SPONTANEOUS IMBIBITION CHARACTERISTICS OF FONTAINEBLEAU SANDSTONE BY SECONDARY AND TERTIARY RECOVERY

By

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The undersigned hereby certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled “SPONTANEOUS IMBIBITION CHARACTERISTICS OF FONTAINEBLEAU SANDSTONE BY SECONDARY AND TERTIARY RECOVERY” by Sunny Saini in partial fulfilment of the requirements for the degree of Master of Applied Science.

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Dedicated to my Family

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ABSTRACT

Spontaneous imbibition of water into Fontainebleau Sandstone matrix because of capillary gradient is an important mechanism for oil recovery from Fontainebleau Sandstone reservoirs. Spontaneous imbibition characteristics of Fontainebleau Sandstone core were determined by measuring the Wettability Index of four Fontainebleau Sandstone core samples under laboratory conditions. This was done by utilizing a combination of a Benchtop Relative Permeameter Flooding System and Amott Cups. The specimen had a diameter of 38mm and a height of 47mm. Permeability and porosity of the cores varied from 12 to 14 mD and 10 to 14% respectively. The fluids and chemicals used were kerosene, synthetic brine and Sodium dodecyl sulphate. Amott's method was used to measure the wettability index. This method consists of four steps: (1) brine flooding, (2) spontaneous imbibition of brine, (3) kerosene flooding, (4) spontaneous imbibition of kerosene.

One core was saturated with kerosene and then flooded with brine, followed by spontaneous imbibition of brine. Similarly, another core was saturated with brine and then flooded with kerosene, followed by spontaneous imbibition of kerosene. Similar procedures were used for other two cores except the addition of surfactant to the synthetic brine. All cores were then cleaned and re-saturated for spontaneous imbibition of kerosene and brine. All Experiments were performed under laboratory temperature conditions. Oil and water wettability values were obtained along with secondary and tertiary oil recoveries. These values were used to calculate the wettability index of Fontainebleau sandstone cores. Spontaneous imbibition characteristics of the cores obtained from the experimental data indicate that Fontainebleau Sandstone formation is a potential candidate for Secondary and Tertiary oil recovery by water injection and spontaneous imbibition.

LIST OF ABBREVIATIONS AND SYMBOLS USED

EOR	Enhanced Oil Recovery
OOIP	Original oil-in-place
CO_2	Carbon – dioxide
Υ	Surface tension [dyne/cm]
Θ	Angle of contact [degrees]
l, g, s	liquid, gas, solid
USBM	U.S bureau of mines
NMR	Nuclear Magnetic Relaxation
SEM	Scanning Electron microscopy
ROS	Residual oil saturation
IWS	Irreducible water saturation
S_w	Water saturation [fraction]
S_o	Oil saturation [fraction]
δ_o	Displacement by oil- ratio
V_{wsp}	Water volume displaced by spontaneous imbibition [ml]
V_{wt}	Total displaced water volume [ml]
δ_w	Displacement by water- ratio
V_{osp}	Oil volume displaced by spontaneous imbibition [ml]
V_{ot}	Total displaced oil volume [ml]
K	Permeability [mD]
A	Area of cross-section [cm^2]
Δp	Pressure head loss across the media [psi]
μ	Viscosity [cP]
L	Length [cm]
p_c	Capillary pressure [psi]

p_{nw}	Pressure of the non-wetting phase [psi]
p_w	Pressure of the wetting phase [psi]
Q	Flow rate [cm^3/min]
σ	Interfacial tension [dynes/cm]
WI	Wettability index
T_D	Dimensionless time
t	Imbibition time [mins]
Ø	Porosity [fraction]
μ_o, μ_w	Viscosity of oil and water respectively [cP]
L_c	Characteristic length [cm]
D	Diameter [cm]

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CHAPTER: 1 Introduction

1.1 Introduction

One of the most important recovery mechanisms in hydrocarbon reservoir is spontaneous imbibition, where capillary pressure causes water to invade into water-wet and mixed-wet rock containing oil (Tavassoli et al., 2005). In a reservoir rock, the major amount of reservoir fluid is stored in the matrix but is not accessible because of low permeability. Comparatively, fracture system has higher permeability. Most of the fluid flows out from the fracture system leaving behind a major amount in the matrix. Spontaneous imbibition process facilitates the draining out the excess fluid from the rock matrix. Two main modes of spontaneous imbibition are, counter-current spontaneous imbibition, in which the displacing wetting fluid flows in the opposite direction from the produced non-wetting fluid, and co-current spontaneous imbibition, in which the wetting phase and non-wetting phase are flowing in the same direction. The reservoir rock can be oil-wet, water-wet, or mixed wet. There are certain surface active components in the crude oil which can alter the wettability of the rock from oil-wet to water-wet and vice versa. Rate and extent of spontaneous imbibition provides a measure of wettability that is dependent on surface energy. However, the mechanism of imbibition is complex and many factors beside wettability affect the rate of spontaneous imbibition and displacement efficiency (Morrow, 2001). In the petroleum industry, there is a strong interest in prediction and improvement of oil recovery from fractured reservoirs. Measurement of oil recovery by spontaneous imbibition is widely applied for characterization of wettability and prediction of oil recovery from fractured reservoirs (Mai et al., 2006; Thomas et al., 2008).

Crude oil production from the reservoir can be categorized into primary, secondary and tertiary recovery. Primary recovery is the production of oil by native energy such as gas drive or natural water drive. The differential pressure available from reservoir forces to recover oil gradually falls with the life of the reservoir and becomes insufficient to force oil to the production wells (Chen, 2011). In this case, secondary recovery methods are applied to the reservoir. Fluid is injected into the reservoir to maintain the reservoir pressure, thereby replacing or increasing the natural reservoir drive. This is normally achieved by water-injection or gas-injection. At the end of secondary recovery, a significant amount of oil is still left in the reservoir. To extract the remaining oil from the reservoir, tertiary oil recovery methods are applied. Tertiary recovery methods are also called Enhance oil recovery (EOR) methods. EOR can be divided into thermal, gas, and chemical methods. Selection of these methods depends on the type of reservoir and availability of injection fluid.

Fontainebleau sandstone rock from south Paris basin has a significant hydrocarbon potential which leads to the motivation of this research work. The composition of Fontainebleau sandstone is 99.8% silica (mainly quartz crystals). The core samples were provided by VINCI technologies. Fontainebleau sandstone core samples were subjected to spontaneous imbibition and forced imbibition methods to determine the wettability characteristics of the reservoir rock.

1.2 Research Objective

In this research, the main objective was to determine the spontaneous imbibition characteristics of Fontainebleau sandstone cores by secondary and tertiary recovery methods. This included determination of (1) water wettability index, (2) oil wettability index, and (3) wettability index of the core by secondary and tertiary recovery. Another objective of this research was to observe the change in wettability of the core by the use of a surfactant.

1.3 Enhanced Oil Recovery

Enhanced Oil Recovery is a generic term referring to techniques for increasing the amount of crude oil that can be recovered from an oil field. Using EOR, 30-60% of the reservoir's original oil can be extracted (Trinity, 2006). Normally, only 5-30% of the original crude oil can be produced by the pressure energy stored in the reservoir. This particular phase of oil recovery is known as Primary Oil Recovery (Standnes, 2001).

During production, Water Injection is the usual method to maintain the reservoir pressure. The injected water maintains the pressure above the bubble point ensuring that no gas is liberated in the reservoir and pushes the oil in front of the water towards the production well (Standnes, 2001). The water flooding method usually increases the oil recovery to a total of 40-60% of original oil-in-place (OOIP). This phase of oil production is known as Secondary Oil Recovery. During water flooding, oil is recovered at a steady increasing water-oil ratio at the production wells. When the water-oil ratio becomes high, oil cannot be produced in a cost effective way and the field has reached its economical limits (Standnes, 2001). At this point there is still 40-60% of OOIP left in the reservoir, mainly because of rock properties and unfavourable wettability conditions. This residual oil left in the reservoir after the secondary oil recovery phase becomes the target for the Enhanced Oil recovery (EOR) methods. Since EOR methods follow the secondary oil recovery phase, they are sometimes called Tertiary Oil Recovery Methods (Standnes, 2001). Figure 1.1 shows the enhanced oil recovery process.

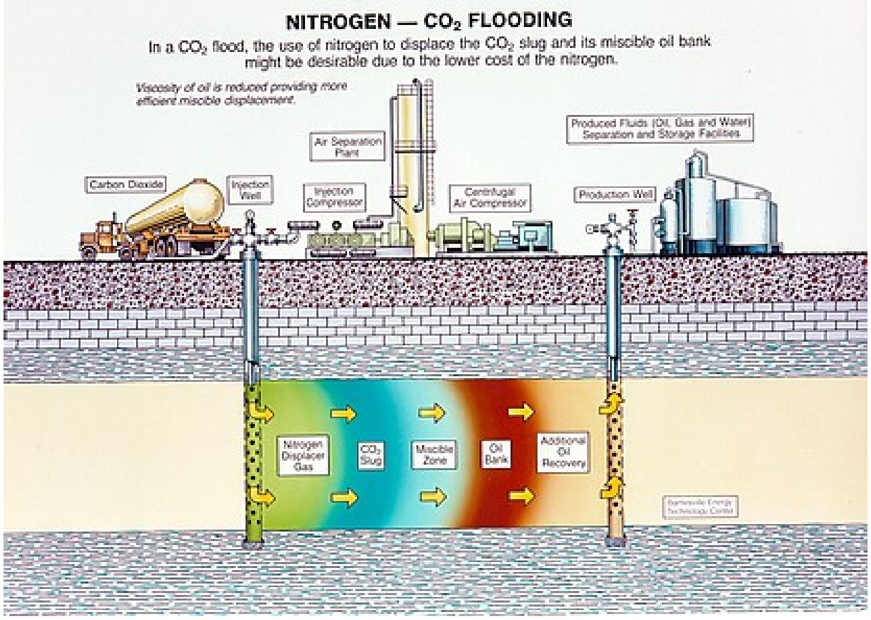


Figure 1.1 Nitrogen-CO_2 Flooding (Trinity, 2006).

Three major EOR methods have been found to be commercially successful to varying degrees:

Thermal Recovery, which involves introduction of heat such as injection of steam to lower the viscosity of heavy viscous oil and improve the flow through the reservoir.

Gas Injection, which uses gases such as natural gas, nitrogen or carbon-dioxide that expand in the reservoir to push additional oil to the production well, or other gases that dissolve in oil to lower its viscosity and increase its flow rate.

Chemical Injection, which uses long chain polymers to increase the effectiveness of water flooding, or surfactants that help lower the surface tension and prevent the oil droplets from moving through a reservoir. Each of these techniques has been hampered by its relatively high cost and, in some cases, by the unpredictability of its effectiveness (Trinity, 2006).

1.4 Fractured Reservoirs

Naturally fractured reservoirs are heterogeneous porous media which comprises matrix blocks and fractures. Most of the fluid is stored in the matrix blocks, but the matrix has a low permeability (Fujiwara, 1989). On the other hand, the fractures store less amount of fluid, but have extremely high permeability. Most of the reservoir fluid flows from the matrix blocks into the wellbore through the permeable fractures. Therefore, the producing capacity of a naturally fractured reservoir is governed by the matrix and fracture system fluid transport capacity (Fujiwara, 1989). Figure 1.2 shows the model of matrix and fracture system. In the early 1950's, production from the highly fractured Spraberry field in west Texas turned attention towards the mechanism known as Spontaneous Imbibition of water into the matrix block as an efficient way to increase oil recovery from fractured reservoirs (Standnes, 2001).

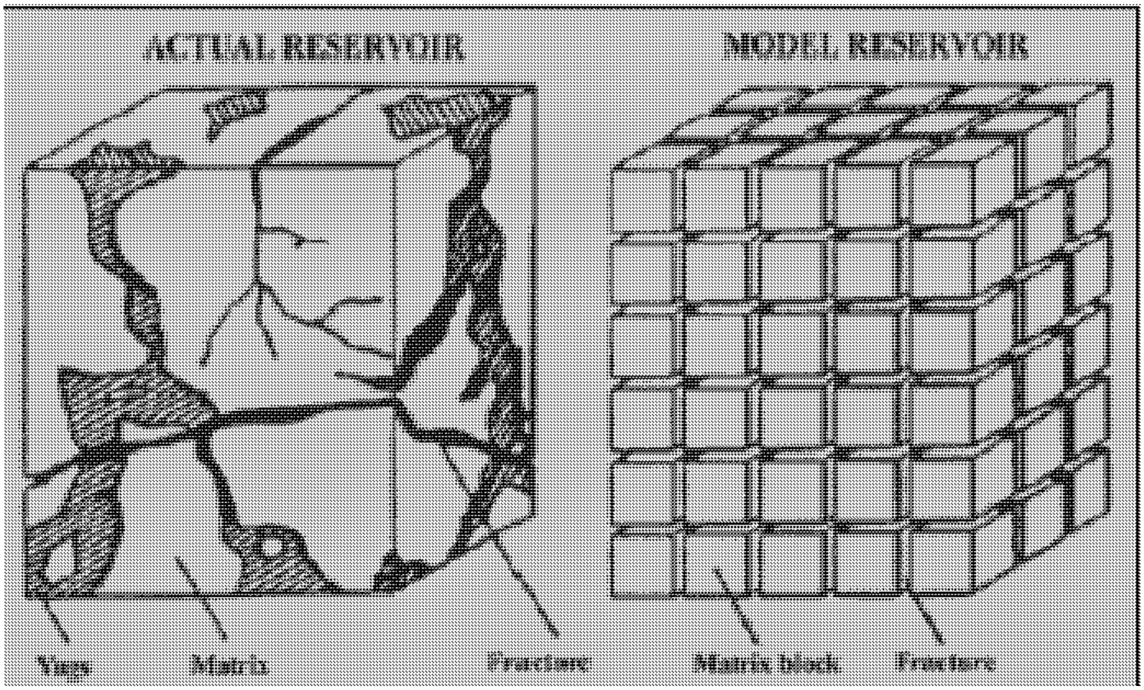


Figure 1.2 Naturally fractured reservoir (Fujiwara, 1989).

In case of water-wet reservoir rock, water imbibes spontaneously into the matrix block and pushes the oil out to the fracture system. This mechanism is currently referred to as the most important method to increase the displacement efficiency in fractured reservoirs (Standnes, 2001). However, this method does not work efficiently in case of oil-wet reservoir rocks because of the negative capillary pressure and absence of spontaneous imbibition of water. Mixed-wet cores imbibe both water and oil spontaneously and it becomes arbitrary which phase is chosen as wetting one. If the porous media is oil-wet, oil flows into the medium and reduces the water saturation (Standnes, 2001).

Chapter: 2 Fundamentals

2.1 Wettability

Wettability can be defined as the tendency of one fluid to spread or adhere to a solid surface in the presence of other immiscible fluids (Standnes, 2001). The fluid with the highest affinity for the solid surface is called the wetting fluid, whereas the other is called non-wetting fluid (Standnes, 2001). When two fluids are in contact with each other, their equilibrium configuration depends on the surface tension between each pair of the three phases as shown in Figure 2.1. Each surface tension acts upon its respective interface and defines the angle Θ at which the liquid contacts the surface (Glover, 1998; Mungan, 1964; Schembre et al., 1998; Yildiz et al., 1998). This is called the wetting angle of the liquid to the solid. Table 2.1 shows the contact angle and interfacial tension for common fluid-fluid interfaces.

