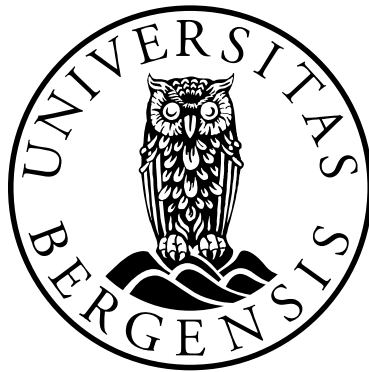


# Enhanced Oil Recovery by Combined Low Salinity Water and Polymer Flooding

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Dissertation for the degree philosophiae doctor (PhD)  
at the University of Bergen

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## Scientific Environment

The research presented in this dissertation has been conducted at the Centre for Integrated Petroleum Research (Uni Research CIPR) and Department of Chemistry at the University of Bergen, in Bergen, Norway during the period of 2010-2013. This research is part of the PETROMAKS program which was sponsored by the Research Council of Norway. Professor Arne Skauge was the main advisor for this PhD project. Dr. Kristine Spildo and Dr. Tormod Skauge were the co-advisors.





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*To the memory of Shaba...*





## **Preface**

This dissertation is submitted to the Department of Chemistry and the Faculty of Mathematics and Natural Science at the University of Bergen in partial fulfilment of the requirements for the degree of Doctor of Philosophy. This research work has been conducted at the Centre for Integrated Petroleum Research (CIPR) and the University of Bergen during the period of September 2010 to August 2013. The project was part of the PETROMAKS program initiated and supported by the Research Council of Norway.

The primary objective of this study was to investigate the increased oil recovery by low salinity waterflooding and improve the understandings on mechanism(s) believed to be the reason for low salinity effect (LSE). Moreover, it was also the interest to study and examine the synergistic effect of combined low salinity waterflooding and polymer injection on further oil recovery improvement through reducing residual oil saturation.

This dissertation consists of two main parts. Part one includes seven chapters and provides the background for enhanced oil recovery mechanisms especially polymer flooding and low salinity waterflooding. Also the summary of main results obtained during this research work and related conclusions are provided in part one. Part two in this dissertation is the included papers and an internal report.



## **Abstract**

World energy demand is continuously increasing as the developed and developing countries consume more energy to keep their growing industries running. Significant portion of the energy demand is supplied by fossil energies, especially crude oil. Thus, to meet the world energy demand, it is necessary to increase the oil reserves and oil production capacities. This goal is achievable by either exploration/development of new oil reservoirs, or by improving the recovery efficiency of the current producing or mature reservoirs by applying enhanced oil recovery (EOR) processes.

Enhanced oil recovery processes are applied to recover oil not produced by natural energy drives of the reservoir. The natural reservoir drives could normally produce one third of the oil, usually two third of oil in the reservoir is left behind and trapped in pore structures of the reservoir due to rock/fluid interactions. The trapped oil could be mobilized and recovered if the rock/fluid interactions altered to favourable state. The favourable state may be achieved by implementing EOR processes and through, among others, wettability alteration, weakening the capillary forces, strengthening the viscous forces.

During the last 10-15 years low salinity waterflooding (LSW) as an emerging EOR process, has been extensively investigated both in experimental and field pilot scales. Although the EOR potential for LSW has been proven, however the mechanism or mechanisms behind low salinity effect (LSE) is still open for further discussions. So far, several mechanisms have been proposed as the reasons for LSE, but no one conclusively explains all observations reported for low salinity injection.

This research study has mainly concentrated on the improving the understandings about mechanisms believed to be the reason for low salinity effect with stress on wettability alteration mechanism. Also the aim in this work was to investigate if combination of low salinity water and polymer results in synergistic effect on residual oil mobilization and final oil recovery.

It is generally reported in the literature that low salinity shifts the wettability towards more water-wet state, and therefore oil polar components are released, mobilized and produced by low salinity water. The results from this study shows that the initial wettability state of the porous media is a key parameter for low salinity effect as less water-wet cores gave better oil recovery by LSE. Moreover and contrary to the general belief in the literature, wettability indicators in this study showed shift to less water-wet state by low salinity injection. The wettability indicators were used in this study include end point relative permeabilities, frontal advancement behaviour obtained by in-situ saturation monitoring, and relative permeability and capillary pressure curves obtained from simulation of experimental results. This study concludes that depending on the initial wettability of the porous media the wettability shift by low salinity effect could be either towards more water-wet or less water-wet state. The optimum wettability state is where the minimum residual oil saturation and maximum oil recovery may be obtained. This study also showed that injection of low salinity water at initial water saturation (secondary mode LSW) is more efficient than low salinity injection at residual oil saturation (tertiary mode LSW).

Furthermore, combination of low salinity water and polymer injection or alternatively nano-sized polymer particles revealed considerable synergy between two EOR processes. The combined effect was even more significant (more than 50% reduction in residual oil saturation after waterflood) when the low salinity environment was established at initial water saturation ( $S_{wi}$ ) rather than at waterflood trapped oil saturation ( $S_{or}$ ). This synergistic effect can be attributed to improved banking of low salinity mobilized oil that is a combined effect with low salinity oil mobilization. The results are encouraging as the concentration of the polymer used in this study was very low (300 ppm) and only gave slight change in mobility ratio.

Under the experimental conditions in this study, also nano-size polymer particles (LPS: Linked Polymer Solution) exhibit similar EOR potential. Low salinity combined with LPS gave similar additional oil recovery effect as low salinity polymer, even though the mechanisms for LSW and LPS are different than for LSW and polymer.

# List of Publications

## Paper 1:

**Shaker Shiran, B.**, and Skauge, A. (2012): “Wettability and Oil Recovery by Low Salinity Injection”, Paper SPE 155651 prepared for presentation at the SPE EOR Conference at Oil and Gas West Asia, 16-18 April, Muscat, Oman.

## Paper 2:

**Shaker Shiran, B.**, and Skauge, A. (2013): “Enhanced Oil Recovery (EOR) by Combined Low Salinity Water/Polymer Flooding”, *Energy & Fuels*, 27, 3, 1223-1235.

## Paper 3:

Skauge, A., and **Shaker Shiran, B.** (2013): “Low Salinity Polymer Flooding”, Paper A14 prepared for presentation at 17<sup>th</sup> European Symposium on Improved Oil Recovery, 16-18 April, St. Petersburg, Russia.

*This Paper from the EAGE IOR Symposium in St. Petersburg, Russia was selected as one of the best from this conference.*

## Paper 4:

**Shaker Shiran, B.**, and Skauge, A. (2014): “Similarities and Differences of Low Salinity Polymer and Low Salinity LPS (Linked Polymer Solutions) for Enhanced Oil Recovery”, *Journal of Dispersion Science and Technology*, Accepted author version posted online: 08 Jan 2014. Published online: 08 Jan 2014.

## Internal Report:

**Shaker Shiran, B.**, and Skauge, A. (2013): “In-Situ Saturation Monitoring and Simulation Study of Low Salinity Waterflooding”, Submitted to the Centre for Integrated Petroleum Research (CIPR).

## Summary of Paper Content

**Paper 1** investigates the effect of initial wettability state of porous media and clay content on increased oil recovery by low salinity injection. Berea and Bentheimer

outcrop sandstones with different initial wettability and clay content were selected to perform tertiary mode low salinity floods. The different initial wettability states were established in the cores by systematic ageing with crude oil at elevated temperature. The results from both core materials are compared in this paper based on the effect of their initial wettability and clay content.

**Paper 2** presents and compares the results obtained from secondary mode and tertiary mode low salinity waterflooding in Berea cores at water-wet and mixed wet conditions. The experimental results also were simulated to investigate the direction of wettability alteration by low salinity injection. Also in this paper the synergistic effect of combining low salinity waterflooding and polymer injection was investigated in secondary and tertiary modes.

**Paper 3** examines the combined effect of low salinity water and low salinity polymer injection in Berea and Bentheimer cores at different wettability states. Also oil mobilization potential of low salinity polymer is compared the oil mobilization potential of low salinity polymer particles, e.g. linked polymer solutions (LPS).

**Paper 4** reports the flow behavior of single phase and two phase polymer and linked polymer solution (LPS) injection in Berea and Bentheimer cores under low salinity and high salinity conditions. The main focus in this paper was to investigate the similarities and differences of propagation of polymer and linked polymer solutions in the porous media and their potential to mobilize residual oil after low salinity injection.

**Internal Report** introduces the results obtained from in-situ saturation monitoring of secondary low salinity versus high salinity waterflooding. The aim was to investigate frontal advancement behavior of low salinity and high salinity floods and to detect local saturation change, the source of increased oil recovery, and possible wettability shift by low salinity injection. The experimental results including in-situ saturations were used as inputs to simulate the process and find relative permeability and capillary pressure curves in order to detect the direction of wettability shift.

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# CHAPTER 1

## INTRODUCTION

### 1.1 Oil Supply and Demand

The first commercial oil well was drilled by Edwin Drake in northwestern Pennsylvania in 1859 (Dickey, 1959). Since then, oil has been remained as the world's main energy source and the demand for this energy source is still increasing. Based on the outlook for long term oil demand published in 2012 by the Organization of Petroleum Exporting Countries (OPEC), the need for oil will increase to 107 million barrel per day in 2035, from the current value of about 90 million barrel per day.

In order to meet the continuously increasing oil demand and keep sustainable oil supply, the ultimate recoverable oil reserves should be increased. This could be achieved by replacing the produced oil by new reserves from new discoveries as well as applying enhanced/improved oil recovery (EOR/IOR) methods to maximize oil recovery from current mature oil fields by minimizing the trapped oil left behind in the reservoirs. Exploration and development of new oil reserves is cost and energy intensive and requires new installations and infrastructure. Also there are only few number of large scale oil discoveries during recent years compared to the past. In contrast, EOR/IOR methods are utilizing existing installations and facilities of the developed oil reservoirs. These methods are more energy efficient and are expected to play a major role in future oil supply.

### 1.2 Oil Recovery Maximizing

In mature oil fields, after primary and secondary oil recoveries which are mostly governed by the reservoir original pressure, pressure maintenance schemes and waterflooding, considerable amount of oil is trapped in the pore networks of the porous media by capillary forces exist in pore scale. To achieve maximized oil

recovery in these fields, the capillary forces responsible for oil entrapment must be overcome. During last 4-5 decades different EOR/IOR methods have been designed and implemented in order to efficiently recover oil left in the reservoir after waterflooding projects. These methods include variety of physical, chemical, and technical processes and procedures which lead to increased final oil recovery and accelerated rate of oil recovery from the reservoirs.

It is worth noting that there is a subtle difference between IOR and EOR methods. The IOR methods include all processes and procedures that affect economically increased oil recovery and cover primary, secondary, and tertiary stages of oil recovery. These recovery methods deal with both mobile and immobile oil left in the reservoir. The EOR methods mostly refer to tertiary oil recovery methods which could mobilize the immobile oil trapped in pore structure of the porous media. The most commonly applied EOR methods include but not limited to water based processes (polymer flooding, surfactant flooding, alkali/surfactant/polymer flooding), gas based processes (miscible gas injection, nitrogen (N<sub>2</sub>) and CO<sub>2</sub> injection), thermal processes (in-situ combustion), and combination of these processes (water alternating gas (WAG), hot water injection, steam injection, foam injection).

### **1.3 New EOR Processes**

During the last 10-15 years, low salinity water (LSW) injection or smart waterflooding has been given a great interest as new water based tertiary oil recovery process (Morrow and Buckley, 2011). Extensive experimental researches as well as some field pilot studies have verified the validity and potential of low salinity injection as tertiary recovery process. The reason for categorizing the low salinity injection as an EOR method is that this process targets the immobile residual oil saturation left trapped after conventional high salinity waterflooding.

The brine used in low salinity injection includes substantially lowering the salt concentration compared to the connate water of the reservoir (diluted brine) or modification of brine composition. The low salinity injection is carried out in both

secondary mode and tertiary mode injections. In secondary mode, the low salinity water is injected at initial water saturation ( $S_{wi}$ ), while in tertiary mode the low salinity injection follows the conventional high salinity waterflooding at residual oil saturation ( $S_{or}$ ) condition.

It is well known from the literature that the low salinity environment, used as pre-flush, is beneficial for the application of other well established EOR processes such as surfactant flooding and polymer flooding (Lake, 1989). Therefore the extension of low salinity water in combination with surfactant flooding and polymer flooding is of great interest to investigate the synergy between these different EOR methods. These combined processes which also are called hybrid EOR techniques, may lead to even higher oil recoveries than by the individual processes.

#### **1.4 Scope and Objectives of the Current Study**

Numerous experimental results have been reported in the literature, varying from many promising results to limited or no effects of low salinity. The principal mechanism(s) responsible for low salinity effect (LSE) and the optimal conditions, under which increased oil recovery by low salinity brine injection may or may not be observed, are still unidentified. Many papers have been published dealing with and discussing the possible mechanism(s) behind enhanced oil recovery by low salinity (LS) injection. The more papers presented, the more diversity is introduced to the proposed mechanisms for LSE. Therefore understanding the underlying mechanism(s) for LSE and identifying the necessary and sufficient conditions to observe or not observe LSE remains as a challenging path for further studies and investigations.

The experimental research presented in this PhD dissertation, is devoted to investigate the mechanism(s) behind the low salinity effect with focus on wettability alteration mechanism. Furthermore, the examination of the combined effect of low salinity polymer solution on increased oil recovery was the matter of interest in this research. The primary objectives of this study were to investigate the mechanisms behind low salinity waterflooding and study if there was a positive synergy of combining low

salinity with polymer flooding. The thesis addresses effect of initial wettability states, rock permeability, and clay content on low salinity water flood. It also discusses secondary versus tertiary low salinity with respect to additional oil recovery. Studies have been made to test if the combination of low salinity water and polymer has synergistic effect on increased oil recovery, and if so investigate the oil mobilization and fluid flow properties for low salinity polymer. The outcrop Berea and Bentheimer core plugs with different permeabilities and different mineralogies (especially kaolinite content) were selected to conduct the displacement experiments. The core plugs were also aged with crude oil at elevated temperature to establish initial wettability states other than water-wet state.

This dissertation consists of seven chapters, four published papers and one internal report. Chapter 2 is dealing with an overview of the basic reservoir engineering concepts including different oil recovery mechanisms and processes. Chapter 3 has been devoted to the rock wettability and its effect on the efficiency of the enhanced oil recovery (EOR) processes. In chapter 4, the application and mechanisms of polymer and linked polymer solutions (LPS) for increased oil recovery is discussed. Chapter 5 describes the EOR potential of the low salinity water injection and the mechanisms proposed as the reasons for the low salinity effect (LSE). The main results obtained in this PhD study, and the related discussions are presented in chapter 6. Chapter 7 presents the concluding remarks and the recommendations for further studies to improve the understandings of the low salinity effect. The published papers and the internal report are presenting the main findings during the course of this PhD study.

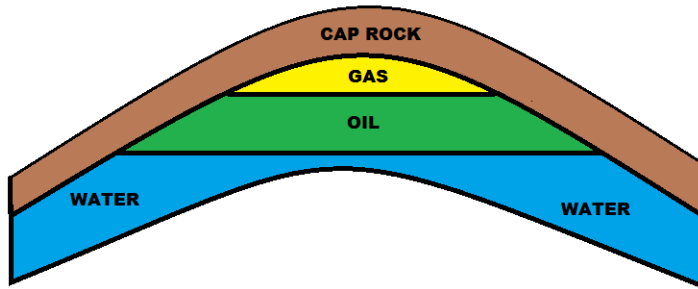
## CHAPTER 2

# BASIC RESERVOIR ENGINEERING CONCEPTS

### 2.1 Oil Migration and Accumulation

There are three necessary needs for an oil reservoir to be present: a source rock where the oil is generated, a reservoir rock where the oil is accumulated, and an impervious trap called cap rock, which works as a barrier to prevent escape of oil from the reservoir (Selley, 1985). After generation of oil through conversion of the organic material under catagenesis reaction in dominantly sedimentary rocks (source rock), due to the pressure gradients mainly governed by overburden compaction of the sediments, oil moves to and is accumulated in the reservoir rock.

The process of oil movement from the source rock to the reservoir rock is called primary migration. The reservoir rock must be porous and permeable in order to be a good candidate for oil accumulation. The movement of oil within the reservoir after accumulation is referred to as secondary migration. The main contributor to the secondary migration is buoyancy which is the result of density difference between gas, oil and water. The distinction between primary and secondary migration processes is based on petroleum migration through different pore sizes and lithology as well as the difference in state of petroleum distribution (Tissot and Welte, 1978). Figure 2-1 illustrates a typical anticlinal reservoir with gas cap at the top, oil at the middle and water at the bottom of the reservoir.



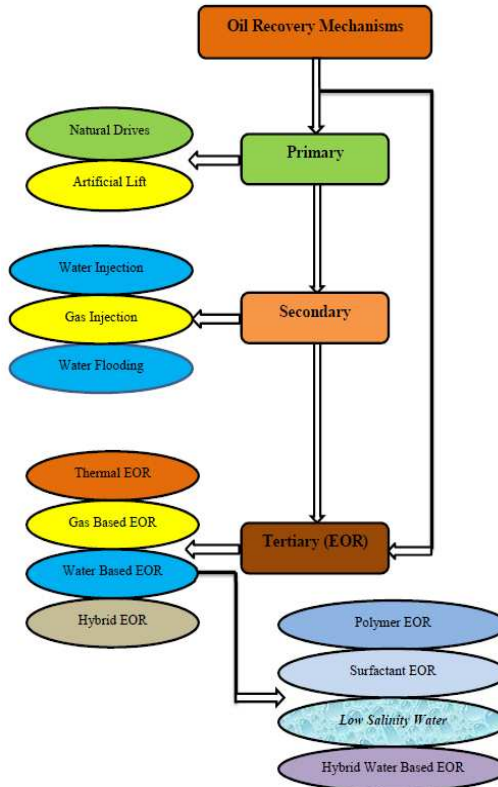
**Figure 2-1** Schematic of an anticlinal reservoir, with the illustration of fluid distributions based on density difference during secondary migration.

Most of the oil reservoirs are in sedimentary rocks. Sandstones, carbonates and shales are the sedimentary rock types. The reservoir rocks are dominantly in sandstones and carbonates (limestone, dolomite), while the shales normally behave as cap rocks in the reservoir. About 60 percent of world oil reserves are trapped in carbonate reservoirs and the remaining 40 percent are in sandstones. Compared to sandstone reservoirs which are highly homogeneous, the carbonate reservoirs are significantly heterogeneous and naturally fractured, and therefore the prediction of the behavior of such reservoirs is extremely challenging (Schlumberger, 2008).

## 2.2 Mechanisms of Oil Recovery

Oil is normally produced from the reservoir through three different stages, known as primary recovery, secondary recovery and tertiary recovery. Depending on the characteristics of the reservoir and its physical and chemical properties as well as recovery potential at each recovery stage, in some reservoirs, tertiary recovery techniques could be implemented right after the primary oil recovery. In some cases, especially for the extra heavy oil reservoirs, the primary and/or secondary recovery

stages would be skipped because of the low recovery potential of such reservoirs in these stages. In such cases, the tertiary recovery stage is the first and possibly the only stage for economical oil recovery (Lake, 1989). The general classification of oil recovery mechanisms is presented in Figure 2-2.



**Figure 2-2** General classification of oil recovery mechanisms.

### 2.2.1 Primary Oil Recovery

The primary oil recovery is a recovery stage that oil is produced from the reservoir by the natural displacement energy exists in the reservoir. The source of this natural energy comes from different driving forces depending on the characteristics of the oil

reservoir. These driving forces include depletion drive, rock and fluid expansion drive, water drive (aquifer drive), gas cap drive, gravity drainage drive, and combinations of these driving mechanisms (Ahmed and McKinney, 2005). These mechanisms will precisely be described in following subsections.

Early identification of the responsible drive mechanism(s) of the reservoir is crucial in order to determine the primary recovery potential of the reservoir and deploy a suitable plan for further development of the reservoir in secondary and tertiary recovery stages.

### **2.2.1.1 Depletion Drive**

Depletion drive mechanism which is also referred to as solution gas, dissolved gas or internal gas drive, is the dominant mechanism when the liberation and expansion of gas as a consequence of oil production and pressure decline is the main source of energy in the reservoir.

### **2.2.1.2 Rock and Fluid Expansion Drive**

In the reservoirs with a pressure above bubble point pressure, the main drive mechanism is the expansion of rock and fluids (water and oil) due to their compressibilities. These reservoirs which are also called under-saturated reservoirs, experience a rapid pressure decline because the compressibility of oil/water and rock is fairly low. This is also the reason for poor efficiency and low primary recovery factor in the reservoirs with this drive mechanism.

### **2.2.1.3 Water Drive**

In the reservoirs with water drive as principal driving mechanism, the source of driving energy is acquired from the aquifers bound the reservoir from the bottom (bottom drive) or laterally (edge water drive). In such reservoirs water fills the pore



spaces initially filled with oil, and displace oil upwards to production wells. Depending on the characteristics of the reservoir, water drive mechanism could result in very high oil recovery with very low pressure decline during the life time of the reservoir. These reservoirs are also subjected to higher water production which depend on production water/oil ratio (WOR), could affect the reservoir economic limits.

#### **2.2.1.4 Gas Cap Drive**

The driving energy in the gas cap drive reservoirs is provided by the expansion of the gas gap exists above the oil column in the reservoir. The gas cap itself could exist as primary or secondary gas cap. The expansion of gas cap results in displacing the oil downwards to production wells. The efficiency of the gas cap drive mechanism depends mainly on the size of the gas cap. The reservoirs with gas cap drive are subjected to high produced gas/oil ratio (GOR).

#### **2.2.1.5 Gravity Drainage Drive**

Gravity drainage or gravity segregation drive mechanism is a driving force for primary oil recovery caused by density differences between gas, oil, and water present in the reservoir. This drive mechanism is very slow since the long period of time is needed for segregation of fluids and obtaining equilibrium state in the reservoir. Therefore this mechanism results in high oil recovery in long term periods.

