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Thermal, compositional, and salinity effects on wettability and oil recovery in a dolomite reservoir

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THERMAL, COMPOSITIONAL, AND SALINITY EFFECTS ON
WETTABILITY AND OIL RECOVERY IN A DOLOMITE RESERVOIR

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science in Petroleum Engineering.

in

The Craft and Hawkins Department of Petroleum Engineering

by

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This work is dedicated to my loves: Reza and Ava

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NOMENCLATURE

- **V**: Velocity
- **μ** : Viscosity
- **Θ** : Contact angle
- **ΔP** : Pressure drop
- **q_o** : Rate of oil production
- **K**: Permeability
- **K_{ro}** : Oil relative permeability
- **K_{rw}** : Water relative permeability
- **S_{wi}** : Initial water saturation
- **S_{ro}** : Residual oil saturation
- **μ_o** : Oil viscosity
- **A**: Area of reservoir
- **h**: Pay zone thickness
- **ϕ** : Porosity
- **PV**: Pore volume

ABSTRACT

Low salinity and composition effects in improving oil recovery in sandstone reservoirs are known. However, these effects have not been thoroughly studied for the carbonate reservoirs. Because of the lack of the clay minerals in the carbonate rocks, the mechanisms for the improved oil recovery with low salinity, brine composition, and temperature may not be the same as those for sandstones. This experimental study attempts to investigate the effects of low salinity, brine composition, and temperature on wettability and oil recovery in a dolomite reservoir. Also, it is attempted to confirm that wettability alteration is the main mechanism for improvement of oil recovery.

The experiments for this study were performed at both ambient and reservoir conditions as well as at a temperature of 250°F using two different techniques, Dual-Drop Dual-Crystal (DDDC) and coreflooding. Water-advancing contact angle was measured using the DDDC technique to characterize reservoir wettability with different salinities including twice, 10, 50 and 100 times diluted brines. Also, the effect of brine composition on wettability was investigated with Yates synthetic brine, Yates synthetic brine without sulfate, and brines containing sulfate in different concentrations. In addition, the effect of temperature on wettability was investigated using DDDC technique. Coreflood experiments were carried out using a dolomite core to determine aging time, to measure the oil recovery, and to confirm whether an optimal salinity brine and an optimal composition of brine obtained contact angle measurements improve the oil recovery compared with Yates synthetic brine. Oil-water relative permeabilities were generated by history matching the oil recovery and pressure drop data obtained from the coreflood experiments.

The experimental results showed that the wettability was altered from strongly oil-wet to intermediate-wet by diluting the Yates synthetic brine by about 50 times and increasing the amount of sulfate in Yates synthetic brine from 2.2 g/l to 4.4 g/l. Also, increasing the temperature to 250°F had a significant effect on wettability and changed the wettability from oil-wet to intermediate-wet. Coreflood results confirmed the wettability alteration to intermediate-wet and also demonstrated improvements in oil recovery induced by the optimal salinity and optimal brine composition.

1. INTRODUCTION

1.1 Background

The economic significance of carbonate reservoir is enormous. More than half of the world's remaining oil exists in carbonate reservoirs (Akbar et al. 2001). These reservoirs are among the most complex reservoirs to characterize, model and manage. They are characterized by rather low primary oil recovery; therefore, the enhanced oil recovery potential of these reservoirs is high. Many carbonate reservoirs are believed to be oil- wet and have very low permeability, so the enhanced oil recovery from such reservoirs poses a great challenge.

Among the techniques developed and applied to improve oil recovery, waterflooding is an inexpensive oil recovery process and is so far the most widely applied method for improving the oil recovery.

Waterflooding is a process of injecting water into oil reservoirs. Traditionally, it was practiced for pressure maintenance after primary depletion. Composition of water was not considered as an important factor influencing the amount of oil recovered. However, over the last decade substantial studies have shown that composition of injected water has an important effect on crude oil- brine- rock interactions in a favorable way to increase oil recovery (Austad et al. 2005; Fathi et al. 2010; Fathi et al. 2011; Fernø et al. 2011; McGuire et al. 2005; Nanji et al. 2011). Waterflooding improves the oil recovery not only through the physical processes, of maintaining reservoir pressure and sweeping the mobilized oil to the producing well by the injected of water, but also through the chemical process. Therefore, modifying the brine chemistry of the injection water can significantly influence the observed recovery.

Extensive studies in the recent literature on crude oil- brine- rock systems has shown that injecting low salinity brines may have a significant impact on oil recovery from sandstone

reservoirs. It is confirmed (Morrow et al. 1998; Buckley and Liu 1996; Jadhunandan and Morrow 1995; Yildiz and Morrow 1996; Yildiz et al. 1999; Tang and Morrow 2002; Morrow and Buckley 2011) the effect of low salinity brines is related to the presence of clay minerals. Some reported studies (Yildiz et al. 1999; Tang and Morrow 1999, 2002; Morrow and Buckley 2011) have excluded carbonates from this effect, because of the absence of clay minerals, even though the potential for carbonates has not been carefully studied. Contrary to these results, the impact of low salinity on oil recovery in composite rock samples was studied by Saudi Aramco in Saudi Arabian carbonate reservoirs Yousef et al. (2011, 2012, 2011 a, 2011 b, 2011 c); consequently, a substantial increase in oil recovery was reported. Also, some reported studies (Austad et al. 2012; Yousef et al. 2011, 2012, 2011 a, 2011 b, 2011 c) have shown that oil recovery from carbonates is dependent on the ionic composition of the injection water. They reported that oil recovery in carbonates is increased by addition of sulfate to the injected water (Austad et al. 2005; Austad 2008; Peimao and Tor 2005; Zekri et al. 2001; Yousef et al. 2011, 2012; Webb et al. 2005; Larger et al. 2007; Austad et al. 2012; Zheng et al. 2007; Alotabi and Naser-El-Din 2009; Strand et al. 2006; HØgnesen et al. 2005).

Waterflooding has several advantages compared with EOR methods, including:

1. Higher oil recovery with minimal investment in current operations,
2. Applicability at the early life cycle of the reservoir
3. Faster payback, even with relatively low incremental oil recovery

Although it is widely accepted that brine salinity and composition may play a role in increasing oil recovery from carbonate reservoirs, underlying the mechanism of this increase is unclear. The main conclusion of most previous studies is that wettability alteration (overcoming the strong rock–oil adhesion interactions) from oil-wet to water-wet in carbonate reservoirs is the

main reason for the enhancement of the oil recovery (Zhang et al. 2007; Bagci et al. 2001; Yousef et al. 2010; Zekri et al. 2012). On the other hand, wettability is reported as a possible driving mechanism for significant increase in oil recovery. Wettability is defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids. Wettability, spreading, and adhesion play an important role in determining the ultimate oil recovery from petroleum reservoirs. Based on the previous studies, it is confirmed that reservoir wettability and consequently microscopic displacement efficiency are affected by brine composition and salinity. However, the knowledge of the effects of brine salinity and composition on establishing and altering wettability in carbonate reservoirs is quite limited. Therefore, the presented study aims to quantify the effects of brine salinity and composition on wettability and oil recovery by making reproducible contact angle measurements and by relative permeability determination using corefloods.

1.2 Objectives

The specific objectives of this study are:

1. To determine the wettability behavior of dolomite rock by measuring water- advancing contact angle in different rock-brine-oil systems using the Dual- Drop- Dual-Crystal (DDDC) technique at both ambient and reservoir conditions.
2. To experimentally investigate the influence of brine salinity on wettability in dolomite rock-brine-oil systems by measuring the water- advancing contact angle.
3. To experimentally investigate the influence of brine composition, specifically the sulfate ion concentration in brine, on wettability in dolomite rock-brine-oil system as determined by measuring the water- advancing contact angle.

4. To experimentally determine the optimal brine composition and salinity using the DDDC technique at both ambient and reservoir conditions.
5. To experimentally study the effect of temperature on wettability by measuring water-advancing contact angle in dolomite rock-brine-oil systems using DDDC technique at reservoir conditions.
6. To determine the aging time by running the corfflooding experiments using the Yates synthetic brine-Yates oil- dolomite core systems.
7. To conduct coreflood experiments to investigate the effect of brine salinity and composition on wettability and ultimate oil recovery at reservoir condition.
8. To compare oil recovery obtained by injecting the synthetic reservoir brine to the core with that obtained by injecting an optimal salinity brine and an optimal composition brine.
9. To experimentally confirm that wettability alteration is the main mechanisms to improve the oil recovery using the DDDC and corfflooding methods.

1.3 Methodology

To achieve the objective of this study, Yates crude oil was used as oil phase. The reservoir pressure and temperature were 700 psi and 82°F, respectively. Also, the viscosity and density of Yates crude oil were 12.8 cp and 0.875 gr/cc, respectively. Synthetic reservoir brines were prepared by adding the calculated amounts of various salts to deionized water (DIW) to match the reservoir brine compositions. Silurian dolomite was used to represent the Yates rock.

The objectives of this study require use of two different experimental techniques including Dual-Drop Dual-Crystal (DDDC) technique to describe rock-fluid interactions in terms of water-advancing contact angle and coreflooding method to measure oil recovery and oil-

water relative permeabilities. The DDDC technique provides an accurate and reproducible measurement of the water-advancing contact angle that presents wettability. When water advances over an area of the solid surface that was previously occupied by the oil, the water-advancing contact angle can be measured. It has been used to represent wettability since the mode of its measurement is similar to the nature of fluids flow in the reservoir in the sense that when oil is produced, injected or resident water advances over the rock surface previously occupied by the oil (Rao 1999). When the oil adheres to the rock surfaces, the large advancing contact angle will be measured. Large advancing contact angle does not mean that oil spreads on the surface.

Many of previous studies (Zekri et al. 2001; Yousef et al. 2011, 2012, 2011 a, 2011 b, 2011 c; Zhang et al. 2007; Webb et al. 2005; Larger et al. 2007; Austad et al. 2012; Zhang et al. 2007) investigated the effect of sulfate ions on wettability and oil recovery in carbonate reservoirs and found that the sulfate ion plays a crucial role on wettability alteration based on their experiments. Therefore, this study investigated the effect of brine composition by applying five brine solutions with different sulfate ion concentrations. Also, to study the effect of low salinity, five different versions of reservoir brine were used in separate experiments, starting with regular brine and ending with 100 times diluted brine. For all these experiments, Dual-Drop Dual- Crystal (DDDC) contact angle measurement technique was used to measure water-advancing contact angles at both ambient and reservoir conditions. This was done to investigate the wettability and its alterations induced using different brine salinities and compositions. DDDC technique was used at high temperature 250°F in addition to the reservoir temperature 82°F to investigate the effect of temperature on wettability as the Yates reservoir (with an oil API gravity 30) was considered to be a candidate for steam injection.

In this study, three coreflooding experiments, including Yates fluids- dolomite rock, brine with 4.4g/l sulfate and 50 times diluted brine were carried out at aging time 10 days to determine the impact of brine salinity and composition on relative permeability and oil recovery. Also, by conducting corefloods, we could attempt to correlate wettability alteration inferred from contact angle experiments with those from relative permeability interpretation and their effects on oil recovery compared with Yates synthetic reservoir brine.

Initial water saturation, residual oil saturation, and endpoint relative permeabilities were measured through coreflood experiments along with pressure and recovery profiles. A coreflood simulator was then used to calculate oil-water relative permeabilities by history matching the pressure drop and recovery data obtained from the coreflood experiments. Finally, the relative permeability variations were interpreted using Craig's rules of thumb (Craig, 1971) to characterize wettability alterations induced by optimal brines.

The significant contributions of this study are to experimentally show that changing brine salinity and composition can alter wettability, thereby enhancing oil recovery from a dolomite rock- fluids system.

2. LITERATURE REVIEW

Several technologies and practices so far have been used to improve the oil recovery by waterflooding, such as multilateral wells, infill drilling, improved reservoir characterization and modern monitoring and surveillance, and others. Traditionally, the role of brine composition and salinity on wettability and oil recovery has not been studied in detail. However, over the last decade extensive studies have shown that brine composition and salinity can affect crude oil-brine-rock interactions in a favorable way to improve oil recovery. In recent years, Not only the effect of brine salinity and composition on wettability and oil recovery has been applied in sandstone reservoirs but also the effect of low salinity waterflooding has been applied to carbonate reservoirs. As it is shown in Figure 2-1, the number of publications and presentations to study the effect of low salinity on oil recovery has increased in recent decades (Morrow and Buckley, 2011).

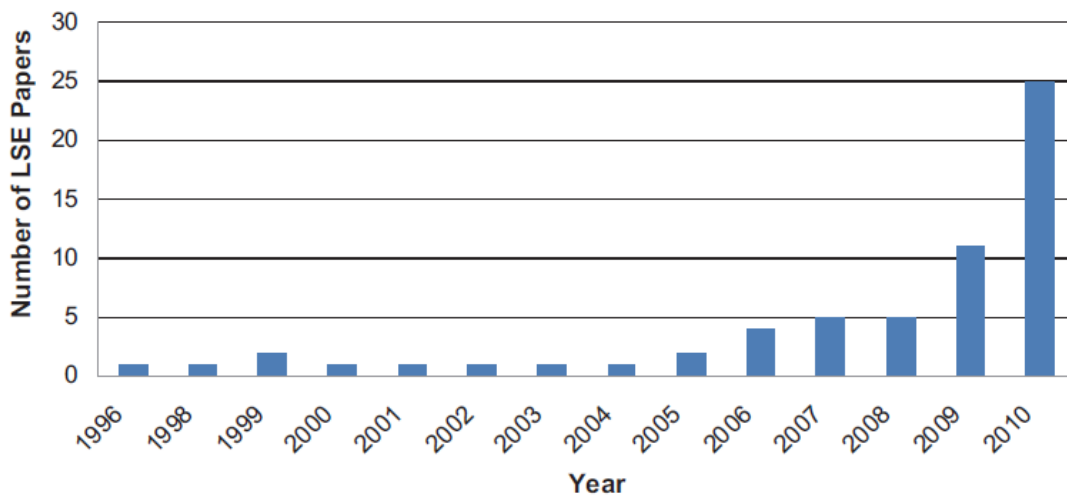


Figure 2-1: The increased number of publications and presentations studied on low salinity effect show the interest in low salinity effect (Morrow and Buckley 2011)

2.1 Brine Composition and Salinity

The concept of injecting low salinity water into petroleum reservoirs has been addressed since the 1960s. Based on the literature review, brine salinity and composition has a significant effect on the reservoir wettability and oil recovery. It was reported that water chemistry influences the stability of water films and sorption of organic oil components on mineral surfaces through at least two mechanisms. The water chemistry could change the charge on the rock surface and affect the rock wettability and/ or changes in the water chemistry could dissolve rock minerals and affect the rock wettability. Therefore, the optimal salinity and composition in the injection water may yield high oil recoveries.

Muhammad (2001) investigated the effect of brine composition in solid-liquid-liquid systems using the Wilhelmy Plate technique for Yates crude oil. It was reported that when the concentration of monovalent salts in the aqueous phase increased from 2 % to 20%, water-advancing contact angle increased by about 50°. He further reasoned that as the concentration of salts increased, the water film on the rock surface between the drop phase and the rock substrate weakened.

McGuire et al. (2005) investigated the effect of low salinity on residual oil saturation using the single well chemical tracer tests in the Alaska field. It was demonstrated that low salinity decreased the residual oil saturation significantly and increased the original oil in place (OOIP) from 6 to 12%, resulting in an increase in waterflood recovery of 8 to 19%.

Zheng (2012) investigated the effect of brine salinity and composition on wettability using the Dual- Drop- Dual- Crystal (DDDC) technique in gas- condensate- reservoirs. Multi-component and single salt- brine systems were used. It was concluded that the effect of brine salinity and composition on wettability was insignificant since measured water advancing

contact angles were in the range of about 140° to 165° which show a strongly oil- wet nature of a gas- condensate fluid.

Yousef et al. (2011, 2012, 2011 a, 2011 b, 2011 c) reported that brine salinity and composition, and also reservoir temperature have significant impact on carbonate surface charge. They reported these parameters have a substantial impact on rock wettability, and ultimately has potential to enhance oil recovery in carbonate reservoirs.

Austad et al. (2012) also reported a laboratory study showing low salinity effect (LSE) from core material sampled from the aqueous zone of a limestone reservoir. They observed 2-5 % increment in oil recovery by flooding the cores with diluted formation water or diluted seawater.

2.2 Driving Mechanisms

In the past two decades most of the studies have been focused on understanding the underlying drive mechanisms of low salinity waterflooding. Wettability alteration has been suggested as one of the driving mechanisms for improved oil recovery by altering the salinity and ionic composition of the injected water based on laboratory experiment results in carbonate reservoirs (Kaminsky and Radke 1998; Austad et al 2008; Yousef et al. 2010; Zekri et al. 2012). Carboxylic acids present in crude oil are the most important wetting parameters for carbonate reservoir (Standnes and Austad 2000a).

Hirasaki (1991) proposed that wettability alteration depends on the value of the critical disjoining pressure and thus on the stability of the water-film that is in direct contact with the rock. Where the capillary pressure is above the critical disjoining pressure, components may deposit from the oil and bind onto the rock surface leading to wettability alteration. Also, Kaminsky and Radke (1998) explained wettability variation in reservoir process that wettability

change may not only be dependent on the stability of the wetting- water film but also on the ability of components from the crude oil to diffuse through the wetting film and adsorb onto or spread on the rock surface.

Figure 2-2 shows a schematic model of the chemical mechanism suggested for wettability alteration in carbonate surface.

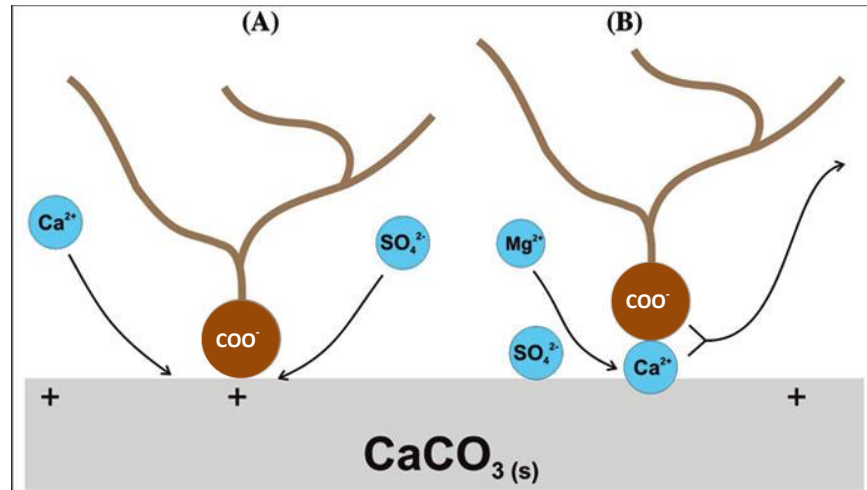


Figure 2-2: Schematic model of the wettability alteration. A) Proposed mechanism when Ca^{2+} and SO_4^{2-} are active. B) Proposed mechanism when Mg^{2+} and SO_4^{2-} are active (adopted from Zhang et al. 2007)

According to this model, negatively charged carboxylic acid components, COO^- , of crude oil are adsorbed on positively charged chalk surface due to anion exchange capacity of carbonate. Sulfate ions adsorb on the rock surface when seawater is injected into the systems. This will change the surface charge, so that some of the adsorbed crude oil may leave the rock surface. Also, the adsorption of sulfate ions onto the chalk surface decreases the positive charge of the surface, which causes an excess of calcium ions to be close to the surface. Calcium ions react with the negatively charged carboxylic group, $-\text{COO}^-$, so that some of the adsorbed crude oil leaves the rock surface due to ion-binding between calcium ions and carboxylic group. At high temperature ($> 90-100\text{ }^\circ\text{C}$), magnesium may assist in the wettability alteration process. It

becomes more reactive because of dehydration, and displaces both calcium and calcium-carbonate complexes $[-\text{COOCa}]^+$ on the chalk surface in the presence of sulfate (Figure 2-2 B). According to the above described schematic model of wettability alteration, key ions (Ca^{2+} , Mg^{2+} , and SO_4^{-2}) alone could not increase the oil recovery. However, Karoussi and Hamouda (2007) reported that water saturated with Mg^{2+} ions (without SO_4^{-2} and Ca^{2+} ions) could also increase the oil recovery in the spontaneous imbibition experiments from chalk core plugs. They investigated the effect of ion-free water and water containing Mg^{2+} or SO_4^{2-} on wettability alteration at elevated temperature on carbonate rock. They suggested using both experimental observations and calculations obtained from DLVO theory that fine detachment is one of the mechanisms that alters the wettability of the rock at elevated temperatures. Also they reported that presence of magnesium ions indicates a more stable water film and requires an increase in the capillary pressure to rupture the water film as the temperature increases.

