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Master's Thesis Effect of Brine Concentration on Flow Properties in Two Types of Carbonate Rocks – Ekofisk Chalk and Iranian Limestone

Study of Chemical Effect of Brine
Composition on Flow Properties on
Carbonate Rocks

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**Norwegian University of Science and Technology
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By
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Trondheim, Norway 2012

Preface Page

This master thesis was based on experimental investigation of the effect of brine concentration on flow properties in two types of carbonate rocks by imbibition and water flooding process, as secondary method of enhanced oil recovery (EOR).

I hereby declare that the master's thesis on petroleum engineering has been performed in accordance with the regulations at the Norwegian University of Science and Technology (NTNU), Department of Petroleum Engineering and Applied Geophysics.

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Statement of the Author

On this master thesis on petroleum engineering all information and ideas expressed such as literature reviewed, laboratory experiment, results obtained and discussion including conclusion and recommendation here are product of my efforts and knowledge and do not reflect the opinion and suggestion of any third party.

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Dedication

This work on petroleum engineering is dedicated to my beloved wonderful wife and daughter, mother and sisters for their patience and moral supports, I will always be grateful for your loving gesture. Your inspirations have always helped me to succeed in life.

Thank you for all your love, guidance and support, which were source of my motivation to work very hard.

Special gratefully goes to Pål Skalle, Associate Professor of Institute of Petroleum and Technology (IPT) and Project Coordinator for Mozambique, and also to Isabel Chuvambe, Director of Project Development of National Petroleum Institute (INP) of Mozambique.

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Summary

The displacement of oil from reservoir rock pore spaces is a function of many interacting variables, amongst which the reservoir wetting state has been shown to be one of the important affected by the rock lithology, oil chemistry and brine salinity. A finding from previous research says that the injection brine into oil saturated core plug increased oil recovery. Based on this the objective of this master thesis is to investigate the effect of brine concentration on flow properties in two types of carbonate rocks for enhanced oil recovery (EOR) through imbibition and water flooding processes.

The methodology used to evaluate the effect of brine concentration (BC) and chemical composition (CC) for oil recovery consisted on two stages. The first stage covers the literature review regarding the effect of brine concentration and chemical composition, including carbonates (chalk and limestone) characteristics. The second stage is related to the laboratory experiment which was performed using n-Decane oil, six (6) brines with different concentrations and chemical composition and the six (6) core plugs where four (4) “chalks” from Ekofisk (Norway) and the other two (2) “limestones” from Iranian field. The experiment was carried out in the laboratory of Institute of Petroleum and Technology (IPT), the materials, chemicals products, apparatus and equipments, methodology and procedures were provided by the IPT laboratory.

To carry out the laboratory experiments, initially the two cores from Iranian were cleaned before being used. Different properties of brines, cores and oil were measured using different methods and procedures; and results were computed. Next, each core was saturated with one type of brine and after that flooded by n-Decane oil for establishment of initial water saturation and determination of volume of oil produced by drainage process at room temperature conditions at one bar. After that, all cores were aging about 15 days at room temperature condition. Finally, each core was flooded using brine by imbibition process at room temperature conditions.

Results achieved were computed and discussed based on the literature review and compared with “A salinity (AS) Ekofisk core reference case” and similar studies. From this study was observed that the matrix block has a high porosity. The average porosity was about 40.24% of the volumes of large pores. The average absolute permeability was about 3.73 mD which is low because the microporous dominate the pore network. The average brine density (ρ) was about 1.026 g/cm³ and pH was about 7.25. The initial water saturation varies between 14.58 to 28.50% and residual oil saturation among 22.49 to 62%. The sleeve pressure in the cylinder was kept from 15 to 28 bar. During waterfloodig was observed that the breakthrough pressure drop and time to increases when the oil recovery increase.

The highest original oil in place (OOIP) was achieved in the low salinity (LS) core which was about 68.46% and the lowest was recorded in the C salinity (CS) core which was around 26.71%. The reason of the high and the low recovery is related with the effect of brine concentration and chemical composition of Sodium, Calcium, Magnesium and Sulphate, added in the solution. The main driving mechanism for low salinity waterflooding is believed to be multi component ionic exchange made possible by the expansion of electrical double layer. The permeability and porosity of the cores can be pointed as other factor. In general, it was shown that there is an increase in oil recovery as the salinity decreases.

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1.1 Introduction

Majority of the world's remaining oil resources are located in carbonate reservoirs, which are usually prove more difficult for crude oil production than conventional sedimentary reservoirs. A possible mechanism that may improve the recovery of oil from carbonate reservoirs is the injection of low-salinity fluids. It has been proposed that this process alters the surface chemistry of the pores and hence changes the wettability, which leads to achieve higher oil recovery.

Studies reported by Robertson, Eric P., (2007) cited that there is may be an optimal composition of the total dissolved solids (TDS) in the injection water that would yield the highest oil recovery. The composition could involve many variables with respect to ionic composition and brine concentration but current knowledge of how and when water composition can be manipulated to increase oil recovery is limited. Therefore, the system oil/water/rock interactions determines displacement efficient and are highly complex.

Nevertheless, laboratory study observations such as those referred above were sufficiently encouraging to justify further studies aimed at the field application. In the light of previously study mentioned earlier, the objective of the present work is to investigate the effect of brine concentration and chemical composition on flow properties in two types of carbonate rocks, four from Ekofisk, North Sea in Norway and two from Iranian, Ismari outcrop fields.

This study will help in getting more depth understanding of brine concentration (BC) and chemical composition (CC) for enhanced oil recovery (EOR) on carbonates reservoirs, especially on chalk and limestone rocks by imbibition and water flooding process.

The methodology used for this study consisted firstly on review a consistent physio-chemical theory related to the brine concentration (BC) and chemical composition (CC) for oil recovery on carbonates especially in chalk and limestone rocks. Secondly, a laboratory experiment was carried out to evaluate the effect of brine concentration and chemical composition on core flooded for enhanced oil recovery (EOR) by imbibition and waterflooding processes.

The work is made up of five chapters. The first chapter is an introduction of the work, which gives the background and objectives of the research work. This is followed by a detailed literature review which describes different parameters treated in work and characterizes the carbonates reservoir rock. The third is the heart of the work, where gives a detailed description of the laboratory experiment, which includes a description of materials and apparatus, methodology and procedures used. The four presents the results and discussion of the laboratory experiment and goes ahead to give a detailed discussion of the experimental results. The last includes conclusion and recommendations for the further future works.

1.2 Background

This study topic titled “effect of brine concentration (BC) on flow properties in two types of carbonate rocks” it is expansion part of the project course of reservoir engineering performed in the first semester of 2012 which was named “laboratory investigation of low salinity water flooding (LSW) on carbonate reservoir rock (chalk).

The objective of the project course was to investigate how much oil could be recovered from low salinity water flooding process. The laboratory experiment was carried out at room temperature conditions. Two core plugs from Iranian outcrop field one type of brine concentration and n-Decane oil. The experiments results achieved demonstrated that the formation has low permeability around 0.32 mD and high porosity about 47.95% and the oil recovery obtained was high.

1.2.1 Previous Works Carried Out On Brine Concentration and Chemical Composition

In this subsection is presented some researches work regarding brine concentration and chemical composition, as key points for the present laboratory experiment:

Studies on impact of brine salinity and ionic composition for oil recovery by water flooding from carbonate rocks demonstrated that at high temperatures ($>90^{\circ}\text{C}$) and by seawater injection can be improved oil recovery (IOR) from chalks. Also was observed that the ions Sulphate (SO_4^{2-}), Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) are key seawater and have the capability to change the rock surface charges, release absorbed carboxylic oil components, change rock wettability and improved oil recovery.

When Mohan, K., et. al., (2011) found that one of the conditions of change in wettability at the high temperature ($> 90^{\circ}\text{C}$) in carbonates is because of brine composition. However, these mechanisms are not active at a low reservoir temperature of 52°C . Hiorth, A., et. al., (2010) from laboratory studies proposes that the mineral dissolution maybe can be controlling factor in the brine-oil-chalk interaction.

Yousef, A.A.; et. al., (2010) have studied the impact of ion composition on carbonates cores (not chalk) at 100°C and they found out that there were incremental oil recoveries of about 10% for 10 times diluted seawater over that of the original seawater. The key mechanism was identified to be the wettability alteration toward a more water-wet state. Other studies shown that, the change in the injection brine composition can improve oil recovery (IOR). Moreover, others experience demonstrated that oil recovery can result in increase with reduction of injection brine composition from 15000 to 1500 part per million (ppm) and the content of total dissolved solid (TDS) from 30000 to 1000 ppm. However, the change in salinity depends of the relative permeability (K_r).

Research performed by Yousef, A.A., et. al., (2011) on carbonate reservoirs using a new method, smart water flooding as have showed that tuning salinity and ionic composition of the injected water on carbonate reservoir can have favorably effect on oil/brine/rock interactions, alter rock wettability, enhance microscopic displacement efficiency and eventually improved water flood recovery.

1.3 Objectives

What is the Objective of this Study?

The objective of this study is to investigate the effect of brine concentration on flow properties in the two types of carbonate rocks “Ekofisk Chalk and Iranian Limestone” to evaluate how can be increased the oil recovery through manipulation of the injection brine concentration and chemical composition by imbibitions and water flooding as enhanced oil recovery (EOR) method.

Why Do we Need this Study?

In reservoir engineering practices has been given consideration to the effect of chemical composition of the salt in the injection water on waterflood displacement efficiency or to the possibility of increased oil recovery through manipulation of the injection water composition. Previous studies have been shown that there are increasing evidences that injection of low salinity brine (LSB) has a significant impact on the amount of oil displaced. However, the exact mechanism by which this occurs is an unsettled issue. Therefore, it is the great goal of this research to investigate how this process could impact on oil recovery from two type of carbonate rocks (4 chalks) from Ekofisk Field, North Sea, Norway and (2 limestones) from Iranian outcrop field at field scale.

How to Investigate the Effect of Brine Concentration?

To evaluate the effect of brine concentration and chemical composition first of all literature related to carbonate reservoir rock, parameters that control oil displacement into the reservoir and the chemical composition of brines, were reviewed. Laboratory experiment was performed using six core plugs carbonates (4 chalks and 2 limestones) and n-Decane oil. The six brines solution with different concentrations and chemical composition were prepared. The chemical components used are constituted by Potassium Chloride, Sodium Chloride, Calcium Chloride, Magnesium Chloride, Sodium Sulphate, and Bicarbonate.

For this laboratory experiment it was proposed, to aging the cores, to apply both imbibition and water flooding processes, in other to maximize the oil production and the final oil recovery at room temperature conditions. Finally, the results of petrophysical, and physio-chemical parameters calculated related to the salinity of the water flooding process to enhanced oil recovery (EOR) were discussed based on the literature reviewed and laboratory investigation results obtained. The experimental results also were compared with similar studies reported within literature.

Expected Results from this Work

On this study were used four (4) new chalk and two (2) limestone already usage. In order, to evaluate and understand which parameter; both brine concentration and chemical composition has an effect on flow properties and most efficient on chalk rocks by imbibition and water flooding process. Therefore it was expected that the oil recovery must be higher for low salinity as compared to the high salinity. This work is also done so that we can observe the chemical effect on oil recovery in the chalk samples when imbibition and water flooding process are used to enhanced oil recovery.

Chapter Two: Literature Review

2.1 Introduction

This chapter captures literature review related to the carbonates characteristics, parameters definitions and descriptions of characteristics of dynamic properties to understand the mechanism behind the effect of brine concentration. According to the definition, the dynamic properties of the reservoir rocks are related with one, two or more features that can be affected by the fluids in the reservoir rock.

The dynamic properties of the reservoir rock are: porosity (Φ), temperature (T), pressure (P), viscosity (μ), density (ρ), permeability (K), relative permeability (K_r), capillary pressure (P_c), interfacial tension (γ) and wettability (W), water, oil and gas; saturations, and pore size distribution. Those parameters determine the mechanisms that affect the brine concentration and chemical composition on flow properties on carbonate reservoir.

2.2 Characteristics of Carbonate Rock

Carbonate reservoirs are characterized by extremely heterogeneous porosity (ϕ) and permeability (K). These heterogeneities are caused by the wide spectrum of environments in which carbonates are deposited and subsequent diagenetic alteration of the original rock fabric. The carbonate reservoir present sufficient void space (ϕ) to contain hydrocarbons and adequate connectivity of these pore spaces to allow transportation over large distances permeability.

Carbonate reservoirs can be fractured or non-fractured. Carbonate reservoirs tend to be most oil-wet or mixed-wet according to Anderson, W., (1985) and Buckley, J.S., et. al., (1998). Current recovery techniques, such as waterflooding, recover only 40-50% of the original oil in place (OOIP). In non-fractured carbonates; the recovery is much smaller than in fractured oil-wet and low-permeability carbonates reservoirs.

Several studies revealed that close to 50% of the world proven petroleum reserves are located in carbonates, which usually show a rather low oil recovery factor less than 30%. This is mainly due to the fractured nature of these reserves. Akbar, M., and Vissapragada, B., (2000 & 2001); and Roehl, P.O., and Choquette, P.W., (1985), reported that almost 60% of the world's remaining oil lies within carbonates reservoirs.

Recent studies reported by Mohan, K.; Gupta, R., and Mohanty, K.K., (2011) found that the wettability of carbonate reservoirs tend to be oil-wet, leading to lower oil relative permeability (K_r) and lower oil recovery in the life of a waterflooding mode. Sharma, G., and Mohanty, K.K., (2011) reported that due to microscopic oil trapping and macroscopic by-passing, waterflooding in carbonate reservoirs is often poor. Therefore, to improved oil recovery from oil-wet, low-permeability carbonates reservoirs is a great challenge.

Høgnesen, E.J.; Strand, S., and Austad, T., (2005) reported that in contrast to the sandstone reservoir, literature data indicate that about 80-90% of the worlds carbonate reservoirs show a negative capillary pressure, that is they are preferentially oil-wet.

It is documented also that the permeability of the matrix blocks is often in the range of 1-10 mD. Thus, the improved oil recovery (IOR) potential from this type of reservoir is very high.

Some studies show that 60% of worldwide oil reserves are located in carbonate reservoirs. The total oil recovery does not exceed generally 10%. Processes currently used for improved oil recovery from carbonate reservoirs includes miscible gas injection, water alternate gas (WAG), simultaneous water alternate gas (SWAG), foam-assisted WAG, microbial EOR, steam injection, carbon dioxide (CO₂) flooding, alkaline-surfactant-polymer (ASP) flooding, injection carbonated water, alkaline without surfactant and low salinity water flooding (LSW).

Carbonates reservoirs are divided on two main groups of sedimentary rock namely, limestone and dolomite. Chalk is a pure limestone sedimentary rock, as illustrate in figure 2.1.

2.2.1 Description of Chalk Rock

It is comprised of a sequence of mainly soft, white, very fine-grained extremely pure limestones which are commonly 300 - 400 meters thick. These rocks consist mainly of coccolith biomicrites, as illustrate in figure 2.1. They are formed from the skeletal elements of minute planktonic green algae, associated with varying proportions of larger microscopic fragments of bivalves, foraminifera and ostracods.

The planktonic coccoliths and many of the foraminifera (the planktonic species) lived floating in the upper levels of the oceans. When they died their skeletons sank to the bottom, combining with the remains of bottom living bivalves, foraminifera and ostracods, to form the main components of the chalk.



Figure 2.1: Shows the Nitzana chalk curves situated at Western Negev, Israel are chalk deposit formed at the Mesozoic era's Tethys Ocean; outcrop chalk on England; and a scanning electron microscope of a coccolith.

Chalk can also be referred to as compounds including Magnesium Silicate and Calcium Sulphate. Chalk has greater resistance to weathering and slumping than the clays with which it is usually associated, thus forming tall steep cliffs where chalk ridges meet the sea.

2.3 Definitions and Characterization of Petrophysics and Petrochemistry Parameters

This section presents definitions and characterizes the dynamic properties of the reservoir rock. This will be presented succinctly to give a good insight.

2.3.1 Porosity

Porosity (ϕ) is one of the most important parameters in formation evaluation and calculation of reserves. Density, neutron and acoustic logs are the basic materials for porosity calculation. Normally, the relationships between conventional three porosity logs (density, neutron and acoustic logs) and core analysis porosities are established based on the principle of volume physical model to extract reservoir porosity. By concept, the porosity is defined as a percentage or fraction of void to the bulk volume (V_b) of the rock, as reported by Xiao, L., et. al., (2011).

In reservoir engineering, only the interconnected or effective porosity (ϕ_e) is of interest since this is the only capacity which can make a contribution to flow. The measurements can be done in the laboratory on core samples, applying different methods, whereby actual conditions are simulated as closely as possible prior to measurement, or in-situ via suites of electric logs such as neutron porosity (ϕ_n), density and sonic logs. Therefore, the porosity can be calculated by equation 2.1, through interconnected void space or pore volume (V_p) divided by bulk volume (V_b).

$$\phi = \frac{V_p}{V_b} \quad (2.1)$$

Studies results also show that the porosity it is difficult in establishing a single model for porosity calculation in complex lithologic reservoirs.

2.3.2 Permeability

The permeability is a parameter that measure under turbulent flow conditions of the ease with which fluid flows through a porous rock, and is a function of the degree of interconnection among the pores.

Studies carried out by Lager, A., et. al., (2006) regarding salinity on carbonate reservoir revealed that there was a reduction in permeability when the injection brine salinity was less than 1550 part per million (ppm) of total dissolved solid (TDS). This reduction in permeability was observed when the low salinity brine (LSB) replaced the initially permeating high salinity brine. They concluded from others studies that the release process is primed by a combination of extremely low salinity and high pH. They also found that little change in permeability when fluids with increasing pH were injected until an injection pH of 9 was reached. At $\text{pH} > 11$ a rapid and drastic decrease in the permeability was observed implying that severe damage was caused on contact with the high salinity fluid and the absence of salts in the solution as cited by

The permeability reduction occurs if the ionic strength of the injection brine is equal or less than, the critical flocculation concentration (CFC), which is strongly dependent on the relative concentration of divalent cations, such as ion Calcium (Ca^{2+}) and Magnesium (Mg^{2+}). These cations have the function of stabilizing the clay by lowering the zeta potential resulting in the lowering of the repulsive force.

The relationship between porosity and permeability the following situations were commonly encountered on carbonate rock:

- (a) highly porous rock type has very low or negligible permeability (<1 mD), because microporous dominate the pore network;
- (b) vuggy rocks have a high volume of large pores, but permeability (K) remains low (<10 mD), since these vuggs are isolated within a microporous matrix;
- (c) a rock type with moderate porosity 15-20% has excellent K (>100 mD), because the pore network is homogeneous and well connected (partially cemented oolitic grainstone);
- (d) an extremely low porosity rock 2-5% presents good permeability (K) because of the presence of the well connected fracture network.

The permeability of a medium in mili Darcy's (D) can be computed using Darcy law, equation 2.2 where Q is the flow rate of fluid through the porous medium in cm^3/s ; μ is the dynamic viscosity of the fluid in centipoises (cPs); P_1 and P_2 are pressures applied inlet and outlet of the core, in atm; L is the length of the core, in cm; and A is the cross sectorial or area of the fluid, in cm^2 .

$$k = \frac{QL\mu}{A(P_1 - P_2)} \quad (2.2)$$

2.3.3 Rock Compressibility

The rock compressibility (C_r) quantifies the relationship between the stress applied on a body and the resulting change in volume (V). In the case of a non-porous solid there is only one compressibility stated as given by formula 2.3. Where V represents the body volume, P is the pressure applied to it and the upper index refers to the body volume when there is no any pressure applied.

$$C = \frac{-1}{V} \frac{dV}{dP} \quad (2.3)$$

The equation 2.3, supposes that the system will hold under the same temperature during the whole change in pressure and considers compressibility as a positive value when the body volume diminishes while or subjected to compression.

The rock compressibility is an important property of rocks specially in the case of stress sensitivity formations in which flow of fluids in porous media during production is attached to reservoir formation strain and displacement or when the local stress are re-organized due to infill or exploratory well drilling. Because of this, compressibility values and behavior must be known in order to accomplish the reservoir behavior during exploitation and production processes correctly.

Carvajal, J. M., et. Al., (2010) from their laboratory experiment demonstrated that rock compressibility behavior depend on both stress path and stress state.

The rock compressibility (C_r) on tested samples decreases as stress pathway. Their results show that as mean stress applied on rock increases the compressibility decreases and that for low mean stress values the decrease on compressibility is faster than for higher stress values. Finally, micro-fracturing density increases both the stress sensitivity and the initial value of rock compressibility but this increase is not as drastic as the one due to stress pathways.

2.3.4 Pore Size Distribution

The concept of the pore size distribution was been an attempt to characterize the intricate geometry of the flow channels in porous media. Because pores in a porous medium are interconnected it is impossible to describe exactly what is meant by a “pore” and, therefore, the term pore size distribution requires further amplification.

As documented by Klinkenberg, L.J., (1957) the visual method for the determination of pore size distribution “the pore” is considered to be the hole between the grains as observed on thin sections or on a polished surface of the rock under a microscope,. A pore size distribution should not be based on the idea that a core should, under all circumstances, behave as a bundle of straight non-interconnected capillaries of the same pore size distribution.

2.3.5 Forming a Transition Zone and Capillary Pressure

Wael, A., et. al., (2007) showed that a homogeneous formation exhibits a zone of transition from high oil saturation (S_o) at the top to high water saturation (S_w) at the bottom (blue curves), see in figure 2.2. This saturation transition has its origin in the capillary pressure (P_c) which is the difference between the water and oil pressures at the interface and is given by equations 2.4, 2.5 and 2.6.

$$P_c = P_{nw} - P_w \quad (2.4)$$

Where P_{nw} is the pressure in the non-wetting phase and P_w is the pressure in the wetting phase.

$$P_c = g * h * \rho \quad (2.5)$$

Then ρ represent the density difference between phases, g is the gravitational acceleration and h is the height of capillary rise.

$$P_c = \frac{2\gamma\cos\theta}{r} \quad (2.6)$$

Where γ is the interfacial tension, θ is the contact angle and r is the inner radius of capillary.

In a capillary tube, forces from water-wetting (WW) surface, cause water to rise (left side), displacing oil, but if the tube inner surface is oil-wetting (OW), the oil will push water down (right side). The wetting forces, and therefore capillary pressure, are inversely proportional to the capillary radius. The capillary rise, h , is determined by the balance of wetting forces and the weight of fluid displaced from the bulk-fluid interface. Translating this to a porous formation, there is a free water level (FWL) defined, where the capillary pressure between water and oil is zero.

Since porous rocks have a distribution of pore and pore throat size – similar to a distribution of capillary tubes at any given height above the free water level (FWL), the portion of the size distribution that can sustain water at that height will be water-saturated.

At greater height, the buoyancy of oil in water provides greater capillary pressure (P_c) to force water out of smaller voids. In a water-wet formation (left side), the oil/water contact is above the free water level (FWL), indicating that pressure must be applied to force oil into the largest pores. In an oil-wet formation (right side), the contact is below the free water level (FWL), signifying that pressure must be applied to force the water phase into the largest pores.

The oil/water contact (OWC) divides the zone containing mostly oil from the one containing mostly water.

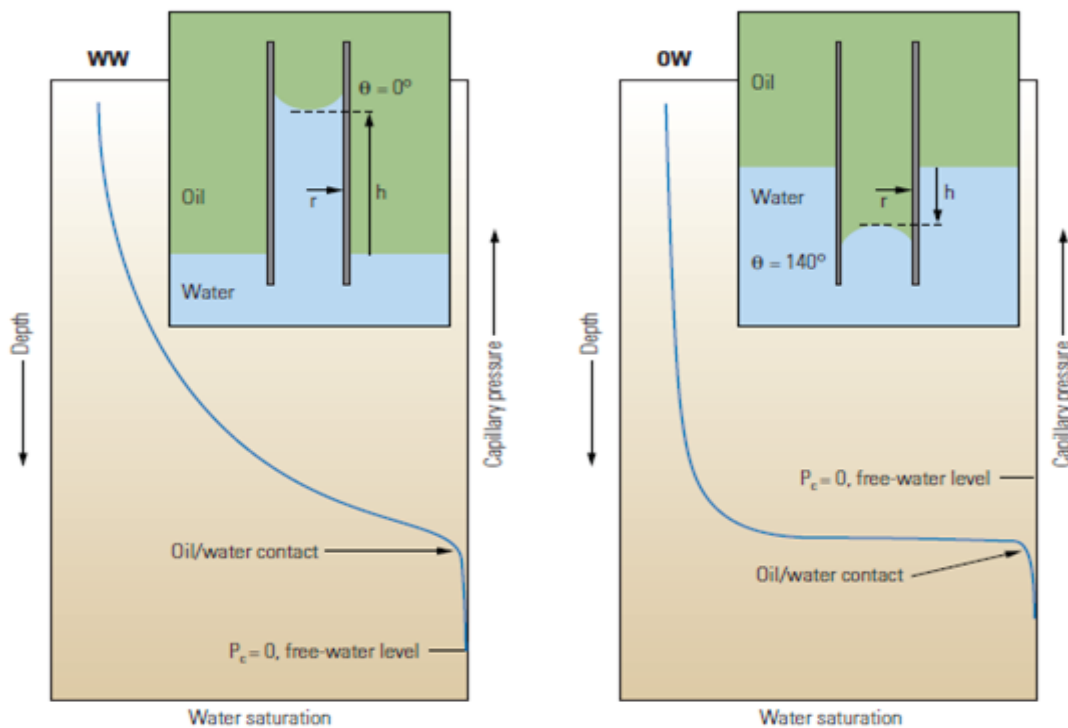


Figure 2.2: Illustrates the forming a transition zone on water-wet (WW) and oil-wet (OW) conditions, by Wael, A.; et. al., (2007).

Moreover, literature data reported by Namba, T., and Hiraoka, T., (1995) defined the capillary pressure (P_c) force as the pressure in oil phase (P_o) minus the pressure in the water phase (P_w), as showed by equation 2.7.

$$P_c = P_o - P_w \quad (2.7)$$

Thus, the capillary pressure can be either positive (water-wet) and negative (oil-wet) depending on the wettability preference. Also, reported by Tabary, et. al., (2009) that the low permeable rocks usually have larger absolute capillary pressure $|P_o - P_w|$ than high permeable rocks. It was reported that the capillary pressure is positive if any rock is water-wet and negative in the oil-wet case.

