

The sum of the effective permeabilities of the fluids content on the sample will be close to the absolute permeability but not necessarily equal.

According with the range given by (Tiab & Donaldson, 2004) the permeability from the cores in this work is judged as poor or fair.

2.1.6.1 RELATIVE PERMEABILITY

Relative permeability curves and their associated parameters are very important for the oil recovery (Lake, 1989). If it is consider a flow of several incompressible, single component phases in a one dimensional, linear, permeable medium and the flow is steady state, Darcy law may be integrated over a finite Δx distance, then:

$$u_j = \frac{-\lambda_j \Delta \Phi_j}{\Delta x}$$

$u_j = \text{Flux of phase } j$

$\lambda_j = \text{mobility of phase } j$

$\Delta \Phi_j = \Delta(P_j - \rho_j g D_z), \text{Potential difference}$

$\Delta x = \text{distance}$

λ_j (mobility) can be decomposed into:

$$\lambda_j = k \left(\frac{k_{rj}}{\mu_j} \right)$$

$k = \text{Absolut permeability}$

$k_{rj} = \text{Relative permeability to the phase } j$

$\mu_j = \text{Phase } j \text{ viscosity}$

Or into:

$$\lambda_j = \frac{\mu_j}{k_j}$$

$k_j = \text{Phase permeability}$

Another definition:

$$k_j = k k_{rj}$$

k_j is a tensorial property in three dimensions. The relative permeability to a phase decreases as the saturation of that phase also decreases (Lake, 1989; Ahmed, 2001). The relative permeability to a phase disappears much before that phase saturation gets to zero. If the relative permeability of a phase is zero, it does not flow. At that point the saturation cannot be reduced anymore. To reduce the "trapped" oil

saturation (residual oil saturation) is one of the objectives of the enhanced oil recovery which will be described and defined further in the point 2.3.

The residual oil saturation (S_{or2}) is the oil remaining behind in a very deep water swept region of the permeable medium (Lake, 1989); the remaining oil saturation (S_{oR2}) is the oil left after any water flood, superficial or deep. In other words, the residual oil saturation is less or equal than the remaining oil saturation. (i.e. $S_{oR2} \geq S_{or2}$). The trapped water saturation (S_{wr1}) is the irreducible water saturation. Exists also the connate water saturation, this is the water saturation in the reservoir naturally, many times S_{wr1} is actually equal to the connate water saturation.

2.1.6.2 END POINT RELATIVE PERMEABILITIES.

End point relative permeabilities are the constant relative permeability of a phase at the other phase's residual saturation (Lake, 1989). The word relative in the name of the K_r functions indicates the phase permeability has been normalized by some quantity. As the definition implies we take the normalized permeability to be the absolute permeability to some reference fluid (usually 100% air or water) though this is not always the case in the literature. This choice of normalizing factor means the end point permeabilities will usually be less than 1.

The endpoint values are measures of the wettability. The nonwetting phase exists in isolated globules that occupy the center of the pores (Lake, 1989). Trapped wetting phase, occupies the crevices between rock grains and coats the rock surfaces. For this reason the trapped nonwetting phase is a bigger obstacle to the wetting phase than

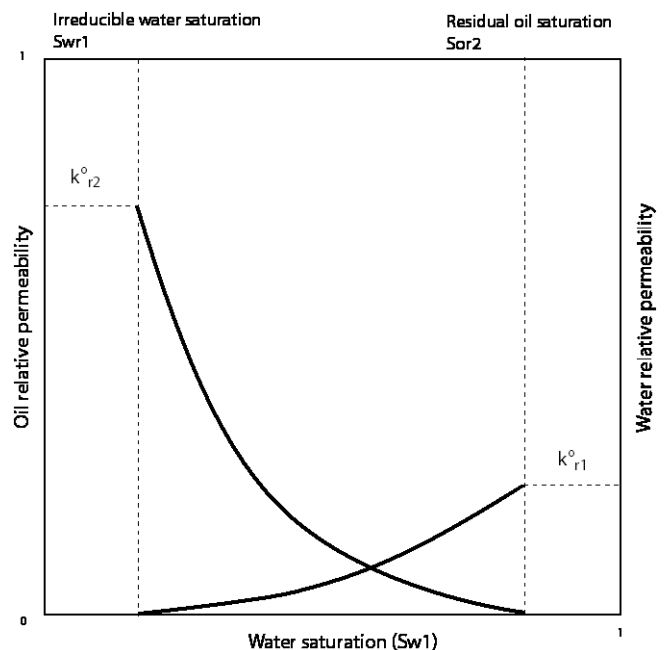


FIGURE 1 WATER – OIL RELATIVE PERMEABILITIES (LAKE, 1989)

the trapped wetting phase is to the nonwetting phase. The ratio of wetting to nonwetting endpoints proves to be good qualitative measure of the wettability of the medium. The permeable medium in the Figure 1 is water wet since k_{r1} is less than k_{r2} .

Others take the crossover saturation (where $k_{r2}=k_{r1}$) of the relative permeabilities as a more appropriate indicator of wettability (Lake, 1989). It is less sensitive to the value

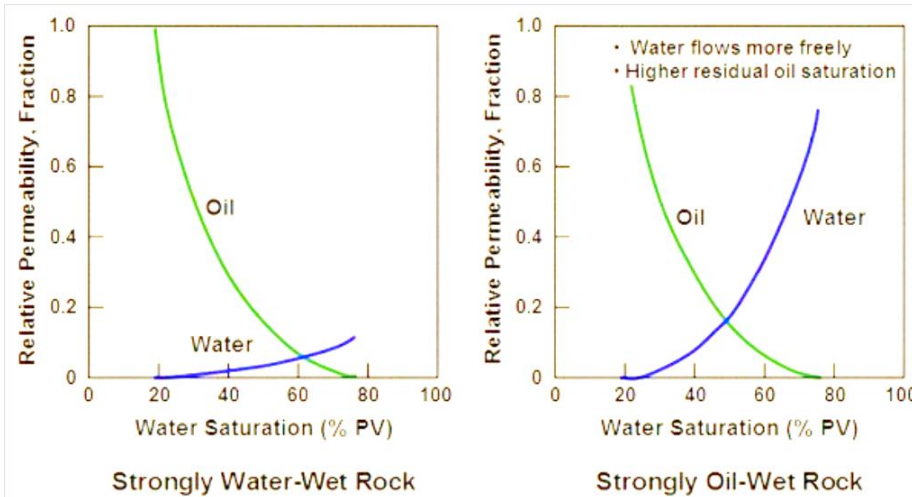


FIGURE 2 RELATIVE PERMEABILITY CURVES FOR STRONGLY WATER-WET AND OIL-WET (ANON., 2013)

of the residual phase saturations. Fig 2 illustrates both the shift in the crossover point and the movement of the water endpoint relative permeability as a function of wettability.

The Figure 2 also illustrates that relative

permeability can change by several factors over a normal saturation range.

When a water flooding occurs both phases (oil and water) flow, the k_{rO} decrease from high, while the oil saturation decrease also. The water relative permeability k_{rW} starts low and increases as water saturation increases (Abdallah, et al., 2007). As water occupies small pores that had oil before eventually all paths will be filled with water and the oil will stop flowing. The oil is disconnected, encapsulated in the pores (since the paths are “blocked” with water now) this will make that the final k_{rW} has lower values than the original k_{rO} . The oil trapped is the goal in this experimental work. It can be produced by reducing IFT, increasing the pressure gradient or viscous force.

K_r curves become less curved when IFT is reduced (Abeyasinghe et al, 2012). Surfactant flood (which will be described later) shift the k_{rO} curve to the right in both water wet and mixed wet conditions. The increased in k_{rO} indicates an accelerated oil production at mixed wet conditions. (Abeyasinghe et al, 2012).

2.1.6.3 ROLE OF RELATIVE PERMEABILITIES AND THE CAPILLARY NUMBER

Relative permeability (k_r) and capillary pressure (P_c) curves can be estimated by history matching the experimental data from the core floods using Sendra simulator (Abeyasinghe et al, 2012). Sendra utilizes a fully implicit black oil formulation based on Darcy's law and continuity equation. Water-oil k_r curves can be obtained by parameter estimation using LET- correlation (Lomeland et al, 2005)

1 The endpoint relative permeabilities increase as the capillary number increases, and the residual saturation decrease until each endpoint is close to 1. (Baviere, 1991) "A high capillary number results in greater recovery and it can be increased by lowering the IFT or making the pressure drop larger" (Lake, 1989)

2 The curvatures of the relative permeability and saturation curves change very slowly with the capillary number

3 The relative permeability of the phase depends only on its own saturation

2.2 SURFACTANTS

Surfactants have two separated portions that are hydrophilic and hydrophobic; both parts together are called amphiphilic. Usually the hydrophobic is a long chain hydrocarbon radical, with 8- 18 carbon atoms, possible associated with naphthenic or aromatics. (Baviere, 1991). "... they are chemical substances that adsorb on or concentrate at a surface or fluid/fluid interface when present at low concentration in a system. They alter the interfacial properties significantly; in particular, they decrease the surface tension, or IFT. In general they consist of a hydrocarbon portion (non polar) and a polar, or ionic portion." (Green, 1998)

In a representative way the hydrocarbon part is call the "tail" (lipophilic) interacts very little with the water and the ionic part which is polar, interacts strongly with the water

molecules, this is the “head” (hydrophilic) (Donaldson, 1985). The hydrocarbon can be a straight or a branched chain molecule.

The balance between the hydrophilic and hydrophobic parts gives the characteristics of a surface active agent. The measured hydrophilic/lipophilic balance (HLB) indicates the tendency to solubilize in oil or water. Low HLB tends to be more soluble in oil and then it forms water in oil emulsions.

When we want to increase the oil solubility then it should be increase the influence of the nonpolar end, the lipophilic, this can be done by increasing the molecular weight of the end, also decreasing branches, or decrease the influence of the polar end by decreasing the number of polar moieties (Lake, 1989).