According to Young`s Equation:

$$\gamma_{lg} \cos\theta = \gamma_{sg} - \gamma_{sl} \tag{2.1}$$

Where,

ϒ = Surface Tension, dyne/cm
ϴ = Angle of Contact, degrees
l = Liquid
g = Gas
s = Solid

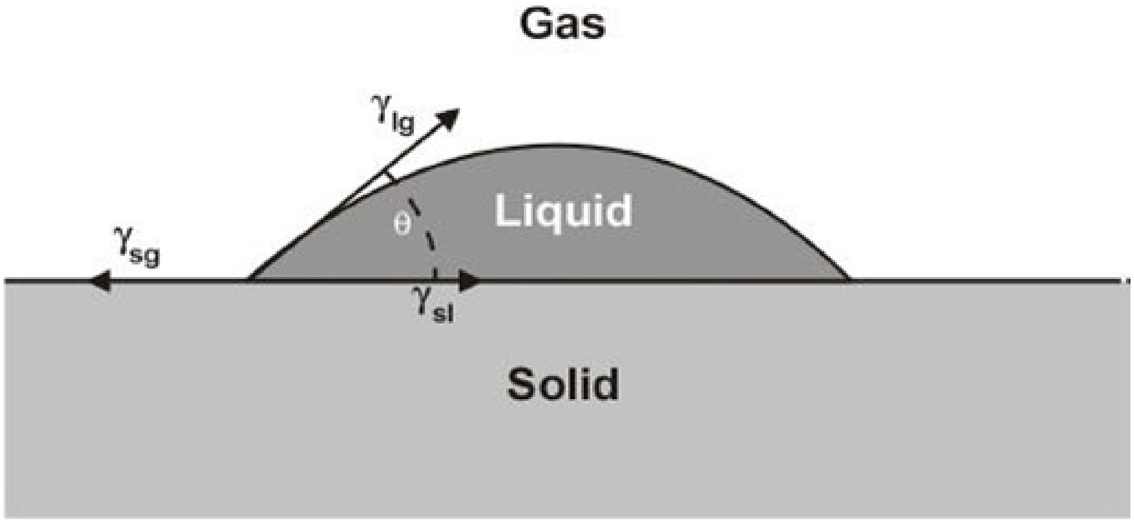


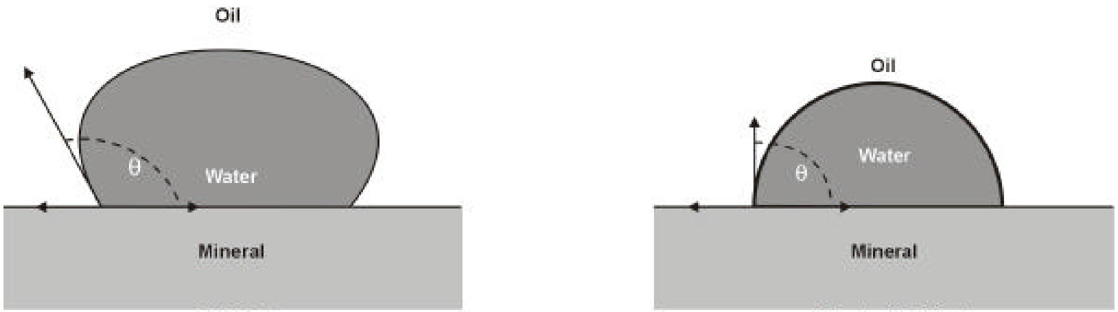
Figure 2.1 Liquid-solid-gas wetting angle (Glover, 1998).

Table 2.1 Contact angle and Interfacial tension for common fluid-fluid interfaces (Glover, 1998).

Interface	Contact Angle, Θ, Degrees	Cos Θ	Interfacial Tension, dynes/cm
Air-Water	0	1.0	72
Oil-Water	30	0.866	48
Air-Oil	0	1.0	24
Air Mercury	140	-0.765	480

2.1.1 Types of Wettability in Porous Medium

The contact angle ϴ can vary between 0 and 180 degrees depending on the relative affinity for the fluids towards the surface. A contact angle of less than 90 degrees indicates that a surface has higher affinity for water than for oil, and it is classified as water wet (Standnes, 2001). If the contact angle is greater than 90 Degrees, the surface has higher affinity for oil than for water, and it is termed as oil wet (Standnes, 2001). If the contact angle is equal to 90 Degrees, both fluids have equal affinity for the surface, and it is termed a neutral wet or mixed wet (Standnes, 2001). Figure 2.2 shows the contact angle for various wetting properties.



Oil Wet
Wetting Angle > 90 degrees

Neutrally Wet
Wetting Angle = 90 degrees

Water Wet
Wetting Angle < 90 degrees

Totally Water Wet
Wetting Angle = 0 degrees

Figure 2.2 Wetting angle for various wetting properties (Glover, 1998).

2.1.2 Wettability Measurements

Several methods are used to determine the wettability of a rock to various fluids. The main ones are:

- **Microscopic Observation -** Rock samples are directly observed and wetting angles are measured. Petrographic microscope or SEM fitted with an environmental stage is used. Measurements are difficult and good data rely on luck more than judgement (Glover et al., 1998).

- **Amott Wettability Measurements -** This is a macroscopic mean wettability of a rock to a given fluid. The amount of fluid imbibed forcibly and spontaneously by a rock sample is measured. It has no validity as an absolute measurement but is used in the industry to compare wettability of various core plugs (Glover, 1998).

- **US Bureau of Mines Method –** This is a macroscopic mean wettability of a rock to a given fluid. The USBM method is similar to the Amott's method but considers the required work for forced displacement. This method is used in industry to compare various core plugs (Glover et al., 1998).

- **NMR –** This method is used to determine the fractions of core that are water wet and oil wet in a core with fractional wettability. The nuclear magnetic thermal relaxation time for water protons in porous media is used to find the wettability. The use of magnetic thermal relaxation time is taken from the observation that the porous media surfaces can significantly reduce the measured relaxation time (Anderson, 1986).

2.1.3 Quantitative Method

Amott Method

The combination of spontaneous imbibition and forced imbibition process is used in the Amott method to determine the average wettability of a core. Various fluids and reservoir cores can be used in the test. The Amott method states that the wetting fluid will imbibe spontaneously into the core, displacing the non-wetting fluid (Anderson, 1986). The influence of other factors, such as relative permeability, viscosity, and the initial saturation of the rock is reduced by using the ratio of fluid displaced by spontaneous imbibitions to forced imbibition (Anderson, 1986).

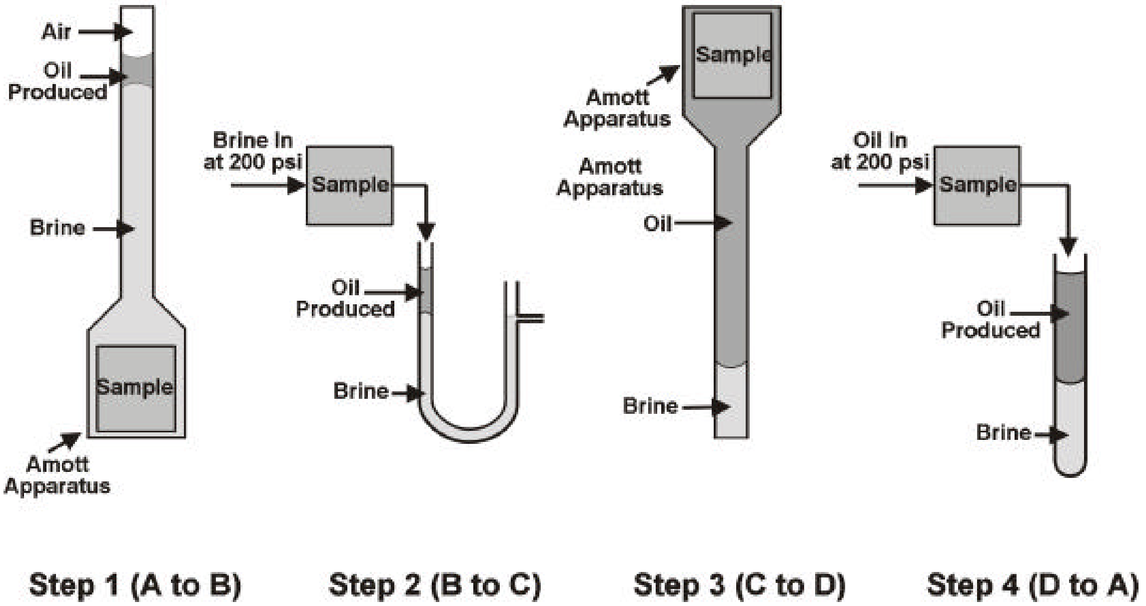


Figure 2.3 Amott wetting technique (Glover, 1998).

A core sample is prepared by centrifuging under brine until the residual oil saturation, ROS, is reached. According to Figure 2.3, the Amott wettability measurement consists of the following four steps: (1) immerse the core in oil, and measure the volume of water displaced by spontaneous imbibition (A to B); (2) centrifuge the core in oil until the irreducible water saturation, IWS, is reached, and measure the total amount of water displaced, including the water displaced by water imbibition (B to C); (3) immerse the core in brine, and measure the volume of oil spontaneously displaced by the imbibition of water (C to D); and (4) centrifuge the core in oil until ROS is reached, and measure the total amount of oil displaced (D to A) (Anderson, 1986).

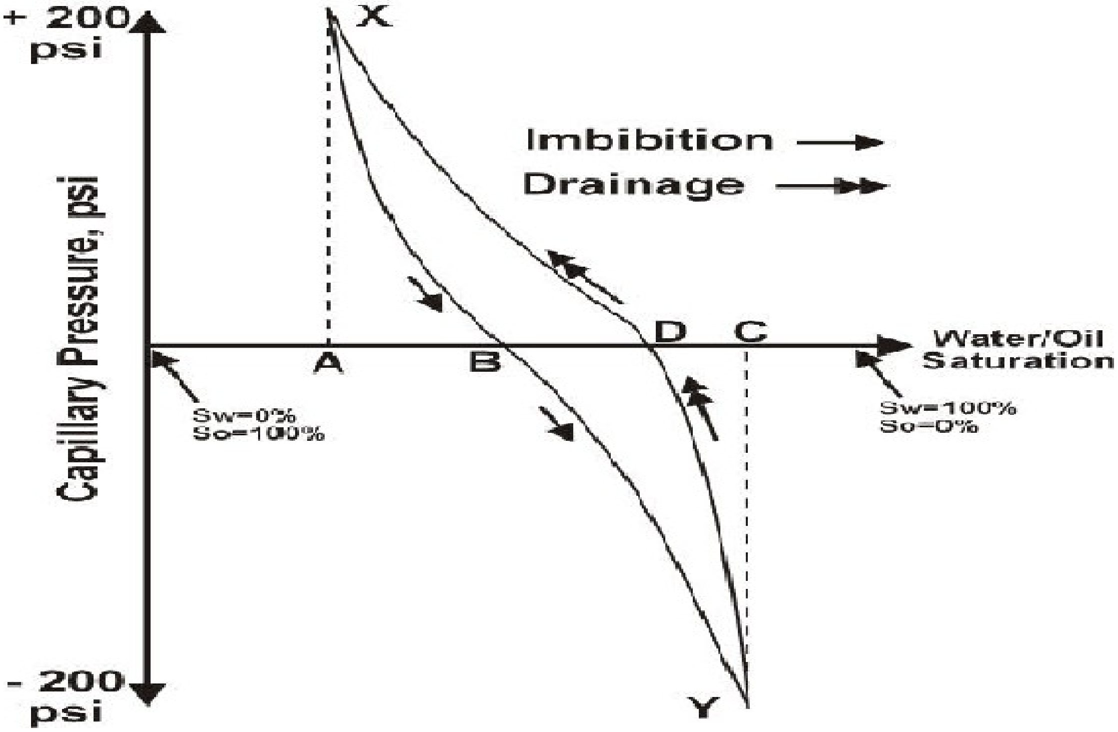


Figure 2.4 Wettability test data (Glover, 1998)

According to Figure 2.4, AB gives oil produced in step 1; BC gives oil produced in step 2; CD gives water produced in step 3; and DA gives water produced in step 4. The test results are expressed by:

(1) "Displacement by oil-ratio", the ratio of water volume displaced by spontaneous imbibition of oil, $V_{wsp,}$ to the total water volume displaced by oil imbibition and forced displacement, V_{wt} (Anderson, 1986).

$$\delta_o = \frac{V_{wsp}}{V_{wt}} \tag{2.2}$$

(2) "Displacement by water-ratio", the ratio of oil volume displaced by spontaneous water imbibition, $V_{osp,}$ to the total oil volume displaced by imbibition and forced displacement, V_{ot} (Anderson, 1986).

$$\delta_w = \frac{V_{osp}}{V_{ot}} \tag{2.3}$$

Amott chose an arbitrary time period of 20 hours for the spontaneous oil and water imbibition steps in this method. At the end of the experiment the so called Amott-Harvey wettability index is calculated, which states that the wettability index is the displacement by water ratio minus the displacement by oil ratio:

$$I = \delta_w - \delta_o = \frac{V_{osp}}{V_{ot}} - \frac{V_{wsp}}{V_{wt}} \tag{2.4}$$

The wettability index varies from +1 for complete water wetness to -1 for complete oil wetness. Wettability of the core is water wet when $+0.3 \leq I \leq 1$, Mixed wet when $-0.3 \leq I \leq 0.3$, and oil wet when $-1 \leq I \leq 0.3$ (Anderson, 1986).

2.2 Darcy's Law

The flow of a fluid through a porous medium is often modeled using Darcy's Law. It states that the fluid flow between two points is directly proportional to the pressure difference between two points and the ability of the media to impede the flow. Flow impeding factor is referred to as permeability (Ahmed, 1946). In other words, Darcy's law is a simple relationship between discharge rate through a porous media and the pressure drop over a given distance. Diagrammatic representation of Darcy's Law is given in Figure 2.5.

According to Darcy's law;

$$Q = \frac{KA}{\mu}\frac{\Delta P}{L} \tag{2.5}$$

Where,

Q = Flow rate through the porous media, cm^3/sec

K = proportionality constant, or permeability, Darcy

μ = Viscosity of the flowing fluid, cP

ΔP = Pressure drop over the media, atm

L = Length of the porous media, cm

A = Cross-sectional area across which flow occurs, cm^2

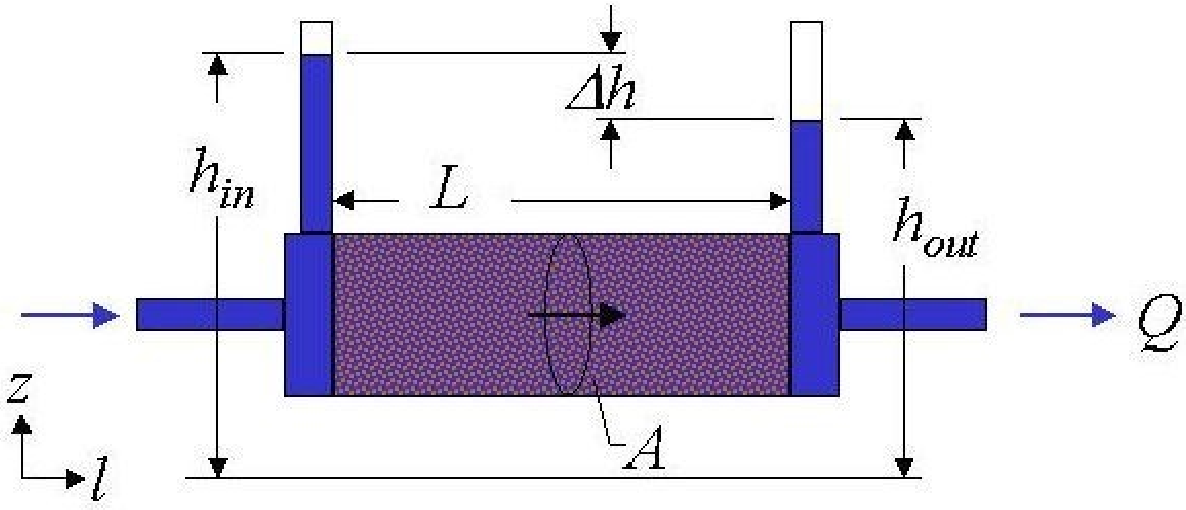


Figure 2.5 Diagrammatic representation of Darcy’s Law (Brown, 2003)

Darcy’s Law applies under the following conditions:

- Laminar (viscous) flow
- Steady state flow
- Incompressible fluids
- Homogeneous formation

According to Darcy’s law, a fluid flowing with the flow rate of 1 cm^3/s through a cross-sectional area of 1 cm^2 with a viscosity of 1 cP and pressure gradient at 1 atm/cm will have the permeability value of 1 mD (Ahmed, 1946).

2.3 Surface and Interfacial Tension

When two immiscible fluids are in contact with each other, it becomes necessary to consider the effect of the forces at the interface. The term surface tension is used to describe the acting forces when a liquid and gas come in contact with each other. On the other hand, when two liquids are in contact with each other, the acting forces are called interfacial tension (Abrams, 1975). Diagrammatic representation of surface and interfacial tension is shown in Figure 2.6. Surfaces of liquids act like thin films which possess little strength but resists being broken.