For water-wet fractured reservoirs, the capillary forces are the main driving forces of spontaneous imbibition and contribute to the replacement of oil by water

2.3.6 Capillary Pressure and Relative Permeability

By definition, relative permeability (K_r) is the ratio of effective permeability (K_{eff}) of a particular fluid at a particular saturation to absolute permeability (K_a) of that fluid at total saturation. The relative permeability (K_r) is dimensionless and is a non-linear function of fluid saturation.

Wael, A., et. al., (2007) demonstrated that the capillary pressure and relative permeability (K_r) for water-wet and mixed-wet conditions as shown in the figure 2.3 contrast possible capillary pressure (red) and relative permeability curves for water, relative permeability of water, K_{rw} , (blue) and oil, K_{ro} , (green) for water-wet and mixed-wet reservoirs. The first curve to consider is the primary drainage capillary pressure curve (dotted), which indicates a certain pressure in the oil phase that is required before a substantial displacement of water can occur. Since most reservoirs are considered to be water wetting when oil first migrates, this curve is also used for the mixed-wet condition.

The other curves (dashed=increasing S_w , solid=increasing S_o) these differ based on the wettability change due to oil contact with the surfaces in the large pore spaces. In the strongly water wetting saturation, the capillary pressure curves stays positive over most of the saturation range, while in the mixed-wet case, its sign has both positive and negative portions, signifying that some parts of the surface imbibe water and others imbibe oil. The relative permeability of oil (K_{ro}) values are less at low water saturation (S_w) in the mixed-wet case, because the oil is in competition with water in the large pores. Similarly, the relative permeability of water, (K_{rw}) at high water saturation (S_w) is reduced in the water wetting (WW) case because the oil preferentially occupies the large pores.

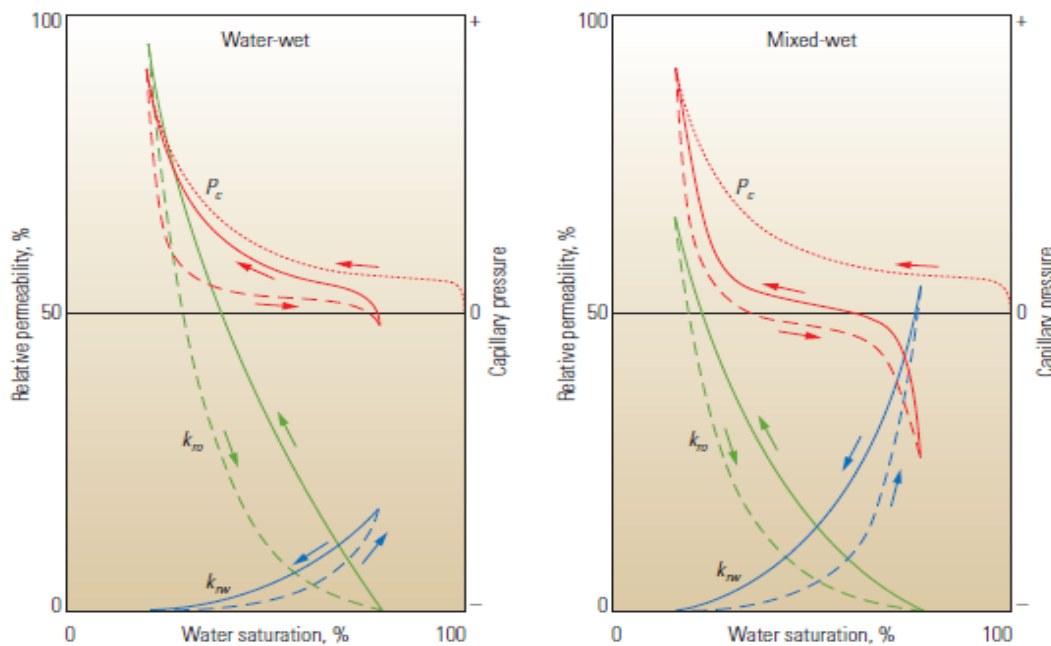


Figure 2.3: Presents the capillary pressure and relative permeability for water - wet and mixed-wet conditions, by Wael, A.; et. al., (2007).

The relative permeability (K_r) of the oil, gas and water phases are expressed by equations 2.8, 2.9 and 2.10 where K_o is the oil permeability, K_g the gas permeability and K_w the water permeability, in mD.

$$K_{ro} = \frac{K_o}{K_a} \quad (2.8)$$

$$K_{rg} = \frac{K_g}{K_a} \quad (2.9)$$

$$K_{rw} = \frac{K_w}{K_a} \quad (2.10)$$

The relative permeability (K_r) of fluid phase varies between zero and one. In multiphase flow studies, the relative permeability plays an important and crucial role in understanding of fluid flow behavior in porous medium. The relative permeability trends are of great importance when undesirable water or gas flow is anticipated in an oil reservoir. The relative permeability is influenced by saturation, saturation history, pore geometry, temperature, and wettability, viscous, capillary and gravitational forces.

The absolute permeability (K_a) of reservoir rock is a unique number but in contradiction permeability is a set of values that depend on fluid saturation. Several correlations have been derived so far in oil industry to calculate relative permeability values for each fluid phase. From special core studies together with petro physical studies relative permeability data can be obtained. Well tests serve as good source for effective permeability (K_{eff}) of fluids under actual reservoir conditions. It is very important to understand that relative permeability (K_r) characteristic of reservoir fluids usually change from one place to another. Various rock facies in a reservoir may exhibit every different relative permeability (K_r) trends.

2.4 Saturation Phase

2.4.1 Water Saturation

Saturation is defined as relative amount of water, oil and gas in the pores of a rock, usually as a percentage of volume (V). Water saturation (S_w) is the fraction of water in a given pore space. It is expressed in volume/volume, percent or saturation units. The saturation is known as total water saturation if the pore space is the total porosity, and the effective water saturation if the pore space is the effective porosity. If used without qualification, the term usually refers to the effective water saturation.

2.4.2 Establishment of Initial Water Saturation

The initial water saturation (S_{wi}) is essential for proper reserves evaluation, it informs decisions on which zones to complete in order to obtain water-free product, and influences a variety of productivity and formation damage issues. The most common methods of saturation S_{wi} determination are electrical log resistivity measurements and direct saturation measurement on in-situ core samples. In the laboratory it is made by porous plate method which only allows the water enter through it for a certain pressure interval up to 1 bar to 0.6 bar on top. The establishment of S_{wi} takes 7 days of applying porous plate method and it can be calculated using equation 2.11.

$$S_{wi} = 1 - S_o \quad (2.11)$$

2.4.3 Moveable Oil Saturation

Moveable oil saturation (S_{om}) is the volume of hydrocarbon per unit volume of rock that can be moved on production, measured in volume/volume or porosity units. It is the maximum possible reduction in oil saturation (S_o) into the reservoir rock, and can be calculated through summation of initial oil saturation (S_{oi}) and residual oil saturation (S_{or}) as given by the equations 2.12 and 2.13.

$$S_{om} = S_{oi} - S_{or} \quad (2.12)$$

$$S_{om} = 1 - S_{wi} - S_{or} \quad (2.13)$$

2.4.4 Residual Oil Saturation

The residual oil saturation (S_{or}) is defined as the oil that does not move when fluids are flowing through the rock in normal conditions, for primary and secondary recovery, and invasion. It is the oil that cannot be reducible even under any conditions, always remains in the reservoir rock.

2.4.5 Irreducible Water Saturation

Irreducible water saturation (S_{wir}) is the water that always remains immiscible, and cannot be miscible even under any condition in the reservoir rock. It is equivalent to the minimum water saturation (S_w) found from capillary pressure (P_c) curves determined from special core analysis (SCAL) the typical capillary pressure (P_c) and water saturation (S_w) curves relationships.

2.4.6 Reservoir Fluid Saturation

It is related with initial saturations of water (S_{wi}) and oil (S_{oi}) that can be calculated by equation 2.14.

$$S_{wi} + S_{oi} = 1 \quad (2.14)$$

2.4.7 Interfacial Tension

It is the thin film between two fluids not or well miscible. The interfacial tension (γ) can be between oil-water, oil-gas and gas-water systems. Some previous researches work reported that the surfactants can be used to lower the interfacial tension between oil and water and increase the capillary number to mobilize residual oil blods.

2.4.8 Contact Angle

The angle formed between the solid-liquid interface and the liquid-vapor interface is referred to as the contact angle (θ). A contact angle can be measured by producing a drop of liquid on a solid. The Young's equation 2.15 and figure 2.4 are used to describe the interactions between the forces of cohesion and adhesion, and measure what is referred to as surface energy.

$$\gamma_{so} = \gamma_{sw} + \cos \theta * \gamma_{ow} \quad (2.15)$$

The quantitative method of contact angle (θ) measurement consist of an oil drop surrounded by water on a water-wet surface (*left*) that forms a bead. The angle contact is approximately zero.

On an oil-wet surface (*right*), the drop spreads, resulting in a contact angle of about 180° . An intermediate-wet surface (*center*) also forms a bead, but the contact angle comes from a force balance among the interfacial tension (γ) terms, which are the surface-oil (γ_{so}) and surface-water (γ_{sw}) terms, respectively, and oil-water (γ_{ow}) terms. Figure 2.4 shows the contact angle of an oil drop surrounded by water on a water-wet surface (left) forms a bead, intermediate-wet surface (center) and oil-wet surface (right).

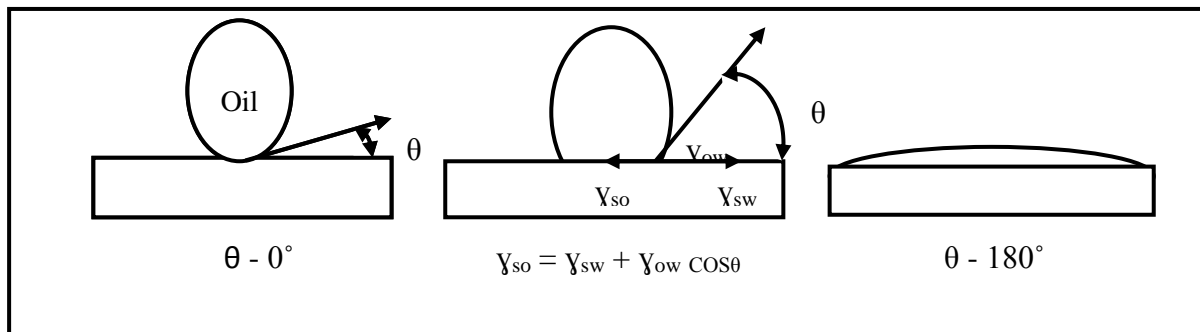


Figure 2.4: Shows the contact angle of an oil drop surrounded by water, by Wael, A.; et. al., (2007).

2.4.9 Pore Surface Roughness

Studies performed on pore surface by Wael, A., et. al., (2007) concluded that the apparent contact angle measured from the average surface plane, can differ significantly from the true contact angle (θ) at a locally inclined surface (top). Even if a pore is water-wetting (WW), the surface water may not be a double layer, but could be thicker due to pore rugosity (bottom), as shown on figure 2.5. At an asperity, the surface forces are more favorable for displacing the double layer than elsewhere on the surface.

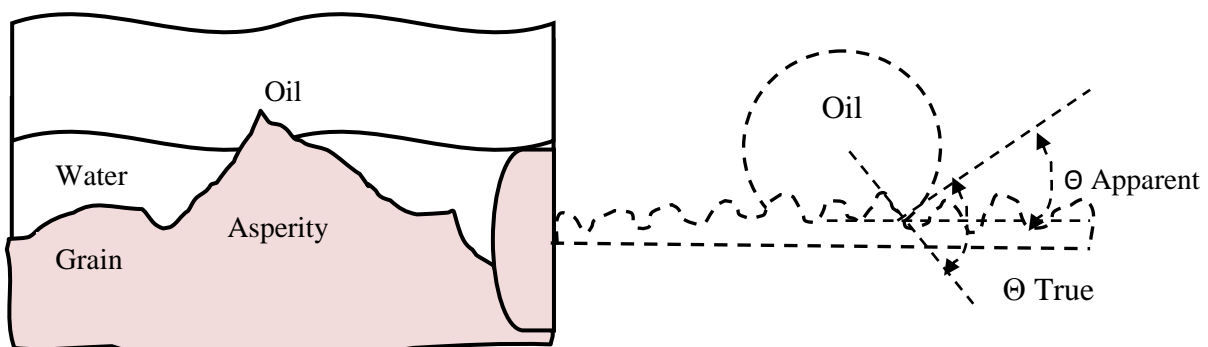


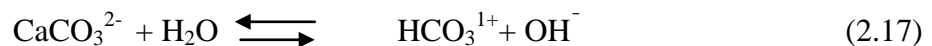
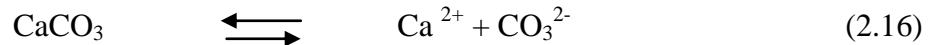
Figure 2.5: Represents the pore surface roughness, by Wael, A.; et. al., (2007).

2.4.10 pH Variation

The majority of petroleum reservoirs contain Carbon Dioxide (CO_2) which will act as a pH buffer, rendering an increase of pH up to 10 unlikely if not impossible in most reservoirs.

From these researches works have shown that a rise in pH during low salinity laboratory experiment has benefit on increases of oil recovery. This rise in pH, is due two concomitant reactions: carbonate dissolution and cation exchange. The dissolution of carbonates (i.e. calcite and/or dolomite) results in an excess of hydroxyl anion (OH^-), and cation exchange occurs between clay minerals and the invading water.

Therefore, the dissolution reactions are relatively slow and dependent on the amount of carbonate material present in the rock, as showed by equations 2.16 and 2.17.



However, cation exchange occurring on the clay minerals, and to a much lesser extent quartz, is faster. The mineral surface will exchange Hydrogen (H^+) cation present in the liquid phase with cations previously absorbed. This will lead to a decrease in H^+ concentration inside the liquid phase resulting in a pH increase. The mechanisms active at the front where alkaline water is displacing acidic crude oil include:

- (a) reduction of oil/water interfacial tension;
- (b) wetting alteration of the matrix grains;
- (c) formations of water drops inside of oil phase, and
- (d) drainage of oil from the volume (V) between alkaline water drops to produce an emulsion containing very little oil.

If a pH above 9 is achieved inside petroleum reservoir this would be equivalent to an alkaline waterflood. Experiment shows that high pH is not responsible for the increase in oil recovery due to the injection of water with low salinity. Figure 2.6 shows the diverse adhesion mechanism occurring between clay surface and crude oil.

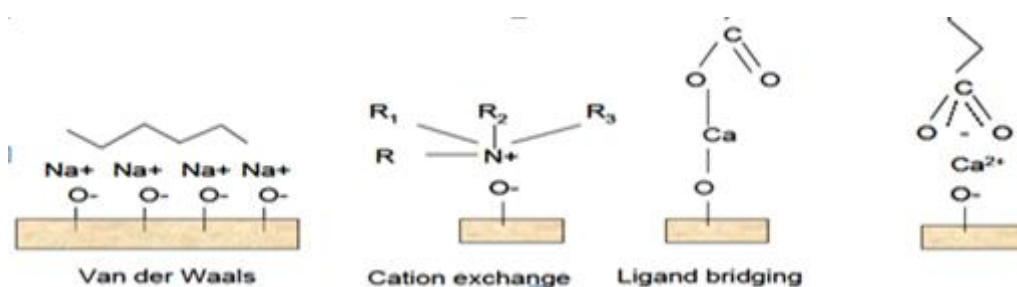


Figure 2.6: Shows the representation of the diverse adhesion mechanism occurring between clay surface and crude oil, by Lager, A.; et. al., (2006).

The pH is beneficial when it is higher than 7 and no effect, if was less than 7, for oil recovery (OR) on water-wet system. The pH is measured after the effluent is collected. Alkali can be used to generate in-situ surfactant with acid oils and increase pH to lower surfactant adsorption as cited by Mohan, K., et. al., (2011).

2.4.11 Fines Migration

Studies reported that released fines, migrate with the flowing fluid and are subsequently captured at pore throats or pore constrictions, causing formation damage. While Lager, A., et. al., (2006) found results that in the presence of high salinity brine (HSB), clays are undisturbed and retain oil their oil wet nature leading to poorer displacement efficiency. When in contact with low-salinity water, clay particles detach from the pore surface.

Ashraf, A.; Hadia, N.J., and Torsæter, O., (2010) have reported that for oil recovery different phenomena can contribute for example by increase in pH (alkalinity), the presence of fines migration and multi-component ionic exchange (MIE) during low salinity water flooding (LSW) can be improved oil recovery (IOR).

2.4.12 Clays

Clays are defined as are hydrous aluminum silicates whose molecular lattice can also contain magnesium, potassium, sodium, and iron in decreasing prevalence. Clay minerals constitute 40% of the minerals in sediments of sedimentary rocks. Some properties of clay are:

- (a) they are generally located on the pore grain surfaces,
- (b) they have a large specific surface area, and
- (c) they are chemically reactive.

Clays affect the enhanced oil recovery (EOR) processes by influencing the medium permeability (K) or by changing the ionic state of the resident fluids. Also, was documented by Lake, L.W., (1989) that among the most interesting characteristic of clay is the ability of clays to exchange cations with fluids in the pore space.

2. 4.13 Temperature Variation

Indications from previous researches found out that the reservoir temperature will conform to the regional or local geothermal gradient with a normal value being 1.6 °F/100 ft. This is because of the large thermal capacity of the rock matrix, which comprises about 80% of the bulk reservoir volume. Also, the very large area for heat transfer conditions within the reservoir may be considered isothermal in most cases.

Idowu, J., et. al., (2011) have showed from studies, that the imbibition rate and oil recovery (OR) increases as the temperature (T) increases due to a strong adsorption of Sulphate (SO_4^{2-}) and Calcium (Ca^{2+}) onto chalk surface. The work also, concludes that temperature, low salinity water and the potential determine ions plays a very important role in the increase oil recovery in the reservoir.

Hamouda, A.A, and Karoussi, O., (2008) and Yousef, A.A., et. al., (2011) carried out researches work on chalk rocks in high temperature reservoirs in order to observe the temperature effect on oil recovery the results showed that it is not only the injected fluid temperature that affects the oil recovery rate and ultimate oil recovered, but also the temperature difference between injected fluid and reservoir temperature. Above the critical temperature, an adverse effect of temperature is observed, where the relative permeability (K_r) indicates a more oil-wet behavior. Above 80 °C (tested at 130 °C) the intersection of relative permeability is shifted toward lower water, where less oil recovery is obtained.

This observation also is neither supported by interfacial tension (γ) nor contact angle (θ) as a function of temperature, as both show a decrease with temperature favoring higher oil recovery.

Studies on chalk, shows that the condition necessary to trigger the effect include oil with high polar components, Sulphate free formation water whose temperature can be higher than 90 °C, and high concentration of key seawater ions in the injected water. Also, it is proposed that at higher temperatures, these ions become more reactive with the chalk rock surface, and this will induce the substitution of Calcium (Ca^{2+}) on the rock surface by Magnesium (Mg^{2+}).

Also studies related to chemical interaction between seawater and chalk performed by Austad, T., (2008) and Høgnesen, E.J., et. al., (2005) concluded that adsorption of cation Ca^{2+} onto the chalk surface increased during the absorption of Sulphate (SO_4^{2-}) because the initial positive charge of the chalk surface decreased. Thus, adsorption of anion SO_4^{2-} onto the chalk surface causes excess of ion Ca^{2+} to be close to the surface. While the Sulphate is very efficient as wettability modifying agent towards carbonates, at elevated temperatures.

2.5 Brine Concentration and Chemical Effect

2.5.1 Brine Concentration

Injection of brine with well selected ionic composition in carbonate reservoir has been developed into an emerging EOR technology, aiming for improved microscopic sweep efficiency with reduction in the remaining oil saturation (S_o). When brine of low salinity, is injected into the reservoir, oil recovery is seen to be improved to as much as 15%, although the mechanism of low salinity brine (LSB) in reservoirs still remains unsettled.

Experiments performed by Webb, K.J., et. al., (2005) found that at ambient or reduced conditions using dead fluids and addition of Sulphate at sea-water concentrations modifies the rock wettability (W) to increase water-wet behavior. Idowu, J., et. al., (2011) reported that one important effect of the low salinity water is its ability to alter relative permeability (K_r) which consequently improves the wettability of the reservoir, usually changing it to a more water-wet state. They also found that the potential determining ions play a very important role in wettability alteration in carbonates. Furthermore, they documented that the adsorption of anion Sulphate (SO_4^{2-}) onto chalk surface facilitates the adsorption of Sulphate (SO_4^{2-}) charged carboxylic material by changing the surface chalk in the presence of SO_4^{2-} increases the concentration of cation Ca^{2+} close to the chalk surface which facilitates a reaction with the carboxylic group.

Zahid, A., et. al., (2010) have shown that waterflooding performance is dependent on the composition of injecting brine solution. From research carried out on chalk to understand IOR on chalk using surfactant solutions and later using the modified sea water, the results shows that wettability alteration towards more water wetting (WW) conditions to be the reason for improvement in oil recovery. Bagci, S., et al. (2001) performed laboratory work to observe the effect of brine composition on oil recovery by waterflooding process using Sodium Chloride (NaCl), Potassium Chloride (KCl) and Calcium Chloride (CaCl_2) brines.

Also Yousef, A.A., et. al., (2011) found that the mechanisms of salinity mainly linked to presence of clay minerals, oil composition, the presence of formation water with high concentration of divalent cations for example Calcium (Ca^{2+}) and Magnesium (Mg^{2+}), and the salinity level of the low salinity water can be in the range of 1000 to 5000 part per million (ppm).

While Pu, H., et. al., (2010) concluded from experiment that increase in Sulphate ion content of the effluent brine confirmed the dissolution of anhydrite, for all three rock types, namely: eolean sandstone, dolomite and calcite.

Zhang, Y., et al., (2007) demonstrated from both laboratory experiment and field tests that by injection of brine with different salinity for reservoir cores, a large increase in oil recovery was observed for secondary recovery by injection of low versus high salinity. They concluded that increase in pressure drop across the core was closely related to increase in oil recovery for both secondary and tertiary modes. Studies reveals that if proper consideration is given to the quality of the ionic composition of the injected water by lowering its total dissolved solid (TDS), oil recovery can be greatly enhanced, and residual oil saturation (S_{or}) immensely reduced.

2.5.2 Multiple-Component Ionic Exchange

In understanding of low salinity in terms of multiple-component ionic exchange (MIE) between absorbed crude oil components, cations in the in-situ brine and clay mineral surfaces, the enhanced oil production and associated water chemistry response must be consistent with the MIE mechanism proposed. It must be also noted that the MIE between clay mineral and the injected brine is responsible for the improvement in oil recovery (OR) arising from the injection of low salinity water, as cited by Lager, A., et. al., (2003).

Several examples of improved oil recovery by injection of low ionic strength brine have been reported for both outcrop and field cores samples by Tang, G.Q., and Morrow, N.R., (1997) and (2002). They demonstrated that the conditions necessary for improved oil recovery are such as the type of oil and rock, composition of the formation and injected water, and initial water saturation (S_{wi}) However, are still far from understood. Also, they show that most laboratory relative permeability (K_r) tests and displacement tests are done using synthetic formation water as both the formation and injected water rather than using formation water.

2.5.3 Acid Number

Independent study carried out by Zhang, P., and Austad, T., (2005) and Austad, T., (2008) concluded that the acid number (AN) of the crude oil is the most important wettability parameter for chalk and the acid number of the crude oil usually decreases as the reservoir temperature increases due to decarboxylation at high temperatures. Therefore, carbonate reservoirs appear to be more oil-wet as the reservoir temperature decreases, which is opposite to sandstone.

In an experimental carried seawater used as the base imbibing fluid, and model Ekofisk formation water used as initial water present in the cores and where the cores aged in crude oils with different acid number ranking between (0.17 ~ 2.07 mg KOH/g oil) and at a variety of temperatures ranging from 40 - 20 °C following major observations were observed:

- (a) good relationship between the new wetting index and oil recovery was achieved;
- (b) the water-wet fraction of the chalk surface must be above 0.6 for spontaneous imbibition to occur;
- (c) sulphate in the imbibiting fluid appeared to have a wettability modifying effect, especially at low water-wet conditions; and
- (d) cationic surfactant of the type $[\text{R-N}(\text{CH}_3)_3]^+$ dissolved in the imbibiting fluid IOR significantly especially close to neutral wetting conditions.

Høgnesen, E.J., et. al., (2005) from regard wetting properties of chalk as important factor, they documented that the most important factor was the acid content in the crude oil determined by the acid number(AN). Thus, carbonate reservoir at high temperature usually contain crude oils with a lower AN, and may therefore act somewhat more water-wet.

2.5.4 Chemical Reaction of Chalk

When a drop of dilute hydrochloric acid is placed on a piece of chalk, the acid reacts with the calcite and forms bubbles of carbon Dioxide (CO_2). This "fizz" reaction is a characteristic of limestone. When heated, the calcium carbonate in Chalk decomposes to lime, or calcium oxide. Many geologists carry a small bottle of dilute hydrochloric acid into the field for a rapid and easy identification of limestone.

2.5.5 Effect of Chemical Composition on Chalk

Zahid, A., et. al., (2010) have reported that using an anionic surfactant in combination with Sodium carbonate for enhanced oil recovery (EOR) by spontaneous imbibition from oil-wet carbonate rocks, the carbonate ion to be a potential determining ion at high pH. During alkaline flooding when oil containing organic acids is flooded with alkaline water a high oil recovery (OR) efficiency, can be achieved provided a bank of viscous oil/in/water emulsion forms in-situ. The amount of additional oil recovered depends on the pH and salinity of the water and the type and amount of organic acid contains, as well as on the amount of fines in the porous medium, as demonstrated by Cooke, Jr. C.E., et. al., (1974).