2.2.1 CLASSIFICATION AND STRUCTURE OF SURFACTANTS

They can be classified to the ionic nature of the head (Green, 1998) (Baviere, 1991):

- Anionic: In aqueous solution the molecule ionizes, and then the surfactant has a negative charge. It is classified as anionic for the negative charge on the head group.
- Cationic: In aqueous solution, ionization occurs and the head group has a positive charge.
- Nonionic In this one there is no ionization, usually the head group is larger than the tail group.
- Zwitterionic: This surfactant has two ionic groups of opposite charge.

Anionics and nonionics have been used as surfactants in EOR processes. Anionics because they are more stable, have low adsorption on rock, and can be manufactured economically and they are relatively cheap compared with the cationics or non-ionics (Bortolotti, et al., 2010). Nonionics have been used primary as cosurfactants. They can handle high salinity brine but their properties are not as good as anionics. Cationics are not used because they get adsorbed strongly on sandstone reservoir rocks, although cationic surfactants are effective (70% recovery) in imbibing water into originally oil

wet cores at concentrations higher than their CMC (Seethepalli, et al., 2004). Cationic surfactant had the capacity to reverse the rock to its water-wet wettability by forming ion-pairs with the dissociated adsorbed anion materials in the aqueous phase. Then this surfactant removes the material that was adsorbed on the rock wall, which leaves the surface less oil-wet (Bortolotti, et al., 2010).

The most common surfactants used in micellar/polymer flooding are sulfonated hydrocarbons (Green, 1998). "...the term 'crude oil sulfonates' refers to the product when a crude oil is sulfonated after it has been topped. 'Petroleum sulfonates' are sulfonates produced when an intermediate-molecular-weight refinery stream is sulfonated, while 'synthetic sulfonates' are the product when a relatively pure organic compound is sulfonated. Crude oil and petroleum sulfonates have been used for low salinity application (less than 2 to 3 wt% NaCl). These surfactants have been widely used because they are effective at attaining low IFT, relatively inexpensive, and reported to be chemically stable." (Green, 1998)

Practical surfactants for EOR have some water solubility (Green, 1998). The characteristics and structure of petroleum sulfonates suitable for EOR applications depends on the chemical composition of the feedstock, degree of sulfonation, and average number of sulfonate groups attached to each molecule.

2.2.2 EVALUATION OF SURFACTANTS:

For the experimentally evaluation of surfactants (Seethepalli, et al., 2004) has performed these studies:

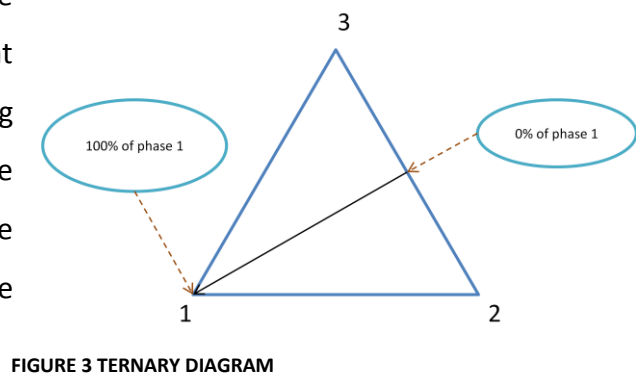
- Phase behavior study.
- Interfacial tension measurement: The presence of the in situ surfactants in the aqueous phase generated can decrease in IFT. IFTs of the order of 10-2 mN/m and lower are capable of mobilizing oil by buoyancy.

- Wettability tests: there where changes with wettability is observed, in the case of cationic surfactant it was necessary about 1wt% to get the change to intermediate to water-wet.
- Adsorption: The adsorption of anionic surfactants decrease in the presence of Na_2CO_3 . That type of surfactant has a plateau of adsorption which is over the CMC. The adsorption of anionic surfactants can be suppressed by the use of alkali.

2.2.3 PHASE BEHAVIOR

2.2.3.1 TERNARY DIAGRAM

It is a plot that can represent more composition information in a mixture, at fixed temperature and pressure, consisting of three components (Lake, 1989). The composition of the mixture will be represented as a point on a plot of the mole fraction of components. The whole plane



is made up of points that represent the component concentration of all possible mixtures (Lake, 1989). As the figure 4 shows, along the line, the percentage of the component 1 vary in a constant manner from 0% (the farthest point in the line from the apex) to 100% exactly in the apex. It works in the same way for the rest of the components (2 and 3).

For the surfactant-brine-oil phase behavior it is conventionally represented in this ternary diagram with the convention 1=brine, 2=oil, 3=surfactant. The phase behavior is strongly affected by salinity (Winsor, 1954).

At low salinity a typical surfactant will usually have good solubility in aqueous phase and poor in oil. Then a composition that is close to the brine-oil boundary will split in

two phases, one with pure oil, and a microemulsion phase with brine, surfactant and some oil. The tie lines have a negative slope. This is called Winsor type I system, a lower-phase microemulsion, or a type II (-) (II for the phases that could be form, and “-” for the direction of the slope in the tie lines) (see Figure 5).

On the other side high salinity will usually have in certain way a mirror image of this behavior. The electrostatic forces drastically decrease the surfactants solubility in the aqueous phase. As a result we will obtain two phases, one with the brine, and the other with a microemulsion phase that contains most of the surfactant and some brine solubilized in the oil phase. This is called Winsor type II, upper-phase microemulsion, or a type II (+) (now the tie lines have a positive direction slope since the point is now in the brine apex).

The best for a higher oil recovery is the type II (-), where the oil is solubilized in the brine, but still the effect of IFT is an important matter to achieve this goal. IFT is very important especially in the intermediate salinities case. This point is called Winsor type III, a middle-phase micro emulsion, or a type III. In this state three phases exist, water, oil, and microemulsion. IFT between water-emulsion and emulsion-oil is present. The mixture contains phase environments from type II (-) and type II (+) (Lake, 1989).

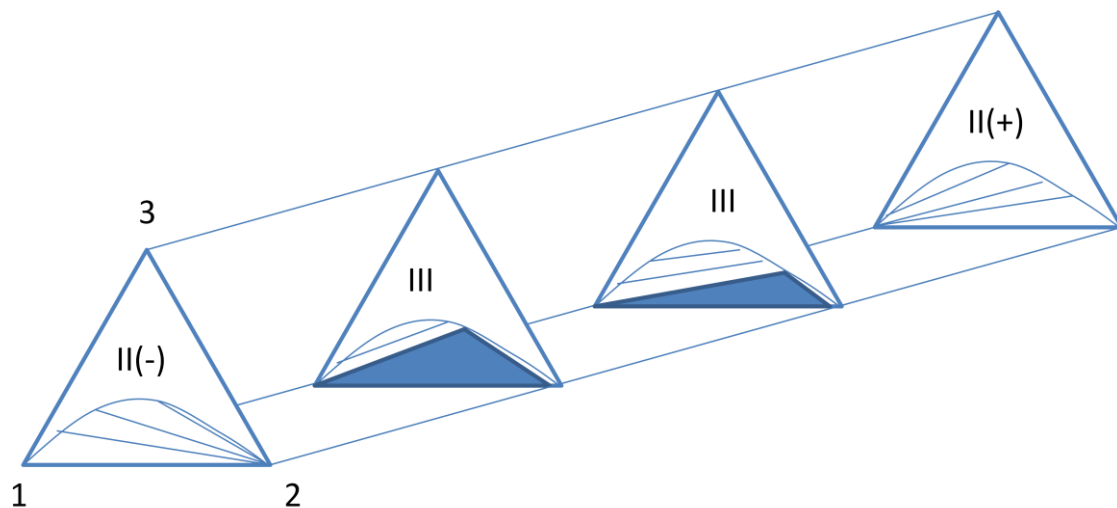


FIGURE 4 DIAGRAM OF MICELLAR-POLYMER PHASE BEHAVIOR (LAKE, 1989)

2.2.4 MECHANISMS INVOLVED IN OIL DISPLACEMENT BY SURFACTANT SOLUTIONS

The oil recovery potential by surfactant flooding is described by the capillary desaturation curve (CDC). This curve gives the variation of the residual saturation (S_{or}) as function of N_c . The curve has a plateau in S_{or} at when the N_c is low, then, it is reached the critical N_c (N_{cc}), after that, it will decrease. The decrement can be achieved with surfactant that can reduce the IFT (Abeyasinghe et al., 2012).

Some mechanisms involved in the displacement of oil by surfactant solutions can be:

2.2.4.1 IMMISCIBLE DISPLACEMENT UNDER LOW INTERFACIAL TENSION CONDITION

There are four regions or zones in the porous media while flooding with surfactant solution. This immiscible flow that is displacing the oil will form areas inside the rock (Baviere, 1991).

- a) Two phase flow of oil and water under initial conditions in the reservoir.
- b) The oil bank. If the surfactant displaces the oil, then a region of oil flowing at a higher saturation than the initial will appear. This two phase flow region is the oil bank.
- c) The two or three phase flow of oil, brine and microemulsion, where the low interfacial tension exist.
- d) The polymer. Not used in this document.

2.2.4.2 MOBILITY CONTROL

The base criterion for a displacement is that each bank is less mobile than the one is displacing. The total relative mobility is the sum of the mobilities (relative permeability

over viscosity). Usually it is add oil or a polymer to increase the viscosity since only surfactant and brine are not enough to get enough mobility (Baviere, 1991).

To Decrease mobility ratio increases areal, vertical and displacement sweep efficiency. The control of the mobility affects the distribution of the slug. This can prevent the slug to become disperse: fingering, channeling, mixing cross flow or other mechanism. Fingering occurs in low tension process than in most others because the low tension help to get little or none stabilization of the fingers. If the mobility ratio decreases the sweep efficiency is improved (Baviere, 1991) .

2.2.4.3 FLUID AND ROCK INTERACTIONS

Some important interactions are: adsorption, cation exchange, precipitation-dissolution phenomena, capillary phenomena, dispersion. These interactions affect the retention of surfactant. A description of some of them:

Adsorption: It is caused by the attraction between the surfactant molecules and the mineral surfaces. The forces that act for this to happen can be, Van der Waals, electrostatic forces and hydrogen bonding. They can be different according with the type of surfactant or with the nature of the mineral. It depends on temperature, electrolyte composition, pH, surfactant concentration, oil concentration. The conditions that bring the solubilization of the oil and brine in a microemulsion phase are also the cause of the tendency into lower adsorption.