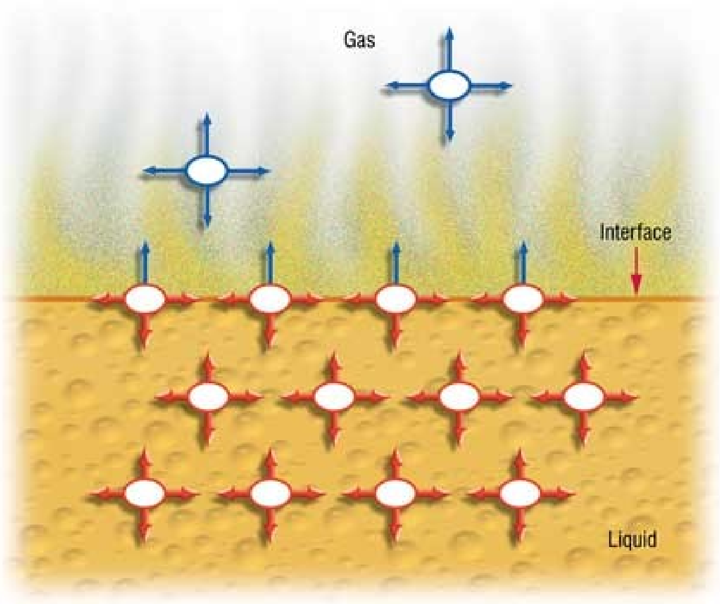


Figure 2.6 Diagrammatic representations of surface and interfacial tension (Fitch, 2002)

It is believed that this behaviour is caused by attraction between molecules within a given system. Molecules are attracted to each other in proportion to the product of their masses and inversely as the squares of the distance between them. The surface and interfacial tension is denoted by the symbol σ and the SI unit as N/m (Ahmed, 1946).

2.4 Capillary Pressure

The combined effect of surface and interfacial tension of the rock and fluids, geometry, pore size, and the wetting characteristics of the system is referred to as the capillary forces. When two immiscible surfaces get in contact with each other, the curved surface between them tends to adjust into the smallest possible area per unit volume. This holds true whether the fluids are oil and water, water and gas, or oil and gas. A discontinuity in pressure exists between the immiscible fluids, which depends on the curvature of the interface separating the fluids. This pressure difference is called capillary pressure and it is referred by p_c (Ahmed, 1946).

$$p_c = p_{nw} - p_w \tag{2.6}$$

Where,

p_c = Capillary pressure, psi.

p_{nw} = pressure of the non-wetting phase, psi.

p_w = pressure of the wetting phase, psi.

In a porous medium, the displacement of one fluid by another is either aided or opposed by the surface forces of capillary pressure. In order to maintain the porous medium as partially saturated with non-wetting fluid while it is exposed to wetting fluid, the pressure of the non-wetting fluid has to be maintained at a value greater than that in the wetting fluid (Ahmed, 1946).

2.5 Permeability

The property of the porous media that measures the capacity and ability of the formation to transmit fluids is termed as permeability. Rock permeability is regarded as an important rock property because it describes the directional movement and the flow rate of the fluid in the formation. Relative permeability is a very important factor in case of multiphase flow in porous media. Relative permeability varies with different factors. For example, Overburden pressure reduces the permeability. Permeability of the core may be altered during the core cutting process, or during the cleaning process. The problem occurs due to reactive clays. The core sample may not represent the reservoir rock because of the reservoir heterogeneity.

Certain conditions are followed for the measurement of relative permeability. The flow must be laminar, there should not be any reaction between the rock and the fluid, and there must be single phase flow through the rock. Permeability is measured by passing a viscous fluid through a core sample and then measuring the flow rate and pressure drop. Effective permeability is the ability of porous media to transmit fluid when its saturation is less than 100% of the pore space. Relative permeability is the ratio of effective permeability of a given phase, say oil, in presence of another phase, water or gas, to the absolute permeability (Ahmed, 1946).

2.6 Spontaneous Imbibition

Spontaneous imbibition is a process in which the wetting fluid replaces the non-wetting fluid in a porous media by capillary action. Capillary pressure is the product of curvature, C, and the interfacial tension σ. Imbibition plays a key role in many types of oil recoveries, including thermal recovery by steam injection, alternate action of gas and water, and water flooding of reservoirs. Spontaneous imbibition can be classified into co-current and counter current imbibition. Co-current when both the wetting and non-wetting fluid move in one direction, and counter current when the wetting and non-wetting fluid move in opposite directions. Oil recovery by spontaneous imbibition of brine is an important mechanism in fractured reservoirs, especially when the reservoirs have low permeability. Imbibition also leads to the measurement of the wettability of porous medium. The imbibition rate depends on the porous media and its fundamental properties. In naturally fractured reservoirs, the imbibition forces should be strong enough for surfactant-enhanced water flooding (Darvish et al., 2000; Xie et al., 2001; Jadhunandan et al., 1991)

2.6.1 Scaling of Spontaneous Imbibition

Scaling of laboratory results to the reservoir condition is the most widely used approach in order to determine oil recovery. Viscous forces, gravity forces, and capillary forces are the most important forces governing the flow of oil and water during oil production (Morrow, 1979). In spontaneous imbibition viscous forces have less significance when compared to gravity and capillary forces. Scaling helps in predicting the field implications of laboratory experiments. Spontaneous imbibition is driven by only capillary forces, which implies that the reservoir rock should be water-wet. Systems having different fluid properties should take the same time to reach the recovery level as long as certain conditions are fulfilled (Mattax and Kyte, 1962). To understand better Mattax and Kyte proposed a scaling group:

$$T_D = 1.8849 \times 10^{-2} \times t \times \sqrt{\frac{K}{\phi}} \times \frac{\sigma}{\sqrt{\mu_w \times \mu_o}} \times \frac{1}{{L_c}^2} \tag{2.7}$$

Where T_D = dimensionless time, t = imbibition time in mins, K = permeability in mD, φ = fractional porosity, σ = interfacial tension in dynes/cm, μ_o = oil viscosity in cP, μ_w = water viscosity in cP, and L_c = characteristic length in cm.

$$L_c = \frac{Ld}{2\sqrt{d^2+2L^2}} \tag{2.8}$$

Where, L = length of the core and d = diameter of the core.

Some assumptions are made for the equation 2.7; (1) capillary pressure and oil/water viscosity ratios must be duplicated; (2) sample shape must be identical; (3) relative permeability function must be different; (4) gravity effect must be neglected. Oil produced from fractured reservoirs give different bulk flow between fractures and reservoir matrices for different matrix pore size, shape and boundary. The smaller the ratio of volume to open surface area, the faster will be the imbibition rate (Zhang et al., 1996). The rate of increase in wetting phase saturation is dependent on interfacial tension, viscosities of water and oil phase, detailed pore structure, core geometry and boundary conditions that determine wettability. Fresh core samples lose more oil during the brine imbibition process, which is strong evidence that the reservoir is strongly water wet with the contact angle close to zero. Measurement of spontaneous water imbibition is a widely applicable method for determining wettability (Rapopport, 1955).

Morrow et al., (2001) provided an analysis of imbibition into a capillary tube, which demonstrates the basic competition between capillary driving force and viscous resistance for flow that is clearly co-current.

Consider a capillary tube of radius, r, containing a meniscus of a perfectly wetting liquid. The capillary pressure, P_c, is equal to:

$$P_c = \frac{2\sigma}{r} \tag{2.9}$$

According to Poisenille equation:

$$\frac{\Delta P}{L} = \frac{8\mu v}{r^2} \tag{2.10}$$

Where, ΔP = pressure drop, L = length, μ = viscosity, v = mean velocity, r = radius of the tube.

If a capillary tube is being invaded by a fluid of viscosity, μ, displacing a gas with negligible viscosity, then the driving pressure is P_c and the viscous resistance is proportional to the invaded length. Combining equation (2.9) and (2.10):

$$v = \frac{2\sigma}{r}\frac{1}{L}\frac{r^2}{8\mu} = \frac{\sigma r}{4\mu L} \tag{2.11}$$

The velocity, v, is dL/dt and so, on integrating, we get:

$$L^2 = \frac{\sigma r t}{2\mu} \tag{2.12}$$

If the tube length is L_{max} then fractional length filled, L/L_{max} is:

$$\left(\frac{L}{L_{max}}\right)^2 = \frac{\sigma r t}{2\mu L_{max}^2} \tag{2.13}$$

If the invading and receding fluid have same viscosity, the mean velocity of the advancing interface becomes constant and:

$$\frac{L}{L_{max}} = \frac{\sigma r}{4\mu L_{max}^2} t \tag{2.14}$$

Thus, imbibition into a tube will be scaled by a dimensionless time defined by:

$$t_{Dt} = \frac{\sigma r t}{f(\mu_w,\mu_o) L_{max}^2} \tag{2.12}$$

2.7 Surfactants

Surfactants are amphiphilic molecules containing two parts with different properties towards water. Long hydrophobic hydrocarbon chains bounded to the hydrophilic group represent the usual structure of the surfactant, which is either charged, or non-charged. In standard terminology, the hydrophilic portion is called the head group and the hydrophobic group is called the tail. The hydrocarbon chain can be saturated, straight, branched, or aromatic. The charge of the hydrophilic group plays an important role in classifying the surfactant. Based on the charge of the hydrophilic group, the surfactant is anionic or cationic. If the hydrophilic part only contains polar groups, then the surfactant is non-ionic. A surfactant is zwitter-ionic when it contains both positively and negatively charged groups in the same molecule. Surfactants can change the surface or interfacial properties between two immiscible fluids by lowering the interfacial surface energy (Hou et al., 2006).

It is well known that cationic and anionic surfactants have the ability to interact and create so-called ion-pairs (Eksborg et al., 1973). Such surfactant systems have been studied recently in more detail and are referred to as catanionic surfactant mixtures (Karlsson, 2001). Examples of different types of surfactants are;

Anionic Surfactants – sulphates, sulphonates, phosphates, carboxylates, and stearate.

Cationic Surfactants – pyridium, imidazolinium, piperidinium, and sulphonium compounds.

Amphoteric Surfactants – Aminocarboxylic acids.

Non-Ionic Surfactants – Alkyl-, Alkyl-aryl, acyl-, polyol ethers Alanolamides.

Chapter: 3 Resources

3.1 Porous Media

Fontainebleau sandstone cores from south Paris basin, France were used to carry out the spontaneous and forced imbibition experiments. Fontainebleau sandstone has significant hydrocarbon and carbon-dioxide storage potential. Fontainebleau sandstone has been widely studied and some research studies of other rocks have been validated using results of this sandstone (Robin and Rosenberg, 1995; Robin, 2001; Guillot et al., 1994). Four core samples, cylindrical in shape, were used for the experiments. Cores were labelled as 18G, 18H, 18 I and 18L. Physical properties of the core sample are summarized in Table 3.1. These core samples were new from VINCI technologies, therefore the conventional cleaning procedures were not followed for the spontaneous imbibition experiments. Figure 3.1 shows the Fontainebleau core samples used for the experiments.

Figure 3.1 Fontainebleau sandstone core

Table 3.1 Physical properties of the core samples used in the experiment.

Core Sample	Core Length, (inches)	Core Diameter, (inches)	Dry weight, (g)	Wet weight, (g)	Porosity, ϕ	Permeability, (mD)	Pore Volume, (mL)
18G	3	1.5	128	133	0.12	13.33	6.6
18H	3	1.5	127	133	0.11	13.33	6.5
18I	3	1.5	128	133	0.12	13.33	6.7
18L	3	1.5	132	133	0.11	13.33	6.5

3.2 Fluid System

Oil

Oil used for the experiment was Kerosene with a density of 0.81g/mL at 20°C. Kinematic viscosity of oil at the same temperature was 2.19 cSt. Kerosene was selected for the experiment because it is the best substitute for other kinds of oil in lab experiments. It is also economical and readily available. Kerosene has also been used in more published work related to petroleum studies (Hatiboglu and Babadagli, 2008; Al-Suhaili and Faisal, 2012; Shokrollah and Behbahani, 2004).

Brine

Synthetic brine was prepared to use in the imbibition experiments. The composition of brine used in the experiments comprises 4wt% NaCl and 0.5wt% $CaCl_2$ (Morrow, 1999). The salts were weighted accurately and dissolved in distilled water using a magnetic stirrer. The kinematic viscosity of brine, 1.31 cSt, was measured using Ostwald viscometer. The density of Brine, 1034 gm/cm^3, was measured using hydrometer. The interfacial tension between brine and oil is 48 dyne/cm (Glover, 1998).

Surfactant

Sodium dodecyl sulphate, an anionic surfactant, was used in the imbibition experiments by tertiary recovery. The composition of the surfactant used was 0.2wt% (Samanta, 2011). The salt was weighted accurately and mixed with brine using a magnetic stirrer. The kinematic viscosity of surfactant and brine mixture, 1.22 cSt, was measured using Ostwald viscometer. The density of surfactant and brine mixture, 1032 gm/cm^3, was measured using hydrometer.

3.3 Core Cleaning

The core samples were cleaned by injecting the pore volume of toluene in order to dissolve oil. After injecting toluene, the core samples were injected against pore volume of alcohol to dissolve all components of oil. Later on, the core samples were subjected to distilled water injection in order to rinse the samples. Cleaned cores were then dried in an oven under 60°C for about 24 hours. The core cleaning procedures were carried out under laboratory conditions of 1 atm and 20°C.

CHAPTER: 4 Equipment and Resources

4.1 Core Saturation Equipment

A vacuum oven was used to saturate core samples with kerosene or brine for the imbibition experiments as shown in Figure 4.1. Cores were immersed in the beaker containing kerosene or brine and kept in the vacuum oven for a period of 1 week.

Figure 4.1 Vacuum Oven

4.2 Water-Flooding Equipment

All water flooding experiments were performed using a Benchtop Relative Permeameter BRP 350 from VINCI technologies as shown in Figure 4.2. The flooding experiments were performed with a confining pressure between 800-900 psi, back pressure between 65-70 psi, and injection flow rate of 5cm^3/min. Optimum pressure condition were used in all experiments to facilitate water flooding. The distilled water pump was used to push the piston in order to facilitate water injection from the cylindrical tank.

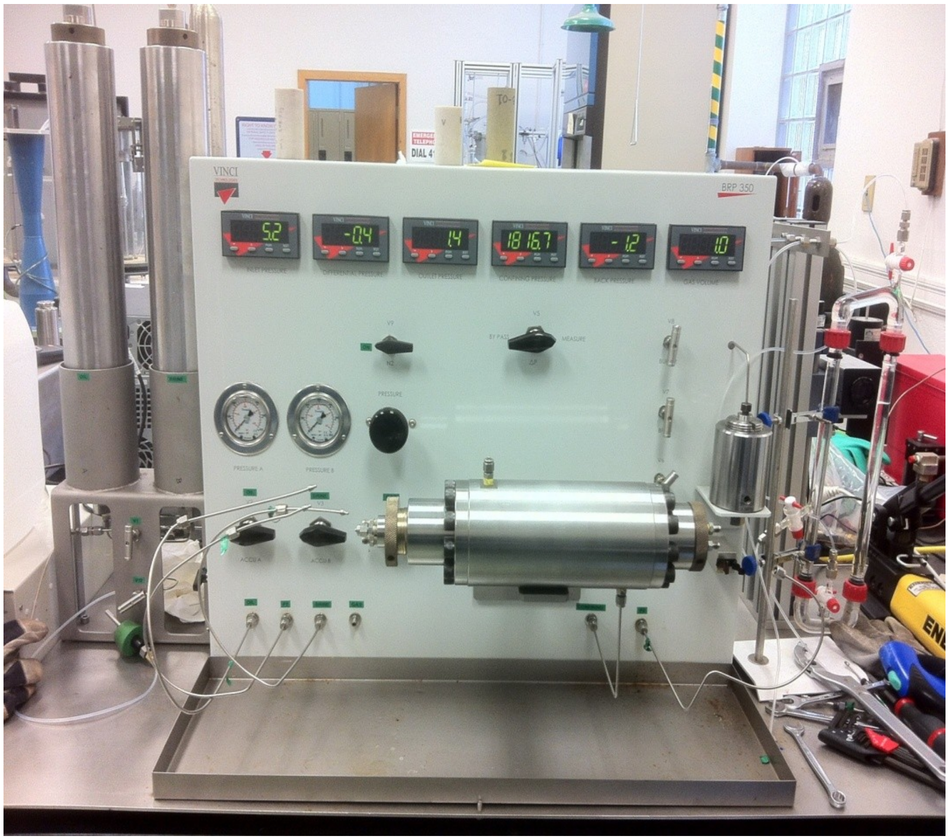


Figure 4.2 Benchtop Relative Permeameter (BRP 350)

4.3 Spontaneous Imbibition Equipment

All spontaneous imbibition experiments were conducted in Amott's cup as shown in Figure 4.3. Sample cores were placed in a vertical position in the Amott's cup and surrounded by imbibition fluid. The experiments were carried out at laboratory conditions of 1 atm and 20°C.

