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Dedication

This thesis is dedicated to Street Children in Ghana as a contribution to the worthy course of fighting hunger, deprivation and poverty.

Acknowledgement

I express my sincere gratitude to God for giving me the needed strength and wisdom to complete this project. Further appreciation is extended to the government of Ghana for awarding me scholarship to study in the University of Stavanger (UiS). I would also want to thank Professor Ingebret Fjelde for his help, guidance, advice and kindness as my supervisor in this thesis. Finally, I express my profound gratitude to all International Research Institute of Stavanger (IRIS) laboratory personnel for their willingness to help me and keep my company in the laboratory during my experimentation.

Abstract

The influence of brine chemistry, salinity and composition on the retention of polar oil components onto reservoir rock mineral surface in relation to low salinity water flooding (LSWF) was studied and evaluated in this piece of work using ultra-violet visible (UV-Vis) spectroscopy. Five different brine compositions; sea water (SW), formation water (FW), LSW1 (FW diluted 100 times), LSW2 (FW diluted 1000 times) and KCl low salinity brine were studied and their effect on the retention of polar oil components was evaluated. Research was further extended to investigate the effect of the amount of acidic components in crude oil on the retention of polar oil components in LSWF. Two sets of diluted crude oil samples were investigated and evaluated; untreated stock tank oil (STO) and treated STO (Crude oil containing reduced amount of acidic components). Initial experiments were conducted to prepare a standard absorption curve and flooding experiments were carried out to study the retention of polar oil components. This thesis also evaluated the importance of the results obtained to field application.

It was observed in this work that the retention of polar oil components is a strong function of brine salinity and chemistry. The retention of polar oil components was highest when the reservoir rock in equilibrium with low salinity water (LSW1 and LSW2) was flooded with diluted STO. Earlier works stated that LSW1 and LSW2 contain higher total concentration of divalent cations onto the reservoir mineral surface than SW and FW. High total concentration of divalent cations onto reservoir rock minerals enables more polar components to be bonded onto the mineral surface through cation bridging. Also, generally, SW reported lower retention of polar oil components onto the reservoir rock surface compared to FW. SW contains less amount of Ca^{2+} than FW. In cation exchange, Ca^{2+} is given high replacing preference than other divalent cations such as Mg^{2+} which implies that Ca^{2+} plays a more significant role in cation bridging than Mg^{2+} which could also be the reason for the increased retention observed with FW than SW. KCl low salinity brine reported the lowest retention of polar oil components.

Two brine compositions (FW and KCl brine) were set up to investigate the effect of the amount of acidic components present in STO on retention of polar oil components. STO was treated with potassium silicate ($\text{Si}_2\text{O}:\text{K}_2\text{O}$) to reduce acidic components present. Results obtained indicated that retention of polar oil components was sensitive to the amount of acidic components present in STO. Retention of polar oil components was higher when the column was flooded with STO

containing reduced amount of acidic components. It has been reported in literature that an increase in base/acid ratio of STO decreases the stabilization of the water-film on the mineral surface due to increased attractive forces. The treated STO has high base/acid ratio due to the reduction of the amount of acidic components it contains. KCl brine reported the lowest retention of polar oil components because it contains no divalent cations to bond polar oil components onto the rock surface through multi-components ion exchange (MIE) and cation bridging.

This work is very useful for evaluating the low salinity effect of crude oils and reservoir rocks. It provides a simple, cheaper but effective technique of selecting the optimum salinity and composition of brine required to give good results in LSWF.

It was observed that there is retention of polar oil components during the flooding experiments. The retention of polar oil components was dependent on the composition of brine in equilibrium with the reservoir rock column. The amount of acidic components present in STO also affects the retention of polar oil components onto reservoir rock minerals. STO with reduced amount of acidic components reported higher retention of polar oil components compared to untreated STO.

Estimating retention with UV-Vis spectroscopy within 400nm wavelength could not detect all the polar components present. It is therefore recommended that further work should be carried out to measure retention within other ranges of wavelength. Also UV-Vis Spectroscopy do not give specific measurement of retention but it is only able to compare the amount of polar components in two samples. There is therefore the need to seek improvement by adopting methods capable of estimating retention of polar components more specifically.

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Nomenclature

Abbreviations

AN	Acid Number
CEC	Cation Exchange Capacity
COBR	Crude Oil/Brine/Rock
CPO	Cumulative Produced Oil
CSTO	Concentration of Stock Tank Oil
DF	Dilution Factor
EOR	Enhanced Oil Recovery
GC	Gas Chromatography
IFT	Interfacial Tension
IOIP	Initial Oil in Place
IOR	Improved Oil Recovery
LSWF	Low Salinity Water Flooding
MIE	Multi-Component Ion Exchange
MS	Mass Spectrometry
NSO	Nitrogen, Sulphur and Oxygen
OOIP	Original Oil in Place
PV	Pore Volume
UV-Vis	Ultra-Violet Visible

Symbols

The definition of each symbol is followed by its SI units

A	Absorbance, A
b	Path length of the cuvette, cm
c	Concentration of the solution, M
E	Overall displacement efficiency, volume fraction
E_D	Microscopic displacement efficiency, volume fraction
E_v	Macroscopic displacement efficiency, volume fraction
F_c	Capillary force, N
F_v	Viscous force, N
g	Gravity acceleration constant, cm/s^2
K	Absolute permeability, md
K_o	Effective permeability to oil, md
K_{ro}	Relative permeability to oil, md
K_{rw}	Relative permeability to water, md
K_w	Effective permeability to water, md
M	Mobility ratio, dimensionless
N_{ca}	Capillary number, dimensionless
P_c	Capillary pressure, mPa
P_{cow}	Oil-Water capillary pressure, mPa
P_o	Pressure of the oil phase, mPa
P_w	Pressure of the water Phase, mPa
r	Capillary radius, mm
S_o	Oil saturation, volume fraction or %
S_{or}	Residual oil saturation, volume fraction or %
S_{orw}	Residual oil to waterflood, volume fraction or %
S_{wi}	Initial water saturation, volume fraction or %
S_{wr}	Irreducible water saturation, volume fraction or %

V	Interstitial Velocity, cm/s
Θ	Contact angle, degrees
ε	Molar absorptivity, $M^{-1}cm^{-1}$
μ_o	Oil phase viscosity, cP
μ_w	Water phase viscosity, cP
ρ_o	Oil phase density, g/cm^3
ρ_w	Water phase density, g/cm^3
λ_d	Mobility of the displaced fluid, md/cP
λ_D	Mobility of the displacing fluid, md/cP
λ_i	Mobility of fluid phase i , md/cP
σ_{os}	IFT between oil and solid surface, dynes/cm
σ_{ow}	IFT between oil and water, dynes/cm
σ_{ws}	IFT between water and solid surface, dynes/cm
σ_x	Standard deviation, dimensionless
$\langle x \rangle$	Arithmetic mean, dimensionless

1. Introduction

Low salinity waterflooding (LSWF) is an enhanced-oil-recovery (EOR) technique in which the chemistry of the injected brine is controlled with the aim of improving oil recovery (Jerauld *et al.*, 2008). Waterflooding is applied worldwide to improve oil recovery. Experiments in the laboratory and field pilot applications have demonstrated that there is an improved recovery associated with LSWF compared to conventional waterflood practices. The technology of LSWF is fast gaining grounds in the industry because of its simplicity, low cost and environmental friendly benefits.

Unfortunately, there is no single widely accepted explanation to the numerous evidence of increased oil recovery associated with LSWF. Bernard (1967) explained that sweep efficiency improvements caused by clay hydration were responsible for the increased oil recovery. Tang and Morrow (1999) attributed the increased oil recovery to desorption of mixed-wet fines containing oil droplets from the pore walls when low salinity water is injected. McGuire *et al.* (2005) believed that oil recovery increase was due to in-situ surfactant generation by low salinity water injection. Lager *et al.* (2006) also suggested that multi-component ionic exchange (MIE) between the mineral surface and the invading brine is responsible for the reported improved oil recovery associated with LSWF.

Lack of a single plausible general mechanism to explain the basis for improved oil recovery observed in LSWF both in the laboratory and field pilot operations has craved the interest of various researchers and stakeholders. Over the past decade, research into LSWF has increased tremendously as seen in the various papers published annually and the conferences organized yearly. Intensive work by pioneers (Morrow, 1990; Jadhunandan and Morrow, 1995; Buckley *et al.*, 1998) and other authors paved the way for various research groups to build on and uncover new findings. As complex as the subject might seem, various successes has been achieved in the past decade even though there is still much to be understood on LSWF.

The mechanism by which wettability alteration affect oil recovery especially by LSWF has been studied by many authors (Morrow, 1990; Jadhunandan and Morrow, 1995; Tang and Morrow,

1997; Buckley *et al.*, 1998; Nasralla *et al.*, 2011) .Most of these authors believe that wettability alteration has an effect on oil recovery by LSWF. It is however not yet certain how wettability alteration directly or indirectly explains the improved recovery recorded in LSWF operations.

It has been reported by many authors (Morrow, 1990; Jadhunandan and Morrow, 1995; Basu and Sharma, 1997; Buckley *et al.*, 1998) that, desorption of polar oil components from the surface of rock mineral during LSWF could cause wettability alteration. The amount of polar components present in the crude oil and the conditions that favour the retention of these components could therefore have a pronounced effect on wettability of the mineral surface and therefore oil recovery by LSWF.

Cation exchange capacity of the mineral, the composition of the injected brine, the amount of polar components in the crude oil and the quality of the crude oil solvent have all been cited as factors that affect the retention of polar oil components during LSWF (Jadhunandan and Morrow, 1995; Basu and Sharma, 1997; Buckley *et al.*, 1998; Lager *et al.*, 2006). Fjelde *et al.* (2013) studied the retention of polar oil components on various reservoir rock minerals in equilibrium with brines at different salinities and composition.

UV-Vis spectroscopy gives the absorbance spectra of a compound in solution or as a solid (Oliva and Barron, 2010) . This method observes the absorbance of light energy or electromagnetic radiation, which excites electrons from the ground state to the first singlet excited state of the compound. The colour of crude oil is closely related to the amount of polar components it contains. The more polar components are present, the darker is the colour of the sample. The concentration of polyaromatic hydrocarbons (PAH) will also affect the absorption. Therefore, UV-Visible Spectroscopy can be applied to estimate the amount of polar components in an oil sample (Fjelde *et al.*, 2012). By applying UV-visible spectroscopy, it is possible to measure absorbance of the light.

This work is focused on using the UV-Vis spectroscopy analysis technique introduced by Fjelde *et al.* (2013) to study how the composition and chemistry of the injected brine and the amount of acidic components in the crude oil affects the retention of polar oil components onto reservoir rock mineral surfaces. This research was carried out to study mechanisms related to LSWF.

2. Problem Definition and Objectives

Problem Statement

LSWF is fast gaining popularity and attracting attention as an enhanced oil recovery (EOR) technique because of cost and environmental safety. Research is still ongoing to study some mechanisms related to LSWF as interest in the subject continue to grow over the past decade.

The wettability of a rock is greatly affected by the retention or adsorption and or desorption of polar oil components on the mineral surface. It has been documented in literature that improved recovery associated with LSWF is very sensitive to wettability changes (Jadhunandan and Morrow, 1995; Basu and Sharma, 1997; Buckley *et al.*, 1998). Unfortunately, there is no widely accepted mechanism that completely describes how wettability alteration affects recovery by LSWF and there is also no much understanding about the basic factors affecting the retention of polar oil components onto mineral surface during LSWF.

Objectives

The objectives of this research work are

1. To investigate the retention of polar oil components onto reservoir rock mineral surface in relation to LSWF.
2. To determine how the retention of polar oil components onto reservoir rock mineral surface is affected by the salinity and composition of the injected brine in equilibrium with the rock and the amount of acidic components present in the crude oil.

This thesis opens with the theory which present literature and explains fundamental concepts required to understanding the subject matter, then the experimentation processes are described and linked with the results obtained. Finally, the results from experiments are discussed in relation to the proposed objectives and field relevance.

3. Theory

3.0 General Introduction

This chapter introduces the fundamental concepts of oil recovery and how the various concepts discussed explain the subject of LSWF. The purpose is not to elaborate the details of all the subjects in oil recovery but to build a basic foundation that will introduce most of the terms required to adequately understand the subject matter of this thesis.

All concepts discussed assumes two phase oil-water system with each section explained in relation to LSWF.

3.1 Oil Recovery

Chronologically, Green and Willhite (1998) categorized oil recovery into three subdivisions: primary, secondary and tertiary recovery. However, because many reservoir production operations do not follow this chronological sequence, the term “tertiary recovery” is now replaced by a more complete term “enhanced oil recovery” (EOR). Another widely used term is “improved oil recovery” (IOR) which includes EOR but also encompasses other activities such as reservoir characterization, improved reservoir management, and infill drilling. Figure 1 shows a simple schematic representation of the sequential stages of oil recovery.

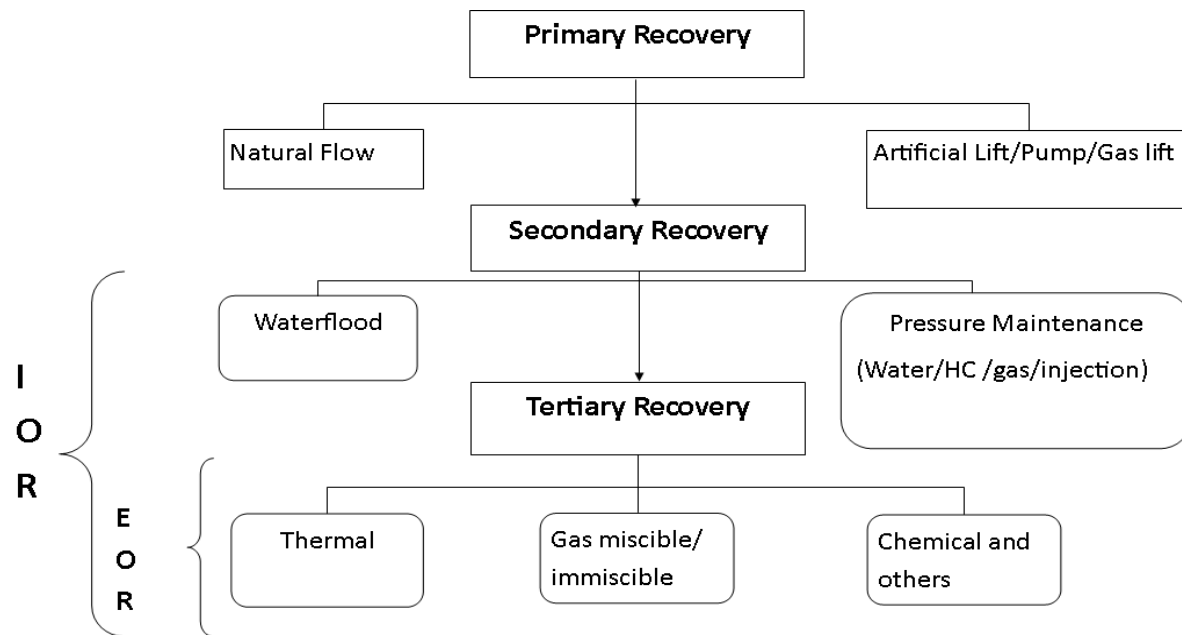


Figure 1 Sequential Stages of Oil Recovery (Stosur *et al.*, 2003)

3.1.1 Primary Recovery

In primary recovery, fluids are produced by the natural energy of the reservoir (Stosur *et al.*, 2003). Green and Willhite (1998) mentioned the underlying natural energy sources as;

- a) Solution-gas drive
- b) Gas-cap drive
- c) Natural water drive
- d) Fluid and rock expansion
- e) Gravity drainage

Primary oil recovery is usually between zero to over 50% of the original oil in place (OOIP), and it depends mainly on the type of hydrocarbon and the reservoir drive mechanism (Ali and Thomas, 1996).

3.1.2 Secondary Recovery

Secondary recovery is started when natural reservoir energy is depleted to the extent that there is no enough energy to commercially lift fluids (Green and Willhite, 1998). When natural energy of the reservoir falls, or becomes too small for economic oil recovery, energy need to be added to the reservoir to permit additional oil recovery (Stosur *et al.*, 2003). The additional energy is usually in the form of injected water or gas.

Secondary recovery is widely accepted to mean water flooding, and can vary from zero (oil sand) to a few per cent (heavy oils) to 20-50% of the initial oil in place (IOIP) for light oil (Ali and Thomas, 1996).

3.1.3 Tertiary Recovery (EOR)

When secondary recovery is no longer enough to support commercial fluid production, supplemental energy of a different kind permits additional oil recovery (Stosur *et al.*, 2003). This energy is usually added to the natural or physical displacement mechanisms of the primary or secondary methods. Improved fluid flow within the reservoir is usually induced by addition of heat, chemical interaction between the injected fluid and the reservoir fluids, mass transfer and/or altering the oil properties in such a way that the process enhances oil movement through the reservoir. They are often referred to as EOR processes.

Some of the frequently used EOR processes are (Green and Willhite, 1998);

- a) Mobility control processes (provides stable mobility ratios to improve macroscopic displacement efficiency e.g. polymer and foam injection).
- b) Chemical processes (chemicals injected to displace oil by interfacial tension (IFT) reduction, e.g. surfactant and alkaline injection).
- c) Miscible processes (injection of fluids that are miscible with the oil in the reservoir e.g. injection of hydrocarbon solvents or CO₂).
- d) Thermal processes (injection of thermal energy or in-situ generation of heat to improve oil recovery e.g. steam injection and in-situ combustion).
- e) Other processes e.g. microbial-based techniques, immiscible CO₂ injection and mining of resources at shallow depths.

3.1.4 Low Salinity Waterflooding (LSWF)

LSWF is an EOR technique in which the composition of the injected water is controlled with the aim of improving oil recovery (Jerauld *et al.*, 2008). Waterflooding is applied worldwide to improve oil recovery. Experiments in the laboratory and field applications demonstrated that, there is an improved recovery associated with LSWF compared to conventional waterflood practices.

LSWF may be applied either as a secondary recovery technique or as a tertiary recovery method (McGuire *et al.*, 2005; Lager *et al.*, 2008; Seccombe *et al.*, 2008). Low salinity water such as fresh water from rivers may be injected during initial stages of production with the aim of maintaining reservoir pressure and moving oil towards production wells for eventual production. In such a case, the purpose of injecting low salinity water is to sweep out the reservoir macroscopically. LSWF may also be employed as an EOR technique to reduce residual oil saturation in the reservoir rock. In this situation, the aim of applying LSWF is to increase microscopic sweep efficiency. However, the two processes are mostly connected.