The increase in adsorption is dependant of the increase in surfactant concentration until CMC is reached. For this reason, surfactants are usually used at least in to orders of magnitude larger than CMC. So the electrolytes end up been the variable that can control the adsorption for a particular reservoir.

Cation exchange: Occurs when one of the injected fluids differs in electrolyte composition from the initial fluid that saturated the rock. This always happens in anionic surfactant.

Capillary phenomena: The trapping of microemulsion can be greater than the oil since the oil is nonwetting and the microemulsion is the wetting phase, the wetting phase is

the one held more tightly than nonwetting phases. This residual microemulsion saturation can be high even at very low interfacial tension.

2.2.5 MICELLES AND MICROEMULSIONS

When the surfactant molecules dissolve in water they form a monolayer. This monolayer formed lowers surface tension as function of the excess surfactant concentration (Baviere, 1991).

At the correct saturation and temperature, surfactant molecules aggregate into micelles, with the HC parts towards inside in a dynamic equilibrium with the non micellated molecules. (Baviere, 1991) Micelles form a concentration called Critical Micelle Concentration and it is identified by a change in the properties of the solution. The micellization helps to increase the surfactant solubility. According to (Baviere, 1991) There can be:

Type 1: If the oil exceeds the solubilization capacity of micelles, then there is an excess of oil that has traces of water and surfactant. Micelles can solubilize oil in the interior of them. These are the solutions named S1 by Winsor.

Type 2: Micelles can be inverted in oil, with their hydrophilic part directed to inside of the aggregate. So it's called S2 Winsor or type 2 if there is an excess of water phase.

Type 3: When we pass gradually from S1 to S2 to an intermediate state where oil and water are continuous phases. In the presence of an excess of oil and water the type 3 appears.

In a very low concentration the dissolved surfactant molecules are dispersed as monomers but when the concentration is increased to a certain point they tend to form aggregates called micelles. This specific concentration is called the Critical Micelle Concentration (CMC). Above this surfactant concentration there is still some monomers concentration, but even if the concentration is increased over the CMC the concentration of monomers won't change. (Green, 1998)

A definition of a microemulsion used in oil recovery processes is "... a stable, translucent micellar solution of oil and water that may contain electrolytes and one or more amphiphilic compounds." (Green, 1998)

It is known that the rate of a chemical reaction can be very sensitive to the nature of the reaction environment. Reactions involving polar or ionic transition states can be especially sensitive to the polarity of the reaction medium (Myers, 1999). It is normal that chemical reactions, especially the ones in which the reactant may be soluble in water and the other in oil, can exhibit a significant enhancement in rate when carried out in the presence of surfactant micelles. The presence of the micellar species can provide a beneficial effect through two possible mechanisms:

The palisades region of the micelle is a representation of a transition zone between a polar aqueous environment, which may be either the bulk phase or the micellar core, and a non polar hydrophobic region. This gradient in polarity can serve as a convenient area of intermediate polarity perfect to increase reactant interaction or for optimizing the exergics of transition state formation.

To Increase potential for the micelle to solubilize a reactant that would not normally have significant solubility in the reaction media. In other words, it can serve as a source of reactant that increases the available concentration. The enhancement that has been reported is what makes this system very attractive for potential practical applications.

Microemulsions are composed of two mutually immiscible liquid phases, one spontaneously dispersed in the other with the assistance of one or more surfactants or cosurfactants (Myers, 1999). While microemulsions of two non aqueous liquids are theoretically possible usually they have at least one aqueous phase. The systems may be water continuous (o/w) or oil continuous (w/o), this will be determined by the surfactant system employed, temperature, electrolyte levels, the chemical nature of the oil phase, and the relative ratios of the components. Most microemulsions, especially those employing an ionic surfactant require the addition of a cosurfactant to be able to get the ITF properties necessary to become a microemulsion.

Microemulsions and macroemulsions can exist with either the oil or the water being the continuous phase. The characteristics of the system will, of course be different in each case (Myers, 1999). The correct use of the phase diagram allows establishing not only the component ratios necessary to produce a microemulsion, but also the component forming the continuous phase.

The difference between microemulsions and conventional emulsions or macroemulsions is very clear. Even if a macroemulsion can be kinetically stable for long periods of time, at the end it will experience phase separation in order to get to the minimum interfacial free energy (Myers, 1999). The surfactants or polymers will make this time to be longer but the thermodynamic forces remain unchanged. Microemulsions on the other hand appear to be thermodynamically stable, assuming no change. They are different in many characteristics, including the size of droplets, and the mechanical requirements to be prepared. In a droplet size order from smallest to the biggest we will have: Solutions, micelles, swollen micelles, micro emulsions, and then macro emulsions and suspensions at the end of the list as the biggest droplets.

The major interest in these fluids is that it is possible to pass continuously from the case of a micro-emulsion in which oil is the continuous phase to one in which the water is. This then suggest that a true miscible displacement of oil by water may be possible. (Green, 1998)

The principal properties of micro emulsions are: reasonable compatibility with the various reservoir fluids and complex rheological properties (Latil, 1980).

It has been seen the emulsification performance plays an important part in the oil recovery for surfactant flooding (Zhu, et al., 2013). Apparently the increase on oil recovery is direct influenced by the increase of the emulsification index, even if the IFT level is not that low (Shiau, et al., 2012).

2.3 ENHANCED OIL RECOVERY

EOR generally refers to oil recovery after the one obtained through natural energy from the reservoir and external mechanism to inject energy. It includes many processes like water flooding (which by itself is known as a secondary recovery), caustic flooding, hydrocarbon injection, carbon dioxide flooding, micellar-polymer flooding, and many thermal methods. In this case we will refer mainly to the micellar-polymer flooding process (Donaldson, 1985; Lake, 1989). When these methods become not economical then it is applied an enhanced oil recovery technique, (or before getting to this point), known as tertiary recovery designed to recover the residual oil (Donaldson, 1985).

We can divide oil recovery as:

Primary recovery: Hydrocarbons are recovered from a field by means of the well drilled into the reservoir. The pressure in the well is higher than the weight of liquid column, so the well flows when it is opened (Baviere, 1991).

Secondary recovery: To produce extra oil than primary recovery, the pressure in the reservoir is maintained by injecting another fluid. This technique has two objectives: to maintain the pressure and to push the oil in the reservoir towards the producing well. For this type of recovery the water flooding is very common. Water or brine is physically incapable of displacing oil as a total from a reservoir rock. Capillary forces acting will retain some of the oil. This residual oil saturation can range from 15 to 40% for that reason is an important target for tertiary oil recovery (Donaldson, 1985)

Tertiary recovery: After primary and secondary techniques have been used, sometimes tertiary recovery is used to get the remaining oil, using more sophisticated systems. In simple words, the purpose of this technique is to increase the displacement efficiency. It can focus on producing the oil that remains in part of the reservoir that was not swept by the displacing fluid. Or also can focus on increasing the sweep efficiency. Some techniques can do both.

In the new fields the trend is to plan exploitation as a whole instead of steps, so they start with secondary recovery even though it is still possible to continue with primary.

Techniques to improve the displacement efficiency or sweep efficiency could be used at the beginning instead of wait for the reduction of production. This is called enhanced oil recovery (Baviere, 1991; Donaldson, 1985).

2.4 WATER FLOODING

It is a secondary oil recovery process where the water or formation water is injected into the rock to push the oil that has been left there after the primary recovery. (Agbalaka, et al., 2008) When water flooding occurs on strongly water-wet rocks the water is imbibed into the small pores while the oil is expelled to the big ones and then displaced in front of the injection wave, so there is a “uniform front”, i.e. only the oil phase moves (Agbalaka, et al., 2008). At certain point some of the water covers the whole pore wall leaving some oil spheres trapped, since it is surrounded by the water then there is not enough pressure to compress that sphere and make it pass through the pore throat. This disconnected residual oil exists as small globules in big pores, or as a community of pores that are surrounded by water.

In strongly oil-wet systems the two fluids (oil and water) behave in the inversed way than the strong water-wet case (Agbalaka, et al., 2008). Water flooding is not very efficient in strong oil wetting rocks. When water flooding is applied the water forms continuous channels or fingers inside the big pores (not touching the walls) pushing the oil that was there.

Wettability is the most important determinant for the recovery efficiency in water flooding (Agbalaka, et al., 2008). Also water flooding is affected by the oil-water relative permeabilities, which are also in function of wettability. The most generally accepted method to see the wettability effect in the water flood is with these relative permeability measurements.

The best oil recovery is when is in an intermediate-wetting state. (Agbalaka, et al., 2008)

Dong, (Dong, et al., 2006) found any effect of the rock wettability on the oil recovery in the case of surfactant-polymer flooding in sandstones. Contrasting with water flooding which confirm with (Agbalaka, et al., 2008) that it is very important.

2.5 MICELLAR-POLYMER FLOODING

Micellar-polymer flooding or surfactant flooding is any injection of a surface-active agent (surfactant) that can improve the oil recovery. Micellar flooding does not take into account processes like alkaline flooding or other where the main goal is not to reduce the capillary forces to get oil recovery (Lake, 1989). The process usually involves: surfactant, cosurfactant (alcohol), hydrocarbons, water and electrolytes or polymers (polymers are not used in this series of experiments for this thesis). The surfactant can obtain ultralow IFTs lower than 10^{-3} dynes/cm for a specific crude oil/reservoir-brine by formulating a microemulsion system (Lake, 1989). The surfactant is the main component in the micellar system, it sets a limit in the number of possibilities in composition, along with: the cosurfactant (if is needed), brine salinity, oil composition and reservoir temperature (Green, 1998). Each reservoir oil/brine needs a different formulation. To be able to have an important reduction in the residual oil saturation it is necessary to get an IFT of 10^{-3} dynes/cm

In general the micellar/polymer process is a tertiary displacement (Green, 1998). It is executed after water flood is ending (Abdelhady, 2007). A primary slug with micellar solution at a specified volume is injected. This volume is variable. It can be 3% to 30 % of the flood pattern. The micellar solution has very low IFT with the crude oil so it mobilizes the trapped oil and form an oil bank in front of the slug. Also has low IFT with brine and it is displaced also. Because oil is initially at residual saturation in a tertiary flood, there won't be oil production until the oil bank reaches the end of the system.