Zhang, P., and Austad, T., (2005) reported that preliminary imbibition test showed that increasing the Sulphate concentration in the imbibiting fluid on improving oil recovery on oil-wet carbonates (chalk) by wettability modification. The ionic species for brine analyses are Sodium (Na^+), Magnesium (Mg^{2+}), Calcium (Ca^{2+}), Potassium (K^+), Chloride (Cl^-), Iodide (I^-), SO_4^{2-} and Carbonate (HCO_3^-) Moreover Zhang, et. al., (2007) and Tina, et. al., (2009) have observed that the anion Sulphate (SO_4^{2-}) as a potential determining ion for improved oil recovery, IOR, in chalk reservoirs. This anion must act together with cations Mg^{2+} and Ca^{2+} because anion SO_4^{2-} alone is not able to increase spontaneous imbibition.

2.5.6 Chemical Mechanism for Low Salinity

Some studies carried out by Alotaibi, M.B.; and Nasr-El-Din, H.A., (2009) have reported that the salinity concentration level used by US Geological Survey classifies saline water into three categories, namely:

- (a) slightly saline water contains between 1000 to 3000 ppm;
- (b) moderately saline water contains roughly 3000 to 10000 ppm; and
- (c) highly saline water has around 10,000 to 35000 ppm of salt.

On the other hand, seawater has a salinity of roughly 35000 ppm. However, it varies from one place to another.

The chemical equilibrium is established at temperature, pressure and reservoir pH, between absorbed polar components of the oil and inorganic cations Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) of the formation brine. Initially, both acid and basic organic materials are absorbed onto the clay together with inorganic cations, especially Calcium (Ca^{2+}).

The initial pH of the reservoir formation water maybe can be between 5 to 6 due to dissolved Carbon Dioxide (CO_2) and Sulphurous acid (H_2S). This low pH environment enhances the adsorption of both acidic and basic components onto the clay surface as cited by RezaeiDoust, A., et. al., (2010).

When the low salinity (LS) is injected into the reservoir with ion concentration much lower than that in the initial formation brine especially Calcium (Ca^{2+}), the equilibrium associated with the brine/rock interaction is disturbed, and a net desorption of cations occurs. Therefore, to compensate for loss of cation, proton, hydroxyl (H^+), from the water close to the clay surface adsorb onto the negative sites of the clay, (i.e. substitution of Ca^{2+} by Hydroxyl (H^+) is taking place. This creates a local increase in pH close to the clay surface. The local surface increase in pH close to the clay surface causes reactions. Figure 2.7 illustrates the chemical mechanism. Upper, desorption of basic material. Lower, desorption of acidic material. The initial pH at reservoir conditions may be in the range of 4 – 5.

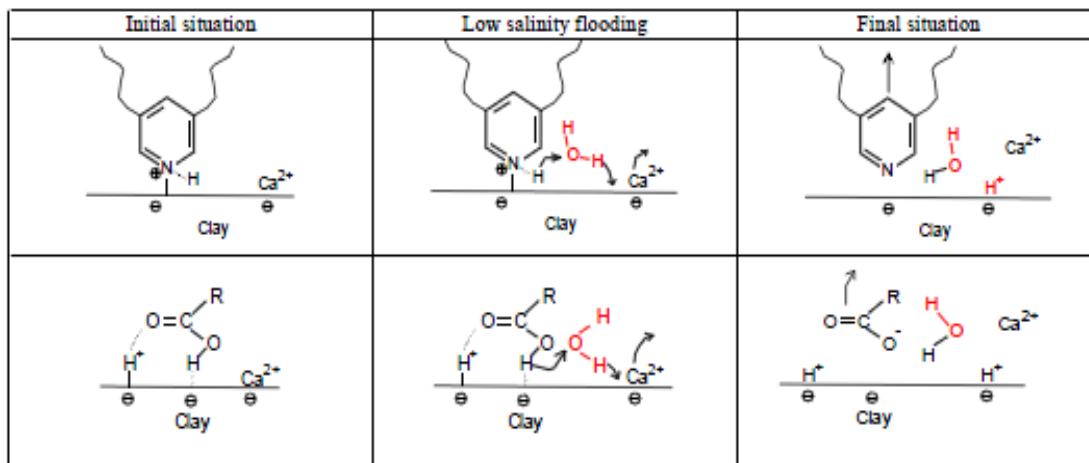


Figure 2.7: Represents the proposed chemical mechanism for low salinity for EOR effects, by RezaeiDoust, A.; et. al., (2010).

2.6 Wettability

2.6.1 Concept of Wettability

Wettability (W) as applied to an oil reservoir describes the tendency of a fluid to adhere or absorb onto a solid surface in the presence of another immiscible fluid.

It can be also described as a measurement of the affinity of the rock surface for the oil or water phase. It is the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids as cited by Zhang, P., and Austad, T. (2005), and Vledder, P., et. al., (2010). It can be defined as phenomenological as the fraction of the rock surface that is coated by absorbed hydrocarbons.

A conventional parameter for characterize it is the wettability index (W). For $W=0$, the porous medium is completely water-wet (zero hydrocarbon coating) and for $W=1$, the porous medium is completely oil-wet (complete hydrocarbon coating). The wettability if is about 0.5 characterizes mixed wetness.

The rock wettability is a major factor controlling the location, flow and distribution of fluids in a reservoir. Hydrocarbon recovery results from the competition between capillary and viscous forces and gravity. Low salinity flooding is a way to improved oil recovery (IOR) by manipulation the wettability towards more water-wet state.

2.6.2 Characteristics of Wettability

The wettability it is the preferences of a solid to contact one liquid or gas, known as the wetting phase, rather than another. The wetting phase will tend to spread on the solid surface and a porous solid will tend to imbibe the wetting phase, in both cases displacing the non-wetting phase. Rocks can be water-wet, oil-wet or intermediate-wet. The intermediate state between water-wet and oil-wet can be caused by a mixed-wet system, in which some surfaces or grains are water-wet and others are oil-wet, or a neutral system, in which the surfaces are not strongly wet by either water or oil. Both water and oil wet most materials in preference to gas, but gas can wet sulfur, graphite and coal.

The wettability affects relative permeability (K_r) electrical properties, nuclear magnetic resonance relaxation times and saturation profiles in the reservoir. The wetting state impacts waterflooding and aquifer encroachment into a reservoir. Reservoir wetting preference can be determined by measuring the contact angle (θ) of crude oil and formation water on silica or calcite crystal or by measuring the characteristics of core plugs in either an Amott Imbibition Test United State Bureau Mines (USBM) test.

The maximum relative oil recovery on IOR of the strong oil-wet into carbonatic rock is obtained when the Amott–Hervey Wettability Index (W) is close to zero or when the reservoir rock turns into a neutral-wet condition. When the $W > 1$, the reservoir rock turns into a water-wet state and if $W < 1$, the reservoir rock turns into an oil-wet condition. Theoretically, strong water-wet reservoir rock is the optimal condition for oil production: water occupies the small pores and adheres to the rock surface, whereas oil flows through the large pores and is produced easier. However, this condition is scarcely found in carbonatis reservoir, which normally yield very low recovery factor. Also, reported that the application of enhanced oil recovery (EOR) in carbonatic reservoirs requires many considerations and accurate preliminary studies to minimize possible risks that could turn EOR operations into a failure as cited by Bortolotti, V., et. al., (2010).

Graue, A., et. al., (1998) reported that oil composition, surface rock mineralogy, history of the fluids exposed to the rock surface, pore roughness, water saturation (S_w), and water composition are all critical parameters affecting wettability (W) alteration. One reason that makes very difficult to increase the recovery factor (RF) of carbonatic reservoirs is rock wettability, especially when it is in the range from moderate to strong oil-wet.

The wettability affects most of the petrophysical properties of reservoirs rocks including capillary pressure, relative permeability, waterflood behavior, electrical properties, and enhanced oil recovery.

Most reservoir rocks are water-wet since they were originally formed in marine or lacustrine sedimentary environments. During hydrocarbons migration, reservoir rocks can be reversed to oil-wet conditions because of electrical charges of the grains that attract the oppositely charged components contained in the migrating hydrocarbon phase. Carbonatic reservoir rocks normally show a moderate to strong oil-wet condition. Also found that alkaline substances and some surfactants have the capability to reverse the oil-wet reservoirs into a more favorable condition for improved oil recovery (EOR).

Buckley, J.S., (1998) showed that the wetting preference is influenced by oil components, the brine chemistry and the mineral surface, as well as the system temperature, pressure and saturation history. Also, they believe that oil composition is very important to changing the wettability of a naturally water-wet surface, because any wettability-altering components and the crude oil cannot attach to the solid surface and alter the wetting tendency toward oil-wet.

Austad, T., et. al., (2008) concluded that surfaces active components in seawater, such as magnesium (Mg^{2+}), Calcium (Ca^{2+}) and Sulphate (SO_4^{2-}) play an important role in both wettability modification and chalk rock mechanics. In that sense, injection of seawater into chalk must be regarded as a tertiary oil recovery technique. Figure 2.8 shows the schematically the model of the suggested mechanism for the wettability alteration induced by seawater. Proposed mechanism when main Ca^{2+} and SO_4^{2-} are active at lower temperature (left), and mechanism when Mg^{2+} and SO_4^{2-} are active at higher temperature (right).

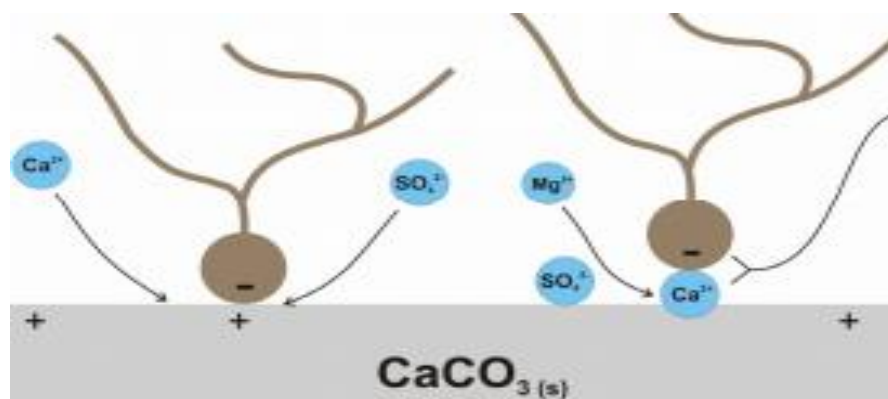


Figure 2.8: Shows the schematic model of the suggested mechanism for the wettability alteration induced by seawater. by Austad, T.; et. al., (2008).

Jadhunandan, P., and Morrow, N.R., (1995) and Tang, G.Q., and Morrow, N.R., (1997) have been observed that the composition of the water can have a significant impact on the wettability and oil recovery.

2.6.3 Wetting in Pores

The three conditions of wetting show the similar saturations of water and oil. Figure 2.9 represents the schematic model. The water-wet case, oil remains in the center of the pores. The reverse condition holds if all surfaces are oil-wet. In the mixed-wet case, oil has displaced water from some of the surfaces, but still in the centre of water-wet pores.

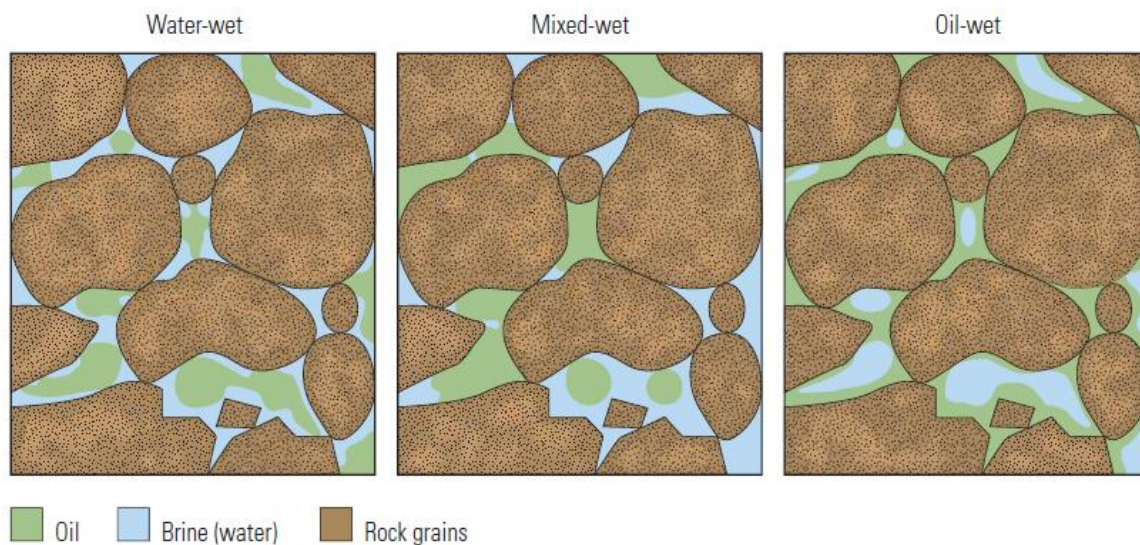


Figure 2.9: Shows the wetting in pores model, water-wet case (left), mixed-wet case (center) and oil-wet case by Wael, A.; et. al., (2007).

2.6.4 Water - Wet and Oil - Wet Texture Model

Figure 2.10 shows the textural model of water and oil on the wet state. The water-wet pores filled with oil and water (*top left*) are represented in the textural model as randomly distributed oblate spheroids placed in a background of a complex reflective index (CRI) model medium (*top right*). In an oil-wet rock, oil is in contact with the grains and surrounds conductive brine (*bottom left*). Brine is predominantly situated in the center of the pores. In the textural model, this is represented as spheroids with oil surrounding water (*bottom right*).

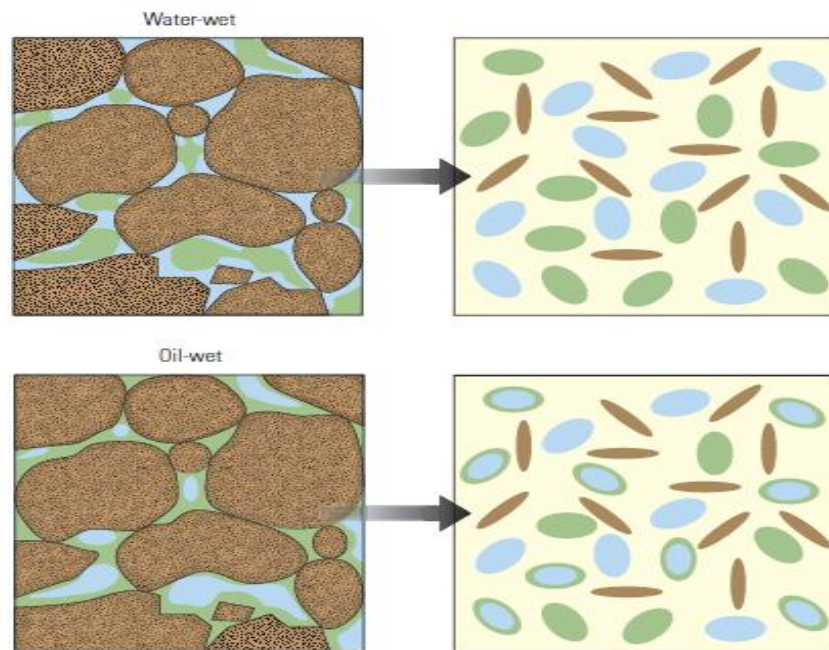


Figure 2.10: Represents the textural model of water and oil on the wet state, by Wael, A.; et. al., (2007).

2.7 Wettability Classification

2.7.1 Oil - Wet Core

Pertaining to the preference of a solid to be in contact with an oil phase rather than water or gas phase. Oil-wet rocks preferentially imbibe oil. Generally, polar compounds or asphaltenes deposited from the crude oil onto mineral surfaces cause the oil-wet condition. Compounds in oil-base mud also can cause a previously water-wet rock to become partially or totally oil-wet.

2.7.2 Water-Wet Core

It is related to the adhesion of a liquid to the surface of a solid. In water-wet conditions, a thin film of water coats the surface of the formation matrix, a conditions that is desirable for efficient oil transport. Treatments that change the wettability of the formation from water-wet to oil-wet can significantly impair productivity. Describe the preference of a solid to be in contact with a water phase rather than an oil or gas phase. Water-wet rocks preferentially imbibe water. Generally, sandstones and carbonates are water-wet before contact with crude oil, but may be altered by components of the crude oil to become oil-wet. Certain minerals, as well as different crystallographic faces of the same mineral, may be variably prone to being oil-wet or water-wet.

2.8 Amott Index and USBM Tests

The Amott test is one of the most widely used empirical wettability measurements reservoir cores in petroleum engineering.

The method combines two spontaneous imbibition measurements and two forced displacement measurements. This test defines two different indices: the Amott water index (I_w) and the Amott oil index (I_o).

The two Amott indices are often combined to give the Amott–Harvey Index (AI). So, the it is a number between zero (0) and one (1) that describes wettability of a rock in drainage processes. The Amott index is defined as the displacement by water ratio minus the displacement by oil ratio, as showed in the equation 2.18.

$$AI = I_w - I_o \quad (2.18)$$

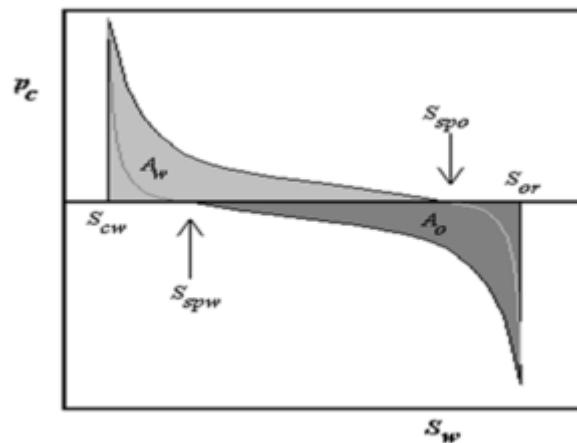


Figure 2.11: Gives the Amott–Harvey Index (AI) and USBM number calculation [III].

These two indices are obtained from special core analysis (SCAL) experiment (porous plate or centrifuge) by plotting the capillary pressure (P_c) curve as a function of the water saturation (S_w) as shown on figure 2.11. The amott water index (I_w) and amott oil indx (I_o) are calculated by equations 2.19 and 2.20, respectively.

$$I_w = \frac{S_{spw} - S_{cw}}{1 - S_{cw} - S_{or}} \quad (2.19)$$

Where S_{spw} is the water saturation for a zero capillary pressure (P_c) during the imbibition process, S_{cw} is the irreducible water saturation and S_{or} is the residual oil saturation after imbibition.

$$I_o = \frac{S_{spo} - S_{or}}{1 - S_{cw} - S_{or}} \quad (2.20)$$

Where S_{spo} is the oil saturation for a zero capillary pressure (P_c) during the secondary drainage process, S_{cw} is the irreducible water saturation and S_{or} is the residual non-wetting phase saturation after imbibitions.

As referred by Okasha, T.M., et. al., (2003) a rock wettability is defined as:

- (a) a water-wet when the AI is between 0.3 and 1;
- (b) weakly water-wet when the AI is among 0 and 0.3;
- (c) weakly oil-wet when the AI is between - 0.3 and 0; and

(d) oil-wet when the AI is among -1 and - 0.3.

If a sample spontaneously imbibes only brine, it is considered water-wet. Similarly, if it imbibes only oil, it is considered oil-wet. If the sample imbibes neither, it is described as neutrally wet.

2.9 Drainage and Imbibition Processes

2.9.1 Drainage Process

It is defined as the process of forcing a non-wetting phase into a porous rock. Oil migrates into most reservoirs as the non-wetting phase, so initial charging of the reservoir is a drainage process.

2.9.2 Imbibition Process

It is known as the process of absorbing a wetting phase into a porous rock. Imbibition is important in a water drive reservoir because it can advance or hinder water movement, affecting areal sweep. Spontaneous imbibition refers to the process of absorption with no pressure driving the phase into the rock. It is possible for same rock to imbibe both water and oil, with water imbibing at low in situ water saturation, displacing excess oil from the surface of the rock grains, and oil imbibing at low in-situ oil saturation (S_o), displacing excess water. An imbibition test is a comparison of the imbibition potential of water and oil into a rock. The wettability of the rock is determined by which phase imbibes more.

The process of water sucking into a porous medium by the action of capillary forces is referred to spontaneous imbibition. The role of imbibition has been recognized in numerous types of recovery processes including alternate injection of water and gas, also steam injection through the imbibition of condensed water and waterflooding of heterogeneous reservoirs as reported by Tabary et. al., (2009). The imbibition capillary pressure (P_c) characteristics are key to describing recovery characteristics in fractured carbonates as they control fracture matrix interactions as well as oil drainage from oil wet pore surfaces. Any wettability modification to a more water-wet system will therefore be identifiable in the imbibition capillary pressure data, as cited Webb, K.J., et. al., (2005).

Zhang, P., and Austad, T., (2005) reveals that spontaneous imbibition of water into the carbonate matrix blocks is believed to be the key mechanism for improved oil recovery (IOR) by waterflooding process. Also, for carbonates, imbibition tests changing sulfate concentrations have a significant influence on the oil recovery rate.

The recovery of oil by spontaneous imbibition of brine into the reservoir rock is very important for fractured reservoirs where reserves are mainly held in very low permeability matrix blocks. Under water injection or aquifer drive, subsequent recovery of oil from the rock matrix, if any, is mainly dependent on spontaneous imbibition of water, and is a relatively slow process, as documented by Tabary et. al., (2009).

2.10 Waterflooding Process as an Enhanced Oil Recovery (EOR) Method

The life of an oil well goes through three distinct phases where various techniques are employed to maintain crude oil production at maximum levels. Therefore the primary importance of these techniques is to force oil into the wellhead where it can be pumped to the surface. The three stages of oil field development are: primary recovery - when oil is forced out by pressure generated from gas present in the oil.

Secondary recovery - when the reservoir is subjected to water flooding or gas injection to maintain a pressure that continues to move oil to the surface, and tertiary recovery, also known as enhanced oil recovery (EOR) introduces fluids that reduce viscosity and improve flow.

These fluids could consist of gases that are miscible with oil typically Carbon Dioxide (CO₂), cyclic steam injection (huff'n puff), fire flooding (air or oxygen injection), polymer solutions, gels, surfactant-polymer formulations, alkaline-surfactant-polymer formulations, microorganism formulations, hot water injection, steam assisted gravity drainage (SAGD), foams, low salinity waterflooding (LSW). Enhanced oil recovery (EOR) is a generic term for using sophisticated techniques for increase the amount of crude oil that can be extracted from an oil field. Using enhanced oil recovery 30-60% or more of the reservoir's original oil can be extracted compared with 20-40% using primary and secondary recovery techniques.

The primary recovery typically provides access to only a small fraction of a reservoir total oil capacity. Secondary recovery techniques can increase productivity to a third or more. Tertiary recovery EOR enables producers to extract up to over half of a reservoir's original oil content, depending on the reservoir and the EOR process applied.

The production can be increased after a decline in pressure from the water drive or pressure maintenance, by a techniques called water flooding, which is the injection of water through injection well to push crude oil toward producing wells.

Water is pumped into the productive layer at injection pressure through bore holes in a volume equal to (or greater than) the volume of oil extracted. The formation energy in the deposit is kept at the optimum level. The original lifetime of the well is prolonged, which greatly reduces the amount of drilling operations and consequently reduces the cost of oil. But in some cases, natural gas often produced simultaneous with the oil is re-injected to maintain reservoir pressure, thus driving oil into the wellbore as documented by Al-Anazi, B.D., (2007).

The waterflooding is widely used to improve oil recovery (IOR) from oil reservoirs but, except to avoid formation damage, is largely designed without regard to the composition of the brine injected. It is showed that changes in injection brine composition can improve recovery, thereby, introducing the idea that the composition of the brine could be varied to optimize waterflood recovery, according to Jerauld, G.R., et. al., (2006). While Webb, K.J., et. al., (2005) shown from their studies that waterflooding recovery is dependent on the composition of injected brine in clastic reservoirs.

During waterflooding different forces control fluid flow in porous media including viscous, capillary and gravity forces. The capillary forces are the most dominant at the waterflooding, and create residual oil saturation (S_{or}).

As cited by Yousef, A.A.; Al-Saleh, S., and Al-Jawfi, M., (2011) to mobilize the residual oil, a significant reduction in capillary forces is required. Capillary forces are a function of fluid-fluid, and fluid-rock interactions. Interfacial tension (γ) measurements between oil and water, and rock wettability measurements (i.e. contact angle) are typically used to measure these interactions.

Figure 2.12 shows the schematic diagram of water flooding apparatus where [1] is air supply, [2] reduction valves, [3] core holder, [4] core sample, [5] manometers, [6] sleeve pressure and [7] liquid-volume measurement.

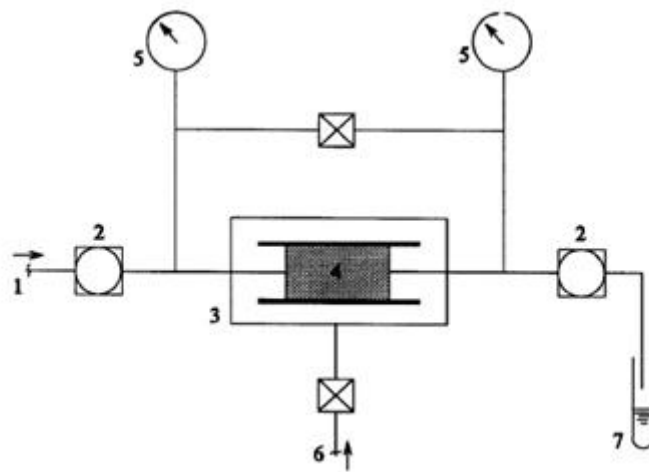


Figure 2.12 Represents the schematic diagram of water flooding, by Ole, T., and Abtahi, M., (2003).

2.10.1 Waterflooding Process Advantages

Waterflooding process by all measures has been the most successful method recovering oil from reservoir. The key ground for success of waterflooding includes:

- (a) water is an efficient injectant for displacing oil of light to medium gravity;
- (b) water is relatively easy to inject into oil-bearing formations;
- (c) water it is available and most importantly inexpensive; and
- (d) waterflooding involves much lower capital investment and operating costs, leading to favorable economics compared to others EOR methods.

It follows that there may be cases where attention to injection water composition could lead to increased oil recovery (OR) and a likely increase in the economic profitability of a waterflood. The method represents higher profitability due to substantially lower capital requirement.