3.2 Displacement Forces

Physically, three competing forces determine the flow of fluids in porous media.

- a) Capillary forces
- b) Viscous forces
- c) Gravity forces

The relative magnitude of these three competing forces determines whether fluids flows through the porous media or gets trapped.

3.2.1 Capillary Forces

When two immiscible fluids are in contact in the interstices of a porous medium, a pressure discontinuity exists across the curved interface separating the two fluids (Torsaeter and Abtahi, 2003). This difference in pressure P_c is the capillary pressure, which is pressure in the non-wetting phase minus the pressure in the wetting phase. Mathematically, capillary pressure can be expressed as

$$P_c = P_{non-wetting} - P_{wetting} \quad (3.1)$$

Thus, the capillary pressure may have either positive or negative values. For a two phase oil-water system, capillary pressure is defined as

$$P_c = P_o - P_w \quad (3.2)$$

Where P_c is the capillary pressure, P_o , P_w are the oil and water phase pressures respectively.

The capillary pressure in a typical oil/water system where oil is the non-wetting phase is further defined by Green and Willhite (1998) as

$$P_c = P_o - P_w = \frac{2\sigma_{ow}\cos\theta}{r} \quad (3.3)$$

Where σ_{ow} is the interfacial tension (IFT) across the oil and water interface, θ is the contact angle and r is the radius of the capillary or pore channel. The interfacial tension is the contractile force per unit length that exists at the interface of two immiscible fluids such as oil and water.

Strong capillary forces during water flooding might trap oil and cause relatively high residual oil saturation. From equation 3.3, trapping of oil can be reduced by lowering of the IFT by injection of surfactants or reducing $\cos\theta$ by inducing a wettability alteration.

LSWF may cause wettability alteration through desorption of polar oil components from the reservoir rock surface thereby affecting $\cos\theta$. McGuire *et al.* (2005) mentioned that LSWF leads to in-situ surfactant generation which causes eventual reduction of IFT and this will reduce capillary pressure and improve fluid flow.

3.2.2 Viscous Forces

Viscous forces in a porous medium increases the magnitude of the pressure drop that occurs when a fluid flows through the medium (Green and Willhite, 1998). Fluid flows through a porous medium when the viscous force dominates the capillary and gravity forces.

The viscous force is related to the capillary force through the dimensionless group called capillary number. The capillary number is defined for water displacing oil as

$$N_{ca} = \frac{F_v}{F_c} = \frac{v\mu_w}{\sigma_{ow}\cos\theta} \quad (3.4)$$

Where, N_{ca} is the capillary number, F_v represents the viscous forces, F_c is the capillary force, v is the interstitial velocity and μ_w is the viscosity of the water phase.

From equation 3.4, high capillary number is required to displace fluids. According to Green and Willhite (1998), waterfloods operates at conditions where $N_{ca} < 10^{-6}$. At these value of N_{ca} , residual oil cannot be displaced by water. However, if N_{ca} can be increased to say $N_{ca} > 10^{-5}$, residual oil can be mobilized. N_{ca} is usually increased by increasing the interstitial velocity, by increasing the injectant viscosity (adding polymers), by reducing the IFT (injecting surfactants) or inducing a wettability change to reduce the contact angle.

Injecting low salinity water into the formation will reduce the IFT between water and oil (McGuire *et al.*, 2005). LSWF may also cause desorption of polar oil components from the pore walls, altering the wettability of the mineral surface. Therefore LSWF could increase N_{ca} and enhance fluid flow through the porous medium.

3.2.3 Gravity Forces

Gravity forces are dominant in reservoirs where there exists high density difference between the coexisting fluids (injected and displaced fluids) or in cases where there exist a low IFT between the fluids in contact.

According to Torsaeter and Abtahi (2003), the hydrostatic pressure of a liquid with density ρ is dependent on the elevation z as follows

$$\frac{dP}{dz} = \rho g \quad (3.5)$$

For an oil-water system, the capillary pressure then becomes

$$\frac{dP_c}{dz} = (\rho_w - \rho_o)g \quad (3.6)$$

Where, ρ_w and ρ_o are the water and oil phase densities respectively and g is the acceleration due to gravity.

Gravity segregation will occur when density difference between injected and displaced fluids are so significant to induce a component of fluids flow in the vertical direction even when the main direction of fluid flow is expected in the horizontal plane (Green and Willhite, 1998).

Low salinity water has lower density than high salinity water (Fjelde *et al.*, 2012). Injecting low salinity water into the reservoir could therefor cause gravity segregation depending on the difference between the injected brine and the formation brine. However, when a large field is considered, the effect of this segregation could be negligible compared to other forces acting on the fluids.

3.3 Wettability

Wettability is the tendency of one fluid to preferentially adhere to a solid surface in the presence of a second fluid (Green and Willhite, 1998). When two immiscible fluid phases are placed in contact with a solid surface, one phase usually is attracted to the solid more strongly than the other phase. The more strongly attracted phase is called the wetting phase.

Rock wettability has an impact on the nature of fluid saturations and the general relative permeability characteristics of a fluid/rock system (Green and Willhite, 1998). Changes in the wettability of a rock will affect the electrical properties, capillary pressure, relative permeability, dispersion, and simulated EOR (Anderson, 1986).

3.3.1 Measurement and Types of Wettability

Contact angle is the best wettability measurement method especially when pure fluids and artificial cores are used since there is no tendency of the measured wettability getting altered by surfactants or other compounds (Anderson, 1986). It is not possible to measure contact angle in porous media because of the difficulty in obtaining smooth surfaces. However, contact angle measurements can be used to study mechanisms in the laboratory.

When a drop of water is placed on a surface in contact with oil, a contact angle is formed with values ranging from 0 to 180° [0 to 3.14 rad] (Anderson, 1986). A typical oil/water/solid system is shown in Figure 2. The surface energies in the system are related by Young's equation,

$$\sigma_{ow} \cos \theta = \sigma_{os} - \sigma_{ws} \quad (3.7)$$

Where, σ_{ow} is the IFT between oil and water, σ_{os} is the IFT between oil and solid surface, σ_{ws} is the IFT between water and the solid surface and θ is the contact angle measured.

By convention, the contact angle θ is measured through the water. As shown in Figure 2, when the contact angle is less than 90° [1.6 rad], the surface is preferentially water-wet, and when it is greater than 90° [1.6 rad], the surface is said to be preferentially oil-wet. Table 1 summarizes the approximate relationship between wettability and contact angle presented by Anderson (1986). However, Morrow (1990) mentioned that reservoir wettability is not a simply defined property and therefore classification of reservoirs as either water-wet or oil-wet is oversimplification. This is because reservoir rock surfaces are made up of different combination of minerals with each section of the rock surface presenting different wettability to the fluids in contact with the rock.

Table 1 Relationship between Wettability and Contact Angel (Anderson, 1986)

	Water-wet	Neutrally wet	Oil-wet
Contact angle (Minimum)	0°	60-75°	105-120°
Contact angle (Maximum)	60-75°	105-120°	180°

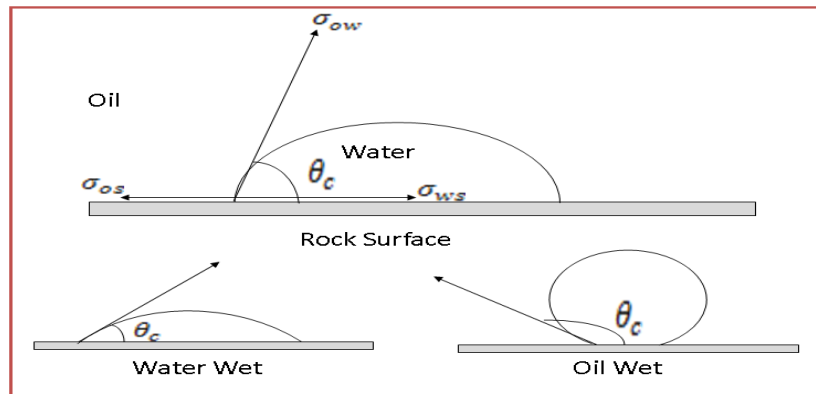


Figure 2 Wettability of Oil/Water/ Solid system (Anderson, 1986)

3.3.2 Mechanism of Wetting Alteration by Crude Oil

Basu and Sharma (1997) and Buckley *et al.* (1998) mentioned that crude oil can be separated into two components on the scale of polarity:

- I. The heavy polar components fraction (mainly asphaltenes and resins), which is the major surface-acting components.
- II. The oil which acts as the solvent environment for the polar fraction.

In a crude oil/brine/rock system, Buckley *et al.* (1998) identified four main associations:

- Polar interactions: polar components such as asphaltenes adsorb directly onto the rock surface in the absence of water film.
- Surface precipitation: asphaltenes and other heavy components precipitate out of the crude oil to act on the rock surface. This association is likely to be more pronounced in poor solvent crude oils.
- Acid/base interactions: will occur where charges at oil/brine and brine/rock interfaces changes the pH of the system.
- Ion binding: divalent ions such as Ca^{2+} and Mg^{2+} tend to bind oil components to brine and rock.

Any conditions that favour these interactions can render the rock more oil-wet and the water film becomes very unstable as the oil components gain access to the rock surface. Basu and Sharma (1997) studied the effect of salinity on the thin water film and they realized that increasing salinity of brine actually made the film less stable and the surface more oil-wet. Also both Basu and Sharma (1997) and Buckley *et al.* (1998) and many other authors in literature agrees that most of the surface activity is directly associated with the amount of polar components in the crude oil.

3.3.3 Wettability Effects on Recovery by LSWF

The mechanism by which wettability alteration affect oil recovery especially by LSWF has been studied by many authors (Morrow, 1990; Jadhunandan and Morrow, 1995; Tang and Morrow, 1997; Buckley *et al.*, 1998; Nasralla *et al.*, 2011). One of the explanations proposed is the electric double layer mechanism.

The electric double layer mechanism proposes that the rock surface is overlain by a thin film of water and the wettability of the rock depends on the stability of this thin water film (Morrow, 1990). A stable thin water film will render the rock surface more water-wet. For the thin water film to be stable, the oil/brine and brine/rock interfaces must have the same polarity. The film thickness which has been found to be generally much less than 100nm, is determined by a balance between Van der Waals attractive forces and repulsion by electrostatic and hydration forces.

Nasralla *et al.* (2011) explained that change of electric charge at oil/brine and brine/rock interface caused by low salinity water is the primary reason for wettability alteration on mica surfaces. They reported from laboratory experiments that low salinity water increases repulsion of the oil/brine and brine/rock interfaces and renders the rock more water-wet which then is the cause of increased recovery.

3.4 Relative Permeability and Capillary Pressure Curves

Fluid saturation distribution and fluid flow through porous media are strongly affected by the relative permeability and capillary pressure relationships (Green and Willhite, 1998). Recent advances in reservoir modeling also tried to investigate the effects of salinity on capillary pressure and relative permeability curves.

3.4.1 Relative Permeability curves

Relative permeability is defined as the ratio of the effective permeability of the fluid at a given saturation to a base permeability (Amyx *et al.*, 1960). The base permeability may be defined as absolute permeability, K , the permeability of the porous medium saturated with a single fluid, air permeability, K_{air} or effective permeability to non-wetting phase at irreducible wetting phase saturation.

Mathematically,

$$K_{ro} = \frac{K_o}{K} \quad (3.8)$$

$$K_{rw} = \frac{K_w}{K} \quad (3.9)$$

Where, K_{ro} and K_{rw} are the relative permeability of the porous medium to oil and water respectively. K_o and K_w , are the effective permeability of oil and water respectively and K is the permeability at 100% saturation of one of the fluid phases.

Typical relative permeability curves for water-wet and oil-wet rocks, as function of wetting phase saturation are presented in Figure 3.

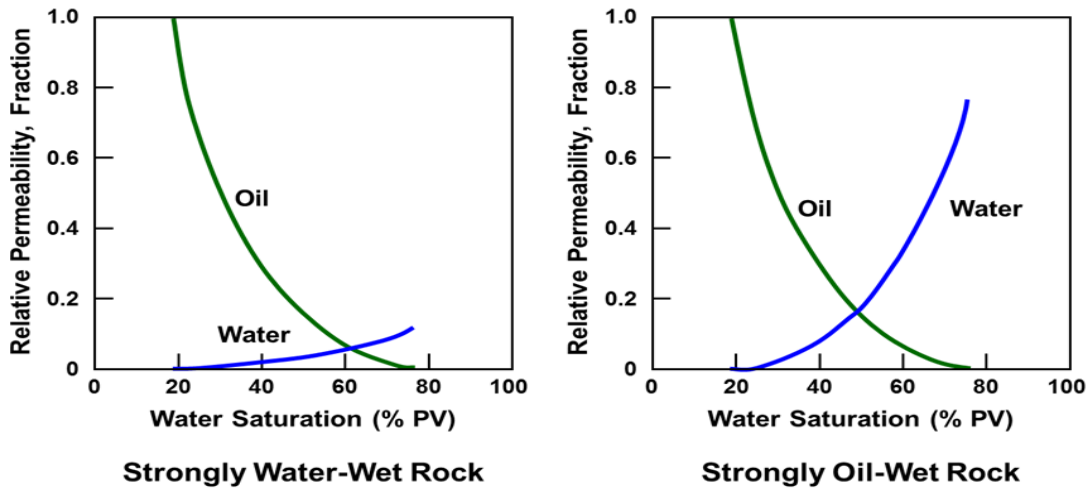


Figure 3 Relative Permeability Curves, Water-wet and Oil-Wet (Glover, 2013)

In a strongly oil-wet system, water is expected to flow easier than in a strongly water-wet system. Some of the factors that affect relative permeability are; fluid saturations, geometry of the pore spaces and pore size distribution, wettability and fluid saturation history (imbibition or drainage).

3.4.2 Salinity Effects on Relative Permeability curves

Jerauld *et al.* (2008) studied the effect of salinity on relative permeability and capillary pressure curves. They modeled the salinity dependence of relative permeability and capillary pressure curves with simple empirical correlations. These correlations give a good background and understanding of fluid flow in LSWF.

Some assumptions of the model:

1. Salt is modeled as an additional single-lumped component in the aqueous phase. Salt can therefore be injected and tracked and also the viscosity and density of the aqueous phase is dependent on salinity.
2. Relative permeability and capillary pressure are a function of salinity but this dependence disappears at high and low salinities. High and low-salinity relative permeability curves are made inputs and shapes are then interpolated between.

Equations of the model:

$$K_{rw} = \theta K_{rw}^{HS}(S^*) + (1 - \theta)K_{rw}^{LS}(S^*), \quad (3.10)$$

$$K_{row} = \theta K_{row}^{HS}(S^*) + (1 - \theta)K_{row}^{LS}(S^*), \quad (3.11)$$

$$P_{cow} = \theta P_{cow}^{HS}(S^*) + (1 - \theta)P_{cow}^{LS}(S^*), \quad (3.12)$$

$$\theta = (S_{orw} - S_{orw}^{LS}) / (S_{orw}^{HS} - S_{orw}^{LS}), \quad (3.13)$$

$$S^* = (S_o - S_{orw}) / (1 - S_{wr} - S_{orw}), \quad (3.14)$$

Where K_{rw} and K_{row} is water and oil relative permeability respectively, P_{cow} is oil/water capillary pressure, S_o is oil saturation, S_{orw} is residual oil to waterflood, S_{wr} is irreducible water saturation and θ is a dimensionless measure of low-salinity Vs. high salinity character. HS and LS indicate high salinity and low salinity respectively.

θ , has a value between 0 and 1. θ is 0 at low salinity and 1 at very high salinity. Interpolation is made between low salinity and high salinity relative permeability and capillary pressure curves depending on the value of θ chosen. Figure 4 is a typical graph depicting the salinity dependence of relative permeability curves.

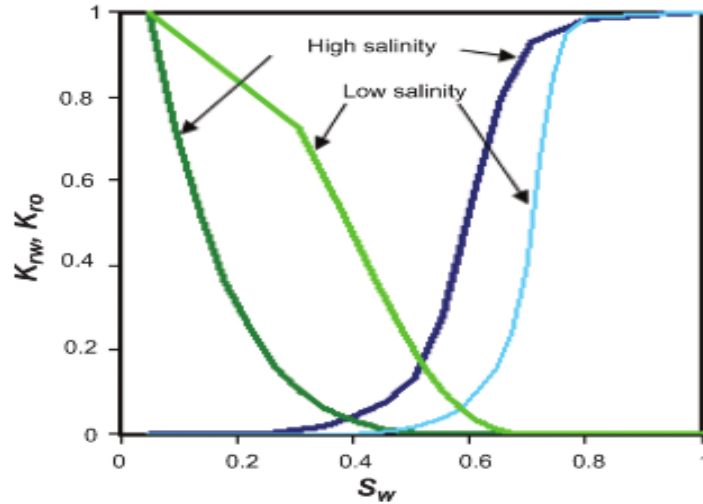


Figure 4 High and Low salinity relative permeability Curves (Jerauld *et al.*, 2008)

3.5 Oil Recovery and Relative Permeability Curves

The overall displacement efficiency of an oil recovery displacement process can be viewed as the product of microscopic and macroscopic displacement efficiencies (Green and Willhite, 1998). In equation form,

$$E = E_D E_v \quad (3.15)$$

Where E = overall displacement efficiency, E_D = microscopic displacement efficiency expressed as a fraction and E_v = macroscopic (volumetric) displacement efficiency expressed as a fraction.

Microscopic displacement implies the mobilization of oil at the pore scale (Green and Willhite, 1998). Thus, E_D can be viewed as a measure of the effectiveness of the displacing fluid in moving the oil within spaces in the rock where the displacing fluid interacts with the oil. E_D is reflected in the magnitude of the residual oil saturation, S_{or} , in the regions contacted by the displacing fluid. E_D can be defined as

$$E_D = \frac{(1 - S_{or})}{(1 - S_{wi} - S_{or})} \quad (3.16)$$

Where S_{wi} is the initial water saturation.