Bagci et al. (2001) investigated the effect of brine composition on oil recovery by waterflooding in limestone cores. They indicated that the injected brine with different composition in waterflooding can provide a possible and economically feasible approach to increase oil recovery. To achieve to this result, brines with two different concentrations of 2 and 5 wt% of NaCl, CaCl₂, KCl and binary mixture of them were used. Oil recovery increased by decreasing the salinity of injected water, and the highest oil recovery of 35.5% of original oil in place (OOIP) was obtained for 2% KCl brine. Wettability alteration was indicated as a reason for improving oil recovery. Adjustment of the composition of injected brine could have a significant effect on improving oil recovery by wettability alteration. They also reported the higher pH in low salinity effluent brine samples that was caused by ion exchange reaction.

Austad et al. (2008) studied the effect of brine composition and temperature on oil recovery by carrying out several laboratory experimental studies of water injection and using different core plugs on North Sea chalk reservoirs. It was shown that Ca^{2+} , Mg^{2+} , and SO_4^{-2} are the responsible ions for improving the oil recovery in chalk reservoirs at high temperatures (above 90 °C). It was also reported that wettability alteration is a key reason for the improvement of oil recovery based on these experimental results. They suggested a schematic model of the chemical mechanism describing wettability modification and enhanced water weakening of chalk. According to their model, the ions adsorb to the rock surface, which changes the surface charge so that the adsorbed crude oil may be removed from the rock.

It was reported that sulfate-containing fluids such as seawater can change the wettability of carbonates to more water-wet state. A possible hypothesis on this mechanism described is that sulfate ions will be attracted to positively charged chalk surface if the injection water contains Ca^{+2} and SO_4^{-2} , consequently a reduction of the positive surface charge will prevail. More Ca^{+2} can be adsorbed onto the surface because of a reduction of electrostatic repulsion (Zhang and Austad 2006; Dost et al. 2009; Altoibe et al. 2009)

Yousef et al. (2010) proposed that wettability alteration is the main mechanism for extensive oil recovery by smart waterflooding in carbonate reservoir. They mentioned both surface charges alteration and improving the connectivity between rock pore systems are two different approaches causing wettability alteration. It was explained that even though diluting the seawater will reduce the concentration of key ions (SO_4^{-2} , Ca^{+2} and Mg^{2+}), presence of anhydrite in carbonate rock matrix will provide in-situ generation of SO_4^{-2} which is probably important for wettability alteration. Beside in-situ generation of SO_4^{-2} , dissolution of anhydrite will also improve the connectivity among the macropore and micropore. Because of this effect, dilute

seawater will be able to access pores that were not accessible by regular seawater, and eventually improve oil recovery.

Zekri et al. (2012) investigated the effect of low salinity on wettability by measuring the contact angles using the sessile drop method for carbonate rocks. It was indicated most likely wettability alteration is the mechanism responsible for the improved oil recovery by LoSal technology. Also, the results showed that increasing the sulfate concentration increases the water wetness of the chalky and microcrystalline limestone.

2.3 Effect of Sulfate Ion and Temperature on Wettability Alteration and Oil Recovery on Carbonate Reservoirs

Reported studies experimentally have shown that the sulfate ion is the key ion in carbonate reservoirs affecting wettability, and consequently improving the oil recovery alone, without expensive surfactant. It was also reported significant additional increase in oil recovery was observed with increasing the concentration of sulfate ion as well as the temperature (Austad et al. 2005, 2008; Peimao and Tor 2005).

McCaffery (1972) studied the effect of temperature on water-advancing contact angle for different quartz-hydrocarbon-brine systems at 300 psi. They reported that by increasing the temperature, contact angle was decreased. That means temperature can change the wettability in favorable way.

Hjelmeland and Larrondo (1986) investigated the effect of temperature on oil-water interfacial tension and contact angles on a calcite surface. They used the single-crystal technique of enlarging and reducing the oil drop volume to measure water-receding and water-advancing contact angles. They experimentally showed that increasing the temperature has a significant effect on wettability alteration since the oil-wet nature of the calcite surface changed to water-wet by increasing the temperature from 71.6°F to 140°F.

Anderson (1986) investigated the effect of temperature on wettability. He concluded that core becomes more water-wet when the temperature increases. He reported two reasons for wettability alterations with increasing the temperature, including increasing the solubility of wettability–altering compounds and decreasing the IFT and the contact angle.

Lichaa et al. (1995) used several methods including receding contact angles on smooth calcite surfaces, Amott tests, USBM tests, and the combined Amott-USBM tests using reservoir core samples to investigate the effect of temperature rise on wettability alteration. The measured receding contact angles showed a steady decline for three different rock-fluids system by increasing the temperature. Therefore, they concluded that the calcite surface becomes preferentially more water-wet when temperature increases. Also, their USBM tests on restored carbonate cores indicated that wettability changed from oil-wet to intermediate or water- wet by increasing the temperature from 77 °F to 167 °F.

Wang and Gupta (1995) used modified pedant drop method to study the effect of temperature and pressure on contact angle at pressures ranging from 200 to 3,000 psi and temperature from room temperature to 200°F for crude oil-brine-quartz-calcite systems. They reported that contact angle increased by increasing the pressure and increased by increasing temperature for quartz surface, but decreased with temperature for the carbonate system.

Rao (1999) investigated the effect of temperature on contact angles on a calcite surface using DDDC technique, and reported that water-advancing angle decreased as the temperature of the oil-brine-calcite system increased. Also, it was confirmed that when the temperature in the contact angle cell was increased, the calcium carbonate precipitated out of the synthetic brine on the quartz surface and changed the wettability of the system. This is because by increasing the temperature, the solubility of calcium, sulfate and magnesium carbonates in brine decreases and

deposits on crystal surface. Therefore, this process changes not only the brine composition but also changes the texture and composition of the solid surface used in the contact angle tests.

Al-Hadhrami and Blunt (2000) summarized the effect of temperature on wettability alteration in oil-wet fractured carbonate reservoirs by steamflooding or hot-water injection. It was shown that as temperature increases the wettability changes from oil-wet to water-wet.

Zekri et al. (2001) investigated the effect of brine salinity by decreasing the salinity of the systems and effect of brine composition by increasing the amount of sulfate concentration of the system on wettability in chalky limestone media. They concluded that salinity is not a critical factor in wettability alteration but the presence of the small amount of sulfate in the water might shift the wettability toward water-wet. On the other hand, they showed a system with relatively low salinity (salinity similar to the seawater) was an oil-wet system. With the same salinity system, i.e. seawater with sulfate concentration of 4048 ppm, they showed that system moved towards a water-wet. They experimentally concluded that sulfate is the most important ion in changing the wettability and eventually oil recovery.

Hognesen et al. (2005) investigated spontaneous imbibition into oil-wet carbonates. They used reservoir limestone, outcrop chalk cores, seawater and formation water at high temperature conditions. They indicated that sulfate present in the injection brine can change the wettability from oil-wet to water-wet. Also, they indicated that with an increase of temperature, sulfate ion concentration can improve the oil recovery even more.

Jens et al. (2005) conducted spontaneous imbibition experiments using Stevens Klint outcrop chalk core plugs at different temperatures (70, 90, 110 and 130°C). Both the concentration of sulfate and temperature increased oil recovery. By increasing the temperature from 90 to 130 °C, the average oil recovery increased from 22 to 45%.

Zhang and Austad (2005 and 2006) stated that surface reactivity of potential determining ions (sulfate, calcium, and magnesium) increases with increase in temperature. They stated by increasing the temperature, more negative charges are created due to adsorption of SO_4^{2-} with co-adsorption of Ca^{2+} on carbonate surface. This improves wettability alteration process, and eventually enhances oil recovery.

Strand et al. (2005, 2008) and Fathi et al. (2010) proposed that SO_4^{2-} will adsorb on a positively charged chalk surface during imbibition of seawater into a chalk rock sample. As a result, the bond between rock surface and negative oil component will fail. More Ca^{2+} ions will be able to adsorb to the rock surface because of a decrease in the positive surface charge, eventually allowing release of more of the negative oil component. Also, they mentioned that as temperature increased, this effect became more pronounced and this explains the correlation between oil recovery and temperature observed in spontaneous imbibition tests.

Webb et al. (2005) and Larger et al. (2007) compared recovery from a North Sea carbonate core sample using sulfate free simulated formation brine with seawater, which contains sulfate, to study the effect of sulfate ion on wettability. They showed that seawater was able to improve the wettability of the carbonate system, changing the wettability of the rock to a more water-wet state, and consequently improve the oil recovery. On the other hand, a clear improvement in oil recovery was observed with seawater in comparison with the formation water. This result was made based on the saturation change distinguished in the spontaneous imbibition tests between simulated formation and seawater.

Strand et al. (2006) experimentally investigated the effect of seawater (containing sulfate ions) on oil recovery for limestone core plugs. It was reported that oil recovery did not increase when the concentration of SO_4^{2-} was increased 3 times the concentration in seawater. However,

spontaneous imbibition studies on chalk have reported that when the concentration of SO_4^{-2} increased, the oil recovery improved (Austad et al., 2005; Peimao and Tor 2005).

Zhang et al. (2007) also carried out spontaneous imbibition experiments to investigate the impact of Mg^{2+} ions on oil recovery. It was observed that Mg^{2+} without SO_4^{-2} resulted only in minimal extra oil recovery, whereas Mg^{2+} along with SO_4^{-2} resulted in a significant increase in oil recovery. Neither SO_4^{-2} nor Ca^{+2} alone were able to improve oil recovery under spontaneous imbibition. Therefore, SO_4^{-2} can increase the oil recovery only in the presence of either Ca^{+2} or Mg^{2+} .

Alotabi and Naser-El-Din (2009) indicated seawater can increase the oil recovery in carbonate reservoirs, changing the rock wettability toward more water wet. They reported that multi- component ion exchange is an important parameter in improving oil recovery during waterflooding in carbonate reservoirs. They also mentioned that multi-component ion exchange does not need low salinity water to decrease the residual oil saturation because there is no expandable electronic double layer in carbonate reservoir due to lack of clay.

Punternold et al. (2009) performed both spontaneous imbibition and forced flooding experiments with chalk core plugs injecting different mixtures of seawater and produced water. Oil recovery did not change with different mixtures of seawater and produced water at 50°C and 70°C. However, oil recovery showed slight improvement for the different mixtures at 90 °C. The fluids containing sulfate ions appeared to give 5-10 % higher oil recovery compared to the produced water containing no sulfate. Also, it was reported that Seawater was more efficient than produced water above 100 °C.

Alotaibi and Naser-El-Din (2009) confirmed that solubility of Ca^{2+} ions increased as the temperature increased, the calcium left the carbonate lattice, and that changed carbonate surface

charge to more negative. Therefore, an increase in temperature tends to make the core more water-wet. On the other hand, an increase in temperature tends to increase the solubility of wettability-altering compounds such as Ca^{2+} , Mg^{2+} , and SO_4^{-2} . Also, they reported that the effect of pressure on wettability was not significant.

Yousef et al. (2011, 2012, 2011 a, 2011 b, 2011 c) indicated that injecting seawater containing sulfate ion is able to alter carbonate surface charge toward more negative, leading to more interactions with water molecules, and ultimately change rock wettability. Also they studied the temperature effect on surface charge of carbonate rock using the zeta potential technique. Zeta potential measurements showed more negative charges. Surface reactivity of key ions (Ca^{2+} , Mg^{2+} , and SO_4^{-2}) increased with increase in temperature, adsorption of SO_4^{-2} with co-adsorption of Ca^{2+} on carbonate surface occurred, and that created more negative charges. The solubility of Ca^{2+} ions increased as the temperature increase, the calcium left the carbonate lattice, and that changed carbonate surface charge to more negative (Rodriguez and Araujo, 2006; Alotaibe et al., 2011). This presents one potential mechanism for rock wettability alteration. Another proposed mechanism for wettability alteration is microscopic dissolution due to presence of anhydrite which could enhance the connectivity between macropore and micropore.

Also, Zeta potential measurements suggested that diluting seawater has a significant tendency to alter carbonate rock surface charges toward more negative-state. Alteration of surface charge to negative-state will release adsorbed carboxylic oil components (negative charge components) from the rock surface, alter the rock wettability, and eventually improve oil recovery (Yousef et al. 2011, 2012, 2011 a, 2011 b, 2011 c).

Austad et al. (2012) and Zhang et al. (2007) indicated that sulfate-containing fluids such as seawater can alter the wettability of carbonates to a more water-wet state. It was concluded by them that since carbonate has anion exchange capacity because of positively charged surface, SO_4^{-2} may adsorb to it, changing the wettability of carbonates to a more water wet state.

2.4 Wettability and Contact Angle

Wettability is the tendency of one fluid to spread on or adhere to a rock surface in the presence of other immiscible fluids. Wettability has a significant effect on multiphase rock fluid interactions. It affects primary recovery, residual oil saturation, the shape of the relative permeability curves, the distribution of fluids in a reservoir and their displacement behavior in the porous space. On the other hand, changes in the wettability of cores have been reported to affect electrical properties, capillary pressure, waterflood behavior, relative permeability, dispersion and simulated EOR (Anderson, 1986). Wettability depends on the surface roughness, brine composition, and oil composition. Therefore, by manipulating the brine composition we could achieve the desired wetting condition.

Donaldson et al. (1969) examined the effect of wettability on oil recovery by running coreflood tests. Chemical treatment was used to change core wettability. They concluded that capillary pressure, relative permeability and recovery efficiency of waterflooding changed by changing wettability. They also suggested that wettability of the system should be known for proper understanding of the test data.

Rao et al. (1992) examined the effect of initial core wettability on waterflood oil recovery by conducting coreflood tests including water-wet, intermediate-wet and oil-wet reservoir systems. The highest oil recovery was obtained for an intermediate-wet system and the lowest oil recovery was obtained for an oil-wet system during waterflooding. They also reported that

miscible gas flooding led to the possible development of a mixed-wettability condition in some cases that resulted in increased waterflood oil recovery in successive cycles.

There are several methods for measuring the wettability of a system (Anderson, 1986). Contact angle (θ) is one of the most common methods to measure rock wettability. For oil-water-rock systems, Young's equation is applied to define the reservoir wettability in terms of contact angle, which explains the mechanical equilibrium relationship between interfacial tensions at the three phase contact.

For rock- oil- water systems of petroleum engineering interest, Young's equation is given as:

$$\sigma_{so} = \sigma_{sw} + \sigma_{wo} \cos\theta \tag{1}$$

Where θ is the equilibrium contact angle at the oil- water- solid contact line and σ_{wo} , σ_{so} and σ_{sw} are the interfacial tensions of the oil-water interface, the solid-oil interface, and the solid-water interface. Three-phase contact line is defined as the intersection of a solid surface with the interface between two immiscible fluids. A “moving“ contact line often appears when one fluid displaces another immiscible fluid along a solid surface. The corresponding contact angle is called dynamic contact angle Figure 2-3.

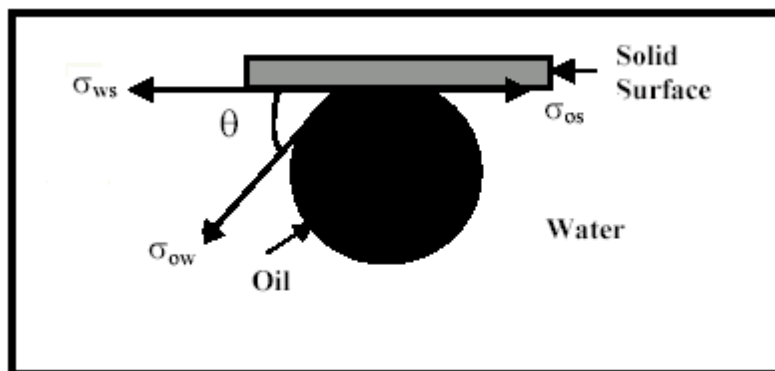


Figure 2-3: Contact angle at oil-water-solid interfaces (Rao and Girard, 1996)

The general conventional classification of contact angle is (Anderson, 1986): Water-wet, 0-75; intermediate-wet, 75~115; and oil-wet, 115~180.

Although there are several methods to measure contact angles such as sessile drop techniques, Wilhelmy plate technique, modified pendant drop method, the sessile drop volume alteration method, etc., these methods have some inherent problems. To overcome the problems related to these contact angle measurement techniques, Rao and Girard (1996) reported a new technique to measure contact angle called the Dual-Drop Dual-Crystal (DDDC) technique. In this technique, two separate crude oil drops are placed on two parallel crystal surfaces held by horizontal and vertical arms of an optical cell. Both oil drops on the two crystal surfaces are aged, so the water film between the crude oil drops and crystal surfaces is drained with the help of the buoyancy forces to attain adhesion equilibrium. By turning the lower crystal upside down and mingling the two oil drops, the advancing and receding contact angles can be measured by shifting the lower crystal laterally, which also helps in monitoring, without any ambiguity, of the three phase contact line (TPCL) movement within the areas previously occupied by crude oil. A schematic diagram of the DDDC technique and monitoring TPCL movement are shown in Figure 2-4 and 2-5. The contact line movement is reproducible by moving the oil drop back to the original position.

Xu et al. (2006) used the DDDC technique to study the effect of fluids composition and rock mineralogy on the water-receding and the water-advancing contact angle for different rock-oil-water systems at reservoir conditions. The dolomite-Yates live oil-Yates synthetic reservoir brine system showed the intermediate-wet behavior ($\theta_a = 95^\circ$) using the DDDC technique conducted at 2,785 psi and 82°F. The quartz-Yates live oil-Yates synthetic reservoir brine system showed weakly water-wet behavior ($\theta_a = 60^\circ$) in the DDDC test conducted at 2,495 psi and 82°F

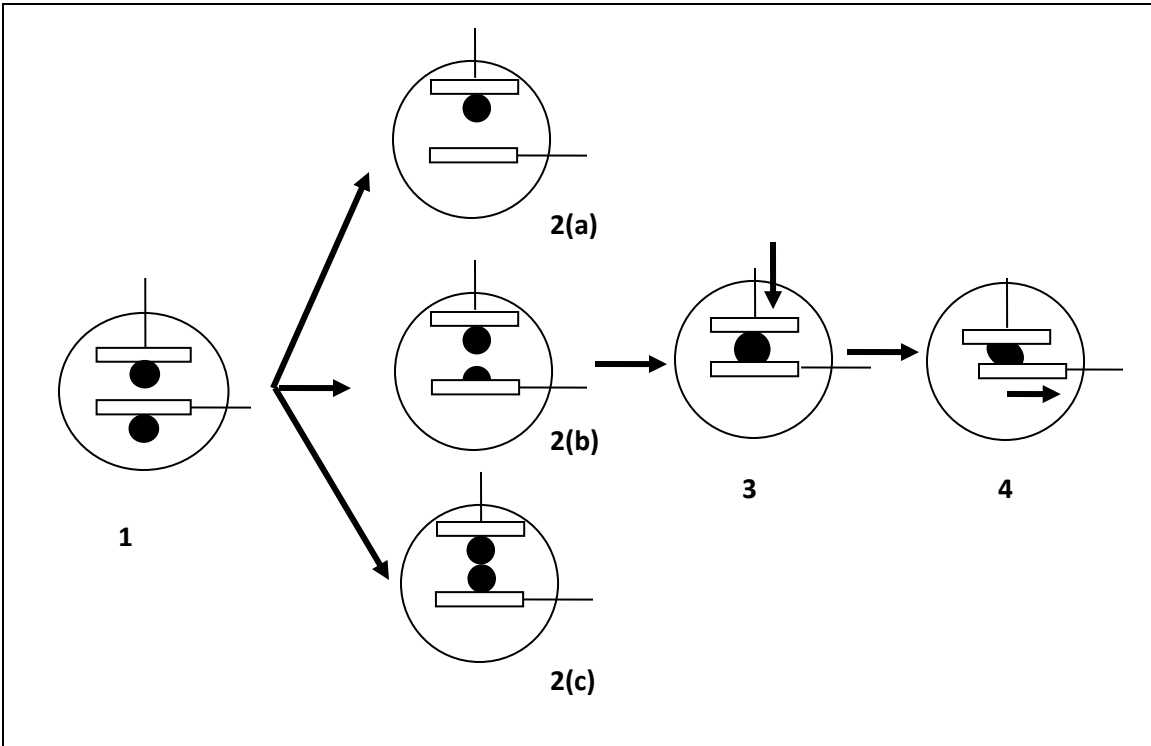


Figure 2-4: Schematic depiction of the dual-drop dual-crystal (DDDC) technique (Rao and Girard, 1996)

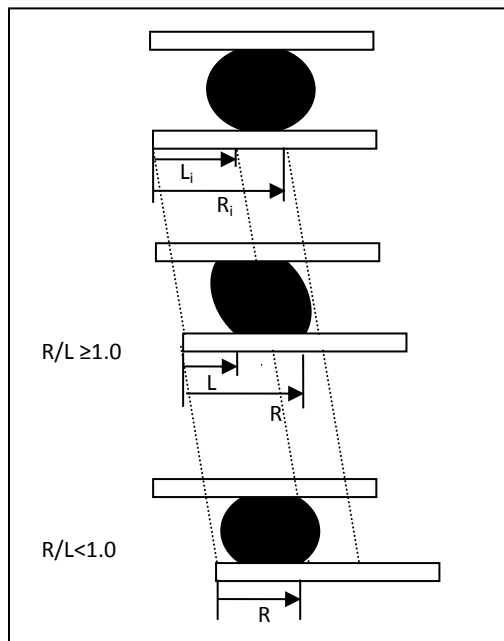


Figure 2-5: Method of monitoring contact line movement in the DDDC technique (Rao and Girard, 1996)

2.5 Measurement of Relative Permeability

Relative permeability explains the ability of the porous media to conduct one fluid in the presence of two or more fluids. The oil-water flow characteristics in reservoirs can be predicted by relative permeabilities.