As referred by Webb, K.J., et.al., (2004) many laboratory coreflood studies have shown increased oil recovery is achieved by waterflooding using low salinity water, compared with injection of seawater or high salinity produced water. The reasons for this improved oil recovery are thought to be due to effective wettability changes and/or controlled removal of clay constituents.

Chapter Three: Laboratory Experiment

3.1 Introduction

As was discussed in the chapter two gave a literature background to the carbonates characteristics, the concepts and characteristics of dynamic properties of the reservoir rock that affect the oil production and ultimate oil recovery using imbibition and waterflooding process. This chapter will describe and explain the procedures and methodology carried out in the laboratory experiment, for enhanced oil recovery (EOR) by imbibition and waterflooding mode. Thus, both imbibition and waterflooding process is mechanisms key for oil recovery of original oil in place.

Work done during the laboratory experiment will be described in terms of procedures and methodology applied used for the core plug analysis experiment. Measured and calculated were the relevant parameters, such as: effective porosity by (helium gas and saturating liquid), air permeability and absolute permeability, dynamic viscosity, density and pH. Also computed were pore volumes, initial water saturation, residual oil saturation, including recovery factor (RF) of original oil in place. Figures showing material and apparatus used for each experiment, tables of data and results are also presented.

3.2 Definitions and Characteristics of Core Plugs, Routine and Special Core Analysis

3.2.1 Core Plugs

Many literatures revealed that a core plugs or samples are taken from a conventional core for analysis. Core plugs are typically 1 to 1 ½ inch or 2.54 to 3.81 cm in diameter and 1 to 2 inch or 2.54 to 5.08 cm long. Core plugs are ordinarily cut perpendicular to the axis of the core or parallel to the axis, called horizontal and vertical plugs, respectively, when cut from a vertical wellbore. Therefore the core plugs it is used for core analysis which is performed through routine core analysis (RCAL) and special core analysis (SCAL) methods.

3.2.2 Routine Core Analysis

The set of measurements normally performed on core plugs or whole core. These generally include porosity, grain density, horizontal permeability, fluid saturation and a lithologic description. The RCAL often includes a core gamma log and measurement of vertical permeability. Measurements are made at room temperature and at either atmospheric confining pressure, formation confining pressure, or both. The RCAL is distinct from SCAL.

3.2.3 Special Core Analysis

The laboratory study of a sample of a geologic formation usually reservoir rock taken place during or after drilling of a well. Economic and efficient oil and gas production is highly dependent on understanding key properties of reservoir rock, such as porosity (ϕ), permeability (K), and wettability (W).

Geoscientists have developed a variety of approaches, including log and core analysis techniques, to measure these properties. Core analysis is especially important in shale reservoirs because of the vertical and lateral heterogeneity of the rocks. Core analysis can include evaluation of rock properties and anisotropy; organic matter content, maturity, and type; fluid content; fluid sensitivity; and geomechanical properties. This information can be used to calibrate log and seismic measurements and to help in well and completion design, well placement, and other aspects of reservoir production.

3.3 Description of Laboratory Experiment

The laboratory investigation had as its objective, to evaluate the effect of brine concentration (BC) in the flow properties for enhanced oil recovery (EOR) by spontaneous imbibitions and waterflooding process.

In evaluating the effect of brine concentration (BC) we used completely water-wet and weakly water-wet corefloods phases. First of all, two cores were cleaned with methanol at 65 °C afterwards with toluene at 110 °C and after that dried at 60 °C within oven. After that were measured and determinate porosity and the air permeability of the core plugs. Also we measured the dry weights for saturation determination. Six core plugs were used including six brines with different concentration or salt solution as well as different composition on 1000 ml of distilled water.

After that, the core samples were saturated with brine having different concentrations and chemical compositions under vacuum. I also, used n-decane oil which was filtered before being used to avoid problems during waterflooding mode. Both, spontaneous imbibitions and waterflooding process were performed at room temperature conditions and using 2 ml/min of flow rate.

3.3.1 Equipments of the Experiment

The equipments presented below were used on the experiment investigation. The principle, procedures and methodology for each equipment were described in each experiment.

Equipments of the Experiment

- Cores Holders
- Hassel Cell
- Soxhlet apparatus
- Vacuum Eksikator
- Pump KNAUER “Advanced Scientific Instrument”
- Oven “Termarks”
- Filter

Analytical Equipments

- Analytical Weight
- Air Permeability
- Helium Porosimeter
- Pycnometer
- Capillary Viscosimeter
- pH Meter Lab

3.4 Methodology of the Experiment

3.4.1 Materials

The material used in this experiment includes six core floods with different dimensions of length and diameters, six brines with different concentrations and chemical composition, including n-decane oil type.

3.4.2 Core Properties

A total of six carbonate core plugs were used, where four were drilled and cut off in the NTNU laboratory. The chalk piece comes from Ekofisk outcrop and the other two cores come from the Iranian outcrop. The cores were then prepared in different dimensions of which lengths were around 4.02 to 7.00 cm and diameters vary between 3.70 to 3.86 cm. The porosity measured were around 30.93 to 45.33% and permeability, about 0.799 to 5.31 mD. The core properties are presented on table 3.1.

<i>Table 3.1: Presents the cores properties including the dry and wet weights</i>								
Core Name	Diameter D (cm)	Length L (cm)	Porosity ϕ (%)	Air Permeability K (mD)	Weight Dry W_d (g)	Weight Wet W_w (g)	Weight Brine ΔW (g)	Target Study
LS	3.77	4.47	45.26	4.32	72.51	96.31	23.80	Chemical effect
MS	3.70	4.17	45.33	4.43	63.91	85.02	21.11	Chemical effect
HS	3.78	4.36	44.99	4.11	70.81	93.89	23.08	Chemical effect
AS	3.77	7.00	44.94	5.31	112.97	150.97	38.01	Chemical effect
BS	3.83	5.18	30.93	3.41	110.48	128.23	17.75	Chemical effect
CS	3.86	4.02	36.20	0.80	99.89	109.78	9.89	Chemical effect
Average	3.79	4.87	41.27	3.73	88.26	110.27	22.27	

3.4.3 Cleaning and Core Preparation

For the total six core (carbonates) samples, two needed to be cleaned before used. Also cleaned were the two samples from Iranian outcrop because before were used and what the core had is unknown.

The chalk samples were cleaned with Methanol at 98.5% of purity by submerging the cores for about 7 hours using Soxhlet extraction apparatus at around 65 °C. After that it was removed and the methanol replaced by Toluene. The cores were next cleaned with Toluene at 98% of purity at about 110 °C in the same apparatus. It was subjected to 6 hours to clean with toluene and after at least 16 hours, the cores were observed to be clean. The core were then taken-out and placed in the oven for 3 days at 60 °C so as to remove the humidity and dry out.

After the two cores had being dried, the six cores were labeled as low salinity (LS), moderate salinity (MS), high salinity (HS), A salinity (AS), B salinity (BS) and C salinity (CS) as shown in figure 3.1. In the (left) shows the chalk cores before being cleaned and in the (right) the core after being cleaned and named. Figure 3.2 Shows the apparatus used for clean them.

The dry weight (W_d) and wet weight (W_w) including the mass values were measured using Analytical weight as shown on the figure 3.3. The weights values are also presented on table 3.1.

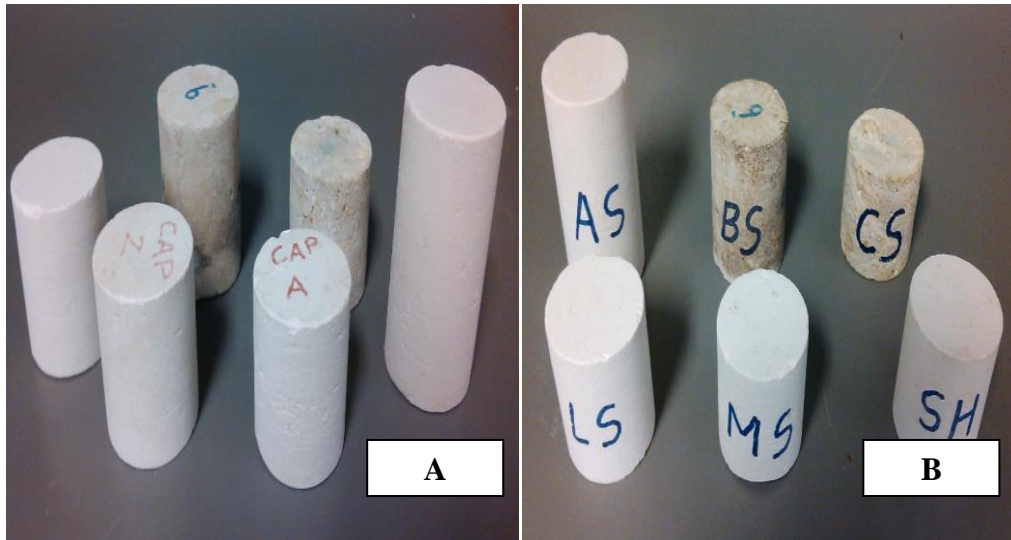


Figure 3.1: Shows the 6 cores used in the experiment before being cleaned (A) and after being cleaned (B).

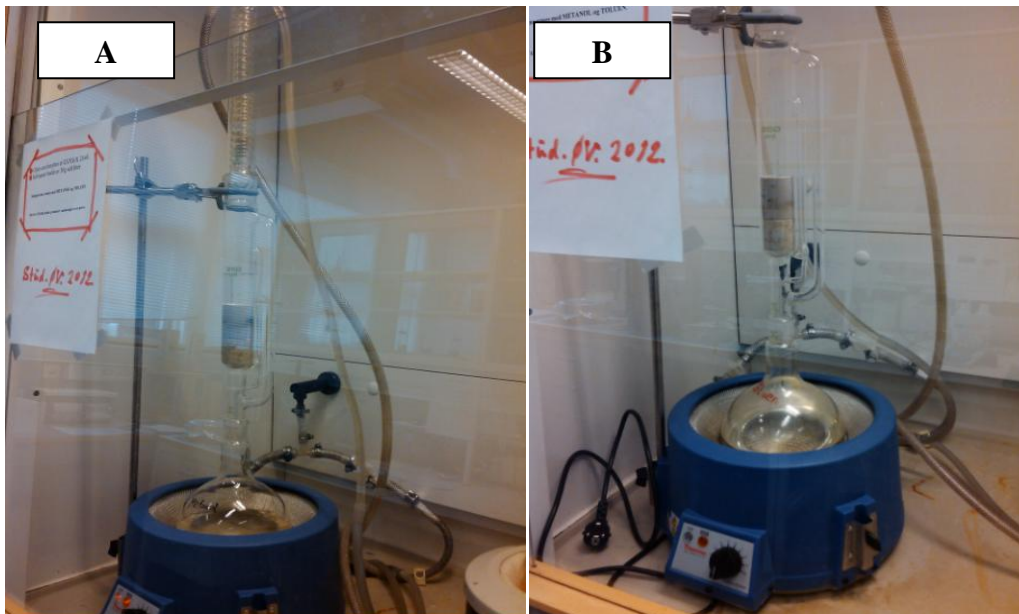


Figure 3.2: Shows the two cores samples inside of the Soxhlet extraction apparatus used to clean them with Methanol at 65 °C on 6 hours (A) and with toluene at 110 °C on 12 hours (B).



Figure 3.3: Gives the analytical weight used for dry and wet weights the cores and brines mass weight.

3.5 Brine and Oils Properties, and Brine Concentration

3.5.1 Brine Properties

The six brines concentration used have different chemical composition and were brine named: low salinity concentration (LSC), moderate salinity concentration (MSC), high salinity concentration (HSC), A salinity concentration Ekofisk (ASCE) reference case, B salinity concentration (BSC) and C salinity concentration (CSC). The viscosity (μ) and density (ρ) of brine at room temperature conditions are presented in table 3.2.

Table 3.2: Gives the properties of brines concentration

Type of Brine Name	Mass Brine m (g)	Quantity V (cm ³)	Density ρ (g/cm ³)	Viscosity μ (cPs)	Total Dissolved Solid TDS (g/l)
LSC	38.641	1000	1.021	1.014	18.91
MSC	38.652	1000	1.019	1.019	14.77
HSC	38.657	1000	1.021	1.017	12.70
ASCE	79.037	1000	1.048	1.065	25.61
BSC	35.084	1000	1.022	0.997	15.39
CSC	59.047	1000	1.030	1.066	18.91
Total	289.12	6000	6.161	6.178	106.29
Average	48.19	1000	1.03	1.029	17.72

3.5.2 Oil Properties

The n-Decane oil was used and the density and viscosity were measured. In all cases the oil was filtered before being used. The oil properties are presented on table 3.3.

Table 3.3: Presents the n-Decane oil properties		
Oil Sample	Density at 22.7 °C	Viscosity at 22.7 °C
Units	ρ (g/cm ³)	μ (cPs)
N-decane	0,718	0,879

3.5.3 Brines Composition

The six brines used were designed LSC, MSC, HSC, ASCE reference case of all brines studied, BSC and CSC. Then the amount of Sodium Chloride, Magnesium Chloride and Calcium Chloride including other chemical products the chemical composition was determined and adjusted for each brine sample. The chemical compositions of brine concentration studied are presented on table 3.4.

Table 3.4: Gives the chemical composition of different brines including the Ekofisk reference case						
Component i	LSC	MSC	HSC	ASCE	BSC	CSC
units	g/l	g/l	g/l	g/l	g/l	g/l
KCl	0.39	0.39	0.39	0.00	0.00	1.17
NaCl	9.87	10.35	10.59	15.74	10.35	9.87
CaCl ₂ *2H ₂ O	0.52	0.52	0.52	9.27	2,08	0.00
MgCl ₂ *6H ₂ O	1.08	1.08	1.08	0.60	0.00	3.63
Na ₂ SO ₄	6.93	2.31	0.00	0.00	0.62	2.65
NaHCO ₃	0.12	0.12	0.12	0.00	2.34	1.59
TDS (g/l)	18.91	14.77	12.70	25.61	15.39	18.91

On the brine LSC the the concentration of sodium Sulphate is 3 times higher rather than in the brine MSC. The concentration of Sodium Chloride is lower compared with the concentration in the brines assigned MSC and HSC. The brine assigned MSC has a medium value of concentration of Sodium Chloride compared with the concentration in the brines labelled LSC and HSC. The Sodium Sulphate is 100% compared with the concentration in the reference case.

The brine named HSC is without Sodium Sulphate. The concentration of Sodium Chloride is high compared with the concentration in the brines LSC and MSC. The brine labelled ASCE is the reference case obtained in the Ekofisk outcrop field.

For the brine assigned BSC, the concentration of Calcium Chloride and Sodium Bicarbonate are higher compared with all brines concentrations prepared. The concentration of Potassium Chloride and Magnesium Chloride are zero. In the brine called CSC the concentration of Potassium Chloride is 3 times higher than concentration of the brine HSC and Magnesium Chloride is higher compared with all brines prepared. The concentration of Calcium Chloride is zero. Sodium Bicarbonate is approximately mid value of all concentration prepared.

3.5.4 pH Determination

The pH was measured using a pH meter Lab at 21.8 °C where before starts the measurement the pH meter was calibrate to pH=4.0 with buffer solution. Therefore, each brine solution was directly introduced into the a production tube or through a pH meter and into tube. The results of measurement are presented on table 3.5.

Table 3.5: Shows the results of pH of brine measured at 21.8 °C

Brine	pH
LSC	6.76
MSC	7.74
HSC	7.75
ASCE	6.12
BSC	7.09
CSC	8.06
Average	7.25

3.6 Brine and Oil Preparation

3.6.1 Brine Preparation

The 6 brine solutions with different concentration and composition were prepared by adding a different amounts of Sodium Chloride (NaCl) at 99.5% of purity, Calcium Chloride (CaCl₂ 2H₂O) at 99% of purity, Magnesium Chloride (MgCl₂ 6H₂O) at 100.2% of purity, Sodium Bicarbonate (NaHCO₃) at 99% of purity, Potassium Chloride (KCl) at 100% of purity and Sodium Sulphate (Na₂SO₄) at 99.7% of purity to the distilled water. The brine type and the core sample were saturated according to the order presented in table 3.6.

Table 3.6: Gives the weights and total dissolved solid of brine concentration used for each solution

Core Name	Brine Name	Weight Dry W _d (g)	Weight Saturated W _w (g)	Weight Brine W _b (g)	Total Dissolved Solid TDS (g/l)
LS	LSC	72.51	96.31	23.80	18.91
MS	MSC	63.91	85.02	21.11	14.77
HS	HSC	70.81	93.89	23.08	12.70
AS	ASCE	112.96	150.97	38.01	25.61
BS	BSC	110.48	128.23	17.75	15.39
CS	CSC	99.89	109.78	9.89	18.91
	Total	530.56	664.2	133.58	106.29
	Average	88.43	110.7	22.26	17.72

3.6.2 Oil Preparation

As referred previously in the point 3.5.2 and table 3.3 on this chapter, the n- Decane oil was used for flooding. Before used, it was filtrated using a 5 μm filter paper, to remove solids and contaminants to reduce experimental difficulties during core flooding experiment. Also their density (ρ) and viscosity (μ) were measured at room temperature conditions (22.7 $^{\circ}\text{C}$).

3.8 Brine and Oil Density Determination

The density (ρ) of brine solution and oil were measured using Pycnometer method at room temperature conditions about 22.7 $^{\circ}\text{C}$ which consisted on measurements of comparison of weights of a Pycnometer without the solution brine and oil and the Pycnometer with solution brine and oil respectively. Then, the results of brine density are presented on table 3.2 and appendix A, table A - 1 for brines and table 3.3 and appendix A, table A - 2 for oil.

3.9 Brine and Oil Viscosity Determination

The viscosity (μ) of oil and brine were determinate by the capillary viscosimeter apparatus at room temperature conditions about 23.7 $^{\circ}\text{C}$. Then, the procedure applies kinematic viscosity (ϑ) determination which is suitable for Newtonian liquids. Usage surface tension of 20 to 30 mN/min and acceleration of the fall of 9.8105 m/s^2 and the constant K_1 and K_2 are referred to the timing marks during the visual survey of the meniscus passage. The kinematic viscosity in mm^2/s of liquid can be computed using the instrument constant as given by equations 3.1 and 3.2.

$$\vartheta = K_1 t_1 \quad (3.1)$$

$$\vartheta = K_2 t_2 \quad (3.2)$$

Where t_1 and t_2 are the flow times in seconds. Then the dynamic viscosity (μ) can be computed by the equation 3.3 where ϑ_{av} and ρ_{av} are average kinematic viscosity and average density of the liquid respectively.

$$\mu = \rho_{\text{av}} \vartheta_{\text{av}} \quad (3.3)$$

The results computed were already presented on the point 3.5.1 in the table 3.2. Figure 3.4 shows the capillary viscosimeter for measurements used, and brine solution and n-Decane oil dynamic viscosity determination.



Figure 3.4: Shows the Viscosimeter apparatus.

3.10 Measurement Methods and Data Analysis

Next are presented methods used for measurements and determination of different parameters during the experiments.

3.10.1 Porosity Determination Method

The porosity was measured through Helium (He) gas porosimeter method using porosimeter apparatus as shown in figure 3.5. The principle of gas expansion follows Boyle's law. The method involves introducing the core sample into the core holder in vertical direction and injecting the Helium gas to the core.

From the equipment, the values of volume of the matrix without the core (V_1), in cm^3 and the value of volume of the matrix with the core (V_2), in cm^3 were read. The measurements were performed at room temperature conditions, and the back pressure sleeve (BPS) was kept until 10 bars in the Helium (He) gas cylinder. The estimated volume of grain and non connected pores (V_g), in cm^3 were calculated using equation 3.4.

$$V_g = V_1 - V_2 \quad (3.4)$$

The pore volume of the core (V_p) in cm^3 was computed from equation 3.5, as shown below.

$$V_p = V_b - V_g \quad (3.5)$$

An estimated bulk of volume of the core (V_b), in cm^3 was obtained using equation 3.6, where L is the length of the core, in cm and D is the diameter of the core, in cm.

$$V_b = 3,14 \left(\frac{D}{2}\right)^2 L \quad (3.6)$$

The effective porosity of the core flood was calculated using equation 2.1. The results of the measurements and the effective porosity calculations are presented in table 4.1, in the chapter four.



Figure 3.5: Shows the Helium porosimeter apparatus (Core Laboratories, Inc.) used for measurements of the volumes V_1 and V_2 .

3.10.2 Air Permeability Determination Method

The air permeability was measured by constant head permeameter apparatus as shown in figure 3.6 using Hassler cell method. The method consists of pressure regulated by the upstream and downstream values on the side of Hassler cell and measurement of the air flow in the flow meter.

The experiment was carried out at room temperature conditions and the back pressure sleeve (BPS) was kept to 15 bars in the Nitrogen (N_2) cylinder. The 6 cores plugs were introduced and removed into the coreholder using vacuum. To start the measurements, the pressure gradient (ΔP) was fixed to 3 bars because the air flow at the core sample must be laminar.

Four (4) iterations of pressure inlet (P_1) and outlet (P_2) including the air flow rate (Q) were performed. Except for the core assigned CS that were carried out only three (3) iterations. During the measurements 1 bar was added to both pressures in each run.

Also the increment was fixed in 0.5 bar for both pressures for each iteration. The flow rate in liter/minute that was passing through the core into the coreholder was read in the flow meter. It was observed that the flow rate increase when both pressures increases gradually.

The core CS was considered for only 3 runs because during the measurements pressures was not showing to be increasing proportional with the air flow rate. The pressure outlet (P_2) shows lower values rather than pressure inlet (P_1). The pressure drop (ΔP) was fixed to 4.5 bar and the air permeability was calculated using Darcy's law as represented by equation 3.7 where A is the core area, in cm^2 , P_a is the absolute pressure in bar, and the μ viscosity of the fluid, in centipoise (cPs).

$$K = \frac{2Q\mu LP_a}{AP_1 - P_2} \quad (3.7)$$

The results of measurements and air permeability calculations are presented on tables (4.2, 4.3, 4.4, 4.5, 4.6 and 4.7) in the chapter four.



Figure 3.6: Shows the Constant Head Permeameter apparatus used to measuring pressures (P_1) and (P_2) and air flow rate.

3.10.3 Establishment of Initial Water Saturation

The initial water saturation (S_{wi}) of all core plugs was determined by saturating liquid method using vacuum Eksikator apparatus.

Each core sample was saturated with their brine solution and equilibrated at room temperature conditions for at least 15 days. The initial water saturation (S_{wi}) was established by injection of n-Decane oil. The brine solution and n-Decane oil were filtrated using a 4 μm filter paper, before being used to prevent clogging of the pore space.

3.10.4 Core Saturation and Effective Porosity Determination

The core sample needed to be saturated with composition brine solution for establishment of initial water saturation (S_{wi}). The initial water saturation for all cores was determined by liquid saturating method.

To determine the effective porosity by liquid saturating method each core length, diameter, dry and wet weights were measured. Next, different brine solutions were prepared using 1000 ml of distilled water (H_2O) and six chemical products previously mentioned. Before saturation all six brine solutions were filtered using 0.45 μm filter paper. Once again, the pump was left running about 20 minutes. After that, the core were introduced into the beaker under vacuum Eksikotor (container) apparatus as showed in figure 3.7 and left vacuum about 20 minutes at 100 mbar pressure to remove air, water and particles in the core and open the pores space. Afterwards the brine solution was placed into the beaker until the core to be submerged 100%. Then, in closed system the cores were left to be saturated about 1 hour at 1 bar pressure gauge and at room temperature conditions. Finally each core was removed and their wet weights were measured.

Next, the pore volume (V_p) was calculated for each core by comparison of the weights of a dry and saturated core. The results of effective porosity are presented in table 4.8 on the chapter four.



Figure 3.7: Shows the vacuum Eksikotor (extractor) apparatus used for core saturation.

3.11 Water flooding Procedure

In water flooding experiments solution brines play an important role in oil recovery (OR) processes and the “displacement fluids”.

These fluids needed to be prepared for water flooding experiments for displacement of brine to oil or from oil to brine through porous medium. In this study have been defined two different displacement fluids by drainage and imbibitions processes.

To proceed with the experiment all tubes were thoroughly cleaned with toluene before the experiment, to wash away eventual remains of oil. This was then washed with methanol to remove any remains of water. The experiment was carried out in the conditions to prevent air into the tube and followed first brine at room temperature conditions 22 °C and using a flow rate about 2 ml/min. Lower flow rate was during waterflooding used because the core used has low permeability.

3.11.1 Drainage and Imbibition Processes

The initial water saturation (S_{wi}) was established by injection of n-Decane oil. The brine solution and n-Decane oil were filtered using a 4 μm filter paper. Before imbibitions, brine and oil were filtered to prevent clogging the tube and pores space. For all cores were computed the flow rate, absolute injectivity and absolute permeability. When carried out this measurements the flow rate was fixed at values of 0.5, 1.0 2.0 and 3.0 ml/min respectively, in the pump. Each flow rate was used to find out about one average pressure drop from different values of pressure drop. The average drop pressure was found by summing different values read in the pressure meter. Therefore 3 or 4 iterated average pressure drop was used to compute 3 or 4 absolute injectivity and absolute permeability respectively. The flow rate (Q) was determined using equation 3.8 where V is the volume, in cm^3 and A is the section area of the core, in cm^2 .

$$V = \frac{Q}{A} \quad (3.8)$$

The absolute injectivity (I_{abs}) and absolute permeability (K_{abs}) were estimated using equations 3.9 and 3.10 respectively where K_{abs} was computed based on the Darcy's law using data measured in the laboratory.

$$I_{abs} = \frac{V_w}{\Delta T A \Delta P} \quad (3.9)$$

$$K_{abs} = \frac{\mu_w V_w L}{A \Delta P \Delta T} \quad (3.10)$$

Where V_w is the water production in each time, in cm^3 , ΔT is the time, in seconds, ΔP is the pressure drop, in bar, L is the length of the core, in cm and μ_w is the water viscosity, in centipoises (cps).