Macroscopic displacement efficiency describes how effective the displacing fluid(s) is contacting the reservoir in a volumetric sense (Green and Willhite, 1998). E_v is a measure of how effectively the displacing fluid sweeps out the volume of a reservoir, both areally and vertically, as well as how effectively the displacing fluid moves the displaced oil towards the production wells.

3.5.1 Mechanisms of Secondary Recovery

The aim of supplementary recovery is to increase the natural energy of the reservoir, usually by displacing hydrocarbons towards the producing wells with some injected fluid (Dake, 1978). The most common fluid injected is water because of its availability, low cost and high specific gravity which facilitates injection.

The basic mechanics of oil displacement can be understood by first studying the mobility ratio of the fluids. The mobility ratio of any fluid is defined as

$$M = \frac{\lambda_D}{\lambda_d} \quad (3.17)$$

Where mobility of the fluid phase, λ_i , is defined as

$$\lambda_i = \frac{K K_{ri}}{\mu_i} \quad (3.18)$$

And where, λ_D = mobility of the displacing fluid phase and λ_d = mobility of the displaced fluid phase.

The mobility ratio, M, is a dimensionless quantity. The mobility ratio, affect both areal and vertical sweep, with sweep decreasing as M increases for a given volume of fluid injected (Green and Willhite, 1998). Also, M affects the stability of a displacement process with flow becoming unstable when $M > 1.0$.

If $M \leq 1$ it means that, under an imposed pressure differential, the oil will be able to travel with a velocity equal to, or greater than that of the water (Dake, 1978). Since it is the water which is pushing the oil, there is therefore, no tendency for the oil to be by-passed which results in the sharp interface between the fluids.

3.5.2 Influence of EOR on Relative Permeability curves

Tertiary flooding targets recovering the oil remaining in the reservoir after a conventional secondary recovery project, such as water drive project (Dake, 1978). Dake (1978), explains how

EOR techniques could have effect on the relative permeability curves, Figure 5. After an ideal water drive K_{ro} is zero when $S_o = S_{or}$, point A, and the oil will not flow. Two possibilities for improving the situation and initiating fluid flow;

The oil is displaced with fluids soluble in it. This will result in the increase of oil saturation above S_{or} . This is equivalent to moving from point A to B on the normal relative permeability curve which eventually produces a finite K_{ro} and the oil becomes mobile.

Another option is to use fluids that can reduce interfacial tension or have the ability to alter properties between oil and fluids. This method involves the use of miscible or semi-miscible fluids to reduce the residual oil saturation to a very low value, S'_{or} .

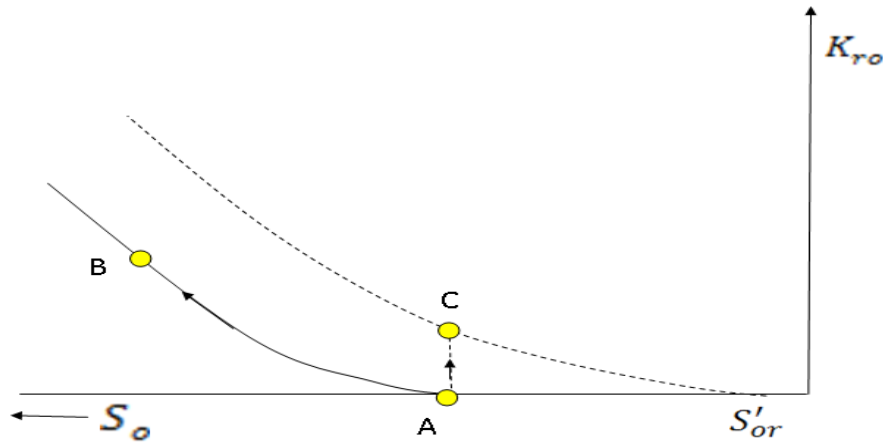


Figure 5 Illustrating two methods of mobilizing remaining oil after conventional waterflood (Dake, 1978)

One of the mechanisms of LSWF (McGuire *et al.*, 2005) proposes that during LSWF, the IFT between injected fluid and the oil is reduced leading to the mobilization of residual oil.

3.6 Crude Oil/Brine/Rock Interactions

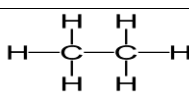
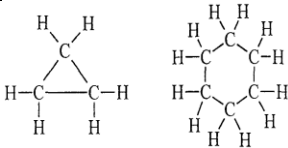
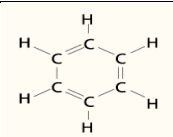
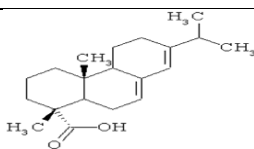
The interaction between crude oil, brine and the reservoir rock are very complex (Jadhunandan and Morrow, 1995; Basu and Sharma, 1997). Therefore studying the various components involved in this reactions and interactions is crucial to understanding some of the mechanisms underlying oil/brine/rock reactions. Oil recovery by waterflooding and LSWF is strongly dependent on the interactions between oil, brine and rock. No single explanation exist as to how these interactions affect recovery by LSWF and this even makes it more important to consider. Retention of polar oil components is also a strong function of both physical and chemical reactions between oil, brine and the reservoir rock.

3.6.1 Crude oil

Crude oils are complex mixtures of hydrocarbons and polar organic compounds of oxygen, sulphur and nitrogen and sometimes also contains metal-containing compounds such as vanadium, nickel, iron and copper (Skauge *et al.*, 1999). Crude oils have many components of different structures and no two oils are exactly the same in their composition.

There are four major groups of compounds which are commonly present in crude oil: paraffins, naphthenes, aromatics, resins and asphaltenes. Table 2 gives examples of crude oil components.

Table 2 Chemical Composition of Crude Oil

Compound	Examples	Properties
Paraffins (C_nH_{2n+2})		Straight and branched chains
Naphthenes (C_nH_{2n})		Closed ring structures
Aromatics (C_nH_{2n-6})		Basic hexagonal ring structures
Resins and Asphaltenes		Fused aromatic rings; NSO impurities

3.6.2 Brine

The composition and chemistry of both connate brine and injected brine has been shown to have effect on crude oil/brine/rock interaction, wettability, interfacial tension, relative permeability and capillary pressure curves (Jadhunandan and Morrow, 1995; Basu and Sharma, 1997).

Typical compounds used to prepare synthetic brines in the laboratory include water, NaCl, Na_2SO_4 , $NaHCO_3$, KCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$ and $SrCl_2 \cdot 6H_2O$. Examples of these synthetic brines are formation water (FW), Sea water (SW), and low salinity waters (LSW).

The presence of some divalent cations such as Ca^{2+} and Mg^{2+} could greatly affect the wettability of reservoir rocks and therefore influence recovery of oil (Anderson, 1986).

Effect of Brine on Retention of Polar Components

According to Fjelde *et al.* (2012) and Omekeh *et al.* (2012), brines with high total concentration of divalent cations onto the rock surface will give high retention of polar oil components in aging with crude oils. Polar oil components are held onto the rock surface by these cations through cation bridging.

3.6.3 Sandstone Rocks

Sandstones are clastic sedimentary rocks composed mainly of sand-sized minerals or rock grains (Alden, 2013). The formation of sandstones involves two main stages. First, a layer or layers of sand accumulate as a result of sedimentation either from water (stream, lake or sea) or from air (as in a desert). Finally, the sand becomes sandstone when it is compacted by pressure or overlying deposits and cemented by the precipitation of minerals within the pore space or between the sand grains.

Sedimentology

Sandstones consist of mainly two types of materials according to Alden (2013);

- a) The matrix: Very fine material, which is present within interstitial pore space between the framework grains.
- b) Cement: Mineral matter introduced later that binds the siliclastic framework grains together.

Mineralogy

The two dominating minerals in sandstone are quartz and feldspar (Alden, 2013). The other minerals are clays, hematite, ilmenite, amphibole, mica, lithic fragments, biogenetic particles and heavy minerals.

The cement materials are mainly calcite, quartz (silica), clays and gypsum. They either bind the matrix or fill in pore space.

Clay Minerals

Clay minerals are hydrous aluminium phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths and other cations (Alden, 2013).

There main groups of clay minerals are:

1. **Kaolinite group** - includes kaolinite, dickite, nacrite, and halloysite; formed by the decomposition of orthoclase feldspar (e.g. in granite).
2. **Illite group**- also includes hydrous micas, phengite, brammalite, celadonite, and glauconite (a green clay sand); formed by the decomposition of some micas and feldspars; predominant in marine clays and shales.
3. **Smectite group**- also includes montmorillonite, bentonite, nontronite, hectorite, saponite and sauconite; formed by the alteration of mafic igneous rocks rich in Ca and Mg; weak linkage by cations (e.g. Na^+ , Ca^{2+}) results in high swelling/shrinking potential.
4. **Glauconite**: Glauconite is a greenish mineral of the mica group, a hydrous silicate of potassium, iron, aluminum, and magnesium, usually found in sedimentary rocks as an accessory mineral (Merchant, 2009). A typical chemical representation of glauconite is $(\text{K,Na})(\text{Al,Fe,Mg})_2(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2$. Glauconite can contain high amounts of Smectite which is an expanding clay mineral when it comes into contact with water (Deer, 1992).
5. **Vermiculite**

About 97% of all petroleum reservoirs contain clay minerals and silica fines (Hill, 1982). These clays are platey and rod-like structures that are loosely attached to the sand grains of the reservoir. The size of clay particles is defined as less than four microns in diameter, whereas the size of migratory fines may be as large as 50 microns. These small particle sizes result in high surface areas, making clay minerals to react readily and rapidly with fluids introduced into a sedimentary rock.

3.7 Proposed Mechanisms underlying LSWF

Since Martin (1959) first observed that the composition of the flood water and the presence of clay could affect oil recovery, the studies of LSWF has been widely accepted with several authors, institutions and companies proposing different mechanisms to explain the process. Over the past years, several mechanisms have been proposed and several papers have been written on the subject to either support some of the proposed mechanisms or refute them. With studies keep intensifying each year, there has not been a widely accepted mechanism to explain the process of LSWF. It is therefore safe to take notice that all the proposed mechanisms discussed here are still widely opened to debate.

3.7.1 Clay Hydration

Bernard (1967) attributed increased recovery observed for fresh water floods compared to brine in experiments performed on both synthetic cores and outcrop cores to the hydration of clay. He explained that, the fresh water causes clay in the rock to swell and the pore space available to oil and water is decreased leading to increased recovery. He further explained that, the observed increase in recovery could have been caused by the dispersion of clay into fine particles by fresh water. These particles move along the created channels of flow and subsequently plug them up. New flow channels are established after the flow channels are completely or partially plugged. Additional oil is recovered as these new channels are flooded out. He therefore concluded that, when hydratable clays are present, a fresh floodwater can produce more oil than brine. The fresh water hydrates the clays and lowers the permeability as a result of which the floodwater generates a relatively high pressure drop.

3.7.2 Fine Migration

Tang and Morrow (1999) proposed that the migration of clay fines could be the major reason for the observed increased in recovery associated with LSWF. They mentioned that, in water flooding, crude oil can remain as drops which adhere to fines at the pore walls as part of the trapped oil fraction during displacement. The mixed-wet clay particles are removed from the pore walls with the flowing oil and get deposited at the oil-water interface. When low salinity water is injected, the electrical double layer in the aqueous phase between particles is expanded and the tendency of the floodwater to remove fines is increased and so oil recovery is increased. They also assumed that, partial removal of mixed-wet fines from pore walls to give locally heterogeneous wetting might have also been a possible cause of the observed increase in recovery.

However, Lager *et al.* (2006) reported that experience gained from BP LSWF corefloods, showed increased recovery with no observations of fine migration or significant permeability reductions.

3.7.3 Saponification

McGuire *et al.* (2005), reported that the generation of surfactants from the residual oil at elevated pH levels is major LSWF recovery mechanism. They explained that, as low salinity water is injected into the core, hydroxyl ions are generated through reactions with the minerals native to

the reservoir and pH is increased to about 7 to 8 range up to pH of 9 and more. The increased in pH therefore causes the process to behave in a similar way like alkaline flooding, reducing IFT between the reservoir oil and water, increasing the water wettability of the reservoir and therefore resulting in incremental recovery of oil. They also mentioned that, low salinity water injected into the reservoir appear to alter the properties of crude oil.

McGuire *et al.* (2005) also tried to use the mechanism of saponification to explain why not so much high recovery was observed in the case of high salinity waterflooding. They explained that, in high salinity processes, presence of divalent cations (Ca^{2+} and Mg^{2+}) will precipitate the natural surfactants in crude oils and prevent them from increasing oil recovery. Low salinity water will always have low concentrations of these divalent cations. Provided the low salinity water is quite soft, the surfactants remain effective.

It has been reported in literature that a high acid number ($\text{AN} > 0.2$) is needed to generate enough surfactants to reduce wettability reversal and/or emulsion formation. There is however reported cases of improved oil recovery by LSWF with crude oils with acid numbers $\text{AN} < 0.05$. Also Lager *et al.* (2006) reported that, experiments on North Slope core sample only showed an increase in pH from 5-6 with an increase in oil recovery. They also mentioned that most reservoirs contain CO_2 and H_2S gases which will act as a pH buffer, rendering an increase of pH up to 10 unlikely.

3.7.4 Multi-Component Ion Exchange (MIE)

Lager *et al.* (2006) cited that multicomponent ion exchange occurring between the brine, oil and rock surface could be the possible mechanism that explains the observed increased in oil recovery associated with LSWF. They explained that, on an oil-wet surface, multivalent cations at a clay surface will bond to polar compounds present in the oil phase (resin and asphaltenes) forming organo-metallic complexes. At the same time, some organic polar compounds will be adsorbed directly to the mineral surface thereby enhancing the oil wetness of the clay surface. During the injection of low salinity brine, MIE will take place, removing organic polar compounds and organo-metallic complexes from the surface and replacing them with uncomplexed cation. This will make the clay surface more water-wet and result in improved oil recovery.

The mechanism of MIE could explain some of the interesting observations made in the studies of LSWF over the past years such as (Lager *et al.*, 2006):

1. Why LSWF does not work when a core is acidized and fired as the cation exchange capacity of the clay mineral might have been destroyed.
2. Why LSWF has no effect on mineral oil as no polar compounds are present to strongly interact with the clay minerals surface.
3. Why there is no direct relationship between the oil acid number and the amount of oil recovered.

3.7.5 Electric Double Layer (EDL)

BP workers Lee *et al.* (2010) proposed and tried to validate a mechanism called the electric double layer mechanism. They mentioned that the distribution of ions around clay particle forms a double layer; an adsorbed layer close to the clay surface and a diffuse layer containing ions which are in Brownian motion. During wettability restoration, the polar and ionic species within the crude oil can be attracted or adsorbed to the surface through some defined interactions. For a negative clay surface, positive charge molecules will be adsorbed strongly and in the presence of multivalent ions, negative charged adsorbates may also be held by cation bridging. They mentioned that, during LSWF, the divalent cations are exchanged for monovalent cations which no longer hold the oil to the surface. The water layer adjacent to the surface then thickens as the double layer expands as the salinity decreases driving the clay surface more water-wet and more oil is recovered.

Nasralla *et al.* (2011) also conducted studies that support the electric double layer mechanism.

3.7.6 Chemical Mechanism

Austad *et al.* (2010) recently proposed a chemical mechanism to explain some of the processes observed in LSWF. They assumed that, at reservoir conditions, the pH of formation water is about 5 due to dissolved acidic gases like CO₂ and H₂S and therefore initially both acidic and basic organic materials are adsorbed onto the clay together with inorganic cations, especially Ca²⁺, from the formation water. The clay therefore acts as a cation exchanger with relatively large surface area. When low salinity water is injected into the reservoir with an ion concentration much lower than that of the initial formation brine, the equilibrium associated with the brine-rock interaction is disturbed, and a net desorption of cations, especially Ca²⁺, occurs.

To compensate for the loss of cations, protons, H^+ , from the water close to the clay surface adsorb onto the clay, a substitution of Ca^{2+} by H^+ then takes place. This creates a local increase in pH close to the clay surface. A fast reaction between OH^- and the adsorbed acidic and protonated basic material will cause desorption of organic material from the clay. This eventually improves the water wetness of the rock and increased oil recovery is observed.

This mechanism seems to be an extension of the MIE mechanism proposed by Lager *et al.* (2006). Studies are still on going to affirm or refute this mechanism.

3.7.7 Conditions Required for LSWF

With many proposed mechanisms of LSWF, there are still no clear-cut worldwide accepted criteria for applying LSWF.

Lager *et al.* (2006) explained that both crude oil and clay-bearing reservoir rocks are required for low salinity effect. They reported that low salinity effect is not seen in strongly water-wet, clay-free porous media with mineral oil.

Seccombe *et al.* (2008) also mentioned that recovery by LSWF is a function of water chemistry and formation mineralogy. They tried to correlate Kaolinite content of the rock and LSWF recovery.

Studies conducted on LSWF almost share some common background even though some of them still disagree with one another. Some of the conditions necessary for effective application of LSWF can be summarized as follows:

1. Presence of clay minerals (Kaolinite)(Lager *et al.*, 2006; Seccombe *et al.*, 2008).
2. Crude oil containing polar components (Lager *et al.*, 2006).
3. Weakly water-wet surface (Jadhunandan and Morrow, 1995; Nasralla *et al.*, 2011; Fjelde *et al.*, 2012)
4. Optimal temperature and pressure (Nasralla *et al.*, 2011)
5. Presence of connate brine with multivalent ions (Lager *et al.*, 2006).

The presence of these conditions does not guarantee that improved recovery will be observed by LSWF. The process of LSWF is more complex and no single explanation exists to describe its conditions fully.

3.8 Some Mechanisms Governing Retention of Polar Oil Components

Many authors (Crocker and Marchin, 1988; Jadhunandan and Morrow, 1995; Skauge *et al.*, 1999; Nasralla *et al.*, 2011) all agree that the wettability of a rock is a strong function of the amount of polar components present in the crude oil. Therefore any condition which directly or indirectly affects the wettability of a crude oil/ brine/ rock (COBR) system will also affect the retention of polar oil components on the rock surface and vice versa. From these deductions, it has been reported that the retention of polar oil components in a COBR system is closely affected by the type and quality of crude oil, the composition of brine, initial water saturation S_{wi} , aging temperature, the amount of divalent cations (Ca^{2+} and Mg^{2+}) present and the type of rock (Jadhunandan and Morrow, 1995).