Figure 4.3 Amott's cup

Chapter: 5 Experimental Measurements

5.1 Spontaneous Imbibition of Core 18G

Core sample 18G was saturated with kerosene by keeping the immersed sample in the vacuum oven for one week. After the core saturation, the wet weight of the core sample was measured to find the pore volume. During the initial phase of imbibition, the saturated core was placed vertically inside Amott's cup and surrounded by synthetic brine with all sides subjected to imbibition. The experiment was carried out at laboratory conditions of 1 atm and 20°C. The amount of oil recovered was measured at different time intervals and a graph of oil recovered against imbibition time was plotted. The total spontaneous imbibition time was 150 hours (6.25 days). After the experiment, core sample 18G was cleaned and dried in an oven under 60°C for about 24 hours. The core sample was then used for the next phase of experiment. Figure 5.1 shows the interface between brine and the recovered oil.

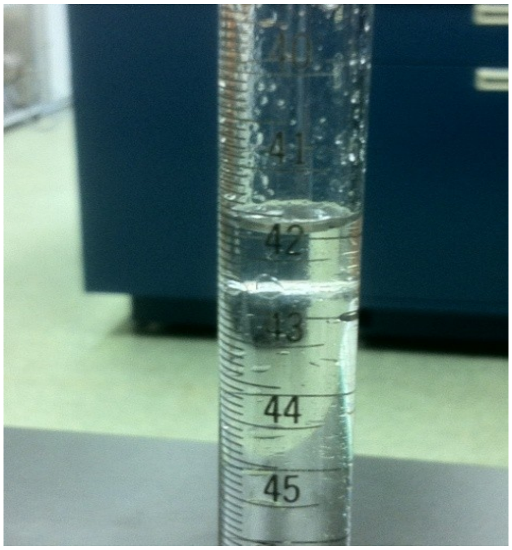


Figure 5.1 Oil recovered by spontaneous imbibition of core 18G.

5.2 Spontaneous Imbibition of Core 18H

Core sample 18H was saturated with synthetic brine by keeping the immersed sample in the vacuum oven for one week. After the core saturation, the wet weight of the core sample was measured to find the pore volume. During the initial phase of imbibition, the saturated core was placed vertically inside Amott's cup and surrounded by kerosene with all sides subjected to imbibition. As shown in Figure 5.2, the Amott's cup was kept in an inverted position because the density of brine is more than the density of kerosene. Hence, the recovered volume of brine settles down at the bottom of the Amott's cup. The experiment was carried out at laboratory conditions of 1 atm and 20°C. The amount of brine recovered was measured at different time intervals and a graph of brine recovered against imbibition time was plotted. The total spontaneous imbibition time was 150 hours (6.25 days). After the experiment, core sample 18H was cleaned and dried in an oven under 60°C for about 24 hours. The core sample was then used for the next phase of experiment.

Figure 5.2 Brine recoveries by spontaneous imbibition of core 18H and 18L.

5.3 Spontaneous Imbibition of Core 18I

Core sample 18I was saturated with kerosene by keeping the immersed sample in the vacuum oven for one week. After the core saturation, the wet weight of the core sample was measured to find the pore volume. During the initial phase of imbibition, the saturated core was placed vertically inside Amott's cup and surrounded by synthetic brine with all sides subjected to imbibition. Sodium Dodecyl Sulphate, an anionic surfactant, was added to synthetic brine prior to the experiment. The experiment was carried out at laboratory conditions of 1 atm and 20°C. The amount of oil recovered was measured at different time intervals and a graph of oil recovered against imbibition time was plotted. The total spontaneous imbibition time was 150 hours (6.25 days). After the experiment, core sample 18I was cleaned and dried in an oven under 60°C for about 24 hours. The core sample was then used for the next phase of experiment. Figure 5.3 shows the recovery of oil by spontaneous imbibition after the addition of surfactant.

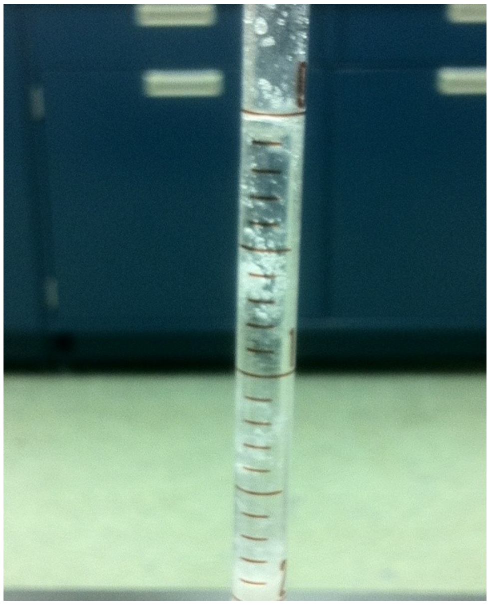


Figure 5.3 Oil recovered by spontaneous imbibition of core 18I.

5.4 Spontaneous Imbibition of Core 18L

Core sample 18L was saturated with synthetic brine by keeping the immersed sample in the vacuum oven for one week. Sodium Dodecyl Sulphate was added to the synthetic brine prior to the experiment. After the core saturation, the wet weight of the core sample was measured to find the pore volume. During the initial phase of imbibition, the saturated core was placed vertically inside Amott's cup and surrounded by kerosene with all sides subjected to imbibition. The Amott's cup was kept in an inverted position because the density of brine is more than the density of kerosene. Hence, the recovered volume of brine settles down at the bottom of the Amott's cup. The experiment was carried out at laboratory conditions of 1 atm and 20°C. The amount of brine recovered was measured at different time intervals and a graph of brine recovered against imbibition time was plotted. The total spontaneous imbibition time was 150 hours (6.25 days). After the experiment, core sample 18L was cleaned and dried in an oven under 60°C for about 24 hours. The core sample was then used for the next phase of experiment.

5.5 Water Flooding of Core 18G Followed by Spontaneous Imbibition

Core sample 18G was saturated with kerosene by keeping the immersed sample in a vacuum oven for one week. A Benchtop Relative Permeameter (BRP 350) from VINCI Technologies was used for the flooding experiment. The core sample was loaded in the core holder and the flooding tank was filled with synthetic brine. The confining pressure of the system was set between 800-900 psi and back pressure was set between 65-70 psi. The injection flow rate was 5cm^3/min. A displacement pump, shown in figure 5.5, was used to force the piston in order to inject brine through the pipelines. Figure 5.4 shows the core holder of BRP 350.

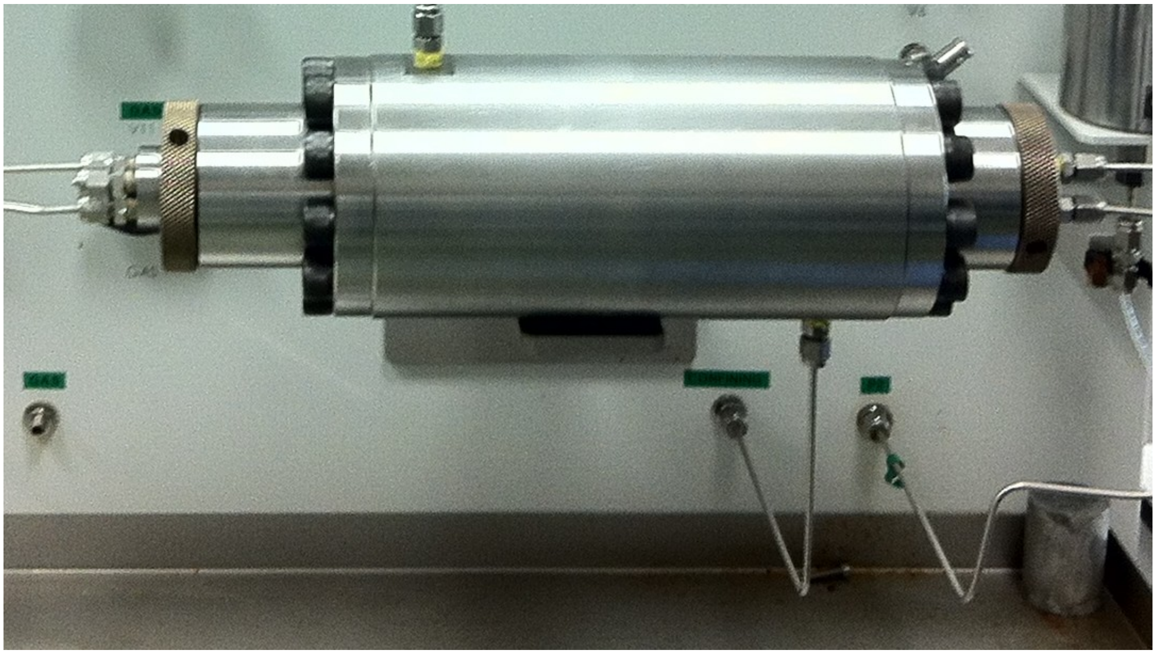


Figure 5.4 Core holder (BRP 350)

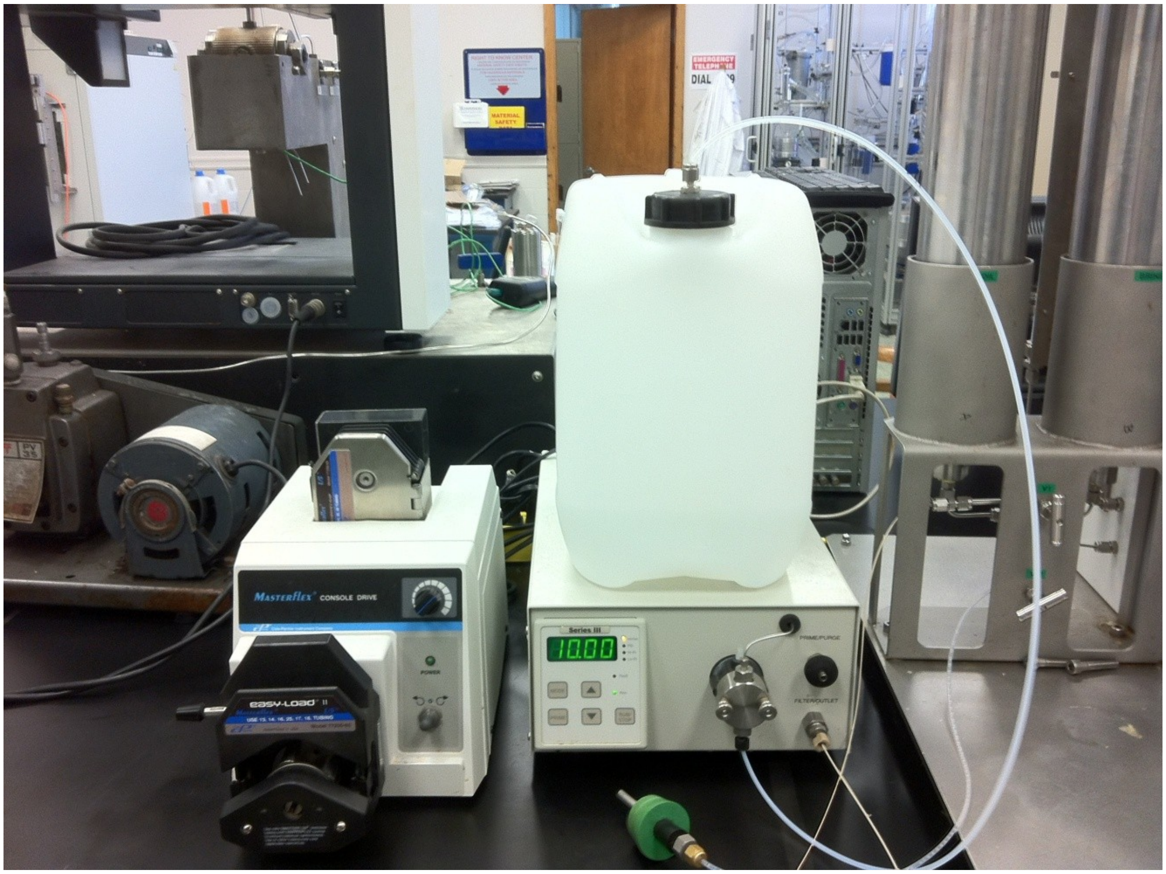


Figure 5.5 Displacement pump

Once the inlet pressure exceeded the outlet pressure, the water flooding process was initiated and the core sample was subjected to counter current flow of synthetic brine. As shown in Figure 5.6, the resulting mixture of brine and oil was introduced into a separator. The separator was already filled with kerosene and brine prior to the experiment. The initial level of the interface was recorded. VINCI Acquisition (V2.3) software was used to record the rise in the level of kerosene in order to determine the volume of oil recovered after water flooding. The core sample was subjected to the water flooding process for 48 hours. The experiment was carried out at a laboratory temperature of 20°C. Figure 5.7 shows the VINCI Acquisition (V2.3) software that was used to detect the interface between oil and brine in the separator.

After water flooding, the core sample was taken out of the core holder and placed vertically inside Amott's cup. The core sample was surrounded by synthetic brine with all sides subjected to imbibition. The experiment was carried out at laboratory conditions of 1 atm and 20°C. The amount of oil recovered was measured at different time intervals and a graph of oil recovered against imbibition time was plotted. The total spontaneous imbibition time was 150 hours (6.25 days). Figure 5.8 shows the spontaneous imbibition of the core sample 18G after the water flooding experiment.

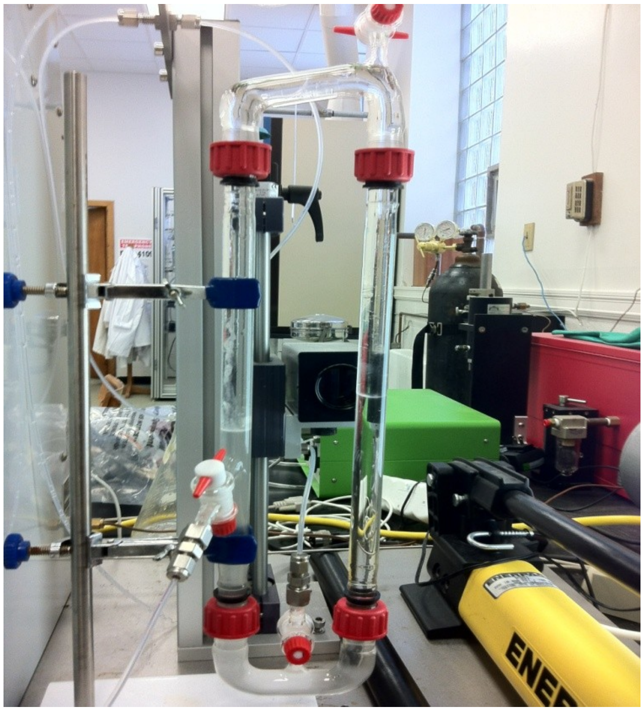
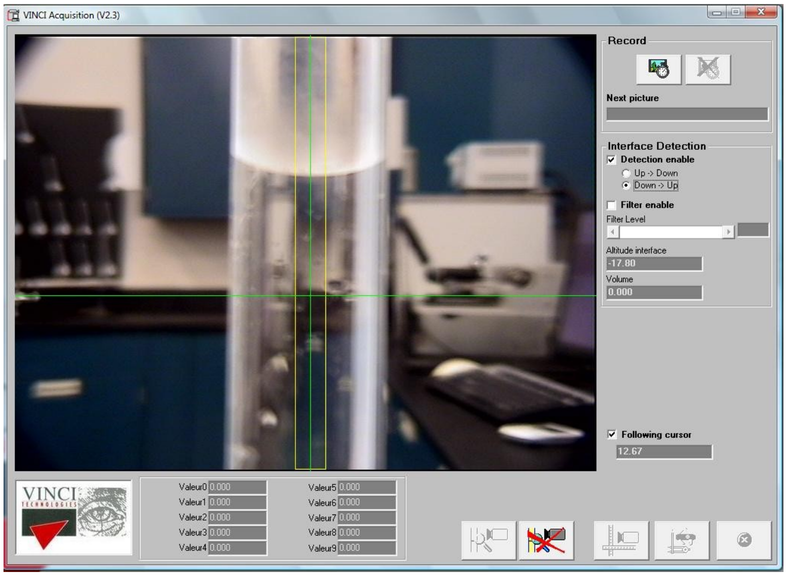