For establishment of absolute injectivity, firstly all cores were flooded with brine solution before flooding with n-Decane oil. The sleeve pressure (SP) was maintained from 15 to 25 bar in the core holder according to the variation of the streaming pressure into the system. The Sleeve pressure was applied to tighten the space between core and the core holder plastic, forcing injection of brine solution and avoid formation of gas at 10 bar and back pressure. The core is flooded by two different fluids: brine solution with different concentration and n-decane oil. The fluids are made ready inside of three aluminum cylinders. The pump forces the brine inside to flow out from the top using Exsol D-60 oil as driving force.

During drainage, the flooding process used the n-decane as the displacing phase and the flow rate was fixed to 2 milliliter per minute in the pump for all cores samples. The flooding process was carried out until no more production water was obtained. The pressure drop cross the sample core and the flow rate were monitored continuously during all measurements performed. The flooding apparatus is showed in figure 3.8.

The result of first drop brine and oil pressure measurements datas and calculation of I_{abs} and K_{abs} are presented on tables 4.9 and the volume of produced oil by drainage process are given in table 4.12 on the chapter four.

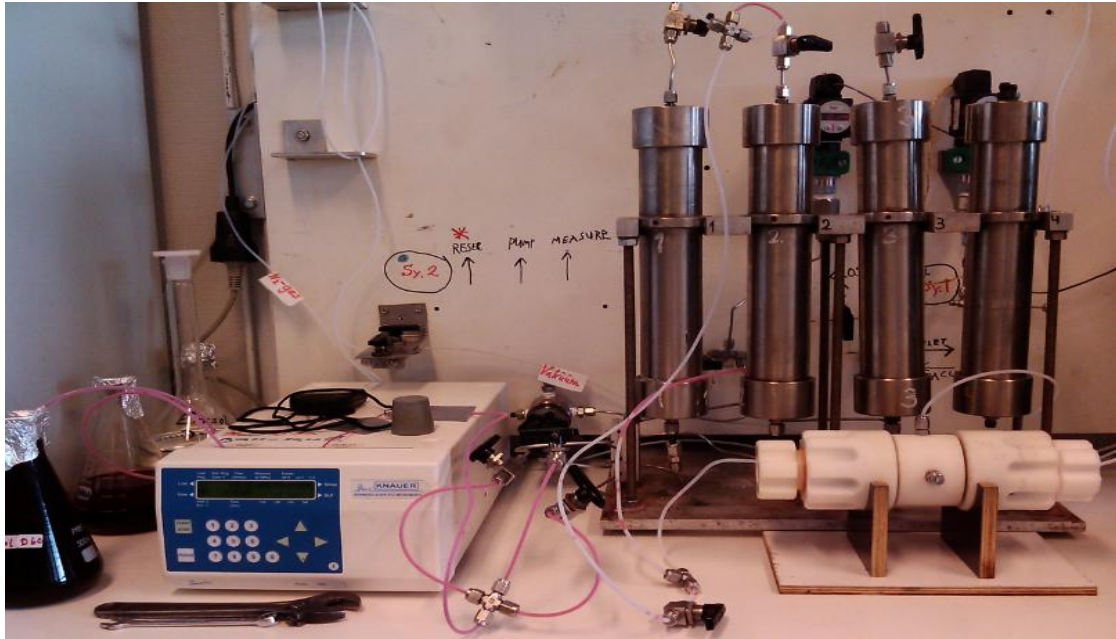


Figure 3.8: Illustrates the water flooding apparatus used for the experiments in drainage and imbibition.

3.12 Aging the Core floods

The aging process makes the conditions of the cores move like reservoir conditions. After establishment of initial water saturation (S_{wi}) by displacement with n-Decane oil, the core is ready for aging. The cores were removed from the core holder plastic and completely submerged into n-Decane oil in the plastic container. The plastic container was completely sealed and held at room temperature conditions (about 22 °C) for 15 days. During the aging process, the cores were surrounded with n-Decane oil and a amount of surface-active components from the oil will adsorb onto the outermost surface of the core. After that all cores were ready for imbibitions process.

3.13 Imbibition Processes

The brine solution brine was first injected until oil recovery was stabilized. The pressure drop that cross the core plug and oil production was monitored continuously. The injection brine was then switched when no more oil production is obtained to evaluate the effect of brine concentration on the flow properties for secondary method of oil recovery. Then for each brine solution was injected in the production fluids into the tube were measured and used for calculating the recovery factor (RF).

Next, were computed the original oil in place (OOIP) in cm^3 by drainage process, volume of oil produced (V_{op}) in cm^3 and recovery factor (RF) by imbibition process and finally the residual oil saturation (S_{or}) in percentage (%) from equations 3.11, 3.12 and 3.13 respectively, where V_p is the pore volume and S_{wi} is the initial water saturation.

$$\text{OOIP} = V_p(1 - S_{wi}) \quad (3.11)$$

$$\text{RF} = \frac{V_{op}100}{\text{OOIP}} \quad (3.12)$$

$$S_{or} = \frac{\text{OOIP} - V_{op}}{V_p} \quad (3.13)$$

The injected pore volume (inject v_p) is given by the equation 3.14 where ΔT is the cumulative time in minutes, Q is the flow rate in cm^3 per minute and V_p is the pore volume in cm^3 .

$$\text{Injected } v_p = \frac{\Delta T Q}{V_p} \quad (3.14)$$

Chapter Four: Results and Discussion

4.1 Introduction

This chapter presents the results and discussion of the measurements and calculations of different parameters referred to the previous chapters. The results are discussed according to different values obtained and are also compared with the results achieved on the A salinity concentration Ekofisk (ASCE) reference case and also other references reviewed. Here the results obtained observed based on the following contents are presented: effective porosity, air permeability and absolute permeability (by water) calculated, pore volume, initial water saturation and residual oil saturation, aging of the cores, volume of oil produced and injected pore volume, drainage, imbibition and waterflooding processes, including recovery factor of original oil in place (OOIP).

4.1.1 Effective Porosity By Helium Porosimeter

Table 4.1 shows the results of the volumes measured and effective porosity calculated.

Table 4.1: Gives the results of the volumes measured and porosities calculations

Lithology "	Core Name	Diameter D (cm)	Lenght L (cm)	Volume Without V_1 (cm ³)	Volume With V_2 (cm ³)	Grain Volume V_g (cm ³)	Bulk Volume V_b (cm ³)	Pore Volume V_p (cm ³)	Porosity ϕ (%)
Chalk	LS	3.77	4.47	61.00	33.70	27.30	49.87	22.57	45.26
Chalk	MS	3.70	4.17	61.00	36.50	24.50	44.81	20.31	45.33
Chalk	HS	3.78	4.36	61.00	34.10	26.90	48.90	22.00	44.99
Chalk	AS	3.77	7.00	90.00	47.00	43.00	78.10	35.10	44.94
Limestone	BS	3.83	5.18	68.00	26.80	41.20	59.65	18.45	30.93
Limestone	CS	3.86	4.02	61.00	31.00	30.00	47.02	17.02	36.20
Average		3.79	4.87	67.00	34.85	32.15	54.73	22.58	41.27

The measurements were performed at room temperature conditions and the back pressure sleeve (BPS) was kept until 10 bars in the Helium cylinder. The result of effective porosity obtained for all core floods varies between 30.93 to 45.33% which is very high. The average porosity achieved was about 41.27%. The result of porosity obtained on chalk showed that the matrix block presents high porosity which was around 45% because the vuggy rocks have a high volume of large pores, but permeability remains low (<10 mD). Studies carried on chalk from the Ekofisk field achieved the similar results (Høgnesen, E.J.; Strand, S., and Austad, T., 2005). For the limestone-2 the porosity value is a little bit high. The average achieved was about 33.57%. This results may be because of presence of micro porous dominate the pore network and permeability remains very low (< 1mD).

4.1.2 Air Permeability Measurement

The air permeability was measured by constant head permeameter apparatus using Hassler cell. The back pressure sleeve (BPS) was kept to 15 bars in the Nitrogen (N₂) cylinder and performed at room temperature conditions. During the measurements it was observed that the pressure varied with air flow rate. Also, was observed that when both pressure increased gradually the air flow rate also increases. The results calculated, shows that the air permeability is very low and varies between 0.80 to 5.31 mD. The average achieved in chalk was around 4.54 mD and for limestone was about 2.11 mD. The average air permeability obtained was around 3.73 mD which mean that more pressure inlet (P₁) was needed to inject into the core plug because the chalk formation it is very tight.

Tables 4.2, 4.3, 4.4, 4.5, 4.6 and 4.7 gives the results of air permeability (K) in mD and average pressure drop (1/P_m) in atm⁻¹ computed.

From cross plot between the air permeability (K), in mD and average pressure (1/P_m), in atm⁻¹ (see figure 4.1), it was showed that the air permeability of the core LS was around 4.32 mD and table 4.2 gives respective results computed.

Table 4.2: Gives the result of the pressure measurement and air permeability computed of the core LS

Core LS Units	Diameter D (cm)	Lenght L (cm)	Area A (cm ²)	Pressure In let P ₁ (atm)	Pressure Out let P ₂ (atm)	1/P _m P (atm ⁻¹)	P ₁ ² -P ₂ ² P (atm)	Flow Rate Q (l/min)	Flow Rate Q (cm ³ /s)	Air Permea K (D)	K mD
1	3.77	4.47	11.16	3.948	0.987	0.10	14.613	0.310	5.167	0.0051	5.07
2	3.77	4.47	11.16	4.442	1.481	0.08	17.535	0.350	5.833	0.0048	4.77
3	3.77	4.47	11.16	4.935	1.974	0.07	20.458	0.390	6.500	0.0046	4.56
4	3.77	4.47	11.16	5.429	2.468	0.06	23.380	0.430	7.167	0.0044	4.40
										Average	4.70

By plotting the air permeability (K), in mD against average pressure (1/P_m), in atm⁻¹ (see figure 4.1), it was observed that the air permeability of the sample MS was about 4.43 mD and table 4.3 provide the results calculated.

Table 4.3: Presents the result of the pressure measurement and air permeability calculated of the core MS

Core MS Units	Diameter D (cm)	Lenght L (cm)	Area A (cm ²)	Pressure In let P ₁ (atm)	Pressure Out let P ₂ (atm)	1/P _m P (atm ⁻¹)	P ₁ ² -P ₂ ² P (atm)	Flow Rate Q (l/min)	Flow Rate Q (cm ³ /s)	Air Permea K (D)	K mD
1	3.70	4.17	10.75	3.948	0.987	0.10	14.613	0.320	5.333	0.0051	5.07
2	3.70	4.17	10.75	4.442	1.481	0.08	17.535	0.370	6.167	0.0049	4.89
3	3.70	4.17	10.75	4.935	1.974	0.07	20.458	0.410	6.833	0.0046	4.64
4	3.70	4.17	10.75	5.429	2.468	0.06	23.380	0.450	7.500	0.0045	4.46
										Average	4.76

From cross plot between the air permeability (K), in mD versus average pressure ($1/P_m$), in atm^{-1} (see figure 4.1), it was shows that the air permeability of the core plug HS was around 4.11 mD and table 4.4 shows the results computed.

Table 4.4: Gives the result of the pressure measurement and air permeability computed of the core HS

Core HS Units	Diameter D (cm)	Lenght L (cm)	Area A (cm^2)	Pressure In let P_1 (atm)	Pressure Out let P_2 (atm)	$1/P_m$ P (atm^{-1})	$P_1^2-P_2^2$ P (atm)	Flow Rate Q (l/min)	Flow Rate Q (cm^3/s)	Air Permea K (D)	K mD
1	3.78	4.36	11.22	3.948	0.987	0.10	14.613	0.300	5.000	0.005	4.76
2	3.78	4.36	11.22	4.442	1.481	0.08	17.535	0.340	5.667	0.004	4.50
3	3.78	4.36	11.22	4.935	1.974	0.07	20.458	0.380	6.333	0.004	4.31
4	3.78	4.36	11.22	5.429	2.468	0.06	23.380	0.420	7.000	0.004	4.17
										Average	4.43

Through plotting between the air permeability (K), in mD against average pressure ($1/P_m$), in atm^{-1} (see figure 4.1), it was shows that the air permeability of the AS was about 5.31 mD and table 4.5 gives the results computed.

Table 4.5: Shows the result of the pressure measurement and air permeability computed of the core AS

Core AS Units	Diameter D (cm)	Lenght L (cm)	Area A (cm^2)	Pressure In let P_1 (atm)	Pressure Out let P_2 (atm)	$1/P_m$ P (atm^{-1})	$P_1^2-P_2^2$ P (atm)	Flow Rate Q (l/min)	Flow Rate Q (cm^3/s)	Air Permea K (D)	K mD
1	3.77	7.00	11.16	3.948	0.987	0.10	14.613	0.240	4.000	0.0061	6.15
2	3.77	7.00	11.16	4.442	1.481	0.08	17.535	0.270	4.500	0.0058	5.76
3	3.77	7.00	11.16	4.935	1.974	0.07	20.458	0.300	5.000	0.0055	5.49
4	3.77	7.00	11.16	5.429	2.468	0.06	23.380	0.340	5.667	0.0054	5.44
										Average	5.71

Cross plot among the air permeability (K), in mD versus verage pressure ($1/P_m$), in atm^{-1} (figure 4.1), it was shows that the air permeability of the sample BS was about 3.41 mD and table 4.6 provide the results achieved.

Table 4.6: Presents the result of the pressure measurement and air permeability calculated of the core BS

Core BS Units	Diameter D (cm)	Lenght L (cm)	Area A (cm^2)	Pressure In let P_1 (atm)	Pressure Out let P_2 (atm)	$1/P_m$ P (atm^{-1})	$P_1^2-P_2^2$ P (atm)	Flow Rate Q (l/min)	Flow Rate Q (cm^3/s)	Air Permea K (D)	K mD
1	3.83	5.18	11.52	3.948	0.987	0.10	14.613	0.210	3.500	0.004	3.86
2	3.83	5.18	11.52	4.442	1.481	0.08	17.535	0.240	4.000	0.004	3.67
3	3.83	5.18	11.52	4.935	1.974	0.07	20.458	0.270	4.500	0.004	3.54
4	3.83	5.18	11.52	5.429	2.468	0.06	23.380	0.300	5.000	0.003	3.44
										Average	3.63

Through the cross plot among the air permeability (K), in mD and average pressure ($1/P_m$), in atm^{-1} (see figure 4.1) it was observed that the permeability of the core CS was around 0.80 mD which is very lower compared with others core plugs. Table 4.7 gives the results computed.

Core CS Units	Diameter D (cm)	Lenght L (cm)	Area A (cm ²)	Pressure In let P ₁ (atm)	Pressure Out let P ₂ (atm)	1/P _m P (atm ⁻¹)	P ₁ ² -P ₂ ² P (atm)	Flow Rate Q (l/min)	Flow Rate Q (cm ³ /s)	Air Permea K (D)	K mD
1	3.86	4.02	11.70	5.429	0.987	0.08	28.49	0.11	1.83	0.0008	0.79
2	3.86	4.02	11.70	5.626	1.184	0.07	30.25	0.12	2.00	0.0008	0.81
3	3.86	4.02	11.70	6.021	1.579	0.07	33.75	0.13	2.17	0.0008	0.79
										Average	0.80

Figure 4.1 gives the plot between air permeability and pressure.

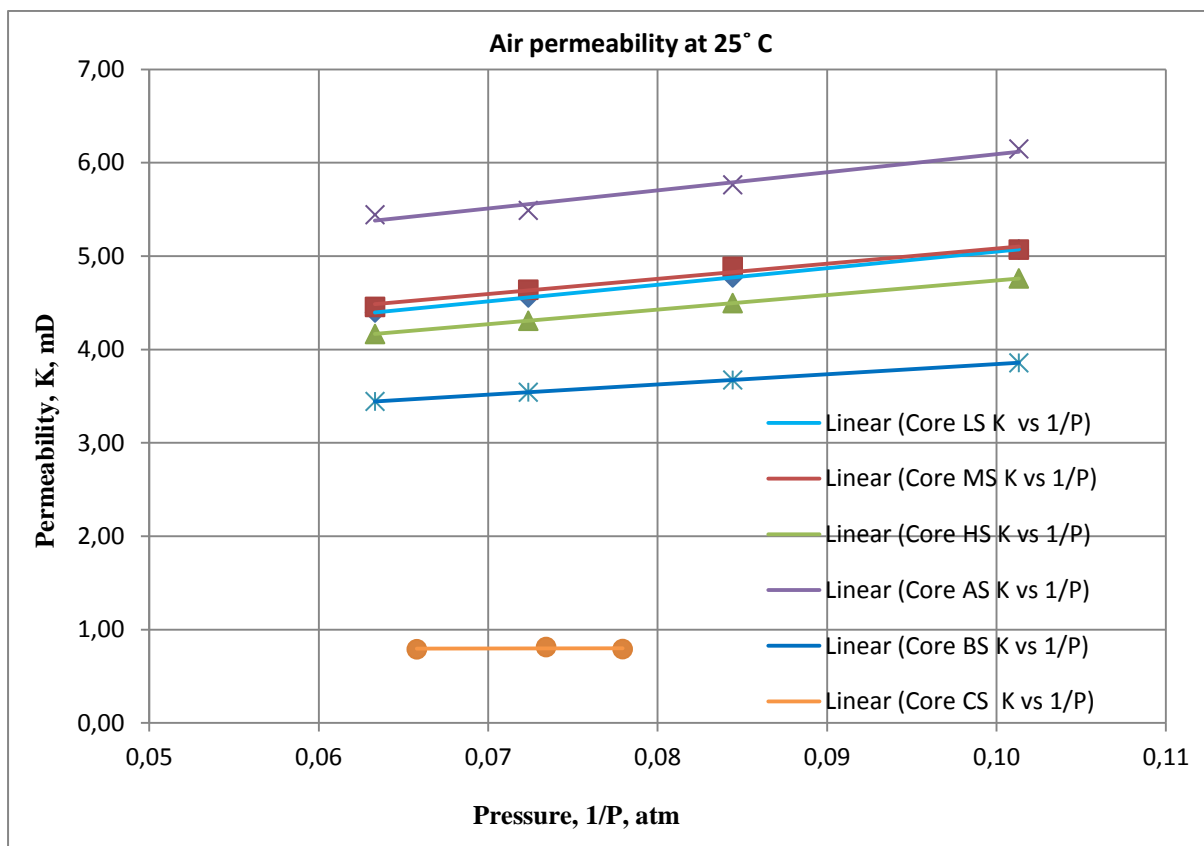


Figure 4.1: Represents the cross plot between air permeability and pressure.

The plot result of core CS show horizontal line. However, from the comparison with other core the results achieved shows that there a relationship between permeability and pressure. Also shows that there is a direct correlation between data calculated.

Comparative study performed by (Høgnesen, E.J.; Strand, S., and Austad, T., 2005) was achieved similar results and demonstrated that the permeability it is between (1 -10 mD) and others studies showed that is less than (< 1 mD) which is very lower. On this study we can consider that the results of air permeability are satisfactory because the values shows the same behavior with those achieved in the Ekofisk study.

Below the figure 4.2 gives the relationship between permeability and porosity. From the results achieved we can conclude also that the link between porosity and permeability is not straightforward in carbonates and is difficult to predict. Studies shows that there is common microporosity in carbonates, high proportion on non-effective porosity and high contrasts in permeability is also common in carbonate. Therefore, the primary hydrocarbon recovery is commonly lower. The variation in permeability is controlled by variation in porosity and pore size distribution. From observation, the values are favourable to higher porosity and lower permeability. From comparative studies carried out on carbonate evaluation of permeability and porosity it can be considered that may be the rock type could be packstone/wackstone. Therefore from the figure 4.2 shows that the correlation between values is about of 80 %, which is very satisfactory.

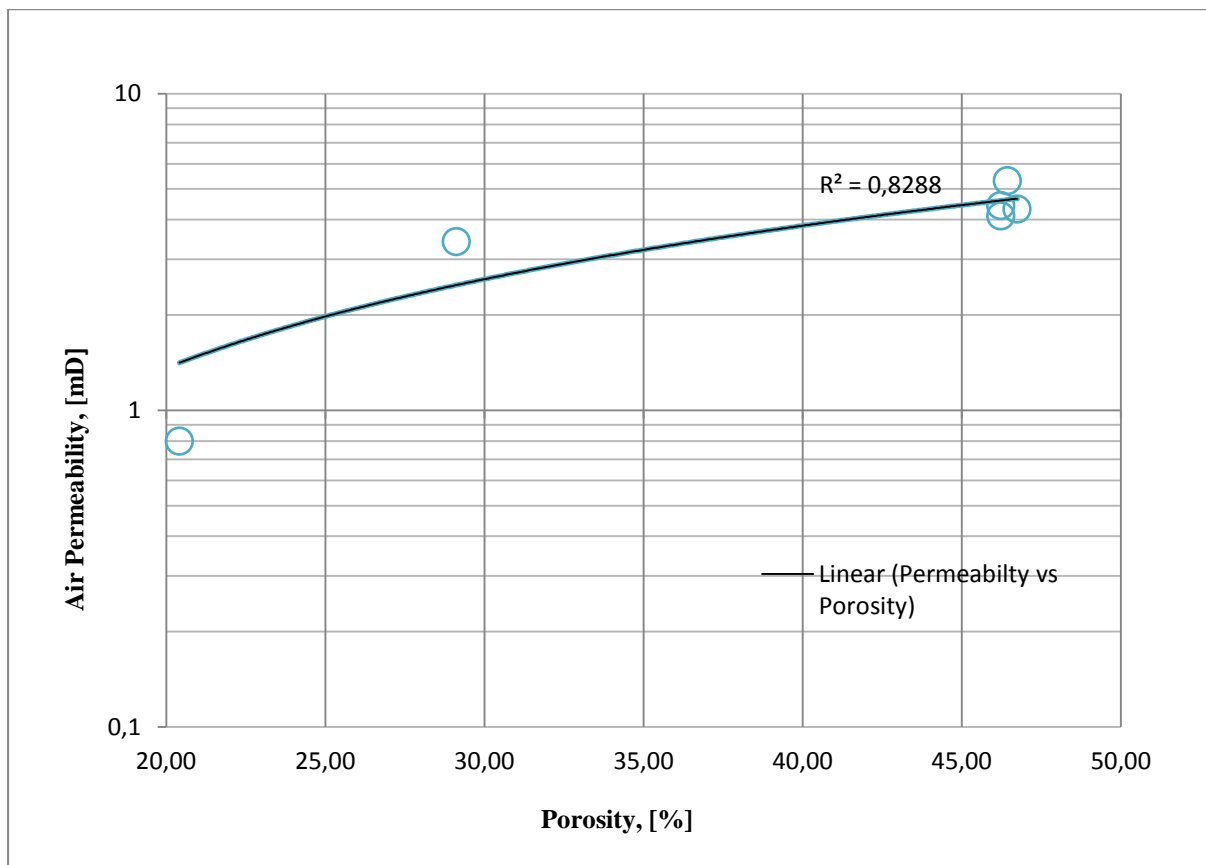


Figure4.2: Shows the relationship between permeability and porosity.

4.2 Porosity Determination by Saturating Liquid Method

The effective porosity determination by liquid saturating method consists on measurements of the length, diameter, dry and wet weights. To proceed was measured 1000 cm³ of distilled water (H₂O) to prepare six brine solutions with different concentrations for each core plug using six (6) chemical products. The pore volume (V_p) was calculated for each core by comparison of the weights between a dry and saturated core.

The calculated results of effective porosity are given on table 4.8 below and appendix C, table C-1 gives the comparison between Helium gas and saturating liquid methods.

Table 4.8: Presents the results of the effective porosity calculated using liquid saturation method

Lithology "	Core Name	Diameter D (cm)	Lenght L (cm)	Weight Dry W_d (g)	Weight Wet W_w (g)	Weigth Brine W_b (g)	Density Weight ρ_w (g/cm ³)	Pore Volume V_p (cm ³)	Bulk Volume V_b (cm ³)	Porosity ϕ (%)
Chalk	LS	3.77	4.47	72.51	96.31	23.80	1.021	23.31	49.87	46.74
Chalk	MS	3.70	4.17	63.91	85.02	21.11	1.019	20.72	44.81	46.23
Chalk	HS	3.78	4.36	70.81	93.89	23.08	1.021	22.61	48.90	46.23
Chalk	AS	3.77	7.00	112.96	150.97	38.01	1.048	36.27	78.10	46.44
Limestone	BS	3.83	5.18	110.48	128.23	17.75	1.022	17.37	5.65	29.12
Limestone	CS	3.86	4.02	99,89	109.78	9.89	1.030	9.60	47.02	20.42
Average		3.79	4.87	88.43	110.70	22.27	1.027	54.73	54,73	39.20

The results of effective porosity obtained shows that the formation have higher porosity which ranks between 20.42 and 46.74% with on average of about 39.20%. The results of the four (4) Ekofisk chalk computed by helium porosity method gives quite similiar results with the study performed in the Ekofisk field. The Iranian core plugs also shows a little bit higher results about 29%, except one that is showing lower value about 20% (core CS). The difference between values achieved may be as a result of differents methods used for the measurements or related to the presence of small particle and fine migrate present in the brine that can block the core pores and also low permeability.

4.3 Density

The densities were measured at 22.7 °C, the results achieved ranked between 1.019 to 1.048 g/cm³ for brines and about 0.718 g/cm³ for n-Decane. The A salinity concentration Ekofisk (ASCE) reference case and C salinity concentration (CSC) showed higher values of density. Therefore, the higher density values can be related to the mass of total dissolved solid (TDS) added in the brine solution. In comparison with normal brine that is around 1.02 g/cm³ at room temperature condition the study results shows that the values are accurate. Table 3.2 and appendix A, table A – 1 and table A -2 gives the results of density calculated of brine and oil, respectively.

4.4 Viscosity

The viscosity of brine and oil were measured at 23.7 °C and the results computed are presented on table 3.2 and appendix A, table A – 3. The results calculated of brine vary between 0.997 to 1.066 cps and of n-Decane around 0.879 cps. The brines ASCE and CSC achieved higher values and the lower was registered on the brine BSC which is around 0.997 cps. Figure 4.3 represent the relationship between the density and viscosity. The cross plot between densities against viscosity shows only one point crossed by the straight-line.

However, the correlation between data indicates a direct relationship and also shows that the correlation achieved is around 70%, which can be considered acceptable.