3.8.1 Influence of Crude Oil

The composition and quality of crude oil affects the retention of polar oil components (Jadhunandan and Morrow, 1995; Buckley *et al.*, 1998; Skauge *et al.*, 1999). Crude oil with high composition of asphaltene and resins will retain more on reservoir rocks through direct adsorption and drive the COBR system towards a more oil-wet condition (Crocker and Marchin, 1988). Similarly polar oil components will easily precipitate out of a crude oil with poor solvent component and get adsorbed directly on the rock surface (Buckley *et al.*, 1998). Heteroatom (NSO) compounds have been indicated as relatively more strongly adsorbed and hence more important in wettability behaviour. Crude oils containing more NSO compounds makes a COBR system most oil-wet than those containing less NSO compounds (Crocker and Marchin, 1988). Oil with high degree of aromaticity would be expected to contain a larger content of polar compounds as the polarity of the oil as a solvent increases with increasing aromatic content. Oil with high paraffinic character would not be a good solvent for polar components and it is expected to contain low concentration of NSO compounds and asphaltenes (Skauge *et al.*, 1999). Retention of polar oil components is higher for crude oil with high base/acid ratio. An increase in acid number is expected to increase the stability of the water film covering the rock surface due to increased repulsive forces between the oil-water and the rock-water interfaces. Similarly an increase in the base number is expected to decrease the stabilization of the water-film due to increased attractive forces.

3.8.2 Effect of Brine Composition

The composition of brine also affects the retention of polar oil components. Experiments conducted by Jadhunandan and Morrow (1995) revealed that adsorption of polar oil components on rock surfaces depends strongly on the amount of calcium, Ca^{2+} present in the brine. Adsorption of polar oil components was higher for a system containing high concentrations of Ca^{2+} . Studies conducted by Fjelde *et al.* (2012) and Omekeh *et al.* (2012) also indicated that retention of polar oil components is high for systems with high total divalent ion concentration. More polar components are held to the rock surface through cation bridging and ion binding.

3.8.3 Aging Temperature

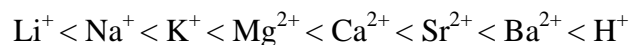
Experiments conducted by Jadhunandan and Morrow (1995) indicated that high aging temperature drives a COBR system towards more oil-wet. Nasralla *et al.* (2011) also studied the adsorption of oil components on mica surfaces and found that high aging temperature was associated with an equally high adsorption of oil components onto mica surfaces.

3.8.4 Initial Water Saturation

The initial water saturation in equilibrium with the rock has also been found to closely affect the retention of oil components on rock surfaces (Jadhunandan and Morrow, 1995). Increase in initial water saturation decreases the adsorption of oil components on rock surfaces. Experiments conducted by Crocker and Marchin (1988) also found that adsorption of oil components on wet Berea resulted in values up to one-third as much as those for the dry Berea. Therefore initial water saturation is also a basic requirement for retention of polar oil components on rock surfaces.

3.8.5 Cation Exchange Capacity and Type of Rock

Cation exchange capacity (CEC) of clay is the ability of clay minerals to exchange cations adsorbed to the naturally negative charged external surfaces and between the layers of the clay structure (Hamilton, 2009). CEC is a measure of the clay's ability to attract and hold cations from a solution. The forces that attract and hold the cations in solution are electrostatic and van der Waals forces. Some cations will be adsorbed more strongly than other cations. The relative replacing power of a particular cation depends on its strength of binding. According to (IDF, 1982), the relative replacing power of cations at room temperature is:



3.8.6 Interaction between Irons and Mineral Surfaces during LSWF

According to Lager *et al.* (2006), cation exchange processes can affect four different possible mechanisms of organic matter adsorption onto clay mineral surface during LSWF. These four adsorption mechanisms includes; cation exchange, ligand bonding and cation and water bridging.

Cation Exchange

Adsorption by cation exchange occurs when molecules containing quaternized nitrogen or heterocyclic ring replace exchangeable metal cations initially bound to clay surface (Lager *et al.*, 2006). In this process, cations of like charge are exchanged equally between a solid surface such as clay and a solution, such as brine containing various ions.

Ligand Bonding

Ligand bonding basically describes the direct bond formation between a multivalent cation and a carboxylate group (Lager *et al.*, 2006). These bonds are stronger than cation bridging and cation exchange bonds. Ligand bonding often will lead to the detachment of organo-metallic complexes from the mineral surface.

Cation Bridging

Cation bridging is a weak adsorption mechanism and mostly forms between polar functional group and exchangeable cations on the clay surface (Lager *et al.*, 2006). This mechanism is more effective when there is high total divalent cation on the clay surface.

Water Bridging

Water bridging involves the complexation between the water molecule solvating the exchangeable cation and the polar functional group of the organic molecule (Lager *et al.*, 2006). Water bridging mostly occurs if the exchangeable cation is strongly solvated (i.e. Mg^{2+}).

4. Pre-Experimental Work

4.0 Brief Introduction

This chapter seeks to introduce the various methods and approaches adopted in the experiments conducted in this work and further justifies the reasons for which those particular techniques were chosen from a pool of similar available techniques. The processes are described briefly with emphasis on their limitations and capabilities. The chapter ends with introduction to error analysis where the various methods of quantifying error in experimental work are analyzed.

4.1 Evaluation of Methods used for determination of Polar Oil Components

Some methods by which polar components in oil can be determined both qualitatively and quantitatively include:

1. Mass spectrometry (MS)
2. Gas chromatography (GC)
3. UV-visible spectroscopy (UV-Vis) and
4. Visual observation of colour changes

These approaches can analyze the amount of polar organic compounds qualitatively present in oil or their total concentration.

4.1.1 Mass Spectrometry (MS)

Mass spectrometry is an analytical tool used for measuring the molecular mass of a sample (Ashcroft, 2012). The functionality of mass spectrometers can be divided into three fundamental parts:

1. The **ionisation source**: inside the ionisation source, the sample molecules are ionised.
2. The **analyser**: The ions are extracted into the analyser region of the mass spectrometer where they are separated according to their mass (m) -to-charge (z) ratios (m/z).
3. The **detector**: The separated ions are detected and this signal sent to a data system where the m/z ratios are saved and stored together with their relative abundance for presentation in the format of a m/z spectrum.

The molecular masses for large samples such as biomolecules can be measured to within an accuracy of 0.01% of the total molecular mass of the sample (Ashcroft, 2012). For small organic molecules, the molecular mass can be measured to within an accuracy of 5 ppm or less. This

approach was not selected for analysis in this work because there is no MS instrument available at IRIS laboratory.

4.1.2 Gas Chromatography (GC)

Gas Chromatography (GC) is used to separate volatile components of a mixture. The GC process can be explained as follows (See Figure 6) (Murphy, 2013).

A small amount of the sample to be analyzed is injected into the injector and the injector is set to a temperature higher than the boiling point of the component. Components of the mixture evaporate into the gas phase inside the injector. A carrier gas, such as helium, flows through the injector and pushes the gaseous components of the sample onto the GC column. Within the column, separation of the components takes place. After components of the mixture move through the GC column, they reach a detector. Ideally, components of the mixture will reach the detector at varying times due to differences in the partitioning between mobile and stationary phases. The detector sends a signal to the chart recorder which results in a peak on the chart paper. The area of the peak is proportional to the number of molecules generating the signal.

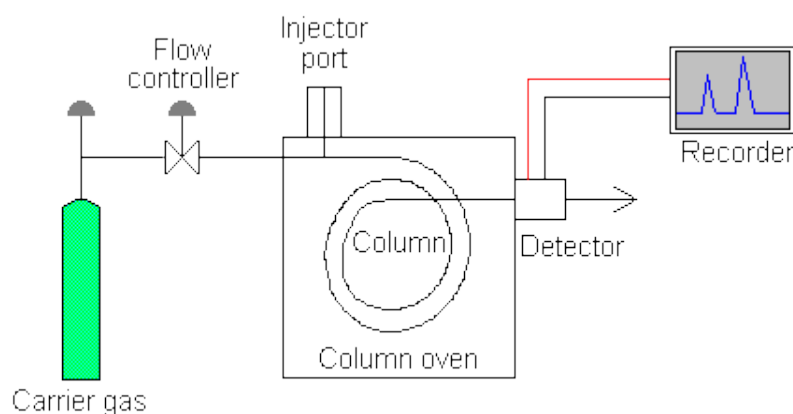


Figure 6 Gas Chromatography (Murphy, 2013)

The procedure is usually well suited for compositional analysis of organic material, thus it can be applied for the determination of the composition of oil. The range of detectability and accuracy depends on the detector used. GC method can detect only volatile compounds. Most of the components in crude oil are not volatile.

4.1.3 UV-Visible Spectroscopy (UV-VIS)

Ultraviolet-visible (UV-vis) spectroscopy is used to obtain the absorbance spectra of a compound in solution or as a solid (Oliva and Barron, 2010). This technique observes the absorbance of light energy or electromagnetic radiation, which excites electrons from the ground state to the first singlet excited state of the compound. The UV-vis region of energy for the electromagnetic spectrum covers 1.5 - 6.2 eV which also corresponds to a wavelength range of 800 - 200 nm. The Beer-Lambert Law (Equation 4.1) is the principle underlying absorbance spectroscopy. Absorbance A (arbitrary units, A) of a single wavelength is proportional to b , the path length of the cuvette or sample holder (usually 1 cm) and c , the concentration of the solution (M) and all are related by the molar absorptivity of the compound or molecule in solution ϵ , ($M^{-1}cm^{-1}$).

$$A = \epsilon bc \quad (4.1)$$

There are three types of absorbance instruments used to collect UV-vis spectra:

1. Single beam spectrometer.
2. Double beam spectrometer.
3. Simultaneous spectrometer.

A typical UV-Vis instrument has a light source (usually a deuterium or tungsten lamp), a sample holder (the cuvette) and a detector, but some have a filter for selecting one wavelength at a time (Oliva and Barron, 2010). Figure 7 is an illustration of the single beam instrument which has a filter or a monochromator between the source and the sample to analyze one wavelength at a time.

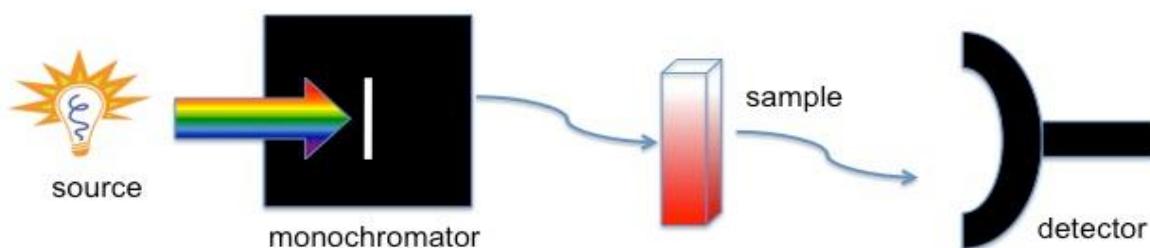


Figure 7 Illustration of a single beam UV-vis instrument (Oliva and Barron, 2010)

Information that can be extracted from a UV-Vis Spectroscopy

Both qualitative and quantitative information of a given compound or molecule can be obtained from UV-Vis spectroscopy (Oliva and Barron, 2010). It is however advisable to use a reference cell to zero the instrument for the solvent in which the compound is dissolved. To extract quantitative information on the compound, the instrument should be calibrated using known concentrations of the compound in question in a solution with the same solvent as the unknown sample.

To construct an acceptable calibration curve, at least three or more concentrations of the compound will be required (Oliva and Barron, 2010). The selected concentrations should start at just above the estimated concentration of the unknown sample and should go down to about an order of magnitude lower than the highest concentration.

The colour of crude oil is a function of the amount of polar components it contains. The more polar components are present, the darker is the colour of the sample. Therefore, UV-Visible Spectroscopy can be applied to estimate the amount of polar components in an oil sample (Fjelde *et al.*, 2012). By using UV-visible spectroscope, it is possible to measure absorbance of the light. Absorbance is defined as the ratio between light intensity in the absence of the sample and the intensity when the sample is present (Harris and Bashford, 1987).

Limitations of UV-Vis Spectroscopy

UV-vis spectroscopy works well on liquids and solutions, but does not give very good results for samples of suspension of solid particles in liquid because the sample will scatter the light more than absorb the light (Oliva and Barron, 2010).

UV-Vis spectroscopy does not provide exact concentrations values for different heteroatoms, but gives a possibility of comparing different samples with each other and with a reference sample (Harris and Bashford, 1987).

Absorbance is not linear at higher concentrations because the Beer-Lambert law is not valid. Harris and Bashford (1987) recommend determining the linear range of absorbance with concentration by measuring absorbance of reference solutions.

Choice of Solvent and Cuvette

Every solvent has a UV-Vis absorbance cut off wavelength (Oliva and Barron, 2010). The solvent cut off is the wavelength below which the solvent itself absorbs all of the light. It is therefore good practice to choose solvent whose absorbance cut off does not fall on the same wavelength where the compound under investigation is thought to absorb. Table 3 contains various common solvents and their absorbance cut-offs.

Table 3 UV absorbance cut-offs of various common solvents.

Solvent	UV-Absorbance Cut-off (nm)
Acetone	329
Benzene	278
Dimethylformamide (DMF)	267
Ethanol	205
Toluene	285
Water	180

The cuvette (the sample holder) will also have a UV-Vis absorbance cut-off (Oliva and Barron, 2010). Glass will absorb all of the light higher in energy starting at about 300 nm, therefore if the sample absorbs in the UV, a quartz cuvette should be selected as the absorbance cut-off is around 160 nm for quartz (Table 4).

Table 4 Usable wavelength of different types of cuvettes commonly used

Material	Wavelength Range (nm)
Glass	380-780
Plastic	380-780
Fused quartz	Below 380

To obtain reliable data, the peak of absorbance of the compound must be at least three times higher in intensity than the background noise of the instrument (Oliva and Barron, 2010). Using higher concentrations of the compound in solution can reduce this source of error.

4.1.4 Visual Observation

The amount of polar oil components present in oil will influence its colour (Fjelde *et al.*, 2013). If the colour difference between experimental sample and reference samples is significant, Visual evaluation of retention of polar oil components can be used. Usually, when there is retention, the experimental sample will be lighter in colour than the reference oil sample. The clearer the contrast, the more retention has taken place. This method however is prone to large errors since it is based solely on personal judgment.

4.2 Basic Error Analysis

Every laboratory experiments involve taking measurements of physical quantities and these measurements most often are not perfectly accurate (Climers, 2012). The deviation of the measured value from the true value of the quantity may arise from different sources. Much effort may be put into refinement of technique or into improvement of the instruments, but this can only decrease the error in magnitude but never eliminated it entirely. Therefore the statement of the result of any laboratory measurement is complete only if there is indication of how much error the measurement might contain. To properly account for the degree of uncertainty in a laboratory experiment, there is the need to know the types of errors, the ways to reduce the errors, and how to treat the data obtained properly.

4.2.1 Introduction to Error Analysis

Error in a scientific measurement can be defined as the inevitable uncertainty that characterizes that measurements (Taylor, 1982). Error analysis therefore is the study, quantification and evaluation of uncertainty in measurements. Errors cannot be entirely eliminated by being careful and following all the due processes in the laboratory and therefore the best way of dealing with error is to know their sources and possible ways for minimizing their occurrence. Complete studies of error analysis will require much more time and space than it is viewed in this work. What this work covers is therefore the basics required to quantify and evaluate error.

Two key words often used in error analysis are accuracy and precision.

Accuracy

The accuracy of any measurement signifies how close the measured value comes to the true value (Climers, 2012). Accuracy therefore defines how correct the measured value is.

Precision

The precision of a scientific measurement refers to the agreement among repeated measurements (Climers, 2012). Precision measures how closely two or more measurements agree with other (Carlson, 2000). Precision is sometimes referred to as “repeatability” or “reproducibility”. A measurement described as highly reproducible tends to give values which are very close to each other of the measurements.

4.2.2 Types and sources of Experimental error

Basically, experimental error can be grouped into three major categories,

Personal Errors: These are errors that arise from personal bias or carelessness in reading an instrument, in recording observations, or in calculations (Climers, 2012). Reading a value from a scale involves lining up an object with the marks on the scale and it depends mostly on the position of the eye and personal judgment. This type of error therefore originates from human mistakes. Personal errors are significant, but they can be minimized by conducting the experiment several times much more carefully each time (Carlson, 2000).

Systematic Errors: These are errors that affect the accuracy of a measurement (Carlson, 2000). Systematic errors are associated with specific instruments or techniques (Climers, 2012). Improperly calibrated instruments are one of the sources of this type of error. Reducing systematic errors depends mainly on the skill and experience of the experimenter to detect and to prevent or correct them.

Random Errors: These are errors that affect the precision of a measurement (Carlson, 2000). Random errors result from unknown and unpredictable variations in the experimental situation (Climers, 2012). Unpredictable fluctuations in temperature or in-line voltage are the examples of random errors. They are sometimes referred as accidental errors. Random errors can be minimized by repeating the measurement a sufficient number of times or by improving the experimental technique.

4.2.3 Methods of quantifying error

The results of an experiment must be reported in a way that indicates the accuracy and precision of the experimental measurements. Some common ways to describe accuracy and precision are described below:

Significant figures

The least significant digit in a measurement depends on the smallest unit which can be measured using the measuring instrument (Carlson, 2000). The precision of a measurement can be estimated by the number of significant digits with which the measurement is reported. Generally, any measurement is reported to a precision equal to 1/10 of the smallest graduation on the measuring instrument, and the precision of the measurement is said to be 1/10 of the smallest graduation.

Relative Error

Relative error measures the accuracy of a measurement by the difference between a measured or experimental value and a true or accepted value (Carlson, 2000).

$$\text{Relative Error} = \left| \frac{\text{Experimental Value} - \text{Accepted Value}}{\text{Accepted Value}} \right| \times 100\% \quad (4.2)$$

If the accepted value of the measured quantity is known the percentage error can be calculated.