Two methods namely steady-state or unsteady-state methods are used to measure relative permeability of a rock to each fluid phase in a core sample. In a steady-state method, a fixed ratio of fluids is forced through the test sample until saturation and pressure equilibrium are established. However, unsteady-state displacement is characterized by the injection of one fluid into a core that contains a low or connate saturation of that fluid and which is intended to displace the mobile portions of a second fluid (Honarpur et al., 1986).

Unsteady-state measurements are used for most laboratory measurements of relative permeability because it can be made more rapidly than steady-state measurements. For the measurement of relative permeability under unsteady-state conditions, the theory developed by Buckley and Leverett (1942) and extended by Welge (1952) is used to calculate relative permeabilities.

2.6 Comparison of the Wettability Obtained from Oil-Water Relative Permeability Curves and the DDDC Contact Angles

Rao (2002) compared the wettability derived from oil-water relative permeability curves and the DDDC contact angles with each other for ten different rock-oil-water systems at their respective reservoir conditions. For eight of the ten systems studied, the wettability appeared to correlate with each other for both methods corefloods and the DDDC contact angle measurements. For the other remaining cases in which both methods did not agree, core-scale heterogeneities and the level of pore inter connectivity were attributed to the observed discrepancies in the results from both methods.

Although it is widely accepted that low salinity and brine composition may increase the oil recovery, the experimental data to determine the effect of low salinity and brine composition in carbonates is quite limited, so more data and mechanistic studies are needed. In this study, reservoir wettability was determined by measuring the water advancing contact angles at both ambient and reservoir condition as well as at high temperature using DDDC techniques for dolomite rock. Also, coreflood tests were conducted to study the effect of brine salinity and composition on oil recovery.

3. EXPERIMENTAL APPARATUSES AND PROCEDURES

To experimentally investigate the impact of brine salinity and composition on wettability and oil recovery, two different methods were used in this study. In the first method, Dual-Drop Dual-Crystal (DDDC) contact angle measurement technique was used to measure the water-advancing contact angle at ambient and reservoir conditions as well as at high temperature condition to investigate the wettability. The advancing contact angle was used to characterize wettability and the rock-oil adhesion interactions present in the system. When the oil adheres to the rock surface strongly, a large advancing contact angle will be measured.

In the second method, coreflood experiments were conducted using the dolomite core to investigate the effect of changing the salinity and ionic composition of the injected brine on oil recovery. Another purpose of running coreflood tests is to determine whether or not an optimal salinity brine and an optimal composition brine obtained from DDDC technique does result in increase in the oil recovery compared to Yates synthetic brine.

The material, equipment apparatuses, and the experimental techniques used in this study are discussed in the following sections.

3.1 Materials

3.1.1 Fluids

Yates crude oil from West Texas was used in this study. Viscosity and density of the Yates stock tank crude oil are 12.8 cp and 0.875 gr/cc, respectively. Yates reservoir temperature and pressure are 82°F and 700 psi, respectively (Ayirala, 2002).

The Yates synthetic brine was prepared by adding different amounts of NaCl, KCl, Na₂CO₃, CaCl₂.H₂O, MgCl₂, Na₂SO₄, and NaHCO₃ to the deionized water. The composition of Yates reservoir brine is listed in Table 3-1.

Table 3-1: Yates synthetic brine composition

Salt	Chemical Name	Yates synthetic Brine(g/l)
NaCl	Sodium Chloride	2.546
KCl	Potassium Chloride	0.0915
Na ₂ CO ₃	Sodium Carbonate	1.43
CaCl ₂ .2H ₂ O	Calcium Chloride Hydrate	1.555
MgCl ₂	Magnesium Chloride	1.87
Na ₂ SO ₄	Sodium Sulfate	2.2
NaHCO ₃	Sodium Bicarbonate	1.09
TDS	Total dissolved solid	10.7825

As it can be seen in Table 3-2, the effect of brine composition on wettability and oil recovery was studied by applying five brine solutions with different sulfate concentrations. This is because based on the literature review, the sulfate ion appears to be one of the most important ions in wettability alteration for carbonate rocks. The reported amount of sulfate ion in Yates reservoir brine was 2.2 g/l. The equivalent total dissolved solids (10.7825 g/l) for all the brine solutions were made by adjusting the quantity of NaCl Table 3-2.

Table 3-2: Brine solution with different sulfate concentrations

Salt (g/l)	Yates synthetic Brine	Brine Solution with different Sulfate concentrations			
	Test 1	Test 2	Test 3	Test 4	Test 5
Na₂SO₄	2.2	0	1.1	4.4	10.7825
NaCl	2.546	4.746	3.646	0.346	0
KCl	0.0915	0.0915	0.0915	0.0915	0
Na ₂ CO ₃	1.43	1.43	1.43	1.43	0
CaCl ₂ .2H ₂ O	1.555	1.555	1.555	1.555	0
MgCl ₂	1.87	1.87	1.87	1.87	0
NaHCO ₃	1.09	1.09	1.09	1.09	0
TDS	10.7825	10.7825	10.7825	10.7825	10.7825

To study the effect of low salinity on wettability and oil recovery, five different versions of reservoir brine, Yates synthetic brine, two times diluted, 10 times diluted, 50 times diluted, and 100 times diluted Yates synthetic brine, were injected to DDDC cell as shown in Table 3-3.

Table 3-3: Brine composition for different salinity

Salt (g/l)	Yates synthetic Brine	2X Diluted	10X Diluted	50X Diluted	100X Diluted
NaCl	2.546	1.273	0.255	0.051	0.025
KCl	0.0915	0.046	0.0092	0.002	0.00092
Na ₂ CO ₃	1.43	0.72	0.143	0.029	0.014
CaCl ₂ .2H ₂ O	1.555	0.777	0.156	0.031	0.016
MgCl ₂	1.87	0.94	0.187	0.037	0.0187
NaSO ₄	2.20	1.1	0.22	0.044	0.022
NaHCO ₃	1.09	0.55	0.11	0.022	0.011
TDS	10.78	5.39	1.08	0.216	0.108

3.1.2 Rock

Silurian Dolomite, purchased from Kocurek Industries, was used to represent carbonate reservoir rock since the Yates reservoir rock type is dolomite. Dolomite rock properties used in this study are presented in Table 3-4.

Table 3-4: rock properties

Rock type	Dolomite
Formation	Thornton
Permeability	45-100 md- brine permeability
Porosity	21%
Homogeneous	No

3.1.2.1 Preparing and Cleaning the Dolomite Rock for Running Experiments

The suitable dolomites substrates were prepared carefully through cutting and polishing followed by cleaning and drying to be used in the Dual-Drop Dual-Crystal (DDDC) contact angle tests. For preparing the dolomite to be used in the ambient condition DDDC cell, the raw dolomite first was cut into appropriate size of 0.9" (L) 0.5" (W) 0.2" (T) in (2.25*1.25 *0.5 cm). However, the size of the upper and lower crystals that was used at reservoir condition DDDC technique was not the same. The upper crystal was cut in the size of 0.4" (L) 0.4" (W) 0.2" (T) in (1.01*1.01*0.51 cm) while the lower crystal was cut in the size of 0.4" (L) 0.25" (W) 0.1" (T) in (1.01*0.64*0.25 cm). The next step after cutting the crystals was to polish them. The crystals were cleaned after polishing as described below. For coreflood tests, the dimensions of core were 6" long and one and 1.5" in diameter.

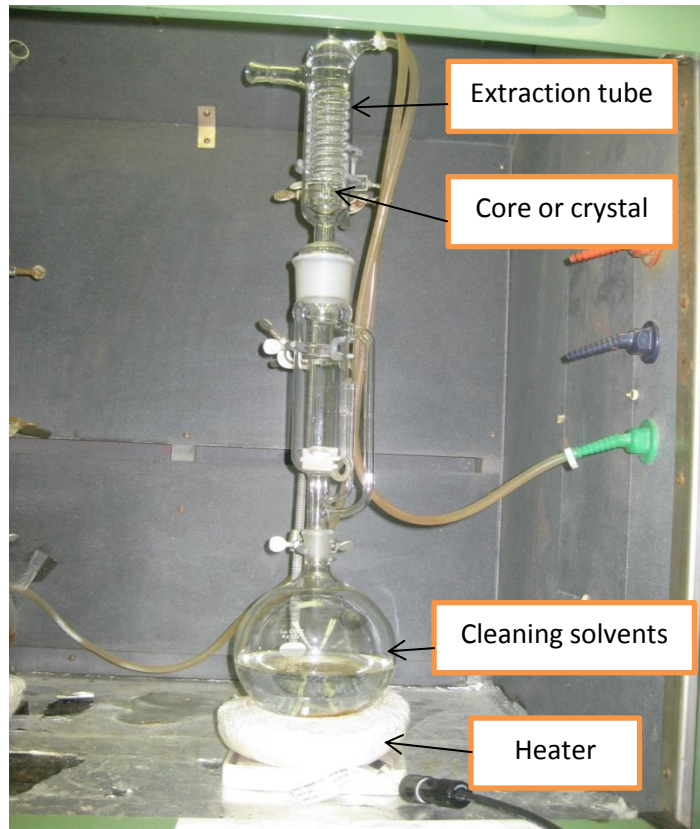


Figure 3-1: Soxhlet extraction cleaning system

Cleaning procedure was the same for both dolomite crystals and core used in this study. First, they were placed in a solution of methanol/ chloroform (13%/87%) and refluxed for 24 hours as can be seen in Figure 3-1. After refluxing, they kept in boiling deionized water (DIW) for 2 hours. Finally, they were dried at room temperature and kept in air-tight glass containers to prevent any deposition of dust particles before the start of experiments.

3.2 Experimental Apparatus

3.2.1 Ambient-Conditions Dual-Drop Dual-Crystal (DDDC) Optical Cell

The ambient DDDC optical cell apparatus was used in this study for carrying out the water-advancing contact angle tests at ambient conditions to determine wettability. The ambient DDDC optical cell and its associated components are shown in Figure 3-2. Two crystal holders, one at the top and the other one at the side, were used to hold rock crystals for measuring the water-receding and the water-advancing contact angles. The upper arm moves in the vertical direction, while the side one moves horizontally. Those arms can rotate on their own axes as well.

There is a needle tip at the bottom of the cell for forming a pendant oil drop and placing it on a rock surface. For injecting oil into the cell, a syringe which is connected to the capillary injection tubing is available. An inlet and an outlet valves are available at the bottom and the top of the optical cell for controlling the influent and effluent, respectively. In addition, the brine solution is taken in a container that is kept at an adequate height to allow flow by gravity. A schematic diagram of the ambient conditions experimental setup is shown in Figure 3-3.

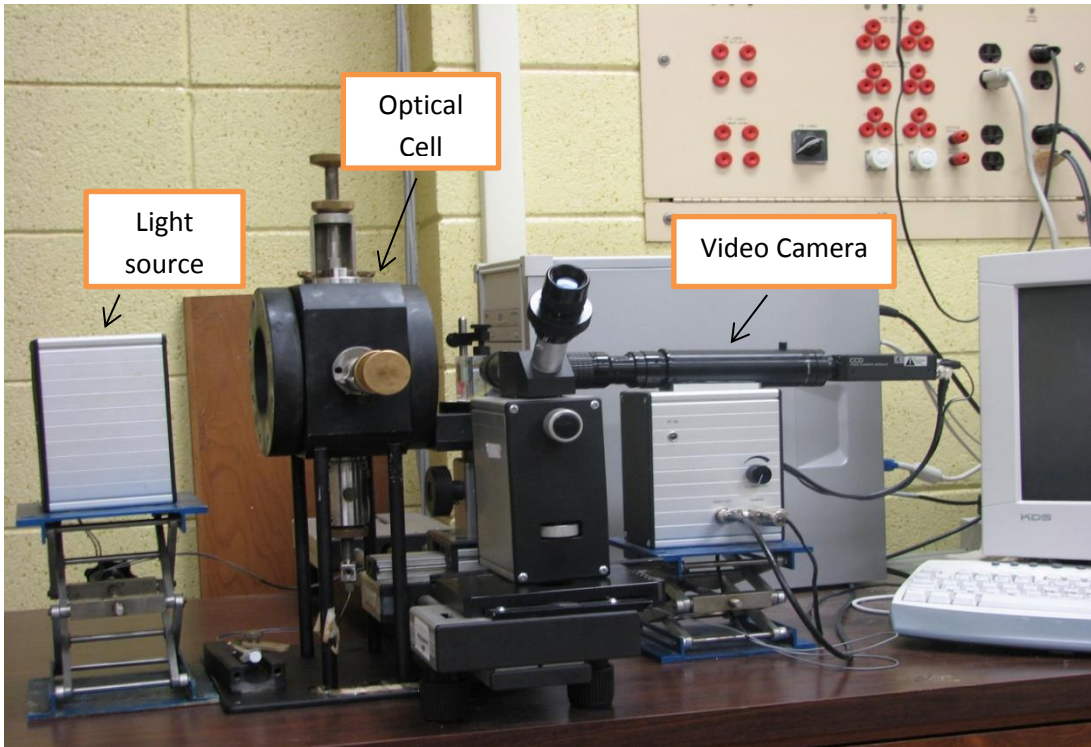


Figure 3-2: Ambient-conditions DDDC optical cell apparatus

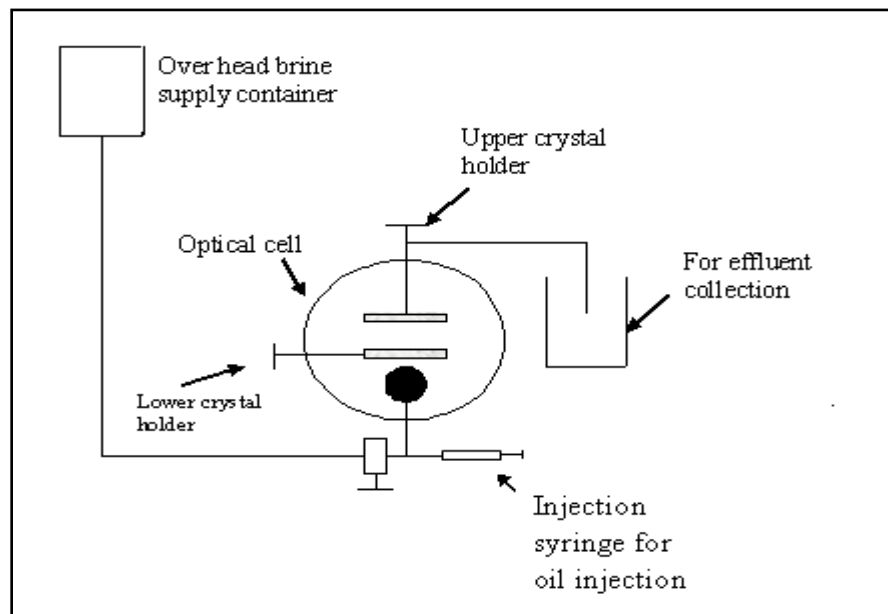


Figure 3-3: Schematic diagram of the ambient-conditions experimental setup

Five steps used for preparation and cleaning of ambient optical cell apparatus included:

1. Deionized water to clean the optical cell
2. Toluene to dissolve oil from the cell and its accessories
3. Acetone to dissolve all the toluene
4. Deionized water to remove any traces of acetone
5. Nitrogen to dry the cell and its accessories

These five steps were applied after finishing each experiment and before starting the new experiment in this study.

3.2.2 High-Pressure High-Temperature (HPHT) DDDC Optical Cell Apparatus

A high pressure and high temperature DDDC optical cell apparatus was used to measure the water-receding and the water-advancing contact angles at reservoir conditions (700 psi and 82°F) and high temperature condition (250°F). This apparatus has four adjustable arms two horizontal and two vertical. One horizontal and one vertical arm that are available to hold the rock crystals are placed one at the top and the other on the side. The third one that is placed horizontal on another side is used to hold a calibration ball. The fourth arm, which is placed at the bottom, has a needle tip which is used to introduce the oil drop to form a pendant drop of oil and place it on crystal surfaces during the high pressure and high temperature DDDC tests. All these arms can rotate as well as move back and forth. This unique cell can hold the pressure and temperature up to 20,000 psi and 400°F, respectively. The other accessories include an oven which is used to adjust temperature, high-pressure/high-temperature floating piston transfer vessels and valves to hold and transport fluids, and an image capturing and analysis system. The image capturing and analysis system includes a high-quality digital camera, a computer equipped with image analysis software, monitor, video recorder and a light source. The high pressure and

high temperature DDDC optical cell apparatus and the schematic diagram of the high pressure and high temperature experimental setup are shown in Figures 3-4 and 3-5, respectively.

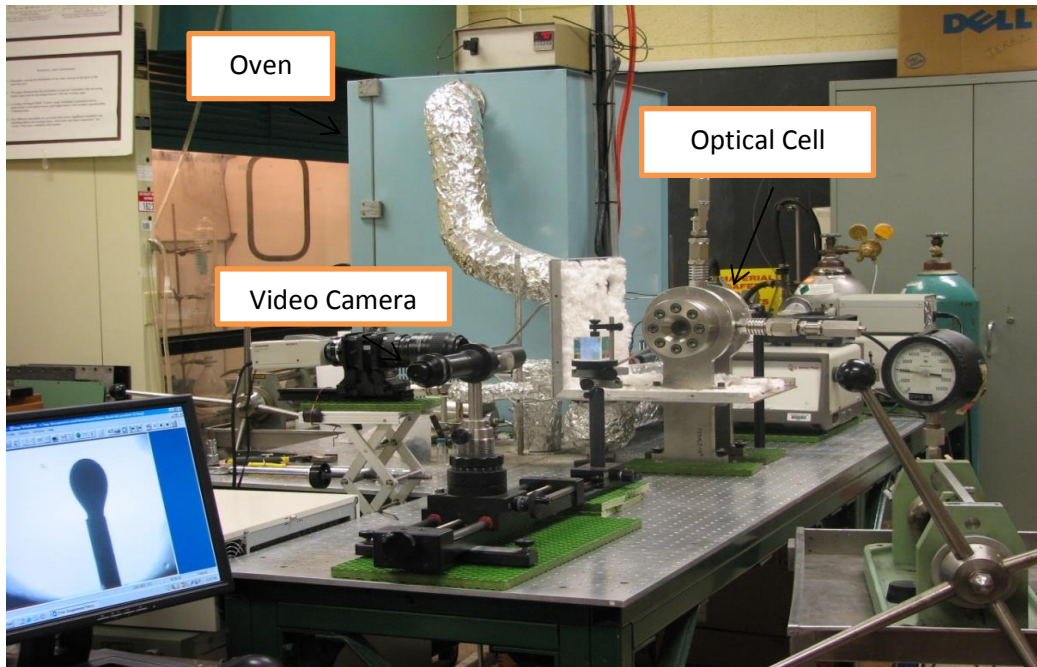


Figure 3-4: The high pressure and high temperature DDDC optical cell apparatus

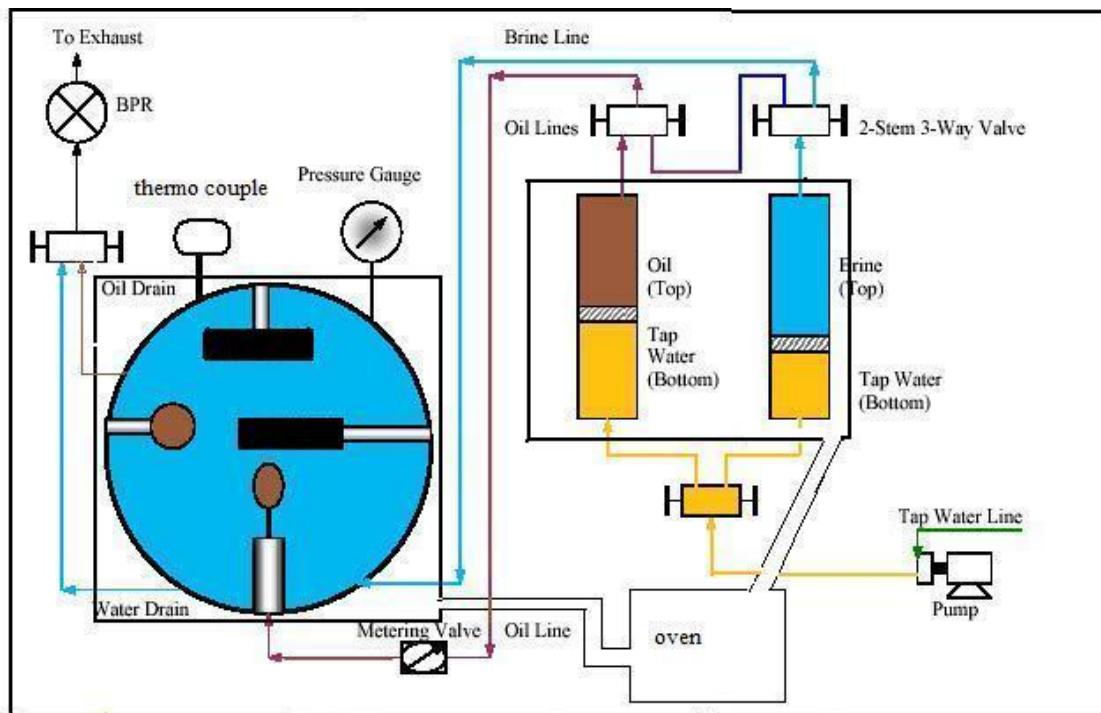


Figure 3-5: Schematic diagram of high pressure and high temperature experimental setup (Xu et al. 2005)

Five steps were used to prepare and clean the high pressure and high temperature DDDC optical cell apparatus in this study. These five steps are brought in below:

1. Deionized water to flush all the wetted parts of the high pressure high temperature DDDC optical cell, tubing, fittings, valves, and transfer vessels
2. Toluene to dissolve any oil traces present in the system
3. Acetone to remove toluene
4. Deionized water to remove any traces of acetone
5. High pressure nitrogen to dry the system

3.2.3 Coreflood Apparatus

A coreflood apparatus was assembled to conduct waterflood (without and with salinity variations) in order to measure endpoint relative permeabilities, initial water saturation and residual oil saturation as well as to obtain data as pressure and recovery versus time. The schematic and actual coreflood setup is shown in Figure 3-6 and 3-7. A dolomite core was placed in the core holder, and fluids in the transfer vessel were injected with a constant rate through the pump at inlet (upstream flowing pressure), while the outlet (downstream flowing pressure) was maintained at the reservoir pressure 700 Psi by using back pressure regulator (BPR). Two pressure gauges for measuring the pressure drop across the core during the floods and one pressure gauge for measuring the annulus pressure were used. A tape heater connected to a voltage controller was used to control and maintain the temperature at reservoir temperature 82°F. The production burette was used to measure oil and water volumes produced at various times during the test.