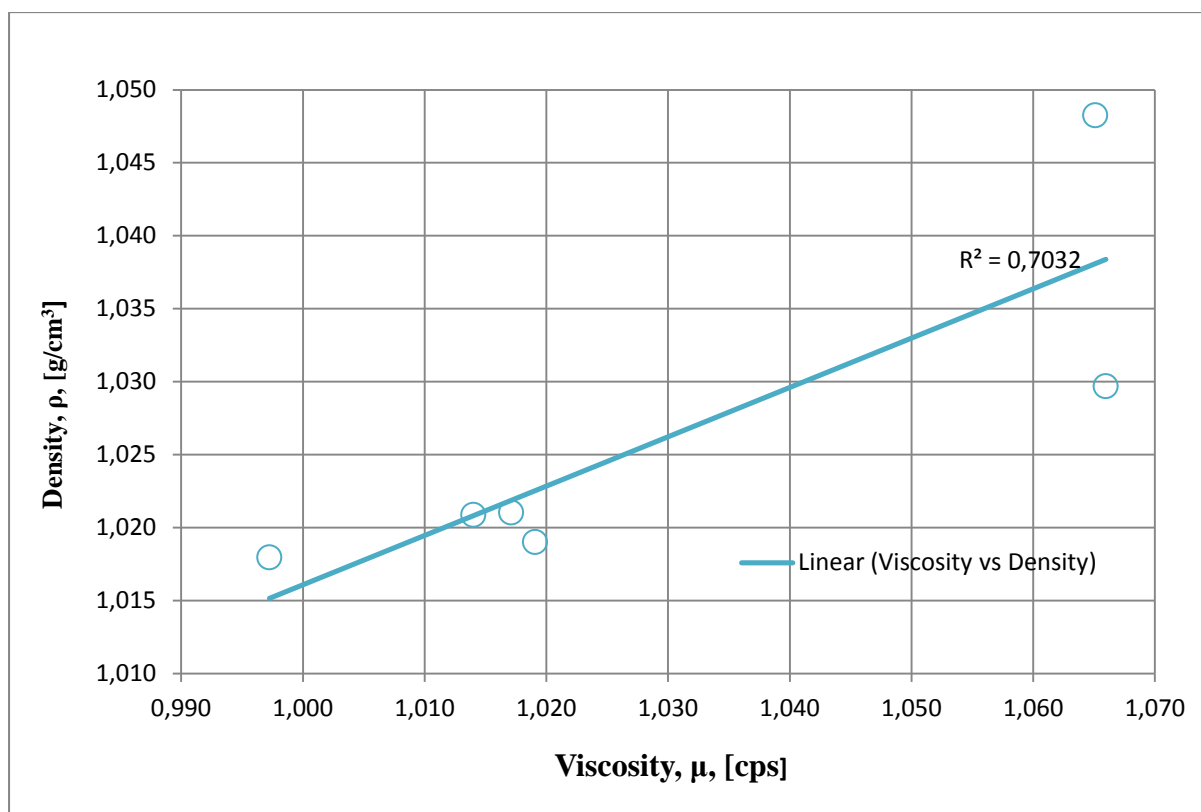


Figure 4.3: Represents the relationship among density and viscosity.

4.5 Brine Solution Behavior

Result showed that the five (5) brine solutions were well mixed, except the solution of brine B salinity concentration (BSC) that was observed to form a precipitate when was added (Calcium Chloride). The precipitate formed was caused may be because of mass of Carbonate (NaHCO_3) added, which is about 0.234%, very higher compared with others brines. Table 3.2 and appendix B, tables B-1 to B – 6 shows the brine compositions used for each brine solution prepared.

4.6 pH

The pH of brines solutions was measured at 21.8 °C. Five (5) brines behave like buffer solution (base), except the brine ASCE reference case that behaves like an acid. The ASCE reference case registered lowest pH which is around 6.12. The low pH may be because of amount of mass of Sodium Chloride added in the solution (1.574 % of NaCl) that is very high. The high pH was found in brine CSC that is about 8.07. Therefore, the highest value of pH achieved can be related of mass of chemical product added in the solution. Were added five (5) chemical products out of six (6) used (Calcium Chloride). The average pH achieved is about 7.25 which is close to neutral.

From comparative studies carried out by (Mohan, K., et. al., 2011) have shows that a rise in pH during low salinity laboratory experiment can be obtained the high oil recovery. Then from this study we can consider that high oil recovery can be achieved using high pH. Table 3.5 gives the results computed.

4.7 Drainage - Water flooding Process

In the water flooding process, the drainage process is crucial stage to create the initial condition for the way that a core plugs behavior as reservoir. Table 4.9 gives the results of lower and higher pressures measured, absolute injectivity and absolute permeability calculated.

Table 4.9: Shows the results of pressures measured, absolute injectivity and absolute permeability calculated

Core Name	I_{abs}			K_{abs}		Waterflooding (Drainage)		
	Lower Pressure Drop P (bar)	Higher Pressure Drop (breakthrough brine) P (bar)	Absolute Injectivity I_{abs}	Absolute Permeability K_{abs} (mD)	Sleeve Pressure P (bar)	Higher Pressure Drop (Breakthrough oil) P (bar)	Lower Pressure Drop P (bar)	Sleeve Pressure P (bar)
LS	1.54	3.78	0.00001	0.0250	15.00	9.72	8.67	15.00
MS	0.18	3.28	0.00010	0.7566	15.00	9.23	8.40	15.00
HS	0.19	1.65	0.00010	0.2271	15.00	10.09	8.62	20.00
AS	0.68	1.60	0.00010	0.3358	15.00	10.48	8.99	20.00
BS	1.06	4.96	0.00010	1.4720	15.00	10.76	9.52	20.00
CS	1.78	5.05	0.00002	0.4230	15.00	16.82	16.82	25.00
Average	0.91	3.39	0.00007	0.5399	15.00	11.18	10.17	19.17

To compute the absolute injectivity (I_{abs}) and absolute permeability (K_{abs}) in mD, were measured the pressures for each three (3) flow rates fixed on (0.5, 1.0 and 2.0) ml/sec and sleeve pressure at 15 bar. During the measurements was observed that for all core plugs the pressure drop was increasing continuously until the breakthrough of brine (see table 4.9 second and third columns). The lower pressure drop recorded ranked from 0.68 bar of the core AS and the higher is about 1.78 bar registered on the CS core. The minimum breakthrough pressure drop of brine was about 1.60 bar recorded on the ASCE core and the maximum breakthrough pressure drop of brine was about 5.05 bar recorded on the CS core from Iran. The values of the I_{abs} for all cores shows approximately the same which are very lower about (0.0001 to 0.00002) almost tending to zero. The lower values achieved may be are related to the pressure drop after breakthrough during water flooding process. For the K_{abs} the lower value computed was about 0.0250 mD in the LS core and the highest value was registered in the core BS which is about 1.4720 mD.

The values of absolute permeability achieved by drainage process are lower compared with the results achieved by air permeability method. By using different methods of measurement can be also achieved different results. However the difference between values should not be so huge. Table 4.10 and appendix C, table C-2 gives the comparison between air permeability and absolute permeability calculated.

Table: 4.10: Gives comparison between absolute permeability and air permeability computed

Lithology "	Core Name	Absolute permeability K_{abs} (mD)	Air Permeability K (mD)
Chalk	LS	0.025	4.320
Chalk	MS	0.757	4.430
Chalk	HS	0.227	4.110
Chalk	AS	0.336	5.310
Limestone	BS	1.472	3.410
Limestone	CS	0.423	0.799
	Average	0.540	3.730

On the basis of comparison of results obtained we can consider that are accurate. However is more secure to use the air permeability method instead of use the liquid method.

4.8 Establishing the Volume of oil Produced

The method of establishing the volume of the oil produced (V_{op}) was discussed in 3.11.1 and 3.13 on chapter three. The volume of water produced is assumed to be the volume of the oil produced. Table 4.9 shows the values of pressure drop monitored continuously during the water flooding using drainage process. During flooding process, it was observed that the pressure drop after breakthrough of oil was decreases for all core plugs, expect in the core CS which remained constant. The minimum and maximum breakthrough pressure drop of oil observed ranking from 8.40 bar in the LS core and 16.82 bar in the CS core. After breakthrough, the minimum pressure achieved was about 8.62 bar in the core HS and around 16.82 bar in the CS core.

For the CS core even after breakthrough the pressure remained constant. The sleeve pressure remained in 15 bar for cores LS and MS. Cores HS, AS and BS experienced increase in pressure up to 20 bar and the CS core reached 25 bar. The increase of sleeve pressure was forced because by increases of the pressure in the system almost close to 15 bar that is the limit fixed or set. The variation of the pressure drop is may be related to the variation of permeability that is considered very low. The core AS has highest permeability and the CS core has the lowest (see table 4.10). Also, it can been seen clearly by porosity (see table 4.8), the core AS has high porosity and the CS core has a low porosity. With low permeability and porosity, more pressure is needed to force the flow rate past through the core because it is very tight. Table 4.11 gives the results of the volume of oil produced (V_{op}).

Table 4.11: Gives the results of the volume of oil produced (V_{op}) calculated.		
Core Name	Initial water Saturation S_{wi} (%)	Oil Produced (Drainage) V_o (cm³)
LS	20.98	18.42
MS	29.19	14.67
HS	16.18	18.95
AS	28.50	25.93
BS	21.47	13.64
CS	14.58	8.20
Average	21.82	16.64

4.8.1 Core LS - Low Salinity Concentration (LSC)

The volume of oil produced (V_{op}) by drainage process achieved is about 18.42 cm³. This brine has the lowest percentage of Sodium Chloride compared with all brines. The brine was prepared adding the following components: 0.039% of KCl, 0.987% of NaCl, 0.052% of CaCl₂*2H₂O, 0.108% of MgCl₂*6H₂O, 0.693% of Na₂SO₄, and 0.012% of NaHCO₃. The pH measured was about 6.78 and computed high porosity. The production achieved can be related to the chemical composition and mass of total dissolved solids (TDS) of Sodium Chloride added in the solution, including high porosity. Appendix B, table B – 1 gives the composition and mass computed of the brine low salinity concentration.

4.8.2 Core MS - Moderate Salinity Concentration (MSC)

The production of oil in the MS core is around 14.67 cm³, lower compared with the production achieved in the core LS and high compared to AS core . The mass of Sodium Chloride used here is a little bit high compared with the LS core. The chemical products used in the brine were: 0.039% of KCl, 1.035% of NaCl, 0.052% of CaCl₂*2H₂O, 0.108% of MgCl₂*6H₂O, 0.231% of Na₂SO₄, and 0.012% of NaHCO₃. The high production obtained maybe related to the pH that is about 7.74, chemical product added in the solution and high porosity. Appendix B, table B – 2 provides the composition and mass estimate of the brine MSC. Figure 4.4 shows the production in tubes achieved in drainage process.



Figure 4.4: Shows the results of oil production in tube of core MS after drainage.

4.8.3 Core HS - High Salinity Concentration (HSC)

The oil production achieved in HS core is about 18.95 cm^3 . This is high compared to the first case. The percentage of Sodium Chloride used in the solution is also high compared with both previous cases (LSC and MSC). The chemical components used in the brine were: 0.039% of KCl, 1.059% of NaCl, 0.052% of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.108% of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.012% of NaHCO_3 and 0.00% of Na_2SO_4 . The presence of ions Sulphate, Calcium and Magnesium and low concentration of Sodium Chloride could be the reason for production obtained. The pH measured is about 7.75 and the porosity is very high. Appendix B, table B -3 gives the chemical composition and mass computed of brine HSC and figure 4.5 just shows the test tubes hardly illustrates the behavior of oil production.

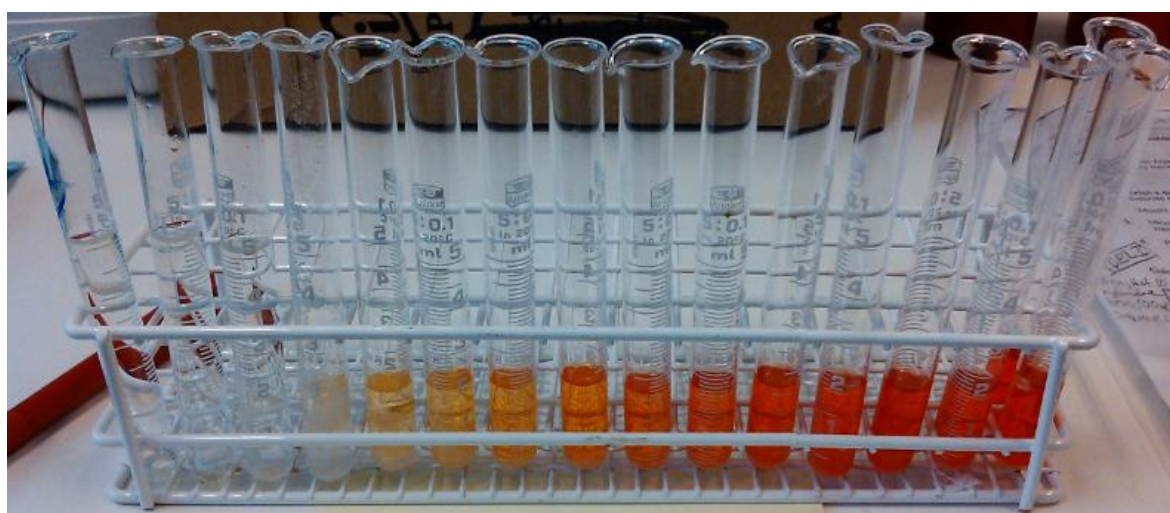


Figure 4.5: Shows the results of oil production tubes of the core HS after drainage.

4.8.4 Core AS - A Salinity Concentration Ekofisk (ASCE) Reference Case

In the AS sample 1.574% of NaCl, 0.927% of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.06% of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were added to make the brine solution. This brine had the highest content of Sodium Chloride compared with all other brines prepared. It also had the lowest pH value of about 6.12 and a high porosity. The oil production achieved was about 25.93 cm^3 . This rate of production could be related to the content of calcium and magnesium. The cations, Magnesium and Calcium can react with the minerals present in the surface of the chalk to release the oil into the pores space. Appendix B, table B – 4 provides the chemical composition and mass calculated of the brine ASCE reference case.

4.8.5 Core BS - B Salinity Concentration (BSC)

The volume of oil produced in the core BS is about 13.64 cm^3 which is the second lowest production achieved in the drainage process. The brine solution was prepared mixing: 1.035% of NaCl, 0.208% of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.062% of Na_2SO_4 and 0.234% of NaHCO_3 , and no KCl and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were added. The low production obtained may be related to the absence of Magnesium Chloride in the solution and low permeability. Appendix B, table B - 5 gives the chemical concentration and mass calculated of the brine BSC.

4.8.6 Core CS - C Salinity Concentration (CSC)

The CS core recorded the lowest production about 8.20 cm^3 of all the cores. The brine solution was made mixing: 0.117% of KCl, 0.987% of NaCl, 0.363% of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.265% of Na_2SO_4 and 0.159% of NaHCO_3 and no $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was added. The low oil production obtained may be related to the absence of Calcium Chloride in the solution and low porosity of the core. Appendix B, table B – 6 shows the chemical composition and mass computed of the brine CSC and figure 4.6 shows the test tubes results of oil production.



Figure 4.6: Shows the results oil production tubes of core CS after drainage.

4.9 Imbibition Process

As detailed in the point 3.13 of the chapter three the process of establishment of imbibition process include the methodology and oil recovery factor (RF) calculation. Table 4.12 presents the results of measurements of breakthrough pressure drop of oil and brine recorded continuously, including sleeve pressure during flooding and aging time.

Table 4.12: Gives the breakthrough pressure drop of oil and brine in the imbibitions process

Imbibition process Name	Flood Date D.M.Y	Flow Rate Q(cm ³ /min)	Pressure Drop Breakthrough of Oil ΔP (bar)	Pressure Drop Breakthrough of Brine ΔP (bar)	Final Pressure Drop ΔP (bar)	Sleeve Pressure P (bar)	Aging Time T (days)
LS	05.07.2012	2	1.12	3.12	7.02	15	15
MS	05.07.2012	2	1.79	2.70	7.78	15	15
HS	05.07.2012	2	1.64	3.48	6.79	15	15
AS	06.07.2012	2	1.46	6.62	11.32	20	15
BS	06.07.2012	2	2.05	8.68	13.21	22	15
CS	06.07.2012	2	16.82	16.83	19.94	28	15

From the table above the minimum value of breakthrough pressure drop of oil obtained was about 1.12 bar for AS core and the maximum breakthrough pressure drop was around 16.82 bar for the core CS. The minimum breakthrough pressure of brine recorded was around 3.12 bar on the core LS and the maximum was about 16.83 bar on the CS core. After breakthrough of brine for all cases the pressure drop continued rising and the lowest was about 7.02 bar obtained on the LS core and the highest was around 19.94 bar achieved in the CS core.

For the three first cases the sleeve pressure was maintained to 15 bar but for the last three cases the sleeve pressure was increased to 20, 22 and 28 bar, respectively because the pressure drop in the system continued rising gradually. The aging process for all the cores consisted in completely submerged the core in plastic recipient with n-Decane oil about 15 days at room temperature conditions. After that it was also flooded at room temperature conditions. Tables 4.13 and table 4.14 shows the final results of parameters calculated of the laboratory experiment which are following: pore volume and injected pore volume, initial water saturation and residual oil saturation, oil produced (V_{op}) in the drainage and imbibition processes, and recovery factor (RF) in % of original oil in place (OOIP).

Table 4.13: Gives results of the laboratory experiment of oil produced in the drainage and imbibitions process and recover factor (RF) in % of OOIP

Core Name	Pore Volume V _p (cm ³)	Initial water Saturation S _{wi} (%)	Residual Oil Saturation S _{or} (%)	Oil Produced (Drainage) V _o (cm ³)	Oil Produced Breakthrough V _{op} (cm ³)	Oil Produced (Vop) (Imbibition) V _{op} (cm ³)	Breakthrough Recovery Factor OOIP (%)	Final Recovery Factor OOIP (%)
LS	23.31	20.98	24.92	18.42	10.00	12.61	54.29	68.46
MS	20.72	29.19	22.49	14.67	7.50	10.01	51.12	68.23
HS	22.61	16.18	34.15	18.95	9.00	11.23	47.49	59.26
AS	36.27	28.50	27.44	25.93	10.30	15.98	39.72	61.63
BS	17.37	21.47	29.42	13.64	5.00	8.53	36.66	62.54
CS	9.60	14.58	62.60	8.20	0.00	2.19	0.00	26.71
Average	21.65	21.82	33.50	16.64	6.97	10.09	38.21	57.80

Table 4.14: Gives the results of injected pore volume(injected Vp) cm³

Core	LS	MS	HS	AS	BS	CS
Injected Vp	3.63	3.93	3.78	4.06	6.19	9.85

On the basis of the results presented in the tables above of each core sample flooded are discussed separately, an explanation how the brine concentration can affect the flow properties in carbonate rock effect of brine on oil recovery in the two (2) types chalk rock applying water flooding method as secondary to enhanced oil recovery (EOR) in the following way:

4.9.1 Core LS - Low Salinity Concentration (LSC)

The LS core was new sample, the initial water saturation was about 20.98% the residual oil saturation achieved was around 24.92% the breakthrough oil recovery factor was about 54.29% and the final oil recovery achieved is about 68.46% which is the highest. This result was expected to be higher compared with other results especially for the Ekosfisk core reference case, which is lower. According literature reviewed lowering salinity brine and increasing the pH will be favorable to higher alkalinity and consequently favorable to higher oil recovery. The concentration of Sulphate, Calcium and Magnesium in solution can be seen as the factor behind to contribute for higher recovery. The main driving mechanism for low salinity waterflooding is believed to be multi component ionic exchange made possible by the expansion of electrical double layer. However were observed during water flooding fines migrate released with fluid flowing and subsequently were captured at pore throats causing formation damage Many literatures have reported that chalks (carbonates) commonly are brittle and easily fractured. Figure 4.7 illustrates the cores LS and MS damaged after being used in imbibition process and appendix D, table D - 1 shows the summary results computed.



Figure 4.7: Shows the samples LS and MS damaged after(imbibition) water flooding process.

4.9.2 Core MS - Moderate Salinity Concentration (MSC)

In the MS core the initial water saturation obtained was about 29.19%, the residual oil saturation achieved is around 22.49% and the volume of oil produced in the drainage is about 14.67 cm³. After early breakthrough the initial oil in place produced was about 51.12% and the final oil recovery was around 68.23%. This value is quite similar to the result achieved in the LS core. From this, shows that the core registered higher oil recovery compared to the AS core reference case. The concentration of Sulphate, Calcium, Magnesium and Sodium Chloride concentration used in the solution, could probably be a factor for that recovery. When these are present in the solution they react with the minerals present in the rock and release the oil present in the void space. Appendix D, table D - 2 gives the final results estimates.

4.9.3 Core HS - High Salinity Concentration (HSC)

The initial water saturation achieved in the HS core was about 16.18%, the residual oil saturation around 34.15% and oil produced in the drainage was about 18.95 cm³. After breakthrough, the initial oil in place was about 47.49% and the final recovery factor was around 59.26%. The oil recovery achieved should be a little bit high compared to the AS core reference case. The reason for this may be because of the chemical composition present in solution and the mass used, is lower compared with the salt added in the brine ASCE. Also the absence of Sulphate could be the key factor of that recovery. However, we can consider that the recovery factor achieved is satisfactory because it is above of 50%. The rock type presents similar properties with the LS, MS and AS cores. Appendix D, table D - 3 gives the summary results computed.

4.9.4 Core AS - A Salinity Concentration Ekofisk (ASCE) Reference Case

The Ekofisk core reference case achieved 28.50% of initial water saturation, 27.44% of residual oil saturation, 25.93 cm³ volume of oil produced in the drainage process and 15.98 cm³ volume of oil produced in imbibition. The initial oil in place after breakthrough was about 39.72% and the final oil recovery was about 61.63% which is also high. The difference of oil recovered compared with the two first cases is about 7 units, which is very high. The brine solution prepared, contained only three components: Sodium, Calcium and Magnesium. The high recovery can be related to the chemical concentration of these three elements. If we compare the results achieved in the HS and AS cores we can observe that are quite similar and the reason of this it is because in the brine solution was approximately added the same amount of chemicals concentration but chemical composition completely different. The presence of Carbonate and Potassium Chloride maybe doesn't make any effect for oil recovery. Figure 4.8 shows the oil production in tubes of the AS core after imbibition process and appendix D, table D - 4 shows the final results calculated.

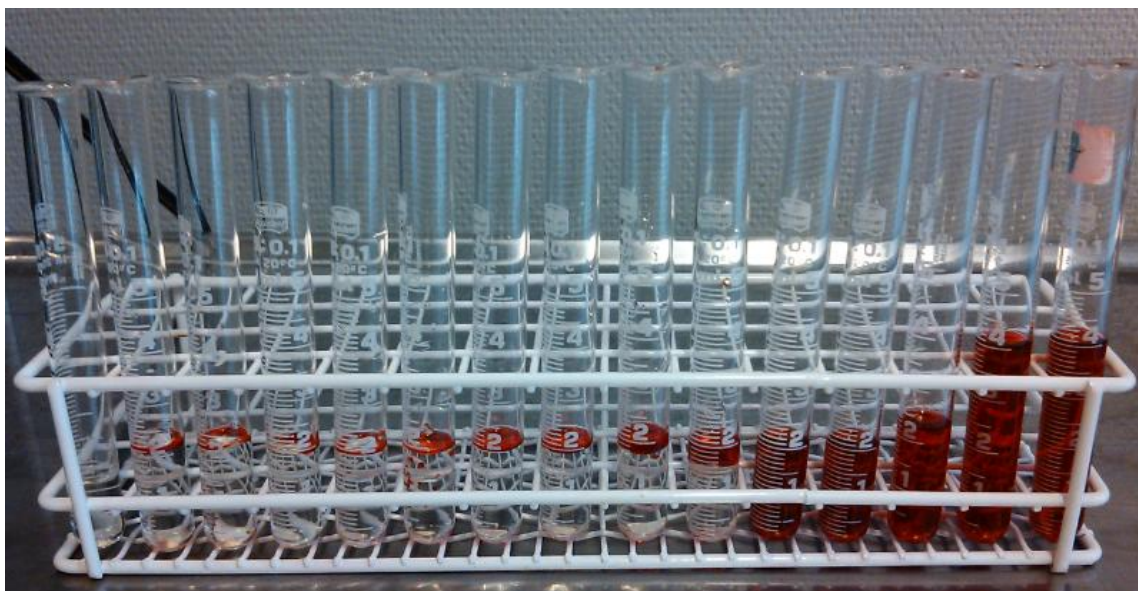


Figure 4.8: Illustrates the results oil production tube of core AS after imbibition.

4.9.5 Core BS - B Salinity Concentration (BSC)

Here the initial water saturation obtained is about 21.47%, the residual oil saturation around 29.42%, the volume of oil produced in the drainage and imbibition were about 13.64 cm³ and 8.53 cm³, respectively. The initial oil in place after breakthrough is about 36.66% and the final recovery is around 62.54%. The high recovery obtained can be justified by the manipulating of elements Sodium, Calcium and Sulphate added in the solution and the chemical composition. The presence of carbonate in greater quantity may be doesn't seen to be an important factor because of the precipitate formed in the solution. A comparison of the results achieved from BS core with LM and LS cores, shows that in the absence of either Calcium or Magnesium or an increase in either one of them can aid in achieving high oil recovery. Appendix D, table D - 5 summarizes the results calculated.

4.9.6 Core CS - C Salinity Concentration (CSC)

The CS core from Iran outcrop field has the lowest permeability and porosity. The initial water saturation was about 14.58%, the residual oil saturation was about 62.60%, the volume of oil produced in drainage about 8.20 cm^3 and in the imbibition was around 2.19 cm^3 . The breakthrough oil production was not observed and the final oil recovery was about 26.71%. This core recorded the lowest initial oil in place, it also recorded high pressure in the system and high sleeve pressure in all experiments carried out. The pH registered was about 8.09. The brine solution prepared were added all chemical used in experiment in high percentage. Except the Sodium Chloride and Calcium Chloride that were not added. The absences of the cation Ca^{2+} may be have decreased the absorption of Sulphate (SO_4^{2-}) in the chalk surface. Consequently, the reaction with the carboxylic group did not take place. As cited by Lager, A., et. al., 2006 high salinity and pH contribute to the reduction in permeability. This low recovery registered could have been influenced by rock properties (low permeability) permeability less than 1 mD. Similar result is supported by Høgnesen, E.J.; Strand, S., and Austad, T., 2005. Figure 4.9 show the results of oil produced in tube after imbibitions and appendix D, table D - 6 shows the summary results estimate.