Percent Difference

If the accepted value of the measured quantity is not known, but the measurements have been repeated several times for the same conditions, the experimental error can be estimated by using the spread of the results. Percent difference measures precision of two measurements by the difference between the measured or experimental values say E_1 and E_2 expressed as a fraction of the average of the two values (Carlson, 2000).

$$\text{Percent Difference} = \left| \frac{E_1 - E_2}{\left(\frac{E_1 + E_2}{2}\right)} \right| \times 100\% \quad (4.3)$$

Mean and Standard Deviation

When a measurement is repeated several times, the measured values are often grouped around some central value (Carlson, 2000). This distribution can be described and represented with two numbers: the mean, which measures the central value, and the standard deviation which describes the spread or deviation of the measured values about the mean.

The mean of a set of N measured values for some arbitrary quantity x , represented by the symbol $\langle x \rangle$, is calculated by the following formula

$$\langle x \rangle = \frac{1}{N} \sum_i^N x_i = \frac{1}{N} (x_1 + x_2 + \cdots + x_{N-1} + x_N) \quad (4.4)$$

Where x_i is the i th measured value of x . The mean therefore is the sum of the measured values divided by the number of measured values.

The standard deviation of the measured values is represented by the symbol σ_x and is given by the formula

$$\sigma_x = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \langle x \rangle)^2} \quad (4.5)$$

The standard deviation is also referred to as the “mean square deviation” and measures how widely spread the measured values are on either side of the mean.

4.2.4 Reporting the Results of an Experimental Measurement

The results of an experimental measurement of a quantity x , is reported with two parts (Carlson, 2000). The best estimate of the measurement is reported as the mean $\langle x \rangle$, of the measurement and the variation of the measurements is reported by the standard deviation σ_x of the measurements. According to Taylor (1982), experimental results is best reported as:

$$x = \langle x \rangle \pm \sigma_x, \quad (4.6)$$

In modern spreadsheets, errors are best represented as error bars. The error is entered as an input as either a fraction of percentage and presented as either a vertical or horizontal bars (Figure 8)

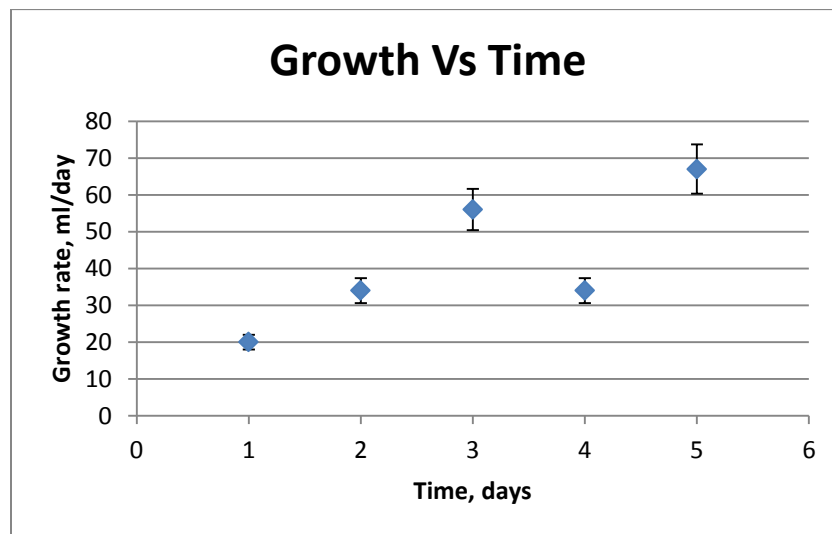


Figure 8 A simple graph showing data with 10% error represented as error bars

5. Experiments

5.0 Objectives of Experiments

The purpose of the experiments is to investigate the retention of polar oil components onto reservoir rock surface and to further find out how the retention of polar oil components on the reservoir rock surface is affected by the chemistry and composition of injected brine. Mechanisms underlying the retention of polar oil components have earlier on been discussed.

The experimentation process was divided into stages:

1. Preparation of Standard Absorption curves
2. Flooding experiments.

5.1 Materials Used in Experiments

This section looks at the various materials used in the experimentation process and reasons for which those materials were chosen specifically for this work. Fluids and rock materials used will be discussed in this section.

5.1.1 Fluids

Stock Tank Oil (STO)

Crude oil of density 0.845 g/ml at 20°C and viscosity of 1.5 cP at 80°C from a field in the North Sea was used in the experiment process. In most experiments, diluted samples of STO were used.

Brine

The compositions of brines used in the various experiments are presented in Table 5. LSW1 and LSW2 were prepared by diluting FW 100 times and 1000 times respectively.

Table 5 Composition of Brine

Salt	FW	SW	LSW1	LSW2	KCl LSW
	[g/l]	[g/l]	[g/l]	[g/l]	[g/l]
NaCl	77.4	23.38			
Na ₂ SO ₄	0.13	3.41			
NaHCO ₃	0	0.17			
KCl	0.42	0.75			0.136
MgCl ₂ ·6H ₂ O	3.56	9.05			
CaCl ₂ ·2H ₂ O	21.75	1.91			
SrCl ₂ ·6H ₂ O	2.25				

Solvent

The solvent used in diluting STO to various volumetric concentrations for both standard absorption curve preparation and flooding experiments was a mixture of toluene and n-decane in the volume ratio 20:80 respectively. The solvent was used to dilute STO before and after flooding in order to obtain UV-Vis spectroscopy reading in the linear range of the standard absorption curve. Diluted STO was injected because the concentration of polar components in STO is so high that it will be impossible to measure the delay in retention of polar components.

5.1.2 Rock

Crushed sandstone reservoir rock which contains high amount of glauconite from a field in the North Sea was used. The crushed rock sample was first cleaned with toluene and methanol in a soxhlet extraction process and then dried in an oven at 80°C for three days. The rock sample was then packed in a column and further cleaned with cycles of toluene and methanol injections before it was used for flooding experiments.

5.2 Standard Absorption Curve

Most of the experiments in this section were carried out in preparation for the flooding experiments.

5.2.1 Preparing Standard Absorption Curve

The standard absorption curve for diluted STO was constructed with a UV-Vis spectroscopy at 400nm wavelength. Different volumetric concentration of STO were prepared by diluting STO with the solvent in the ratio 1:100, 1:200, 1:300, 1:400, 1:600, 1:1000, 1:2000. The absorbance of each sample was measured by UV-Vis spectroscopy at 400nm and the readings were recorded. A graph of absorbance as a function of volumetric concentration of STO was then plotted.

5.2.2 Removing Acid Components from STO

The purpose of this experiment was to investigate how the amount of acidic components in STO will affect the retention of polar oil components onto the reservoir rock surface. The acidic components in STO was removed by adopting a modified form of the method described by Zhang and Austad (2005) and Strelnikova *et al.* (2005). 200 ml of diluted oil sample (STO: Solvent, 1:100) was prepared and about 3g of potassium silicate ($\text{Si}_2\text{O}:\text{K}_2\text{O}$), 48 mesh, was added and stirred for three days at room temperature. On the third day another 3g of potassium

silicate was added to the sample and stirred for three more days. The sample was then filtered to remove potassium silicate from the diluted oil sample.

A standard absorption curve was prepared for the treated oil sample to be used for all dynamic experiments performed with the treated oil sample. The same procedure described for the preparation of standard absorption curve with UV-Vis spectroscopy at 400nm wavelength was followed. The treated diluted oil sample was further diluted to four different volumetric concentrations; 1:400, 1:600, 1:1000 and 1:2000. Absorbance was measured for each sample and the standard absorption curve was constructed.

5.3 Flooding Experiments

The dynamic experiments performed in this work follows the method described by (Fjelde *et al.*, 2012).

5.3.1 Preparations

Steel column with inner diameter 0.96 cm and length 25 cm was filled with the crushed reservoir rock sample. The column was placed in an oven at 80°C at 1 atm. The column was then connected to the pump and piston cell using 1/16'' inner diameter tubing. The reservoir rock was cleaned with at least three cycles of toluene/methanol at 80°C until a clear effluent was obtained. The sketch of the set-up used in the flooding experiments is shown in Figure 9.

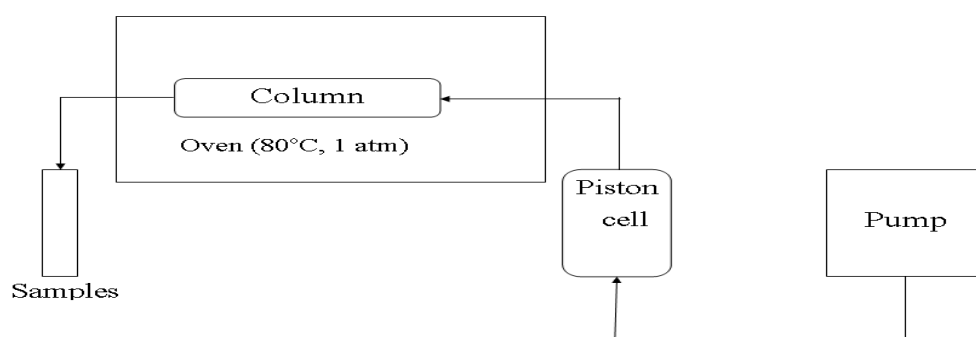


Figure 9 Experimental setup used for flooding experiments

5.3.2 Flooding Procedure

The reservoir rock column was flooded with brine using an injection rate of 0.05 ml/min for approximately 20 hours. Masses of the column before and after brine injection were registered for calculation of pore volume and porosity. After brine saturation, diluted STO (STO: solvent, 1:100) was injected using an injection rate of 0.05 ml/min for 8 hours. Effluent samples (2 ml) were collected for determination of the concentration of the polar oil components.

5.3.3 Calculation of Pore Volume and Porosity

The cross-sectional area of the column is defined as

$$A = \frac{\pi}{4} D^2 \quad (5.1)$$

And therefore the bulk volume of the column will be calculated as

$$V_{bulk} = A \cdot l \quad (5.2)$$

Where A is the cross-sectional area of the column, D is the inner diameter of the column, l is the length of the column and V_{bulk} is the bulk volume of the column

The pore volume of the packed column saturated with brine was calculated as

$$PV = \frac{m_{column+saturated\ sample} - m_{column+dry\ sample}}{\rho_{brine}} \quad (5.3)$$

Where $m_{column+saturated\ sample}$ is the mass of the column containing the brine-saturated rock sample, $m_{column+dry\ sample}$ is the mass of the column packed with the dry rock sample, ρ_{brine} is the density of brine and PV is the pore volume and, \emptyset is porosity of the rock in the column.

The porosity of the rock, \emptyset is then calculated as

$$\emptyset = \frac{PV}{V_{bulk}} \times 100\% \quad (5.4)$$

5.4 Analytical Method

The linear range of the standard absorbance curve was determined by measuring the absorbance as a function of STO concentration in diluted samples at wavelength 400 nm.

Once the absorbance of diluted effluent sample was measured, estimates of volumetric concentration of STO in the sample were read from the standard absorption curve. The volumetric concentration of STO in the sample was then plotted against dimensionless

cumulative produced oil (Cumulative produced oil/pore volume) and compared to the volumetric concentration of the reference oil and the extent of retention was ascertained.

5.4.1 Calculation of Presented Data

This section presents the calculations made to arrive at the plotted data. The calculations were done as simple as possible.

Cumulative produced oil (CPO), ml

2ml of effluent oil samples were collected regularly during flooding and analyzed for absorbance. Cumulative produced oil refers to an arithmetic summation of produced oil collected at regular interval.

$$CPO_i = \sum_{n=1}^i (\text{Effluent samples collected}) \quad (5.5)$$

Where, CPO_i , is the CPO (ml) after collecting $n = i$ samples.

The CPO calculated was converted into a dimensionless value by dividing with measured pore volume (PV).

$$\text{Dimensionless } CPO_i = \frac{CPO_i}{PV} \quad (5.6)$$

The absorbance values measured are average data of the 2ml effluent sample collected. Therefore the estimated CPO must also be an average. The average CPO values were calculated as.

$$\text{Average } CPO_i = \frac{CPO_i + CPO_{i-1}}{2} \quad (5.7)$$

Where, CPO_i , is the CPO after collecting the sample $n = i$ and CPO_{i-1} is the CPO of the previous sample $n = i - 1$.

Concentration of STO (CSTO) in Diluted Effluent Sample, ml/ml

The volumetric concentration of STO in the sample was estimated from the standard absorption curve. Absorbance in the linear range of the standard absorption curve is fitted with a straight line whose equation is determined. The equation of the straight line is presented as shown in Equation 5.8.

$$Absorbance = k(CSTO) + c, \quad (5.8)$$

Where k and c are constants.

First the effluent oil sample collected is diluted and the absorbance is measured. Once the absorbance of the diluted sample is measured, the equation is inverted and CSTO estimated as shown in Equation 5.9.

$$CSTO = \frac{Absorbance - c}{k} \quad (5.9)$$

The unit of CSTO is ml of STO/ ml of Solvent.

After the concentration of STO in the diluted effluent sample is estimated, the value obtained is multiplied by the dilution factor to obtain the volumetric concentration of the undiluted effluent sample originally collected during flooding.

$$CSTO \text{ of effluent sample} = DF \times CSTO \text{ of diluted effluent sample}$$

Where DF is the dilution factor or the number of times the collected effluent sample was diluted to obtain readings in the linear range of the standard absorption curve.

Retention, ml

The amount of polar oil components retained on the mineral surface was evaluated as the difference between the CSTO of injected diluted STO and the CSTO of the produced effluent sample.

$$Retention = CSTO_{Reference\ oil} - CSTO_{Effluent\ Sample} \quad (5.10)$$

By assuming the solvent part is not retained on the rock surface, the unit of Retention will be ml.

5.4.2 Error Estimation and Graphing

The major source of error in this work was absorption measurement. In measuring the absorption of each sample, measurements were made ten times and the standard deviation was then calculated. Data was reported as the mean value and the standard deviation calculated.

$$x = \langle x \rangle \pm \sigma_x, \quad (5.11)$$

The error, which is the standard deviation expressed as percentage is then presented in the form of error bar.

6. Results and Discussion

6.0 General Introduction

During the various experimentation processes, numerous results were obtained. This section is aimed at explaining most of the results obtained from the experiments conducted in section 5 and further try to link these observations to their relevance in field applications.

6.1 Standard Absorption Curve

The volumetric concentration of STO of samples whose absorbance was measured for the preparation of the standard absorption curve are 1:100, 1:200, 1:300, 1:400, 1:600, 1:1000 and 1:2000. Figure 10 is a picture illustrating the diluted samples used for preparing the standard absorption curve. By visual observation, the samples become lighter in colour as the volumetric concentration of STO in the sample decreases.



Figure 10 Diluted Samples used to determine Standard Absorption curve. The concentration of STO decreases from left to right in this picture.

After the absorbance of each sample was measured by UV-Vis spectroscopy at 400nm and the readings recorded, a graph of Absorbance as a function of CSTO was plotted to find out the points that fall in the linear range. From Figure 11, it can be observed that the injected diluted sample (in red maker) does not fall in the linear range. Therefore effluent samples collected after flooding were diluted to obtain measurements at 400nm. The reasons behind some higher concentrations falling outside the linear curve can be explained with the Beer's law discussed earlier. The Beer's law assumes that there is a linear relationship between the Absorbance A , the molar concentration of the solution, c , and b , the path length of the cuvette assuming the molar

absorptivity of the molecules in the solution ϵ , is constant. At some higher concentrations, the assumption that the molar absorptivity is constant fails and the absorptivity is no longer constant. This situation causes the curve to deviate from the linear range. To obtain reading in the linear range, the said solution must be further diluted.

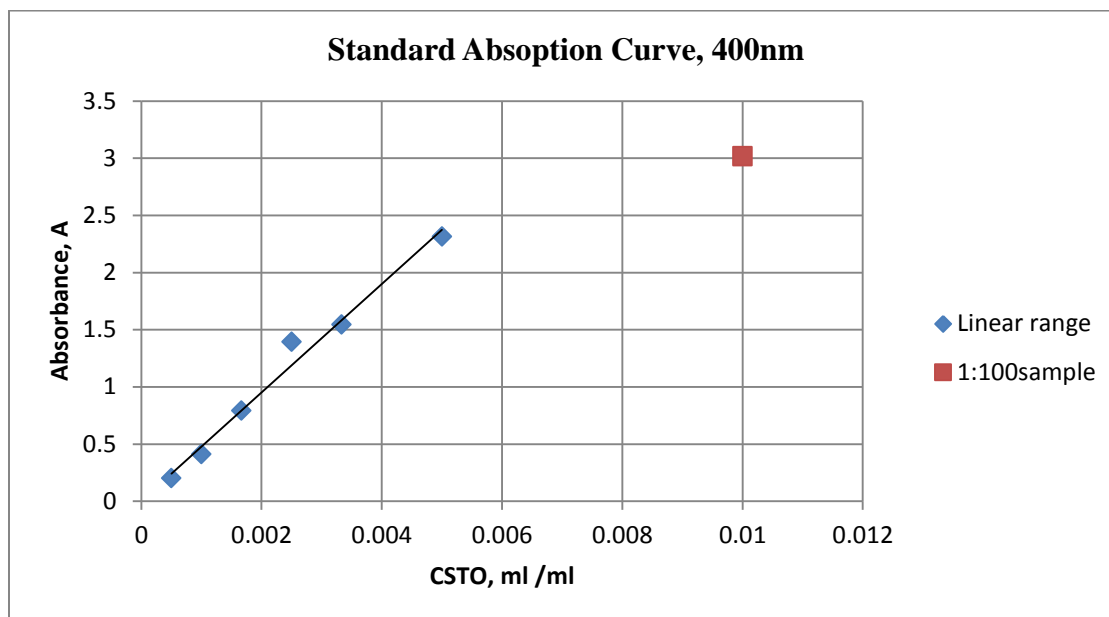


Figure 11 Standard absorption curve measured at 400nm wavelength

6.1.1 Standard Absorption curve for Untreated STO

Figure 12 illustrates the standard absorption curve prepared with the untreated STO. The points were fitted with the best straight line and the equation of the line determined along with the correlation coefficient, the R^2 value. An acceptable R^2 value of 0.9831 was obtained for the fit.