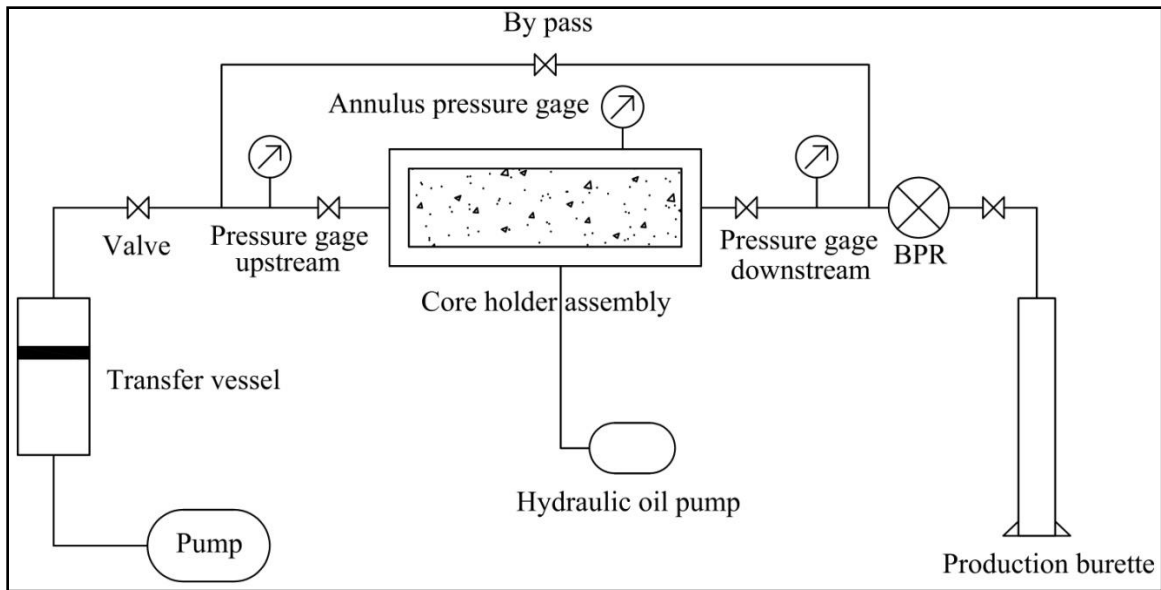


Figure 3-6: schematic of coreflood experimental setup

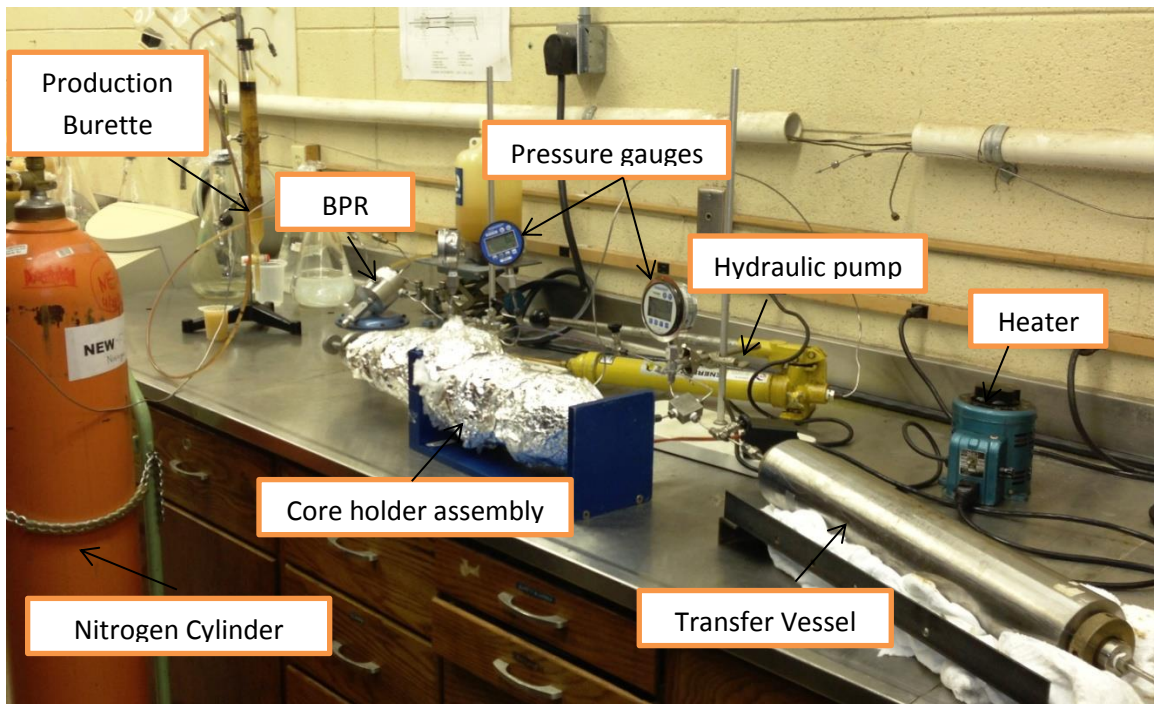


Figure 3-7: Coreflood apparatus

3.3 Experimental Procedure

3.3.1 Contact Angle Measurement Using the Dual- Drop Dual- Crystal Technique

In this study for determining the wettability of different oil-brine-rock systems, Dual-Drop Dual-Crystal (DDDC) technique was used to measure water-advancing contact angle at

ambient, reservoir (82°F and 700 psi) and high temperature conditions (250°F and 700 psi). The procedures of measuring contact angles using DDDC technique are described as below.

Two previously prepared and cleaned crystals were mounted, one in the lower horizontal holder and the other in the upper vertical holder. After filling the cell with brine, oil was injected into the cell through the injector tip located in the bottom of the optical cell. Two separate drops were placed on the two crystals and aged for 24 hours to achieve solid-fluids equilibrium.

After 24 hours, the lower crystal was turned upside down. Then there are three possible ways that a drop could behave: 1) The drop remains attached to the surface due to adhesion, 2) A part of the oil drop floats to the top of the cell because of the buoyancy, while leaving behind a part of the oil on the surface, and 3) All of the oil drop detaches from the lower crystal without leaving any oil on the surface. In the first two cases, the upper crystal is brought down to merge the two oil drops, and in the third case the oil drop on the upper crystal is brought down to contact the same area that was previously occupied by the previous oil drop (Figure 3-8). Then the lower crystal was moved laterally to observe the movement in contact line. As the contact line moves, it enables the measurement of water-advancing contact angle (θ_a) as water advances over a previously oil occupied area. All of the contact angles were measured at different times until they show negligible change. This procedure is repeated until at least two successive shifts yield similar water-advancing contact angles.

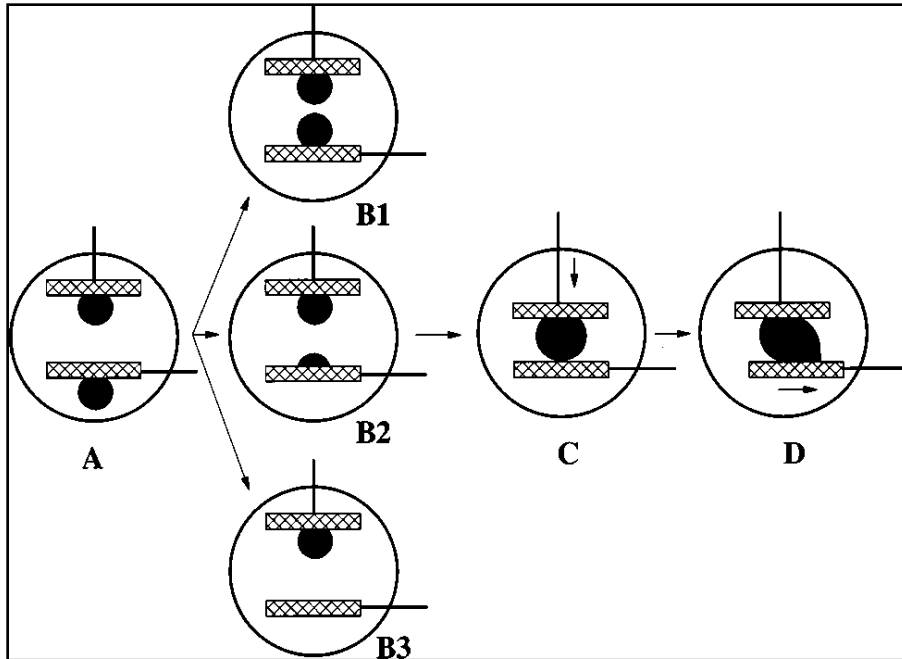


Figure 3-8: Schematic depiction of the dual-drop-dual-crystal (DDDC) contact-angle technique (Rao, 1999)

Even though the procedures mentioned above are the same for both ambient and reservoir conditions, there are some differences. For ambient condition, brine was taken in a large container, which was kept at a sufficient height above the cell to allow liquid to flow through plastic tubing by gravity, while for the reservoir condition tests, the brine was taken in a transfer vessel and filled into the cell using a constant flow rate pump. Also, for reservoir condition, after the optical cell was filled with brine, it was heated up and then pressurized to obtain the desired temperature and pressure conditions. After achieving constant pressure and temperature conditions, a few drops of oil were injected into the aqueous phase for attaining the oil-water interaction equilibrium.

3.3.2 Coreflood Procedure

The coreflood apparatus was used to estimate oil recovery, residual oil and water saturation and the end-point effective permeabilities. The series of experiments conducted in this study are shown in Table 3-5.

Yates crude oil and Silurian dolomite core were used for all sets of experiments conducted using the coreflood methods.

Table 3-5: List of experiments conducted using coreflooding method

Set	Aging time period	Different brine	Salinity (g/l)	Amount of Sulfate (g/l)
1	10 days	Yates synthetic brine (2.2 g/l sulfate content)	10.78	2.2
2		Brine with 4.4 g/l sulfate	10.78	4.4
3		50 times diluted brine	0.216	0.044

For conducting the coreflood experiments in this study, several steps including pore volume and porosity determination, absolute permeability determination, establishing initial condition, and waterflood were performed in sequence.

3.3.2.1 Pore Volume and Porosity Determination

The core was wrapped with a layer of Teflon tape and then placed inside of the coreholder. To check if there is any leak in the core system, the core system was placed under vacuum using a vacuum pump. The core system was checked to maintain vacuum for a few hours. If not, it indicates that there is a leak in the core system that should be fixed by repeating previous steps until pressure does not change. Yates synthetic brine was then injected into the core at a very low rate 0.1 cc/min by opening the inlet valve and closing the outlet valve. When the core was completely saturated with brine, the pressure would rapidly increase. At this point, the volume of injected brine was recorded and then the pore volume (PV) and porosity were calculated using the following calculations.

$$\text{Pore volume (PV)} = \text{Injected volume} - \text{Dead volume} \quad (2)$$

$$\text{Bulk volume} = \text{Area of core} * \text{length of the core} \quad (3)$$

$$\text{Porosity} = \frac{\text{Pore volume}}{\text{Bulk volume}} \quad (4)$$

As it can be seen from the above equations, pore volume was calculated by subtracting the injected fluid volume from the dead volume and porosity was calculated by dividing the pore volume over the bulk volume.

3.3.2.2 Absolute Permeability Determination

Brine was injected through the core at three different flow rates of 1, 1.5, and 2 cc/min for 4 pore volume each and then the stabilized pressure drops (Δp) were averaged for each flow rate to obtain the absolute permeability (K_{abs}) using the Darcy's law.

$$\text{Darcy's law: } q = \frac{KA\Delta p}{\mu\Delta X} \quad (5)$$

$$\text{Absolute permeability: } K_{\text{abs}} = \frac{q\mu\Delta X}{A\Delta P} \quad (6)$$

3.3.2.3 Establishing Initial Condition

After the absolute permeability test, oil was injected into the core with a flow rate of 2 cc/min for 4 pore volumes. After third pore volume, no brine would be observed in the effluent indicating connate water saturation (S_{cw}) was reached. Then, the brine produced was measured and used to calculate the connate water saturation. For measuring effective permeability (K_{eff}), the flow rate was changed to 3 and 4 cc/min and injected for four pore volume each. Effective permeability was calculated using the Darcy's equation after reaching the constant pressure drop for each. Having both the absolute and effective permeabilities, the endpoint oil relative permeability would be calculated by following equation. The core was then left aging for 10 days to obtain the natural wettability before conducting the corflood experiments.

$$\text{End point relative permeability: } K_{\text{ro}}^* = \frac{K_{\text{eff}}}{K_{\text{abs}}} \quad (7)$$

3.3.2.4 Waterflood

Waterflood tests were conducted after aging the core at initial water saturation to produce oil, to determine oil recovery and oil-water relative permeabilities. In order to avoid contamination and reduce the dead volume, before waterflooding, all lines were flushed with the fluid about to be injected. The volume of oil in these lines could not be considered because it was produced from the lines not from the core itself. Brine was injected at a flow rate of 2 cc/min for 4 pore volumes. For measuring effective permeability (K_{eff}), the flow rate was changed to 3 and 4 cc/min and injected for four pore volume each. Effective permeability was calculated using the Darcy's equation after reaching a constant pressure drop for each flow rate. Having both the absolute and effective permeabilities, the endpoint water relative permeability could be calculated. The residual oil saturation and oil recovery were calculated by measuring the volume of oil produced. At this point, the core would be ready for the next waterflood test.

Leas and Rappaport (1953) linear coreflood criterion ($LV\mu \geq 1$, where L is system length in centimeter, μ is displacing phase viscosity in centipoises, and V is velocity in centimeters per minute) was used to calculate the minimum stable volumetric flow rates to be used in each of the experiments to ensure flood is stable and recoveries are not dependent on injection flow rate.

3.4 Experimental Design

The ambient-condition DDDC technique was used to measure the water-advancing contact angles for all nine tests mentioned in section 3-1-1 to determine the effect of brine salinity and composition on wettability. After that, the tests display significant wettability effects were chosen to be run at reservoir conditions (82°F, 700 psi) using HPHT DDDC technique. In order to investigate the effect of temperature on wettability, those experiments conducted using

high pressure high temperature DDDC technique at reservoir conditions were also conducted at high temperature conditions (250°F, 700 psi).

Coreflood tests were used to investigate the effect of brine salinity and composition on oil recovery by carrying out three coreflood experiments using the optimal brine composition and brine salinity obtained from the DDDC technique.

3.5 Coreflood Simulator to Determine Oil-Water Relative Permeabilities

The main purpose of conducting the coreflooding experiments is to quantify recoveries and to determine the oil-water relative permeabilities from which wettability alterations were interpreted. To achieve to this purpose, a coreflood simulator was used to estimate oil-water relative permeabilities by matching the data obtained from the coreflood experiments. The pressure drop is computed by deriving the saturation profile in the core and thereby calculating the total mobility along the length of the core. This model estimates relative permeabilities by minimizing the sum-of-squares of the weighted deviations of the experimental pressure and production histories from the calculated values. Craig's rules of thumb (Craig, 1971) were used to interpret the relative permeability curves to infer wettability alterations.

4. RESULTS AND DISCUSSION

The results of dynamic contact angle measurements using Dual- Drop Dual- Crystal tests at ambient, reservoir, and high temperature conditions, and oil recovery using the coreflood tests are presented in this chapter. The results are divided and discussed in the following 4 sections.

In section 4-1, the experimental results of Dual- Drop Dual- Crystal technique conducted at ambient condition have been presented. Wettability was determined in these tests by measuring water-advancing contact angles using different salinity and composition of brine.

In section 4-2, the results of the experiments conducted at reservoir conditions (700 psi and 82°F) using the Dual- Drop Dual Crystal technique have been presented and discussed.

In section 4-3, the experimental results of the effect of temperature on wettability using DDDC technique have been presented and discussed. This was done by measuring the water-advancing at high temperature conditions (700 psi and 250°F).

In section of 4-4, the effect of brine salinity and composition on oil recovery have presented and discussed. This was done by conducting coreflood tests at reservoir conditions using the optimal brine salinity and composition obtained from DDDC tests at reservoir conditions. The results obtained from a coreflood simulator for estimating oil-water relative permeabilities by history matching experimental data on oil recovery and pressure drop have also been discussed in the section of 4-4.

4.1 Wettability and Dynamic Contact Angles at Ambient Conditions

The ambient condition DDDC tests for determining the wettability of the Yates crude oil-brine–dolomite systems were conducted by changing the salinity and composition of brine. On the other hand, the role of dissolved salts and the amount of sulfate ion on stabilization of aqueous wetting film trapped between oil phase and rock surface was investigated using the

DDDC tests by measuring the change of water-advancing contact angle. The 24-hour aging time for all the experiments was selected since most of the wettability changes happen during the initial 24 hours of exposure (Rao, 1996). The results from the ambient condition tests are presented in following sub-sections.

4.1.1 Effect of Brine Composition on Wettability at Ambient Conditions



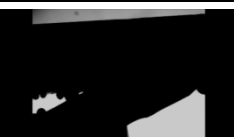


As it can be seen in Table 4-1, five different brines with different amount of sulfate were used in this study to investigate the effect of brine composition on wettability for dolomite rock and Yates crude oil. There were always distinct differences between advancing and receding contact angles, but no consistent trends were obtained.

The DDDC results showed that for Yates crude oil-dolomite-Yates synthetic brine systems, the measured water-advancing angle was 158° , indicating a strongly oil-wet nature Table 4-1 and Figure 4-1. This measured water advancing angle, 158° , was similar with measured water advancing angle reported by Vijapurapu (Vijapurapu and Rao, 2003) for the same Yates rock-fluids system. The effect of brine with 4.4 g/l sulfate on wettability was significant as the water-advancing contact angle changed from 158° for Yates brine to 115° for brine with 4.4 g/l sulfate- indicating a shift in wettability from strongly oil-wet to intermediate-wet.