The micellar solution must be design to get a favorable mobility between the slug and the oil bank, so the viscosity is adjust to make this possible. Sometimes it is added a polymer to increase the apparent viscosity. For this reason the process has the potential to increase the volumetric sweep efficiency and also the microscopic displacement efficiency.

Sometimes on a reservoir a preflush is injected before the solution which contains a sacrificial adsorbent to be taken by the rock and fill the adsorption sites and avoid the surfactant to get lost in the rock (Green, 1998). The amount of surfactant in lab tests is 100% of the flood pattern but in the field this is not possible. A micellar solution is relatively expensive so it is used a limited volume. The rest of the volume is a less expensive fluid, used as a displacement for the micellar slug. It is not possible to use only brine because it doesn't have the necessary mobility to drag the surfactant slug, a solution of polymer in water should be used.

3. PROCEDURE

The procedure for surfactant flooding in chalk cores is similar to the one used in Keller's paper. (Kellerhals, 1979).

3.1 MATERIAL

3.1.1 BRINE

The composition of the formation water (FW) used in the dynamic experiments is given in Table 1

Salt	FW (g/l)
NaCl	36.81
KCl	0.31
MgCl ₂ 6H ₂ O	4.48
CaCl ₂ 2H ₂ O	33.25

TABLE 1 BRINE COMPOSITION

3.1.2 CRUDE OIL

As crude oil a stock tank oil (STO) from a field in the North Sea was used. The oil from this location is classified as light crude oil with approximately an API gravity of 37.5. The crude was filtered through a 0.45µm filter at 60°C before use in the experiments.

3.1.3 SURFACTANTS

3.1.3.1 SURFACTANT WITH WETTABILITY ALTERATION PROPERTIES (SWA1)

The surfactant product for wettability alteration is synthesized from coconut and containing dodecyl and tetradecyltrimethyl ammonium. The active content of the product is 50% weight and it contains 35- 40% isopropanol. It was used a solution of 1%wt (active ingredient) in FW. The properties can be seen in Table 2

Components	SWA1
Type	Surfactant
Trimethylammonium chloride	50%
2-Propanol	37%
Water	13%
Physical & Chemical Properties	
Appearance	Liquid
Color	Light yellow
Physical state/Odor	Propanol
pH	6-9
Boiling point	80°C
Flash point	17°C
Density	890 Kg/m ³
Viscosity	19mPas

TABLE 2 WETTABILITY ALTERATION SURFACTANT PRODUCT PROPERTIES

3.1.3.2 SURFACTANT WITH IFT REDUCTION PROPERTIES

The characteristics of the surfactants with interfacial reduction properties are stated on the Table 3

Components	SIFT2	SIFT3	SIFT1
Type	Sulfonate	Anionic Olefin	Anionic Olefin
Water	64-80%	58-60%	63-86%
Internal Olefin Sulfonate	20-30%	30-35%	16-25%
Internal Olefin	<3%	---	<3%
Sodium Hydroxide	<0.5%	1-5%	0.5-2.5% 2- Butoxyethanol
Sodium sulfate	<2.5%	5-10%	<2.5
Physical & Chemical Properties			
Appearance	Clear	Clear	Viscous Liquid
Color	Amber	Clear	Amber
Physical state/Odor	Liquid	Liquid	Alcoholic
Form	Liquid	Liquid	Liquid
pH	9-12 (5% in water)	11-12 (as it is)	9-12 (5% dilution)
Freezing point	<-9.4C	----	-1°C
Boiling point	100°C	>100°C	93.3°C
Flash point	93.9°C	93.9°C	98.9°C
Specific gravity	1.045 g/mL	1.0697 g/mL	1.02 g/mL
Viscosity	700 cP	<500 cP	2500cP

TABLE 3 IFT SURFACTANT PRODUCT PROPERTIES

Three surfactant products were used in the surfactant systems with IFT reduction. Solubility and phase behavior were evaluated for each surfactant product. Two surfactant products (SIFT1 and SIFT2) were tested to be used in combination by mixing in different ratios in FW.

In the solubility test we had 10ml samples of the surfactant prepared with FW at 1%w and stored in an oven at 90°C for 3 days. If visually it can be seen that there is no precipitation, then 10mL of STO crude oil were added and mixed. Three days later it was evaluated if there was precipitation due to the oil mixture. (Shiau, et al., 2012; Wang & Mohanty, 2013) This applies for all surfactant solutions.

For the evaluation of the surfactants solutions SIFT1 and SIFT2 that could work as a mixture in a solution, it was necessary to find out the best ratio between the lipophilic and the hydrophilic. For that reason some extra tests were done and observed. These solutions were storage for 3 days also on an oven at 90°C and were prepared with:

- Different salinities: half and double salinity for FW.
- Different ratios: SIFT1 and SIFT2 were mixed in ratios of 100/0, 75/25, 50/50, 25/75 and 0/100

The result of the test for SIFT1 and SIFT2 was that these components have a strong reaction with the FW salinity; they are not very soluble with high salinity. To help solubilization it was added 5%w isopropanol as a cosurfactant. The relation 0/100 of SIFT1/SIFT2 was the one with no precipitation, the clearest. Although the solution had an oleic residue. The 100% SIFT2 solution was then separated from its oleic residue and passed through a titration process to analyze if the 1% active component from the surfactant was still in the solution (see Figure 5). So the SIFT2 solution with 5% isopropanol at normal salinity from FW was used in the flooding and the SIFT1 was discarded for insolubility.

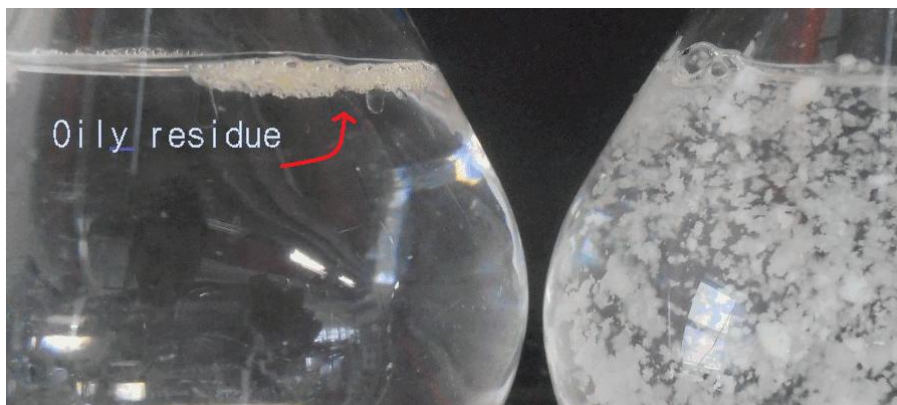


FIGURE 5 SIFT2 (TO THE LEFT) AND SIFT1

3.1.4 ROCK

Liege outcrop chalk rock was used as analogous to reservoir chalks

Liege chalk typical properties have been reported to be (Risnes, 1999):

- Age: Upper Campanian.
- Average porosity: 40%
- Silica content: less than 2%
- Permeability: 1-2 mD

These properties classify the chalk as high porosity and low strength chalk.

3.2 VISCOUS FLOODING EXPERIMENTS

The flooding experiments were carried out at 90°C by using the experimental set up in Figure 5. The piston cell contained different solutions that were injected depending on the step in the experiment: FW, Oil, Surfactant with wettability alteration properties, or Surfactant with IFT alteration properties.

The surfactant for wettability alteration (SWA1) reduce the IFT down to 1 ml/min, while the surfactants for reduction of IFT (SIFT 1, 2 and 3) reduce the IFT down to 0.01ml/min (reference Personnel Communication Ingebret Fjelde, 2013)

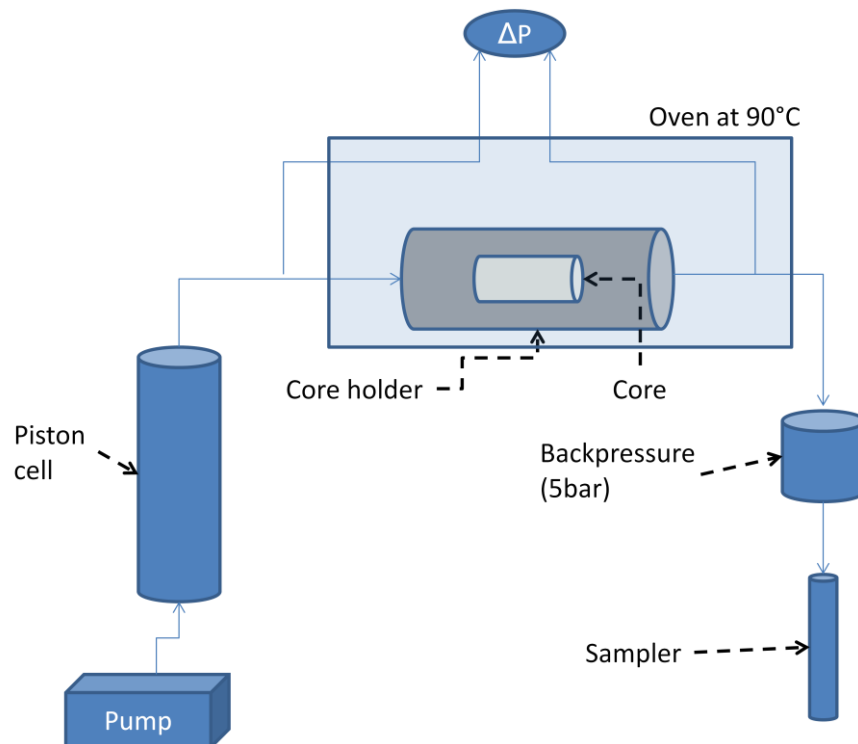


FIGURE 6 VISCOUS FLOODING EXPERIMENT SETUP

In the laboratory the original condition of 100% water saturation is simulated by saturating a core specimen with brine (Donaldson, 1985).