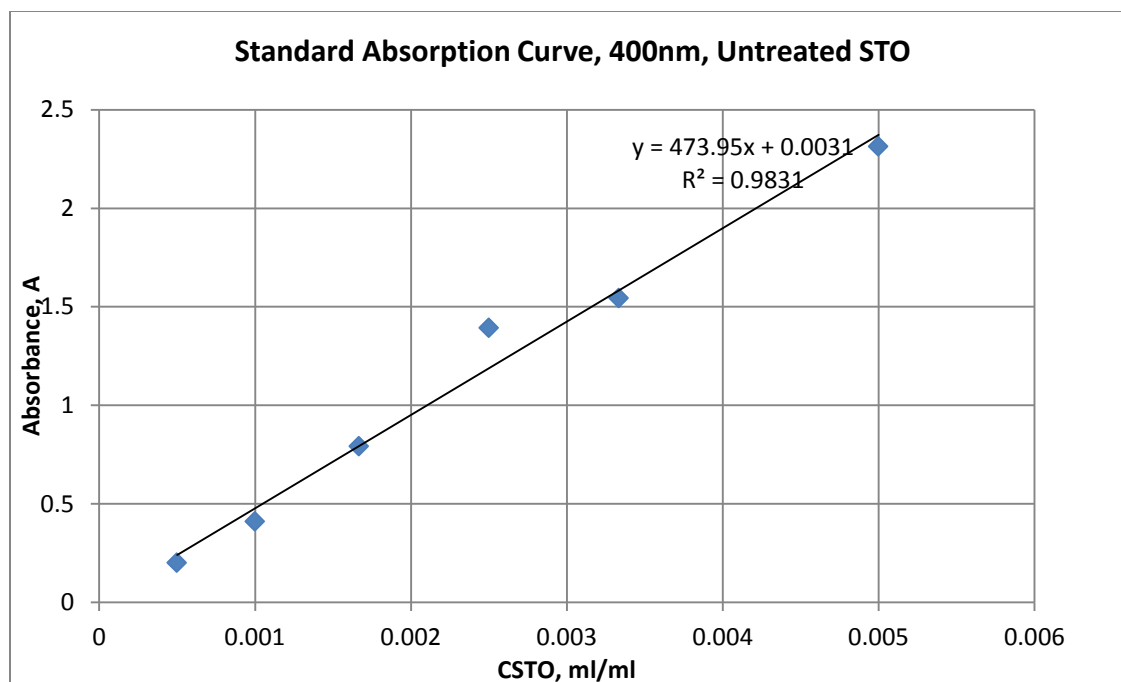


Figure 12 Standard Absorption curve of untreated STO

The standard absorption curve will be used to estimate the volumetric concentration of effluent oil samples collected during flooding experiments in order to estimate the amount of retention.

6.1.2 Standard Absorption Curve for Treated STO

A separate standard absorption curve was prepared for the treated oil sample to be used for all dynamic experiments performed with the treated oil sample. The same procedure described for the preparation of standard absorption curve with UV-Vis spectroscopy at 400nm wavelength was followed. The treated diluted oil (1:100 volumetric concentrations) was further diluted to four different samples at a ratio of; 1: 400, 1: 600, 1: 1000 and 1:2000. Absorbance was measured for each sample and the standard absorption curve was plotted. These specific four samples were chosen because most of the absorbance measured in the linear range falls in this range of volumetric concentration. Figure 13 is the standard absorption graph for the treated oil.

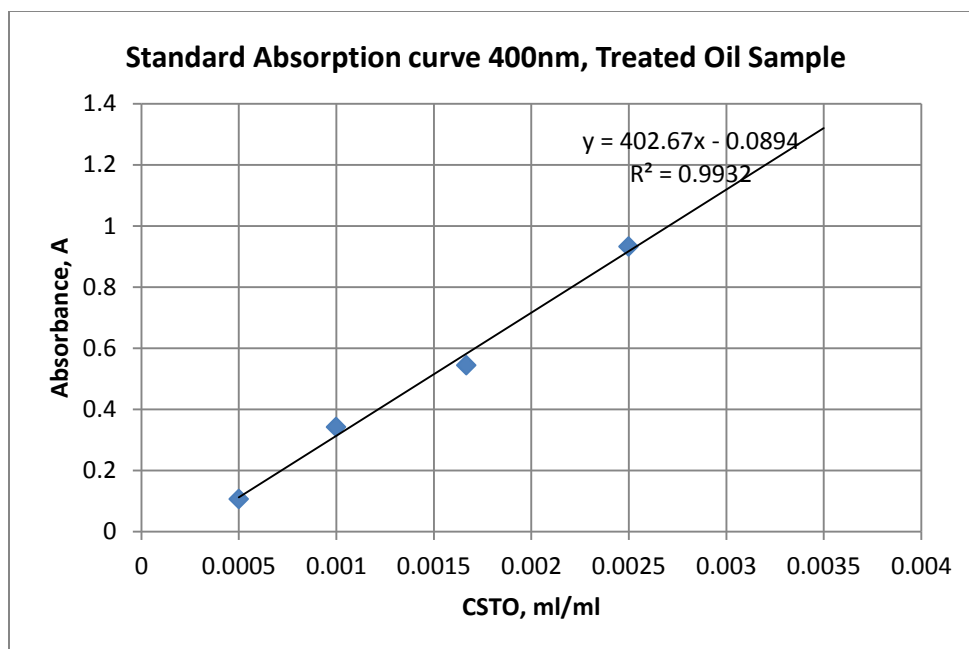


Figure 13 Standard Absorption Curve measured at 400nm for treated oil sample.

6.1.3 Standard Absorption Curve compared, Treated Vs Untreated STO

The STO was treated to reduce acidic components. Figure 14 compares the standard absorption curve for treated and untreated oil. The standard absorption curve for the treated oil shifted a bit down compared to the standard absorption curve of the untreated oil. Again, the Beer-Lambert Law explains the reason behind this observation. The treated oil contains reduced amounts of acidic components and therefore it has a lower molar concentration of polar oil components compared to the untreated oil. The absorptivity is still practically constant and so both curves still remain linear in these volumetric concentrations. However, the treated oil has lower concentration at each point because of the removal of acidic components and this explains why the curve shifted a bit down.

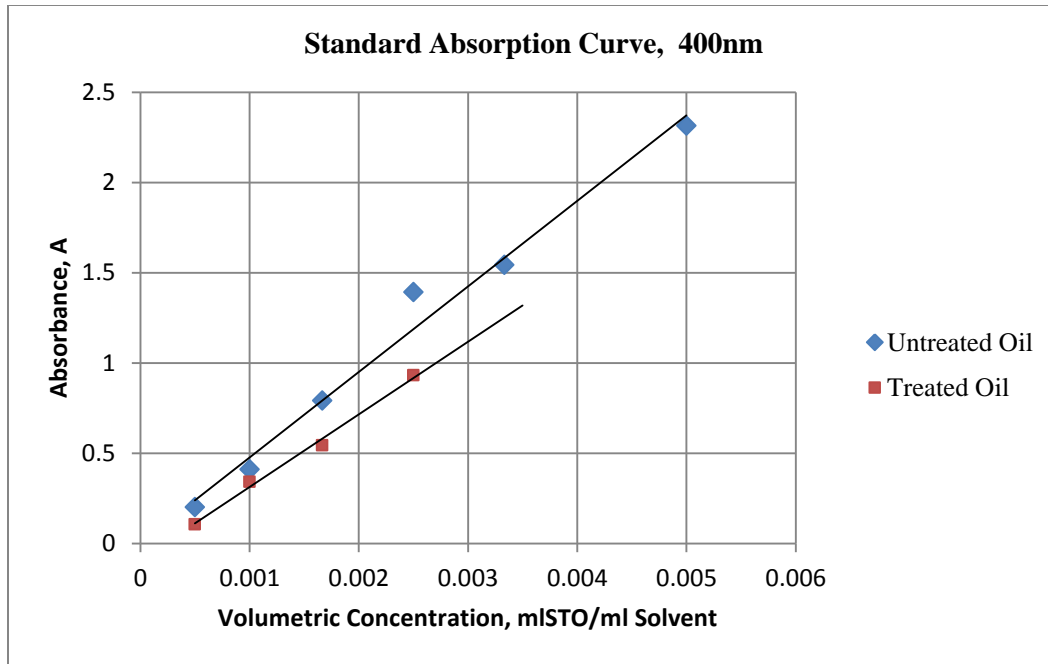


Figure 14 Standard Absorption curve, Treated STO vs untreated STO

6.2 Flooding Experiments

The crushed reservoir rock used for the flooding experiments was packed in a metal column. Table 6 presents the physical dimensions of the column.

Table 6 Physical dimensions of the column

Length, cm	25
Diameter, cm	0.96
Area, cm ²	0.7238
Bulk Volume, cm ³	18.10

Dynamic experiments were conducted by flooding the column with oil sample after the column was saturated with brine. The brines used in flooding experiments were sea water (SW), Formation water (FW), LSW1 (FW diluted 100 times), LSW2 (FW diluted 1000 times) and low salinity water prepared with potassium chloride (KCl). After flooding the column with brine, the pore volume and porosity of the reservoir rock column was measured. Table 7 contains pore volume and porosity of the rock column after flooding the column with different brines. The

method used to pack the columns was found to be acceptable because the porosity of the different columns was found to be rather similar.

Table 7 Summary of pore volume and porosity calculation

Brine	FW	LSW1	LSW2	SW	KCl brine
$m_{\text{column+saturated sample, g}}$	354.70	354.05	353.71	353.78	353.66
$m_{\text{column+dry sample, g}}$	347.48	347.48	346.85	346.64	346.76
$\rho_{\text{brine, @ 80 }^\circ\text{C, g/ml}}$	1.0283	0.9556	0.9523	0.9780	0.9549
PV, ml	7.021	6.875	7.204	7.301	7.228
$\emptyset, \%$	38.79	37.98	39.80	40.33	39.93

Two types of STO samples were used in this experimentation: Untreated STO and treated STO. Effluent samples were collected at regular interval (after 2ml of production) and analyzed with UV-Vis spectroscopy for absorbance after which analysis was conducted on the results to determine retention of polar oil components.

6.2.1 Presentation and analysis of results, Untreated STO

Data obtained from flooding experiments used to analyze and calculate retention are presented in tables in appendices at the end of this work. To compare the retention of polar oil components after flooding the reservoir rock column with different brines, a graph of CSTO as a function of average CPO was plotted for each case. Two curves each are represented on each graph, the effluent sample concentration and the concentration of STO before flooding. The retention of polar oil components during flooding was then calculated by analyzing these graphs. The average error was determined to be 5% and represented as error bars on the plotted graphs.

Formation water (FW)

The composition of FW used in this work was presented in Table 5. The analysis of effluent sample concentration after flooding reference STO (1:100) through reservoir rock minerals in equilibrium with FW is illustrated in Figure 15. Results obtained indicate that there was retention of polar oil components onto reservoir rock minerals when diluted sample of STO was flooded through the column saturated with FW. Retention of polar oil components onto reservoir rock minerals is highest during the early stages of flooding until about 1.5 PV of effluent sample was collected. Early studies conducted by Omekeh *et al.* (2012) and Fjelde *et al.* (2012) revealed that

the total concentration of divalent cations onto clay mineral surfaces will affect the retention of polar oil components. During the early stages of flooding, polar oil components are adsorbed onto the reservoir rock surface mainly through cation bridging and ion binding initiated by the divalent cations in the brine. With process of time, the surface of the reservoir rock mineral gets saturated with polar oil components and the ability of divalent cations to hold more polar components onto the mineral surface is reduced. This explains why there is no significant retention of polar components during the later stages of flooding.

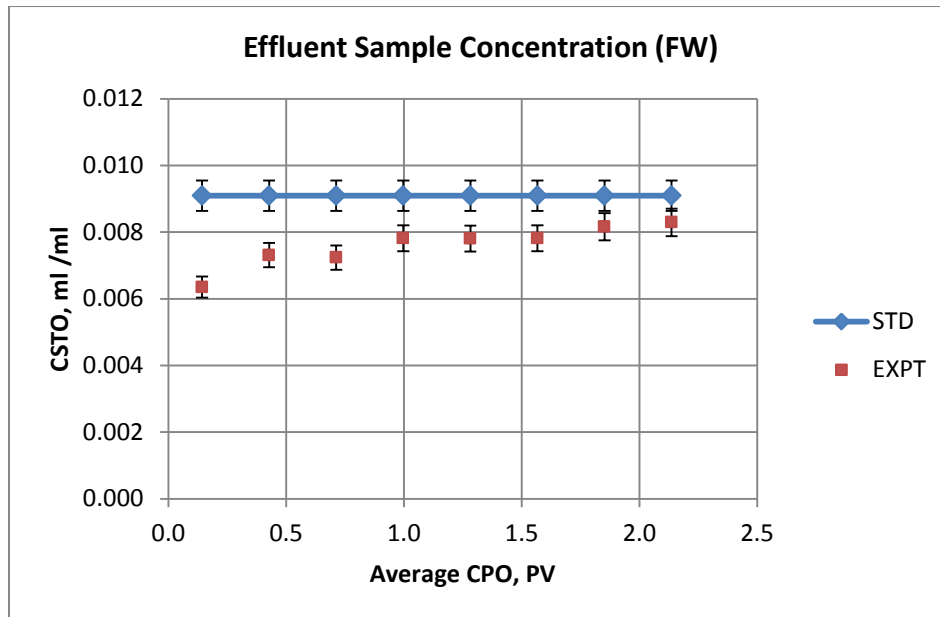


Figure 15 Concentration of STO in effluent sample during flooding reference STO through column saturated with FW

It is also important to mention that the collected effluent samples were diluted five times to obtain acceptable reading within the linear range of the standard absorption curve. The CSTO reading obtained was then multiplied by the dilution factor to get the CSTO of the 2 ml sample originally collected.

LSW1 (FW diluted 100 times)

Low salinity brine prepared by diluting the same FW has earlier been found to contain higher total divalent cations onto the reservoir rock surface (Fjelde *et al.*, 2012; Omekeh *et al.*, 2012). In reference to Figure 16, there is higher retention of polar oil components onto reservoir rock surface in equilibrium with LWS1 than the previous case of FW. Fjelde *et al.* (2013) cited that the retention of polar oil components onto mineral surfaces increases with increasing total

concentration of divalent cations onto clay surfaces. This explains why there is higher retention of polar oil components in the case of LSW1 as compared to the case with FW.

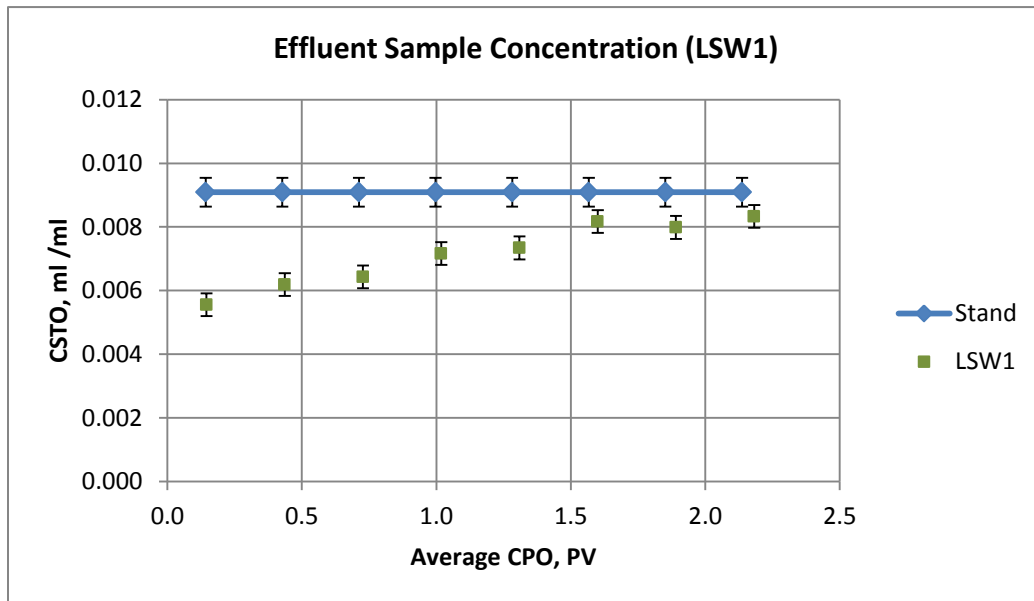


Figure 16 Concentration of STO in effluent sample during flooding reference STO through column saturated with LSW1

However, similar to results obtained after flooding with FW there is only minor retention of polar components observed after producing about 1.5 PV of effluent oil samples.

LSW2 (FW diluted 1000 times)

LSW2 contains higher total concentration of divalent cations onto clay minerals than FW (Fjelde *et al.*, 2012; Omekeh *et al.*, 2012). Referring to Figure 17, there is generally high initial retention of polar oil components onto the surface of the reservoir rock minerals. Retention of polar oil components however begins to decline after about 1.5 PV of effluent samples was collected.

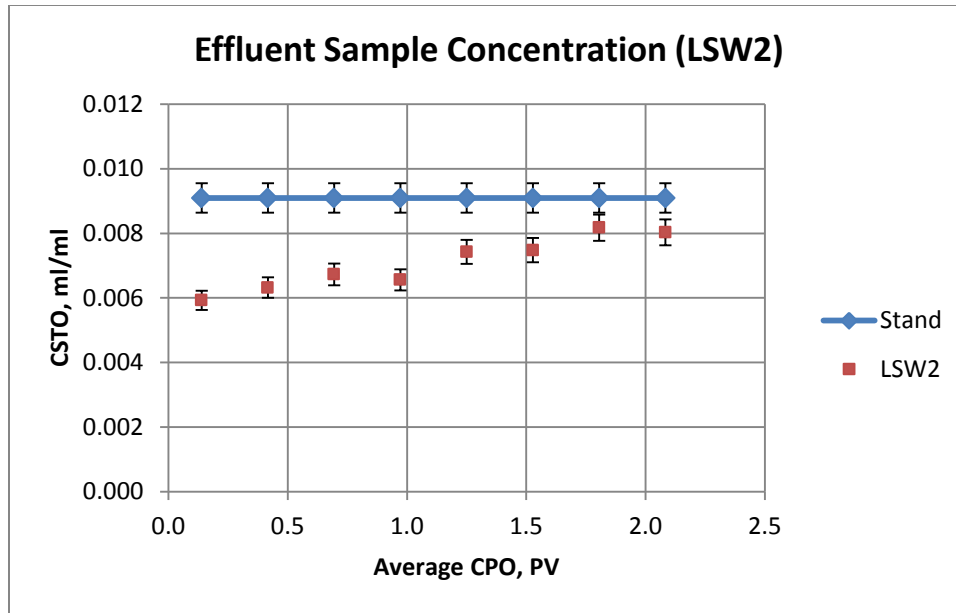


Figure 17 Concentration of STO in effluent sample during flooding reference STO through column saturated with LSW2

Observations here once again confirms the proposal by Fjelde *et al.* (2013) that the retention of polar oil components generally increases with increase in total concentration of divalent ions onto clay surfaces.