The water-advancing contact angle ranged between 153° to 160° for all the brine solutions except for the one with 4.4 g/l sulfate, where the-water advancing angle was 115° . This indicates that for all the cases except for brine with 4.4 g/l sulfate, the system was strongly oil-wet. Therefore, for those cases, changing the amount of the sulfate in the brine solution had a little effect on wettability since there was a small change in water-advancing contact angle. However, for the brine solution with 4.4 g/l sulfate, sulfate had an important effect on wettability

and brought the system from strongly oil-wet to intermediate-wet. This is because the amount of sulfate in the brine, 4.4 g/l, is more than the total amount of magnesium and calcium (3.425 g/l). Therefore, sulfate can be attracted by the positively charged surface and thus more negative charges will be created on the rock surface to cause the oil to leave the surface and to change the wettability to intermediate state. On the other hand, the decrease in water-advancing contact angle is attributed to the ion exchange between the key ions (SO_4^{2-} , Ca^{2+} , Mg^{2+}) present in brine which releases some adsorbed carboxylic oil components from the rock surface, and consequently altering rock wettability to a more water-wet condition (Strand, et al., 2006; Zhang and Austad, 2006; Zhang, et al., 2007).

Table 4-1: Effect of brine composition with different sulfate on dynamic (receding and advancing) contact angles at ambient condition

Test No.	NaCl	TDS (ppm)	pH Before/ After Experiment	Water- Advancing Contact Angle θ_a , deg		Wettability	Water-Receding Contact Angle θ_r , deg
Test1: 2.2g/l SO_4^{2-}	2.546	10782.5	9.29/9.25	158		Strongly oil-wet	29
Test 2: zero SO_4^{2-}	4.746	10782.5	9.31/9.20	154		Strongly oil-wet	30
Test 3: 1.1g/l SO_4^{2-}	3.646	10782.5	9.15/9.03	160		Strongly oil-wet	28
Test 4: 4.4g/l SO_4^{2-}	0.346	10782.5	9.09/9.14	115		Intermediate-wet	40
Test 5: 10.78g/l SO_4^{2-}	0	10782.5	8.07/9.80	153		Strongly oil-wet	35

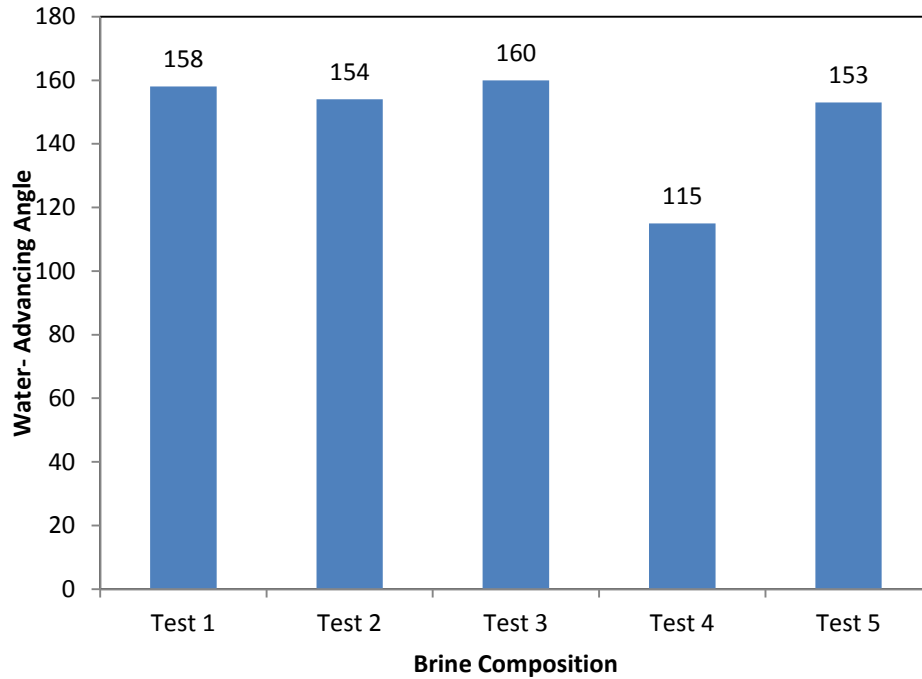


Figure 4-1: Effect of brine composition on water- advancing angle

For the first three tests, with 0, 1.1 and 2.2 g/l sulfate concentration in the brine, a strong oil-wet behavior was observed. For all those cases the total amount of divalent calcium and magnesium cations are higher than the amount of divalent sulfate anions in the systems. Presence of these cations in the brine solution would result in more positive charges on the rock surface. These positive charges would act as attractive sites for the negative ends of the polar components in the crude oil. This may be a reason why the systems were strongly oil-wet for those cases. However, when the amount of sulfate in the system is more than the amount of divalent cations, it has a significant effect on wettability and changes it toward intermediate-wet.

The water-advancing contact angle measured for the brine including 10.782 g/l sulfate, which is equal to the total dissolved salts, was 153°. This means that the system remained strongly oil-wet when sulfate was the only component in the system. Therefore, it appears that

sulfate in the absence of calcium and magnesium ions cannot change the wettability. In other words, sulfate only can change the wettability in the presence of calcium and magnesium ions.

The results obtained in this section are somehow similar to the results obtained by Ligthelm et al. (2009). They investigated how the change in the amount of sulfate and calcium in brine influences wettability alteration for the Middle Eastern Limestone. Three different brines called LS1, LS2 and LS3 were used. Brine LS2 and LS3 were modifications of brine LS1 by increasing the sulfate content and reducing the calcium content, to avoid exceeding the critical solubility constant and precipitation of calcium sulfate. Precipitation of CaSO_4 and CaCO_3 will reduce the calcium and sulfate content of the wettability modifying brine. This consecutively would decrease its wettability modifying power.

The results indicated that brines LS2 and LS3 yielded a response, indicating wettability modification towards increased water-wet state. The absence of a response for brine LS1 is related to the low value for the sulfate to calcium ratio.

Water-receding angles did not change significantly for all the experiments and also pH of the brines before and after conducting the experiments were measured and showed no change for all the experiments except for the one with the 10.782 g/l sulfate. This is because there is no bicarbonate (HCO_3^-) in the brine with only sulfate, which is a crucial ion in determining the system's pH.

4.1.2 Effect of Brine Salinity on Wettability at Ambient Conditions


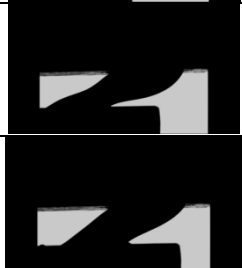
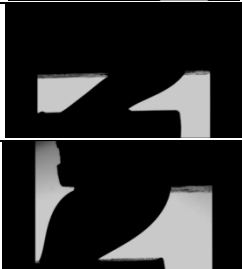


Wettability is a three-phase interaction between rock, oil and brine. The rock surface charge and fluid-fluid interfaces are affected strongly by salinity and pH of brine (Anderson 1986). Diluting the brine decreases the concentration of ions. As a result when the strength of ions in the brine decreases, they do not have that much power to remove water from the crystal

surface and thus oil stays on the water layer instead of the crystal surface. Consequently, this behavior changes the wettability. Also, reducing the salinity changes the solubility of some minerals. Vijapurapu et al. (2002) investigated the effect of salinity on Yates crude oil at ambient conditions. It was reported that low salinity has a significant effect on dynamic contact angles.

In this study, five different versions of reservoir brine, one after another, starting with regular brine and ending with 100 times diluted brine were studied to investigate the effect of salinity on wettability. The results can be seen in Table 4-2.

The advancing contact angle with Yates synthetic brine was 158°, indicating an oil-wet system (Table 4-2 and Figure 4-2). There was no significant change in wettability by diluting the Yates synthetic brine twice and 10 times. However, a significant change was observed in the water-advancing contact angle for 50 and 100 times diluted brine.

Table 4-2: Effect of brine salinity on dynamic (receding and advancing) contact angles at ambient conditions

Type of Brine	Brine Salinity (ppm)	pH Before/ After Experiment	Water- Advancing Contact Angle θ_a , deg	Wettability	Water- Receding Contact Angle θ_r , deg
Yates brine	10782.5	9.29/9.25	158		29
2x diluted	5391.25	9.5/9.36	150		26
10x diluted	1078.25	9.32/9.39	144		27
50x diluted	215.65	9.48/9.3	113		33
100x diluted	107.825	9.18/9.34	125		40

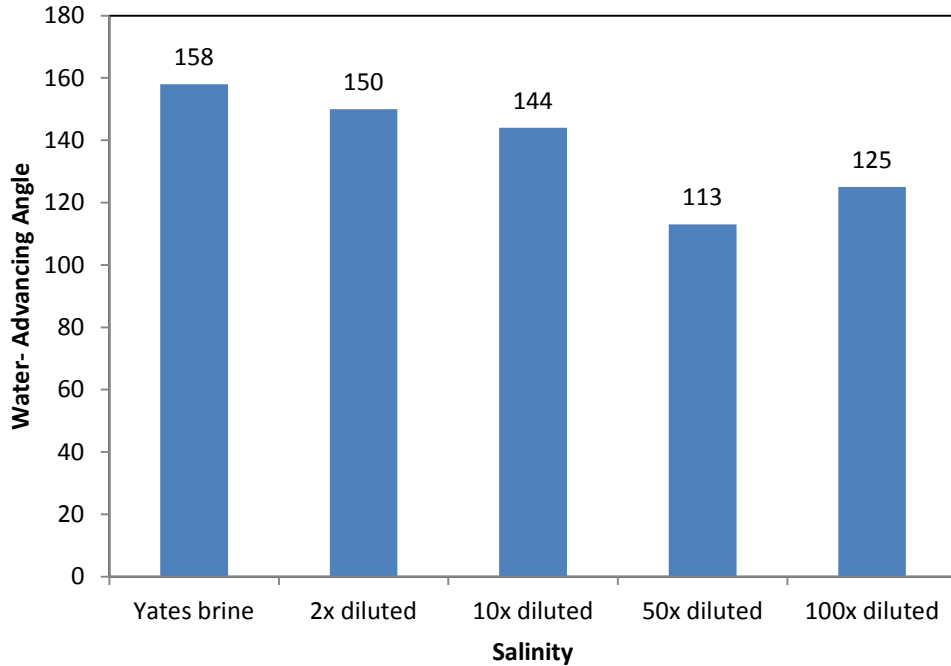


Figure 4-2: Effect of brine composition on water advancing angle

The water-advancing contact angle changed from 158° for the Yates synthetic brine to 150° and 144° for twice and ten times diluted Yates brine, respectively. It means, twice and ten times diluting the brine did not change the system from being oil-wet. This is because the amount of salt in the brines was large enough that caused the thin wetting film of water removed from the dolomite surface and as a result oil adhered on the dolomite surface strongly. A significant change was observed in the water advancing angle with 50-times-diluted brine. The angle changed from 158° to 113°, which indicates that 50 times diluting the Yates synthetic brine changed the wettability of the system from oil-wet to intermediate-wet. The contact angle also changed from 158° to 125° for 100-times-diluted brine indicating the rock wettability showed weakly oil-wet for 100 times diluted brine. The significant change of water-advancing contact angle for 50 and 100 times diluted brine can be explained because the amount of total dissolved solids in the system was quite low and thus there were insufficient ions in the brine to weaken

the thin water film between oil and rock. Also, migration of fines, dissolution and destruction of rock particles could be other possible mechanisms of shifting the system to more water-wet.

The water-advancing angle decreased more for 50 times diluted brine than for 100 times diluted Yates brine and thus it was more effective. This may be because for the 100 times diluted brine the concentration of key ions (SO_4^{-2} , Ca^{2+} and Mg^{2+}) reduced more than a level that they could act as active ions. On the other hand, the amount of salinity in 100 times diluted brine was not able to change the surface charge of the carbonate rock toward more negative, leading to more interactions with water molecules, and eventually altering rock wettability less than that in 50 times diluted brine. This conclusion was in line with other conclusion from other papers (Yousef Jabbar et al, 2013) that “there may be an optimal composition of the dissolved solids in the injection water that would yield the lowest water advancing angle and highest oil recovery”. Also it was confirmed by Alotaibi (2009) that for the best oil recovery there is an optimum salinity level that should not be exceeded to recover more oil.

Changing the water advancing angle toward water-wet state by diluting the brine can be explained through two different mechanisms: (1) Although 50 and 100 times diluted brines will reduce the concentration of key ions (SO_4^{-2} , Ca^{2+} and Mg^{2+}), presence of anhydrite in carbonate rock matrix may provide in-situ generation of SO_4^{-2} which is probably important for wettability alteration; (2) Dissolution of anhydrite will also improve the connectivity among the macro-pores and micro-pores (Yousef et al., 2011). Therefore, those pores that were not connected by Yates synthetic brine can be connected to each other by diluting the brine, and as a result improve the oil recovery.

For all the experiments, water receding contact angles did not change significantly. A measured pH of the brines before and after conducting the experiments was almost constant for all the experiments.

4.1.3 Contact Angle test to Simulate the Coreflood Procedure

In this study for each coreflooding test, a new brine roughly equal to 4 pore volumes was injected to replace the previous brine. However, for conducting the tests using the DDDC technique, the cell was totally washed and cleaned before the subsequent experiments. Therefore, to check whether injecting the new brine into the cell without cleaning it does affect wettability or not, one more experiment was run as follows: First the ambient cell was filled with Yates synthetic brine. After measuring the water advancing contact angle, the crude oil was allowed to stay between the two substrates and then the 50 times diluted brine was injected into the cell. The water advancing angle measured was 112° which was only about 3° less than when it was run after cleaning the cell. It means that flow through test also yield a systematic wettability alteration.

4.2 Wettability and Dynamic Contact Angles at Reservoir Conditions

As it was explained in the section 4-1, nine different experiments with different brine salinity and compositions were conducted at ambient condition using the DDDC technique to investigate the effect of brine salinity and compositions on wettability by measuring water-advancing contact angle. The effect of brine composition on wettability has been summarized in Table 4-1 and Figure 4-1. The brine with 4.4g/l sulfate had a significant effect on wettability and changed the wettability of the system from strongly oil-wet to intermediate-wet. Also, Table 4-2 and Figure 4-2 show the effect of brine salinity on wettability. It was experimentally confirmed that Yates synthetic brine with 50 times and 100 times dilution altered the wettability


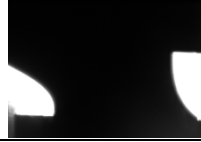


significantly. Strongly oil-wet for the Yates synthetic brine changed to intermediate-wet for 50 times diluted Yates brine and weakly oil-wet for 100 diluted Yates brine. Therefore, to conduct experiments at reservoir conditions (700 psi and 82°F), brine solutions including brine with 4.4 g/l sulfate content, 50 times and 100 times diluted brine were compared with Yates synthetic brine. As it can be seen in Table 4-3 and Figure 4-3, four different experiments were conducted using high pressure, high temperature DDDC technique to investigate whether salinity or brine composition change wettability significantly compared with Yates synthetic brine at reservoir conditions.

4.2.1 Effect of Brine Composition and Salinity on Wettability at Reservoir Conditions

Four different experiments were conducted using DDDC technique at high pressure and high temperature (700 psi and 82°F) to measure water-advancing contact angle in Yates crude oil-different brines–dolomite rock systems in order to investigate the effect of brine salinity and composition on wetting behavior at reservoir conditions.

The results of the high pressure- high temperature DDDC tests are given in Table 4-3. The Yates crude oil-Yates synthetic brine-dolomite systems showed a strongly oil-wet behavior at reservoir conditions (700 psi and 82°) by exhibiting high water-advancing contact angle of 157°. The water-advancing contact angle of 115° for Yates crude oil- brine with 4.4 g/l sulfate-dolomite systems at reservoir conditions showed its intermediate-wet nature. The water-advancing contact angle was measured 112° for the Yates crude oil- 50 times diluted Yates brine- dolomite systems indicating intermediate wet nature. For the Yates crude oil- 100 times diluted Yates brine- dolomite systems, the system was in weakly oil-wet region as the water-advancing contact angle was measured 122°.

Table 4-3: Effect of brine salinity and composition on dynamic (receding and advancing) contact angles at reservoir conditions

Type of Brine	Brine Salinity (ppm)	pH Before/ After Experiment	Water- Advancing Contact Angle θ_a , deg		Wettability	Water- Receding Contact Angle θ_r , deg
Reservoir brine	10782.5	9.29/9.05	157		strongly oil-wet	32
Brine with 4.4g/l SO_4^{2-}	10782.5	9.09/8.99	115		intermediate-wet	41
50x diluted	215.65	9.48/9.12	112		intermediate-wet	38
100x diluted	107.825	9.18/ 9.11	122		weakly oil- wet	28

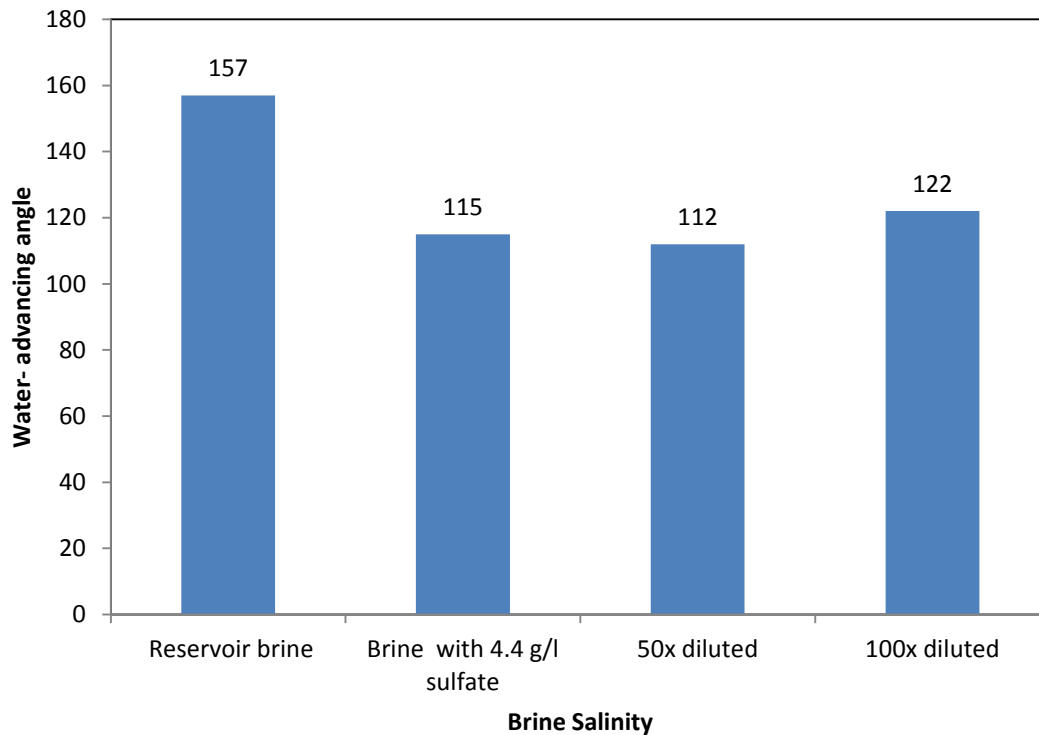


Figure 4-3: Effect of brine composition and salinity on water- advancing angle at reservoir condition

Wettability alteration was experimentally confirmed that is the main mechanism for the reduced water-advancing contact angle. It was concluded that the presence of a relatively stable wetting water film on the rock surface which results in weak adhesion between oil and rock surface would happen by diluting the Yates reservoir brine.

4.2.2 Comparison between Water-Advancing Angles Obtained from both Ambient and Reservoir Conditions

Figure 4-4 displays the difference between water-advancing contact angles obtained using the DDDC technique at ambient and reservoir (82°F, 700 psi) conditions. As can be seen from Figure 4-4, water-advancing contact angles measured at ambient and reservoir conditions were the same or slightly different for all the systems. This is because Yates reservoir temperature is quite low (82°F) or almost close to room temperature at which the ambient tests were conducted.