The core plug is mounted in a core holder and set an overburden pressure of 25 bars to keep the sleeve tight. Then the fluids are not able to slide through the space

between the core and the sleeve. The cores were vacuumed to avoid air in the flooding experiments, and to have an accurate measurement of the pore volume PV.

To calculate the PV FW was injected in the core, the amount was measured by weight and by volume. It should be subtracted from the total FW volume injected the dead volume. The dead volume is the space that is contained between the core holder valves but that do not belong to the core itself. The calculation for that dead volume was approximately 1.1 mL. This step is illustrated by the first rectangle in the top of the Figure 6. PV is obtained when the FW gets to be 10bar in the core.

Sulphate was removed by flowing 5 PV of FW or until the Cell Test (Spectroquant 1.14548.001, analogous to EPA 375.4 and US SM 4500 SO42- E) detect less than 5mg/L (sulphates are known as wettability modifiers, so in order to have results caused exclusively by the surfactant solution it is necessary to eliminate any other source of wettability changes that cannot exist in the real reservoir). The core was in the oven while this step was performed; temperature is not important in this step and is useful to get the core into the right temperature before the next step. The permeability of the FW in the rock was also obtained at this point by means of 3 different rates and their respective stable differential pressure measurements. It is used a 5 bar back pressure, i.e. the net overburden pressure was 20 bar

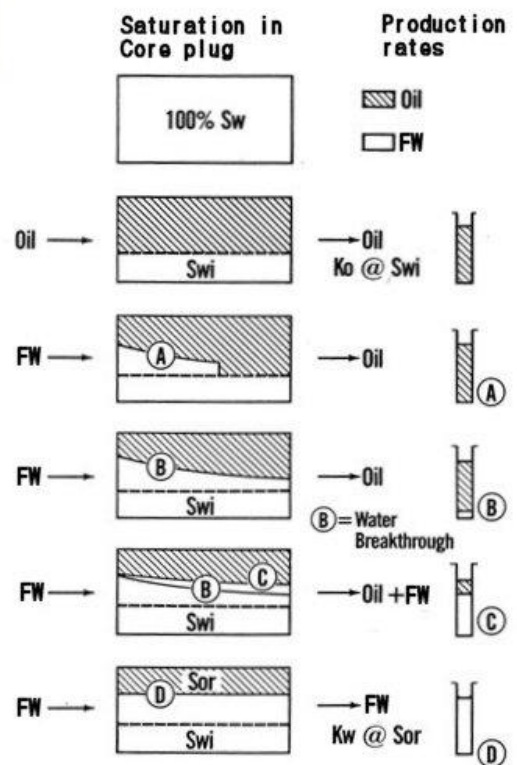


FIGURE 7 FLOODING AND SATURATIONS

The aging with STO. The core plugs in this step are at the correct temperature. Oil was then injected for 90 hours at a 0.07mL/min rate (45 hrs in each direction, i. e. the flow should be inverted after 45 hrs, in order to establish a more homogeneous saturation).

Differential Pressure was measure at all times and also the volume of water produced. To have a more accurate measurement of the water volume it is necessary first bypass oil to clean the tubings from FW. Some dead volume apart from the one existing in the

core holder is also in the system. This “oven-dead-volume” added up to the one from the core holder gets to be 3.46 mL. This oven-dead-volume was subtracted to give the correct result. It will also be useful for the oil measurements since is the same line configuration. At the end of this step we got the initial water saturation S_{wi} . This is the second box in the Figure 6.

At this point the core is ready for the core flooding with surfactant solution or with brine. After any flooding (FW, SWA1, SIFT2, SIFT3) permeability effective to water can be measure using the differential pressure that is taken at all times during the flooding.

The sequence that was taken for the experiments can be seen on Figure 8

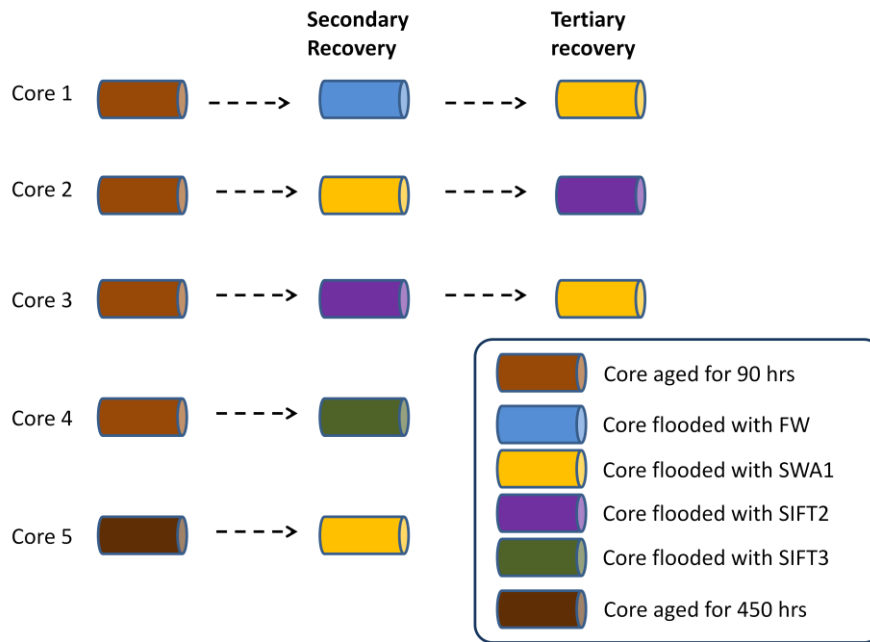


FIGURE 8 SEQUENCE OF EXPERIMENTS FOR CORE PLUGS

The first three cores have had secondary and tertiary recovery while the fourth and fifth did not have tertiary recovery. The fifth core has experienced a much longer aging time 5 times longer than the rest.

Water or Surfactant flooding were carried out at a 0.1ml/min rate. Oil production was measured against time for at least 5PV according to the experiment sequence in Figure 8.

4. RESULTS

In this chapter the results from the core flood experiments are reported. The results and graphs have been corrected for dead volume from the core holder and from the flow lines in the oven in order to get the accurate information from the core only.

Some of the properties that are shown in data tables (4, 5, 6, 7, and 8) have been explained in the previous chapter. The k_o for each core was calculated using the oil viscosity and the differential pressure read from the transducer at the end of the aging time. Analogous to k_o the permeability specific to water was calculated using the viscosity of the fluid and the differential pressure obtained at the end of the floodings.

All core floodings were carried out at 0.1 ml/min rate at 90°C with backpressure of 5bar and overburden of 25bar.

4.1 CORE 1

The Core 1 data are shown in Table 4.

This core was selected to be water flooded as a secondary recovery and after at least 5 PV to carry out the tertiary recovery using the surfactant with wettability alteration properties SWA1. The oil saturation S_o and the differential pressure ΔP across the core are given in the Figure 9

The y axis in the graph is the S_o in percentage. The oil saturation is obtained by the reading of production of oil while the flooding is taking place. In this way we are able to know the amount of oil that remains in the core. It starts at 0PV with the initial oil saturation S_{oi} in this case 0.76 (the saturation of oil obtained at the end of aging time).

Approximately after 0.37 PV's the water breakthrough (WBT) can be observed in the graph. Before this point the production was only oil. After that point traces of oil flow but the main fluid is FW. Refer to Figure to see how WBT behaves in point D. Unfortunately the experiments have to be observed only in working hours because of lab work time regulations for students, so there are missing some points that could not be take for been outside this time. The oil production after WBT, taken from 1PV to 4PV is approximately 0.013 from oil saturation. The ΔP curve shows pressure variance

when the oil is been produced before WBT but after it start to decrease in a constant way, which means that the permeability for the FW is increasing after each PV injected.

After 5PV of FW it was injected a SWA1 solution of FW and surfactant at 1% active component concentration. At the beginning of this flooding represented by the yellow line in the Figure 9 there was a production increase of oil, there is also a variation in the ΔP line. It took approximately one third of PV (100 minutes, 10 mL) to take effect on the core which can represent an interaction with the core minerals. After this sudden production and decrease of ΔP the curve starts to increase and stabilize to around 2500 mBar. The end point permeabilities for water in these floodings are stated in Table 4

Property	Unit	Value
PV	mL	33.6
Bulk Volume	mL	80.4
Porosity	fraction	0.42
Absolute permeability	mD	0.38
Swi	fraction PV	0.24
Soi	fraction PV	0.76
ko(Soi)	mD	0.31
Water flood		
So1	fraction PV	0.42
Kw @ So1	mD	0.14
Krw @ So1	fraction	0.45
Tertiary Surfactant Flood		
So2	fraction PV	0.39
Kw @ So2	mD	0.18
Krw @ So2	fraction	0.60