Sea Water (SW)

Figure 18 illustrates effluent concentration during flooding reference STO sample through the column saturated with SW. Retention of polar oil components was low in this case compared to the previous cases discussed. Sea water used in this work contains higher Mg^{2+} and lower Ca^{2+} (refer to Table 5) compared to FW. In cation exchange capacity, Ca^{2+} has high replacing preference over Mg^{2+} onto the mineral surface. Therefore there is higher total concentration of divalent cations (Ca^{2+}) in FW than SW. Jadhunandan and Morrow (1995) mentioned that high concentration of Ca^{2+} will favour the retention of polar oil components onto the reservoir rock surface and this explains the generally less retention of polar oil components observed for the case of SW compared to FW.

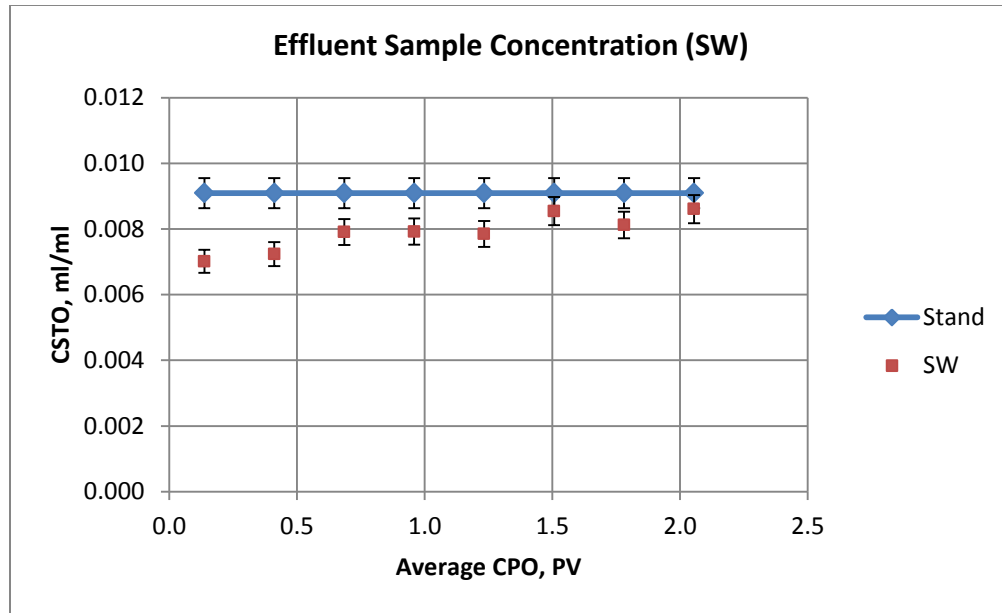


Figure 18 Concentration of STO in effluent sample during flooding reference STO through column saturated with SW

However, the general trend still follows as there is almost only observation of minor retention of polar oil components onto the reservoir rock surface after producing 1.5 PV of oil sample.

KCl Low Salinity Brine

The potassium Chloride (KCl) low salinity water brine was prepared such that it has the same ionic strength as LSW2. The ionic strength of a solution measures the concentration of ions in that solution (Sheng, 2011). The ionic strength of a solution is defined by Sheng (2011) as

$$I = \frac{1}{2} \sum_{i=1}^n C_i Z_i^2, \quad (6.1)$$

Where C_i is the molar concentration of ion i ($M = \text{mol/L}$), Z_i is the charge number of that ion, and the sum is taken over all ions in the solution. For the ionic strength of KCl brine to be equal to the ionic strength of LSW2 brine means,

$$I_{LSW2} = I_{KCl \text{ brine}} \quad (6.2)$$

The mass of KCl in 1L of solution was calculated and the solution carefully prepared for the experiment.

KCl low salinity brine contains no divalent cations. Figure 19 illustrates the effluent sample concentration recorded when the reservoir rock in equilibrium with KCl brine was flooded with

untreated STO. Retention of polar oil components was significantly lower in this case compared to all other flooding experiments conducted with untreated STO.

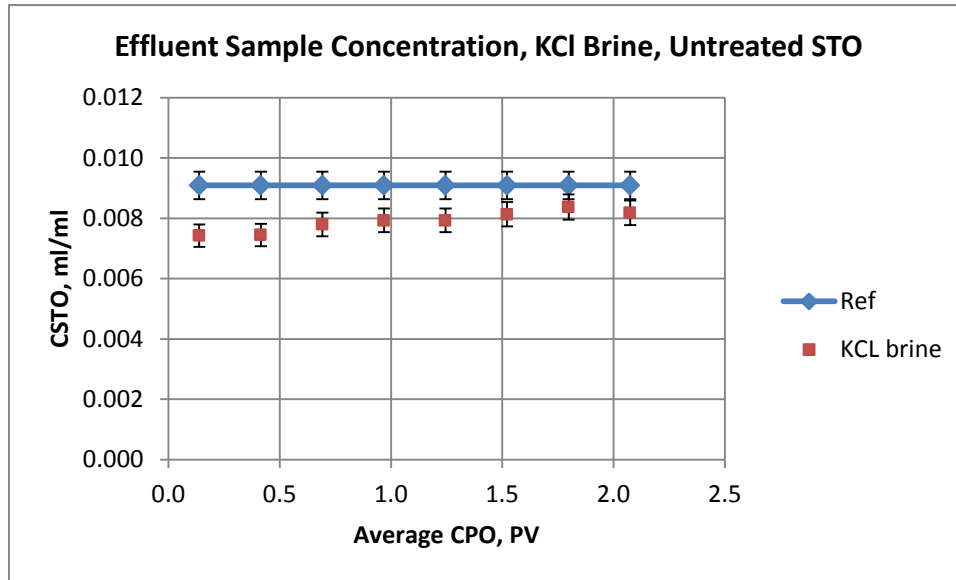


Figure 19 Effect of the amount of acidic components in STO, KCl brine, untreated STO

Because KCl brine contains no divalent ions, it has no significant total divalent cation concentration onto the reservoir rock surface. Adsorption of polar components through cation bridging is therefore significantly very low.

Retention Compared

Figure 20 is a simple graph comparing the retention of polar oil components in all the previously discussed flooding experiments. Generally, retention of polar oil components decreases with increasing amount of PV of effluent samples produced with low retention recorded after 1.5 PV was produced. It can also be observed that generally, retention increases from KCl low salinity brine to SW to FW and then to low salinity water (LSW1 and LSW2). Retention is highest for the case of LSW1 and LSW2 followed by FW and low for the case of SW and very low for KCl brine as seen in the figure.

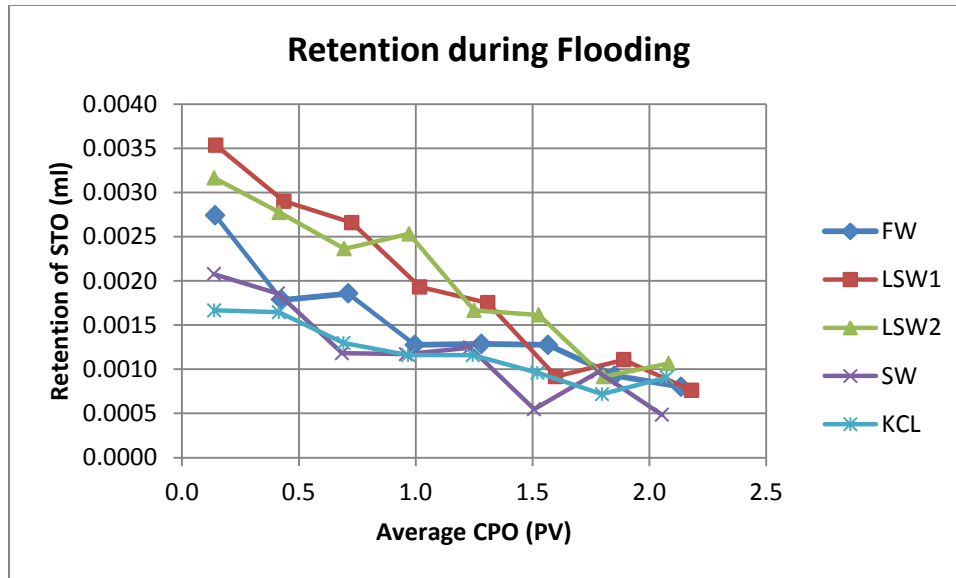


Figure 20 Graph summarizing retention of polar oil components in LSWF

6.2.2 Presentation and analysis of results, Treated vs Untreated STO

This section is aimed at investigating the effects of the amount of acidic components in the crude oil to the retention of polar oil components in relation to LSWF. The treated STO contains reduced amounts of acidic components and therefore has a higher base/acid ratio than the untreated STO. To establish the relationship between the amount of acidic components present in the STO and retention of polar oil components, flooding experiments were conducted with FW and KCl low salinity brine for treated STO and then for untreated STO and the amount of retention was investigated.

Formation Water (FW), Treated vs Untreated STO

FW was chosen as the base case to investigate the effects of the amount of acidic components present in STO on the retention of polar oil components onto reservoir rock mineral surface. Flooding experiments were conducted with treated STO and then with untreated STO and the results were compared. Figure 21 is a graph illustrating the effluent sample concentration in the after flooding with treated STO. There is retention of polar oil components in this case and retention is high at the initial stages of production but gradually retention is reduced at the later stages of flooding.

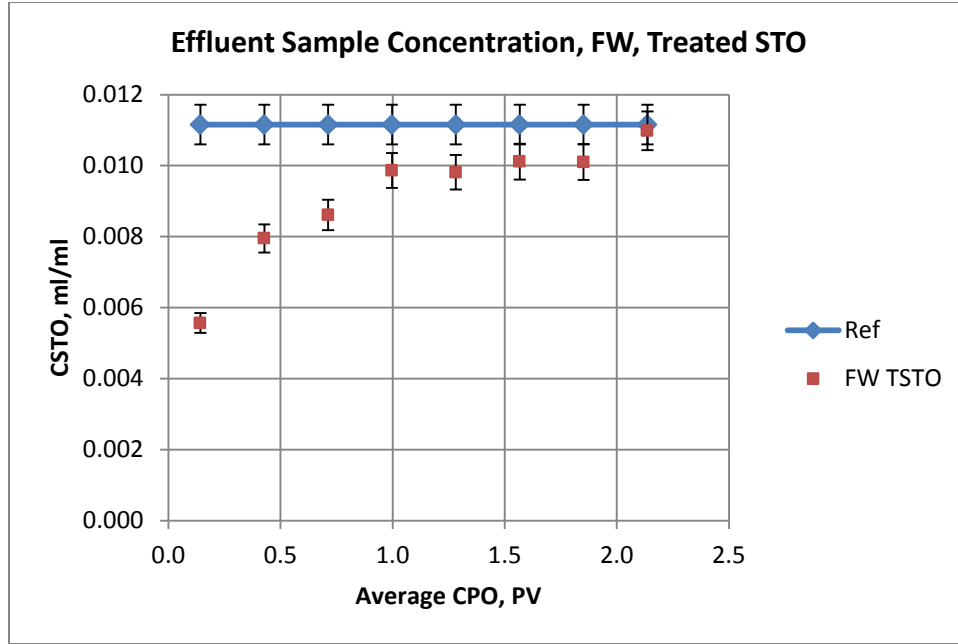


Figure 21 Effect of the amount of acidic components in STO, FW, treated STO

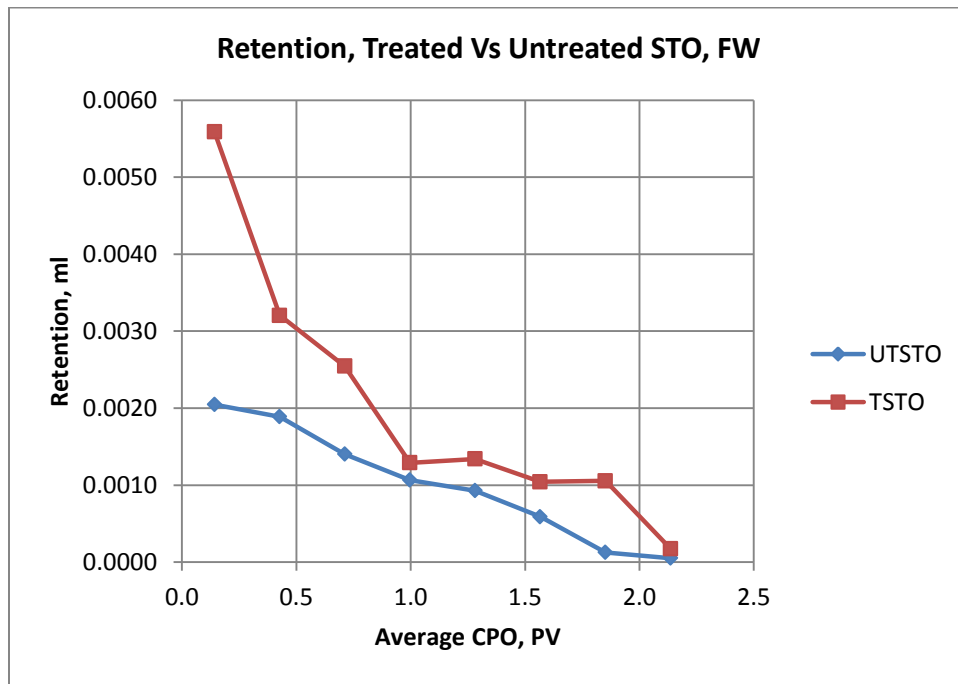


Figure 22 Measure of retention, comparing Treated STO (TSTO) and Untreated STO (UTSTO, FW)

Figure 22 compares the retention of polar oil components onto reservoir rock surface after flooding with treated STO (TSTO) and untreated STO (UTSTO). From the figure, generally

there was high retention of polar oil components in the case of treated STO compared to the case of untreated STO. Skauge *et al.* (1999) studied the effect of base/acid ratio of different crude oils to the adsorption of polar oil components onto clay surfaces and established that there is generally high retention associated with oils with high base/acid ratio. They explained that an increase in the base/acid ratio is expected to decrease the stabilization of the water-film on the rock surface due to increased attractive forces. Treated STO contains reduced amount of acidic components and therefore high base/acid ratio and this explains why there was high retention of polar oil components in the case of treated STO more than untreated STO.

KCl Brine , Treated Vs Untreated STO

Experiments conducted in this section were aimed at demonstrating the effect of the amount of acidic components in STO on retention of polar components onto reservoir rock surfaces when the rock column is saturated with KCl low salinity brine.

Figure 23 illustrate the effluent sample concentration obtained during flooding the column with treated STO. Retention of polar components is significant during the early stages of flooding until about 1 PV of oil is produced. Figure 24 compares the extent of retention recorded by the treated STO and untreated STO during flooding the column in equilibrium with KCl low salinity brine. It can be observed that, generally the treated STO reported a higher retention of polar oil components than the untreated STO. This observation further affirms the earlier claim that increase in base/acid ratio of the crude oil will increase adsorption of polar oil components onto the reservoir rock surface.

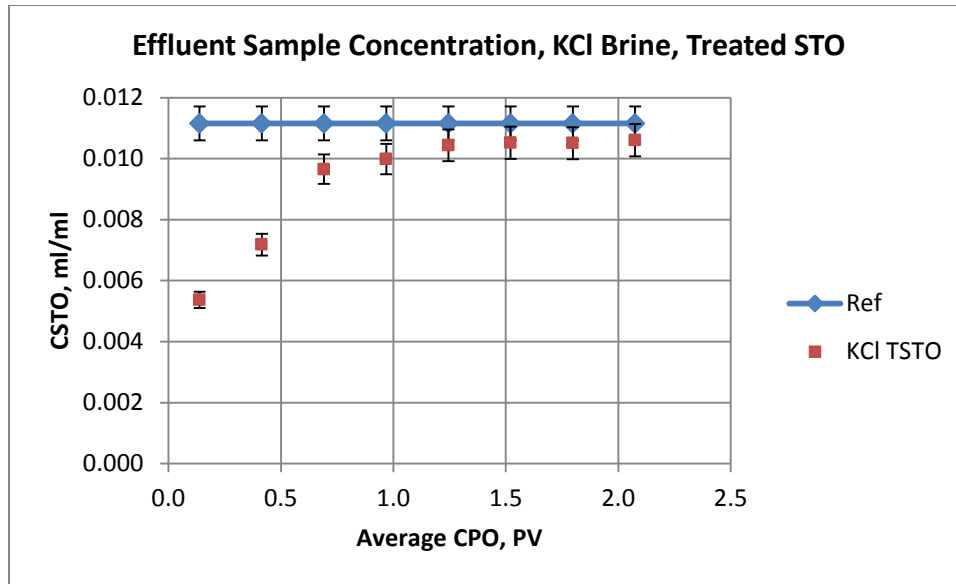


Figure 23 Effect of the amount of acidic components in STO, KCl brine, treated STO

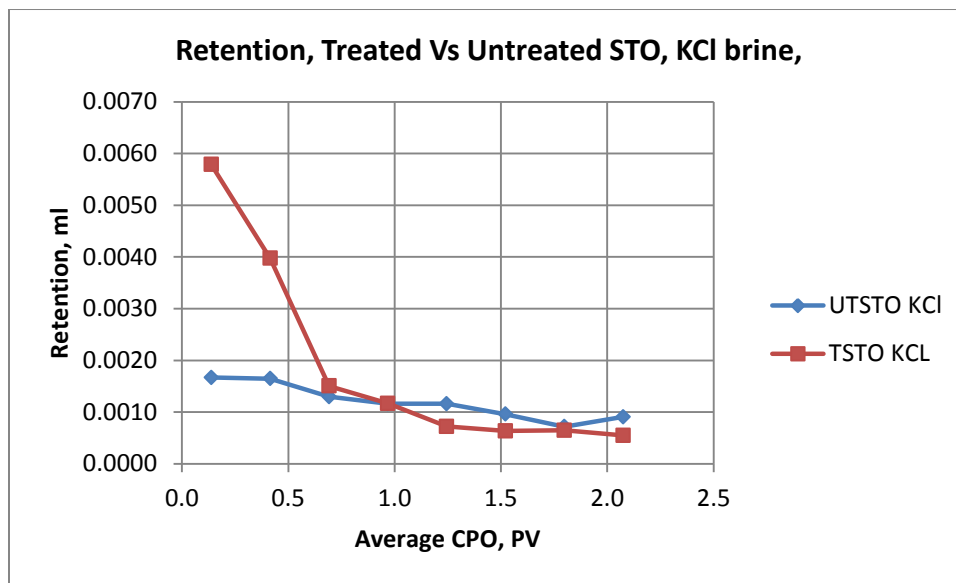


Figure 24 Retention compared, Treated Vs Untreated STO, KCl brine

Another interesting observation from comparing Figure 23 and Figure 24 is that there is no significant change in the retention produced by the treated STO in the two cases of FW and KCl brine. This implies that the retention of polar oil components in the case of treated STO was not significantly influenced by cation bridging. It therefore means that direct adsorption of polar components onto the reservoir rock surface, proposed by Buckley *et al.* (1998) could be the

possible mechanism that dominate in the retention of polar oil components when the acidic components in crude oil is reduced.