#### **2.2.1.6 Combination of Drive Mechanisms**

In many reservoirs it is possible to observe more than one responsible drive mechanism. For example, the reservoir with gas cap and aquifer is benefited from both gas cap drive and water drive mechanisms.

### **2.2.2 Secondary Oil Recovery**

Secondary oil recovery processes are the onset of intervention in the reservoir by applying external energies and forces in order to increase oil recovery. These processes basically include injection of water into the aquifer and/or injection of gas into the gas cap to maintain the original reservoir pressure or prevent rapid pressure decline and thereby supporting the water drive and/or gas drive mechanisms in the reservoir. It is highly recommended to start the pressure maintenance processes (water and gas injection) during the early production life of the reservoir to increase the recovery efficiency and prevent oil entrapment in water and gas invaded zones (Wilkinson et al., 2004).

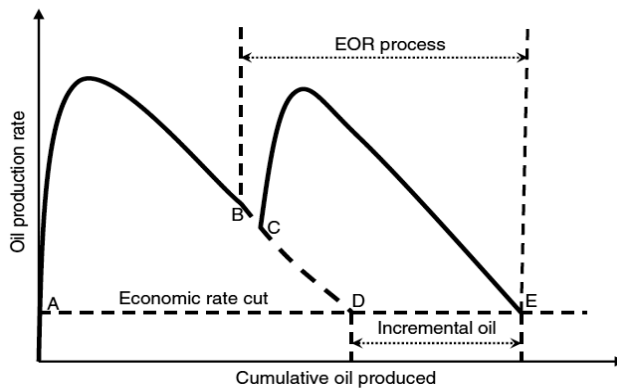
When water, instead of injection into the aquifer, is injected into the oil column in the reservoir, to physically push and displace oil towards the production wells, the process is called waterflooding. Waterflooding is by far the most extensively applied method to maximize oil production from the oil reservoirs. Due to the vast application of waterflooding during the secondary oil recovery stage, the term secondary recovery is almost synonymous with waterflooding. Similar to waterflooding, immiscible injection of gas into the oil column to displace oil to the production wells without resulting in oil swelling, oil viscosity reduction or favorable phase behavior, falls in the category of secondary oil recovery processes (Green and Willhite, 1998).

### **2.2.3 Tertiary Oil Recovery**

After primary and secondary stages of oil recovery, the reservoir drive mechanisms are not strong anymore. At this stage, physical displacement of oil with water and gas injection ends up with high WOR and/or GOR in production well, and the reservoir enters to its depleted phase of lifetime and further oil production would be uneconomic. In such a condition significant amount of oil still remains in the reservoir. Depending on the rock-fluid properties of the reservoir (rock type, permeability, oil viscosity, etc.) and involved drive mechanisms, usually one-third to more than-two third of oil remains trapped in oil reservoirs after primary and secondary recovery

stages. The current average global oil recovery factor (RF) is estimated to be around 35% (Babadagli, 2007). Increasing the recovery factor from current level of 35% to 45% would result in the addition of about one trillion barrel to world's oil reserve (Labastie, 2011).

The key solution and an important tool to extend the economic life time of oil reservoirs, is the application of tertiary oil recovery methods. Tertiary recovery methods, sometimes, are synonymously used with enhanced oil recovery (EOR) processes, however based on definition by Lake (1989); EOR processes are not necessarily restricted to tertiary recovery. Figure 2-3 schematically presents the manner that application of EOR methods would increase the oil production rate as well as extend the economic life time of the reservoirs.



**Figure 2-3** Schematic of incremental oil recovery from an EOR process (Sheng, 2011).

### 2.3 Enhanced Oil Recovery processes: Definitions and Classifications

As it was mentioned before, the term “tertiary recovery” targets the entrapped oil not produced after secondary recovery stage. This term, however, has been source of confusion for years. There are cases (e.g., heavy and extra heavy oils) where the three stage sequential oil recovery classification fails. In such cases tertiary stage recovery

methods are applied for reservoir development with omitting the primary and/or secondary recovery stages. Therefore the term “enhanced oil recovery” (EOR) is more accepted and widely used term rather than “tertiary recovery” (Green and Willhite, 1998).

Another confusion in this category, is the use of term “improved oil recovery” (IOR) as synonymous to EOR. Since early 1990s IOR has been used equivalently with EOR or even instead. Based on the definition by Stosur et al. (2003), IOR refers to any practice that improves oil recovery. IOR therefore includes EOR processes but can also include other practices such as additional technologies dealing with drilling (infill, directional, horizontal), production, operations, reservoir characterization and improved reservoir management (Lake, 2010). In contrast, Sheng (2011) believes that the terms EOR and IOR both refer to only reservoir processes, and any other practices independent of reservoir processes itself (e.g., infill drilling, horizontal wells, and reservoir management) should not be considered as EOR or IOR.

### **2.3.1 Enhanced Oil Recovery processes: Definitions**

Lake (2010) defines enhanced oil recovery (EOR) as “end of the road” that oil is recovered by injection of fluids not normally exist in reservoir. His definition covers all modes of oil recovery processes (drive, push-pull, and well treatments) and most oil recovery agents, but excludes waterflooding and all types of pressure maintenance practices. According to this definition EOR is not necessarily limited to a particular recovery stages (primary, secondary, or tertiary) during the reservoir life time.

EOR processes, according to definition by Green and Willhite (1998), include injection of a fluid or fluids into the reservoir to supplement the natural energy of the reservoir and displace oil to production wells. Moreover, the injected fluids interact with rock-fluid system in the reservoir through physical and chemical mechanisms or creation of thermal energy, which leads to improved conditions for oil recovery. These improved conditions could cover favorable interfacial tension (IFT), wettability

alteration to optimum condition, viscosity reduction, oil swelling or advantageous phase behavior.

Stosur et al. (2003) define EOR as the reservoir processes that produce oil not recovered by secondary methods. They state that the target for EOR is what is left in the reservoir and the focus is on rock/oil/injectant system and the interaction of viscous and capillary forces. By application of EOR processes, the ultimate purpose is to extend economical lifetime of the reservoir and delay the time of reservoir abandonment.

### **2.3.2 Enhanced Oil Recovery processes: Classifications**

Enhanced oil recovery processes could be classified in different ways depending on the mechanisms leading to increased oil recovery, and principal source of energy introduced to the reservoir during each EOR process. Therefore there is no unique classification of EOR processes in the literature and different authors have differently categorized these processes.

Donaldson et al. (1989) classified EOR processes to three main categories: chemical processes, thermal processes, and miscible displacement processes. On the other hand, Lake (1989) stated that, with few minor exceptions, all enhanced oil recovery methods fall into 3 distinct categories including, thermal, solvent, and chemical processes. He also believes that some EOR processes, for example foam injection, could fall into all three categories. Furthermore, the classification of enhanced oil recovery methods presented by Sheng (2011) arranges EOR methods into four categories including thermal recovery, chemical flooding, miscible flooding and microbial EOR. Obviously, these classifications are not conclusive enough and it is possible to combine different EOR processes from different categories in order to gain better EOR response from combined processes.

In this dissertation EOR processes were classified to four categories considering the dominant source of energy inherent to each process. These EOR categories are:

Thermal EOR, gas based EOR, water based EOR, and hybrid (combined) EOR processes.

Thermal EOR generally refers to the processes that are appropriate for the reservoirs with high oil viscosity and low API gravity (e.g., heavy/extra heavy oil). By thermal EOR methods, thermal energy is introduced to these reservoirs in order to reduce the viscosity of oil and enhance the ease of oil mobility towards the production wells. Cyclic steam stimulation (huff and puff), steam or hot waterflooding, steam assisted gravity drainage (SAGD), and in situ combustion are among the most widely applied thermal EOR processes during last few decades (Lake, 1989 and Carcoana, 1992).

In gas based or gaseous EOR processes the essential feature is the use of gas in displacing system. The process is miscible gas injection and involves the injection of hydrocarbon gases as well as non-hydrocarbon gases (e.g., CO<sub>2</sub>, N<sub>2</sub>, and flue gas). The miscible injection of gas results in oil swelling, oil viscosity reduction or favorable phase behavior and therefore increased oil recovery (Stalkup, 1983 and Green and Willhite, 1998).

Water based or aqueous EOR processes are those enhanced oil recovery methods which water is the fundamental element in the structure of the displacing fluid. In these processes the physicochemical properties of water are changed by addition of chemicals or by manipulating the salinity so that the new solution results in increased oil recovery. The most widely used chemicals are polymers and surfactants.

Polymers are added to water to increase the viscosity of the displacing fluid for improving the mobility ratio between displacing and displaced fluids in order to improve the sweep efficiency of the displacement process and decrease the fingering effect (Sorbie, 1991). Polymers are also cross-linked with a metal ion (usually aluminum citrate or chromium acetate) to perform a gel solution, and are applied for water/gas shut-off or blocking the thief zones for injected displacing fluids (strong gels) or microscopic sweep improvement purposes (linked polymer solutions). Application of polymers for EOR will be reviewed in Chapter 4.

Surfactants are added to displacing fluid in order to decrease the interfacial tension (IFT) between oil and displacing fluid and thereby assist in reduction of residual oil saturation ( $S_{or}$ ) entrapped in pore elements due to capillary forces in the reservoir. The addition of surfactant to the injected water results in weakening of the capillary forces by several orders of magnitude, and therefore causes mobilization and release of capillary trapped residual oil, and increased oil recovery (Lake, 1989).

Low salinity or smart water injection (LSW), which is the main area of interest in this study, is an emerging and promising EOR process and includes the dilution or change in the ion composition of injection brine. The salinity gradient between injection brine and connate water leads to increased oil recovery (Morrow and Buckley, 2011).

Hybrid EOR processes in this dissertation refer to the combination of different EOR processes from different EOR categories in order to create a process that results in additional oil recovery over individual processes. According to this definition, EOR methods such as hot water injection, water-alternating-gas (WAG) injection, steam-assisted-gravity-drainage (SAGD), foam-assisted-WAG (FAWAG) and etc. are hybrid processes, because they maintain the combination effect of thermal, water, and gas EOR processes.

Combination of water based EOR processes such as surfactant flooding and polymer flooding with low salinity water injection is emerging practice to benefit from the synergistic properties of different water based EOR techniques and increase the efficiency of oil recovery (Alagic and Skauge, 2010). Low salinity water and hybrid EOR processes will be discussed in more detail in Chapter 5.

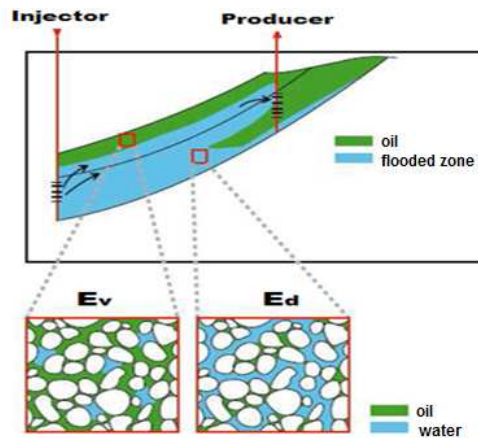
## 2.4 Oil Recovery Efficiency

The total recovery efficiency of any fluid displacement process is given as:

$$E = E_v E_d \dots\dots\dots(2.1)$$

where  $E$  is the total sweep (displacement) efficiency,  $E_v$  is the macroscopic or volumetric sweep efficiency, and  $E_d$  is the microscopic sweep efficiency (Craft et al., 1990 and Lake, 1989). Since both sweep efficiency terms are multiplied by each other, therefore they are equally important in estimation of recovery efficiency and, thus, oil recovery. Figure 2-4 depicts a schematic illustration of a reservoir with macroscopic and microscopic sweep efficiencies.

All EOR processes aim at increasing both macroscopic and microscopic sweep efficiencies. The effective and efficient EOR process is one that to lead the total oil recovery efficiency,  $E$ , to unity. That is, in such an EOR practice, both macroscopic and microscopic sweep efficiencies must approach to unity. Of course in real case EOR projects the total recovery efficiency is much lower than the unity.



**Figure 2-4** Schematic illustration of a reservoir with macroscopic and microscopic sweep efficiencies (NPD.no).

### 2.4.1 Macroscopic Sweep Efficiency

The macroscopic sweep efficiency refers to the quality of the contact between displacing fluid and the oil-bearing parts of the reservoir. Therefore, the frontal movement and stability, and the mobility of the displacing phase are controlled by the



macroscopic sweep efficiency. The macroscopic (volumetric) sweep efficiency, itself, could be reflected as the product of the areal sweep efficiency,  $E_s$ , and the vertical sweep efficiency,  $E_i$ , (Craft et al., 1990):

$$E = E_s E_i \dots \dots \dots (2.2)$$

The areal sweep efficiency in equation 2.2 is the area of the reservoir swept by displacing fluid divided by the total reservoir area. The vertical sweep efficiency is the pore space invaded by displacing fluid divided by the pore space enclosed in all layers behind the location of the leading edge of the front. The areal sweep efficiency is controlled by the geometry of the injection and production wells pattern, mobility ratio and heterogeneity of the reservoir. Vertical sweep efficiency is governed by variation in reservoir properties (e.g., permeability difference in different layers) and the mobility ratio between displacing and displaced fluids (Green and Willhite, 1998).

### **2.4.2 Microscopic Sweep Efficiency**

The microscopic sweep efficiency is concerned with the quality of residual oil mobilization by displacing fluid. Residual oil is trapped in pore elements in the reservoir through an interaction between different forces exist in pore scale. To mobilize the entrapped oil and displace it to the production well, the forces against the oil mobilization must be weakened, while strengthening the forces in favor of the mobilization. The most determining forces in the pore system governing the fluid movement and distribution in the reservoir are: capillary forces, viscous forces, and gravity forces.

#### **2.4.2.1 Capillary Forces**

Capillary forces play a major role in release or entrapment of residual oil in pore spaces and thereby increasing or lowering the recovery efficiency of the displacement process. Having enough knowledge about the significance of these forces is of great

interest for efficient EOR design. In dealing with multiphase systems of immiscible fluids, the effect of forces exist at surface and interfaces must be considered (Amyx et al., 1988).

The capillary forces in an oil reservoir are resulted from the combined effect of surface and interfacial tensions of the rock and fluids, pore size and geometry, and wetting characteristics of the system (Ahmed, 2000). In a multi-phase system (e.g., immiscible water and oil system) in capillary scale, whenever an oil/water interface is curved, the pressure will abruptly increase across the interface to balance the interfacial tension (IFT) forces. This pressure rise is called capillary pressure ( $P_c$ ). By convention,  $P_c$  is defined as the pressure in the non-wetting phase minus the pressure in the wetting phase. For an oil/water system the capillary pressure is always defined as the pressure in oil phase minus the pressure in water phase (Anderson, 1987-a).

The capillary Pressure ( $P_c$ ) is linearly proportional to the interfacial tension between the immiscible fluids and inversely proportional to the radii of curvature, as is given by Laplace (1806):

$$P_c = P_o - P_w = \sigma_{ow} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \dots \dots \dots (2.3)$$

where  $P_c$  is capillary pressure,  $P_o$  is the pressure in oil phase,  $P_w$  is the pressure in water phase,  $\sigma_{ow}$  is the interfacial tension between oil and water, and  $R_1$  and  $R_2$  are the curvature radii of interface between oil and water phases. The capillary pressure for a capillary tube containing oil and water as immiscible phases is expressed as:

$$P_c = \frac{2\sigma_{ow}\cos\theta_{ow}}{r} \dots \dots \dots (2.4)$$

where,  $\theta_{ow}$  is the contact angle measured through the water phase, and  $r$  is the radius of curvature of contact surface.

There are two types of capillary pressure processes: drainage and imbibition. In a drainage process, oil (non-wetting phase) enters to the porous media and displaces the water (wetting phase). The drainage process in hydrocarbon reservoir system simulates the migration of hydrocarbon to initially water saturated porous media. In imbibition

process, water substitutes the oil during spontaneous and forced imbibition processes (Anderson, 1987-a). The spontaneous and forced imbibition processes in capillary pressure curve are beneficial to evaluate the relative significance of capillary and viscous forces during fluid flow in porous media.

#### **2.4.2.2 Viscous Forces**

Viscous forces refer to the pressure gradients associated fluid flow through the reservoir and can be described by Darcy's Law (1856). The viscous forces vary with fluid viscosity, flow velocity, and the length of the flow path. In order for fluid flow through the porous media, the viscous forces must exceed the capillary forces.

#### **2.4.2.3 Gravity Forces**

Gravity forces are taken into account when the density difference between the displacing fluid and the displaced fluid is significant. Gravity forces result in upward movement of lighter fluids and downward movement of dense fluids leading to gravity segregation. In practice the oil reservoirs have pores of such a size that capillary forces are dominant and control the distribution of the fluids, while gravity forces have negligible effect on it. However, in a porous medium with very large pores, gravity could significantly deform the interfaces between fluids (Charles, 1981).

#### **2.4.2.4 Role of Capillary and Viscous Forces on Oil Entrapment and Mobilization**

During waterflooding practices and depending on the structure of the porous media and rock/fluid properties and interactions, considerable portion of oil is left behind and entrapped in pore elements of the reservoir resulting in limited recovery efficiency of the displacement process. The trapped oil is usually referred to as waterflood residual oil. The mobilization and production of this residual oil is the interest of application of

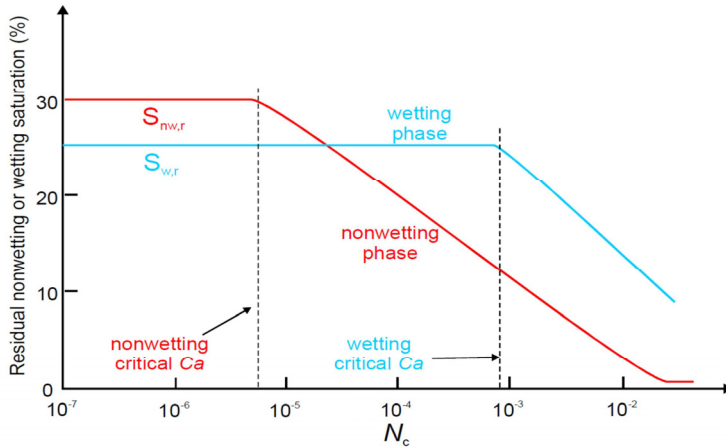
EOR processes. The capillary forces play a major role in trapping of residual oil and must be eliminated in order for higher recovery efficiencies.

The residual oil is achievable if the pressure gradient (viscous forces) due to flow of displacing fluid is enough to overcome capillary forces so that the discrete ganglia of entrapped oil is mobilized (Taber, 1969 and Morrow, 1979). Experimental studies also showed that the mobilization of discontinuous residual oil from pore elements is related to the ratio  $\frac{\Delta P}{L\sigma_{ow}}$ , where  $\Delta P$  is the pressure differential across the length of the porous medium,  $L$ , and  $\sigma_{ow}$  is the interfacial tension between oil and water (Taber, 1969). If the ratio of viscous to capillary force,  $\frac{\Delta P}{L\sigma_{ow}}$ , is increased sufficiently, almost all entrapped residual oil can be produced (Morrow, 1979). The most widely used formula to express the ratio between viscous and capillary forces is expressed as a dimensionless number, called capillary number,  $N_c$ , (Taber, 1969 and Chatzis and Morrow, 1981):

$$N_c = \frac{v\mu}{\sigma_{ow}} = \frac{K\Delta P}{\phi\sigma_{ow}L} \dots\dots\dots(2.5)$$

where  $v$  is the superficial (Darcy) fluid velocity,  $\mu$  is the viscosity of the displacing fluid,  $\sigma_{ow}$  is the interfacial tension between displaced (oil) and displacing (water) fluids,  $K$  is the effective permeability to displaced phase,  $\phi$  is the porosity of the porous medium, and  $\frac{\Delta P}{L}$  is the pressure gradient associated with Darcy velocity.

The plot of change in residual saturation of fluid (wetting or non-wetting) as a function of capillary number variation is called capillary desaturation curve (CDC) as is shown in Figure 2-5. The capillary number at which residual oil starts to be mobilized with increasing of capillary number is called critical capillary number ( $N_{cc}$ ).



**Figure 2-5** The relationship between the residual saturation of the wetting and nonwetting phases as a function of the capillary number (Lake, 1989, re-drawn by Cense and Berg, 2009).

The correlation of capillary number in Figure 2-5 suggests that a capillary number larger than  $10^{-5}$  is required for the mobilization of capillary unconnected and trapped non-wetting (oil) blobs. Based on the definition of capillary number, increasing the displacement flow rate, increasing the viscosity of displacing fluid (e.g., addition of polymer) and/or reduction of interfacial tension between displacing and displaced phases (e.g., addition of surfactant) may lead to decrease in capillary number and thus, the residual oil mobilization.



## CHAPTER 3

# WETTABILITY AND ENHANCED OIL RECOVERY

In this chapter, first the wettability will be defined and different wettability classes possible to be observed in petroleum reservoir rocks will be presented, and then the techniques used in oil industry for wettability measurement will be described. The chapter will be extended to discuss the wettability and contribution of surface forces as well as outlining the factors affecting the wettability of the reservoir rocks. The mechanisms used for wettability alteration and the role of rock wettability on oil recovery will be the last sections of this chapter, respectively.

### 3.1 Definition and Classification of Wettability

Wettability is defined as the desire of a solid to be in contact with one fluid in the presence of other immiscible fluid(s). That is, wettability is the tendency of one fluid to spread on a solid surface in competition with another fluid (Craig, 1971 and Anderson, 1986-a). Concerning the oil reservoir which the main interactions are between the reservoir rock/oil/brine systems, if the reservoir rock prefers to be in contact with brine then the rock is water-wet. In this case water as a spreading (wetting) phase will be present in smallest pores in the reservoir and will dominantly cover the rock surface as a film. In such cases, oil as a non-spreading (non-wetting) phase will occupy the center of larger pores while surrounded by water film. Similarly, in an oil-wet system, oil fills the smallest pores and will cover the rock surface as a film in larger pores, while water will occupy the middle of the larger pores. Therefore, whether the pore surface of an oil reservoir is water-wet or oil-wet is determined by the thickness of the water film between the rock surface and the oil phase (Hirasaki, 1991).