Figure 5.6 Separator



☑ Detection enable

○ Up -> Down

● Down -> Up

☐ Filter enable

Filter Level

Altitude interface -17.80

Volume 0.000

☑ Following cursor 12.67

Valeur0 0.000

Valeur1 0.000

Valeur2 0.000

Valeur3 0.000

Valeur4 0.000

Valeur5 0.000

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Figure 5.7 VINCI Acquisition (V2.3)

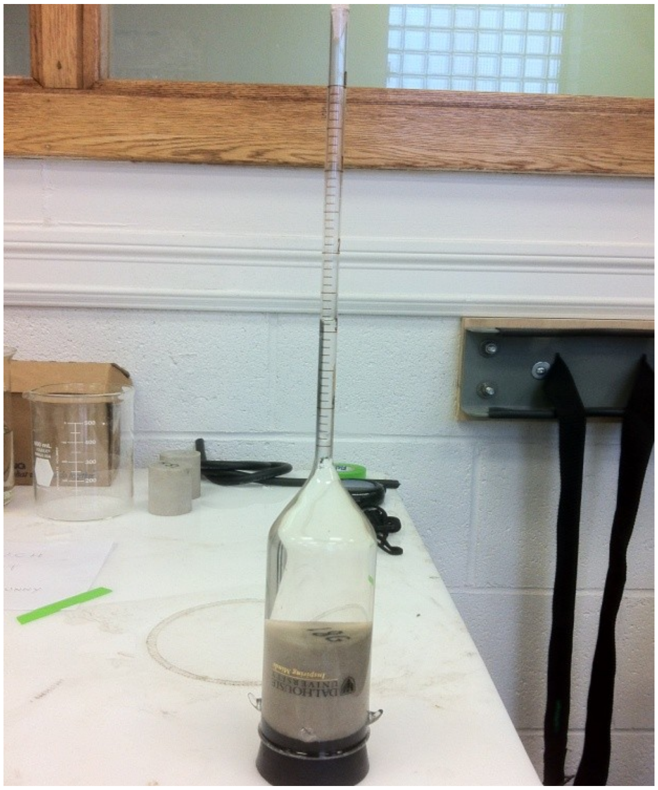

Figure 5.8 Spontaneous imbibition of core 18G

5.6 Oil Flooding of Core 18H Followed by Spontaneous Imbibition

Core sample 18H was saturated with synthetic brine by keeping the immersed sample in a vacuum oven for one week. A Benchtop Relative Permeameter (BRP 350) was used for the flooding experiment. The core sample was loaded in the core holder and the flooding tank was filled with kerosene. The confining pressure of the system was set between 800-900 psi and back pressure was set between 65-70 psi. The injection flow rate was $5cm^3/min$. A displacement pump was used to force the piston in order to inject kerosene through the pipelines.

Once the inlet pressure exceeded the outlet pressure, the oil flooding process was initiated and the core sample was subjected to counter current flow of kerosene. The resulting mixture of brine and kerosene was introduced into a separator. The separator was already filled with kerosene and brine prior to the experiment. The initial level of the interface was recorded. VINCI Acquisition (V2.3) software was used to record the decrease in the level of brine in order to determine the volume of brine recovered after oil flooding. Core sample was subjected to the oil flooding process for 48 hours. The experiment was carried out at laboratory temperature of $20^{\circ}C$.

After Oil flooding, the core sample was taken out of the core holder and placed vertically inside Amott's cup as shown in Figure 5.9. Core sample was surrounded by kerosene with all sides subjected to imbibition. The Amott's cup was kept in an inverted position. The experiment was carried out at laboratory conditions of 1 atm and 20°C. The amount of brine recovered was measured at different time intervals and a graph of brine recovered against imbibition time was plotted. The total spontaneous imbibition time was 150 hours (6.25 days).

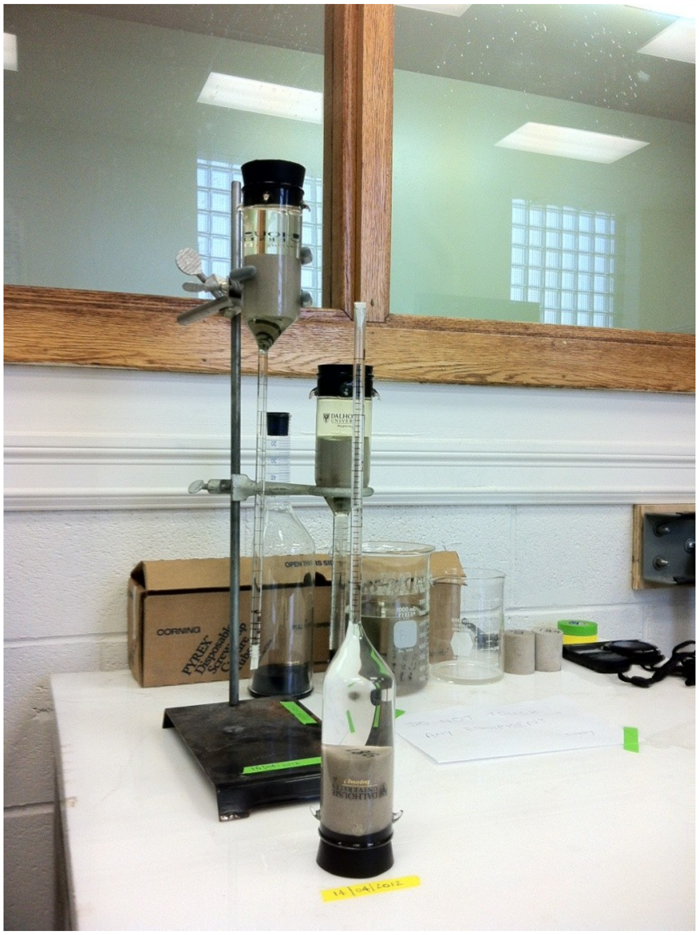

Figure 5.9 Spontaneous imbibition of core 18G, 18H, 18L

5.7 Water Flooding of Core 18I Followed by Spontaneous Imbibition

Core sample 18I was saturated with kerosene by keeping the immersed sample in a vacuum oven for one week. A Benchtop Relative Permeameter (BRP 350) was used for the flooding experiment. The core sample was loaded in the core holder and the flooding tank was filled with brine. Sodium Dodecyl Sulphate was added to the synthetic brine prior to the experiment. The confining pressure of the system was set between 800-900 psi and back pressure was set between 65-70 psi. The injection flow rate was $5cm^3/min$. A displacement pump was used to force the piston in order to inject brine through the pipelines.

Once the inlet pressure exceeded the outlet pressure, the water flooding process was initiated and the core sample was subjected to counter current flow of brine. The resulting mixture of brine and kerosene was introduced into a separator. The separator was already filled with kerosene and brine prior to the experiment. The initial level of the interface was recorded. VINCI Acquisition (V2.3) software was used to record the rise in the level of kerosene in order to determine the volume of oil recovered after water flooding. The core sample was subjected to the water flooding process for 48 hours. The experiment was carried out at laboratory temperature of $20^{\circ}C$.

After water flooding, the core sample was taken out of the core holder and placed vertically inside Amott's cup. As shown in Figure 5.10, the core sample was surrounded by brine, mixed with Sodium Dodecyl Sulphate, with all sides subjected to imbibition. The experiment was carried out at laboratory conditions of 1 atm and 20°C. The amount of oil recovered was measured at different time intervals and a graph of oil recovered against imbibition time was plotted. The total spontaneous imbibition time was 150 hours (6.25 days).

Figure 5.10 Spontaneous imbibition of core 18I

5.8 Oil Flooding of Core 18L Followed by Spontaneous Imbibition

Core sample 18L was saturated with synthetic brine by keeping the immersed sample in vacuum oven for one week. Sodium Dodecyl Sulphate was added to synthetic brine prior to the experiment. A Benchtop Relative Permeameter (BRP 350) was used for the flooding experiment. The core sample was loaded in the core holder and the flooding tank was filled with kerosene. The confining pressure of the system was set between 800-900 psi and back pressure was set between 65-70 psi. The injection flow rate was 5cm^3/min. A displacement pump was used to force the piston in order to inject kerosene through the pipelines.

Once the inlet pressure exceeded the outlet pressure, the oil flooding process was initiated and the core sample was subjected to counter current flow of kerosene. The resulting mixture of brine and kerosene was introduced into a separator. The separator was already filled with kerosene and brine prior to the experiment. The initial level of the interface was recorded. VINCI Acquisition (V2.3) software was used to record the decrease in the level of brine in order to determine the volume of brine recovered after oil flooding. The core sample was subjected to oil flooding process for 48 hours. The experiment was carried out at laboratory temperature of 20°C. After Oil flooding, the core sample was taken out of the core holder and placed vertically inside Amott's cup. The core sample was surrounded by kerosene with all sides subjected to imbibition. The Amott's cup was kept in an inverted position. The experiment was carried out at laboratory conditions of 1 atm and 20°C. The amount of brine recovered was measured at different time intervals and a graph of brine recovered against imbibition time was plotted. The total spontaneous imbibition time was 150 hours (6.25 days).

Chapter: 6 Results and Discussions

6.1 Wettability Index by Secondary Recovery

Core samples 18G and 18H were used to determine the wettability index of the Fontainebleau sandstone core by secondary recovery.

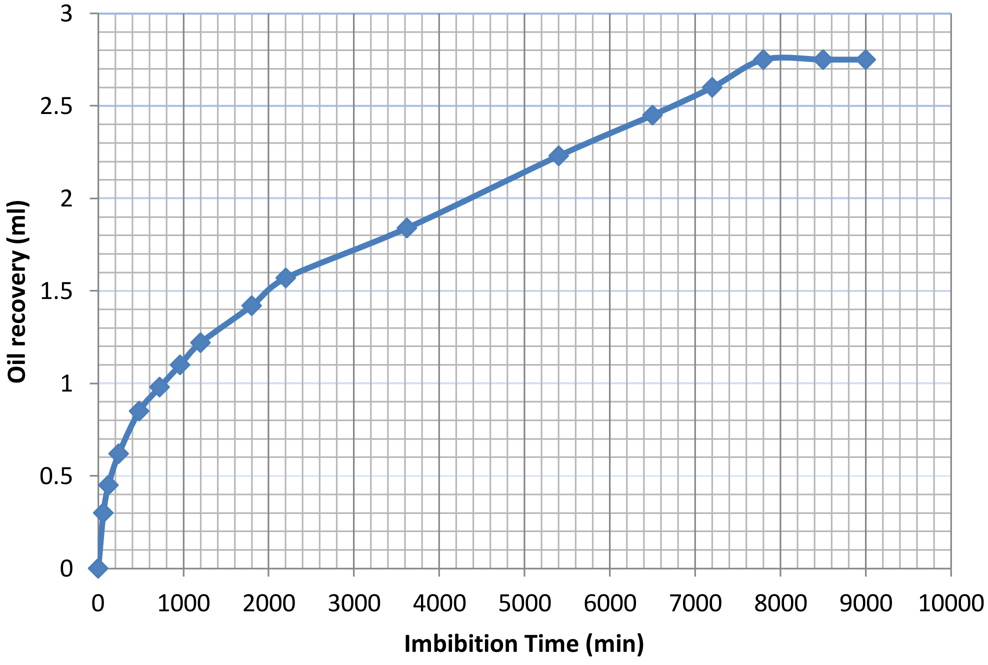

Figure 6.1 Oil recovery vs. Imbibition Time (100% oil saturation – 18G**)**

Figure 6.1 shows the spontaneous imbibition characteristics of core 18G. The plot of oil recovery vs. imbibition time depicts that the rate of oil imbibition was high at the beginning of the experiment and it gradually slowed down over the time period of one week. In fact the volume of oil recovered halted after day 5 of the spontaneous imbibition experiment. The volume of oil displaced by water was 2.75 mL. Since the pore volume of the core sample was 6.6 mL, this result shows that the core is highly water wet in nature. During imbibition, water imbibed spontaneously into the matrix of the core and drove the oil out in a counter current manner because of capillary gradient action. The volume of oil recovered was high in this case.

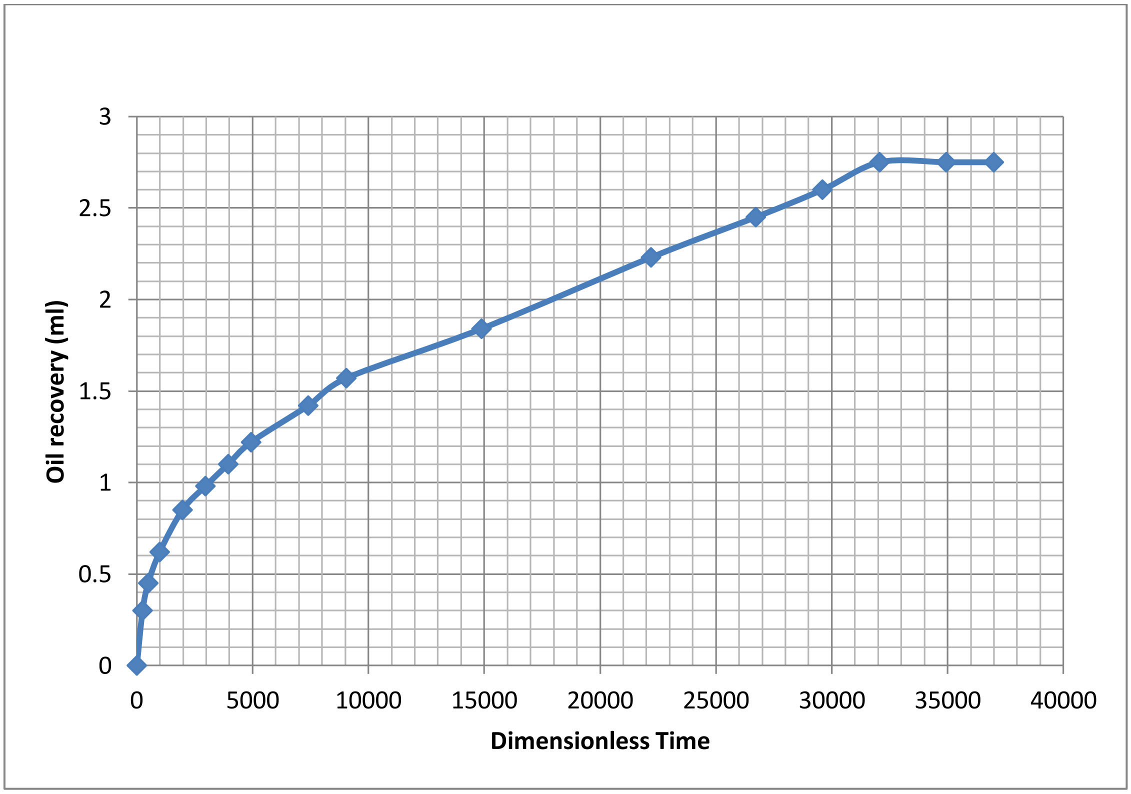

Figure 6.2 Oil recovery vs. Dimensionless Time (100% oil saturation – 18G**)**

Figure 6.2 shows the plot of Oil recovery vs. Dimensionless time. This data assists in correlating the results achieved in laboratory to actual reservoir conditions.

In the next part of the experiment, core 18G was saturated with kerosene and subjected to water flooding experiment. The oil recovered after water flooding was 3.12 mL. Secondary oil recovery technique showed significant recovery in the volume of oil. Same core 18G was then introduced to spontaneous imbibition to recover the remaining oil.