Figure 4.9: Shows the results of oil production in tube of core CS after imbibition.

4.10 Graphical Analysis of Experimental Results

Here are discussed results graphical as shows in figure 4.10 plotting between initial oil in place (OOIP), in % against injected pore volume (injected V_p), in cm^3 , figure 4.11 gives the plotting among initial oil in place (OOIP) in % versus time (ΔT), in min and figure 4.12 shows the cross plot between pressure drop (ΔP), in bar versus injected pore volume (injected V_p), in cm^3 .

Figure 4.10: Shows the plot of Initial oil in place (OOIP) in % against injected pore volume (injected V_p), in cm^3 .

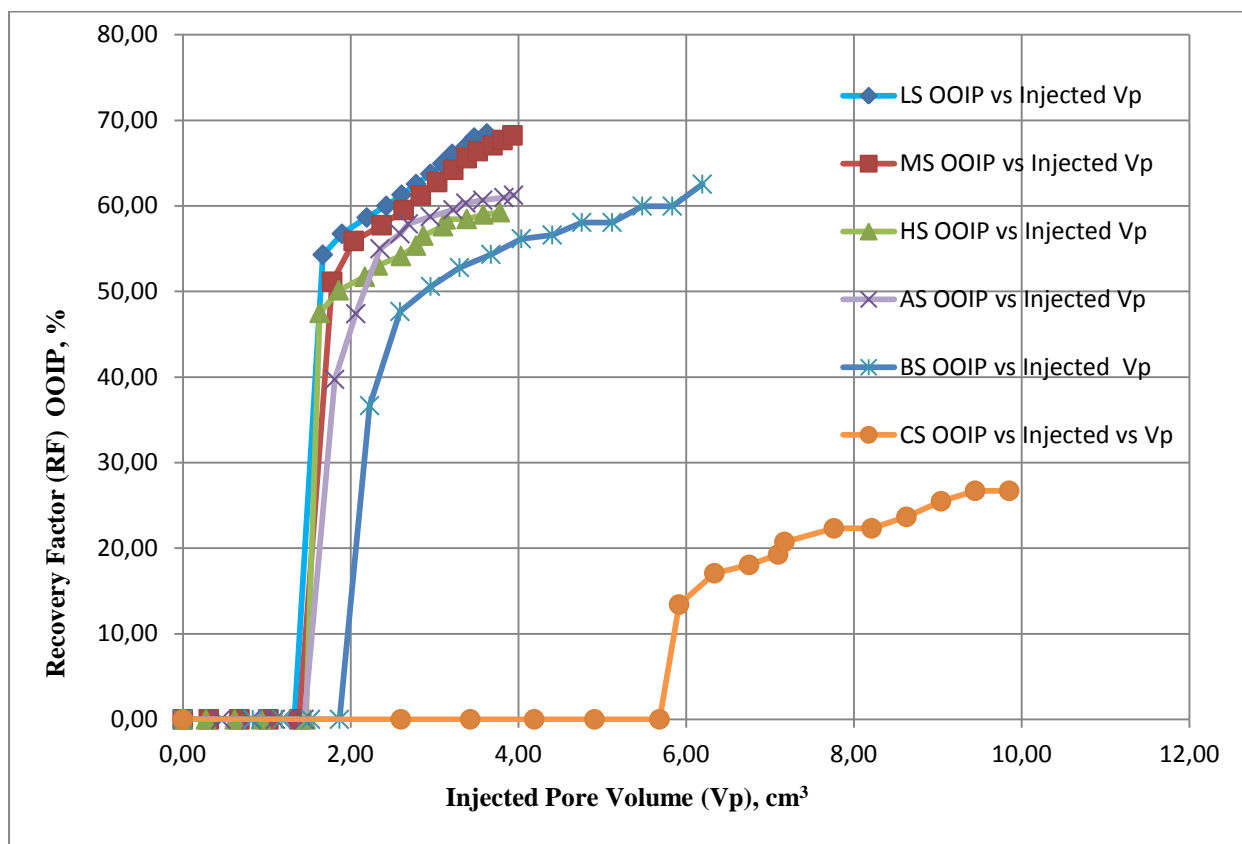


Figure 4.10: Gives the cross plot between Oil Recovery and pore volume injected (V_p injected), cm^3 .

Figure 4.10 is a plot of recovery factor (RF) of initial oil in place (OOIP) and injected pore volume (injected V_p). Starting from zero pore volume (V_p) increases until reaches about 1.2 V_p for LS, MS, HS and AS cores; about 1.87 V_p for BS core and about 5.68 V_p for CS core without any production. But the pump was forcing the brine into core. This can be observed by the horizontal lines that continue increasing in the horizontal direction until breakthrough (first oil drop). Then, suddenly the production increases until breakthrough (first water drop). After that, the production increases for all cores which mean that all lines started to increases gradually until reaches the final oil recovery factor. The lower oil recovery of breakthrough of oil was about 13.66% of the CS core and the highest was around 54.29% for the LS core.

The lowest final recovery was about 26.71% and the highest around 68.46%. By comparison with different references cited by Anderson, W., (1985) and Buckley, J.S., et. al., (1998), Akbar, M., and Vissapragada, B., (2000 & 2001), Buckley, J.S., et. al., (1998) show that oil recovery by water flooding method was about 20 to 60%. However, in this study was estimated to be among 26.71% to 68.46%. Therefore, from this study we can consider that the results achieved are satisfactory. Also similar study carried out by Austad, T.; RezaeiDoust, A., and Puntervold, T., (2010), and Jerauld, G.R., Lin, K.J., and Secombe, J.C., (2006) showed similar results.

Zhang, P., and Austad, T., (2005) reveals that imbibition of water into the carbonate matrix blocks is believed to be the key mechanism for enhanced oil recovery by water flooding process. Also, cited that for carbonates, in the imbibition process the changing in sulfate concentrations have a significant influence on the oil recovery.

The cation exchange between minerals and brine was the primary mechanism behind for improved oil recovery during low salinity brine injection. Appendix D, tables D - 1 to D - 6 gives the final results estimates.

Figure 4.11: Gives the plot of initial oil in place (OOIP) in % versus time (ΔT), in minutes.

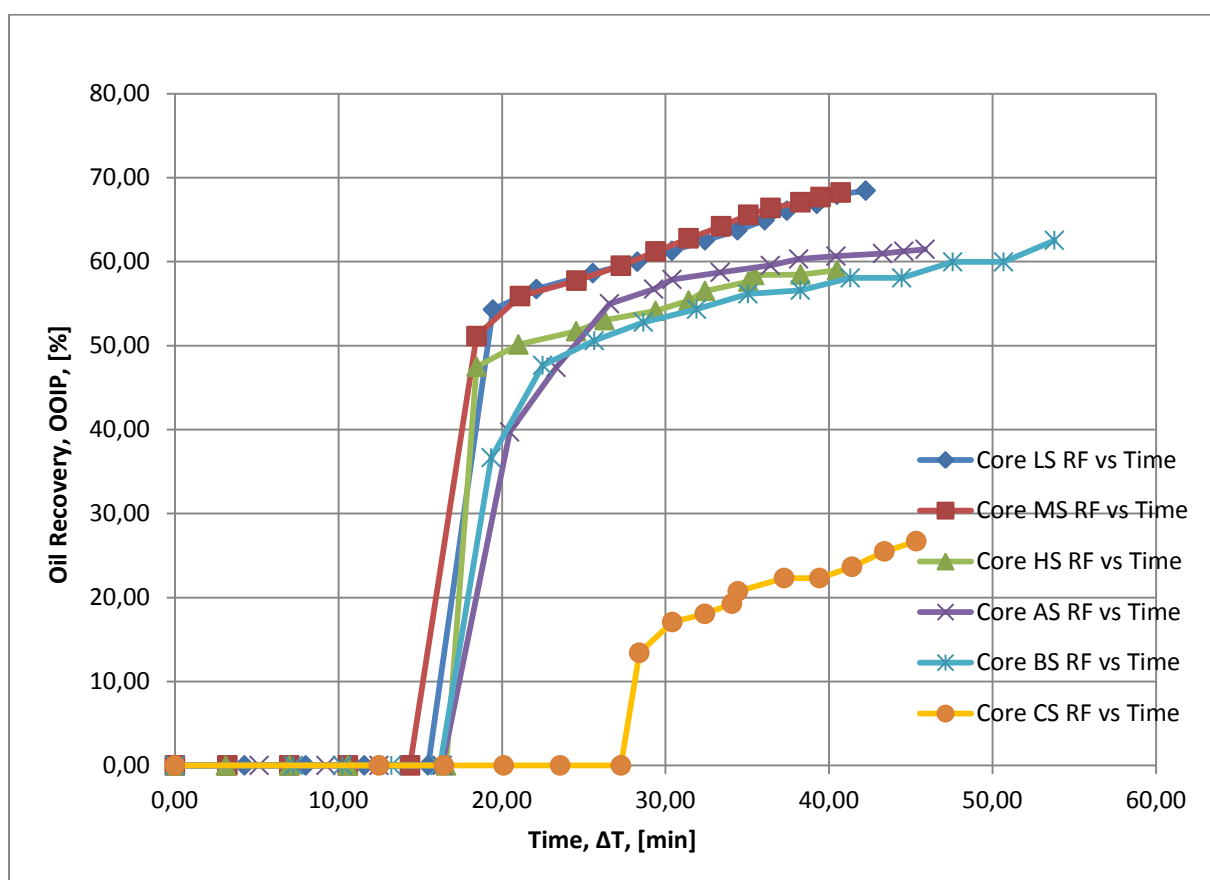


Figure 4.11: Represents the plot between recovery factor (RF) of OOIP in % versus time (min).

Figure 4.11 represents the recovery factor (RF) of initial oil in place (OOIP) in % versus time (ΔT) in min. Here was observed that when brine is injected, for all cases the OOIP increased with time. Beginning from zero time until 27.28 min for the CS core the injection continued until first oil drop was noticed. After breakthrough the lowest time achieved was about 14.38 min from the BS core and the highest time reached was around 53.79 min from the CS core. The final highest recovery was about 68.46% in LS core that was achieved in less than 1 hour, about 42.25 min very lower compared with the BS core that reaches 62.54% of oil in 53.79 min. From the graphic we can see that the four (4) Ekofisk chalks have the same behavior including the AS core reference case. However, the CS core shows lower final recovery in much time about 45.34 min. Also we can observe that the oil recovery achieved is within of range reported data.

Comparative study carried out by Graue, A.; Viksund, B.G., and Baldwin, B.A., (1998) results gives similar behavior. Appendix D, tables D - 1 to D - 6 shows the summary results computed.

Figure 4.12: Gives the cross plot between pressure drop (ΔP), in bar versus injected pore volume (injected V_p), in cm^3 .

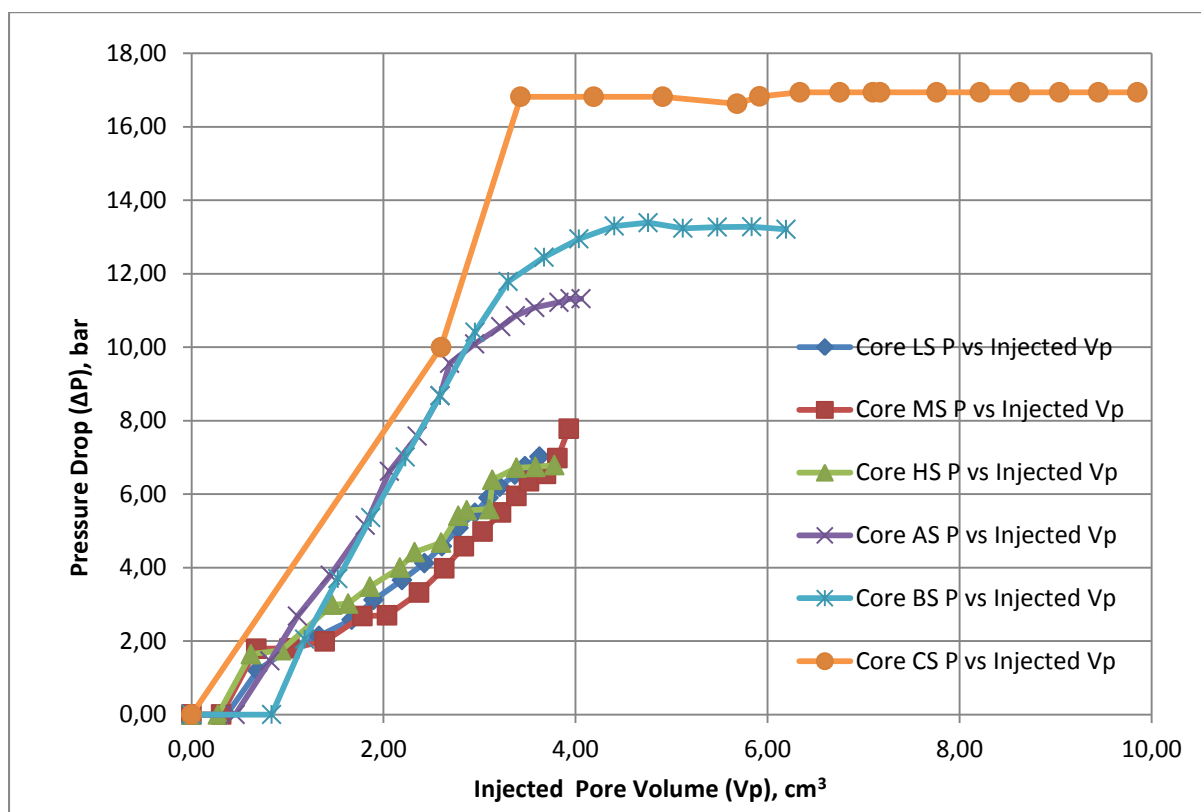


Figure 4.12: Shows the plotting between pressure drop versus pore volume injected (Injected V_p), in cm^3 .

Figure 4.12 shows the cross plot between pressure drop and injected pore volume (injected V_p). From the results, it was observed that when the brine concentration is injected, the pressure drop also increases. For the CS sample from 0 bar the pressure drop increased gradually with the rate of injection until 16.82 bar and from there, it almost remained constant until reached 9.85 V_p and 16.94 bar. The BS sample shows similar behavior to the CS core and gives the second highest pressure drop of about 13.21 bar to reach the final oil recovery when the pore volume was about 6.19 cm^3 . To reach 0.83 V_p the pressure remained constant and from 0.83 V_p increased gradually until reach about 11.79 bar where continues rising slightly and remained constant when the pressure was about 13.21 bar. The CS, BS and AS cores presents almost similar behavior. However, it is noted difference that they have different final pressure drop when compared to each. The LS, HS and MS cores also shows similar behavior, registering low pressure at about 8 bar and injected pore volume of about 4 cm^3 . Therefore, this behavior can be supported by their core properties, including brine concentration and composition that are quite similar. Appendix D, tables D - 1 to D - 6 summarizes the results calculated.

Recommendation

Uncertainties

Various hypotheses have been explained for increases in oil production associated with low salinity water injection related with increasing in pH leading to in-situ saponification and interfacial tension (γ) reduction, emulsion formation, clay migration, and wettability (W), fluid saturations, permeability distribution, residual oil saturation (S_{or}), reservoir temperature (T) and pressure (P). So, the effect of brine concentration (BC) on flow on chalk rock, depends mainly in the understanding the behavior of dynamic properties of the reservoir rock, such as: water saturation (S_w), temperature (T), pressure (P), interfacial tension (γ), viscosity (μ), density (ρ), porosity (Φ), permeability (K), capillary pressure (P_c) and oil/brine/rock system, drainage and imbibition processes, including water flooding method.

On this particular study, the concentration and composition of brine added to prepare each brine solution constitutes our great uncertainty which was key parameters for enhanced oil recovery (EOR) by imbibitions and water flooding method. However, to avoid the high number of uncertainties, four (4) new chalk from Ekofisk field were used and the other two were cleaned with ethanol and after with toluene before being used for do not influence in the results. Also were used different methods to determine porosity and permeability for comparison of results achieved and the methodology and procedures of the laboratory were carefully followed to avoid error during measurements of data.

Based on the results obtained we recommend that during the experiment the procedures and methodology must be well followed to avoid errors on the measurements.

During the experiment the manipulation and/or handling of chalk must be made carefully because the chalk is fragile and can broken easily, also is very weak and susceptible to pore collapse and migration of fines. The limestone is a little bit tight compared with chalk.

We recommend for future work to use new core plugs to decrease the number of uncertainties. However, the cleaning process is key and prevents impurities to influence the results.

More work can be done regarding effect of brine concentration and chemical composition of Sodium, Calcium and Magnesium to evaluate their effect on oil recovery and determines which parameter is key to achieve high oil recovery.

Chapter Five: Conclusion and Recommendation

Conclusion

The laboratory experiment shows results as we expected initially and the conclusions are presented in following way:

The result of effective porosity determined by saturation liquid method differs a little bit with the Helium gas. The porosity by liquid varies among 20.42 to 46.74 % and the porosity computed by Helium gas varies between 30.93 to 45.33 % and the average was about 40.24 %. Therefore, from these results we can conclude that the matrix block has high porosity of the volumes of large pores. The different values obtained of the porosity mostly are caused by the different methods applied in the measurements of the experiment.

The absolute permeability by gas was about 3.73 mD, which remained low, because of micro porous dominate the pore network. So, this result shows that the formation has low permeability. Also shows that those two types of rock had behavior completely different. The chalk is homogeneous rock while the limestone is heterogeneous rock. Therefore, we can say that the results achieved are acceptable compared with similar studies.

From the measurements was observed that the pH measured behaves as solution buffer (base) for 5 brine solutions. Except for the brine A salinity concentration Ekofisk (ASCE) reference case that behavior as a acid which the pH was about 6.12. The maximum pH achieved was about 8.06.

The highest original oil in place (OOIP) was achieved in the low salinity (LS) core which about 68.46 % and the second high oil recovery was recorded in the moderate salinity (MS) core which was about 68.23 %. Both were added the lowest concentration of Sodium Chloride in the solution which was about 0.987 % and 1.035 % respectively. The oil recovery in the A salinity Ekofisk (AS) core reference case was around 61.47 % and the Sodium Chloride added was about 1.574 % which was very high compared with the LS core.

The result obtained in the high salinity (HS) core was about 59.00 % which was satisfactory value compared with the results achieved in the LS and MS cores but not reasonable compared with the AS core, because the amount of salt added was low and consequently should gives high oil recovery. The B salinity (BS) core registered the third highest oil recovery which was about 62.54 %. The lowest recovery was recorded in the C salinity (CS) core which was about 26.71 %. The reason of the high and low recovery it is related with the brine concentration and chemical composition of Sodium, Calcium, Magnesium and Sulphate, added in the brine solution. The permeability and porosity of the cores are also key factor.

During flooding was observed that the pressure drop and time increases when the oil recovery increase and it was also show that there is an increase in oil recovery as the salinity decreases. From the experiment was proved that can be achieved the high oil recovery on carbonate using ambibition and water flooding process.

In conclusion, we can say that, the objective previously set from this study was achieved and the results calculated were considered satisfactory compared with similar studies reported.

Nomenclatures

Symbols

A	Area [cm^2]
cm	Centimeter
C_r	Rock compressibility
D	Diameter, [cm]
I_{abs}	Absolute injectivity
I_o	Amott oil index
I_w	Amott water index
K	Permeability, [md]
K_{abs}	Absolute permeability [mD] or [D]
K_{eff}	Effective permeability, [md]
K_g	Gas permeability, [md]
K_o	Oil permeability, [md]
K_r	Relative permeability, [md]
K_{rg}	Relative permeability of gas, dimensionless
K_{ro}	Relative permeability of oil, dimensionless
K_{rw}	Relative permeability of water, dimensionless
K_w	Water permeability, [md]
mD	Mili Darcy
P	Pressure [bar] or [atm]
Q	Flow rate [cm^3/sec] or [ml/min]
Q	Volumetric flow rate, [cm^3/s]
S_o	Oil saturation, fraction
S_{om}	Moveable oil saturation, fraction
S_{or}	Residual oil saturation after water flooding, fraction
S_w	Water saturation, fraction
S_{wi}	Initial water saturation, fraction
S_{wir}	Irreducible water saturation, fraction
S_{wr}	Residual water saturation, fraction
T	Temperature, [$^{\circ}\text{C}$]
V	Volume, [cm^3]
V_b	Bulk volume, [cm^3]
V_p	Pore volume of the core, [cm^3]
V_w	Water produced [cm^3]
ΔP	Pressure drop [bar] or [atm]
ΔT	Time [sec] or [min]
ρ_w	Density of water inside of rock pores, [g/cm^3]

Abbreviations

A	Cross section area of the core, [cm^2]
AI	Amott–Harvey Index
AN	Acid number [mg KOH/g oil]
AS	A salinity
ASC	A salinity concentration, [g/l]
ASP	Alkaline/surfactant/polymer

<i>BC</i>	Brine concentration
<i>BN</i>	Base number, [mg KOH/g oil]
<i>BPS</i>	Back pressure sleeve, [bar]
<i>BS</i>	B salinity
<i>BSC</i>	B salinity concentration, [g/l]
<i>CC</i>	Chemical composition
<i>CFC</i>	Critical flocculation concentration
<i>CS</i>	C salinity
<i>CSC</i>	C salinity concentration, [g/l]
<i>DNAIA</i>	National Directorate of Environmental Impact Assessment
<i>EOR</i>	Enhanced oil recovery
<i>FWL</i>	Free water level
<i>G</i>	Gas
<i>HS</i>	High salinity
<i>HSB</i>	High salinity brine
<i>HSC</i>	High salinity concentration, [g/l]
<i>IOIP</i>	Initial oil in place
<i>IOR</i>	Improved oil recovery
<i>IPT</i>	Institute of Petroleum and Technology
<i>L</i>	Length, [cm]
<i>LS</i>	Low salinity
<i>LSB</i>	Low salinity brine
<i>LSC</i>	Low salinity concentration, [g/l]
<i>LSE</i>	Low salinity effect
<i>LSW</i>	Low salinity water flooding
<i>MICOA</i>	Ministry for the Coordination Environmental Affairs
<i>MIE</i>	Multiple-component ionic exchange
<i>MS</i>	Moderate salinity
<i>MSC</i>	Moderate salinity concentration, [g/l]
m_w	Mass of wet core, [g]
<i>NG</i>	Norwegian Government
<i>NTNU</i>	Norwegian University of Science and Technology
<i>O</i>	Oil
<i>OOIP</i>	Original Oil In Place
<i>OR</i>	Oil recovery, [%]
<i>OWC</i>	Oil water contact
P_c	Capillary pressure, [bar]
P_o	Pressure in the oil phase, [bar]
P_w	Pressure in the water phase, [bar]
<i>RCAL</i>	Routine core analysis
<i>RF</i>	Recovery factor
<i>RF</i>	Recovery factor, [%]
<i>SCAL</i>	Special core analysis
<i>SP</i>	Sleeve pressure, [bar]
<i>TDS</i>	Total dissolved solid, [ppm] or [g/l] or [mol/l]
<i>USBM</i>	United State Bureau of Mines
V_{op}	Volume of oil produced
<i>W</i>	Wettability index
<i>WAG</i>	Water alternate gas

W_b	Brine weight
W_d	Dry weight, [g]
WO	Oil-wetting formation
WW	Water-wetting formation
W_w	Wet weight, [g]

Greeks Symbols

μ	Viscosity, [cPs]
γ	Interfacial tension, (IFT)
ΔP	Drop pressure of the rock of oil reservoir, [bar] or [atm]
θ	Contact angle
ρ	Density, [g/cm ³]
Φ	Core porosity, [%]

Subscript

a	absolute
b	bulk
c	capillary
d	dry
eff	effective
g	gas
i	initial
i	irreducible
m	moveable
o	oil
p	pore
r	relative
r	residual
w	water
w	wet

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Appendices

Appendix A: Measurements and determination of density and viscosity of brine solution and n-decane oil

Table A - 1: Shows the density determination of brine at 22.7 degrees celsius					
Brines Solution Units	Picnomenter +Brine m (g)	Picnometer Empty m (g)	Mass M (g)	Volume V (cm³)	Density ρ (g/cm³)
LSC	60.969	35.732	25.237	24.721	1.021
MSC	60.923	35.732	25.191	24.721	1.019
HSC	60.973	35.732	25.241	24.721	1.021
ASCE	61.646	35.732	25.914	24.721	1.048
BSC	60.897	35.732	25.165	24.721	1.018
CSC	61.187	35.732	25.455	24.721	1.030
Total	366.595	214.392	152.203	148.326	6.157

Table A - 2: Gives the density calculations of oil at 22.7 degrees celsius					
Brines Solution Units	Picnomenter +Brine m (g)	Picnometer Empty m (g)	Mass M (g)	Volume V (cm³)	Density ρ (g/cm³)
N -Decane	55.621	37.864	17.757	24.721	0.718

Table A - 3: Gives the viscosity measurements and calculations of brine and oil at 23.7 °C