The wettability of rocks could be classified into two main categories: uniform wettability and non-uniform wettability. Uniform wettability could range from

strongly water-wet to strongly oil-wet conditions. If the rock has no strong preference to be in contact with either oil or water, then the rock maintains intermediate or neutral wettability (Anderson, 1986-a).

Non-uniform wettability can also be categorized into three different wettability classes: mixed-wet small (MWS), fractionally-wet (FW), and mixed-wet large (MWL). If smallest pores of the rock are oil-wet, then the rock is mixed-wet small. On the other hand, if the largest pores are oil-wet, then the rock is called mixed wet large. In some instances different parts of a rock sample may have preferences for different wetting phases. In such cases oil-wet or water-wet pores are uncorrelated to the pore sizes. The wettability in these cases is called fractional wettability (Salathiel, 1973 and Skauge et al., 2004).

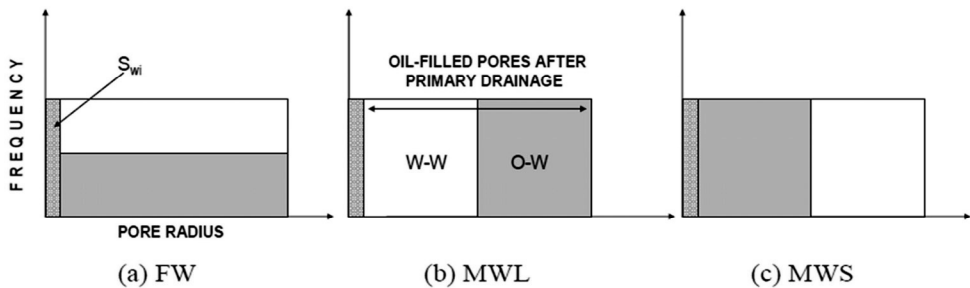
It must be noted that there is a conceptual difference between intermediate-wet system (no strong wetting preference to oil and water) and fractional or mixed-wet systems, where different parts of a rock show different wetting preferences (Anderson, 1986-a). The presence of different wettability classes is schematically presented in Figure 3-1.

For a long time, it was a general belief that all petroleum reservoirs are strongly water-wet. The reason was based on the fact that almost all clean sedimentary rocks are strongly water-wet. Moreover, the sedimentary rocks were deposited in aqueous environments and oil migrated to these rocks later. It was also assumed that connate water prevents polar components from oil to be deposited on the rock surface to change the wettability (Anderson, 1986-a).

Studies by Nutting in 1934 showed that unlike the general belief, it is possible to observe strongly oil-wet wettability state in petroleum reservoirs. Today, it is believed that clean sandstone tends to be strongly water-wet, but many sandstone reservoir rocks are mixed-wet (Mohanty and Miller, 1991). Carbonates however, tend to be more oil-wet (Schön, 2011). A worldwide study of the wettability of fifty oil producing reservoirs (Treiber et al., 1972) showed that 84% of carbonate reservoir rocks were oil-wet, 8% were intermediate-wet and only 8% were water-wet. It was in contrast to 50% oil-wet, 7% intermediate-wet and 43% water-wet for silicate reservoir



rocks. The similar study was performed by Chilingar and Yen in 1983, showing that 80% of the worldwide selected carbonated reservoir samples in their study were either oil-wet (65%) or strongly oil-wet (15%).



**Figure 3-1** Schematic presentation of different wettability classes, likely in a petroleum reservoir (Skauge et al., 2004).

Wettability is an important property of the reservoir rock concerning multiphase flow in porous media. This property influences the oil migration from the source rocks to the reservoir rocks as well as the efficiency of the oil recovery processes throughout the reservoir life. It plays a major role in controlling the location, flow, and distribution of fluids in a reservoir (Anderson, 1986-a, and Morrow, 1990). Therefore better understanding of different wettability states possibly present in a reservoir is crucial for planning an efficient development strategy for the reservoir.

### 3.2 Wettability Measurement Techniques

Several techniques have been presented and used in the literature to recognize different wettability states in reservoir rocks. These techniques include both qualitative and quantitative methods (Anderson, 1986-b). Qualitative wettability measurement techniques are among others, imbibition rates, relative permeability curves, capillary pressure curves, displacement pressure profile, oil recovery profile, and nuclear

magnetic resonance (NMR). In contrast to Anderson (1986-b) which classifies NMR technique as a qualitative method, recently, Chen et al. (2006) and Looyestijn (2008) quantitatively measured wettability by defining a wettability index determined from NMR logs based on the different relaxation characteristics of wetting and non-wetting phases, suggesting that quantitative information about rock wettability could be gained from NMR measurements. The most common used quantitative methods for wettability measurement include contact angle measurements (Neumann and Good, 1979), Amott-Harvey method (Amott, 1959), and USBM wettability method (Donaldson et al., 1969). This section will briefly describe each of these wettability measurement methods.

### 3.2.1 Contact Angle Measurements

Contact angle measurement is the most universal quantitative method to determine the wettability of the flat surfaces. In this method two parallel mineral plates are submerged in brine then a drop of oil is introduced between the plates. If the plates are displaced relative to each other, advancing and receding conditions can be observed. Since water advancing contact angles are relevant to waterflooding therefore these angles are considered as defining wettability (Anderson, 1986-b and Morrow, 1990).

Contact angle ( $\theta$ ) can vary between  $0^\circ$  and  $180^\circ$ . When  $\theta = 0^\circ$ , then water is the spreading fluid and the solid surface is strongly water-wet. If  $\theta = 180^\circ$ , oil spreads on solid and the surface is strongly oil-wet. When the solid surface has no preference for any of the fluids, then the contact angle is  $90^\circ$  and solid surface is neutral or intermediate-wet. The contact angles representing partially water-wet ( $0^\circ < \theta < 90^\circ$ ) or partially oil-wet ( $90^\circ < \theta < 180^\circ$ ) conditions and could be calculated by force balance at the contact angle as given by Young (1805) equation:

$$\sigma_{ow} \cos \theta_{ow} = \sigma_{os} - \sigma_{ws} \dots \dots \dots (3-1)$$

where  $\sigma_{os}$ ,  $\sigma_{ws}$ , and  $\sigma_{ow}$  are interfacial tension between oil-solid, water-solid, and oil-water, respectively.  $\theta_{ow}$  is the contact angle between oil and water. Similar equation

could be written to calculate the contact angle between gas and oil,  $\theta_{go}$ , and the contact angle between water and gas,  $\theta_{gw}$  as:

$$\sigma_{go} \cos \theta_{go} = \sigma_{gs} - \sigma_{os} \dots \dots \dots (3-2)$$

$$\sigma_{gw} \cos \theta_{gw} = \sigma_{gs} - \sigma_{ws} \dots \dots \dots (3-3)$$

where  $\sigma_{gs}$ ,  $\sigma_{go}$ , and  $\sigma_{gw}$  are interfacial tension between gas-solid, gas-oil, and gas-water, respectively. Since, measuring the fluid-solid interfacial tension is difficult (Chaudhury and Whitesides, 1991), therefore by eliminating the fluid-solid interfacial tensions, the following equation which is known as Bartell-Osterhof equation (1927) will be obtained as is shown by equation (3-4). Bartell-Osterhof equation describes the relationship between fluid-fluid interfacial tensions and contact angles in a three phase system.

$$\sigma_{gw} \cos \theta_{gw} = \sigma_{go} \cos \theta_{go} + \sigma_{ow} \cos \theta_{ow} \dots \dots \dots (3-4)$$

**3.2.2 Amott-Harvey Wettability Index**

This method for wettability measurement was introduced by Amott (1959). The basis for Amott test is the fact that the wetting phase will spontaneously imbibe into the core and displace the non-wetting phase. The method includes first displacing of water by oil using centrifuge or pump to reach initial water saturation ( $S_{wi}$ ) as is shown in Figure 3-2. This process is also called primary drainage process. After primary drainage and establishing the initial water saturation, the core plug is submerged in a cell filled with water for spontaneous (free) water imbibition. At the cease of spontaneous water imbibition the change in water saturation is  $\Delta S_{w_{spw}}$ . Then the core is removed from the imbibition cell and mounted in a core holder for further oil production through forced water imbibition process by use of centrifuge or under waterflooding by pump. The change in water saturation in forced water imbibition process,  $\Delta S_{w_{fw}}$ , is also recorded. Therefore the wettability index to water,  $I_w$ , can be calculated by

$$I_w = \frac{\Delta S_{w_{spw}}}{\Delta S_{w_{spw}} + \Delta S_{w_{fd}}} \dots\dots\dots(3-5)$$

Similarly, the wettability index to oil,  $I_o$ , can be defined by measuring the change in water saturation during spontaneous drainage,  $\Delta S_{w_{spd}}$ , followed by forced drainage,  $\Delta S_{w_{fd}}$ , processes:

$$I_o = \frac{\Delta S_{w_{spd}}}{\Delta S_{w_{spd}} + \Delta S_{w_{fd}}} \dots\dots\dots(3-6)$$

The difference in wettability indices to water and oil,  $I_w - I_o$ , is often used to express the wettability by a single number,  $I_{AH}$ , known as the Amott-Harvey wettability index (Morrow, 1990):

$$I_{AH} = I_w - I_o \dots\dots\dots(3-7)$$

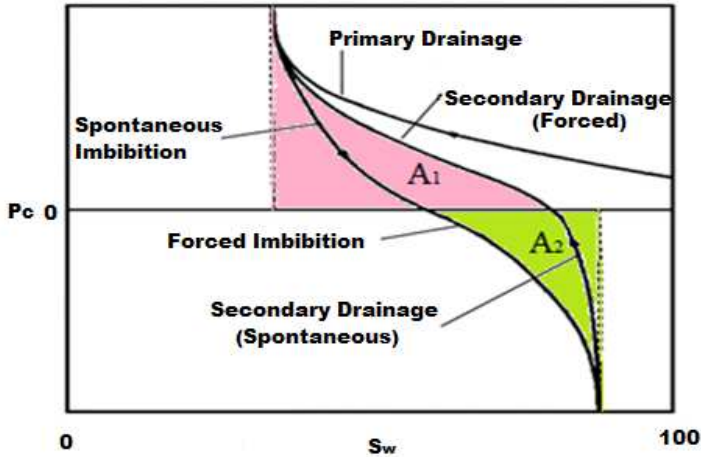
The index varies from +1 for strongly water-wet state to -1 for strongly oil-wet state. As Cuiec (1984) states, the porous media is called water-wet when  $+0.3 \leq I_{AH} \leq 1$ , intermediate-wet when  $-0.3 < I_{AH} < +0.3$ , and oil-wet when  $-1 \leq I_{AH} \leq -0.3$ . One important disadvantage of the Amott test is its slow nature of imbibition processes which could take weeks or even months to complete the imbibition process.

### 3.2.3 USBM Wettability Index

The USBM is the wettability index introduced by US Bureau of Mines and developed by Donaldson et al. (1969). The USBM wettability index ( $I_{USBM}$ ) requires capillary pressure data from forced water imbibition and forced oil drainage steps (usually measured by centrifuge) and is calculated using the following formula:

$$I_{USBM} = \text{Log}\left(\frac{A_1}{A_2}\right) \dots\dots\dots(3-8)$$

Where  $A_1$  and  $A_2$  are the area under forced oil drainage and forced water imbibition capillary pressure curves, respectively (Figure 3-2). If  $I_{USBM}$  is greater than 0, the core is water-wet, and if  $I_{USBM}$  is less than 0, the core is oil-wet. When  $I_{USBM} = 0$ , the wettability of the core is neutral.



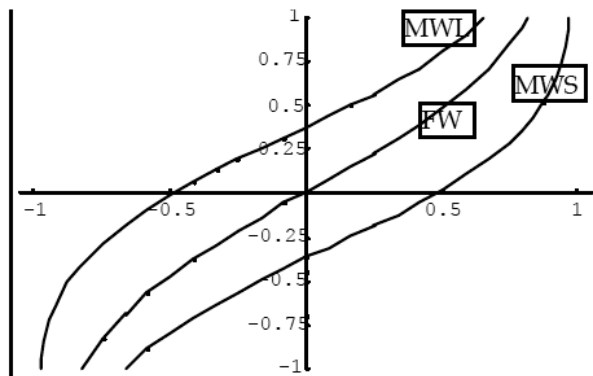
**Figure 3-2** Schematic of spontaneous and forced imbibition and drainage processes used for wettability measurement by Amott and USBM methods (modified from Morrow and Mason, 2001).

### 3.2.4 Fractional and Mixed Wettability Identification: $I_{AH} - I_{USBM}$ Plot

Combination of wettability indices obtained by Amott and USBM methods could increase the resolution of wettability measurements (Sharma and Wunderlich, 1985). Furthermore, the plot of USBM index versus Amott-Harvey index could give useful information about whether the system is fractionally-wet (FW) or mixed-wet (MW). Also based on this plot it is possible to distinguish mixed-wet large (MWL) systems from mixed-wet small (MWS) systems.

In their study of relationship between Amott-Harvey and USBM wettability indices, Dixit et al. (1998) suggested analytical relationships between  $I_{AH}$  and  $I_{USBM}$  indices for different possible wettability states. They distinguished between different wettability

states based on the fraction of oil-wet pores and their distribution within the pore space. In their simplified approach, a uniform pore-size was assumed; accessibility issues were neglected, and phase-trapping was not accounted for. The approach predicted  $I_{AH} = I_{USBM}$  for the fractional-wet case over the range  $-0.5 < I_{AH} < 0.5$ , independent of the type and range of pore size distribution (PSD) or relationship between pore size and volume. Moreover, they concluded that if the larger pores are assumed to become oil-wet, the USBM index will be greater than Amott-Harvey index, indicating more water-wet conditions. Snap-off in the water-wet pores also shifts  $I_{USBM}$  to more water-wet values without affecting the  $I_{AH}$  results. On the other hand, if smaller pores become oil-wet and snap-off is suppressed, then  $I_{USBM} < I_{AH}$  is predicted. Figure 3-3 presents the relationship between USBM-AH wettability indices for the simple analytical model with FW, MWL and MWS wettability types. The validity of the theoretical approach by Dixit et al. (1998) was confirmed by Skauge et al. (2007) where the wettability indices from the North Sea reservoir cores indicated that FW, MWL and MWS wettability states may exist in reservoirs.



**Figure 3-3** The relationship between USBM-AH wettability indices for FW, MWL and MWS wettability types (Dixit et al., 1998).

### 3.3 Wettability and Surface Forces

The wettability of minerals in contact with water and oil could be described by surface forces acting between solid-liquid and liquid-liquid interfaces in a three phase system. The stability of the wetting film on the solid surface and competition among two different liquid phases to reach the rock surface is governed by the force balance present among wetting phase, non-wetting phase, and the solid surface.

The surface forces have three main components including electrostatic, dispersion, and structural forces. The electrostatic forces are the result of osmotic pressure due to the excess counter-ions in the liquid interlayer and depend on brine salinity and pH, composition of crude oil and the mineral. The dispersion component includes the attractive forces result from the London-van der Waals interactions between liquid and mineral surface. The structural forces (e.g., hydration forces) which are also called solvation forces are caused by a change in liquid structure in conditions of confined geometry (Hirasaki, 1991, Basu and Sharma, 1996, Churaev, 2003, and Buckley et al., 1989). The structural forces are short-range interactions compared to the electrostatic and dispersion forces which are long-range interactions (Hunter, 2001).

#### 3.3.1 DLVO Theory

The DLVO theory was introduced to the aqueous colloid dispersions literature by Derjaguin and Landau (in the Soviet Union) and Verwey and Overbeek (in the Netherlands) in the 1930's and 1940's. This theory refers to the stability of the colloid system against aggregation and describes the interactions between attractive van der Waals forces (which lead to the aggregation) and repulsive electrostatic forces in the vicinity of charged colloidal surface in an electrolyte solution. The net interaction force,  $F_{net}$ , is:

$$F_{net} = F_A + F_R \dots \dots \dots (3-9)$$

where  $F_A$  is attractive van der Waals forces and  $F_R$  is repulsive electrostatic forces. The DLVO theory has been widely used in many studies, as a basis, to describe the stability of wetting film (Buckley et al., 1989 and Hirasaki, 1991).

It has been also proven that the DLVO theory is not sufficient to explain the results of wettability experiments with crude oils (Buckley et al., 1989, Basu and Sharma, 1996, Buckley, 1996, and Drummond and Israelachvili, 2002). Buckley (1996) addresses the limitations of DLVO theory which restricts the application of this theory in many practical situations. These limitations prevent application of DLVO theory for interactions with high salinity brines, non-DLVO forces, and interactions involving ions of valence higher than  $\pm 1$ . Basu and Sharma (1996) also presented experimental study which shows that surface forces computed from classical DLVO theory do not match the experimental data at higher brine salinity and pH.

### **3.3.2 Electrical Double Layer**

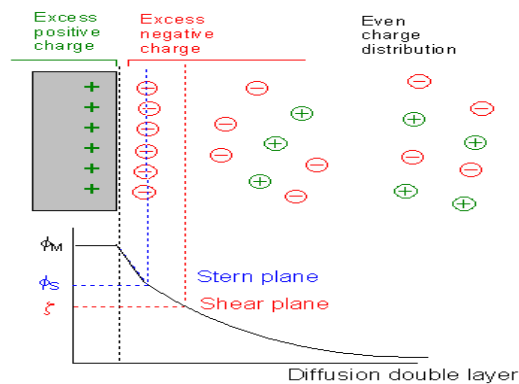
One of the important aspects of interfaces is the electrical charge separation at the interface which plays a crucial role in the stability of the wetting film. The possible origins of charge separation at aqueous interfaces are: preferential adsorption/desorption of lattice ions, specific adsorption of ions, ionization of the surface functional groups, isomorphic substitution, and accumulation/depletion of electrons. The mechanism of charge separation at the interface is so that the surface charge (coions) is neutralized by a layer in the solution containing excess of ions with charge opposite to that of the surface (counterions). The layer of surface coions and opposite counterions is called “electrical double layer” and was first presented by Helmholtz (1879) in a simple model which the counterions directly bind to the surface coions and neutralize the surface charges (Berg, 2010).

The Helmholtz model was later improved by Gouy (1910) and Chapman (1913) known as the Gouy-Chapman model and then by Stern (1924). The Stern model which is the more realistic explanation of physical situation at the interface, the double layer consists of an inner region (Stern layer) where the counterions are adhering to the



surface and are immobile, moving with the particle, and an outer region where the ions are mobile and form the diffuse layer. The plane through the center of the counterions in the stern layer is called “Stern plane”. The density of the counterions decreases with the distance from the surface until the electrical potential becomes zero. The ion concentration at such distance will be the same as the bulk electrolyte solution.

As it is shown in Figure 3-4, within the diffuse layer at a position very close to the surface, there is a “slip plane” or “shear plane” where the electrical potential in this plane is called “zeta potential”. The exact location of the shear plane is not known independently, however it is reasonable to assume that it is not far away from the Stern plane. Therefore zeta potential is assumed identical with the Stern potential and gives a measure of the potential at the beginning of the diffuse layer. The thickness of the electrical double layer is known as “Debye length” and was formulated by (Debye and Hückel, 1923). The Debye length oppositely varies with the salinity and the valence of ions present in the solution.



**Figure 3-4** Illustration of the Stern model of the electrical double layer.

### 3.3.3 Disjoining Pressure

In a three phase system of oil, water and mineral, when the two interfaces approach and interact with each other, the free energy of the system is influenced by the distance

separating the interfaces. The change in energy per unit area as a function of the distance between the interfaces is known as disjoining pressure,  $\Pi$ , and is given by augmented Young-Laplace equation as:

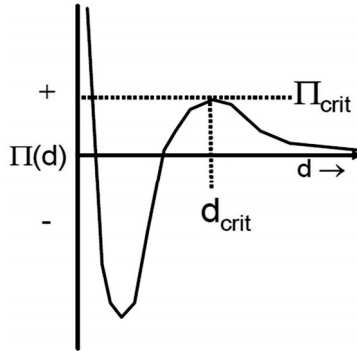
$$P_c = \Pi + 2\sigma_{ow}J \dots\dots\dots(3-10)$$

where  $P_c$  is the capillary pressure between wetting and non-wetting phases,  $\Pi$  is the disjoining pressure in the thin wetting film,  $\sigma_{ow}$  is the interfacial tension between water (wetting) and oil (non-wetting) phases, and  $J$  is the mean surface curvature. The disjoining pressure,  $\Pi$ , is composed of three types of forces: electrostatic forces,  $\Pi_e$ , dispersion forces,  $\Pi_d$ , and structural forces,  $\Pi_s$  (Buckley et al., 1989):

$$\Pi = \Pi_e + \Pi_d + \Pi_s \dots\dots\dots(3-11)$$

Based on equation 3-10,  $\Pi$  will be zero if the distance separating the interfaces is too large. In this case the equation 3-10 will be identical to the common Young-Laplace equation. On the other hand, if one of the bulk phases is a flat solid, the mean curvature of the fluid-fluid interface is zero where the interfaces are parallel, and therefore  $P_c = \Pi$  (Hirasaki, 1991).

If the value of the disjoining pressure is positive (repulsive), then for all values of the separation distance, the wetting film (water film) is stable and the mineral surface will remain water-wet. On the contrary, the wetting film will be unstable if the value of the disjoining pressure is always negative (attractive forces).  $P_c$  in this case exceeds the net forces due to disjoining pressure and surface curvature (Buckley, 1996). As depicted in Figure 3-5, the positive disjoining pressure increases as the interfaces approach each other (separation distance,  $d$ , decreases). The decrease in separation distance and increase in repulsive forces continues until a critical disjoining pressure,  $\Pi_{cr}$ , is reached at a given critical separation distance,  $d_{cr}$ . If the wetting film thins further by more decrease in separation distance, the disjoining pressure will abruptly change from positive to negative values (attraction), and the film will collapse. This will allow non-wetting phase (e.g., crude oil) to be in direct contact with mineral surface and possibly alter the wettability of the mineral surface.