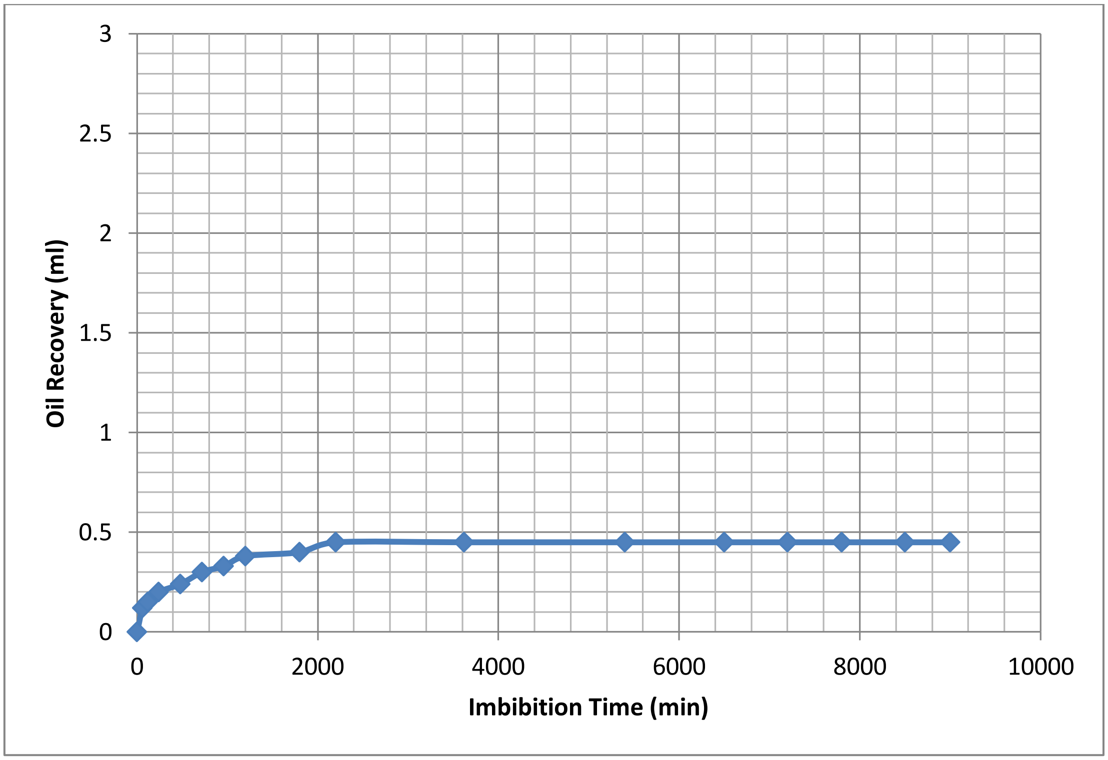

Figure 6.3 Oil recovery vs. Imbibition Time (After water flooding – 18G)

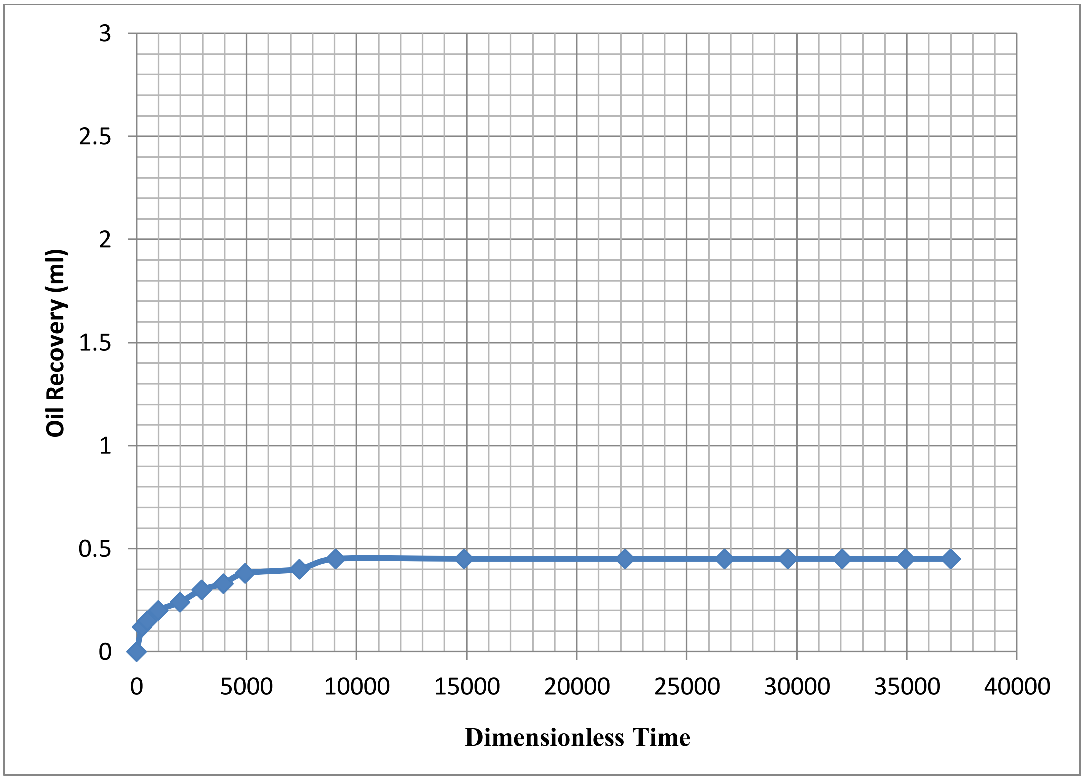

Figure 6.4 Oil recovery vs. Dimensionless Time (After water flooding – 18G**)**

Figure 6.3 shows the spontaneous imbibition results of core 18G after water flooding experiment. The volume of oil recovered in this case was low because most of the oil was recovered during the water flooding phase. The oil recovery by forced imbibition and spontaneous imbibition was 3.12 mL and 0.45 mL respectively, which leads to the total oil recovery of 3.57 mL after water flooding experiment. Figure 6.4 shows the imbibition results after water flooding against dimensionless time.

The ratio of oil volume displaced by spontaneous water imbibition to the total oil volume displaced by imbibition and forced displacement was used in the Ammot's index to calculate the water-wettability index of core 18G. The water-wettability index was calculated to be 0.76. Since the experimental value lies between 0.3 and 1, therefore it shows that the core sample 18G is highly water wet.

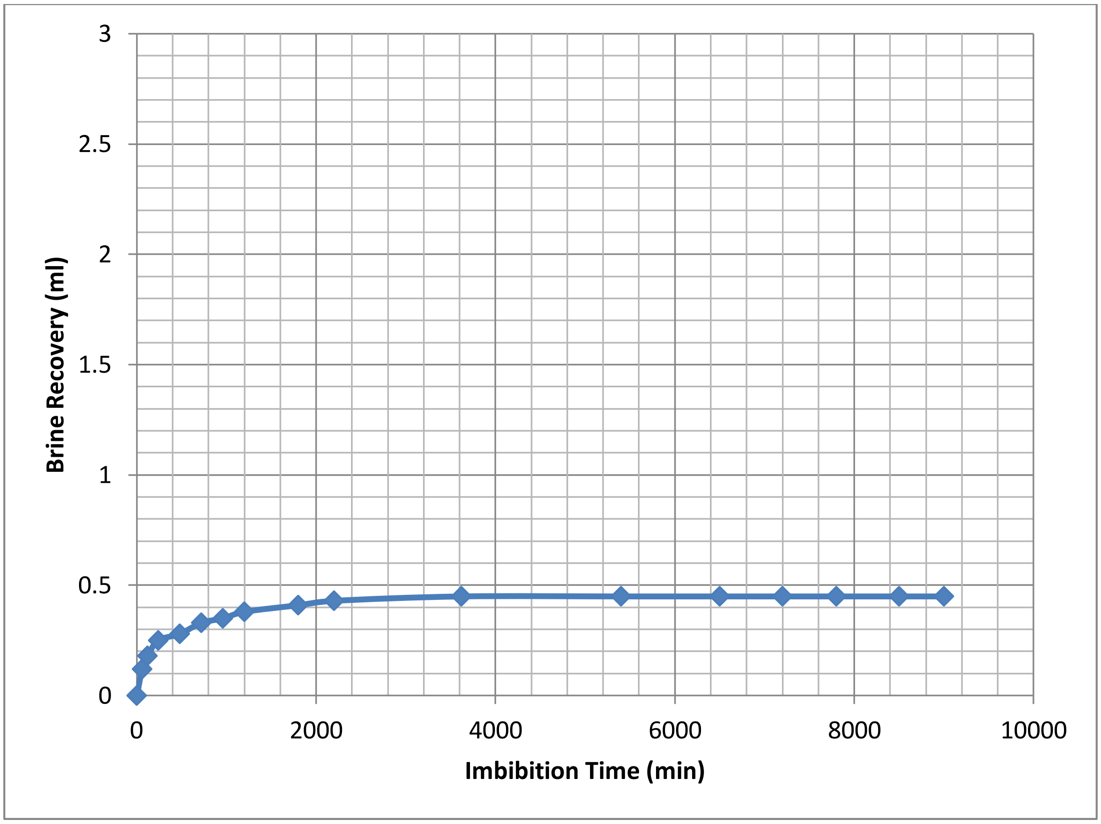

Figure 6.5 Brine recovery vs. Imbibition Time (100% brine saturation – 18H)

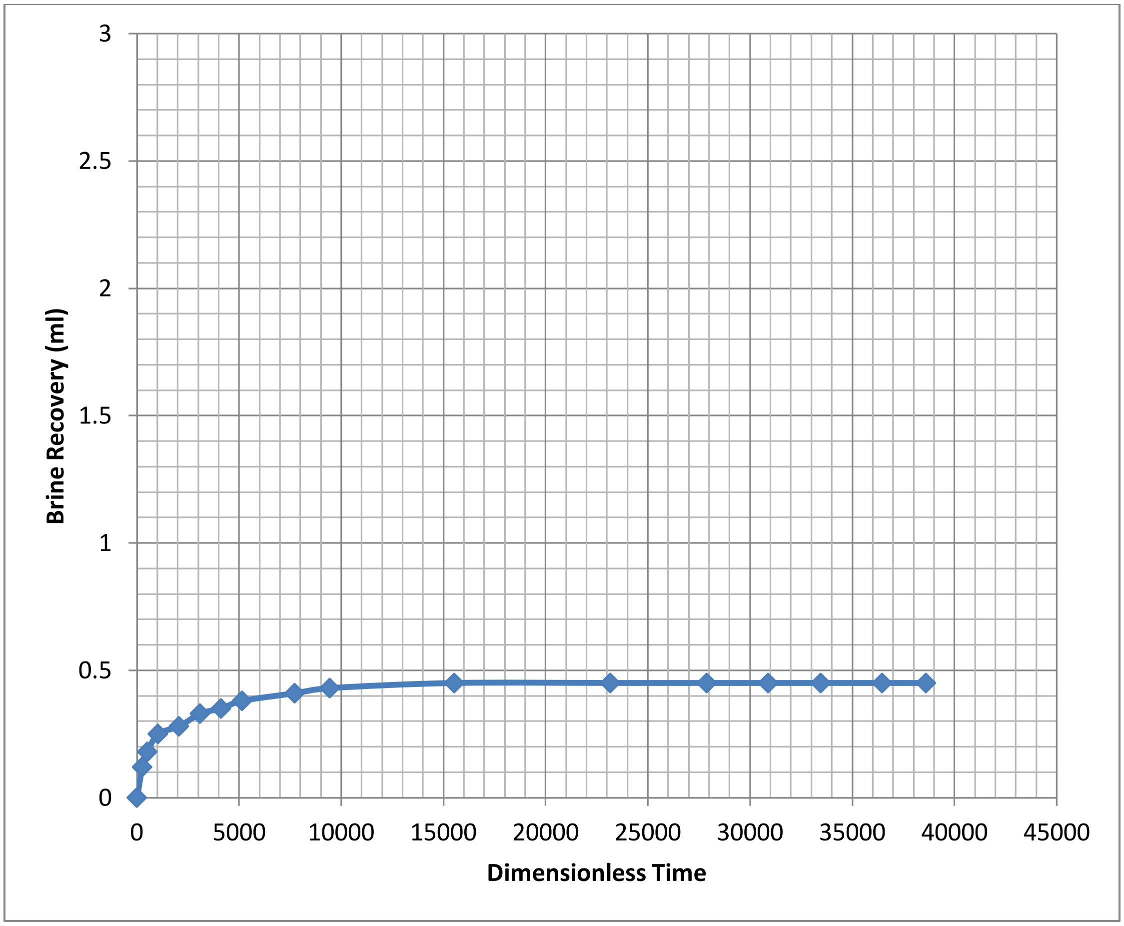

Figure 6.6 Brine recovery vs. Imbibition Time (100% brine saturation – 18H)

Table 6.5 shows the spontaneous imbibition characteristics of core 18H. The core sample was completely saturated in brine solution and imbibed with oil. A low volume of brine was recovered after the imbibition experiment. The recovery process was observed to cease after day 3 of the experiment. The volume of brine displaced by oil imbibition was 0.45 mL. The pore volume of the core 18H was 6.5 mL. Therefore, result showed that the oil could not imbibe spontaneously through the matrix of the core and displace excess brine in a counter-current manner.

Core sample 18H was then again saturated and subjected to oil flooding. The volume of brine displaced by oil flooding was 1.71 mL, which was significantly lower compared to the volume of oil recovered by water flooding of core 18G. The core was then introduced to spontaneous oil imbibition to recover the remaining brine after oil flooding. The volume of brine displaced by oil imbibition in this case was 0, which leads to the total brine recovery of 1.71 mL after water flooding. Figure 6.6 shows the brine recovery plotted against dimensionless time.

The ratio of brine volume displaced by spontaneous imbibition of oil to the total brine volume displaced by oil imbibition and forced displacement was used in Ammot's index to determine the oil-wettability index of core 18H. The oil wettability index was calculated as 0.26. Since the experimental value lies below 0.3, therefore it shows that the core sample 18H is more oil wet core. During the experimental phase, core sample 18H did not show any significant recovery during oil imbibition and oil flooding.

The results of water-wettability index of core 18G and oil-wettability index of core 18H were used in the Amott-Harvy index to determine the wettability index of Fontainebleau sandstone by secondary recovery technique.

Table 6.1 Summary of results by secondary recovery

	18G (Oil Recovery)	**18H (Brine Recovery)**
Spontaneous Imbibition (100% saturation), ml	2.75	0.45
Forced Imbibition, ml	3.12	1.71
Spontaneous Imbibition, ml	0.45	0
Wettability Index	0.76 (Water Wettability Index)	0.26 (Oil Wettability Index)

Results of the first part of experiment are summarized in Table 6.4. The wettability index of Fontainebleau sandstone cores by secondary recovery was calculated and found to be 0.5. Since the experimental value lies between 0.3 and 1, therefore it shows that the Fontainebleau sandstone is a water-wet core.

This result was obtained by using a secondary recovery technique. The result concludes that the Fontainebleau reservoir rock is a water-wet sandstone and a potential candidate for secondary oil recovery by water injection and spontaneous imbibition.

6.2 Wettability Index by Tertiary Recovery

Core samples 18I and 18L were used to determine the wettability index of the Fontainebleau sandstone core by tertiary recovery.