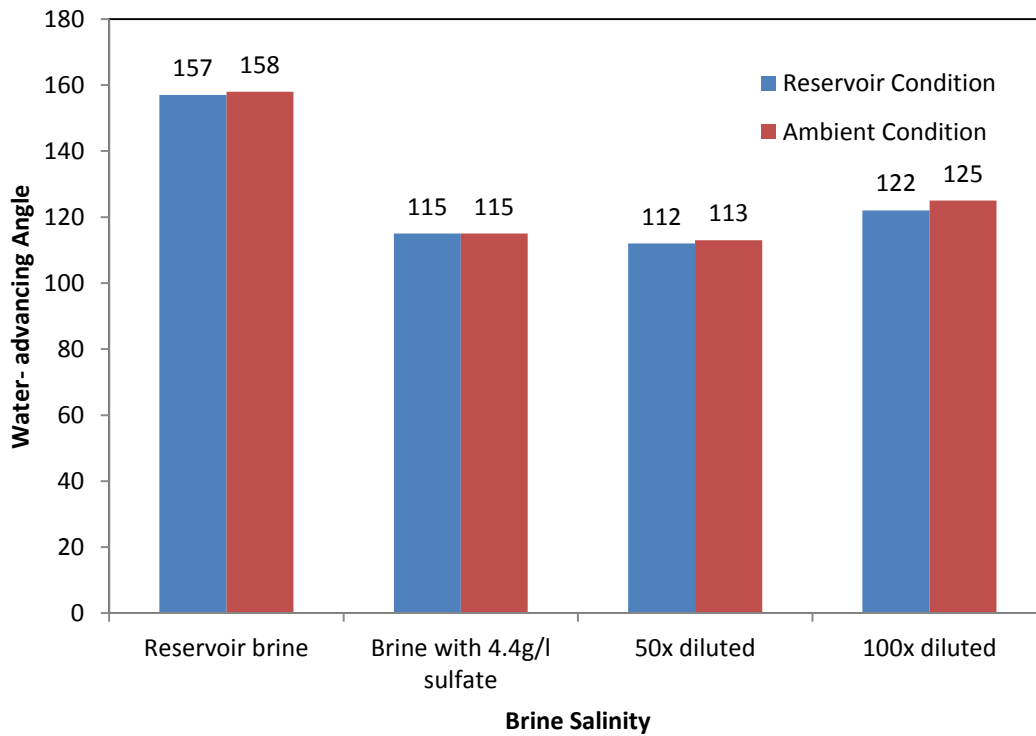


Figure 4-4: Comparison between water-advancing angle obtained for ambient and reservoir conditions

Therefore, the difference between water-advancing contact angle in reservoir and ambient conditions was small. This conclusion is in agreement with findings of other researchers that temperature can change the wettability if it is high and also pressure has little effect on wettability (Anderson 1986, Hejelmend 1986, Wang and Gupta 1995, Rao 1999, al-hadrami and blunt 2001).

4.3 Effect of Temperature on Wettability Using the HPHT DDDC Technique at 250°F





The purpose of investigating the effect of temperature on wettability is to determine if the wettability of the Yates reservoir rock-fluid system is sensitive to high temperatures. Also, for developing thermal production strategies such as steam injection, the characterization of initial wettability and its change with temperature is important.

Based on the literature review, temperature has a significant effect on wettability unlike the pressure. It tends to decrease water-advancing contact angle and make the carbonates more water-wet at higher temperatures. By increasing the temperature not only the oil viscosity will be reduced, but also other variables such as density and viscosity of the individual phases, interfacial properties of oil-water-gas interfacial tensions, and the interfacial energies involving the solid surface and its mineral transformations will be affected. Increasing the temperature has two important advantages: the first is shifting the wettability toward more water-wet in carbonates and the second is that the condensed water from the steam dilutes the native reservoir brine which prevents more expenses for injecting the low salinity of brine to the reservoir in order to recover more oil.

In this study, to determine the temperature effect on wettability, experiments conducted at reservoir conditions (700 psi and 82°F) have also repeated at a temperature of 250°F using the

high-pressure high-temperature DDDC technique. The water-advancing contact angle was measured for all four cases and the results have been shown in Table 4-4 and Figure 4-5.

Table 4-4: Effect of temperature on water- advancing contact angle at 250°

Type of Brine	Brine Salinity (ppm)	pH Before/ After Experiment	Water- Advancing Contact Angle θ_a , deg		Wettability	Water- Advancing Contact Angle at reservoir condition (82°)
Reservoir brine	10782.5	9.05/7	120		weakly oil- wet	157
Brine with 4.4g/l SO ₄ ²⁻	10782.5	8.99/7.4	87		intermediate-wet	115
50x diluted	215.65	9.12/7.7	87		intermediate-wet	112
100x diluted	107.825	9.11/7.3	114		Intermediate-wet	122

The effect of temperature for the 100 times diluted brine-Yates crude oil-Dolomite systems was also noticeable as the water-advancing contact angle decreased from 122° at reservoir condition to 114° at 250°F. Increasing the temperature changed the wettability of the system to intermediate-wet from the weakly oil-wet.

The pH of the brine altered from its initial value ranging between 8.99 and 9.11 to 7–7.7 after increasing the temperature. Therefore, it can be concluded that reduction in water-advancing contact angle by increasing the temperature may be related to calcium, sulfate or magnesium carbonates precipitating out of the brine on the dolomite surface. The possibility of

precipitation of these components on the rock surface was confirmed by pH decreasing 7-7.7 after the experiments.

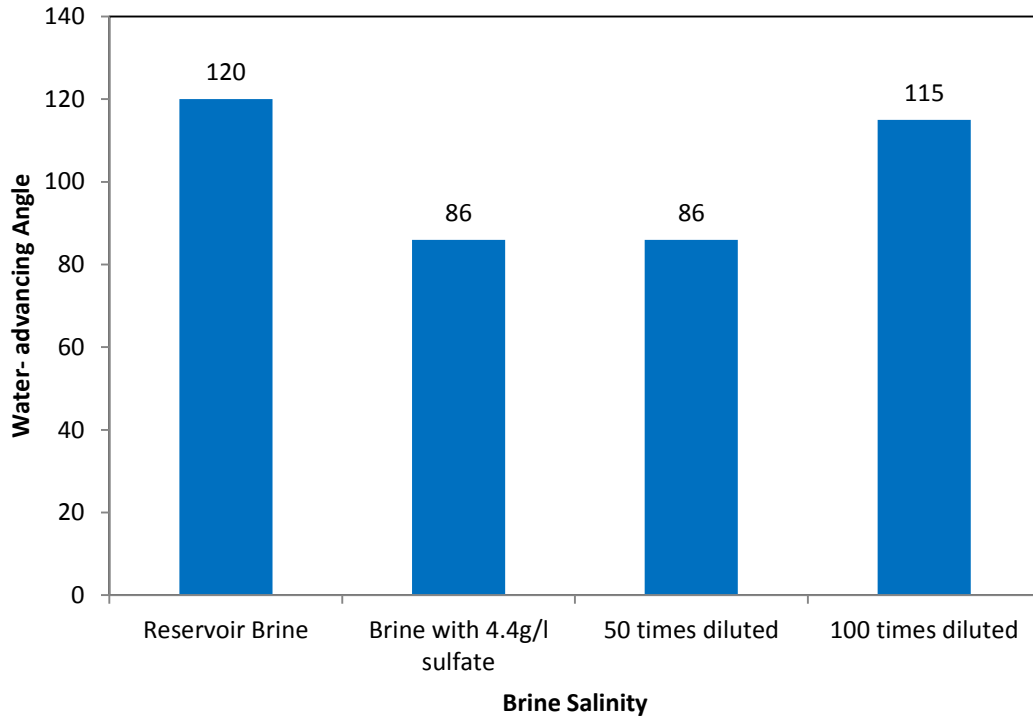


Figure 4-5: Effect of temperature on water-advancing angle at temperature 250°F

Surface reactivity of key ions increased with increase in temperature, adsorption of SO_4^{2-} with co-adsorption of Ca^{+2} on carbonate surface happened, and that created more negative charges (Zhang and Austad 2006; Zhang et al 2007).

The effect of temperature can be explained according to the chemical model that constructed by Hiorth et al. (2010) to predict the surface potential of calcite and the adsorption of sulfate ions from the pore water. At higher temperatures, calcium in the brine reacts with sulfate and anhydrite is precipitated. When anhydrite is formed the aqueous phase loses calcium, and calcium has to be supplied from the rock for the solution to remain in equilibrium with calcite. The source of Ca^{2+} ions must be calcite dissolution. If the calcite dissolution takes places where

the oil is adsorbed, then the oil can be liberated from the rock. The present of magnesium can also help to the dissolution of calcite.

4.3.1 Comparison between Water-Advancing Angles Obtained from Ambient, Reservoir (82°F) Conditions and High Temperature (250°F) Conditions

Figure 4-6 shows the comparison of water-advancing contact angles obtained using the DDDC technique at ambient, reservoir (700 psi and 82°F), and high temperature conditions (700 psi and 250°F).

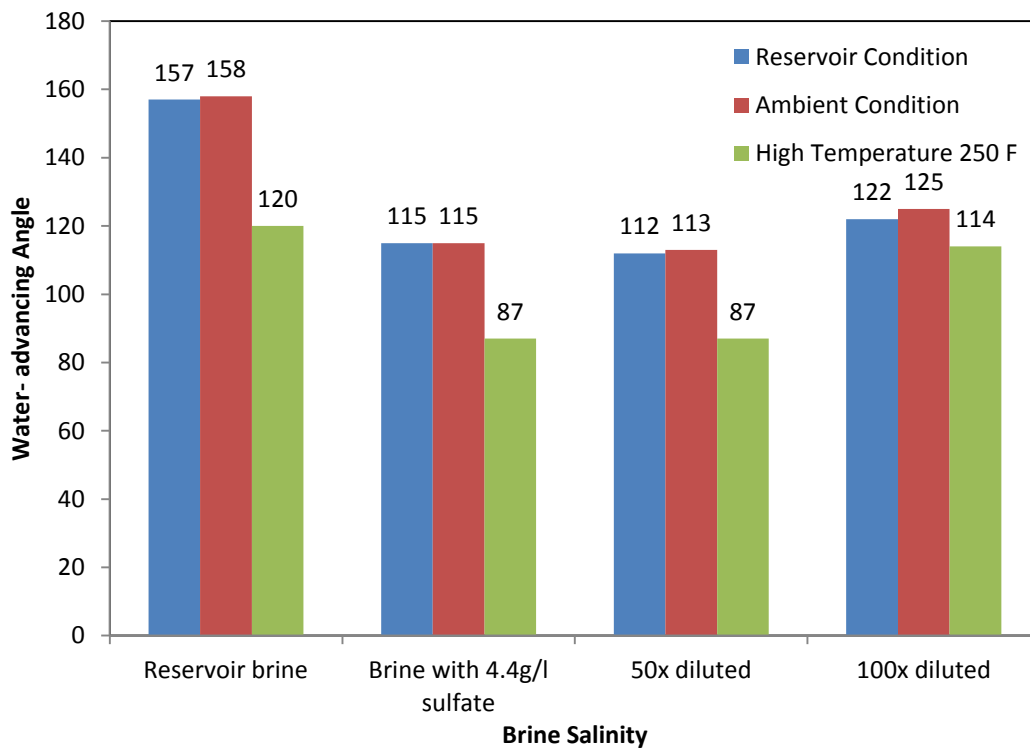


Figure 4-6: Comparison between water-advancing angles obtained for ambient, reservoir (temp 82°F) and high temperature (250°F) conditions

As can be seen in Figure 4-6, there is a significant difference between water-advancing angles measured for high temperature conditions and both ambient and reservoir conditions. Increasing the temperature to 250°F caused a change in wettability in a favorable way for all the tests conducted. Based on the results obtained, it can be concluded that temperature is one of the most important parameters that can change the wettability of the dolomite rock-fluids system in a

favorable way and consequently increase oil recovery. This is because that the affinity of potential determining ions for the dolomite surface increased with temperature, and consequently decreased the water advancing contact angle.

4.4 The Effect of Brine Salinity and Composition on Oil Recovery by Conducting Coreflood Tests at Reservoir Conditions

Many researchers have proposed that the shifting of the wettability state towards less oil-wet state increases the oil recovery. Also, it was experimentally confirmed that the shift towards a water wetting state results in reduction of residual oil saturation. Therefore, in this study coreflood tests were conducted to investigate first the effect of brine salinity and composition on oil recovery and then to determine oil-water relative permeabilities by history matching coreflood data in order to interpret wettability shifts, if any, from relative permeabilities.

Unsteady state relative permeability measurements were conducted in a Dolomite rock-Yates crude oil-Yates brine system. The relative permeability measurements, mainly oil-water relative permeability ratio and oil recovery curves were used to investigate the effect of low salinity and sulfate content on wettability and oil recovery. Initial water saturation, residual oil saturation, the endpoint relative permeabilities and the water saturation at cross-over point that are characteristics of relative permeability were used to infer wettability alterations. The Craig's rules-of-thumb (Craig, 1971) used in this study to interpret wettability alteration are listed in Table 4-5.

Table 4-5: Craig's rules of thumb used for wettability interpretation (Ayirala, 2002)

Criterion	Water-wet	Oil-wet
Initial water Saturation, S_{wi}	>0.25	<0.15
Water saturation at cross-over point	>0.5	<0.5
Endpoint relative permeability to water at S_{or}	<0.3	>0.5
Endpoint relative permeability to oil at S_{wi}	>0.95	<0.7~0.8

Aging time is one of the important variables that influences wettability. Different wettability states can be induced by exposing core sample to crude oil (Jadhunandan and Morrow, 1991; Morrow 1990). In this study, all three coreflood tests were conducted at 10 days aging time.

4.4.1 Relative Permeability and Wettability Measurements for Yates Synthetic Brine-Yates Crude Oil- Dolomite Systems

The history match of oil recovery and pressure drop as well as the resulting relative permeability curve obtained from the simulator for the Dolomite-Yates crude oil-Yates synthetic brine systems are shown in Figures 4-7, 4-8, and 4-9, respectively. Summary of the experimental and simulation of waterfloods are given in Table 4-6. A good history match was obtained for oil recovery and pressure drop versus injected pore volume as it can be seen in Figures 4-7 and 4-8 and Table 4-6.

According to Craig's rules of thumb, the relative permeability curve (Figure 4-9 and Table 4-6) indicates water-wet characteristics for dolomite-Yates synthetic brine-Yates crude oil systems. This was concluded base on the high initial water saturation (S_{wi}) of 0.39 (> 0.25), slightly higher crossover point water saturation ($S_{w,c-o}$) of .58(> 0.50), low endpoint water relative permeability (K_{rw}) of 0.11(< 0.30), and high endpoint oil relative permeability (K_{ro}) of 1(> 0.95) Table 4-8. The wettability derived from the corefloods was totally different from that inferred from the contact angle measurements. Although it was concluded a water-wet characteristics for the Dolomite- Yates synthetic brine- Yates crude oil systems based on relative permeability curve, the water-advancing contact angle measured of 157° using the DDDC technique indicated a strongly oil-wet system Table 4-7.

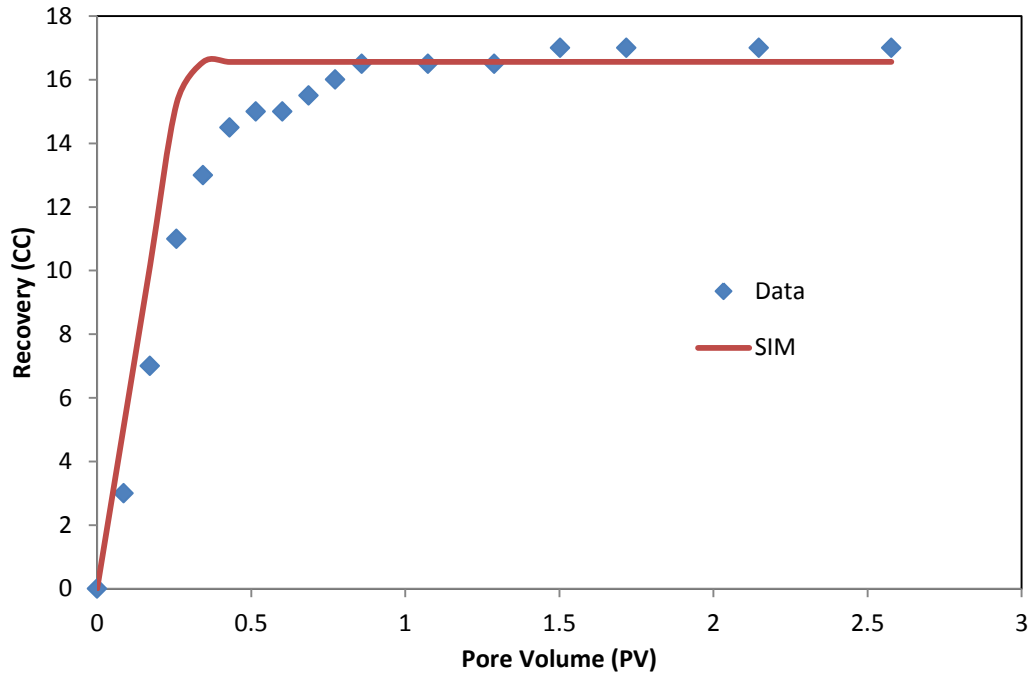


Figure 4-7: History match of oil recovery for the dolomite- Yates synthetic brine - Yates crude oil systems

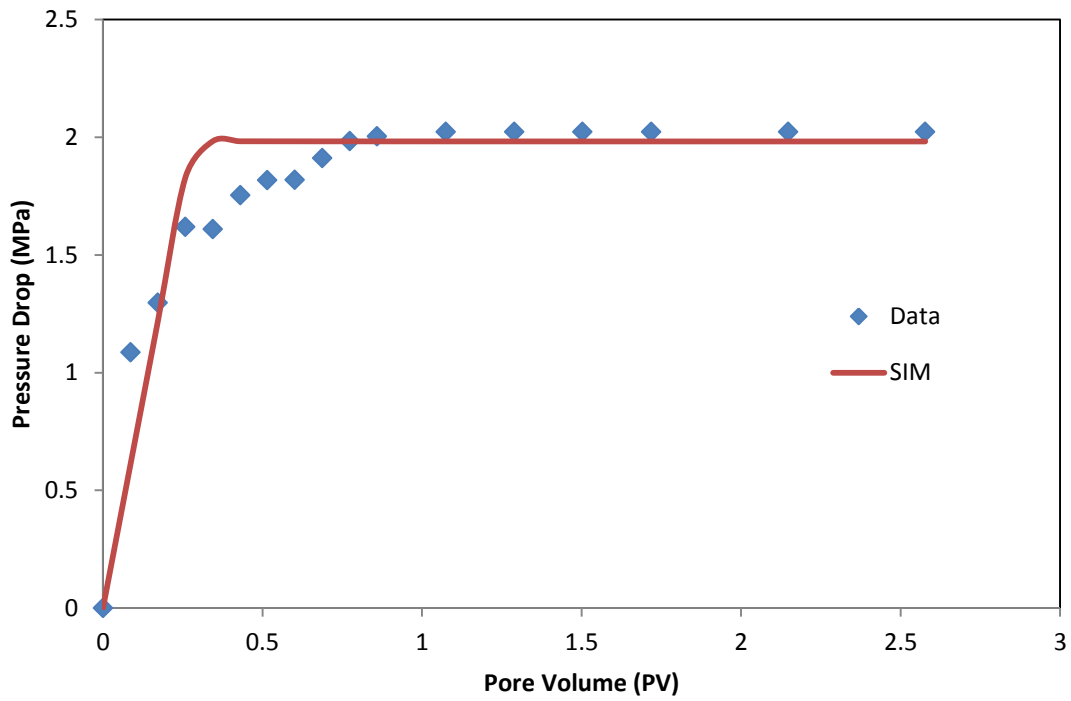


Figure 4-8: History match of pressure drop for the dolomite- Yates synthetic brine - Yates crude oil systems

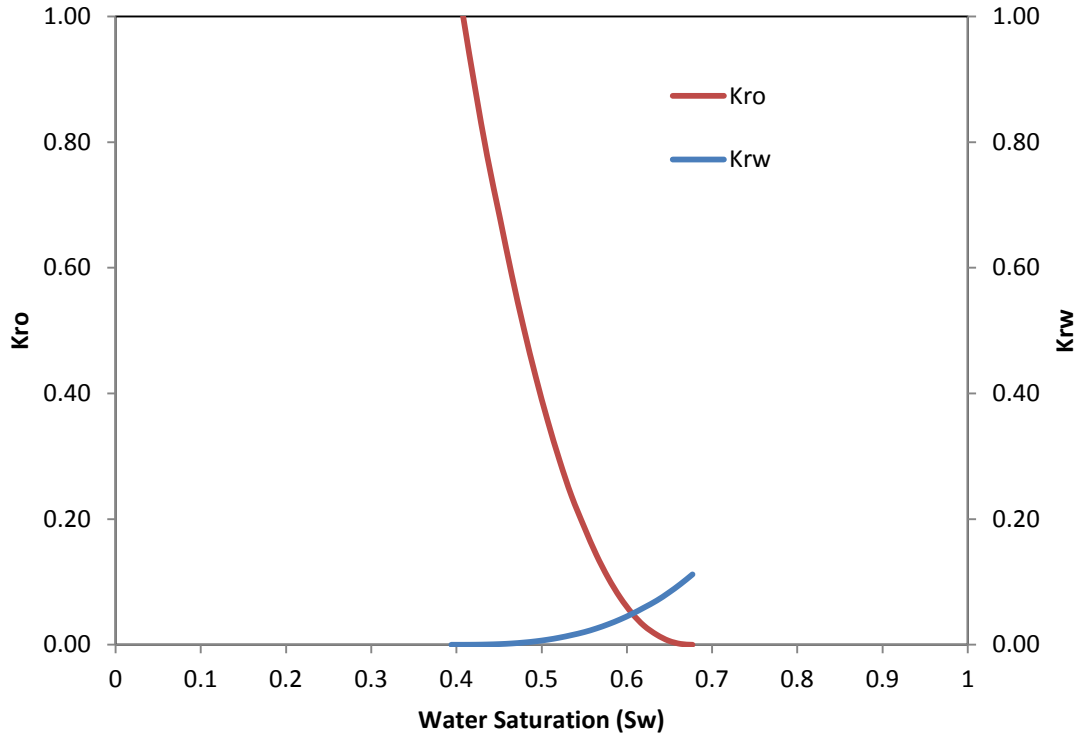


Figure 4-9: Oil-water relative permeabilities for the dolomite- Yates synthetic brine - Yates crude oil systems obtained from a Coreflood Simulator

Table 4-6: Summary of experimental and simulation waterflood results

Brine	Salinity (g/l)	Experimental					Simulation				
		Recovery (%OOIP)	S_{wi}	S_{or}	K_{ro}	K_{rw}	S_{wi}	S_{or}	K_{ro}	K_{rw}	X-over point
Yates brine	10.78	46.7	0.39	0.32	0.96	0.09	0.39	0.32	1	0.11	0.585
Brine with 4.4 g/l sulfate	10.78	73.6	0.42	0.15	0.68	0.12	0.42	0.15	0.68	0.14	0.678
50x diluted	0.216	76	0.45	0.13	1	0.27	0.45	0.13	1	0.26	0.703

The effect of surface roughness on contact angle was reported by Vijapurapu et al. (2002) for the Yates fluids- Berea rock system. They experimentally confirmed the water-advancing contact angle decreases by increasing the surface roughness since the water advancing measured on smooth glass was 166° and 58° on rough surface for Yates crude oil system. Therefore, more aging time should be given to reach solid-fluids equilibrium in coreflood experiments to account for the effect of surface roughness. Also, the discrepancy between two systems can be attributed to the limitations of wettability interpretation from relative permeability using Craig's rules of thumb. The relative permeability may not enable discerning wettability accurately due to the strong impact of rock pore structure on it (Rao 2002). This conclusion is also in agreement with Anderson (1987). It was suggested to measure the wettability independently rather than to rely on Craig's relative permeability rules alone to characterize wettability.