**Figure 3-5** Schematic presentation of disjoining pressure isotherm.

### 3.4 Factors Affecting the Wettability

The initial wettability state of the reservoir rocks could be affected by various parameters through rock/brine/crude oil interactions and under the influence of reservoir pressure and temperature. The detailed discussion of parameters affecting the wettability of reservoir rocks is given by Anderson (1986-a). The important parameters include:

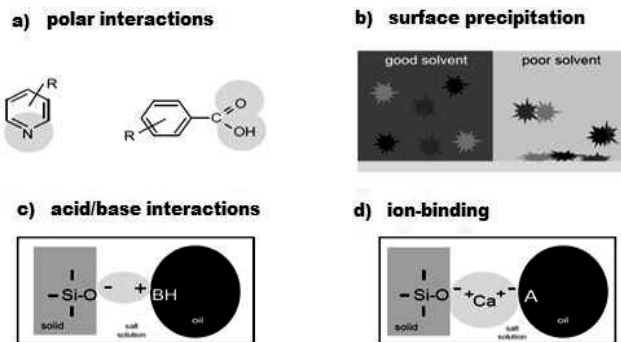
- Type, composition, and geometry of the minerals in the reservoir rocks
- Brine composition, salinity, and pH
- Crude oil composition (content of polar components)
- Composition, salinity, stability, and range of connate water saturation
- Reservoir pressure and particularly reservoir temperature
- Strength of surface forces at rock/brine/crude oil interfaces

### 3.5 Wettability Alteration Mechanisms

Several experimental and theoretical investigations have indicated that the water film separating crude oil from mineral surface is not always stable and the original water wetness of the rock could be altered by destabilization of the water film (Buckley et al.

1989, Hirasaki, 1991). The Stability of water films is governed by the disjoining pressure, which in turn depends on the compositions of COBR system and the applied capillary pressure (Mohanty et al., 1981). Therefore in order to destabilize and rupture the water film, the disjoining pressure must be overcome.

Different mechanisms have been proposed in the literature for the wettability alteration of rock surface through destabilization of water film by crude oil components during crude oil/brine/rock (COBR) interactions. The main categories of COBR interactions which lead to alteration of original water-wetness of the reservoir rock were reported by Buckley (1996) as: polar interactions, surface precipitation, acid/base interactions, and ion binding mechanisms, and are shown schematically in Figure 3-6.



**Figure 3-6** Categories of COBR interactions leading to wettability alteration (Buckley, 1996).

### 3.5.1 Wettability Alteration by Polar Interactions

Experimental evidences show that through direct contact between polar compounds (e.g., asphaltenes) in crude oil and mineral surface, these compounds could adsorb on mineral surface, especially clays. Parameters influencing the adsorption of the polar compounds include the type of clay and its cation exchange capacity, nitrogen content of the crude oil, and the solvent that dissolves the polar compounds (Buckley (1996).

The polar compounds of crude oil have a polar end and a hydrocarbon chain. The polar end contacts the mineral surface in the absence of water film between oil and surface, and the hydrocarbon chain extends to the liquid phase, causing the wettability shift to more oil wetness. If the polar compounds are soluble in water, they can diffuse through the water film to adsorb onto the rock surface. The contact between polar compounds of crude oil and mineral surface through diffusion could happen even at lower solubility in water. This process will result in greater attractive forces and destabilized water film which will make the surface more oil-wet (Morrow et al., 1973, Collins et al., 1983, and Kaminsky and Radke, 1997).

### **3.5.2 Wettability Alteration by Surface Precipitation**

Surface precipitation mechanism for wettability alteration is important when the crude oil is not a good solvent for its asphaltene compounds (Buckley, 1996). The consequence will be the inadequate dissolution of asphaltene compounds in the bulk oil and its precipitation onto the mineral surface. Several studies have shown that precipitation of asphaltenes could change the wettability of the rock surface to less water-wet condition (e.g., Jan et al., 1997, and Al-Maamari and Buckley, 2003). In their study, Jan et al. (1997) observed significant shift in wettability of sandstones due to the precipitation of asphaltenes at lower temperature. The decrease in wettability indices was dependent on the amount and type of asphaltenes adsorbed on the rock surface. The stability of asphaltenes is the dominant factor in overriding the different ionic interaction mechanisms and making rock surface more oil-wet through asphaltene precipitation (Al-Maamari and Buckley, 2003).

### **3.5.3 Wettability Alteration by Acid/Base Interactions**

Presence of connate water plays a crucial role in COBR interactions. The reason is that in the presence of water, both rock and crude oil interfaces become charged (Buckley, 1996). In such a condition polar compounds from both mineral and crude oil can act as

acids or as bases by giving up or gaining a proton (Cuiec, 1975). The acid/base dissociation interactions at the interfaces will affect the surface charges which in turn results in destabilization of the water film at rock surface. If the water film is strong enough, the water-wet condition will be unchanged. If the water film is weak and thin, then it will be collapsed and the adsorption of the ionized oil components onto the rock surface will shift wettability to oil-wet state.

### **3.5.4 Wettability Alteration by Ion-Binding Interactions**

The ion-binding mechanism involves bridging of divalent cations in the brine, such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , between negatively charged oil components and negatively charged sites on the solid surface. This mechanism is possibly the most dominant interaction which results in wettability alteration towards oil-wet condition in sandstone reservoirs containing acidic oil (Buckley, 1996).

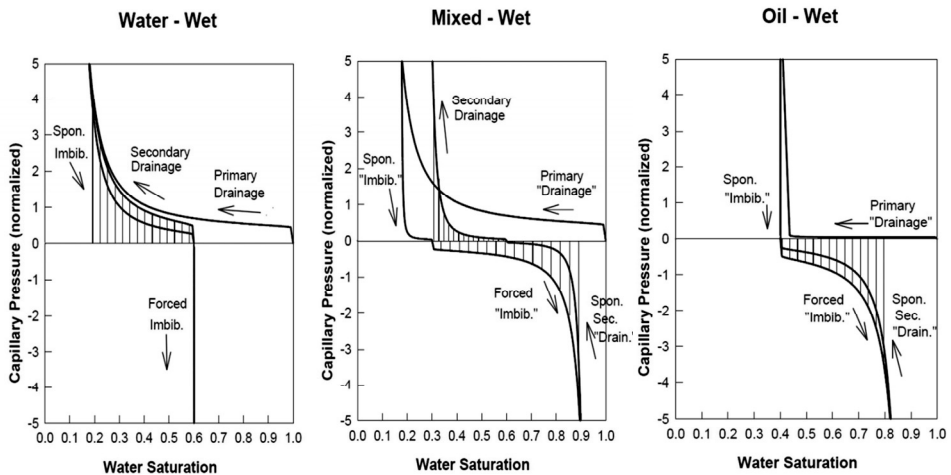
### **3.6 Wettability and Its Effect on Oil Recovery**

As it was mentioned before, wettability controls the location, distribution and flow of fluids through the porous media. Therefore, knowing the reservoir wettability state is crucial for the optimizing oil recovery. The oil/water wetting preference influences many aspects of reservoir performance, particularly in waterflooding and enhanced oil recovery techniques.

To understand the effect of different wettability states of the reservoir rock on oil recovery efficiency one needs to investigate the interplay between wettability and petrophysical properties of the reservoir, especially, the effect of wettability on capillary pressure, relative permeability of the different phases, and residual oil saturation.

### 3.6.1 Wettability and Its Effect on Capillary Pressure Curve

Whether the oil and water in the reservoir distributed in the larger pores or small pores is governed by the wettability of the porous media, and therefore, strongly affects the capillary pressure. If the rock is strongly water-wet, then the spontaneous imbibition of water will be the dominant process in displacing oil, and forced imbibition will not change the oil saturation significantly. On the other hand, for oil-wet cases, spontaneous imbibition of water will have negligible change in oil saturation, and oil will be dominantly displaced by forced imbibition process. As the rock surface becomes more neutrally wetted, the amount of wetting-fluid (water) imbibes during the spontaneous imbibition process would decrease due to the reduction in driving force. In such wettability condition, the non-wetting fluid (oil) would be able to enter smaller pores during the drainage process. Therefore, the transition zone and the area under the drainage capillary pressure curve are reduced. The reason for this is that less work is required for drainage as the wettability for wetting phase diminishes (Anderson, 1987-a). Figure 3-7 shows the relative effect of wettability on the shape of capillary pressure curves.

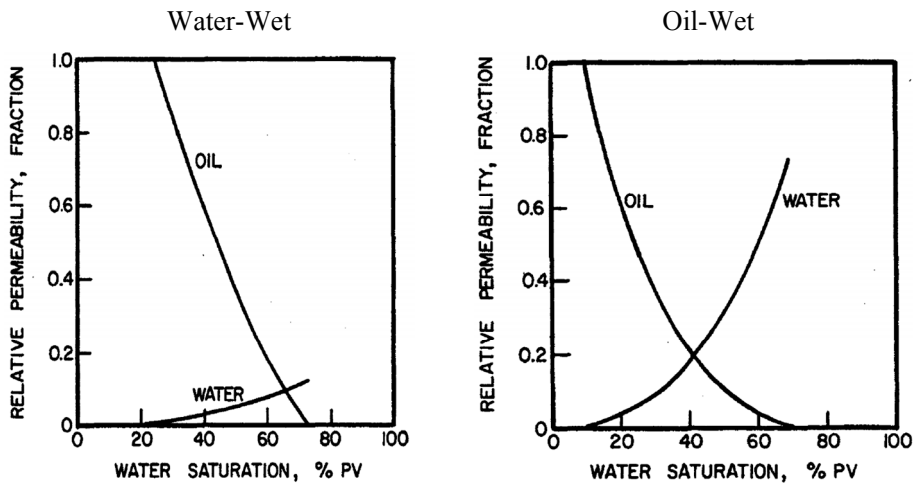


**Figure 3-7** Schematic illustration of capillary pressure variation with different wettability conditions.

### 3.6.2 Wettability and Its Effect on Relative Permeability Curves

Relative permeability is a direct measure of the ability of the porous medium to conduct one fluid when two or more fluids are present. This flow property is the composite effect of pore geometry, wettability, fluid saturation, and saturation history (Anderson, 1987-b).

Wettability state of the reservoir rock also affects the relative permeability of oil and water during two phase flow in porous media. This is due to the fact that wettability controls the location of the fluids in the pore scale. Depending on which fluid is at the centers of the large pores (non-wetting phase) and which one is covering the pore walls as film (wetting phase), fluids will have different flow paths. Wetting phase will flow as film on pore wall, while the non-wetting phase will flow at the center of the channels. This will result lower relative permeability for wetting phase compared to non-wetting phase as shown in Figure 3-8.



**Figure 3-8** Wettability impact on the profile of relative permeability of water and oil (Anderson, 1987-b).



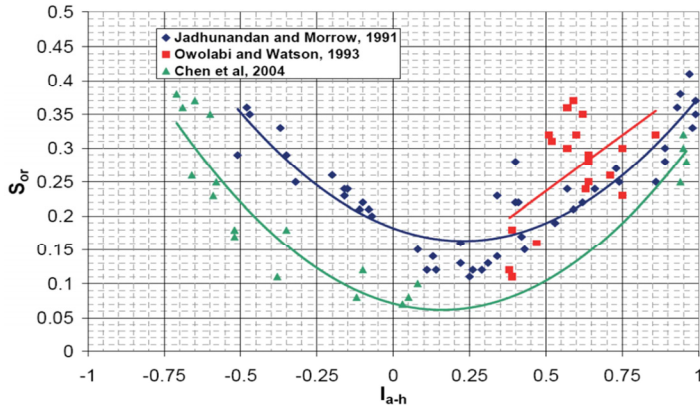
### 3.6.3 Wettability and Its Effect on Residual Oil Saturation

Wettability of the reservoir is a major parameter controlling the oil production profile during waterflooding, the breakthrough of injection water, the final oil recovery, and the residual oil saturation ( $S_{or}$ ) trapped in the pore structure. Therefore identifying the wettability of the reservoir will lead to appropriate implementation of production practices in order to improve the economy of the project.

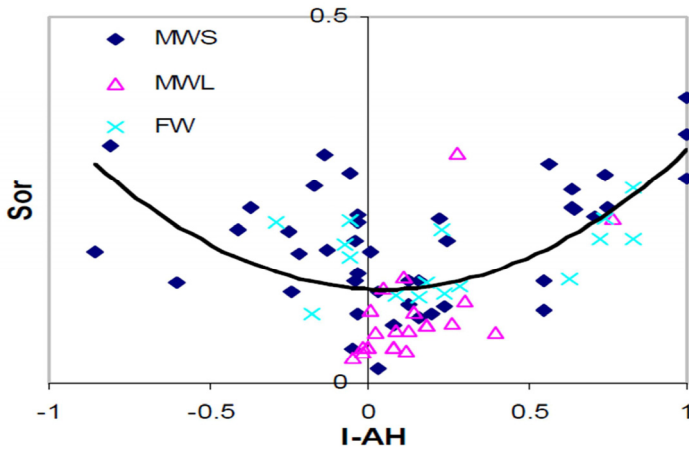
Traditionally it was believed that waterflooding in water-wet systems results higher oil recovery than oil-wet systems (Newcombe et al., 1955, and Coley et al., 1956). In strongly water-wet systems, water breakthrough occurred relatively later compared to oil-wet systems and most of oil produced before breakthrough and only limited oil production was observed after the breakthrough. For strong oil-wet systems the opposite was observed. The breakthrough occurred earlier, limited oil produced before breakthrough and most of oil was produced after substantial amount of water injection after breakthrough. The reason for efficient oil displacement in water-wet systems was related to the strong preference of rock surface for water and associated strong capillary imbibition forces in water-wet systems (Morrow, 1990).

The effect of wettability on oil recovery efficiency of the waterflooding process and residual oil saturation has been extensively investigated during the past decades (Kennedy et al., 1955, Moore and Slobod, 1956, Owolabi and Watson, 1993, Jadhunandan and Morrow, 1995, and Skauge and Ottesen, 2002). These studies indicate that despite the traditional belief, the recovery efficiency of waterflooding increases and the residual oil saturation decreases as the wettability of the porous media shifts from the strongly water-wet or oil-wet states to the intermediate wetting conditions (Figure 3-9 and Figure 3-10).

The reason for lower recovery efficiency and higher residual oil in strongly water-wet porous media is the remaining of oil in the larger pores, where it can be snapped off, or disconnected from a continuous mass of oil by water film, and therefore trapped in pore structure of the porous media.



**Figure 3-9** Effect of wettability on residual oil saturation for Berea Sandstone (Anderson, 2006).



**Figure 3-10** Effect of different intermediate wettability classes on residual oil saturation for North Sea Sandstones (Skauge and Ottesen, 2002).

# CHAPTER 4

## POLYMER AND LINKED POLYMER SOLUTIONS FOR EOR

This chapter will briefly describe the use of polymer and linked polymer solutions in the enhanced oil recovery applications. First, a short introduction to polymer flooding will be provided and the factors affecting the efficiency of a polymer flooding project will be presented. Then the mechanisms involved in polymer flooding process and the concept of inaccessible pore volume will be introduced and finally the application of cross-linked polymer solutions with focus on the application of linked polymer solutions (LPS) will be revisited.

### 4.1 Enhanced Oil Recovery by Polymer Flooding

Polymer flooding includes the addition of large molecular weight water-soluble polymers to injection water in order to increase the viscosity of displacing fluid and improve the adverse mobility ratio. The result will be the dampening of the viscous fingering effect and better sweep efficiency of the displacement process.

Two main types of polymers are more generally used for EOR purposes: synthetically produced partially hydrolyzed polyacrylamides and biologically produced polysaccharides such as xanthan biopolymers. Polyacrylamides are long molecules with a small effective diameter. Therefore they are very sensitive to mechanical shear especially at high flow rates which result in viscosity reduction. These polymers are also sensitive to saline conditions. At high brine salinity, polyacrylamides tend to make the polymer molecules curl up and lose their viscosity-building effect. Unlike polyacrylamides, xanthan polymers are more tolerant to mechanical shear and saline conditions but sensitive to biological degradation in the reservoirs. Both polymers are susceptible to high temperature environments and oxidation by dissolved oxygen in

the injected water, and do not provide long-term stability in such conditions (Sorbie, 1991, and Green and Willhite, 1998).

Xanthan biopolymer solutions reduce the mobility of the injected fluid by increasing its viscosity. These biopolymers are not retained on rock surfaces and therefore propagate through the porous media more readily than polyacrylamides. In contrast, the mobility of injected fluid containing polyacrylamide polymers is reduced by a combination effect of viscosity increase and rock permeability decrease due to the polymer retention (Green and Willhite, 1998).

Many factors and parameters could affect the efficiency of a polymer flooding process either positively or negatively. These parameters could be related to the characteristics of the polymer solution itself, or could be related to the technical, economical and reservoir conditions. The parameters that affect the characteristics of polymer solution and its physico-chemical behavior include but not limited to polymer molecular weight, concentration, degree of hydrolysis and viscoelastic properties of the polymer solution, salinity and pH of make-up brine solution. The lower the salinity and higher the molecular weight and concentration of polymer, the better will be the improved displacement efficiency. Care, definitely, should be taken to avoid technical and economical limitations when preparing polymer solutions with high molecular weight or high polymer concentrations (Sorbie, 1991).

Factors related to technical, economical and reservoir conditions include injectivity problems and shear dependence behavior of polymer, polymer retention/adsorption level and its economic considerations, connate water salinity and pH, rock wettability, and temperature of the reservoir, viscosity of the displaced oil, and finally amount of mobile oil saturation left after waterflooding.

The initial Wettability state of the reservoir rock has crucial impact on the performance of polymer flooding process. The experimental investigations in this work and from the literature indicate that polymer flow behavior in the porous media including pressure build up, polymer retention due to adsorption mechanism,

resistance factor, and residual resistance factor are considerably different for different wettability states.

During a polymer flood in an intermediate-wet reservoir, the injected polymer will interact with significant portions of oil-wet rock. In this case, it is possible that rock wettability will have a considerable effect on polymer adsorption. The adsorption of crude oil components reduces the adsorption sites on rock surface, and therefore, the tendency of polymer molecules to interact with the rock surface is decreased. Higher polymer adsorption on water-wet rock surfaces results in a poor sweep efficiency of polymer solution as a result of retention in porous media and intensification of the trapping of oil in the blocked pores (Sorbie, 1991, Broesta, et al., 1995, Chiappa, et al., 1999).

## 4.2 Mechanisms of Enhanced Oil Recovery by Polymer Flooding

The mechanisms in which the polymer flooding leads to improved volumetric sweep efficiency over waterflooding are outlined by Needham and Doe (1987) as: improving the oil fractional flow, optimizing the mobility ratio of displacing to displaced fluids, and microscopic diversion of displacing fluid to un-swept regions of the reservoir.

### 4.2.1 Polymer Flooding and Fractional Flow Theory

After breakthrough, water and oil flow simultaneously through the porous media until the residual oil saturation is reached. This process depends on relative permeability and viscosity of each phase and is described by fractional flow theory presented by Buckley-Leverett (1942):

$$f_w = \frac{q_w}{q_w + q_o} = \frac{1}{1 + \frac{k_{ro}\mu_w}{k_{rw}\mu_o}} \dots\dots\dots(4-1)$$

and

$$f_o = 1 - f_w \dots\dots\dots(4-2)$$

where  $f_o$  and  $f_w$  are oil and water fractional flow,  $q_o$  and  $q_w$  are oil and water flow rates,  $k_{ro}$  and  $k_{rw}$  are oil and water relative permeabilities, and  $\mu_o$  and  $\mu_w$  are the viscosity of oil and water, respectively.

The addition of polymer to the injection water will increase the viscosity of water and therefore will reduce the permeability to water according to Darcy’s Law. Thus, the fractional flow to water,  $f_w$ , will be decreased while the fractional flow to oil,  $f_o$ , will be increased resulting in improved rate of oil recovery.

It is to be noted that based on the equation 4-1, the positive effect of polymer on oil fractional flow applies only when there is enough mobile oil saturation available and the oil relative permeability is not zero. Otherwise, regardless of any achievable water viscosity, the change in oil fractional flow will be insignificant.

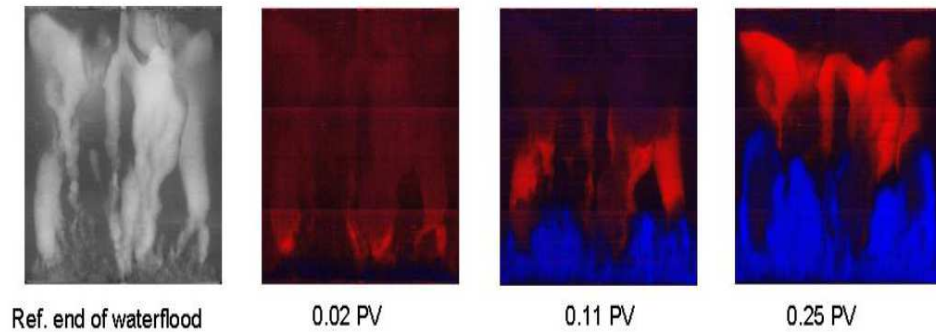
**4.2.2 Polymer Flooding and Mobility Modification**

One of the major drawbacks during waterflooding process is the viscous fingering effect, especially when dealing with heavy viscous crude oils. The fingering effect results when the mobility of the displacing fluid is greater than that of the fluid is displaced. The fingers form at different scales from pore scale to sample scale (Doorwar and Mohanty, 2011).The fingering will cause early breakthrough of the injected water, while the considerable portions of the reservoir are still un-swept (Figure 4-1). In order to sweep oil from the un-swept zones the mobility of the injected water must be reduced. The relative mobility of the displacing phase to the mobility of the displaced phase is termed mobility ratio and was defined by Craig (1971) as:

$$M = \frac{\lambda_w}{\lambda_o} = \frac{k_{rw}(S_{or})\mu_o}{k_{ro}(S_{wi})\mu_w} \dots\dots\dots(4-3)$$

where  $\lambda_w$  and  $\lambda_o$  are the mobility of water and oil phases, respectively. As the equation 4-3 indicates, by increasing the viscosity of water, due to the addition of polymer, the mobility of water and therefore the mobility ratio, M, will be decreased.

The better displacement efficiency and higher oil recovery would be gained when the optimum favorable mobility ratio is achieved, i.e.  $M \leq 1$ .