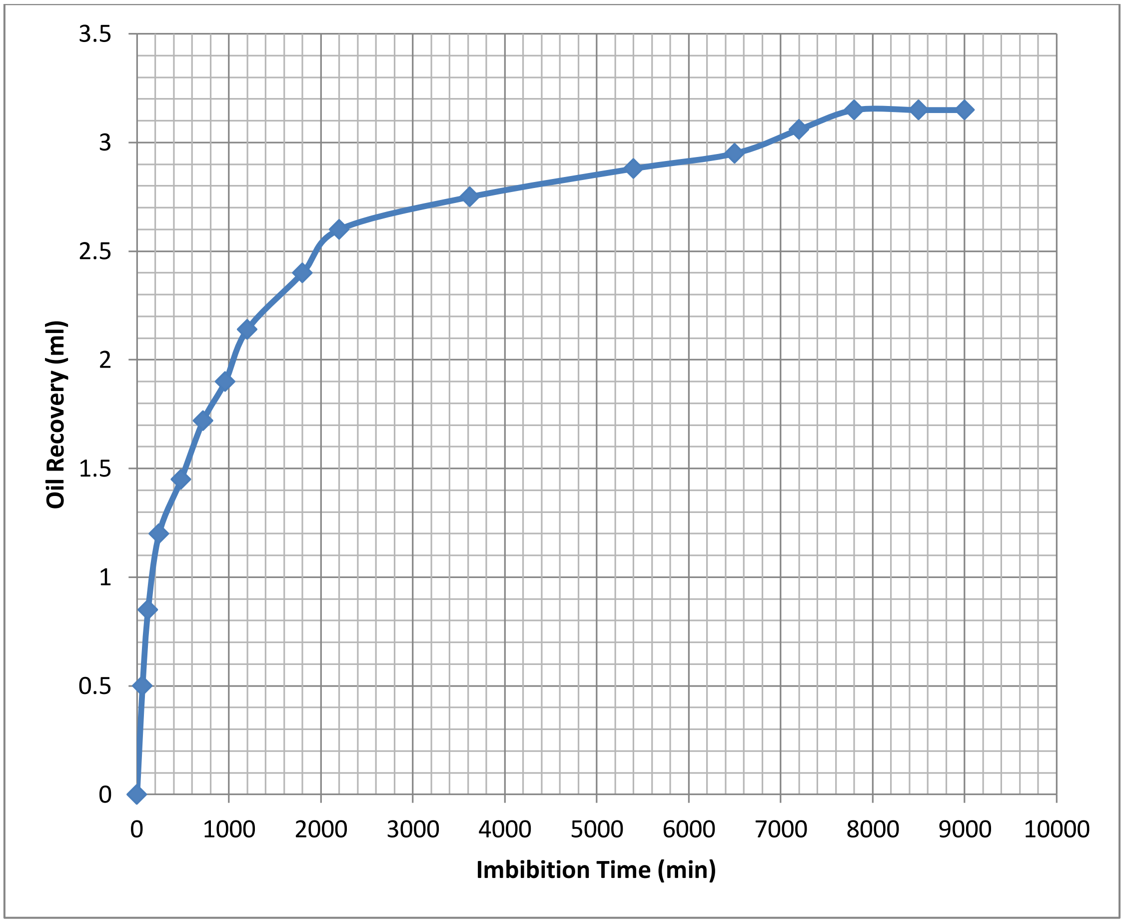

Figure 6.7 Oil recovery vs. Imbibition Time (100% oil saturation – 18I)

Figure 6.7 shows the spontaneous imbibition characteristics of core 18I. Surfactant, sodium dodecyl sulphate, was added to the brine solution before the spontaneous water imbibition experiment. The plot of oil recovery vs. imbibition time depicts that the rate of oil imbibition was relatively high at the beginning of the experiment and it gradually slowed down over the time period of one week. The volume of oil displaced by water was 3.15 mL. Since the pore volume of the core sample was 6.7 mL, result shows that the core is highly water- wet in nature. During imbibition, water imbibed spontaneously into the matrix of the core and drove the oil out in a counter current manner because of capillary gradient action. Volume of oil recovered was high in this case. The recovery of oil was more compared to the volume of oil recovered from core 18G.

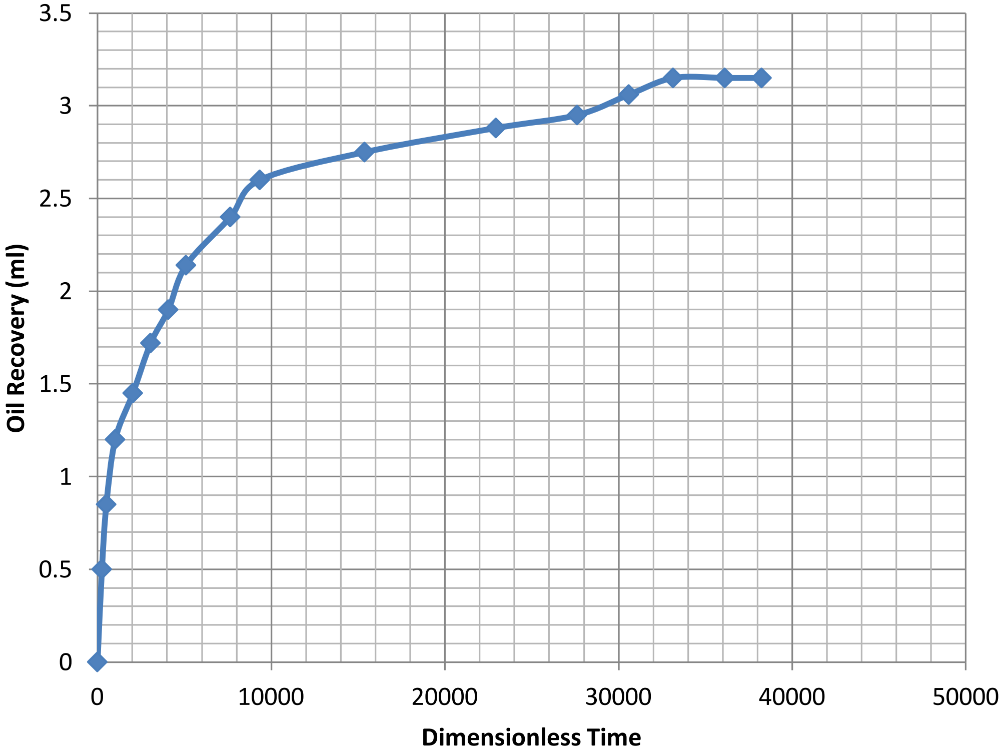

Figure 6.8 Oil recovery vs. Dimensionless Time (100% oil saturation – 18I)

Figure 6.8 shows the plot of Oil recovery vs. Dimensionless time. This data assists in correlating the results achieved in laboratory to actual reservoir conditions.

The core 18I was then saturated with kerosene and subjected to brine flooding. Surfactant was added to the brine solution prior to the experiment. The volume of oil recovered after surfactant enhanced water flooding was 6.11 mL. The recovery was significantly higher than the volume of oil recovered by secondary recovery. The core sample was then introduced to brine imbibition in order to obtain the remaining oil.

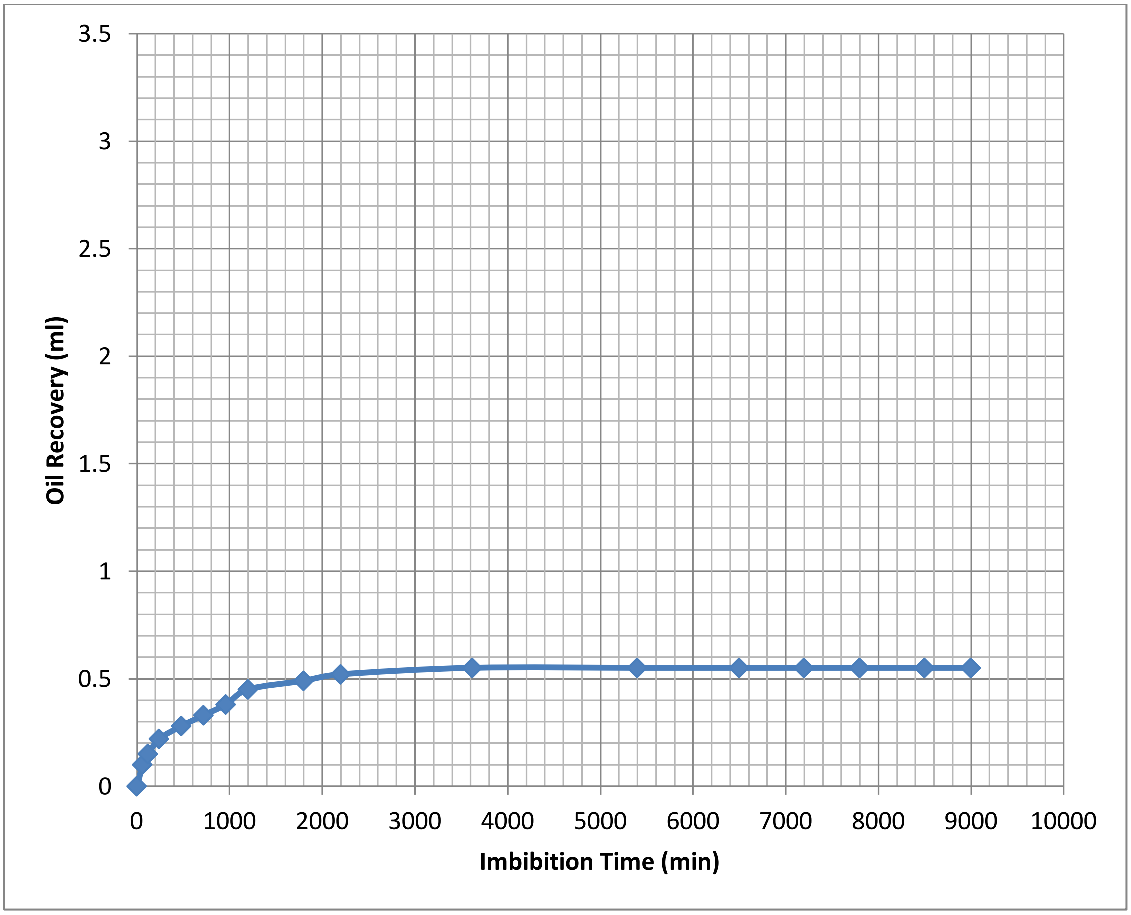

Figure 6.9 Oil recovery vs. Imbibition Time (100% oil saturation – 18I)

Figure 6.9 shows the surfactant enhanced spontaneous imbibition results of core 18I after the water flooding experiment. The volume of oil recovered in this case was low because most of the oil was recovered during the water flooding phase. The oil recovery by forced imbibition and spontaneous imbibition was 6.11 mL and 0.55 mL respectively, which leads to the total oil recovery of 6.66 mL after the water flooding experiment. Figure 6.10 shows the imbibition results after water flooding against dimensionless time.

The ratio of oil volume displaced by spontaneous water imbibition to the total oil volume displaced by imbibition and forced displacement was used in the Ammot's index to calculate the water-wettability index of core 18I. The water-wettability index was calculated to be 0.47. Since the experimental value lies between 0.3 and 1, therefore it shows that the core sample 18G is highly water wet.

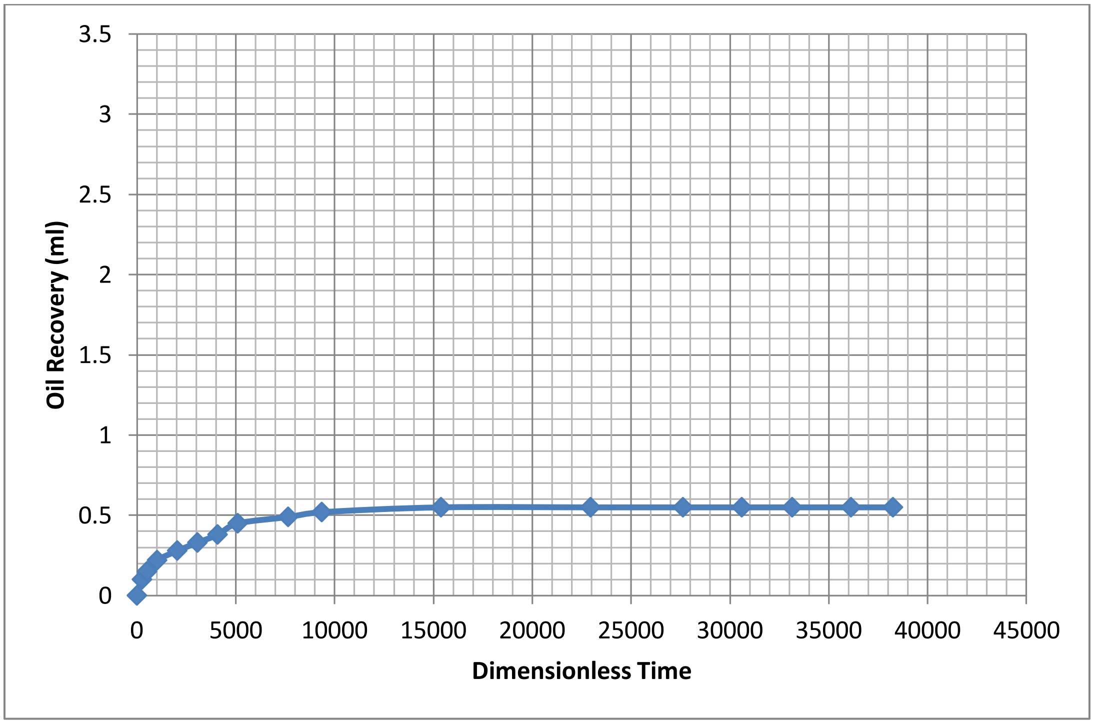

Figure 6.10 Oil recovery vs. Dimensionless Time (100% oil saturation – 18I)

Recovery of oil from the core 18I was comparatively more than the recovery from core sample 18G. This is because, surfactant, sodium dodecyl sulphate, was added to the synthetic brine mixture prior to the spontaneous imbibition experiment. It is observed from the results that surfactant molecules enhanced the oil recovery process. Another observation showed that the surfactant enhanced recovery of oil by water flooding is comparatively more than the surfactant enhanced recovery of oil by spontaneous imbibition. A better explanation is provided as follow:

Capillary number characterizes the ratio of viscous forces to surface or interfacial tension forces.

$$Ca = \frac{\mu v}{\sigma} \tag{6.1}$$

Where, Ca = Capillary number, μ = Viscosity in cP, v = velocity in cm/s, σ = surface or interfacial tension in dynes/cm.

Equation 6.1 shows that the capillary number is inversely proportional to the surface tension between the wetting fluid and the non-wetting fluid. The addition of surfactant reduced the surface tension between the fluids thereby increasing the capillary number. Higher capillary number characterizes high volume of recovery by tertiary recovery.

Water flooding method is driven by viscous pressure gradient mechanism, which is defined as the ratio of pressure drop across the ends of the core to the length of the core. Pressure drop in this case is due to pump energy. On the other hand, Spontaneous imbibition process is driven by capillary pressure gradient mechanism, which depends on the pressure difference between the non-wetting fluid and the wetting fluid and the pore size distribution characteristic. Generally, the average pore diameter determines the average capillary pressure of the porous medium and this is given by Leverett's (1939) equation:

$$Pc = \frac{Pnw - Pw}{r} \tag{6.2}$$

$$r = \sqrt{\frac{8K}{\emptyset}} \tag{6.3}$$

Where, Pc = Capillary pressure in psi, Pnw = Pressure of non-wetting phase in psi, Pw = Pressure of wetting phase in psi, r = Pore size distribution in cm, K = permeability in mD, $\emptyset$ = Porosity.