TABLE 4 DATA FOR CORE 1

Core 1 FW - SWA1

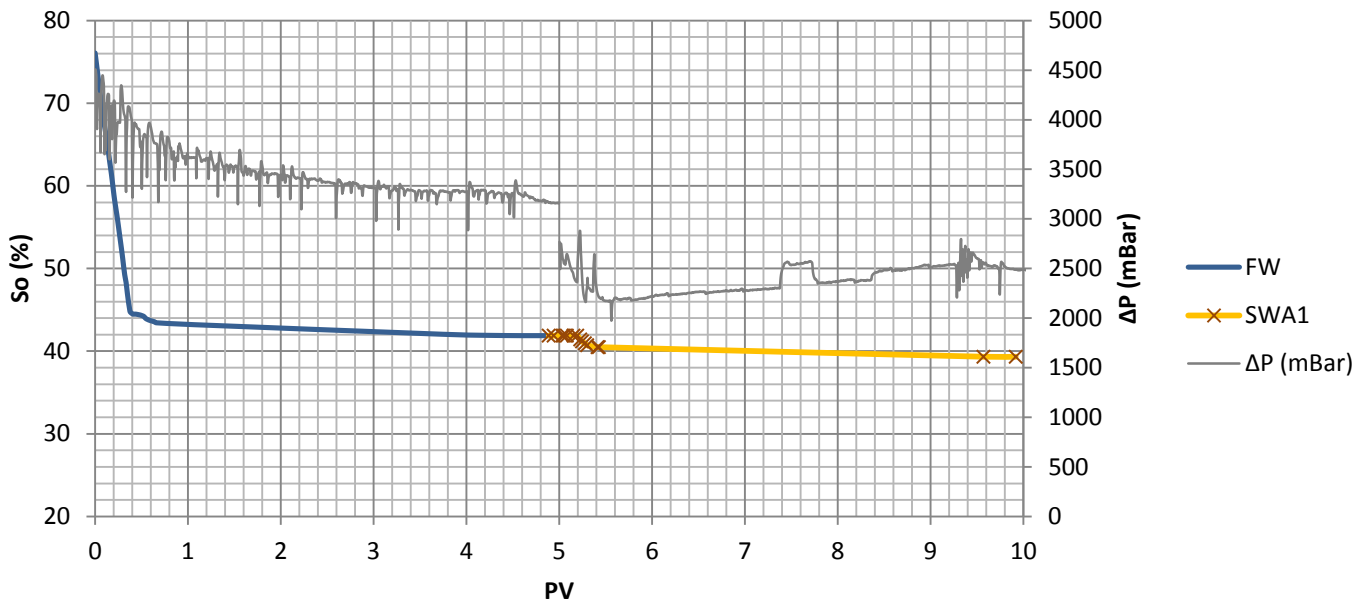


FIGURE 9 OIL SATURATION AND ΔP DURING FLOODING OF CORE 1 WITH FW AND SWA1

4.2 CORE 2

The data from the Core 2 is stated in Table 5

Secondary recovery by surfactant with wettability alteration properties SWA1 was carried out in this core, and after 5 PV the injection of surfactant is switched for surfactant with interfacial tension reduction properties SIFT2. SIFT2 was the result of the phase behavior analysis that is stated in chapter 3. The oil saturation curves and the ΔP curve are in Figure 10

At 0.74 S_o the surfactant flooding began. It produced only oil for 0.48 PV. After that traces of oil in the FW are received in the sampler. The ΔP curve decreases as SWA1 keeps flowing, which makes the effective permeability for the water to increase, as it should be. It is observed also before WBT the ΔP curve have very strong variations. At the end of SWA1 there are other variations, more specifically reductions in ΔP curve, possibly related to other activities realized in the lab. The pressure tends to stabilize around 3bars.

After 5 PV of SWA1 solution injected, the interfacial tension reduction solution SIFT2 was injected in the core. There was no important production for approximately 5 PV. The injection kept going for some PV's more to see if there was some increment, and less than a PV from 5 there was a sudden production which also has a reduction in the ΔP curve. In general the ΔP curve increased its values which might mean some sort of damage cause inside the core, as surfactant solution was injected this damage was increased. The ΔP seems to stabilize around 4bars, which bring the effective permeability for water to 0.12 which is lower than the one from the surfactant flooding for the secondary step with 0.16

Property	Unit	Value
PV	mL	33.1
Bulk Volume	mL	83.35
Porosity	fraction	0.40
Absolute permeability	mD	1.21
Swi	fraction PV	0.26
Soi	fraction PV	0.74
ko(Soi)	mD	0.35
Secondary Surfactant Flood		
So1	fraction PV	0.32
Kw @ So1	mD	0.16
Krw @ So1	fraction	0.13
Tertiary Surfactant Flood		
So2	fraction PV	0.31
Kw @ So2	mD	0.12
Krw @ So2	fraction	0.10

TABLE 5 DATA FOR CORE 2

Core 2 SWA1 - SIFT2

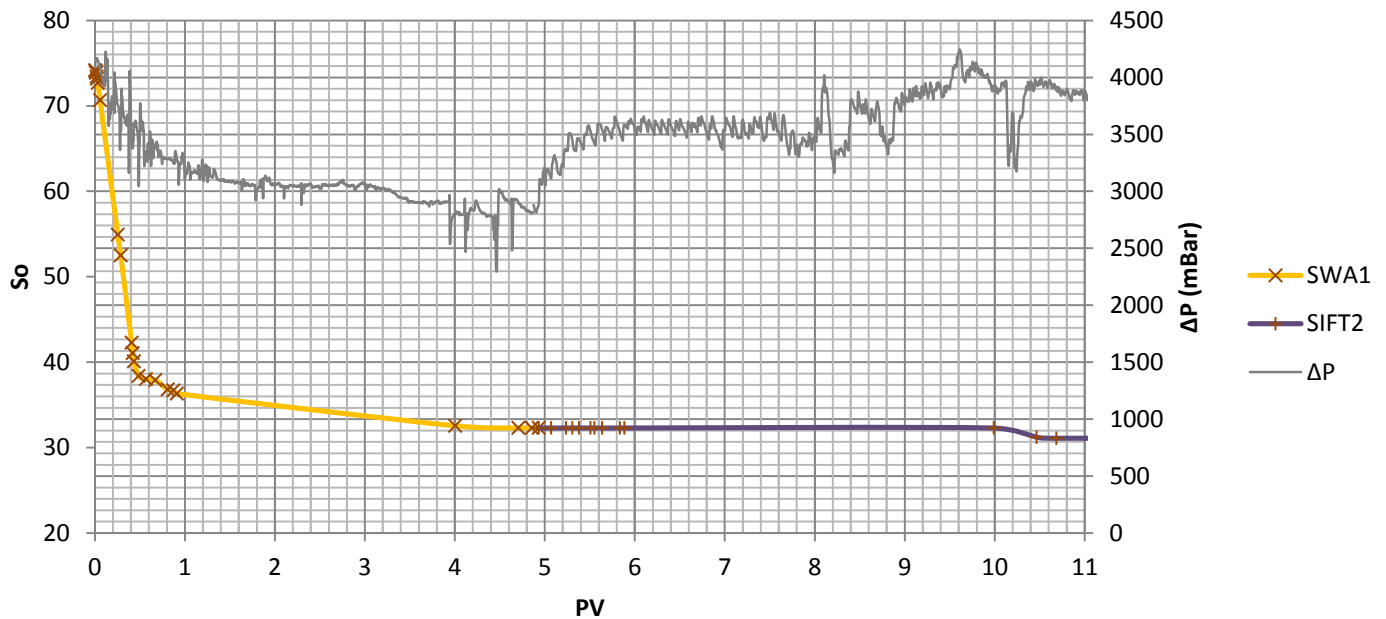


FIGURE 10 OIL SATURATION AND ΔP DURING FLOODING OF CORE 2 WITH SWA1 AND SIFT2

4.3 CORE 3

In the Core number 3 there was injected the SIFT2 as a secondary recovery while the SWA1 was injected as tertiary. In the Core 2 the effect of the SIFT2 could have been reduce by interactions with the SWA1 present in the core. So in this flooding it can be observed the effect of exchanging the sequence of these two surfactant systems.

In Figure 11, WBT in this case was in the sampler after 0.43 PV injected. We don't have more points due to the lab work hour's regulations for students, but in the ΔP curve there are many strong variations which in past cases meant some oil dragging. After 5 PV the system was still producing small amounts of oil in a constant manner, for that reason the time was extended for 3 PV more to observe this reaction.

Finally after 8 PV the injection of the surfactant SWA1 initiated, the production of oil continued with a slightly steeper curve for oil saturation while the ΔP suffer a very drastic decrease which will bring the permeability for water lower.

Property	Unit	Value
PV	mL	33.4
Bulk Volume	mL	81.48
Porosity	fraction	0.41
Absolute permeability	mD	1.08
Swi	fraction PV	0.22
Soi	fraction PV	0.78
ko(Soi)	mD	0.33
Secondary Surfactant Flood		
So1	fraction PV	0.29
Kw @ So1	mD	0.12
Krw @ So1	fraction	0.11
Tertiary Surfactant Flood		
So2	fraction PV	0.28
Kw @ So2	mD	0.16
Krw @ So2	fraction	0.15