**Figure 4-1** Post waterflood polymer injection and improved displacement efficiency. The left hand gray picture is showing water fingered channels at the end of waterflood, red is the oil saturation change and blue is the water saturation change during polymer flooding (Skauge et al., 2012).

### 4.2.3 Polymer Flooding and Microscopic diversion

The application of polymer solutions to improve oil fractional flow behavior or to modify the mobility ratio is much beneficial if it is practiced during the early stages of the waterflooding process, before waterflood residual saturation is reached. Application of polymer solutions to watered-out reservoirs with immobile oil will not result in considerable oil recovery through fractional flow improvement or mobility modification mechanisms. However, flow of high viscosity polymer solution through the previously water flooded pores and channels will reduce permeability in swept zones and will build up resistance to flow in these zones. The consequence will be the diversion of displacing fluid to new un-swept zones and mobilization of residual oil.

Two important terms are widely being used in the literature of polymer flooding to define the significance of resistance build up during polymer flooding. Resistance factor,  $F_r$ , is defined as the ratio of mobility of water to the mobility of polymer

solution. Residual resistance factor,  $F_{rr}$ , is the ratio of water permeability before polymer flooding to the water permeability at post polymer flooding condition. These parameters are the measure of apparent viscosity of polymer solution during the flow in porous media and polymer retention on rock surface, respectively (Sorbie, 1991).

#### **4.2.4 Other Mechanisms**

Since the capillary number is not significantly increased during polymer flooding, therefore many argue that if the polymer solutions are capable of reducing residual oil saturation over waterflooding at microscopic level. Recently, this subject has been the interest of experimental investigations and theoretical interpretations to show that whether polymer flooding could both improve displacement efficiency, and also reduce the residual oil saturation, or it only results in improved displacement efficiency (Wang et al., 2000, Yin et al., 2006, Wu et al., 2007, Cheng et al., 2008, and Huh and Pope, 2008).

Huh and Pope (2008) reviewed the literature on measurements of residual oil saturation by polymer flooding and concluded that the residual oil saturation from polymer flooding practices could be lower than that of waterflooding under certain conditions such as the presence of mobile oil at the end of waterflooding when polymer solution is injected. They emphasize that tertiary mode polymer flooding in a homogenous water wet system does not mobilize the waterflood residual oil. However, secondary mode polymer flooding gives reduction in residual oil saturation by improving the sweep efficiency over waterflood.

Cheng et al. (2008) also investigated the mechanisms of polymer enhanced oil recovery and reported that the results of polymer flooding experiments on four natural cores showed 12% increased oil recovery over water injection. They attributed the increased oil recovery to both improved sweep and displacement efficiencies. They explained their findings by the theory of molecular motion and highlighted the effect of collisions and oscillations between the molecules of polymer solution and oil phase in mobilization of immobile oil.



Sheng (2011) points out another mechanism of increased oil recovery by polymer flooding over waterflooding which is related to the polymer viscoelastic behavior. The interfacial viscosity and therefore shear stress between polymer and oil is greater than that of oil and water. Moreover, since polymer has viscoelastic properties, in addition to shear stress, there is also a normal stress between oil and polymer solution. Therefore, polymer applies a larger pull force on trapped oil droplets and oil films. Thus, “pushed and pulled” out of oil from dead-end pore elements will result reduced residual oil saturation and improved sweep efficiency.

### **4.3 Inaccessible Pore Volume Concept**

The inaccessible pore volume (IPV) indicates the portion of the pore volume that the entrance radii of the pore elements are smaller than the polymer particles (especially when a high molecular weight polymer is used). This volume is mostly occupied by the irreducible or connate water. Inaccessibility of this volume to the polymer would result in the absence of a highly mobile connate water bank, and therefore, the polymer solution would not displace the connate water. This will allow polymer solution to more readily advance and displace oil faster than that of prediction on the basis of pore volume (Dawson and Lantz, 1971). The consequence is a better sweep efficiency of the polymer solution and increased oil recovery. The experimental study by Dawson and Lantz also indicated that about one third of the pore volume in the rock samples was not contacted with the polymer solution, thus was the inaccessible pore volume. This would benefit the polymer flooding process in field scales from the economical point of view. Less contact between rock surface and polymer solution results in less polymer adsorption/retention and therefore the amount of polymer needed for the flooding process will be reduced. One disadvantage associated with inaccessible pore volume is that movable oil droplets in smaller pore will not be contacted with polymer solution and will therefore remain as residual oil saturation.

#### 4.4 Cross-linked Polymer Solutions

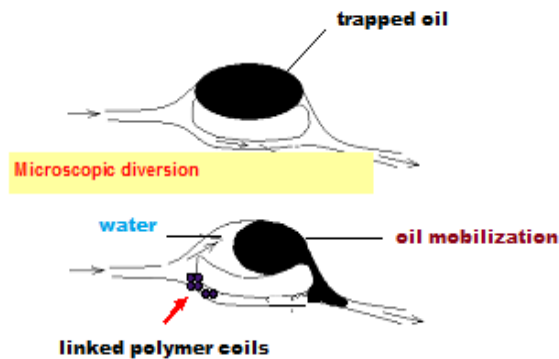
Application of polymer solution for improved oil recovery is not only limited to the improvement in oil displacement and the mobility modification processes. Many reservoirs, due to their geological complexity and heterogeneous characteristics, suffer from high unwanted water and/or gas production in oil wells, or loss of injected EOR solutions in injection wells as a result of presence of thief zones such as high permeable streaks and fractures. In order to improve the economy of the production/injection processes and increase oil production, it is necessary to shut-off the unwanted water/gas production and block the thief zones to prevent the loss of injection fluid.

Gelled polymer solutions have been used widely during the last 30 years as a solution for above-mentioned problems. This process is known in the literature as gel treatment, conformance control, profile modification, in-situ permeability modification, and disproportionate permeability reduction (DPR) process (Huang et al., 1986, Sydansk, 1988 and 1990, Sydansk and Southwell, 2000, Seright and Liang, 1995, Perez et al., 1997, and Willhite and Pancake, 2008).

The gel treatment process consists of injection of an aqueous solution of moderate viscosity containing high molecular weight polymer, usually hydrolyzed polyacrylamide (HPAM), cross-linked with a cross-linking agent such as trivalent cations (e.g.,  $\text{Cr}^{+3}$  or  $\text{Al}^{+3}$ ). The polymer and cross-linker react to form a three dimensional immobile gel structure, which blocks the high permeability zones in the reservoir or reduces the water permeability of such zones. This will result in reduced water/gas production in oil wells and improved displacement efficiency of EOR fluids in injection wells.

The disadvantage associated with immobile strong gels is the quick in-situ gelation time for these gel systems and related high resistance build up against the flow, which prohibits long term gel placements and in depth permeability modifications. Thus, the design of gel solution should be so that to avoid prematurely gelation of gel solution near the wellbore and to allow gel placements deeper in the reservoir.

During the last two decades, numerous experimental studies have been devoted to formulate a cross-linked gel solution for in-depth reservoir treatments. The aim is to improve both conformance and oil mobilization by flow diversion in un-swept parts of the reservoir (Figure 4-2). The new gel systems are named in the literature as weak gels, colloidal dispersion gels (CDG), preformed particle gel (PPG), and linked polymer solutions (Mack and Smith, 1994, Dong et al., 1998, Wang et al., 2003 and 2008, Skauge et al., 2005, Chang et al., 2006, Diaz et al., 2008, Spildo et al., 2009, Ponnapati et al., 2011, and Skauge et al., 2011). The detailed background for these new cross-linked gel systems has been presented in Paper 4.



**Figure 4-2** The proposed mechanism for oil mobilization by log-jamming effect during LPS injection (Bolandtaba et al., 2009).



## CHAPTER 5

# LOW SALINITY WATERFLOODING

This chapter will cover the low salinity waterflooding (LSW) process, which as emerging water based EOR method, has been the center of EOR research attention in recent years. First a short background about low salinity (LS) injection will be provided and the laboratory and field trial observations of low salinity effect (LSE) will be presented. Later the mechanisms proposed to be the possible reasons for increased oil recovery by LS will be introduced and the main agreements and disagreements among researchers will be reviewed. The last part of this chapter will discuss combined low salinity polymer flooding as a new hybrid EOR process.

### 5.1 Low Salinity Waterflooding: History and Observations

#### 5.1.1 Laboratory and Field Observations

Waterflooding is by far the most widely practiced improved oil recovery process with more than 100 years of implementation history. During this century-long period of waterflooding, less attention has been granted to the chemistry of the injection water and its effect on waterflooding performance. The first documented low salinity injection trial goes back to about 70 years ago, when Smith (1942) investigated the effect of fresh water injection into the cores containing Kansas crude oil, and compared the results with the brine injection. The results showed not only no benefit with fresh water compared to the brine injection, but the overall oil recovery was less for fresh water than the brine. In 1959, Martin examined the impact of injection water salinity on oil recovery efficiency by comparing fresh and saline water injection into the sandstone cores. He observed an increased oil recovery by injection of fresh water compared to the saline water. He attributed the increased oil recovery to the swelling, emulsification and migration of the clay particles. Bernard (1967) performed waterflooding experiments with fresh water and sodium chloride (NaCl) brine as the

injection fluids. The results indicated higher oil recovery when fresh water was injected at both connate water saturation and at residual oil saturation. An increased oil recovery in the experiments was associated with increase in pressure differentials. Therefore, he related the observations to the improved microscopic sweep efficiency due to the fines release and migration and possible pore throats blockage. The experimental works performed by Smith (1942), Martin (1959), and Bernard (1967) did not capture the attention of the EOR/IOR researchers until the 1990's.

During the 1990's Morrow and co-workers extensively studied the effect of crude oil/brine/rock (COBR) interactions including salinity gradient and wettability shift on improved oil recovery (Morrow, 1990, Jadhunandan and Morrow, 1995, Yildiz and Morrow, 1996, Tang and Morrow, 1997 and 1999, and Yildiz et al., 1999). Jadhunandan and Morrow (1995) reported experimental results based on more than 50 laboratory waterflood experiments performed on Berea sandstone cores. They showed dependency of rock wettability on brine salinity and composition as well as dependency of oil recovery on wettability state of the porous media. Low salinity effect also was observed by Yildiz and Morrow (1996) where they showed that Berea sandstone aged with Moutray crude oil gave 5.5% higher oil recovery using 2% CaCl<sub>2</sub> brine compared to 4% NaCl + 0.5% CaCl<sub>2</sub> brine. The imbibition tests also indicated that the high salinity brine gave less water-wet conditions than the low salinity brine.

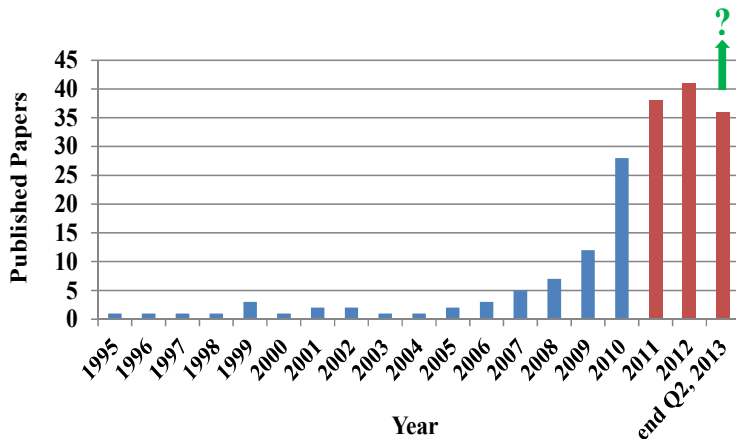
Increased oil recovery with lowering the salinity of the injection water was also observed by Tang and Morrow (1997). They observed wettability shift to more water-wet state by lowering the brine salinity. Moreover, Tang and Morrow (1999) identified the necessary conditions for low salinity effect (LSE) as:

- Presence of connate water
- Presence of significant clay content in the rock
- Mixed-wet wettability state of the rock

Sharma and Filoco (1998) studied the effect of brine salinity and crude oil properties on oil recovery and residual oil saturation and found that presence of polar

components in the oil phase and presence of divalent ions in the connate water are also important necessary conditions for LSE to be observed.

The publications by Morrow and his colleagues on low salinity effect was a major breakthrough to attract the attentions both in laboratory EOR research and field trials for smart waterflooding, and concentrate on better understanding of waterflooding in oil reservoirs. Since then, many publications on low salinity effect ranging from promising observations and possible failures, to presenting the mechanisms believed to be the reasons for LSE, were flowed into the literature. This growth in the interest for low salinity waterflooding (LSW) was even boosted more as LSW was designated as an IOR process at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, since 2006 (Morrow and Buckley, 2011). Figure 5-1 indicates the number of publications reporting low salinity effect during last two decades, showing continuous interest for this water based enhanced oil recovery process.



**Figure 5-1** Continuous increased interest for LSW as water based EOR process (updated from Morrow and Buckley, 2011).

### 5.1.2 Secondary versus Tertiary Mode Low Salinity Injection

Low salinity waterflooding has been tested in both secondary and tertiary modes to assess the effect of injection timing on LSE. In secondary mode practice, low salinity

water is injected at initial water saturation ( $S_{wi}$ ) condition. In Tertiary mode LSW, low salinity water is injected at waterflood residual oil saturation ( $S_{or}$ ), after high salinity waterflooding. Since most of the mature oil reservoirs are currently at high salinity water residual oil saturation state, therefore application of LSW and observation of LSE is highly interested among EOR specialists.

Zhang and Morrow (2006) performed experimental work comparing the secondary and tertiary mode low salinity injection for crude oil/sandstone combinations. They observed improved oil recovery in both injection modes. In some cases they observed improved recovery for secondary mode but not for tertiary mode. Also the results showed increased recovery for secondary mode low salinity injections with variation in initial water saturation. Core plugs with higher initial water saturation, gave better response to secondary mode low salinity flood. Similar experimental studies were performed by Webb et al. (2005 and 2006), Ashraf et al. (2010), Rivet et al. (2010), Gamage and Thyne (2011), Winoto et al. (2012), and Nasralla and Naser-El-Din (2012), all indicating higher increased oil recovery by low salinity injection in the secondary mode compared to the tertiary mode.

### **5.1.3 Low Salinity Injection in Carbonates**

The low salinity waterflooding is a well-studied and well-established process in sandstone rocks compared to the carbonates. The reason to exclude carbonates from the low salinity studies is attributed to the lack of clay content in carbonates compared to the sandstones and decrease in the active ions due to dilution of injection water (RezaeiDoust et al., 2009). Recently, the application of low salinity injection has been extended to carbonate rocks as well.

The studies by Fathi et al. (2010) on outcrop chalk core plugs showed no low salinity effect when the core plugs were imbibed or flooded with diluted brine at elevated temperature. The decrease in the concentration of potential determining ions (divalent ions such as  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $SO_4^{2-}$ ) were postulated to be the reason for lower oil recovery by low salinity injection compared to sea waterflooding. During sea water



injection, divalent ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  react with rock surface and change the surface charges, alter the wettability to more water-wet condition, release the carboxylic oil components from the rock surface and therefore lead to more oil recovery (Austad et al., 2008). However, manipulation of the composition of injection water by increasing the concentration of surface interaction ions (e.g., sulfate ion) could result in additional oil recovery. Sulfate ions are in large quantities present in sea water and adsorb onto the positive sites on the chalk surface. This will weaken the electrostatic repulsion forces, and will provide opportunity to excess  $\text{Ca}^{2+}$  ions to be localized in the vicinity of the rock surface. Positive calcium ions can react with negatively charged adsorbed polar oil compounds to form calcium carboxylate complex which could be possibly released and mobilized and produced during the flooding process (Zhang et al., 2006). The impact of sulfate as a wettability modifier on increased oil recovery by modified injection brine, has been observed and reported by other researchers as well (Webb et al., 2005-b, and Gomari et al., 2006).

Recent studies on low salinity waterflooding concerning carbonates report increased oil recovery by lowering the ionic strength of the injection brine by dilution of high salinity water. During the past five years, Saudi Aramco's Advanced Research Center (ARC) in the Exploration and Petroleum Engineering Centre (EXPEC) has started extensive strategic research program tagged "SmartWater Flood" to find the potential of increasing oil recovery from carbonate reservoirs by tuning the properties of the injection water (e.g., salinity, ionic composition, interfacial tension, and others).

Yousef et al. (2012) examined the smart waterflooding to improve oil recovery in carbonate reservoirs through altering the salinity and ionic composition of the injection sea water. They used composite cores from two of the Saudi Arabian carbonate reservoirs and designed the experimental parameters and procedures so that to reflect the reservoir conditions. The injection sea water was diluted by a factor ranging from 2 to 100-fold and injected to the core in secondary and tertiary modes. The two-fold diluted sea water gave 7% OOIP increased recovery in tertiary mode. The 10-fold and 100-fold diluted sea waterflood increased the incremental recovery factor by 5% and 1.5%, respectively. Secondary mode 10-fold diluted sea water injection recovered 10%

additional oil compared to the sea water injection in secondary mode. Similar results have been reported by other researchers all indicating improved oil recovery by low salinity injection in carbonate rocks, either by diluting the high salinity brine or by manipulation of the determining ions in the injected brine (Zahid et al., 2012, Romanuka et al., 2012, Al-Attar et al., 2013, and Al-Shalabi et al., 2013).

#### **5.1.4 Low Salinity Injection in Field Scale**

Promising achievements from experimental LS injection have been the background for some pilot scale field trials of low salinity waterflooding during the past years. The encouraging feature of the experimental and field low salinity trials is that there is an overall consistency between laboratory results and field observations.

Webb et al. (2004) conducted log-inject-log test to determine the residual oil saturation after waterfloodings with different brine salinities in a sandstone reservoir. The results indicated 25 to 50% reduction in residual oil saturation after waterflooding with low salinity brine. McGuire et al. (2005) reported the results from four sets of single well chemical tracer tests performed in Alaska's North Slope and observed substantial reduction in waterflood residual oil saturation after low salinity water injection. The incremental recovery factor ranged from 6 to 12% OOIP.

Researches in Shell investigated un-intentional low salinity flooding in some Syrian Oilfields with promising results. Vledder et al. (2010) and Mahani et al. (2011) report secondary low salinity injection in the Omar and Sijan fields in Syria leading to improved oil recovery due to the low salinity injection. This observation was supported by the spontaneous imbibition tests and a single well log-inject-log test in an analogue field.

In 2011 Statoil implemented a low salinity injection project in Snorre field in the North Sea. This field passed the screening criteria for low salinity effect and met all the necessary conditions. However, the experimental studies and the field test

indicated a poor potential for low salinity injection at this field (Skrettingland et al., 2011).

Researchers in Saudi Aramco report finalizing the design of several single well chemical tracer tests (SWCTT) to investigate the increased oil recovery potential by their so called SmartWater low salinity injection in Upper Jurassic carbonate reservoir. They successfully completed two field trials where the injection of SmartWater gave 7 saturation units reduction in the residual oil saturation over to the conventional waterflooding. More recently, the first EOR field trial using low salinity water in the giant Burgan oilfield in Kuwait has been documented by Abdulla et al. (2013). They implemented 2 single well chemical tracer tests to measure residual oil saturation ( $S_{orw}$ ) near wellbore region. The test was performed in the region with the best quality rock and the least clay content. They observed an average change of 3 saturation units (23.7% of remaining oil left after effluent waterflood) in residual oil saturation by low salinity injection. There was no formation damage and injectivity problem by reducing brine salinity from 140000 ppm to 5000 ppm. More tests have been planned for the remaining parts of the Burgan field where the reservoir rock contains high amount of clay.

## **5.2 Parameters Affecting the LSE**

Different parameters have been investigated to identify the optimum condition for low salinity effect. The important parameters which have been given much attention in the literature in recent years, include the injection brine composition and ionic strength, connate water composition and saturation, rock type, clay content and type of clays present in the rock material, temperature, initial wettability of the rock surface, and crude oil composition and its acid/base number.

There is no solid agreement in the literature on how these parameters affect the performance of the low salinity injection in different COBR systems. They may influence one single COBR system and assist in LSE but not work in the other COBR systems. Therefore making a general conclusion from observations in one or few

COBR systems and interpreting it as a mechanism behind the low salinity effect could be misleading. Having all necessary conditions available for low salinity may not sufficiently result in LSE (Morrow and Buckley, 2011). For example, kaolinite type clay content has been mentioned in many experimental works as a necessary condition for LSE, and was proposed that the increased oil recovery by low salinity injection is directly proportional to the amount of kaolinite present in the rock (Jerauld, 2006, Lager et al., 2007, and Seccombe et al., 2008). However, there are experimental evidences showing significant tertiary increased oil recovery by low salinity injection in the kaolinite-free rock samples (Cissokho et al., 2009 and Boussour et al., 2009). Furthermore, it is also believed that kaolinite is the least important clay for LSE due to its low cation exchange capacity (Austad et al., 2010). Similar discussions are applicable to some other parameters (e.g., temperature effect or presence of divalent ions in brine solution as reported by Cissokho et al., 2009) with examples and counter examples on supporting or rejecting the impact of these parameters on the improved oil recovery by the low salinity effect.