Table 4-7: Summary of coreflood results and contact angles for the different brines

Brine	Salinity (g/l)	Θ_a / Θ_r			Recovery (%OOIP)
		Ambient	T= 82°F	T= 250°F	
Yates brine	10.78	158/29	157/32	120/-	46.7
Brine 4.4g/l SO ₄ ²⁻	10.78	115/40	115/41	87/-	73.6
50x diluted	0.216	113/33	112/38	87/-	76

4.4.2 Effect of 4.4 g/l Sulfate Content in Brine on Oil Recovery, Relative Permeability and Wettability

To investigate the effect of sulfate ion on oil recovery, coreflood experiment was conducted using brine with 4.4 g/l sulfate. The reason to conduct coreflood experiment with this brine was its significant effect on wettability alteration seen in contact angle measurements discussed section 4-1.

The history match of recovery and pressure drop data versus the injected pore volume obtained from a coreflood simulator during the waterflood for the Dolomite rock-brine with

4.4g/l sulfate-Yates crude oil systems is shown in Figures 4-10 and 4-11. A summary of the simulation and experimental results for endpoints is brought in Table 4-6. It can be seen from Figures 4-10 and 4-11 and Table 4-6 that a good history match was obtained. The effect of the brine with 4.4 g/l on relative permeability curve obtained using the simulator is shown in figure 4-12.

According to the Craig's rules of thumb, the relative permeability curve (Figure 4-12 and Table 4-6) indicated water- wet characteristics for dolomite- brine with 4.4 g/l sulfate- Yates crude oil systems. For this system, initial water saturation ($S_{wi} = 0.42 > 0.25$), cross- over point water saturation ($S_{w,c-o} = 0.67 \% > 0.50$), low endpoint water relative permeability($K_{rw} = 0.13 < 0.3$), and low endpoint oil relative permeability ($K_{ro} = 0.68 < 0.95$) are shown in Table 4-8. The result obtained using the relative permeability curve which indicated a water-wet state was in

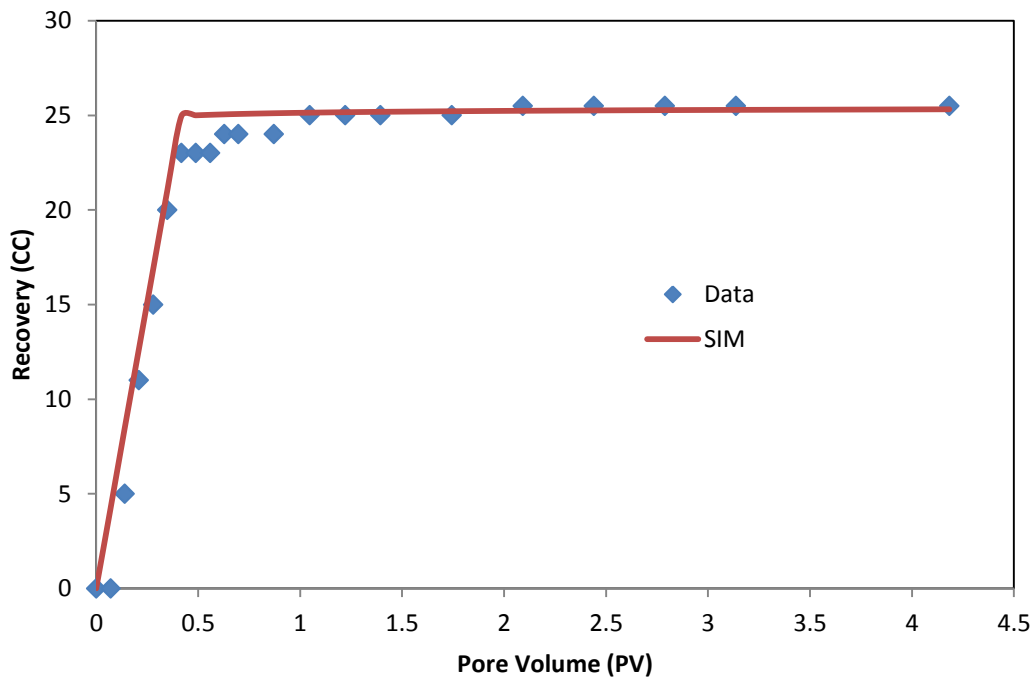


Figure 4-10: History match of oil recovery for the dolomite- brine with 4.4g/l sulfate - Yates crude oil systems

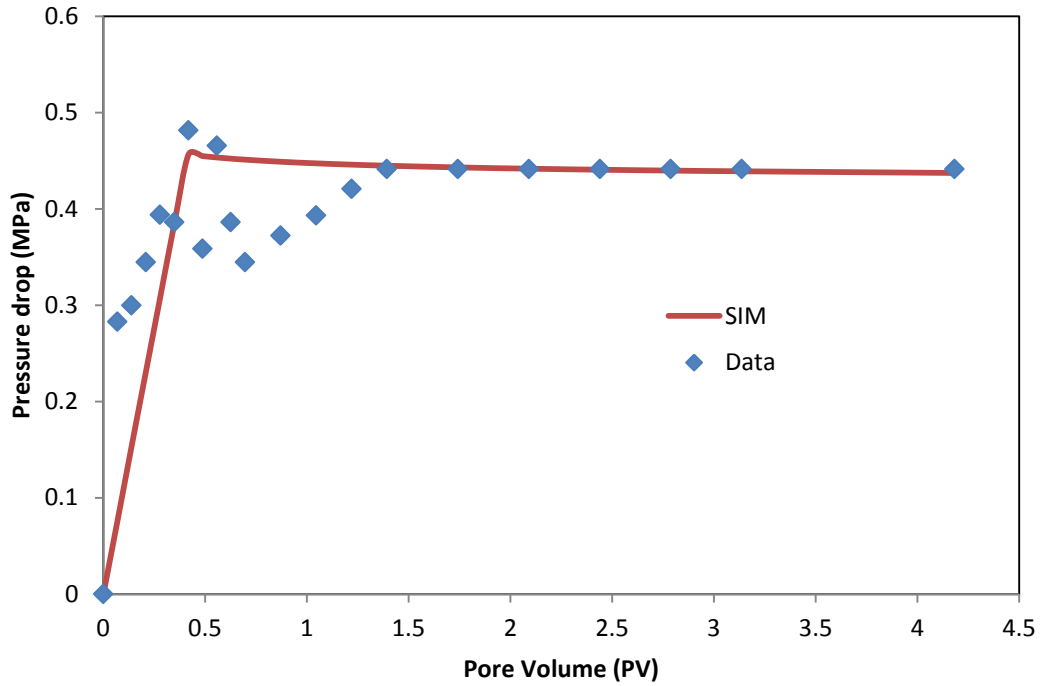


Figure 4-11: History match of pressure drop for the dolomite-brine with 4.4 g/l sulfate - Yates crude oil systems

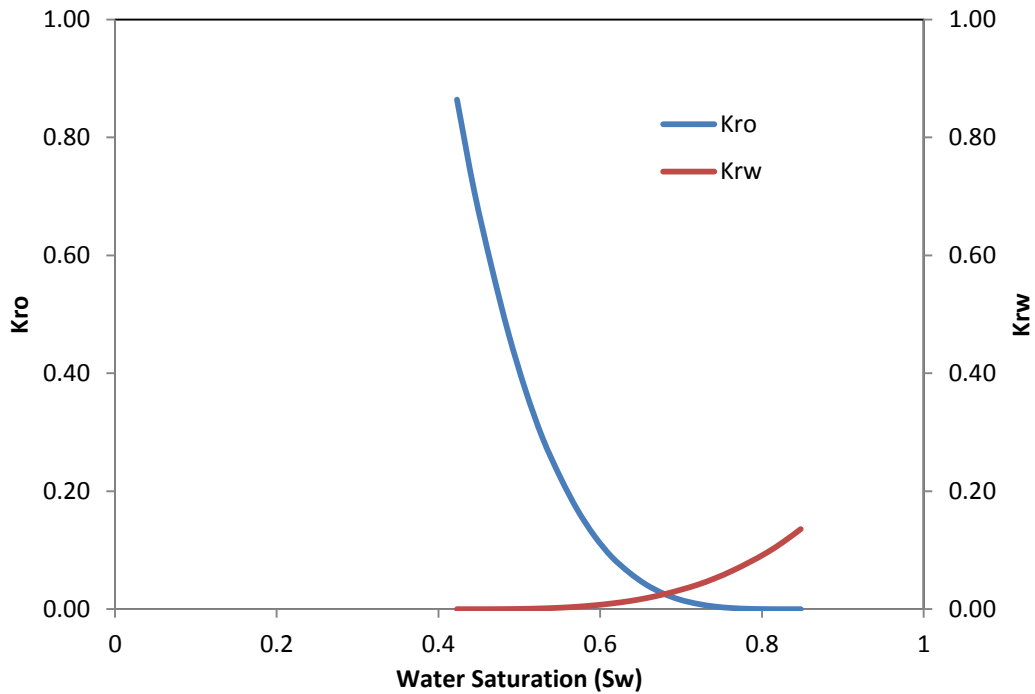


Figure 4-12: Oil-water relative permeabilities for the dolomite-brine with 4.4 g/l sulfate - Yates crude oil systems obtained from a Coreflood Simulator

contrast with the result obtained using the DDDC technique which indicated an intermediate-wet state. All reasons that have brought in section 4-4-1 can be applied here to explain this contrast.

4.4.3 Effect of 50 Times Diluted Brine on Oil Recovery, Relative Permeability and Wettability

From the DDDC technique, it was confirmed that the 50 times diluted Yates synthetic brine had significant effect on wettability alteration and brought the system for the Dolomite-Yates synthetic brine-Yates crude oil systems from strongly oil-wet to the intermediate-wet. Therefore, to investigate the effect of salinity on oil recovery using the coreflood method, 50 times diluted Yates synthetic brine was selected as the inject brine.

The history match of recovery and pressure drop versus the injected pore volume obtained from a coreflood simulator during the waterflood is brought in Figures 4-13 and 4-15 for the Dolomite rock-50 times diluted Yates synthetic brine-Yates crude oil systems. In Table 4-6, the comparison between the result obtained from the simulation and experimental for endpoints is given. A good history match given by the simulator can be seen in Figures 4-13 and 4-14 and Table 4-6. The effect of low salinity on relative permeability curve obtained using the simulator is shown in figure 4-15.

According to the Craig's rules of thumb, the relative permeability curve for the Dolomite rock-50 times diluted Yates brine-Yates crude oil system (Figure 4-15 and Table 4-6) indicated water-wet characteristics ($S_{wi} = 0.45 > 0.25$, $S_{w,c-o} = 0.7 > 0.50$, $K_{rw} = 0.26 < 0.30$, $K_{ro} = 1 > 0.95$). The result obtained using coreflooding and DDDC technique are in disagreement since it was confirmed using DDDC technique that system is in intermediate-wet zone. To know the reasons for this contrast, see the explanation in section 4-4-1.

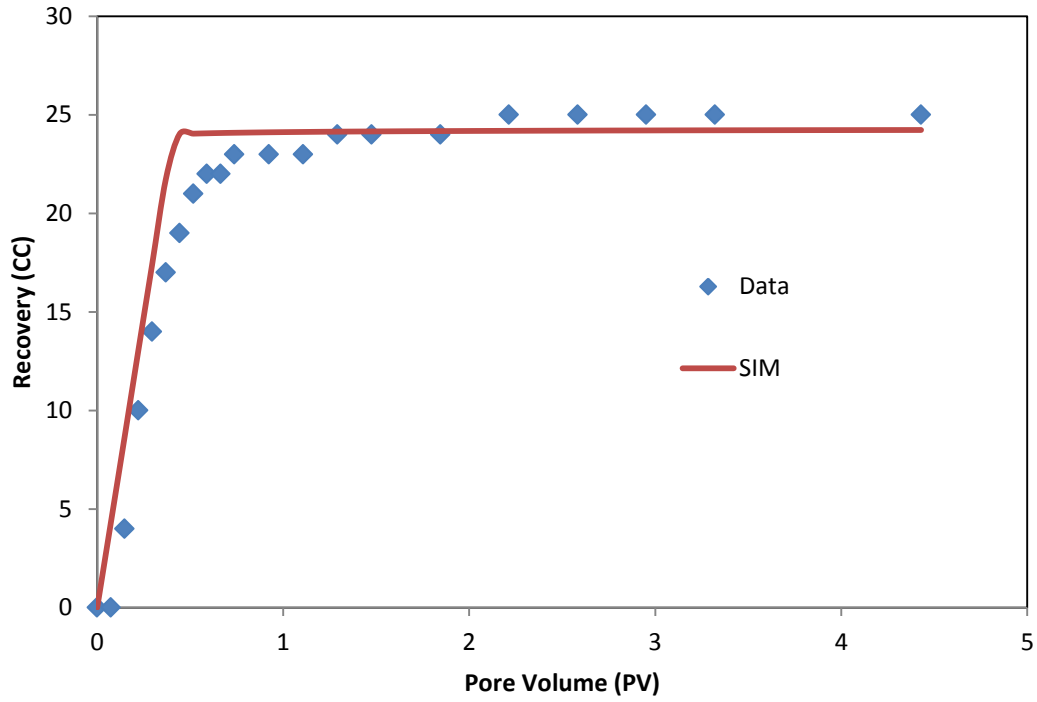


Figure 4-13: History match of oil recovery for the dolomite- 50 times diluted brine - Yates crude oil systems

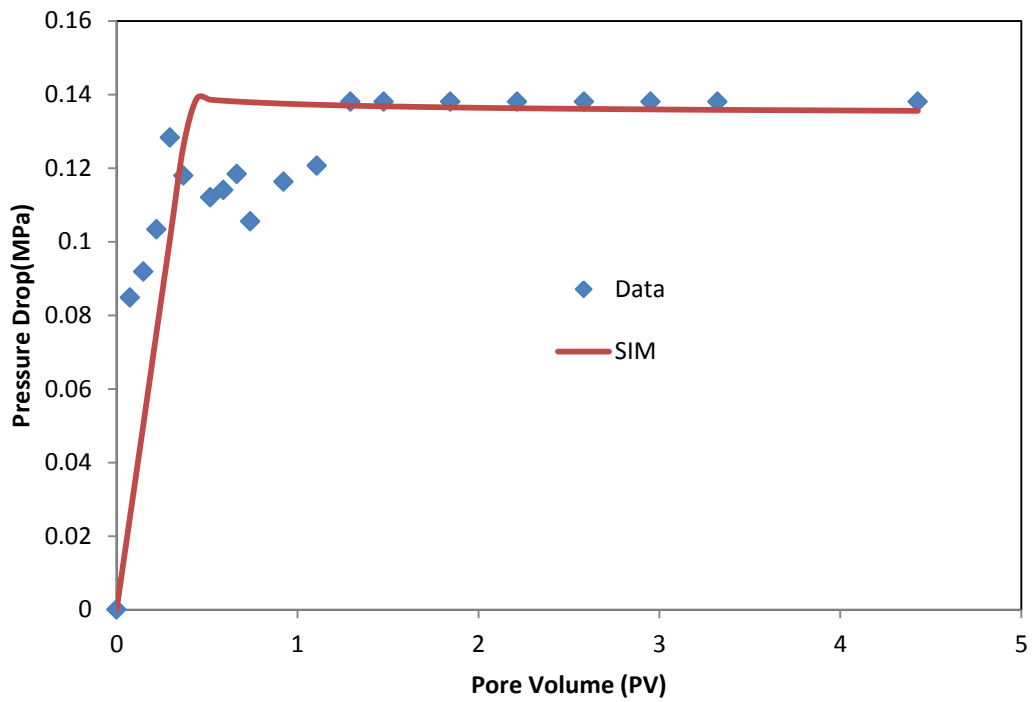


Figure 4-14: History match of pressure drop for the dolomite- 50 times diluted brine - Yates crude oil systems

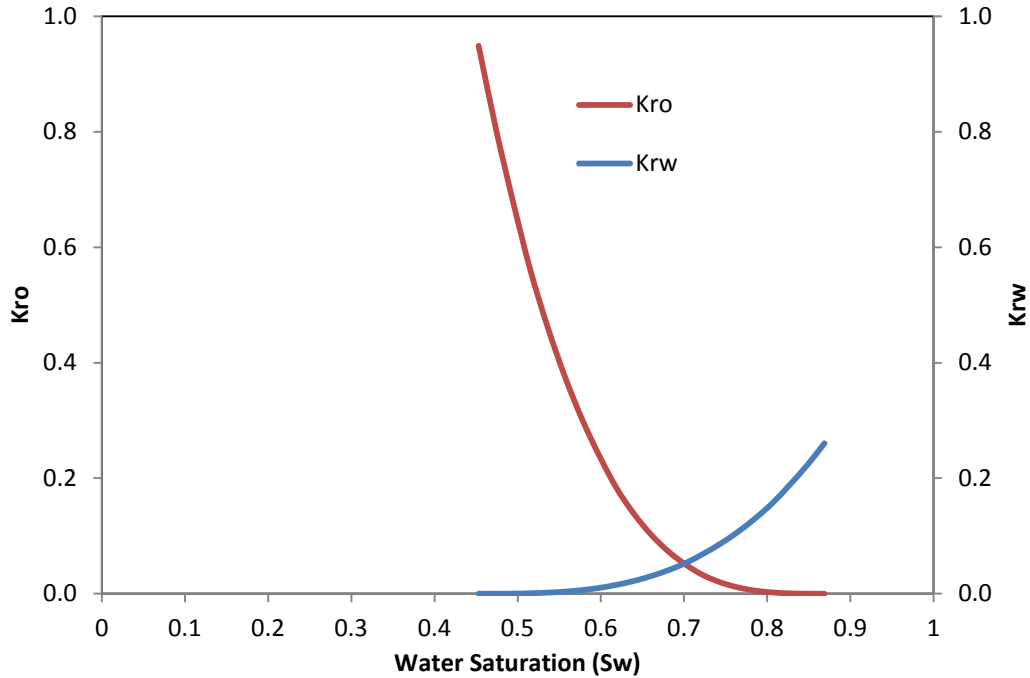


Figure 4-15: Oil-water relative permeabilities for the dolomite- 50 times diluted brine - Yates crude oil systems obtained from a Coreflood Simulator

4.4.4 Comparison between Oil Recovery and Relative Permeability Ratio for All Three Floods

Figures 4-16, 4-17 and 4-18 present the effect of low salinity and amount of sulfate in brine on oil recovery, fractional flow and relative permeability ratio, respectively.

As can be seen from Table 4-6, the oil recovery increased significantly either by increasing the amount of sulfate or decreasing the salinity of the brine in comparison with Yates synthetic brine. The oil recovery increased from 46.7% OOIP to 76% OOIP as the salinity decreased from 10.78 g/l for Yates synthetic brine to 0.216 g/l for the 50 times diluted brine. The recovery increase at low salinity brine is attributed to the wettability alteration that was clearly demonstrated in the contact angle experiments. Also, by increasing the amount of sulfate in the Yates synthetic brine from 2.2 g/l to 4.4 g/l, the oil recovery increased significantly from 46.7%

OOIP to 73.6% OOIP. This increase in oil recovery can also be attributed to the wettability alteration since the result obtained using DDDC technique confirms this conclusion Table 4-7.