TABLE 6 DATA FOR CORE 3

Core 3 SIF2 - SWA1

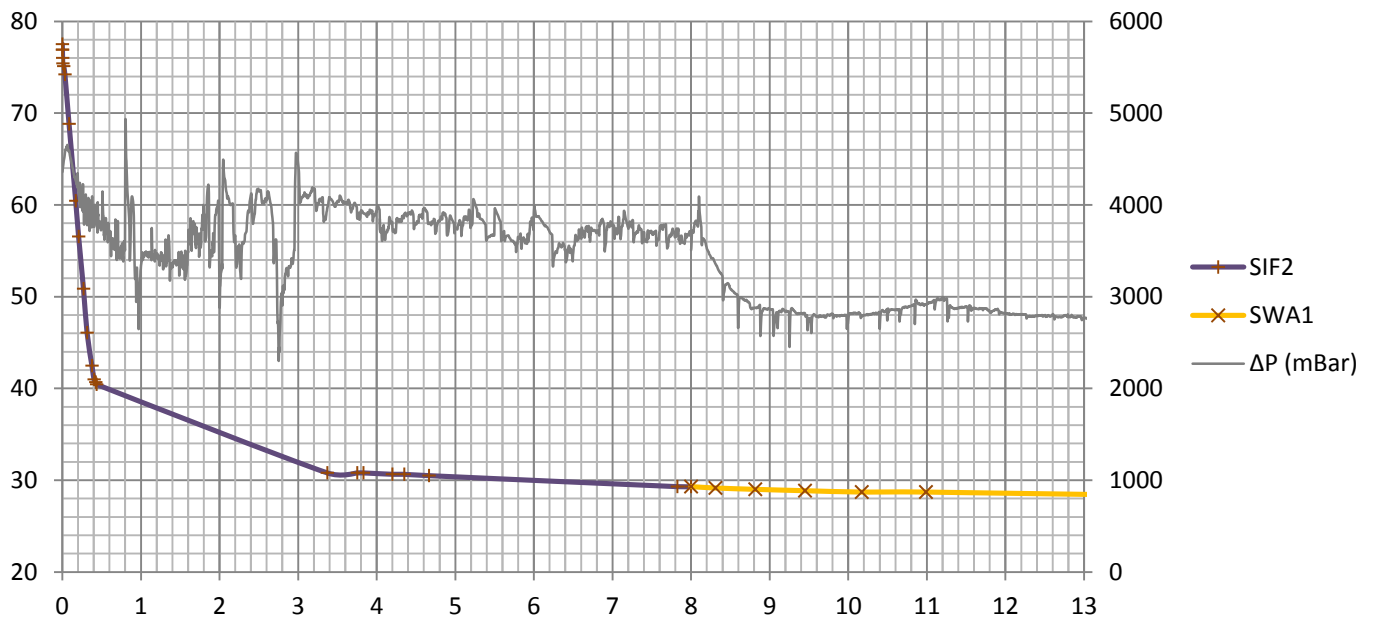


FIGURE 11 OIL SATURATION AND ΔP DURING FLOODING OF CORE 3 WITH SIF2 AND SWA1

4.4 CORE 4

Core 4 was applied a different surfactant with interfacial tension reduction properties. This one was not planned to be mixed with others. SIFT3. When flooding finished, it was injected formation water made by substituting the Cl ions for NO₃ to calculate the real residual water in the core. After each PV volume samples were taken and tested by titration to know the amount of Cl ions contained in the sample. The result showed that the real saturation of water inside the core is not affected by some solubilization of oil in water. Oil do dissolves on the FW but not in important amounts that should take into account.

The injection continued until 7.5 PV to observe an increment on production but it never happened. When the FW with NO₃ was injected there was not important oil production so it is not included in the graph.

In Figure 12 the ΔP curve maximum is around 7 bars. The oil decreased the permeability from very good for water to, not very good for oil. This data can be seen in Table 7. When oil was produced before WBT there are also variations on the ΔP curve after it was reached the limit for the sensor and we see a plane line, but it means the pressure was over that value. Then the pressure decreases increasing the permeability to water.

Property	Unit	Value
PV	mL	31.52
Bulk Volume	mL	79.16
Porosity	fraction	0.40
Absolute permeability	mD	2.38
Swi	fraction PV	0.31
Soi	fraction PV	0.69
ko(Soi)	mD	0.19
Secondary Surfactant Flood		
So1	fraction PV	0.33
Kw @ So1	mD	0.08
Krw @ So1	fraction	0.03

TABLE 7 DATA FOR CORE 4

Core 4 SIFT3

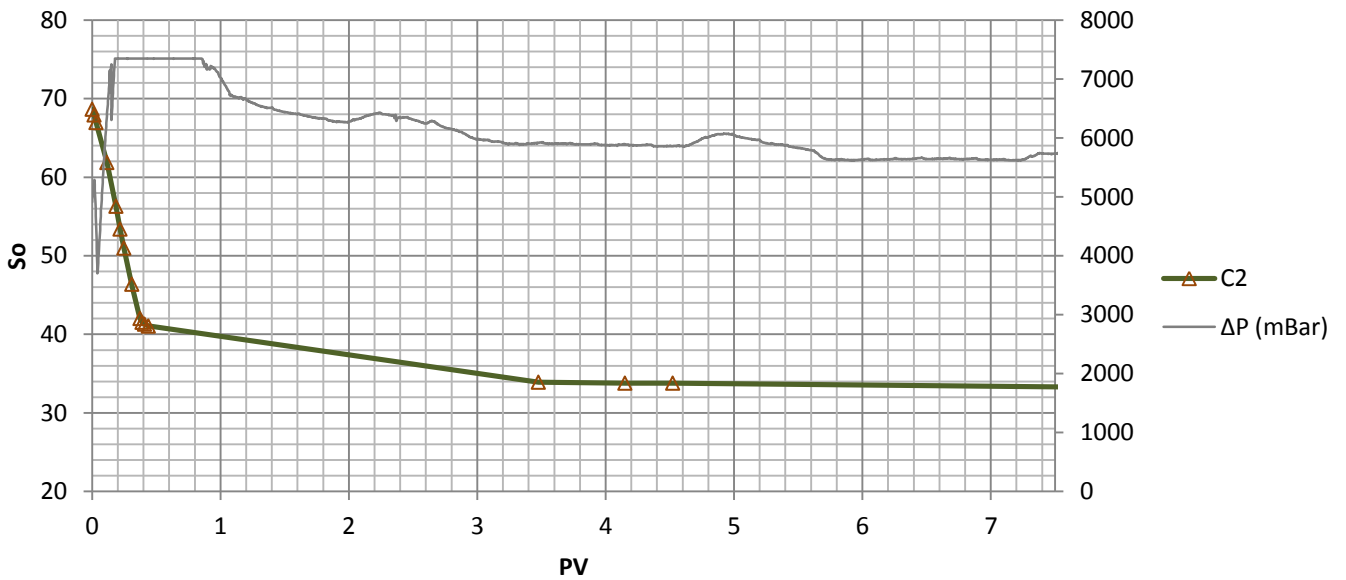


FIGURE 12 OIL SATURATION AND ΔP DURING FLOODING OF CORE 4 WITH SIFT3

4.5 CORE 5

Data for Core 5 can be seen on Table 8

Core 5 went to the normal process for PV measurement and cleaning of sulfates but for the aging process it had been aged for 5 times more than the cores 1-4, this means 450 Hrs of STO been injected at a rate of 0.07mL/min (225hrs in each direction). The longer aging time has been used to observe the behavior of the oil saturation curve with more oil wet rock when a surfactant with wettability alteration properties is used. In this rock we use the surfactant solution SWA1.

The WBT seems to be after about 0.5 PV (see Figure 13). The injection of SWA1 continued for more than 8 PV but there was no important production after 4 PV. The curve ΔP at the beginning of injection shows high variations when there is the highest production of oil. The curve decrease in a constant way until 6 PV then it slightly increases. This increase might mean the flow is starting to make some light damage in the rock.

Property	Unit	Value
PV	mL	31.52
Bulk Volume	mL	78.85
Porosity	fraction	0.40
Absolute permeability	mD	0.40
Swi	fraction PV	0.19
Soi	fraction PV	0.81
k(Soi)	mD	0.33
Secondary Surfactant Flood		
So1	fraction PV	0.39
Kw @ So1	mD	0.15
Krw @ So1	fraction	0.38

TABLE 8 DATA FOR CORE 5

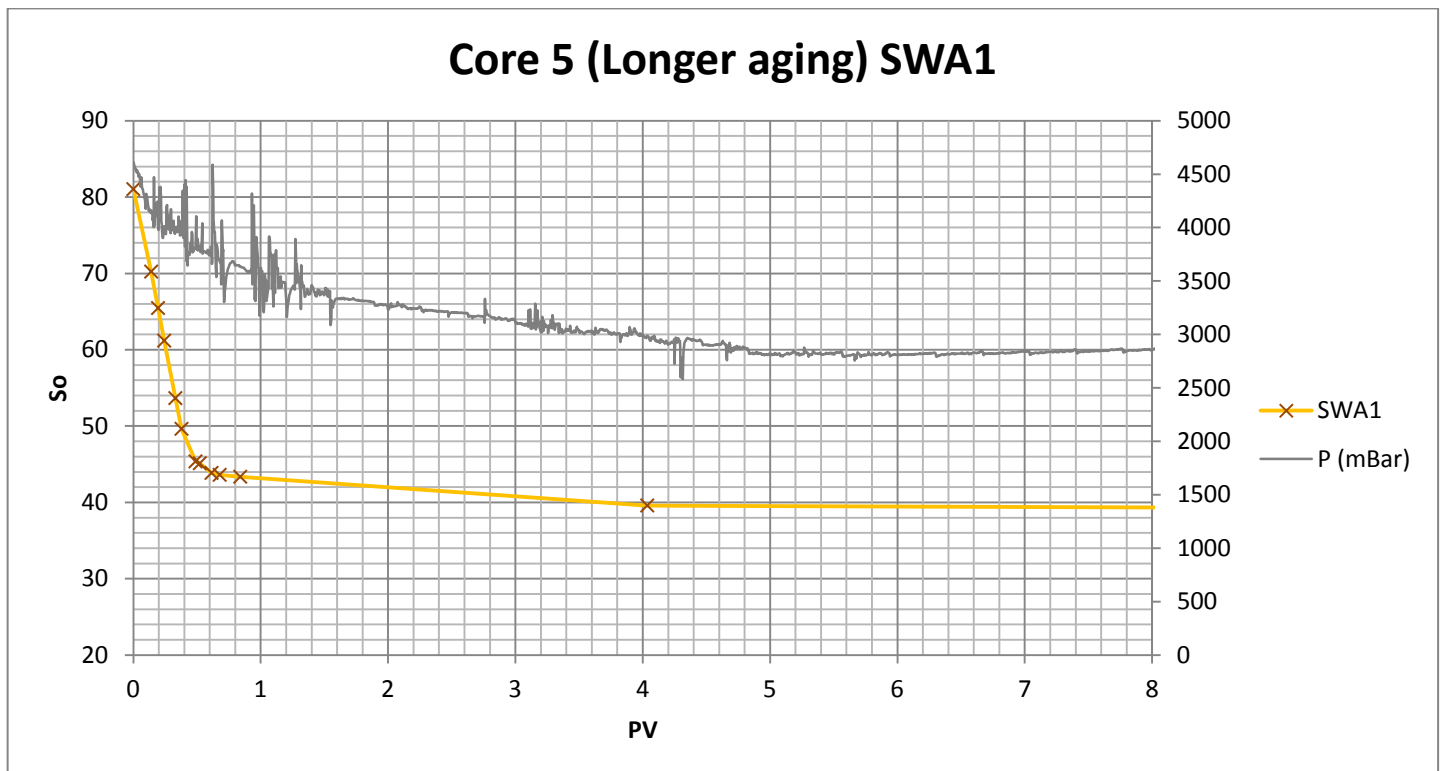


FIGURE 13 OIL SATURATION AND ΔP DURING FLOODING OF CORE 5 WITH LONGER AGING TIME AND WITH SWA1

5. DISCUSSION

In this chapter we compare the different performances of the surfactant systems applied on the cores. The aim is to find the best combination of system and to observe their behavior according to the sequence in the injection order.