### **5.3 Proposed Mechanisms for LSE**

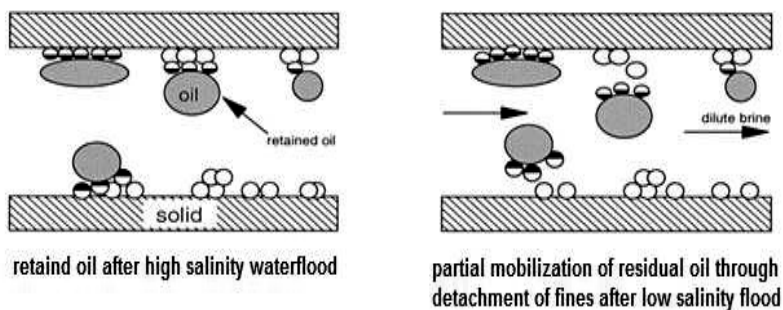
During last 10-15 years extensive research has been conducted aiming at identifying the mechanism or mechanisms under which the low salinity effect is observed. So far several mechanisms have been proposed as the possible reasons for low salinity improved oil recovery. However none of these mechanisms are conclusive to explain all aspects of the observed low salinity effect. Debates and technical discussions still continue among researchers, and experimental evidences supporting or opposing to the proposed mechanisms are growingly being provided to the literature. Some of the proposed mechanisms are more likely the effect of the low salinity injection rather than the cause for LSE. It seems that, most probably, combinations of different mechanisms are contributing together as the reason behind LSE. The mechanisms that have been much debated among researchers are outlined as:

- 1) Fines migration and oil transportation

- 2) Fines migration and microscopic flow diversion
- 3) pH variation
- 4) Wettability alteration
- 5) Double layer expansion
- 6) Multi-component ionic exchange (MIE)

### 5.3.1 Fines Migration and Oil Transportation

Fines migration due to the clay destabilization during fresh water injection was reported by Martin (1957) when he observed the clay-water dispersion in the effluents and suggested that the reduction of the permeability in the core plugs was the result of pore throat blockage by the fines migration. Fines production was also observed in the effluent samples during the low salinity flooding experiments conducted by Tang and Morrow (1999-a). They observed permeability reduction and increased differential pressure during the experiments. They related the fines production to the release and mobilization of mixed-wet clay particles, which in turn assists in the improved oil recovery by reducing the residual oil saturation (Figure 5-2). Moreover, they proposed that detaching the mixed-wet clay particles will lead to the wettability alteration to more water-wet condition.



**Figure 5-2** Fines migration and its impact on residual oil mobilization during low salinity waterflooding (modified from Tang and Morrow, 1999-a).

The low salinity injection, however, is not always associated with fines migration and production. There are evidences of increased oil recovery by low salinity flood with no fines migration or permeability reduction (Lager et al., 2006, Zhang et al., 2007) as well as observation of fines production with no increased oil recovery (Boussour et al., 2009).

### **5.3.2 Fines Migration and Microscopic Flow Diversion**

Microscopic flow diversion due to the clay destabilization and fines mobilization, and consequent high differential pressure, has been proposed in some research works as the reason for improved oil recovery by low salinity injection (Bernard, 1967, Pu et al., 2008, Skauge, 2008, and Alagic and Skauge, 2010). In this case fines are not necessarily produced and observed in the effluents, but they can be moved and displaced inside the porous media, possibly block the pore throats and divert the injected fluid into the un-swept pores. Therefore, the observed increased oil recovery could be the result of improved microscopic sweep efficiency rather than the wettability alteration. Again, the contradictory results have been introduced into the literature indicating significant differential pressure increase with no improvement in the oil recovery (Cissokho et al., 2009 and Boussour et al., 2009). Thus, according to the evidences available in the literature, fines migration is not the determinant mechanism behind low salinity effect, but it could facilitate the LSE in combination with other mechanisms or parameters.

### **5.3.3 Variation in pH and Low Salinity Effect**

Increase in pH associated to the low salinity flooding was first observed by Tang and Morrow (1999-a). The pH increase was attributed to the instability and release of the clay particles due to the salinity gradient during low salinity injection. The increase in pH could be explained by two chemical reactions take place when brine phase is in contact with mineral surface: carbonate dissolution and cation exchange. These

reactions both are accelerated when the brine is low salinity water. Carbonate dissolution is relatively slow, and strongly dependent of the clay fraction. Cation exchange reaction is much faster than carbonate dissolution and occurs between mineral surface and the brine phase. In this reaction,  $H^+$  from the liquid phase is substituted with cations adsorbed on the mineral surface, and leads to the formation of excess hydroxyl ions,  $OH^-$ , in the liquid phase and therefore high pH in the effluent.

Increased oil recovery associated with significant increase in pH observed by McGuire et al. (2005) led them to propose new mechanism reason for LSE. They suggested that low salinity water behaves similar to the alkaline flooding and possibly generates in situ surfactants through the saponification of the acidic compounds in the crude oil, which in turn results in the reduction of the interfacial tension (IFT). The IFT reduction will increase the capillary number and therefore will result in the mobilization and production of the capillary trapped residual oil.

A local pH increase at the water–clay interface was proposed by Austad et al. (2010), who stated that, in a pH-buffered system (e.g., reservoir conditions under which  $CO_2$  acts as the pH buffer), even though the effluent pH might not show any increase, the LSE will be observed because the acid–base reactions are very fast. This is because, a local pH increase close to the clay surface will desorb the organic material from the clay surface and, because of the dynamic nature of the flow conditions, the desorbed material will be transported away from the adsorption sites and the clay surface will become more water-wet.

There are experimental results in contradiction with the proposed LSE mechanism based on pH variation. The alkaline reaction and in situ generation of surfactant needs high acid numbers in the crude oil and high pH values in the liquid phase. However, significant increased oil recovery was reported by Lager et al. (2006) for a North Sea oil reservoir with very low acid number. Moreover, they could not find any correlation between acid number and increased oil recovery by low salinity injection. There are also reports showing improved recovery in the reservoir samples with slight or no change in effluent brine pH (Zhang et al., 2007, and Pu et al., 2008). Experimental

observations also indicate that higher pH in the effluent brine does not always result in the increased oil recovery (Cissokho et al., 2009 and Boussour et al., 2009).

#### **5.3.4 Wettability Alteration**

It is commonly believed that the wettability alteration toward a more water-wet state is the reason for the oil mobilization and production (Tang and Morrow, 1997, Sorbie and Collins, 2010, and Morrow and Buckley, 2011). An improvement in the oil recovery with increasing the water-wetness apparently is in contrast to the assumption that the weakly water-wet to intermediate wet conditions are the most favorable wettability conditions for the oil recovery by waterflooding. However, if the wettability of the core is initially oil-wet to intermediate-wet condition, the observed increase in oil recovery with increasing the water-wetness is reasonable. (Jadhunandan and Morrow, 1995, Skauge and Ottesen, 2002, and Skauge, 2013).

Recent studies on wettability effect and low salinity injection report shifting to a more oil-wet state by low salinity injection (e.g., Sandengen et al., 2011, and Fjelde et al., 2012). Thus, if the wettability alteration is a mechanism for the LSE, it is not always toward a more water-wet state (as most researchers have reported), but it could also be toward a more oil-wet (less water-wet) state as well. The mechanism leading to more oil-wet state is due to the increase in the adsorption of organic components on rock surface with salinity reduction. Since, there is a competition present between the different active species toward the negative sites of the clay; therefore, a negative salinity gradient will increase the adsorption of organic material onto the clay. This will shift the wettability towards the lower water-wetness (Austad et al., 2010).

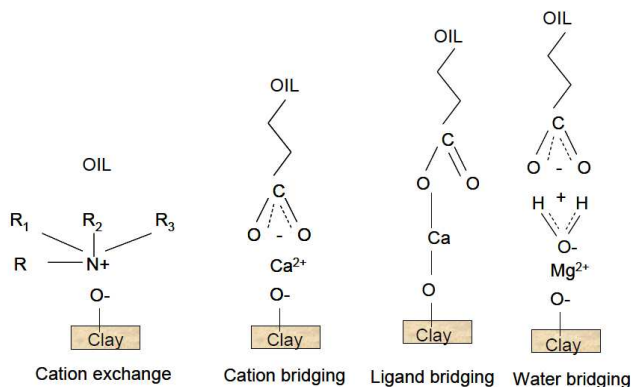
Adhesion mapping studies by Buckley et al. (1997) also showed that there are regions of stability and instability of water films, where non-adhesion or adhesion of crude oil components onto the rock surface could be observed, depending on the brine salinity. This adhesion mapping shows that, under low salinity conditions, water films are unstable and, therefore, adhesion of crude oil components could alter the wettability to a less water-wet state. Therefore, wettability alteration by low salinity injection can be



interpreted as a shift toward either less water-wet or less oil-wet conditions, depending on the initial wettability state of the porous media.

### 5.3.5 Multi-component Ionic Exchange (MIE)

The multi-component ionic exchange mechanism was, first, introduced by Lager et al. (2006) as a theory to explain the increased oil recovery by tertiary mode low salinity injection. They investigated brine composition of the connate water and found that the presence of the divalent cations (e.g.,  $Mg^{2+}$  and  $Ca^{2+}$ ) is the necessary condition for the tertiary LSE. That is, no divalent cations in the connate water, will give no increased oil recovery by LSE. They observed a direct correlation between the retained  $Mg^{2+}$  and the increased oil recovery by LSE. Therefore, the composition of the injected dilute brine solution was suggested to be the main parameter for the low salinity effect. The multi-component ionic exchange could take place through different mechanisms of the adsorption of organic compounds onto the clay minerals (Sposito, 1989). However, the important mechanisms in the low salinity flooding are those involve the divalent cations. These mechanisms are cation exchange, ligand exchange and cation or water bridging (Figure 5-3). The ion exchange theory proposed by Lager et al. (2006) is closely related to the electrical double layer expansion and the ionic exchange process occurs in the double layer region.



**Figure 5-3** Different adsorption mechanisms of oil onto clay surface (Lager et al., 2006).

Although the multi-component ionic exchange theory can explain many experimental observations, however experimental evidences by other researchers (Cissokho et al., 2009) are in contradiction with some of the assumptions in this theory. For example Cissokho et al. (2009) report low salinity effect with injection of 100% monovalent cations. Also they observed that the presence of divalent cations is not always leading to the LSE.

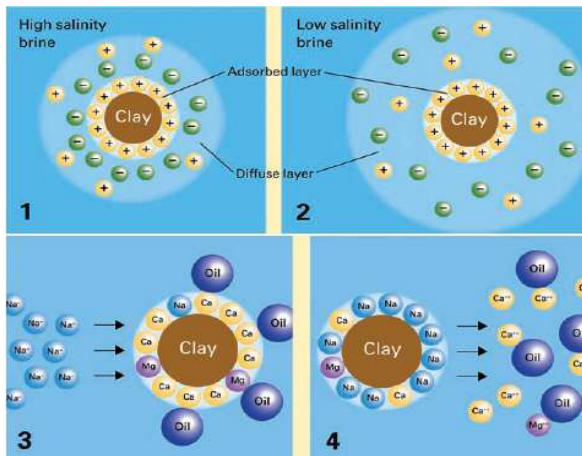
Furthermore, Austad et al. (2010) attributed the reduction of  $Mg^{2+}$  and  $Ca^{2+}$  in the effluents to the precipitation of  $Mg(OH)_2$  or  $Ca(OH)_2$  as a result of a local pH increase during the low salinity water injection. Thus, it is not necessarily the result of the multi-component ionic exchange (MIE) mechanism as was proposed by Lager et al. (2006).

### **5.3.6 Double Layer Expansion**

The concept of electrical charge separation at the interfaces and the definition of the electrical double layer were reviewed in Chapter 3. It was mentioned that the thickness of the electrical double layer which is also called “Debye length” oppositely varies with the salinity and the valence of counterions present in the aqueous phase. That is, in high salinity solutions or solutions with multivalent ions, the electrical double layer will be compressed. In contrast, in diluted solutions where the ionic strength of the solution or valence of the counterions is reduced, the thickness of the double layer is expanded.

The concept of double layer expansion has been used by some researchers to describe the mechanism behind the low salinity effect (Ligthelm et al., 2009, Nasralla et al., 2011, and Nasralla, and Naser-El-Din, 2012). Ligthelm et al. (2009) conducted series of flow experiments by injection of brine solutions of same ionic strength, but with and without divalent cations. They observed increase in the oil recovery when they changed the injection brine containing both monovalent sodium ion and divalent calcium and magnesium to the brine with only pure sodium chloride. They related this observation to the cation exchange mechanism. The increase in the recovery was even

accelerated when sodium chloride brine was diluted 100 times. The effect was attributed to the electrical double layer expansion (Figure 5-4). They postulated that under low salinity water condition, the number of divalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are not enough to act as bridges between negatively charged clay minerals and negatively charged oil-brine interface. In such condition, and based on DLVO theory, the repulsive forces will increase and exceed the binding forces through the multivalent cation bridges. Therefore, the oil polar components may be desorbed from the clay surfaces. Ligthelm et al. (2009) concluded that the expansion of the electrical double layer played dominant role in the increased oil recovery by the low salinity injection compared to the cation exchange mechanism.



**Figure 5-4** Desorption of oil compounds as low salinity brine invades (Frontiers, BP, 2009).

Nasralla, and Naser-El-Din (2012) studied the low salinity effect by measuring the zeta potential under high and low pH values. They found that reducing the pH of the low salinity brine makes the electrical charges at both oil-brine and brine-mineral interfaces weakly negative which in turn reduces the repulsion forces between oil polar components and mineral surface. Therefore to obtain positive effect from the low

salinity injection, the pH of low salinity brine must be high enough to maximize the electrostatic repulsion forces between the mineral surface and polar oil compounds.

#### **5.4 Hybrid LSE-EOR processes**

Hybrid EOR refers to a new combination of EOR methods which gives added incremental recovery over each method applied separately. The most interesting hybrid EOR processes that are recently being investigated include the combination of water based EOR processes such as surfactant flooding and polymer flooding with low salinity water injection (Alagic and Skauge, 2010, and Mohammadi and Jerauld, 2012). Both surfactant and polymer are highly dependent on the brine salinity and favor the low salinity environment. In the low salinity condition, retention of both surfactant and polymer decreases. This results in technically and economically efficient EOR process.

The main idea of the combined low salinity surfactant flood is that a more efficient oil recovery process can be obtained. The low IFT environment established by surfactant would prevent re-trapping of mobilized oil by low salinity water injection. Similarly, addition of polymer to the low salinity water could improve the stability of the LS flood (Tripathi and Mohanty, 2008). Polymer improves the efficient banking of the oil through a favorable mobility ratio, and thus, increasing the displacement efficiency of the low salinity floods.

## **CHAPTER 6**

# **RESULTS AND DISCUSSIONS**

This chapter includes 4 sections. In section 6.1 the main results from the wettability studies will be presented. The summary of the results from core floodings including secondary and tertiary mode low salinity injections will be provided in section 6.2. This section also will cover the in-situ saturation monitoring in type-2 Berea cores and simulation studies of the secondary low salinity versus high salinity corefloods. Section 6.3 is devoted to the presentation and discussion of the results on combined low salinity polymer/LPS floodings. The comparison studies of the propagation and EOR potential of the polymer solution without cross-linker and LPS solutions (polymer with cross-linker) will be presented in section 6.4.

### **6.1 Wettability Studies**

Wettability studies were conducted to establish different wettability states in core plugs to be used for flooding experiments. The cores were aged with crude oil at high temperature (110 °C) for different aging times. The aged cores, then, were analyzed for wettability change using full cycle Amott-Harvey procedure. Other parameters such as the difference in core permeability to oil before and after aging, ion analysis of the effluent brine during the forced drainage, and production profiles were also examined as the additional wettability indicators.

#### **6.1.1 Amott-Harvey and USBM Wettability Indices**

Core plugs from Berea and Bentheimer sandstones were selected for wettability studies. The wettability tests performed on both aged and unaged cores. The detailed results of the wettability studies, including the spontaneous water imbibition in Berea

and Bentheimer cores, capillary pressure curves for Berea and Bentheimer cores, and Amott-Harvey and USBM wettability indices have been presented in Paper 1.

Plots of Amott-Harvey and USBM wettability indices as a function of aging time, and USBM index ( $I_{\text{USBM}}$ ) versus Amott-Harvey index ( $I_{\text{AH}}$ ) are displayed in figures 6-1 and 6-2, respectively. Wettability studies showed that aging the core plugs for different aging times will establish different wettability states. As discussed in Chapter 3, since most of the oil reservoirs are at intermediate or mixed-wet condition, thus, in many experimental studies related to the EOR research, core plugs are aged with crude oil to establish intermediate or mixed-wet condition. Therefore, having estimates for core aging duration would be beneficial to avoid unnecessary long aging periods. The wettability studies in this study showed that for Berea cores the wettability shift to mixed-wet condition requires aging duration of 4-weeks. Under the experimental conditions of this study, the aging duration was 2 weeks for the Bentheimer cores. The aging duration may be different for different fluid-rock systems and especially depends on the reactant agents of both crude oil and rock surface.

It was previously mentioned in Chapter 3 that the combined plot of Amott-Harvey and USBM indices can be used to increase the resolution of the wettability measurements, and differentiate between different wettability classes. Based on Dixit et al. (1998), if the USBM index is greater than Amott-Harvey index, then the larger pores will be oil-wet. In this case the wettability is classified as mixed-wet large. In the cases where the two indices are equal, the wettability is called fractional-wet condition, (shown by the green line in Figure 6-2). On the other hand, if the smaller pores become oil-wet (mixed-wet small), then, the USBM index will be smaller than the Amott-Harvey index. The results of wettability studies in this work indicate that the wettability of the originally water-wet core plugs was shifted to mixed-wet large condition as Figure 6-2 shows greater USBM index compared to the Amott-Harvey index.

### **6.1.2 Other Wettability Shift Indicators**

There are also other indicators for wettability shift than the USBM and Amott-Harvey wettability indices. These indicators include, but are not limited to the oil permeability before and after aging, water imbibition rate, oil production profile and differential pressure buildup during displacement experiments. During wettability studies, one more test was performed as an additional wettability shift indicator. In this test, the effluents of the aged and unaged core plugs (produced brine from the secondary drainage process by centrifuge) were analyzed for the concentration of sodium, magnesium and calcium ions. The ion concentration of the effluent brines were compared to the original ion content in the synthetic sea water (SSW) using a 2100 DV ICP-OES inductively coupled plasma (ICP) instrument.

The unaged core B3 and aged core B4 were selected for ion analysis. The results are shown in Table 6-1. As it is given in this table, the ion content in the effluent from unaged Bentheimer core B3 is higher than the ion content of the original SSW. This is an indication of the reaction between the imbibed water during the spontaneous and forced imbibition processes and the rock surface, which results in ion transfer from rock surface to the bulk fluid. In contrast, the effluent from aged core B4 showed approximately similar ion content as the initial SSW. This implies that aging the core B4 resulted in less reaction between the brine solution in the core and the rock surface. This would be due to the reaction between the adsorption sites on the rock surface and the oil compounds, which results in the covering the rock surface by oil and limiting the contact between the brine and rock surface.

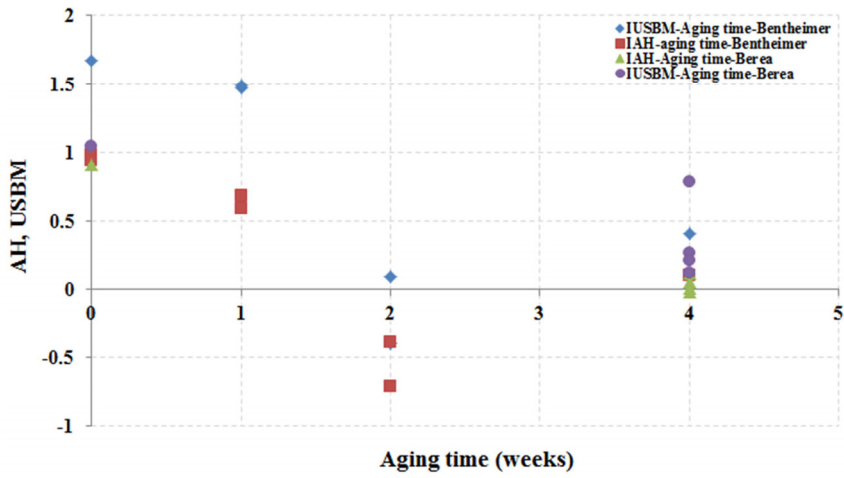


Figure 6.1 Change in wettability indices versus aging duration.

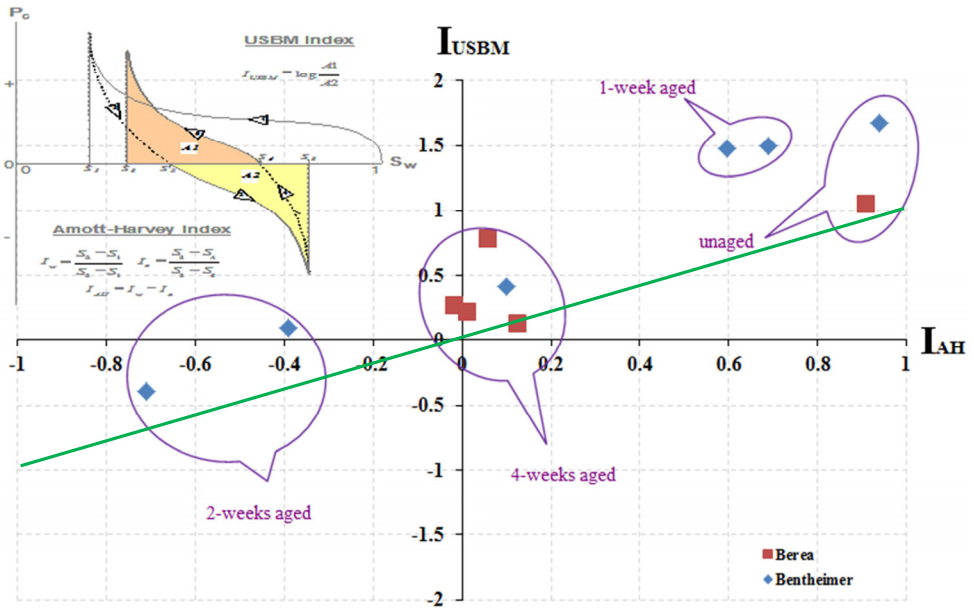


Figure 6-2 The plot of USBM wettability index,  $I_{USBM}$ , versus Amott-Harvey index,  $I_{AH}$ .



**Table 6-1** Ion analysis for the effluent brines of aged and unaged cores after secondary drainage process.

<b>Ion Fluid</b>	<b>[Na<sup>+</sup>], ppm</b>	<b>[Ca<sup>2+</sup>], ppm</b>	<b>[Mg<sup>2+</sup>], ppm</b>
<b>SSW</b>	11156	471	1330
<b>Effluent- unaged B3</b>	14074	617	1747
<b>Effluent- aged B4</b>	11328	516	1416

### 6-1-3 Is the Wettability Alteration Stable?

One of the concerns during the displacement experiments with wettability altered cores is the stability of the established wettability states. Core B2 from Bentheimer core samples and core S12 (will be discussed later in more detail) from Berea samples were selected to verify the stability of the wettability alteration. After a series of floodings, including high salinity/low salinity waterflooding, and polymer/LPS injection, the cores were stored in low salinity water for several months. Then the cores were placed in an Amott imbibition cell for oil imbibition. The imbibed oil was 12 saturation units for core B2, and 11 saturation units for core S12. Considering the formation damage during the long flooding history, especially during polymer/LPS injection in these cores, the oil imbibition, still, was significant and indicated stable wettability alteration of core plugs by aging with crude oil.