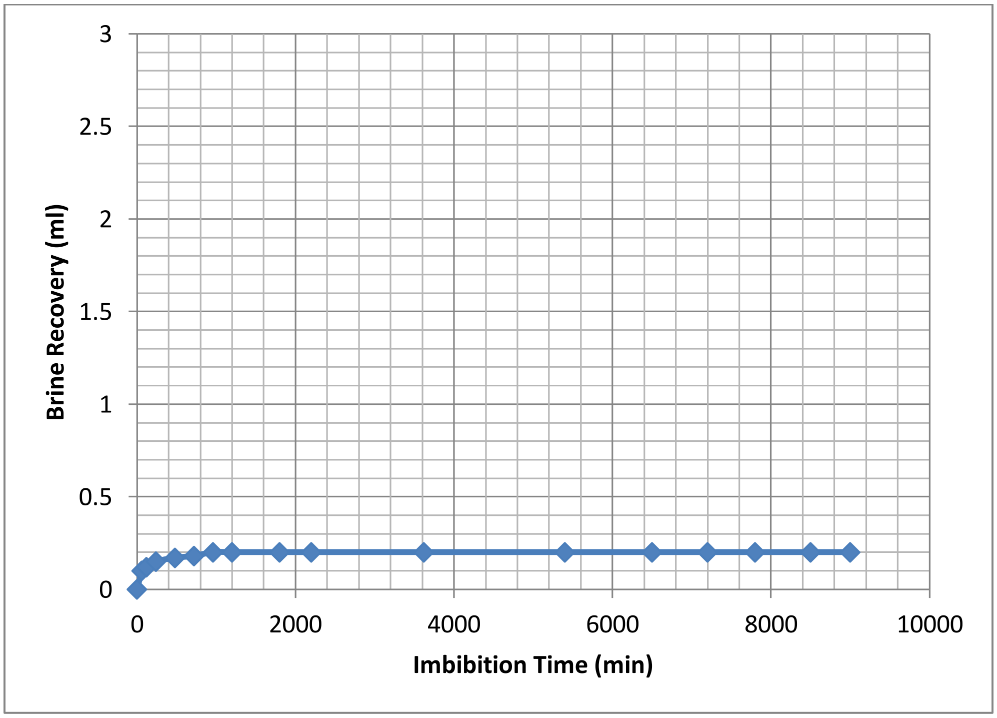

Figure 6.11 Brine recovery vs. Imbibition Time (100% brine saturation – 18L)

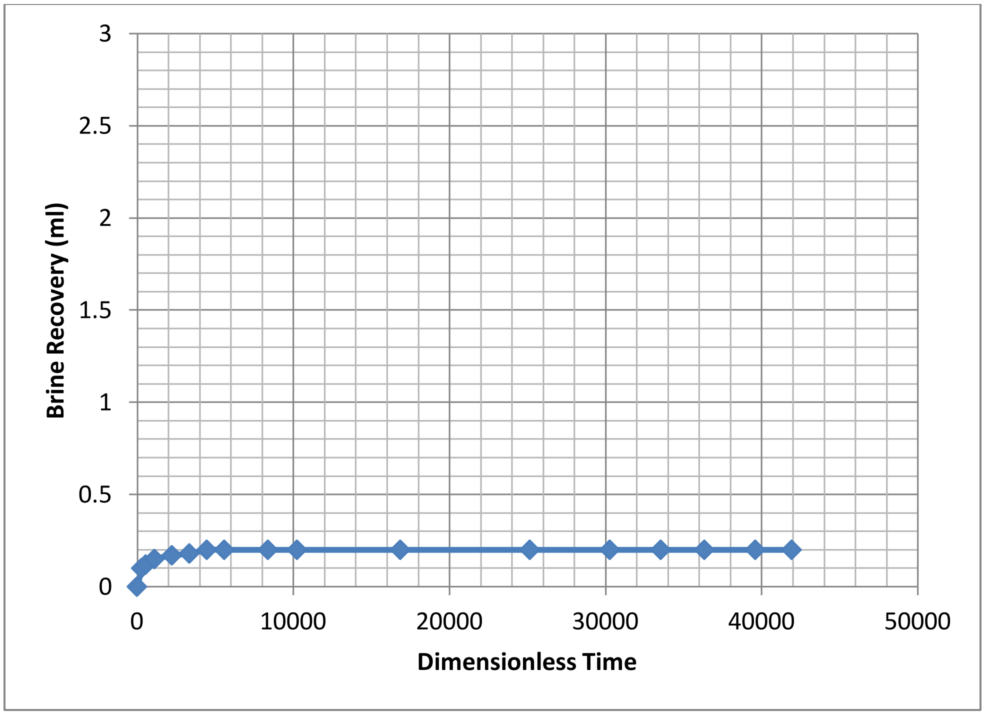

Figure 6.12 Brine recovery vs. Dimensionless Time (100% brine saturation – 18L)

Figure 6.11 shows the spontaneous imbibition character of core 18L. The core sample was completely saturated in brine solution and imbibed with oil. Surfactant was added to the brine solution before saturation. A low volume of brine was recovered after the imbibition experiment. The recovery process was observed to cease after day 2 of the experiment. The volume of brine displaced by oil imbibition was 0.20 mL. The pore volume of the core 18L was 6.5 mL. Therefore, result showed that the oil could not imbibe spontaneously through the matrix of the core and displace excess brine in a counter-current manner.

Core sample 18L was then again saturated and subjected to oil flooding. The volume of brine displaced by oil flooding was 1.91 mL, which was significantly lower compared to the volume of oil recovered by water flooding of core 18L. The core was then introduced to spontaneous oil imbibition to recover the remaining brine after oil flooding. The volume of brine displaced by oil imbibition in this case was 0, which leads to the total brine recovery of 1.92 mL after water flooding.

The ratio of brine volume displaced by spontaneous imbibition of oil to the total brine volume displaced by oil imbibition and forced displacement was used in Ammot's index to determine the oil-wettability index of core 18L. The oil wettability index was calculated to be 0.10. Since the experimental value lies below 0.3, therefore it shows that the core sample 18L is more oil wet. During the experimental phase, core sample 18L did not show any significant recovery after oil imbibition and oil flooding.

The results also shows that the recovery of brine by spontaneous oil imbibition in case of 18L is less than volume of brine recovered from 18H, even after the addition of surfactant, sodium dodecyl sulphate. The explanation for this behavior is given below.

Surfactant reduces the average pore diameter of the porous media. Therefore the addition of surfactant reduced the recovery of brine in case of spontaneous oil imbibition. Moreover, the use of surfactant changes the wettability of the core towards oil-wet thereby reducing the recovery rate by oil imbibition. Another factor affecting the oil imbibition recovery is the decrease in interfacial tension because of the tensioactive property of surfactant in the brine. Decrease in interfacial tension decreases the capillary pressure gradient which is the main driving force of spontaneous imbibition. The volume of brine recovered was less in case of oil imbibition by tertiary recovery process. Figure 6.12 shows the recovery of brine plotted against dimensionless time.

The results of water-wettability index of core 18I and oil-wettability index of core 18L were used in the Amott-Harvey index to determine the wettability index of Fontainebleau sandstone by tertiary recovery technique.

Table 6.2 Summary of results by tertiary recovery

	18I (Oil Recovery)	**18L (Brine Recovery)**
Spontaneous Imbibition (100% saturation), ml	3.15	0.20
Forced Imbibition, ml	6.11	1.92
Spontaneous Imbibition, ml	0.55	0
Wettability Index	0.47 (Water Wettability Index)	0.10 (Oil Wettability Index)

Results of the second part of experiment are summarized in Table 6.8. The wettability index of Fontainebleau sandstone core by tertiary recovery was calculated and found to be 0.37. Since the experimental value lies between 0.3 and 1, therefore it shows that the Fontainebleau sandstone is a water-wet core. The wettability index value is lower compared to secondary recovery because the wettability of the core was shifted towards oil wet by the use of surfactant.

This result was obtained by using the tertiary recovery technique. The result concludes that the Fontainebleau reservoir rock is water-wet sandstone and a potential candidate for tertiary oil recovery by water injection and spontaneous imbibition.

6.3 Comparison of results of published work with those of present work

In addition to this work the mechanism of spontaneous water imbibition in representative reservoir rock samples in the laboratory under varying experimental conditions relating to imbibition experiments with surfactants and without surfactants has been investigated. Peila Chen (2011) published his work on “Surfactant enhanced spontaneous imbibition process in highly fractured carbonate reservoirs”. Silurian dolomite and Guelph dolomite reservoir rock samples were used for imbibition studies and wettability alteration. Cationic surfactant BTC 8358 (n-alkyl dimethyl benzyl ammonium chloride) and anionic surfactant, alcohol based alkoxy sulphonates were used in the imbibition experiments to alter the wettability of the core samples. Crude oil from the field was used to saturate the core samples and synthetic sea water was used as injection brine. Amott’s method was used to determine the oil and water wettability. The Amott-Harvey Index was used to determine the wettability index of the carbonate rock. Results of the experiment are summarized in table 7.1

Table 6.3 Spontaneous and forced imbibition results (Chen, 2011)

	(Oil Recovery)	**(Brine Recovery)**
Spontaneous Imbibition, ml	0.33	0.20
Forced Imbibition, ml	0.91	0.25
Wettability Index	0.266 (Water Wettability Index)	0.444 (Oil Wettability Index)

According to Chen (2011), the wettability of the carbonate rock was determined to be -0.178, which showed that the carbonate reservoir rock was weakly oil wet and the wettability of the rock was shifted towards water wetness.

Standnes (2000) published his work on “Enhanced oil recovery from oil wet carbonate rock by spontaneous imbibition of aqueous surfactant solutions”. In his work it was shown that the cationic surfactants can recover oil from chalk by spontaneous counter-current due to wettability alteration. Cationic surfactants may have comparatively lowered adsorption than anionic surfactants of similar hydrophobic chain length. Cationic and anionic surfactants have the potential to alter the wettability of carbonate rock towards water wetness.

Hatiboglu and Babadagli (2004) published their work on “Experimental analysis of primary and secondary oil recovery from matrix by counter-current diffusion and spontaneous imbibition”. Berea sandstone core samples were used for the experimental work. Fluids used were kerosene, mineral oil, and brine. Anionic surfactant (Alkyl diphenyloxide disulphonic acid) was used to enhance the recovery of oil and imbibition tubes were used to carry out the experiments. Core samples were saturated with oil and imbibed with brine to recover the oil by spontaneous imbibition. The analysis of experimental results showed that the recovery of oil was 45-50% of pore volume after spontaneous imbibition and 60%-65% of pore volume after the addition of surfactant to the brine solution

In the present work, Fontainebleau sandstone core samples were used for carrying out the experiments. Fluids used were kerosene and synthetic brine. Anionic surfactant (Sodium dodecyl sulphate) was used to investigate the effect of surfactant enhance oil recovery and wettability alteration. Amott’s method was used to determine the oil and water wettability index. The Amott-Harvey index was used to determine the wettability indices of Fontainebleau sandstone. The wettability index results clearly showed that Fontainebleau sandstone is highly water- wet and a potential reservoir for recovering oil by secondary and tertiary recovery. Results of the present work also state that the anionic surfactant, sodium dodecyl sulphate, has the potential to alter the wettability of water-wet sandstone towards oil-wet. According to Hatiboglu and Babadagli (2004), high recovery rates were observed from the results of the experiments. The wettability index was not determined but the amount of oil recovery clearly shows that the Berea sandstone is water-wet sandstone core with significant potential of oil recovery by spontaneous imbibition. By comparison with the present work, it is observed that the Berea sandstone and Fontainebleau sandstone falls under the class of Siliciclastic reservoir rocks. Comparison shows that sandstone rocks have high affinity towards water and they are water-wet in nature. One thing observed about Hatiboglu and Babadagli’s work is that it confirms enhanced oil recovery by spontaneous imbibition process is also related by the present study. Referring to the published work of Chen (2011), it is observed that carbonate rocks are oil-wet and sandstone rocks are water wet. Significant oil recovery is obtained by the spontaneous and forced imbibition process. Also, the use of anionic or cationic surfactants alters the wettability of the core from oil-wet to water-wet or vice versa. Both carbonate and sandstone favors oil recovery by secondary and tertiary methods. Consequently the findings of the present study related to wettability alteration are comparable to Chen’s work.

CHAPTER: 7 Conclusions

This part of the thesis presents the conclusions drawn from the work. Also some recommendations for future work are suggested.

7.1 Conclusions

- Core samples have to be saturated completely in order to obtain homogeneous wettability.
- Based on Amott-Harvey wettability index measurements, the Fontainebleau sandstone core is determined to be highly water wet.
- The water wettability index of the Fontainebleau sandstone core is determined to be higher than the oil wettability index.
- Oil cannot imbibe the matrix of Fontainebleau sandstone core and expel water efficiently in a counter current flow.
- Volume of oil recovered from Fontainebleau sandstone core is enhanced by the addition of an anionic surfactant.
- Oil production rate by tertiary recovery is more than secondary recovery.
- Anionic surfactant shows the potential of altering the wettability towards more oil wet.
- Oil recovery by water flooding is comparatively more than oil recovery by spontaneous imbibition.

7.2 Recommendations

Based on the findings of this research, the following recommendations for future work include:

- Detailed investigation of physical-chemical process related to spontaneous imbibition of brine into water wet sandstone at elevated temperature.
- Mixture of cationic and anionic surfactants should be studied for enhanced oil recovery.
- Spontaneous imbibition tests on the cores should be conducted to study the effect of residual gas on imbibition rate and oil recovery.
- Analyze the effect of altered wettability on forced imbibition.
- Forced imbibition of brine into water wet sandstone at elevated temperature.

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APPENDIX

The tables presented below are a summary of the spontaneous imbibition experiments conducted with core samples 18G, 18H, 18L, and 18I.

T-1: Spontaneous imbibition of 18G (100% oil saturation)

Imbibition Time (min)	Oil Recovery (ml)	Dimensionless Time
0	0	0
60	0.3	246.6
120	0.45	493.2
240	0.62	986.4
480	0.85	1972.8
720	0.98	2959.2
960	1.1	3945.6
1200	1.22	4932
1800	1.42	7398
2200	1.57	9042
3620	1.84	14878.2
5400	2.23	22194
6500	2.45	26715
7200	2.6	29592
7800	2.75	32058
8500	2.75	34935
9000	2.75	36990

T-2: Spontaneous imbibition of 18G (After water flooding)

Imbibition Time (min)	Oil Recovery (ml)	Dimensionless Time
0	0	0
60	0.12	246.6
120	0.15	493.2
240	0.2	986.4
480	0.24	1972.8
720	0.3	2959.2
960	0.33	3945.6
1200	0.38	4932
1800	0.4	7398
2200	0.45	9042
3620	0.45	14878.2
5400	0.45	22194
6500	0.45	26715
7200	0.45	29592
7800	0.45	32058
8500	0.45	34935
9000	0.45	36990

T-3: Spontaneous imbibition of 18H (100% brine saturation)

Imbibition Time (min)	Brine Recovery (ml)	Dimensionless Time
0	0	0
60	0.12	257.4
120	0.18	514.8
240	0.25	1029.6
480	0.28	2059.2
720	0.33	3088.8
960	0.35	4118.4
1200	0.38	5148
1800	0.41	7722
2200	0.43	9438
3620	0.45	15529.8
5400	0.45	23166
6500	0.45	27885
7200	0.45	30888
7800	0.45	33462
8500	0.45	36465
9000	0.45	38610

T-4: Spontaneous imbibition of 18I (100% oil saturation)

Imbibition Time (min)	Oil Recovery (ml)	Dimensionless Time
0	0	0
60	0.5	255
120	0.85	510
240	1.2	1020
480	1.45	2040
720	1.72	3060
960	1.9	4080
1200	2.14	5100
1800	2.4	7650
2200	2.6	9350
3620	2.75	15385
5400	2.88	22950
6500	2.95	27625
7200	3.06	30600
7800	3.15	33150
8500	3.15	36125
9000	3.15	38250

T-5: Spontaneous imbibition of 18I (After water flooding)

Imbibition Time (min)	Brine Recovery (ml)	Dimensionless Time
0	0	0
60	0.1	255
120	0.15	510
240	0.22	1020
480	0.28	2040
720	0.33	3060
960	0.38	4080
1200	0.45	5100
1800	0.49	7650
2200	0.52	9350
3620	0.55	15385
5400	0.55	22950
6500	0.55	27625
7200	0.55	30600
7800	0.55	33150
8500	0.55	36125
9000	0.55	38250

T-6: Spontaneous imbibition of 18L (100% brine saturation)

Imbibition Time (min)	Brine Recovery (ml)	Dimensionless Time
0	0	0
60	0.1	279.6
120	0.12	559.2
240	0.15	1118.4
480	0.17	2236.8
720	0.18	3355.2
960	0.2	4473.6
1200	0.2	5592
1800	0.2	8388
2200	0.2	10252
3620	0.2	16869.2
5400	0.2	25164
6500	0.2	30290
7200	0.2	33552
7800	0.2	36348
8500	0.2	39610
9000	0.2	41940

Sample calculation for determining the wettability index

A sample calculation for determining the wettability index of core 18G is done using the equation

$$\delta w = \frac{Vosp}{Vot}$$

$Vosp = 2.75$ ml, $Vot = 3.64$ml

Water wettability index, $\delta w = 0.76$

Similarly, oil wettability index, $\delta o = 0.26$

$$I = \delta w - \delta o = \frac{Vosp}{Vot} - \frac{Vwsp}{Vwt} = 0.76 - 0.26$$

Wettability index of core 18G, I = 0.26

Sample calculation for determining dimensionless time T_D

A sample calculation of dimensionless time for core sample 18G is done using the equation $T_D = 1.8849 \times 10^{-2} \times t \times \sqrt{\frac{K}{\phi}} \times \frac{\sigma}{\sqrt{\mu_w \times \mu_o}} \times \frac{1}{L_c{}^2}$

Calculating dimensionless time for time t=60 minutes,

K= 13.33 mD, ϕ = 0.12, d=3.84 cm, L=4.77 cm

L_c is calculated using the equation $L_c = \frac{Ld}{2\sqrt{d^2+2L^2}}$

=1.18 cm

σ, interfacial tension between brine and oil at laboratory condition is 48 dynes/cm

μ_w and μ_o are the dynamic viscosities. The kinematic viscosities are measured to υ_w= 1.31 cSt and υ_o= 2.19 cSt respectively.

Using the equation $\upsilon = \frac{\mu}{\rho}$, the dynamic viscosities μ_w and μ_o are calculated and substituted in dimensionless time equation.

Finally substituting all the values in the T_D equation, we get T_D = 246.6