5.1 FLOODINGS WITH 90 HRS AGING TIME

Comparison 90 Hrs Aging Time Floods

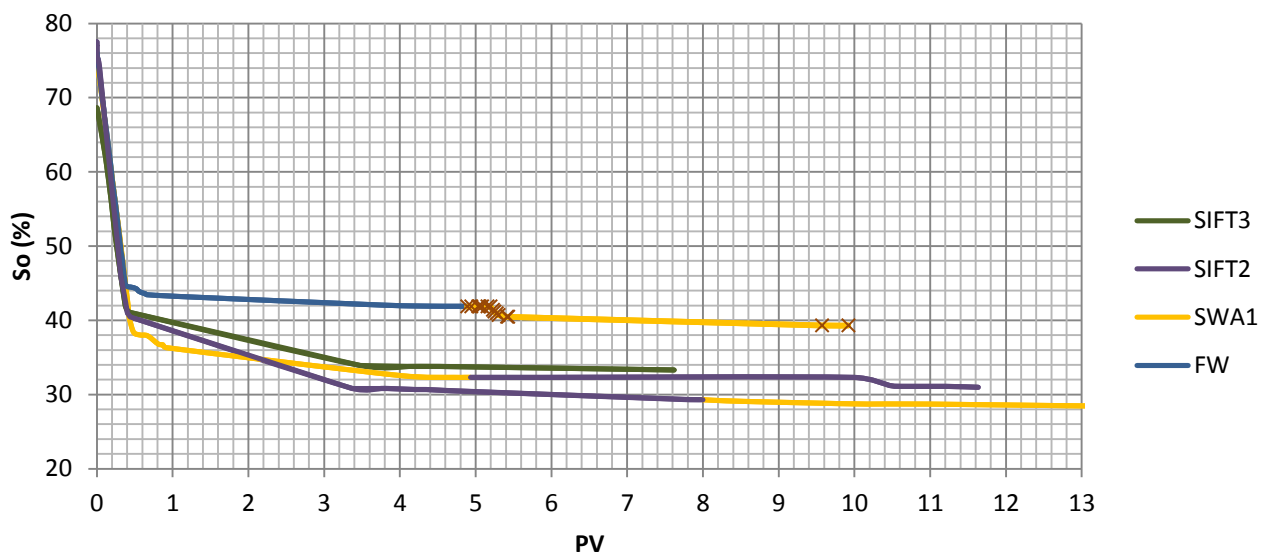


FIGURE 14 90 HRS AGING TIME CURVES FOR OIL SATURATION

When we compare the systems that had the same time for aging (see Figure 14) it is found that the earlier WBT is the SIFT2 system at 0.36 PV, even earlier than the FW and SIFT3 which have WBT at 0.38 PV and the last one is SWA1 at approximately 0.48 PV. The curve for SWA1 is showing the properties of the surfactant. The surfactant change the wettability to more water wet, then the time for water breakthrough is delayed because the water is also filling the small pores in the rock and covering the walls.

Sequences for SWA1 and SIFT2

According with the description from the experiments obtained for Core 2 (with SWA1 first) and Core 3 (with SIFT2 first) in the previous chapter the production of oil was more constant in the Core 3, and even after 8 PV still kept producing. After 8 PV when the injection was switched to SWA1 the slope was maintained. The big difference with the Core 2 is that the reduction of oil saturation stopped after 4 PV. Between these two system sequences could be very obvious that the best occurs when the surfactant with IFT reduction properties is applied. But since it seems there might been a damage in Core 2 (there is an increment of ΔP when it should decrease), then the data could be not trustable, the compatibility between these two surfactants is not a problem since there is no negative reaction in Core 3.

The surfactant solution SIFT3 did not show any improvement in the secondary oil recovery. Compared with the rest of the systems it doesn't seem very effective with this brine/oil system. It is actually the worst system because the initial permeability for that core was the highest in comparative with the rest of the cores. The K_{rw} at the end was the worst of all systems.

5.2 DIFFERENT AGING TIME COMPARISON (CORES 2 AND 5)

Comparing the aging on oil for SWA1 core floodings we can see there is an earlier WBT on the most aged one (Core 5). WBT is seen around 0.35 PV for Core 5 while in the Core 2 we can see WBT around 0.43. This reflects the influence on the aging time and the change of the wettability. When wettability changes to be more oil wetting then the surfactant solution tends to drag less oil. The oil is covering the small pores and the walls of the big pores. So the surfactant solution pushes only the oil from the center of big pores, and gets "faster" to the outlet.

The effect of the wettability modifier surfactant solution stopped after 5 PV with a K_{rw} of 0.38 after 8PV in Core 5 while for Core 2 the maximum K_{rw} was 0.13 after the secondary flood. The saturations for cores 2 and 5 in comparative are in Figure 15

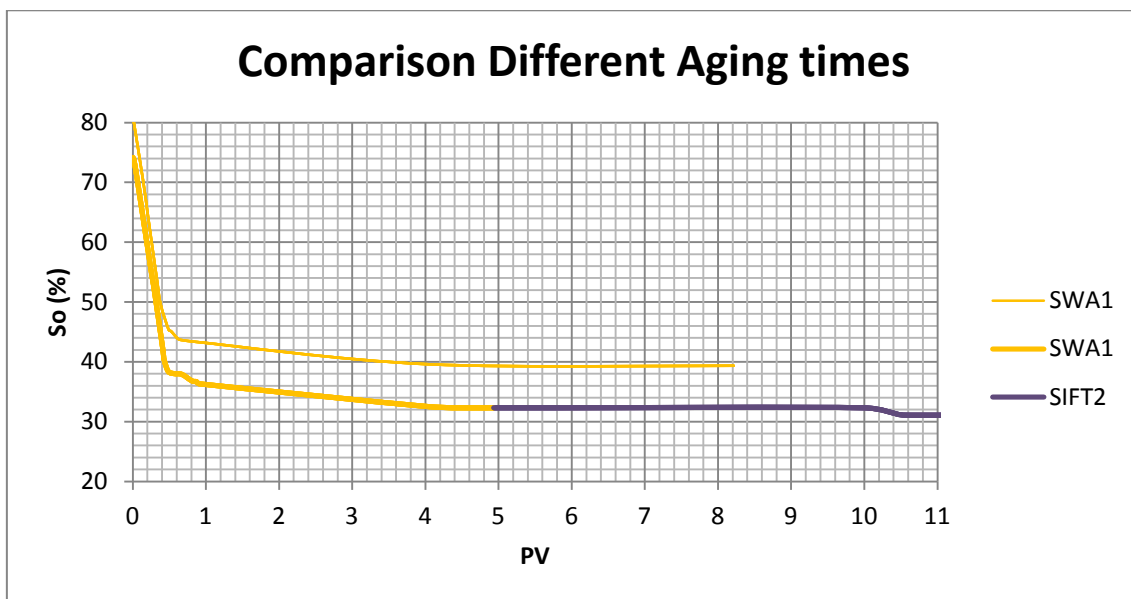


FIGURE 15 90 HRS AGING AND 450 AGING WITH SWA1

It is recommended to repeat the experiments and compare with the same sequence of systems, in order to avoid possible mistakes or damages that could have done to the core. Doing this, the error would be screened easily. Due to the long periods of time that the cores require for aging, and also because the rocks are too brittle, it becomes a process that requires a lot of time.

6. CONCLUSIONS AND FURTHER WORK

Wettability alteration vs water flood

- Wettability alteration system showed a recovery of 3 % additional to oil saturation in tertiary recovery against water flood in secondary recovery.
- Relative permeability increased at S_{or} in secondary recovery from 0.45 for water flood to 0.60 for wettability alteration process in tertiary recovery.
- Wettability alteration system showed a high efficiency as a tertiary process.
- The surfactant system with wettability alteration properties is more effective in rocks that are less water wet. The recovery showed for the less water wet core, it was more than 50% of the oil saturation, as a secondary recovery process compared with the less time aged core with 43%.

Interfacial tension reduction vs water flood

- The processes of interfacial tension reduction got a much higher reduction of oil saturation compared with water flood.

Comparison processes

- When we compare the two systems. The wettability alteration system reached lower oil saturation the first two PV. From there the most effective process seem to be the interfacial tension reduction since it kept reducing the oil saturation while wettability system stop producing oil.

Further work recommended

- Study potential for wettability alteration and IFT reduction by surfactants in chalk also at oil-wet conditions

- Study same surfactant processes for other carbonate reservoir.
- Carry out duplication of experiments of same type as presented in this thesis.

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8. APPENDIX A

Data table from all 5 cores

		Core				
		1	2	3	4	5
Property	Unit	Value	Value	Value	Value	Value
PV	mL	33.6	33.1	33.4	31.52	31.52
Bulk Volume	mL	80.4	83.35	81.48	79.16	78.85
Porosity	fraction	0.42	0.40	0.41	0.40	0.40
Absolute permeability	mD	0.38	1.21	1.08	2.38	0.40
Swi	fraction PV	0.24	0.26	0.22	0.31	0.19
Soi	fraction PV	0.76	0.74	0.78	0.69	0.81
ko(Soi)	mD	0.31	0.35	0.33	0.19	0.33
Secondary Flood						
So1	fraction PV	0.42	0.32	0.29	0.33	0.39
Kw @ So1	mD	0.14	0.16	0.12	0.08	0.15
Krw @ So1	fraction	0.45	0.13	0.11	0.03	0.38
Tertiary Surfactant Flood						
So2	fraction PV	0.39	0.31	0.28		
Kw @ So2	mD	0.18	0.12	0.16		
Krw @ So2	fraction	0.60	0.10	0.15		

TABLE 9 DATA FROM ALL 5 CORES