The wettability studies in this dissertation formed the background for core flooding experiments. These studies indicated how different wettability states could be established with varying the aging duration. The core plugs at different wettability states were used for displacement experiments.

## **6.2 Secondary and Tertiary Mode Low Salinity Waterflooding**

The summary of the main results from low salinity and high salinity waterflooding experiments in secondary and tertiary injection modes are presented in this section. The experiments were conducted on type-1 Berea (low permeability) and Bentheimer sandstones. This section will be extended to also cover the in-situ saturation measurements performed during low salinity and high salinity injections in type-2 (high permeability) Berea sandstone core plugs. The results from simulation studies comparing high salinity and low salinity effects are also included in this section. The simulation studies were conducted using Sendra and Eclipse simulators. A detailed description and discussion of the experiments can be found in papers 1 and 2 and in the Internal Report.

### **6.2.1 Displacement Experiments in Berea Sandstone**

Berea cores at different initial wettability states were used to examine the potential for tertiary mode low salinity injection, as well as to compare secondary and tertiary mode low salinity injection processes. The physical properties of the cores used for this part of the study are given in Table 6-2. The summary of the experimental results is provided in Table 6-3 and in figures 6-3 to 6-4.

As is shown in Figure 6-3, injection of low salinity water in tertiary mode (after secondary high salinity flood) did not increase the oil recovery factor in Berea cores. The lack of a tertiary low salinity effect was observed independent of initial wettability states, however some insignificant oil mobilization was observed in less water-wet cores.

Generally, the oil recovery factor was higher (residual oil saturation was lower) in cores at mixed-wet condition, stating that the oil recovery is increased as the rock wettability shifts towards less water-wet condition, which is consistent with previous observations in the literature (e.g., Jadhunandan and Morrow, 1991). The differential pressure profile for these cores is given in Figure 6-4. The bumps in differential pressure profile represents the flowrate change from initial 0.1 ml/min to 0.2, 0.5, and

1.0 ml/min. Similar pressure profiles was observed during high salinity and low salinity injection in each core. Thr cores with more water-wet condition showed the higher differential pressure.

**Table 6-2** Physical properties of type-1 Berea cores used for displacement experiments.

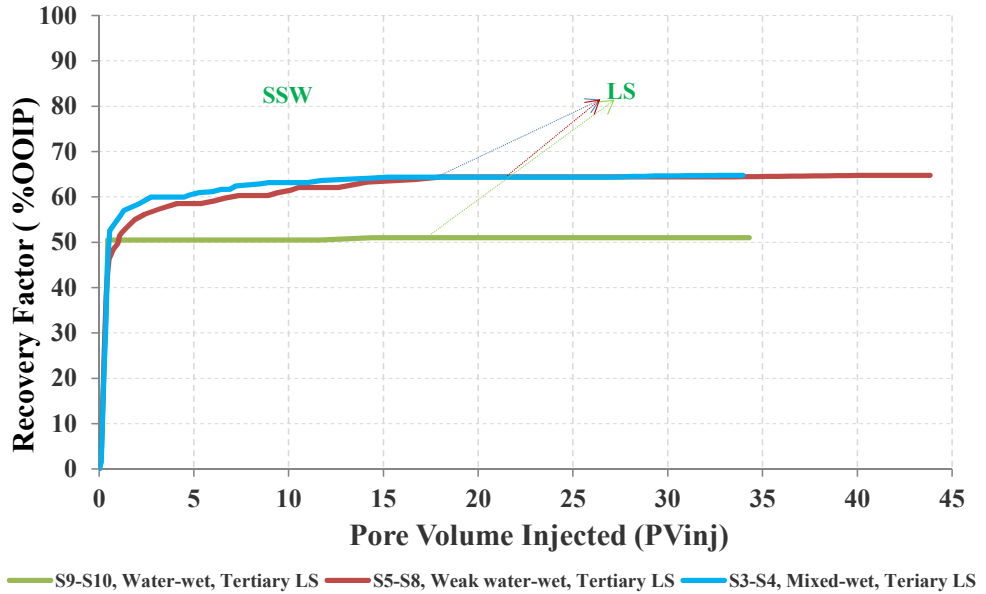
Core ID	L (cm)	D (cm)	PV (ml)	Porosity (%)	$S_{wi}$ (%PV)	$K_w$ (mD)	$K_o@S_{wi}$ (mD)	$^a K_o@S_{wi}$ (mD)
S3-S4	12.34	3.73	25.80	19.13	21	100.07	125.73	77.20
S5-S8	12.16	3.73	24.60	18.51	31	86.13	95.02	76.74
S6-S7	12.44	3.72	25.39	18.78	22	101.02	127.72	93.93
<sup>b</sup> S9-S10	11.90	3.72	25.01	19.28	22	98.38	120.26	-
<sup>b</sup> S11	8.82	3.76	17.77	18.11	22	75.14	89.2	-

<sup>a</sup> Oil permeability after aging

<sup>b</sup> Unaged cores

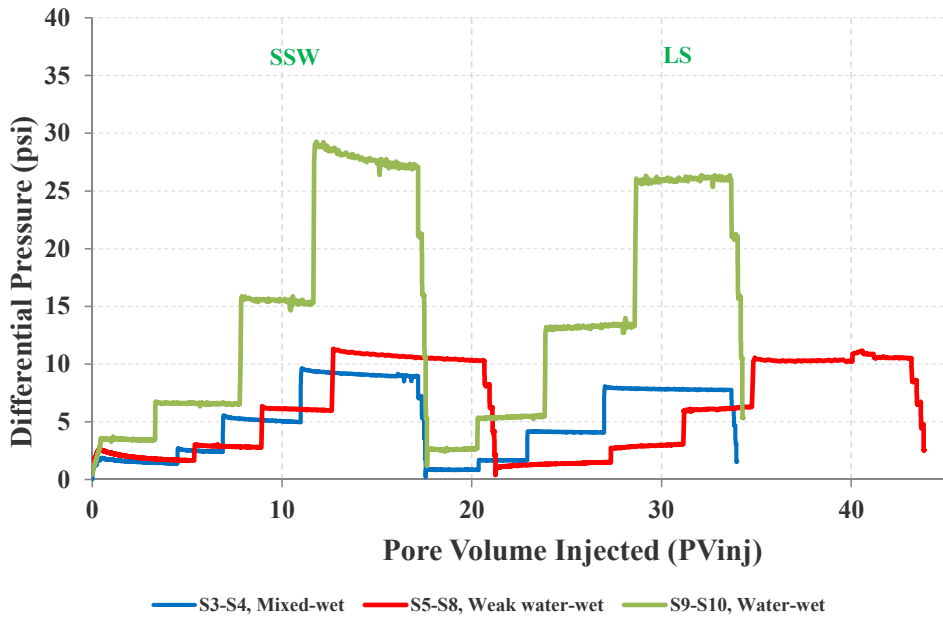
**Table 6-3** Summary of the experimental results obtained from type-1 Berea cores.

Core ID	$S_{wi}$ (%PV)	PV (ml)	$RF_{SSW}$ (%OOIP)	$RF_{LS}$ (%OOIP)	$S_{or}$ (%PV)	$K_{rw}$ ( $S_{or}$ )
S3-S4	21	25.80	64.4	64.8	27.9	0.37
S5-S8	31	24.60	64.4	64.8	24.2	0.33
S6-S7	22	25.39	-	78.1	17.0	0.40
S9-S10	22	25.01	51.0	51.0	38.2	0.11
S11	22	17.77	-	54.3	35.8	0.09

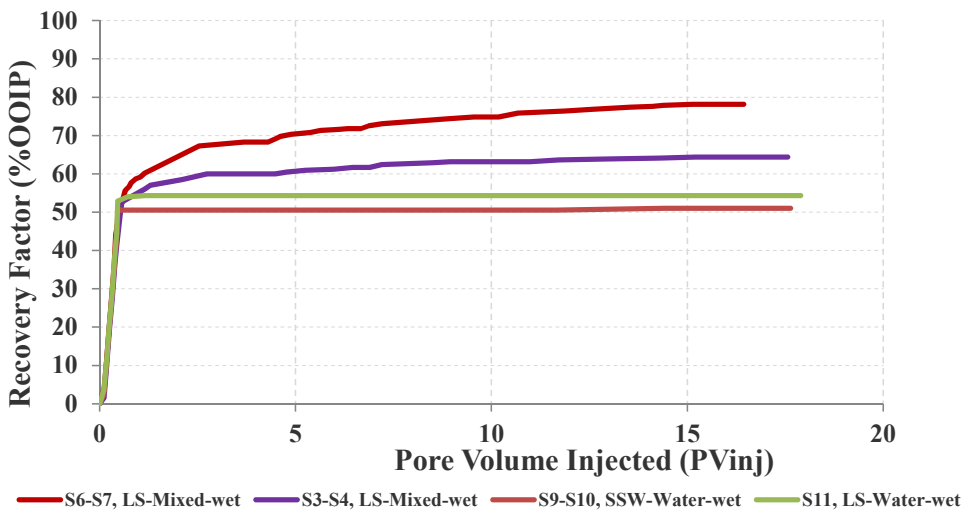


**Figure 6-3** Comparison of oil recovery factor during tertiary mode low salinity injection in type-1 Berea cores at different wettability states.

The comparison of low salinity injection in secondary and tertiary modes was also studied in this dissertation. The summary of the results are provided in Figure 6-5 for mixed-wet and water-wet cores. It seems that the timing of low salinity injection is influencing the efficiency of the flood. Injection of the low salinity water in secondary mode is beneficial at both mixed-wet and water-wet conditions compared to secondary high salinity flood. The effect is more pronounced at mixed-wet conditions as is shown in Figure 6-5. The detailed results of these experiments have been given in Paper 2.



**Figure 6-4** Differential pressure profiles during high salinity and low salinity waterflooding in type-1 Berea cores at different wettability states.



**Figure 6-5** Comparison of the oil recovery factor during secondary mode high salinity (SSW) and low salinity (LS) floodings at mixed-wet and water-wet conditions.

### 6.2.2 Displacement Experiments in Bentheimer Sandstones

Similar to the Berea cores, the kaolinite-free, high permeability Bentheimer cores were flooded at different wettability states. Both Secondary and Tertiary modes were performed in these cores. Table 6-4 gives the physical properties of the core plugs used for flooding experiments. The summary of the experimental results for these cores are shown in Table 6-5 and in figures 6-6 to 6-7.

**Table 6-4** Physical properties of Bentheimer cores used for displacement experiments.

Core ID	L (cm)	D (cm)	PV (ml)	Porosity (%)	$S_{wi}$ (%PV)	$K_w$ (mD)	$K_o@S_{wi}$ (mD)	$^a K_o@S_{wi}$ (mD)
<b>B2-B4</b>	11.88	3.70	32.72	25.60	34	2263.55	1910.40	1571.51
<b>B8-B9</b>	11.76	3.75	31.25	23.99	13	2007.28	1778.42	1489.53
<sup>b</sup> <b>B10-B11</b>	9.99	3.73	26.06	23.81	11	2227.52	2121.17	-
<b>B12-B13</b>	11.77	3.72	30.81	24.08	11	1452.89	1346.84	1293.56
<sup>b</sup> <b>B14-B15</b>	11.75	3.75	30.63	23.63	10	2252.12	2108.07	-

<sup>a</sup> Oil permeability after aging

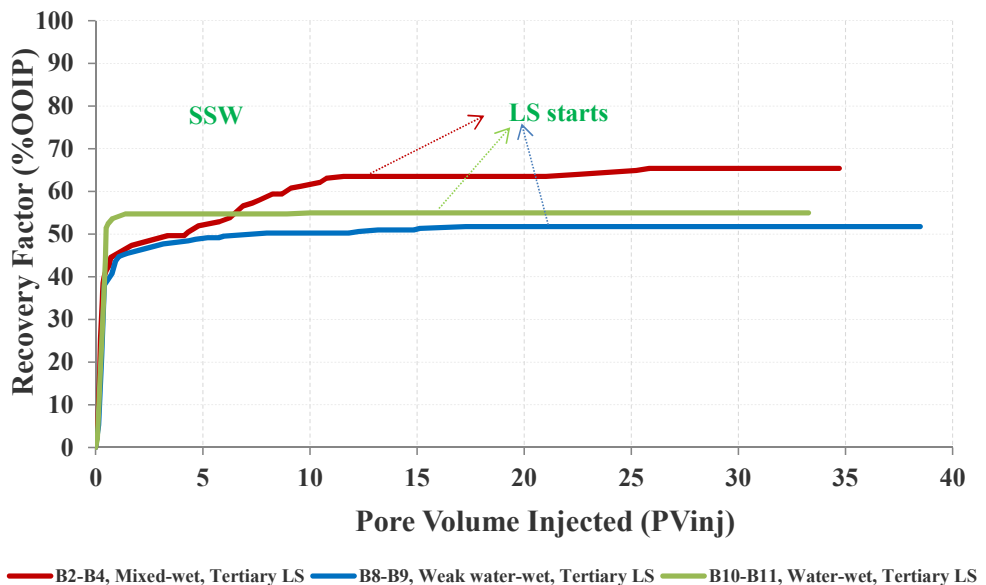
<sup>b</sup> Unaged cores

**Table 6-5** Summary of the experimental results obtained from Bentheimer cores.

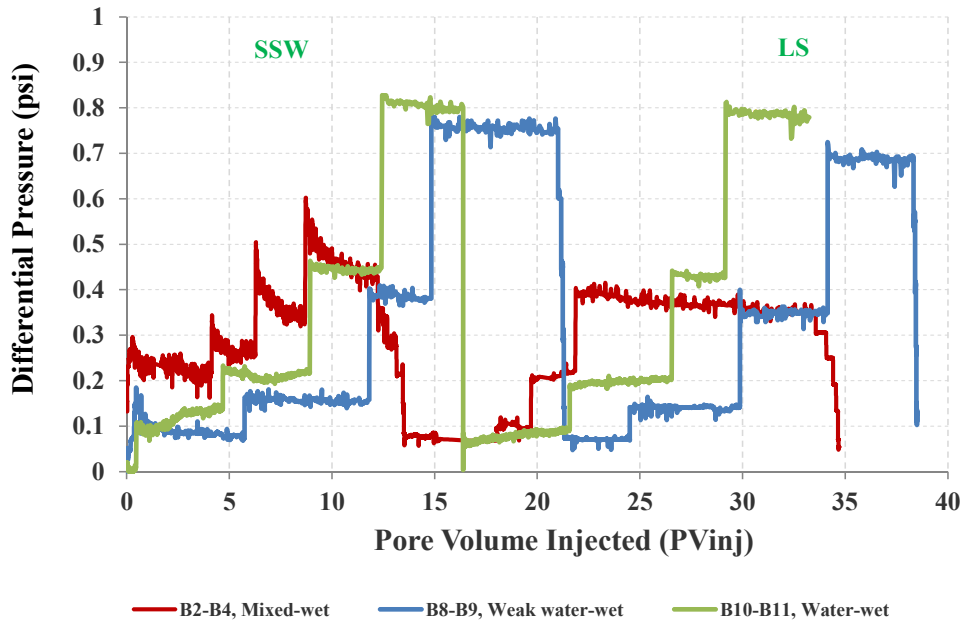
Core ID	$S_{wi}$ (%PV)	PV (ml)	$RF_{SSW}$ (%OOIP)	$RF_{LS}$ (%OOIP)	$S_{or}$ (%PV)	$K_{rw}$ ( $S_{or}$ )
<b>B2-B4</b>	34	32.72	63.5	65.4	23.0	0.4
<b>B8-B9</b>	13	31.25	51.7	52.1	41.6	0.2
<b>B10-B11</b>	11	26.06	54.9	54.9	40.4	0.15
<b>B12-B13</b>	11	30.81	-	61.0	33.5	0.2
<b>B14-B15</b>	10	30.63	56.61	56.61	39.0	0.14

The tertiary mode low salinity injection in Bentheimer cores did not result in significant reduction in residual oil saturation in any wettability condition. However some delayed oil mobilization, up to 2% OOIP, was observed in less water-wet and mixed-wet cores after several pore volumes of low salinity injection at higher flow rate (1.0 ml/min).

Comparing the results from Bentheimer cores to the results from the tertiary low salinity injection in Berea cores indicates that the kaolinite-free, but more oil-wet Bentheimer cores (B2-B4) give better response to the low salinity injection than the Berea cores containing kaolinite minerals at mixed-wet condition (S3-S4). This could be considered as an indication that the impact of initial wettability state of the porous media is more determining than the presence of kaolinite minerals. The literature also reports increased oil recovery by low salinity injection in kaolinite-free porous media (Cissokho et al., 2009 and Boussour et al., 2009). The detailed results of low salinity injection in Bentheimer cores have been presented in Paper 1.



**Figure 6-6** Comparison of oil recovery factor during tertiary mode low salinity injection in Bentheimer cores at different wettability states.

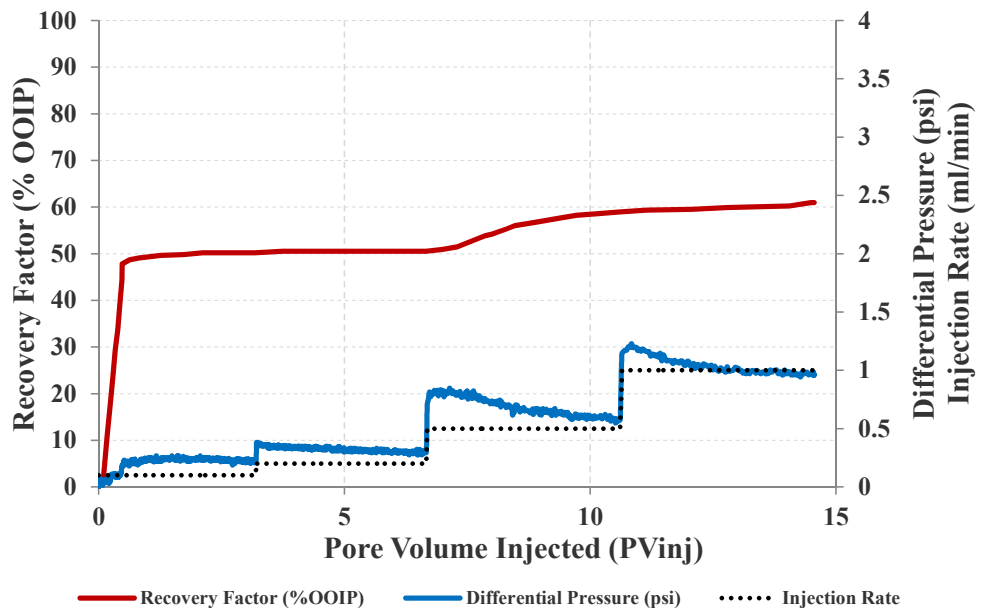


**Figure 6-7** Differential pressure profiles during high salinity and low salinity waterflooding in Bentheimer cores at different wettability states.

Secondary mode low salinity injection was performed in Bentheimer core B12-B13 to investigate the effect of timing of low salinity flood on oil recovery. The result is displayed in Figure 6-8. As the production profile indicates, negligible amount of oil was produced after breakthrough and even when the flow rate was increased to 0.2 ml/min, no extra oil production was observed. The interesting point in this test is the considerable oil production after increasing the flow rate to 0.5 ml/min (about 10% OOIP). One reason for this observation could be related to the so-called capillary end effect phenomena. However, since the extra oil production takes place during almost four pore volumes injection period, and not very quickly, therefore another explanation for this observation might be applicable as well. The cation exchange capacity (CEC) of the rock is directly related to the clay fraction in the rock. The higher the clay content in the rock, and the higher cation exchange capacity of the clay minerals, the higher and faster response to the low salinity injection is expected (Lager



et al., 2006). The Bentheimer cores used in this study had low clay content, and therefore low cation exchange capacity. The lower cation exchange capacity would result in delayed and slow response to the low salinity water injection. The mobilized oil during this slow process may need higher viscous force to be produced as is shown in Figure 6.8. This explanation could be also applied for delayed oil production in tertiary mode low salinity injection in mixed-wet Bentheimer core B2-B4 as is shown in Figure 6-6. In this case the increased oil recovery was observed after long period of tertiary low salinity injection at higher injection rate.



**Figure 6-8** Recovery factor and differential pressure profiles during secondary mode low salinity injection in aged Bentheimer core (B12-B13).

### 6.2.3 Simulation study of the Secondary Mode Displacement Experiments

The production and pressure data from secondary mode high salinity and low salinity water injection at water-wet and mixed-wet conditions were used as input data to

Sendra core flood simulator in order to obtain relative permeability and capillary pressure curves. These curves could be used as wettability indicators to identify the possible wettability shift and its direction during low salinity injection.

The estimated relative permeability and capillary pressure curves indicated shift to less water-wet state with injection of low salinity water in both mixed-wet and water-wet cores (similar to the studies by Sandengen et al., 2011, and Fjelde et al., 2012). This is in contradiction to common belief in the literature, that the low salinity injection shifts the wettability to more water-wetness. The reason for wettability shift to less water-wet condition could be related to the adsorption of organic components on the negative sites of the clay minerals due to the negative salinity gradient. The other reason for this phenomenon is the adhesion of crude oil components due to the instability of the water film under low salinity condition (Buckley et al., 1997). The detailed results of the simulation study to estimate the relative permeability and capillary pressure curves in Berea cores (type-1) have been reported in Paper 2.

#### **6.2.4 In-Situ Saturation Monitoring and Simulation Study of Low Salinity Effect in Type-2 Berea Cores**

The literature is lacking the information on how the additional oil is mobilized by the low salinity injection and how the local saturation of the fluids changed or re-distributed during this process (Skauge, 2013). Therefore, three Berea core plugs from different batch with higher permeability were prepared, coated with epoxy and aged to be used for in-situ saturation monitoring during secondary mode high salinity and low salinity waterflooding. The purpose was to investigate the saturation change during floodings with different salinities and frontal advance of different brines. Also, the aim was to locate the possible in-situ re-distribution of fluids in tertiary low salinity flooding and source of oil production during this process.