6.3 Discussion of results

The relevance of EOR and IOR experimentation and projects is very much dependent on their usefulness and applicability to the ultimate goal of maximizing oil recovery on commercial basis whiles minimizing environment impact. LSWF is emerging as a successful EOR process which is not only effective in oil recovery but also proving good in fighting environmentally problems in oil and gas field work. This section seeks to discuss the contribution of this work to LWSF and EOR practices and the ultimate relevance of this work to field EOR applications.

6.3.1 Results Vs Literature

Many authors (Jadhunandan and Morrow, 1995; Basu and Sharma, 1997; Buckley *et al.*, 1998; Skauge *et al.*, 1999), proposed that there could be adsorption of polar components in crude oil onto rock surfaces which could alter the wettability of the rock. Experiments performed in this work affirmed this claim, showing significant retention of polar oil components onto the reservoir rock surface during flooding. This work did not go further to measure the wettability of the reservoir rocks. The aim was to detect if there is retention of polar oil components and the results proved positive.

Some authors (Jadhunandan and Morrow, 1995; Basu and Sharma, 1997; Nasralla *et al.*, 2011; Fjelde *et al.*, 2013) mentioned that the retention or adsorption of polar oil components onto rock mineral surface is a strong function of the salinity of brine in equilibrium with the rock. Investigations made in this work support this claim. Retention of polar oil components onto reservoir rock surface was a function of the salinity and composition of the brine. Fjelde *et al.* (2013) also mentioned that the retention is high for brines with high total concentration of divalent cations onto clay minerals. In this work, brines with high total concentration of divalent cations gave higher retention of polar oil components. FW, SW and KCl low salinity brine gave lower retention of polar oil components and LSW1 and LSW1 reported the highest retention of polar oil components. Jadhunandan and Morrow (1995), also mentioned that retention of polar oil components onto rock surfaces increases with increase in the concentration of Ca^{2+} in the brine. FW in this work contains more Ca^{2+} than SW. After flooding experiments, it was observed

that FW reported more retention of polar oil components than SW because the later contains less amount of Ca^{2+} .

Lager *et al.* (2006) proposed that MIE is the mechanism that explains oil recovery in LSWF. This work also demonstrated that MIE could play a role in the retention of polar oil components onto reservoir rock surfaces through cation bridging. Brines which give high total concentration of divalent cations onto the reservoir rock surface demonstrated a higher retention of polar oil components. The KCl low salinity brine contains no divalent cations and it demonstrated the lowest retention of polar oil components onto the reservoir rock surface.

Many authors (Jadhunandan and Morrow, 1995; Buckley *et al.*, 1998; Skauge *et al.*, 1999), mentioned that the composition of the crude oil could affect the adsorption of polar oil components onto rock mineral surface. Skauge *et al.* (1999) mentioned that the retention of polar oil components onto rock surface increases with increase in base/acid ratio of the crude oil. This assertion was confirmed in this work as treated crude oil containing reduced amount of acidic components yielded higher retention of polar components than the untreated oil sample.

6.3.2 Limitations of this Work

Like any other practical work, there is an extent to which this work can be applied. To get the maximum benefit of this work, it is very good to know the boundaries within which the methods and processes addressed in this work remain effective. Some of the limitations associated with this work are addressed below;

1. It only gives understanding of the mechanisms affecting the retention of polar oil components in low salinity waterflooding but it is not enough to conclude that a reservoir will be a good candidate for LSWF because this work does not give estimates of oil recovery.
2. This thesis presents a viable method for screening reservoir parameters to determine their response to LSWF but do not guarantee that once a reservoir rock /crude oil system passes this test, it could be a good candidate for LSWF.
3. There are sources of error associated with collecting produced fluids, correct dilution of this produced fluids and reliability of UV-Vis instrument. However, these errors were managed and reduced to some 5%. To obtain reliable and acceptable results from the

methods presented in this work, it is very advisable to identify these sources of error and design mechanisms that will reduce the error to the barest minimum.

4. Retention of polar oil components using UV-Vis spectroscopy was measured within 400nm wavelength which might not have been enough to estimate all polar components present in the samples. There could be some polar components that falls outside this wavelength used to estimate retention.
5. The UV-Vis spectroscopy does not give specific measurement of polar components. It is only good for comparing two samples.

Generally, the methods, procedure and analysis described in this work are reliable and could prove acceptably effective when applied within its operational boundaries.

6.3.3 Field Relevance

The flooding experiments and their results proved very useful to LSWF. The following are few ways by which we could use this work for understanding and applying LSWF.

1. This work is useful in giving first-hand information on the LSWF potential of reservoir rocks. Clay content has been mentioned in the literature as one of the conditions required to obtain low salinity effect. One could use the experimentation process described in this work to select reservoir rocks which have the capability to give positive effect on LSWF.
2. The composition and concentration of crude oil is also very important to obtain LSWF. Wettability which has been cited in many works as the basis of improved recovery seen in LSWF is much dependent on the amount of polar components retained on the mineral surface. Oil with different compositions will give variable effect on LSWF. This work provides a simple method for evaluating the effect of crude oil on retention of polar oil components on the mineral surface.
3. To obtain maximum recovery through LSWF, brine composition is another factor of importance. The method demonstrated in this work provides a simple means to obtain information on the optimum brine composition that needs to be selected to give the right low salinity effect.

Similar methods have been described in the literature but what makes the method described in this work different is;

1. It is cost effective and saves time. Within few days, useful information can be obtained on variables affecting crude oil/brine/ rock interactions.
2. It gives indicative and reproducible results.
3. The experimentation process is flexible and easy to perform

6.3.4 Further Work

This material is relevant to the understanding of retention of polar oil components onto reservoir rock surfaces and its application to LSWF. However, this work can be further expanded to cover other investigations and related topics which could equally prove very relevant to the understanding and application of LSWF. Some of the recommended further research is stated below;

1. The same experiments performed in this work should be expanded to cover other absorption wavelengths of the UV-Vis spectroscopy in order to get a good estimate of the amount of polar components retained. It is also recommended that a more specific method should be employed to study the retention of polar oil components with different chemical structure.
2. It could be relevant to measure wettability alteration caused by the retention of polar oil components in order to link wettability and retention of polar oil components onto reservoir rock surfaces.
3. Estimation of oil recovery was not covered in this work. It will be of good value to measure the amount of oil recovery during flooding in order to know how the retention of polar oil components onto reservoir rock minerals in equilibrium with different brines will affect recovery of oil from the reservoir rock.

7. Conclusions

The experiments conducted in this work were effective in demonstrating and estimating the retention of polar oil components onto reservoir rock surfaces during LSWF. The results obtained from experiments and analysis demonstrated that:

- There is retention of polar oil components onto reservoir rock mineral surfaces during experiments conducted in relation to LSWF. This observation is not new as aging of reservoir rocks with crude oil has been found to change wettability.
- The salinity and composition of brine in equilibrium with the reservoir rock may have significant influence on the retention of polar oil components onto reservoir rock surfaces.
- Multi-component ion exchange, cation bridging and direct adsorption could be the major mechanism that explains the retention of polar oil components onto reservoir rock surfaces during LSWF.
- The amount of acidic components present in the STO may have an effect on retention of polar oil components during LSWF. A decrease in the amount of acidic components in STO will increase the retention of polar oil components onto reservoir rock surface.

This work is useful for conducting quick screening of the low salinity effect of reservoir rocks. It could also be applied to select optimum salinity and composition of brine for LSWF.

UV-Vis spectroscopy measurements could not detect all the polar components present as estimates were made within only 400nm wavelength. Further work carried out to measure retention within other ranges of wavelength, could therefore prove useful. Also UV-Vis Spectroscopy does not give specific measurement of retention but it is only able to compare the amount of polar components present in two samples. It is therefore recommended that methods capable of estimating retention of polar components more specifically should be adopted.

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9. Appendices

A. Standard Absorption Curve Data

Table 8 Experimental Data used to prepare Standard Absorption curves

Vol. Ratio (STO: Solvent)	Vol. Conc. (ml/ml)	Untreated STO	Treated STO
		Absorbance (A)	Absorbance (A)
1:100	0.0100	3.015	
1:200	0.0050	2.314	
1:300	0.0033	1.544	
1:400	0.0025	1.393	0.932
1:600	0.0017	0.792	0.544
1:1000	0.0010	0.41	0.342
1:2000	0.0005	0.201	0.106

B. Flooding Experiment Data, investigating effect of brine composition on retention of polar oil components

Table 9 Effluent sample concentration after flooding column with FW

FW							Reference STO
CPO(ml)	Normalized CPO (PV)	Average CPO(PV)	Absorbance (A)	Diluted Eff. Sample CSTO (ml/ml)	Original Eff. Sample CSTO(ml/ml)	CSTO(ml/ml)	
2	0.3	0.1	0.605	0.0013	0.0063	0.0091	
4	0.6	0.4	0.696	0.0015	0.0073	0.0091	
6	0.9	0.7	0.689	0.0014	0.0072	0.0091	
8	1.1	1.0	0.744	0.0016	0.0078	0.0091	
10	1.4	1.3	0.743	0.0016	0.0078	0.0091	
12	1.7	1.6	0.744	0.0016	0.0078	0.0091	
14	2.0	1.9	0.777	0.0016	0.0082	0.0091	
16	2.3	2.1	0.789	0.0017	0.0083	0.0091	
Reference STO			0.865	0.0018	0.0091		

Table 10 Effluent sample concentration after flooding column with LSW1

LSW1						
CPO(ml)	Normalized CPO (PV)	Average CPO(PV)	Absorbance (A)	Dil. Eff. Sample CSTO (ml/ml)	Orig. Eff. Sample CSTO(ml/ml)	
2	0.3	0.1	0.530	0.0011	0.0056	
4	0.6	0.4	0.590	0.0012	0.0062	
6	0.9	0.7	0.613	0.0013	0.0064	
8	1.2	1.0	0.682	0.0014	0.0072	
10	1.5	1.3	0.699	0.0015	0.0073	
12	1.7	1.6	0.778	0.0016	0.0082	
14	2.0	1.9	0.760	0.0016	0.0080	
16	2.3	2.2	0.793	0.0017	0.0083	

Table 11 Effluent sample concentration after flooding column with LSW2

LSW2						
CPO(ml)	Normalized CPO (PV)	Average CPO(PV)	Absorbance (A)	Dil. Eff. Sample CSTO (ml/ml)	Orig Eff. Sample CSTO(ml/ml)	
2	0.3	0.1	0.565	0.0012	0.0059	
4	0.6	0.4	0.602	0.0013	0.0063	
6	0.8	0.7	0.641	0.0013	0.0067	
8	1.1	1.0	0.625	0.0013	0.0066	
10	1.4	1.3	0.707	0.0015	0.0074	
12	1.7	1.5	0.712	0.0015	0.0075	
14	1.9	1.8	0.778	0.0016	0.0082	
16	2.2	2.1	0.764	0.0016	0.0080	

Table 12 Effluent sample concentration after flooding column with SW

SW					
CPO(ml)	Dimensionless CPO (PV)	Average CPO(PV)	Absorbance (A)	Dil. Eff. Sample CSTO (ml/ml)	Orig. Eff. Sample CSTO(ml/ml)
2	0.3	0.1	0.668	0.0014	0.007
4	0.5	0.4	0.689	0.0014	0.007
6	0.8	0.7	0.753	0.0016	0.008
8	1.1	1.0	0.754	0.0016	0.008
10	1.4	1.2	0.747	0.0016	0.008
12	1.6	1.5	0.813	0.0017	0.009
14	1.9	1.8	0.773	0.0016	0.008
16	2.2	2.1	0.819	0.0017	0.009

Table 13 Data for comparing the extent of retention in various flooding experiments

FW		LSW1		LSW2		SW	
Average CPO(PV)	Retention(ml)	Average CPO(PV)	Retention(ml)	Average CPO(PV)	Retention(ml)	Average CPO(PV)	Retention(ml)
0.1	0.0027	0.1	0.0035	0.1	0.0032	0.1	0.0021
0.4	0.0018	0.4	0.0029	0.4	0.0028	0.4	0.0019
0.7	0.0019	0.7	0.0027	0.7	0.0024	0.7	0.0012
1.0	0.0013	1.0	0.0019	1.0	0.0025	1.0	0.0012
1.3	0.0013	1.3	0.0018	1.3	0.0017	1.2	0.0012
1.6	0.0013	1.6	0.0009	1.5	0.0016	1.5	0.0005
1.9	0.0009	1.9	0.0011	1.8	0.0009	1.8	0.0010
2.1	0.0008	2.2	0.0008	2.1	0.0011	2.1	0.0005

C. Investigating the effect of the amount of acidic components present in STO on the retention of polar oil components

Table 14 Effluent sample concentration after flooding column with FW and untreated STO

FW, Untreated STO						Reference oil
CPO(ml)	Normalized CPO (PV)	Average CPO(PV)	Absorbance (A)	Dil. Eff. Sample CSTO(ml/ml)	Orig. Eff. Sample CSTO(ml/ml)	CSTO(ml/ml)
2	0.3	0.1	0.671	0.0014	0.0070	0.0091
4	0.6	0.4	0.686	0.0014	0.0072	0.0091
6	0.9	0.7	0.732	0.0015	0.0077	0.0091
8	1.1	1.0	0.764	0.0016	0.0080	0.0091
10	1.4	1.3	0.777	0.0016	0.0082	0.0091
12	1.7	1.6	0.809	0.0017	0.0085	0.0091
14	2.0	1.9	0.853	0.0018	0.0090	0.0091
16	2.3	2.1	0.86	0.0018	0.0090	0.0091
	Reference STO (Standard)		0.865	0.0018	0.0091	0.0091

Table 15 Effluent sample concentration after flooding column with FW and treated STO

FW, Treated STO						Reference oil
CPO(ml)	Normalized CPO (PV)	Average CPO(PV)	Absorbance (A)	Dil. Eff. Sample CSTO (ml/ml)	Orig. Eff. Sample CSTO(ml/ml)	CSTO(ml/ml)
2	0.3	0.1	0.359	0.0011	0.0056	0.0112
4	0.6	0.4	0.551	0.0016	0.0080	0.0112
6	0.9	0.7	0.604	0.0017	0.0086	0.0112
8	1.1	1.0	0.705	0.0020	0.0099	0.0112
10	1.4	1.3	0.701	0.0020	0.0098	0.0112
12	1.7	1.6	0.725	0.0020	0.0101	0.0112
14	2.0	1.9	0.724	0.0020	0.0101	0.0112
16	2.3	2.1	0.795	0.0022	0.0110	0.0112
	Reference STO (Standard)		0.809	0.0022	0.0112	0.0112

Table 16 Comparing retention, Treated Vs Untreated STO

Retention, FW, ml		
Average CPO (PV)	Untreated STO	Treated STO
0.1	0.0020	0.0056
0.4	0.0019	0.0032
0.7	0.0014	0.0025
1.0	0.0011	0.0013
1.3	0.0009	0.0013
1.6	0.0006	0.0010
1.9	0.0001	0.0011
2.1	0.0001	0.0002

Table 17 Effluent sample concentration after flooding column with KCl brine, and treated STO

KCl Brine, Treated STO						Reference oil
CPO(ml)	Normalized CPO (PV)	Average CPO(PV)	Absorbance (A)	Dil. Eff. Sample CSTO (ml/ml)	Original Eff. Sample CSTO(ml/ml)	CSTO(ml/ml)
2	0.3	0.1	0.343	0.0011	0.0054	0.0112
4	0.6	0.4	0.489	0.0014	0.0072	0.0112
6	0.8	0.7	0.688	0.0019	0.0097	0.0112
8	1.1	1.0	0.715	0.0020	0.0100	0.0112
10	1.4	1.2	0.751	0.0021	0.0104	0.0112
12	1.7	1.5	0.758	0.0021	0.0105	0.0112
14	1.9	1.8	0.757	0.0021	0.0105	0.0112
16	2.2	2.1	0.765	0.0021	0.0106	0.0112

Table 18 Effluent sample concentration after flooding column with KCl brine, and treated STO

KCl Brine, Untreated STO						Reference oil
CPO(ml)	Normalized CPO (PV)	Average CPO(PV)	Absorbance (A)	Dil. Eff. Sample CSTO (ml/ml)	Original Eff. Sample CSTO(ml/ml)	CSTO(ml/ml)
2	0.3	0.1	0.707	0.0015	0.0074	0.0091
4	0.6	0.4	0.709	0.0015	0.0074	0.0091
6	0.8	0.7	0.742	0.0016	0.0078	0.0091
8	1.1	1.0	0.755	0.0016	0.0079	0.0091
10	1.4	1.2	0.755	0.0016	0.0079	0.0091
12	1.7	1.5	0.774	0.0016	0.0081	0.0091
14	1.9	1.8	0.797	0.0017	0.0084	0.0091
16	2.2	2.1	0.779	0.0016	0.0082	0.0091

Table 19 Comparing retention, Treated Vs Untreated STO

Retention, KCL, ml		
ADCPO (ml/ml)	Untreated STO	Treated STO
0.1	0.0017	0.0058
0.4	0.0016	0.0040
0.7	0.0013	0.0015
1.0	0.0012	0.0012
1.2	0.0012	0.0007
1.5	0.0010	0.0006
1.8	0.0007	0.0006
2.1	0.0009	0.0005