Brines Units	Constant K1 mm ² /s ²	Constant K2 mm ² /s ²	Final time t (min)	Initial time t (min)	Time t1 t (min)	Time t1 t (sec)	Final time t (min)	Initial time t (min)	Time t2 t (min)	Time t2 t (sec)	Brine Density ρ(g/cm ³)	Kinem. Visc. 1 ϑ (cps)	Kinem. Visc. 2 ϑ (cps)	Dinamic Viscosity μ (cps)
LSC	0.001980	0.001635	8.330	0.000	8.330	499.800	18.490	8.330	10.160	609.60	1.021	0.990	0.997	1.014
Average													0.993	
MSC	0.002155	0.001751	7.490	0.000	7.490	449.400	17.310	7.490	9.820	589.20	1.019	0.968	1.032	1.019
Average													1.000	
HSC	0.002452	0.001741	7.060	0.000	7.060	423.600	16.190	7.060	9.130	547.80	1.021	1.039	0.954	1.017
Average													0.996	
ASCE	0.002047	0.001586	17.130	9.010	8.120	487.200	28.010	17.130	10.880	652.80	1.048	0.997	1.035	1.065
Average													1.016	
BCS	0.002430	0.001750	20.460	14.010	6.450	387.000	30.090	20.460	9.630	577.80	1.022	0.940	1.011	0.997
Average													0.976	
CSC	0.002172	0.001707	8.000	0.000	8.000	480.000	18.030	8.000	10.030	601.80	1.030	1.043	1.027	1.066
Average													1.035	1.030
Oil Units	Constant K1 mm ² /s ²	Constant K2 mm ² /s ²	Final time t (min)	Initial time t (min)	Time t1 t (min)	Time t1 t (sec)	Final time t (min)	Initial time t (min)	Time t2 t (min)	Time t2 t (sec)	Brine Density ρ(g/cm ³)	Kinem. Visc. 1 ϑ (cps)	Kinem. Visc. 2 ϑ (cps)	Dinamic Viscosity μ (cps)
N-Decane	0.002430	0.001750	8.260	0.000	8.260	495.600	20.120	8.260	11.860	711.60	0.718	1.204	1.245	0.879
Average													1.225	

Table A - 4: Gives chemical composition datas of brines used

Name Component i	LSC g/l	MSC g/l	HSC g/l	ASCE g/l	BSC g/l	CSC g/l
KCl	0.39	0.39	0.39	0.00	0.00	1.17
NaCl	9.87	10.35	10.59	15.74	10.35	9.87
CaCl ₂ *2H ₂ O	0.52	0.52	0.52	9.27	2.08	0.00
MgCl ₂ *6H ₂ O	1.08	1.08	1.08	0.60	0.00	3.63
Na ₂ SO ₄	6.93	2.31	0.00	0.00	0.62	2.65
NaHCO ₃	0.12	0.12	0.12	0.00	2.34	1.59
TDS (g/l)	18.91	14.77	12.70	25.61	15.39	18.91

Appendix B: Composition and mass (mi) calculated for each brine solution

Table B - 1: Shows composition and mass of the brine low salinity concentration (LSC)									
Component i	MW	MW	LSC	ni	MW	MW	Mass dry	Mass	Mass+ Paper
units	g/mole	g/mole	g/l	moles	g/mole	g/mole	mi (g)	mi (g)	m (g)
KCl	39.098	35.453	0.390	0.010	74.551		0.74	0.744	1.521
NaCl	22.989	35.453	9.870	0.283	58.442		16.54	16.544	17.321
CaCl₂*2H₂O	40.080	35.453	0.520	0.013	110.986	147.020	1.44	1.907	2.684
MgCl₂*6H₂O	24.305	35.453	1.080	0.044	95.211	203.310	4.23	9.034	9.811
Na₂SO₄	22.989	96.060	6.930	0.072	142.038		10.25	10.247	11.024
NaHCO₃	22.989	61.011	0.120	0.002	84.000		0.17	0.165	0.942
Total	172.450	298.883	18.910	0.425	565.228		33.37	38.641	43.303

Table B - 2: Gives the composition and mass of the brine medium salinity concentration (MSC)									
Component i	MW	MW	LSC	ni	MW	MW	Mass dry	Mass	Mass+ Paper
units	g/mole	g/mole	g/l	moles	g/mole	g/mole	mi (g)	mi (g)	m (g)
KCl	39.098	35.453	0.390	0.010	74.551		0.74	0.744	1.521
NaCl	22.989	35.453	10.350	0.400	58.442		23.39	23.386	24.163
CaCl₂*2H₂O	40.080	35.453	0.520	0.013	110.986	147.020	1.44	1.907	2.684
MgCl₂*6H₂O	24.305	35.453	1.080	0.044	95.211	203.310	4.23	9.034	9.811
Na₂SO₄	22.989	96.060	2.310	0.024	142.038		3.42	3.416	4.193
NaHCO₃	22.989	61.011	0.120	0.002	84.000		0.17	0.165	0.942
Total	172.450	298.883	14.770	0.494	565.228		33.38	38.652	43.314

Table B - 3: Gives the composition and mass of the brine high salinity concentration (HSC)									
Component i	MW	MW	LSC	ni	MW	MW	Mass dry	Mass	Mass+ Paper
units	g/mole	g/mole	g/l	moles	g/mole	g/mole	mi (g)	mi (g)	m (g)
KCl	39.098	35.453	0.390	0.010	74.551		0.74	0.744	1.521
NaCl	22.989	35.453	10.590	0.459	58.442		26.81	26.807	27.584
CaCl₂*2H₂O	40.080	35.453	0.520	0.013	110.986	147.020	1.44	1.907	2.684
MgCl₂*6H₂O	24.305	35.453	1.080	0.044	95.211	203.310	4.23	9.034	9.811
Na₂SO₄	22.989	96.060	0.000	0.000	142.038		0.00	0.000	0.777
NaHCO₃	22.989	61.011	0.120	0.002	84.000		0.17	0.165	0.942
Total	172.450	298.883	12.700	0.528	565.228		33.39	38.657	43.319

Table B - 4: Shows the composition and mass of the brine a salinity concentration Ekofisk (ASCE) reference case

Component i units	MW g/mole	MW g/mole	LSC g/l	ni moles	MW g/mole	MW g/mole	Mass dry mi (g)	Mass mi (g)	Mass+ Paper m (g)
KCl	39.098	35.453	0.000	0.000	74.551		0.00	0.000	0.777
NaCl	22.989	35.453	15.740	0.685	58.442		40.01	40.014	40.791
CaCl ₂ *2H ₂ O	40.080	35.453	9.270	0.231	110.986	147.020	25.67	34.004	34.781
MgCl ₂ *6H ₂ O	24.305	35.453	0.600	0.025	95.211	203.310	2.35	5.019	5.796
Na ₂ SO ₄	22.989	96.060	0.000	0.000	142.038		0.00	0.000	0.777
NaHCO ₃	22.989	61.011	0.000	0.000	84.000		0.00	0.000	0.777
Total	172.450	298.883	25.610	0.941	565.228		68.03	79.037	83.699

Table B - 5: Presents the composition and mass of the brine b salinity concentration (BSC)

Component i units	MW g/mole	MW g/mole	LSC g/l	ni moles	MW g/mole	MW g/mole	Mass dry mi (g)	Mass mi (g)	Mass+ Paper m (g)
KCl	39.098	35.453	0.000	0.000	74.551		0.00	0.000	0.777
NaCl	22.989	35.453	10.350	0.399	58.442		23.32	23.316	24.093
CaCl ₂ *2H ₂ O	40.080	35.453	2.080	0.052	110.986	147.020	5.76	7.630	8.407
MgCl ₂ *6H ₂ O	24.305	35.453	0.000	0.000	95.211	203.310	0.00	0.000	0.777
Na ₂ SO ₄	22.989	96.060	0.620	0.006	142.038		0.92	0.917	1.694
NaHCO ₃	22.989	61.011	2.340	0.038	84.000		3.22	3.222	3.999
Total	172.450	298.883	15.390	0.496	565.228		33.21	35.084	39.746

Table B - 6: Shows the composition and mass of the brine c salinity concentration (CSC)

Component i units	MW g/mole	MW g/mole	LSC g/l	ni moles	MW g/mole	MW g/mole	Mass dry mi (g)	Mass mi (g)	Mass+ Paper m (g)
KCl	39.098	35.453	1.17	0.030	74.551		2.23	2.231	3.008
NaCl	22.989	35.453	9.87	0.348	58.442		20.34	20.344	21.121
CaCl ₂ *2H ₂ O	40.080	35.453	0.00	0.000	110.986	147.020	0.00	0.000	0.777
MgCl ₂ *6H ₂ O	24.305	35.453	3.63	0.149	95.211	203.310	14.22	30.365	31.142
Na ₂ SO ₄	22.989	96.060	2.65	0.028	142.038		3.92	3.918	4.695
NaHCO ₃	22.989	61.011	1.59	0.026	84.000		2.19	2.189	2.966
Total	172.450	298.883	18.910	0.581	565.228		42.90	59.047	63.709

Appendix C: Comparison of results of porosity and permeability measurement and calculated

Table C - 1: Shows comparison between porosity computed by helium gas method (A) and liquid saturating method (B)			
Lithology "	Core Name	Porosity (A) ϕ (%)	Porosity (B) ϕ_{eff} (%)
Chalk	LS	45.26	46.74
Chalk	MS	45.33	46.23
Chalk	HS	44.99	46.23
Chalk	AS	44.94	46.44
Limestone	BS	30.93	29.12
Limestone	CS	36.20	20.42
	Average	41.27	39.20

1 - Chalk from Ekofisk and 2 – Limestone from Iranian.

Table C - 2: Gives comparison between absolute permeability and air permeability calculated			
Lithology "	Core Name	Absolute permeability K_{abs} (mD)	Air Permeability K (mD)
Chalk	LS	0.025	4.320
Chalk	MS	0.757	4.430
Chalk	HS	0.227	4.110
Chalk	AS	0.336	5.310
Limestone	BS	1.472	3.410
Limestone	CS	0.423	0.799
	Average	0.540	3.730

1 - Chalk from Ekofisk and 2 – Limestone from Iranian.

Appendix D: Shows the summary results calculated of laboratory experiments

Legend: Breakthrough or

First Oil Drop

First Water Drop

Table D – 1: Shows the summary results of the core LS

Imbibition Process Core LS	Pore Volume V_p (cm ³)	Flow Rate Q (cm ³ /min)	First Oil Pressure Drop ΔP (bar)	First Water Pressure Drop ΔP (bar)	Final Pressure Drop ΔP (bar)	Sleeve Pressure P (bar)	Aging Time T (days)	Initial Water Saturation S_{wi} (%)	Residual Oil Saturation S_{or} (%)	Volume of Oil (Drainage) V_o (cm ³)
05.07.2012	23.31	2	1.12	3.12	7.02	15	15	20.978	24.92	18.42

Parameter Units	Time Step ΔT (min)	Time ΔT (min)	Cumulative Time $\Sigma \Delta T$ (min)	Pressure Drop ΔP (atm)	Volume of Water Injected V_{wi} (cm ³)	Volume of Oil Produced ΔV_{oi} (cm ³)	Total Volume ($\Delta V_w + \Delta V_o$) ΔV_{t_i} (cm ³)	Cumulative Oil Produced ΣV_{oi} (cm ³)	Injected Pore Volume V_p (cm ³)	Recovery Factor (RF) OOIP%
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	4.25	4.25	0.00	0.00	0.00	0.00	0.00	0.36	0.00
2	4.25	3.75	8.00	1.20	0.00	0.00	0.00	0.00	0.69	0.00
3	8.00	3.58	11.58	1.76	0.00	0.00	0.00	0.00	0.99	0.00
4	11.58	3.90	15.48	2.14	0.00	0.00	0.00	0.00	1.33	0.00
5	15.48	3.97	19.45	2.58	-10.00	10.00	0.00	10.00	1.67	54.29
6	19.45	2.66	22.11	3.12	1.55	0.45	2.00	10.45	1.90	56.73
7	22.11	3.45	25.56	3.66	1.65	0.35	2.00	10.80	2.19	58.63
8	25.56	2.72	28.28	4.12	1.75	0.25	2.00	11.05	2.43	59.99
9	28.28	2.12	30.40	4.58	1.76	0.24	2.00	11.29	2.61	61.29
10	30.40	2.02	32.42	5.08	1.77	0.23	2.00	11.52	2.78	62.54
11	32.42	1.99	34.41	5.49	1.78	0.22	2.00	11.74	2.95	63.74
12	34.41	1.66	36.07	5.90	1.78	0.22	2.00	11.96	3.09	64.93
13	36.07	1.36	37.43	6.20	1.79	0.21	2.00	12.17	3.21	66.07
14	37.43	1.83	39.26	6.53	1.85	0.15	2.00	12.32	3.37	66.88
15	39.26	1.23	40.49	6.76	1.80	0.20	2.00	12.52	3.47	67.97
16	40.49	1.76	42.25	7.02	1.91	0.09	2.00	12.61	3.63	68.46
Total	385.19	42.25	427.44	66.14	9.39	12.61	22.00	138.43	36.67	751.52

Table D – 2: Gives the summary results of the core MS

Imbibition Process Core MS	Pore Volume V_p (cm ³)	Flow Rate Q (cm ³ /min)	First Oil Pressure Drop ΔP (bar)	First Water Pressure Drop ΔP (bar)	Final Pressure Drop ΔP (bar)	Sleeve Pressure P (bar)	Aging Time T (days)	Initial Water Saturation S_{wi} (%)	Residual Oil Saturation S_{or} (%)	Volume of Oil (Drainage) V_o (cm ³)
05.07.2012	20.72	2	1.79	2.70	7.78	15	15	29.198	22.49	14.67

Parameter Units	Time Step ΔT (min)	Time ΔT (min)	Cumulative Time $\sum \Delta T$ (min)	Pressure Drop ΔP (atm)	Volume of Water Injected V_{wi} (cm ³)	Volume of Oil Produced Δv_{oi} (cm ³)	Total Volume ($\Delta V_w + \Delta V_o$) ΔV_{ti} (cm ³)	Cumulative Oil Produced $\sum V_{oi}$ (cm ³)	Injected Pore Volume V_p (cm ³)	Recovery Factor (RF) OOIP%
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	3.21	3.21	0.00	0.00	0.00	0.00	0.00	0.31	0.00
2	3.21	3.79	7.00	1.79	0.00	0.00	0.00	0.00	0.68	0.00
3	7.00	3.58	10.58	1.80	0.00	0.00	0.00	0.00	1.02	0.00
4	10.58	3.80	14.38	1.99	0.00	0.00	0.00	0.00	1.39	0.00
5	14.38	4.07	18.45	2.68	-7.50	7.50	0.00	7.50	1.78	51.12
6	18.45	2.66	21.11	2.70	1.30	0.70	2.00	8.20	2.04	55.90
7	21.11	3.45	24.56	3.32	1.73	0.27	2.00	8.47	2.37	57.74
8	24.56	2.72	27.28	3.98	1.74	0.26	2.00	8.73	2.63	59.51
9	27.28	2.12	29.40	4.58	1.75	0.25	2.00	8.98	2.84	61.21
10	29.40	2.02	31.42	4.98	1.77	0.23	2.00	9.21	3.03	62.78
11	31.42	1.99	33.41	5.50	1.79	0.21	2.00	9.42	3.22	64.21
12	33.41	1.66	35.07	5.95	1.80	0.20	2.00	9.62	3.39	65.58
13	35.07	1.36	36.43	6.35	1.88	0.12	2.00	9.74	3.52	66.39
14	36.43	1.83	38.26	6.55	1.90	0.10	2.00	9.84	3.69	67.08
15	38.26	1.23	39.49	6.98	1.91	0.09	2.00	9.93	3.81	67.69
16	39.49	1.23	40.72	7.78	1.92	0.08	2.00	10.01	3.93	68.23
Total	370.05	40.72	410.77	66.93	11.99	10.01	22.00	109.65	39.65	747.44

Table D – 3: Presents the summary results of the core HS

Imbibition Process Core HS	Pore Volume V_p (cm ³)	Flow Rate Q (cm ³ /min)	First Oil Pressure Drop ΔP (bar)	First Water Pressure Drop ΔP (bar)	Final Pressure Drop ΔP (bar)	Sleeve Pressure P (bar)	Aging Time T (days)	Initial Water Saturation S_{wi} (%)	Residual Oil Saturation S_{or} (%)	Volume of Oil (Drainage) V_o (cm ³)
05.07.2012	22.61	2	1.64	3.48	6.79	15	15	16.187	34.15	18.95

Parameter Units	Time Step ΔT (min)	Time ΔT (min)	Cumulative Time $\sum \Delta T$ (min)	Pressure Drop ΔP (atm)	Volume of Water Injected V_{wi} (cm ³)	Volume of Oil Produced ΔV_{oi} (cm ³)	Total Volume ($\Delta V_w + \Delta V_o$) ΔV_t (cm ³)	Cumulative Oil Produced $\sum V_{oi}$ (cm ³)	Injected Pore Volume V_p (cm ³)	Recovery Factor (RF) OOIP%
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	3.12	3.12	0.00	0.00	0.00	0.00	0.00	0.28	0.00
2	3.12	3.88	7.00	1.64	0.00	0.00	0.00	0.00	0.62	0.00
3	7.00	3.58	10.58	1.75	0.00	0.00	0.00	0.00	0.94	0.00
4	10.58	6.00	16.58	2.99	0.00	0.00	0.00	0.00	1.47	0.00
5	16.58	1.87	18.45	3.02	-9.00	9.00	0.00	9.00	1.63	47.49
6	18.45	2.56	21.01	3.48	1.50	0.50	2.00	9.50	1.86	50.13
7	21.01	3.53	24.54	4.00	1.70	0.30	2.00	9.80	2.17	51.72
8	24.54	1.74	26.28	4.42	1.75	0.25	2.00	10.05	2.32	53.03
9	26.28	3.12	29.40	4.68	1.79	0.21	2.00	10.26	2.60	54.14
10	29.40	2.02	31.42	5.41	1.77	0.23	2.00	10.49	2.78	55.36
11	31.42	1.00	32.42	5.56	1.78	0.22	2.00	10.71	2.87	56.52
12	32.42	2.65	35.07	5.59	1.79	0.21	2.00	10.92	3.10	57.63
13	35.07	0.36	35.43	6.39	1.85	0.15	2.00	11.07	3.13	58.42
14	35.43	2.84	38.27	6.72	1.99	0.01	2.00	11.08	3.39	58.47
15	38.27	2.23	40.50	6.74	1.90	0.10	2.00	11.18	3.58	59.00
16	40.50	2.23	42.73	6.79	1.95	0.05	2.00	11.23	3.78	59.26
Total	370.07	42.73	412.80	69.18	10.77	11.23	22.00	125.29	36.51	661.16

Table D – 4: Shows the summary results of the core AS

Imbibition Process Core AS	Pore Volume V_p (cm ³)	Flow Rate Q (cm ³ /min)	First Oil Pressure Drop ΔP (bar)	First Water Pressure Drop ΔP (bar)	Final Pressure Drop ΔP (bar)	Sleeve Pressure P (bar)	Aging Time T (days)	Initial Water Saturation S_{wi} (%)	Residual Oil Saturation S_{or} (%)	Volume of Oil (Drainage) V_o (cm ³)
06.07.2012	36.27	2	1.46	6.62	11.32	20	15	28.508	27.44	25.93

Parameter Units	Time Step ΔT (min)	Time ΔT (min)	Cumulative Time $\sum \Delta T$ (min)	Pressure Drop ΔP (atm)	Volume of Water Injected V_{wi} (cm ³)	Volume of Oil Produced ΔV_{oi} (cm ³)	Total Volume ($\Delta V_w + \Delta V_o$) ΔV_t (cm ³)	Cumulative Oil Produced $\sum V_{oi}$ (cm ³)	Injected Pore Volume V_p (cm ³)	Recovery Factor (RF) OOIP%
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	5.15	5.15	0.00	0.00	0.00	0.00	0.00	0.46	0.00
2	5.15	4.09	9.24	1.46	0.00	0.00	0.00	0.00	0.82	0.00
3	9.24	3.24	12.48	2.68	0.00	0.00	0.00	0.00	1.10	0.00
4	12.48	3.87	16.35	3.79	0.00	0.00	0.00	0.00	1.45	0.00
5	16.35	4.12	20.47	5.15	-10.30	10.30	0.00	10.30	1.81	39.72
6	20.47	2.84	23.31	6.62	0.01	1.99	2.00	12.29	2.06	47.40
7	23.31	3.27	26.58	7.58	0.03	1.97	2.00	14.26	2.35	54.99
8	26.58	2.70	29.28	8.68	1.55	0.45	2.00	14.71	2.59	56.73
9	29.28	1.12	30.40	9.56	1.70	0.30	2.00	15.01	2.69	57.89
10	30.40	2.95	33.35	10.09	1.78	0.22	2.00	15.23	2.95	58.74
11	33.35	3.07	36.42	10.56	1.79	0.21	2.00	15.44	3.22	59.54
12	36.42	1.73	38.15	10.86	1.80	0.20	2.00	15.64	3.37	60.32
13	38.15	2.28	40.43	11.08	1.91	0.09	2.00	15.73	3.58	60.66
14	40.43	2.85	43.28	11.22	1.92	0.08	2.00	15.81	3.83	60.97
15	43.28	1.30	44.58	11.32	1.93	0.07	2.00	15.88	3.94	61.24
16	44.58	1.30	45.88	11.32	1.94	0.06	2.00	15.94	4.06	61.47
Total	409.47	45.88	455.35	121.97	6.06	15.94	22.00	176.24	40.28	679.68

Table E –D: Gives the summary results of the core BS

Imbibition Process Core BS	Pore Volume V_p (cm ³)	Flow Rate Q (cm ³ /min)	First Oil Pressure Drop ΔP (bar)	First Water Pressure Drop ΔP (bar)	Final Pressure Drop ΔP (bar)	Sleeve Pressure P (bar)	Aging Time T (days)	Initial Water Saturation S_{wi} (%)	Residual Oil Saturation S_{or} (%)	Volume of Oil (Drainage) V_o (cm ³)
06.07.2012	17.37	2	2.05	8.68	13.21	22	15	21.473	29.42	13.64

Parameter Units	Time Step ΔT (min)	Time ΔT (min)	Cumulative Time $\sum \Delta T$ (min)	Pressure Drop ΔP (atm)	Volume of Water Injected V_{wi} (cm ³)	Volume of Oil Produced ΔV_{oi} (cm ³)	Total Volume ($\Delta V_w + \Delta V_o$) ΔV_t (cm ³)	Cumulative Oil Produced $\sum V_{oi}$ (cm ³)	Injected Pore Volume V_p (cm ³)	Recovery Factor (RF) OOIP%
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	7.25	7.25	0.00	0.00	0.00	0.00	0.00	0.83	0.00
2	7.25	2.99	10.24	2.05	0.00	0.00	0.00	0.00	1.18	0.00
3	10.24	3.00	13.24	3.70	0.00	0.00	0.00	0.00	1.52	0.00
4	13.24	2.98	16.22	5.36	0.00	0.00	0.00	0.00	1.87	0.00
5	16.22	3.12	19.34	7.01	-5.00	5.00	0.00	5.00	2.23	36.66
6	19.34	3.15	22.49	8.68	0.50	1.50	2.00	6.50	2.59	47.65
7	22.49	3.16	25.65	10.41	1.60	0.40	2.00	6.90	2.95	50.59
8	25.65	3.00	28.65	11.79	1.70	0.30	2.00	7.20	3.30	52.79
9	28.65	3.25	31.90	12.45	1.79	0.21	2.00	7.41	3.67	54.33
10	31.90	3.15	35.05	12.95	1.75	0.25	2.00	7.66	4.04	56.16
11	35.05	3.20	38.25	13.30	1.94	0.06	2.00	7.72	4.40	56.60
12	38.25	3.06	41.31	13.39	1.80	0.20	2.00	7.92	4.76	58.06
13	41.31	3.14	44.45	13.24	2.00	0.00	2.00	7.92	5.12	58.06
14	44.45	3.12	47.57	13.27	1.74	0.26	2.00	8.18	5.48	59.97
15	47.57	3.11	50.68	13.28	2.00	0.00	2.00	8.18	5.84	59.97
16	50.68	3.11	53.79	13.21	1.65	0.35	2.00	8.53	6.19	62.54
Total	432.29	53.79	486.08	154.09	13.47	8.53	22.00	89.12	55.97	653.37

Table D – 6: Shows the summary results of the cCore CS

Imbibition Process Core CS	Pore Volume V_p (cm^3)	Flow Rate Q (cm^3/min)	First Oil Pressure Drop ΔP (bar)	First Water Pressure Drop ΔP (bar)	Final Pressure Drop ΔP (bar)	Sleeve Pressure P (bar)	Aging Time T (days)	Initial Water Saturation S_{wi} (%)	Residual Oil Saturation S_{or} (%)	Volume of Oil (Drainage) V_o (cm^3)
06.07.2012	9.60	2	16.82	16.83	16.94	28	15	14.583	62.6	8.2

Parameter Units	Time Step ΔT (min)	Time ΔT (min)	Cumulative Time $\sum \Delta T$ (min)	Pressure Drop ΔP (atm)	Volume of Water Injected V_{wi} (cm^3)	Volume of Oil Produced ΔV_{oi} (cm^3)	Total Volume ($\Delta V_w + \Delta V_o$) ΔV_{ti} (cm^3)	Cumulative Oil Produced $\sum V_{oi}$ (cm^3)	Injected Pore Volume V_p (cm^3)	Recovery Factor (RF) OOIP%
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	12.48	12.48	10.00	0.00	0.00	0.00	0.00	2.60	0.00
2	12.48	3.97	16.45	16.82	0.00	0.00	0.00	0.00	3.43	0.00
3	16.45	3.66	20.11	16.82	0.00	0.00	0.00	0.00	4.19	0.00
4	20.11	3.45	23.56	16.82	0.00	0.00	0.00	0.00	4.91	0.00
5	23.56	3.72	27.28	16.63	0.00	0.00	0.00	0.00	5.68	0.00
6	27.28	1.12	28.40	16.83	0.90	1.10	2.00	1.10	5.92	13.41
7	28.40	2.02	30.42	16.94	1.70	0.30	2.00	1.40	6.34	17.07
8	30.42	1.99	32.41	16.94	1.92	0.08	2.00	1.48	6.75	18.05
9	32.41	1.66	34.07	16.94	1.90	0.10	2.00	1.58	7.10	19.27
10	34.07	0.36	34.43	16.94	1.88	0.12	2.00	1.70	7.17	20.73
11	34.43	2.83	37.26	16.94	1.87	0.13	2.00	1.83	7.76	22.32
12	37.26	2.16	39.42	16.94	2.00	0.00	2.00	1.83	8.21	22.32
13	39.42	1.99	41.41	16.94	1.89	0.11	2.00	1.94	8.63	23.66
14	41.41	1.98	43.39	16.94	1.85	0.15	2.00	2.09	9.04	25.49
15	43.39	1.95	45.34	16.94	1.90	0.10	2.00	2.19	9.45	26.71
16	45.34	1.95	47.29	16.94	2.00	0.00	2.00	2.19	9.85	26.71
Total	466.43	47.29	513.72	268.32	19.81	2.19	22.00	19.33	107.03	235.73