The physical properties of the three core plugs used for this part of the study are given in Table 6-6. The clay content of these core plugs (type-2 Berea) was similar to the clay content of type-1 Berea cores (Paper 2). These core plugs had higher permeability

compared to the type-1 Berea cores and was assumed to, possibly, have better response to low salinity injection as reported by Zhang and Morrow (2006).

Table 6-7 presents the summary of the experimental results obtained during secondary low salinity and high salinity water injection. Core L1 was flooded with low salinity brine as a secondary mode waterflooding. Core L3 was first flooded with synthetic sea water (SSW) to reach waterflood residual oil saturation ( $S_{or}$ ). At  $S_{or}$ , L3 was flooded with low salinity water to examine possible extra oil recovery by tertiary mode low salinity effect. The in-situ saturation of the cores L1 and L3 was monitored and measured by x-ray scanner while flooding with low and high salinity water.

**Table 6-6** Physical properties of type-2 Berea cores used for displacement experiments.

Core ID	L (cm)	D (cm)	PV (ml)	Porosity (%)	$S_{wi}$ (%PV)	$K_w$ (mD)	$K_o@S_{wi}$ (mD)	$^aK_o@S_{wi}$ (mD)
L1	15.14	3.78	37.92	22.35	27.0	401.08	413.71	183.71
L2	15.18	3.78	37.67	22.08	27.3	406.03	393.86	176.09
L3	15.21	3.76	39.26	23.18	25.6	441.06	502.49	216.01

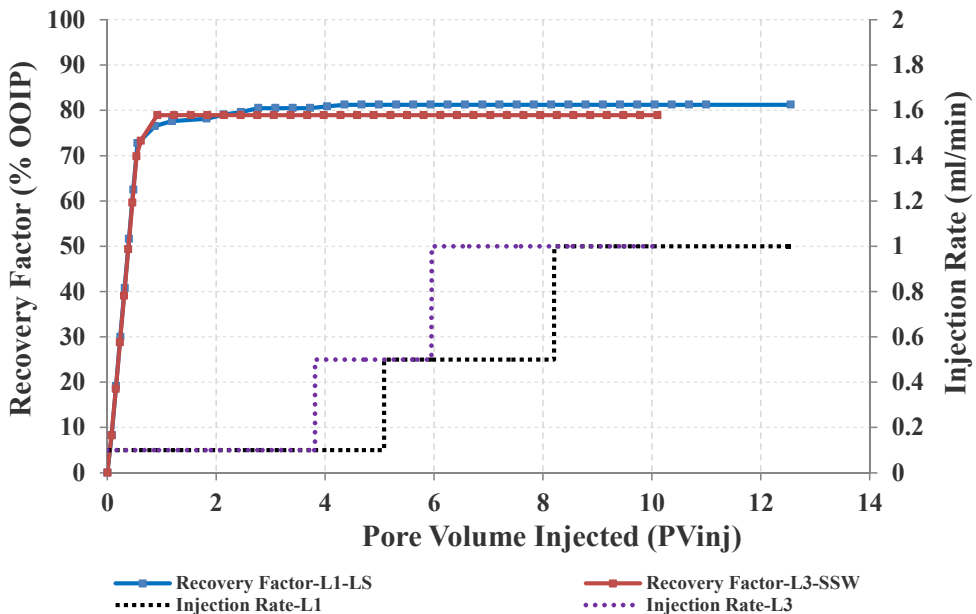
<sup>a</sup>Oil permeability after aging

**Table 6-7** Summary of the experimental results obtained from type-2 Berea cores.

Core ID	$S_{wi}$ (%PV)	PV (ml)	$RF_{SSW}$ (%OOIP)	$RF_{LS}$ (%OOIP)	$S_{or}$ (%PV)	$K_{rw}(S_{or})$
L1	27.0	37.92	-	81.2	13.7	0.14
L2	27.3	37.67	74.2	-	18.7	-
L3	25.6	39.26	78.9	0	15.7	0.15

Figure 6-9 shows the comparison between secondary mode low salinity and high salinity waterflooding in cores L1 and L3, respectively. The oil recovery from both secondary mode high salinity and low salinity flood was significant, though the low salinity injection in secondary mode gave slightly more recovery (about 2% OOIP). Tertiary mode low salinity injection in core L3 did not recover any oil, perhaps due to the efficient oil recovery by synthetic sea water (SSW) injection.

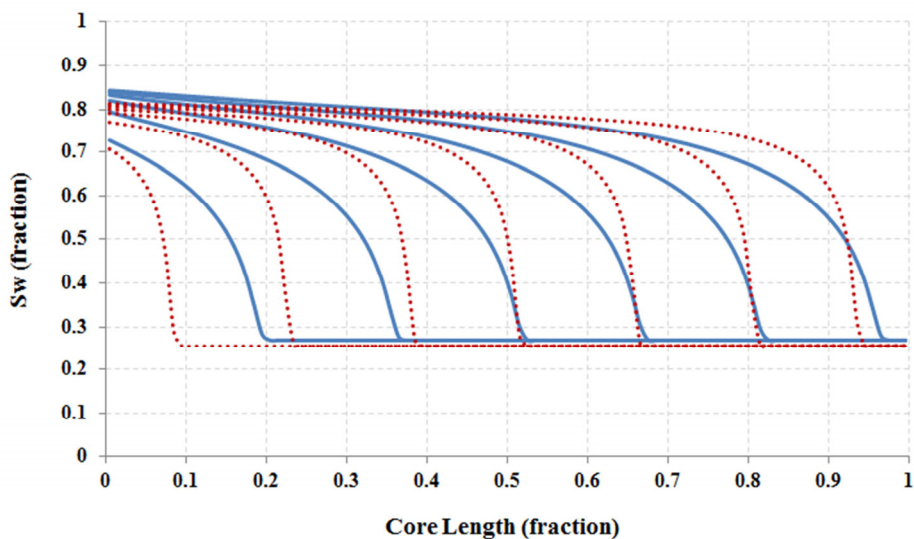
Since the high oil recovery by secondary mode SSW injection in core L3 was unusual (~79% OOIP), a second flood with SSW was conducted (core L2) to examine the reproducibility of the oil recovery by high salinity water injection. The oil recovery from this core was about 74% OOIP showing reasonable agreement with core L3 (Table 6-7). It seems that the combination of crude oil and rock system in this study was optimal for both low salinity and high salinity injections at secondary mode.



**Figure 6-9** Comparison of oil recovery efficiency of the secondary low salinity flood (L1) and secondary high salinity flood (L3).

The experimental data including oil production, differential pressure and in-situ saturation data obtained from L1 and L3 were imported into the core flood simulator, Sendra, to first match the experimental data, and then estimate the oil and water relative permeability and capillary pressure curves based on the best match obtained from the simulator.

The in-situ saturation profiles showed different flow behavior during the low salinity flood in core L1 in comparison to the high salinity flood in core L3. While the frontal slope in low salinity flooded core (L1) varied very gently and was more S-shape, the frontal slope in core L3 was considerably steep (Figure 6-10).



**Figure 6-10** Comparison of the simulated in-situ saturation profiles during low salinity injection into core L1 (blue color) and high salinity injection into core L3 (red color).

The difference in front slope in the cores implies the different frontal advancement behavior during low salinity and high salinity floods. The different frontal advancement behavior might be an indication of different wettability conditions in cores L1 and L3, due to the salinity gradient during the low salinity flooding. Considering that the two cores were prepared and aged in similar condition before

waterflood, it is reasonable to assume that both cores maintained similar initial wettability condition before displacement initiation. In such a case, the wettability shift to less water-wet state due to low salinity effect in core L1 may explain different frontal profile in cores L1 and L3. The estimated relative permeability and capillary pressure curves also showed slightly oil-wet condition for low salinity flooded core (L1) compared to L3.

### **6.3 Combined Low Salinity Polymer/LPS Floodings**

The design of the displacement experiments in this dissertation was such that to flood the cores with low concentration polymer or linked polymer solution (LPS) after secondary and/or tertiary mode low salinity injections. The aim was to investigate the combined effect of low salinity polymer/LPS flooding on further oil mobilization and reduction of the residual oil saturation. The primary postulation was that the combination of low salinity water and polymer/LPS floodings might have synergistic effect on oil recovery, i.e., higher oil recovery than the injection of low salinity water or polymer solution alone. The reason for this postulation is the fact that the EOR processes such as polymer flooding and surfactant flooding often favor to be implemented under low salinity environment. At low salinity condition the retention of polymer or surfactant is decreased and therefore the bulk injection solution could maintain its initial properties long enough during the flooding process (Nelson, 1982, and Sorbie, 1991).

Table 6-8 presents the physical properties of the cores were used to investigate the increased oil recovery by combined low salinity polymer/LPS floodings. These experiments include 5 Berea type-1 and 4 Bentheimer cores; all were used previously for secondary or tertiary mode low salinity waterflooding. Table 6-9 gives the result obtained from combined low salinity polymer/LPS floodings. This table presents the residual oil saturation before low salinity polymer/LPS flooding and after that.

The combined low salinity polymer/LPS injection effect on reduction of residual oil saturation varied from 0% for water-wet Berea cores to more than 50% for secondary

mode low salinity polymer flooding in mixed-wet Berea cores. Strong water-wet Berea cores did not respond to low salinity polymer/LPS injection neither in secondary mode nor in tertiary mode, despite the very high pressure build up (and high residual resistance factor,  $F_{rr}$ ) was achieved in these cores (Figure 6-11). This could be related to the effective trapping of oil due to the snap-off events and formation of strong water films during waterflooding in water-wet cores. The Bentheimer cores at all wettability states responded positively to polymer LPS injection, although the better response was observed in less water-wet cores.

**Table 6-8** Physical properties of the cores used for combined low salinity polymer/LPS floodings.

Core ID	L (cm)	D (cm)	PV (ml)	Porosity (%)	$S_{wi}$ (%PV)	$K_w$ (mD)	$K_o@S_{wi}$ (mD)	$^a K_o@S_{wi}$ (mD)
S3-S4	12.34	3.73	25.80	19.13	21	100.07	125.73	77.20
S5-S8	12.16	3.73	24.60	18.51	31	86.13	95.02	76.74
S6-S7	12.44	3.72	25.39	18.78	22	101.02	127.72	93.93
<sup>b</sup> S9-S10	11.90	3.72	25.01	19.28	22	98.38	120.26	-
<sup>b</sup> S11	8.82	3.76	17.77	18.11	22	75.14	89.2	-
S12	6.90	3.76	15.18	19.81	25	108.90	-	-
B2-B4	11.88	3.70	32.72	25.60	34	2263.55	1910.40	1571.51
B8-B9	11.76	3.75	31.25	23.99	13	2007.28	1778.42	1489.53
<sup>b</sup> B10-B11	9.99	3.73	26.06	23.81	11	2227.52	2121.17	-
B12-B13	11.77	3.72	30.81	24.08	11	1452.89	1346.84	1293.56

<sup>a</sup> Oil permeability after aging

<sup>b</sup> Unaged cores

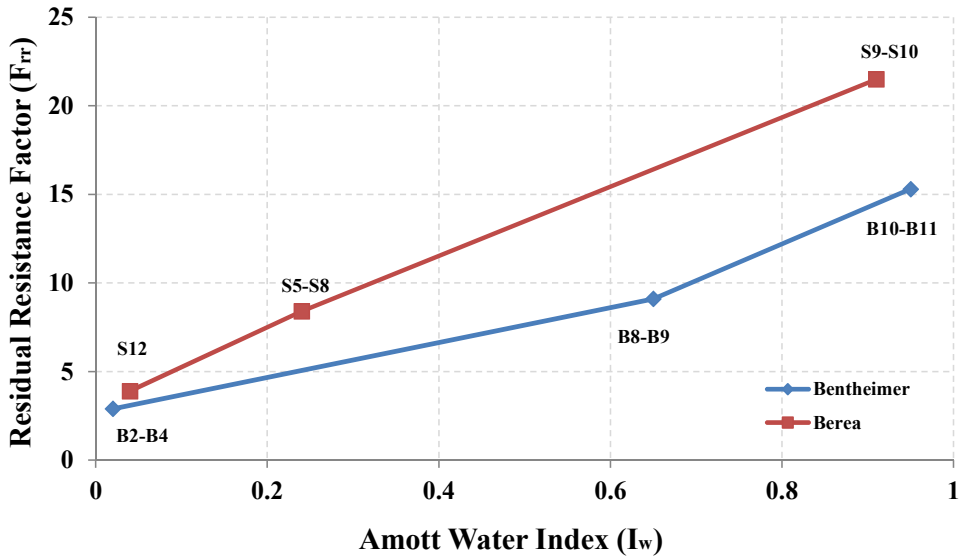
The significant oil recovery due to the polymer flooding was observed in aged Berea cores when the polymer injection was initiated after secondary mode low salinity

flood. The reduction in residual oil saturation was 53 percent in core S6-S7, changing from 17% PV to 8% PV. A second core flood (S12) was conducted to investigate the reproducibility of the high oil recovery in core S6-S7. As indicated in Table 7-11, the reproducibility of the test was confirmed by reducing the residual oil saturation up to 56 percent (reduction in  $S_{or}$  from 16% PV to 7% PV). The results are promising since the residual oil saturation after low salinity flood was extremely low. Thus, the potential for increased oil recovery by combined low salinity polymer system at very low polymer concentration (300 ppm) seems to be encouraging. The results of this study are in line with the very few published results in the literature showing synergistic effect of combining low salinity flood with polymer injection (e. g. Mohammadi and Jerauld, 2012). The detailed results and discussions on the effect of combined low salinity polymer/LPS flooding are given in papers 2 and 3.

**Table 6-9** Summary of the experimental results obtained from combined low salinity polymer/LPS floodings.

Core ID	RF <sub>SSW</sub> (%OOIP)	S <sub>orSSW</sub> (%PV)	RF <sub>LS</sub> (%OOIP)	S <sub>orLS</sub> (%PV)	RF <sub>f</sub> (%OOIP)	S <sub>orf</sub> (%PV)	% Reduction in S <sub>or</sub> after Polymer/LPS
S3-S4	64.4	28.1	64.8	27.9	69.1	24.4	13
S5-S8	64.4	24.5	64.8	24.2	70.1	20.6	15
S6-S7	-	-	78.1	17.0	89.8	8.0	53
S9-S10	51.0	38.0	51.0	38.0	51.0	38.0	0
S11	-	-	54.3	35.8	54.3	35.8	0
S12	-	-	68.7	16.0	85.8	7.0	56
B2-B4	63.5	24.0	65.4	23.0	78.3	14.0	39
B8-B9	51.7	42.0	52.1	41.6	56.2	38	9
B10-B11	54.9	40.0	55.8	39.6	59.0	36.7	7
B12-B13	-	-	61.0	33.5	65.2	29.8	11





**Figure 6-11** Effect of rock wettability on residual resistance factor during polymer flooding.

#### 6.4 The Comparison of the Propagation and EOR Potential of the Low Salinity Polymer and Low Salinity LPS Solutions

One phase and two phase flow experiments were performed to investigate and compare the propagation behavior of 300 ppm low salinity polymer and LPS solutions in water-wet and mixed-wet Berea core plugs. Pressure differentials were recorded to examine how different these two solutions do propagate through cores with different wettability states.

The capability of polymer and LPS solutions to mobilize residual oil trapped after waterflooding was also examined. In water-wet systems both polymer and LPS solutions were not able to mobilize residual oil even with very high pressure differential. In contrast, in mixed-wet cores both polymer and LPS solutions could mobilize and produce residual oil. However polymer injection was more efficient compared to LPS injection, possibly due to waterflooding history before polymer and LPS injection (secondary/tertiary mode low salinity injection). Concerning the oil

recovery potential, LPS did not give more oil recovery over the normal polymer flooding during the course of this study. The propagation and EOR potential of polymer versus LPS solutions is discussed in more detail in paper 4.

## CHAPTER 7

# CONCLUSIONS AND PROPOSAL FOR FURTHER WORK

### 7.1 Conclusions

As it was stated in Chapter 1 (introduction), the intension in this dissertation was to answer some questions on the effect of low salinity injection on increased oil recovery and also investigate possible synergistic effect of combining low salinity and polymer flooding. Based on the results obtained during this study following observations and conclusions can be drawn:

- The results in this study did not show a correlation between low salinity effect (LSE) and the clay content of the porous media contrary to published results in the literature (e.g., Jerauld, 2006, and Lager et al, 2007). The tertiary mode low salinity injection was more positive in Bentheimer cores that did not contain kaolinite minerals, and had lower clay content compared to the Berea cores with higher clay content including kaolinite minerals. Other factors like pore size distribution, aspect ratio and pore structure heterogeneity may also influence the low salinity process. Furthermore, the results of this study showed that the initial wettability state of the porous media is an important parameter in waterflood efficiency of the low salinity injection as more mixed-wet (less water-wet) cores gave better response to the process. The tertiary low salinity injection in more oil-wet Bentheimer cores resulted in higher oil recovery than the intermediate-wet Berea cores containing more clay minerals.
- The oil recovery efficiency of low salinity flood was found to be influenced by the timing of injection. Secondary mode low salinity injection increased oil recovery compared to secondary sea water injection. Injection of low salinity

water after preflush with sea water gave no or negligible reduction in residual oil saturation. This could be explained by effectively trapping and snap off of oil clusters during sea water injection that makes oil mobilization or remobilization much more difficult.

- Wettability alteration towards more water-wet state, as is widely reported in the literature, but seems in this study not to be a key mechanism for the observed low salinity effect in our studies. The estimated wettability indicators in this work showed wettability shift to less water-wet condition, as also previously reported by other researchers (Fjelde et al., 2012). These results are supported by wetting changes observed in adhesion mapping studies performed by Buckley et al., (1997). One of the important parameters influences the low salinity effect is stability of connate water or water film on rock surface. Either weakening or strengthening of the stability of water film may lead to wettability alteration to less water-wetness or more water-wetness, and therefore optimum wettability state for more reduction in residual oil saturation will be obtained. Thus, depending on the initial wettability of the porous media, the wettability shift as a result of low salinity effect could be either towards more water-wet or less water-wet state. Wettability indicators other than end point relative permeabilities are required to detect the direction of the wettability shift.
  
- The in-situ saturation monitoring revealed different frontal advancement behavior when secondary low salinity flood was performed compared to high salinity flood. The frontal advance in low salinity flood was more S-shape, while the frontal advance in high salinity flood was considerably steeper. This observation may also be interpreted as a wettability shift to less water-wet state during low salinity flood.
  
- Stable pressure profile during low salinity flooding and no observed fines production indicates that microscopic flow diversion by fines migration in our cases is not a key mechanism.

- The increased oil recovery by combined low salinity polymer/LPS solutions in water-wet Berea and Bentheimer cores was insignificant as expected and even despite the very high pressure buildup was observed during the polymer/LPS floodings.
- Combined low salinity water-polymer flooding led to very high total oil recovery in mixed-wet cores, probably due to a combined effect of this hybrid EOR process. The results are surprising as the polymer concentration was low and gives only small change in mobility ratio.
- The oil recovery by polymer injection was improved significantly in the case where the low salinity environment was established at initial water saturation ( $S_{wi}$ ) rather than at waterflood trapped oil saturation ( $S_{or}$ ).
- The additional oil recovery by combined low salinity polymer flooding could be attributed to banking of low salinity mobilized oil that is a combined effect with low salinity oil mobilization.
- Nano-size polymer particles (LPS) also gave increase in oil recovery when combined with low salinity waterflooding. The mechanisms for low salinity LPS is expected to be different than low salinity polymer, and is likely coupled to the microscopic diversion of water pathways discussed as the explanation for LPS action.
- Under the experimental conditions in this study, both LPS and polymer solution without cross-linker exhibit similar propagation behavior. This applies for both water-wet and mixed-wet conditions. Both solutions, in this study, assist in additional lowering of residual oil saturation in combination effect with low salinity flood, compared to standard low salinity waterflooding.

## 7.2 Proposal for Further Work

- In-situ saturation monitoring is an appropriate way to follow and measure the saturation change while flooding. It gives vital information on how the flood front advances and informs about the possible in-situ redistribution of the fluids in the core. Therefore it is highly recommended to monitor the in-situ saturation change during secondary and tertiary modes low salinity flooding and polymer injection to detect the differences in frontal advancement during high and low salinity floods, and locate the source of oil production as well as fluid redistributions.
- Low salinity polymer flooding in this study was conducted after low salinity environment was established by low salinity flooding. It is also beneficial to perform polymer flooding under high salinity condition and compare the results to the combined low salinity polymer cases. Furthermore, it is recommended to analyze the effluents for polymer concentration in both low salinity and high salinity conditions to detect the amount of polymer retention in low and high salinity polymer flooding.
- The concentration of the polymer influences the economy of the polymer flooding projects. Also the injectivity of polymer solution at higher concentrations is a crucial challenge for the polymer flooding design. The concentration of polymer in this study was 300 ppm. It is recommended to more systematically perform polymer flooding tests using polymer solutions with concentrations less and higher than 300 ppm and examine the effect on increased oil recovery at lower residual oil saturations similar to the cases in this study.
- The simulation study of combined low salinity polymer flooding in secondary and tertiary modes is recommended to confirm the results from displacement experiments and to get better understanding of the mechanisms control the increased oil recovery by this hybrid method.

- The use of reservoir cores has been reported to give better response to low salinity injection than outcrop core material. Possible due to exposure of outcrop rocks to oxidation and also to low salinity rainwater (Buckley, 2009), which limits the performance of low salinity injection in such rock materials. However, reservoir core are not so easily available, and are less homogeneous and less reproducible for core flood experiment purposes. Therefore, it is necessary to find an appropriate outcrop rock material as a model rock for low salinity injection studies. Investigation to find an alternative outcrop material to Berea (low permeable) and Bentheimer core materials used in this study would be an advantage for extensive study of mechanisms behind low salinity effect, especially in tertiary mode low salinity floods.





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