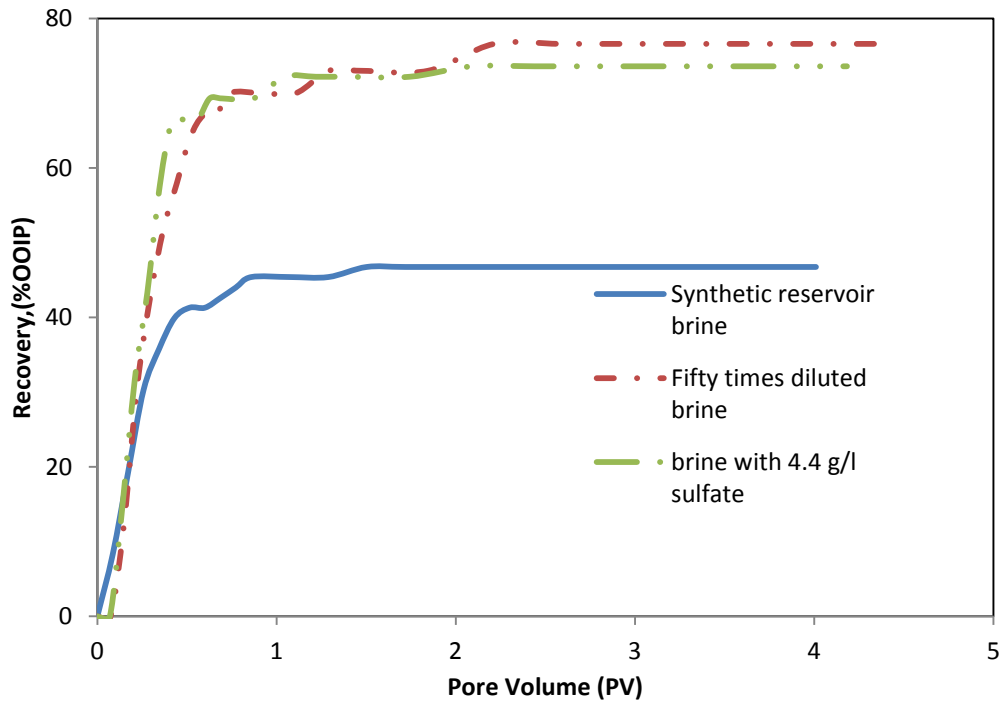


Figure 4-16: Effect of low salinity and amount of sulfate in brine on oil recovery

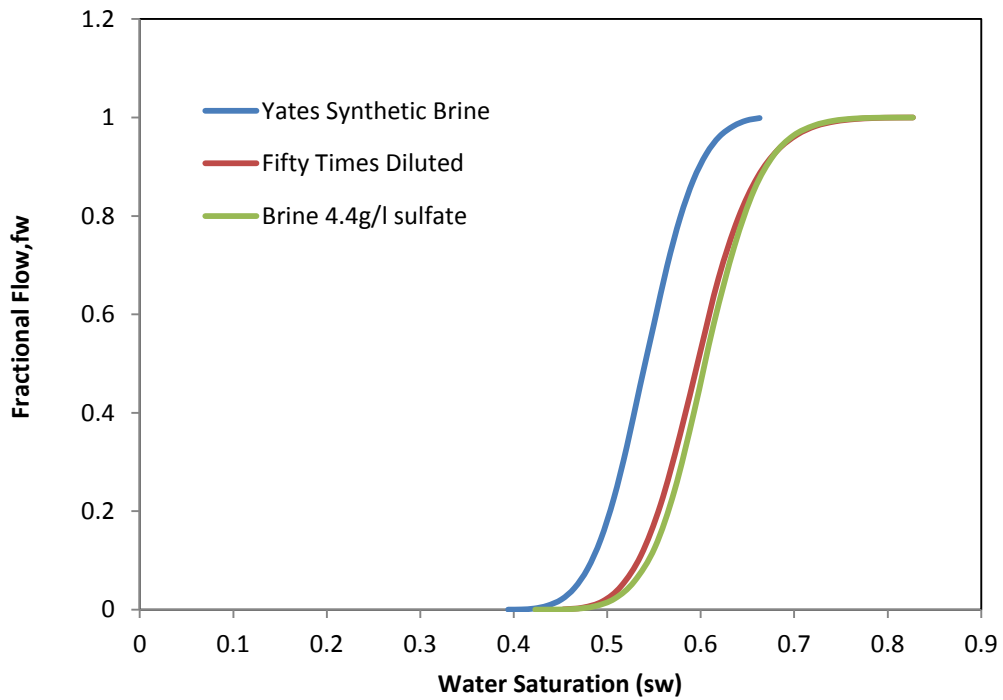


Figure 4-17: Effect of Low salinity and amount of sulfate on fractional flow

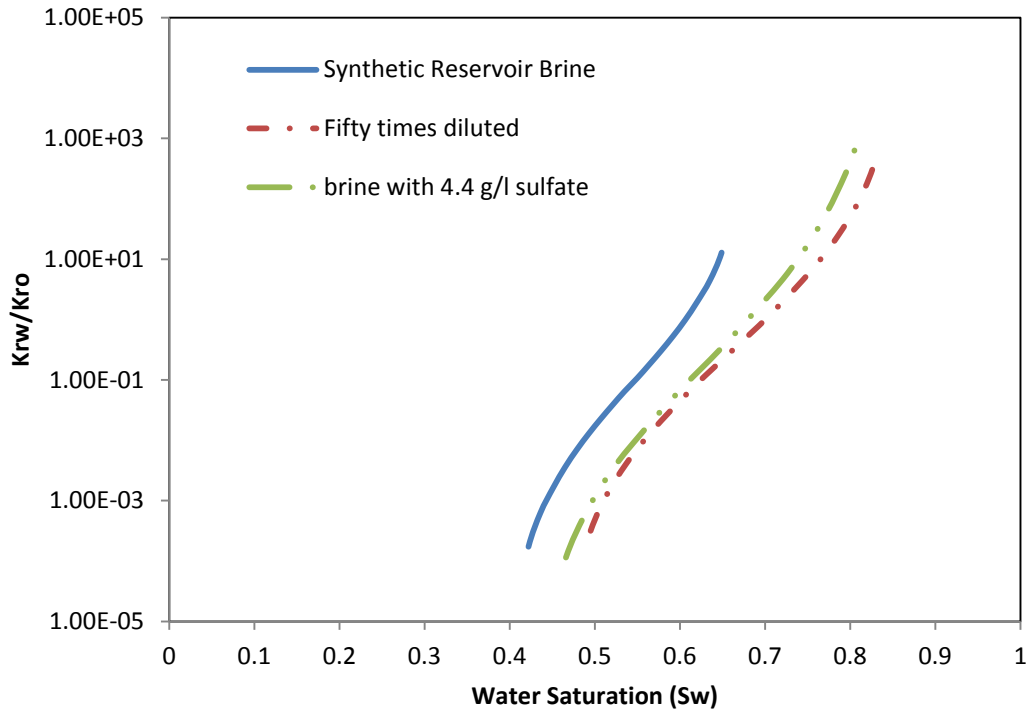


Figure 4-18: Effect of low salinity and amount of sulfate in brine on permeability ratio

There was a significant shift to the left in the water saturation at cross-over point for all the three floods as can be seen from Figure 4-18 and Table 4-6. It decreased from 70% for 50 times diluted brine to 67% for brine with 4.4 g/l sulfate and to 58% for Yates synthetic brine with 2.2 g/l sulfate. These shifts appears to indicate a shift from water-wet to less water-wet or intermediate-wet condition by either changing the salinity or the amount of sulfate in brine.

Fractional flow is another practical method to the assessment of the displacement efficiency of a coreflood. A shift from left to right can be seen in fractional flow curves as shown in figure 4-17. The shift to the right in fractional flow indicates that wettability is changing by changing the salinity and amount of sulfate in brine.

The very high oil recovery obtained by changing the salinity and amount of sulfate showed that the system was neither water-wet nor oil-wet. Therefore, Craig's rules-of-thumb are not strictly applicable to infer wettability shifts for this system as these rules are used only to

distinguish between strongly water-wet and oil-wet systems based on relative permeability curves.

The oil/water relative permeabilities ratio (K_{rw}/K_{ro}) provides another means to interpret the wettability changes (Anderson, 1987; Rao et al. 1992) was also used in this study to infer wettability alteration. As can be seen from Figure 4-18, the relative permeability ratio curves shift to the right by increasing the amount of sulfate. The shift to the right was more pronounced when the salinity of Yates synthetic brine (10.78 g/l) diluted 50 times (0.216 g/l). The most probable mechanism behind this phenomenon is wettability alteration. It means the shift in the relative permeability ratio curves to the right is mostly due to the development of intermediate-wettability or mixed-wettability. The measured advancing contact angle using the DDDC technique on Dolomite rock–brine with 4.4 g/l sulfate-Yates crude oil systems (115°) and also Dolomite rock- 50 times diluted brine- Yates crude oil systems (112°) confirmed the development of intermediate-wettability condition.

The concept of “mixed wettability” was explained by Salathiel (1973) to emphasize the role of the wettability state of the reservoir on oil recovery in an East Texas reservoir. In mixed wettability, the fine pores and grain contacts would be preferentially water-wet and the surfaces of the larger pores are strongly oil-wet. If oil-wet paths were continuous through the rock, water would displace oil from the larger pores and little or no oil would be held by capillary forces in small pores or at grain contacts. He explained the development of mixed-wettability as follow: When oil accumulates in a reservoir, water present in the initially water-wet rock is displaced from the larger pores while the capillary pressure holds water in smaller pores and at grain contacts. After a long time, some organic materials from the oil may deposit on to those rock surfaces that are in direct contact with oil. As a result that process makes those surfaces strongly

oil-wet. This phenomenon leads to the development of so called mixed-wettability. The development of mixed-wettability condition proposed by Salathiel is shown in Figure (Salathiel, 1973).

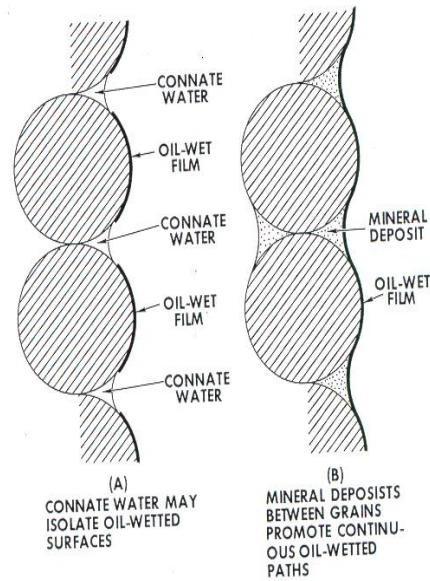


Figure 4-19: Development of mixed-wettability proposed by Salathiel (Salathiel, 1973)

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Low salinity, brine composition, and temperature were experimentally investigated in this study to evaluate their effect on wettability, relative permeabilities, and oil recovery in a dolomite reservoir. The overall conclusions of this work are summarized in this chapter:

1. Previous researches have suggested that wettability alteration is as a key reason for oil recovery improvement in most carbonate reservoirs. The results in this study showed that improvement in oil recovery with sulfate ions and low salinity cannot be explained just by the rock wettability alteration.
2. The reservoir wettability was determined by measuring water- advancing contact angle using the DDDC technique. The water- advancing contact angles of 157° and 156° at ambient and reservoir conditions demonstrated the strongly oil- wet nature of the Yates fluids- dolomite rock.
3. According to the DDDC technique contact angle measurements, the brine containing 4.4 g/l sulfate had the most significant impact on changing the wettability.
4. To investigate the effect of low salinity on wettability alteration using the DDDC technique, the significant wettability alteration was observed with 50 times diluted brine at both ambient and reservoir conditions.
5. At least two mechanisms including 1- Surface charges alteration and 2- Microscopic dissolution of anhydrite can explain the wettability alteration in 50 times diluted brine.
6. The effect of temperature on wettability was significant and water advancing contact angle decreased with increasing the temperature. For both brine with 4.4 g/l sulfate content and 50

times diluted brine, water-advancing contact angle decreased to 86° by increasing the temperature.

7. Displacement of oil by condensed water resulting from steam injection (at higher temperature) may be beneficial through the combined effect of temperature and brine composition on wettability.
8. Coreflood studies were carried out to determine the recovery benefits of low salinity (50 times diluted brine) and sulfate rich (4.4 g/l) brine compared with the base (Yates synthetic brine) coreflood and the role of wettability in recovery. All the coreflood tests gave consistent increase in produced oil, corresponding to reduction in residual oil saturation and increase in water-wetness. The results were in line with previous laboratory tests from other fields.
9. The gradual rightward shift in relative permeability ratio curves indicating wettability alteration to intermediate-wet was induced by brine containing 4.4g/l sulfate and 50 times diluted brine. The water-advancing contact angles measured using the DDDC technique in this system also confirmed the wettability shift to intermediate-wet due to the ability of low salinity and sulfate ions.
10. The coreflood result showed the weakly water-wet nature of the dolomite rock-Yates fluids systems. However, the wettability of this rock-fluids system inferred from DDDC contact angle measurements was strongly oil-wet. This is because Contact angles are measures of the relative affinity of two fluids for a smooth solid surface. In cores, there are additional complexities related to rough surfaces, converging and diverging pore shapes, and heterogeneous mineralogy.

11. The oil recovery increased about 26.9% by increasing the sulfate content in Yates brine from 2.2 g/l to 4.4 g/l.
12. The oil recovery increased 29.3% by decreasing the salinity of the Yates brine from 10.87 to 0.216, respectively.
13. Results from this study indicated that low salinity brine could provide high ultimate oil recovery in carbonate reservoirs. This can avoid extensive investment associated with conventional EOR methods.

5.2 Recommendations

1. Analysis of the mechanisms leading to the enhanced oil recovery under low salinity coreflooding should continue.
2. The effect of the composition of the formation brine should be investigated.
3. Interfacial tension (IFT) should be measured for different salinities, compositions, and temperatures to investigate its effect on brine-crude oil interaction.
4. Based on the literature review, carbonate rocks need longer aging times for equilibrium. Conduct coreflooding in longer aging time and compare the results obtained in the new aging time with those obtained in this study.
5. Use the Zeta potential technique to determine the interaction fluids with dolomite rock at different temperatures as well as different brine salinities and compositions.
6. Outcrop rocks were used for running all the experiments in this study. Conduct the same study using the reservoir rock to investigate that the oil recovery mechanisms are the same for outcrop and reservoir rocks.
7. Add only Ca^{++} to the Test 5 brine and measure the water-advancing contact angle to check whether wettability changes or not.

8. Add only Mg^{++} to the Test 5 brine and measure the water- advancing contact angle to check whether wettability change or not.
9. Add both Ca^{++} , Mg^{++} to the Test 5 brine and measure the water- advancing contact angle to check whether wettability change or not.

REFERENCES

1. Akbar, M., Vissapragada, B., Alghamdi, A.H., Allen, D., Herron, M., Carnegie, A., Dutta, D., Olesen, J.R., Chourasiya, R.D., Logan, D., "A snapshot of carbonate reservoir evaluation", Oilfield Review 21 (2001).
2. Austad, T. and Standnes, D.C.: "Spontaneous Imbibition of Water into Oil-wet Carbonates," SPE, 39 (2003) 363-376.
3. Austad, T., Strand, S., Hognesen, E.J., Zhang, P. "Seawater as IOR Fluid in fractured Chalk," SPE93000, presented at the SPE International Symposium on Oilfield Chemistry, Houston, Texas, February 2-4, 2005.
4. Austad, T., Strand, S., Madland, M., Puntervold, T. and Korsens, R.: "Seawater in Chalk; an EOR and Compaction Fluid," Journal of SPE Reservoir Evaluation & Engineering, 2008, pp. 648-654.
5. Austad, T., Shariatpanahi, S., Strand, S., Black, J., Webb, K.: "Condition for Low Salinity EOR-Effect in Carbonate Oil Reservoirs," Energy Fuels, 26 (1), 2012, pp.569-575.
6. Al-Hadhrami, H. S., Blunt, M. J., "Thermally Induced Wettability Alteration to Improve Oil Recovery in Fractured Reservoirs" Society of Petroleum Engineers, 2000.
7. Alotaibi, M.B., and Naser-El-Din, H.A. 2009. Effect of Brine Salinity on Reservoir Fluids Interfacial Tension. Paper SPE 121569 will be presented at the SPE EUROPEC/EAGE Conference, Amsterdam, The Netherlands, 8-11 June.
8. Alotaibi, M.B., and Naser-El-Din, H.A. 2009. Chemistry of Injection Water and its Impact on Oil Recovery in Carbonate and Clastic Formations. SPE 121565.
9. Alotaibi, M.B., Nasr-El-Din, H.A., and Fletcher, J.J., "Electrokinetics of Limestone and Dolomite Rock Particles," Society of Petroleum Engineers, October 2011.
10. Anderson, W.G., October 1986, Wettability Literature Survey – Part 1: Rock/Oil/Brine Interactions and the Effect of Core Handling on Wettability, J. of Petr. Techn., pp.1125-1144.
11. Anderson, W. G.: "Wettability Literature Survey- Part 5: The effects of Wettability on Relative Permeability," Journal of Petroleum Technology, November, 1987.
12. Ayirala, S.: "Surfactant-Induced Relative Permeability Modifications for Oil Recovery Enhancement," Thesis, The Department of Petroleum Engineering of Louisiana State University.
13. Bagci, S., Kok, M. V. and Turksoy, U.: "Effect of Brine Composition on Oil Recovery by Waterflooding," Petroleum and Technology, 19(3&4), 359-372, 2001.
14. Berner, R.A., "Principles of Chemical Sedimentology" Published by Mcgraw-hill, 1971.

15. Buckley, S.E. and Leverett, M.C.: "Mechanism of Fluid Displacement in Sands," Trans. AIME, 146, 107, 1942.
16. Buckley, J.S., Takamura, K., and Morrow, N.R. 1989. Influence of Electrical Surface Charges on the Wetting Properties of Crude Oils. SPE Reservoir Engineering 4 (3): 332-342.
17. Buckley, J.S. and Morrow, N.R.: "An Overview of Crude Oil Adhesion Phenomena," in Physical Chemistry of Colloids and Interfaces in Oil Production, H. Toulhoat and J. Lecourtier, eds., Éditions Technip, Paris, 2992, 39-45.
18. Buckley, J.S. and Liu, Y.: "Some Mechanisms of Crude Oil/Brine/Solid Interactions," presented at the 1996 International Symposium on Reservoir Wettability and Its Effect on Oil Recovery, Montpellier, France, 11-13 Sept., J. Pet. Sci. & Eng. (in press).
19. Craig, F. F., "The Reservoir Engineering Aspects of Waterflooding," Monograph Series, SPE, Richardson, TX (1971) 3.
20. Donaldson, E.C., Kendall, R.F., Thomas, R.D. and Lorenz, P.B.: "Wettability determination and its effect on recovery efficiency", SPE 2238, SPE Journal, March-1969, pp-13-20.
21. Doust, A.R., Puntervold, T.P., Strand, S. and Austad, T.A.: " Smart Water as Wettability Modifier in Carbonate and Sandstone," Paper presented at 15 the European Symposium on Improved Oil Recovery, Paris, France, April 17-29, 2009.
22. Fathi, J.S., Austad, T. and Strand, S.: " Smart Water as a Wettability Modifier in Chalk: The Effect of Salinity and Ionic Composition," Energy Fuels, 24, 2010, pp. 2,519-2,514.
23. Fathi, S.J., Austad, T., Strand, S.: "Water-Based Enhanced Oil Recovery (EOR) by Smart Water: Optimal Ionic Composition for EOR in Carbonate", Energy & fuels (2011).
24. Fernø, M.A., Grønsdal, R., Åsheim, J., Nyheim, A., Berge, M., Graue, A.: " Use of Sulfate for Water Based Enhanced Oil Recovery during Spontaneous Imbibition in Chalk," Energy & fuels 25 (2011) 1697-1706.
25. Hirasaki, G. J.: "Wettability: Fundamentals and Surface Forces," SPE Formation Evaluation, June 1991: 217-226.
26. Hiorth, A., Cathles, L. M., Madland, M. V.: "The impact of pore water chemistry on carbonate surface charge and oil wettability," Springer Science+ Business Media, 2010.
27. Høgenesen, E. J., Strand, S. and Austad, T.: "Waterflooding of Preferential Oil-Wet Carbonates: Oil Recovery Related to Reservoir Temperature and Brine Composition," paper SPE 94166, presented at the SPE Europe/EAGE Annual Conference held in Madrid, Spain, 13-16 June, 2005.
28. Hjelmeland, O.S. and Larrondo, L.E.: "Experimental Investigation of the Effects of Temperature, Pressure, and Crude Oil Composition on Interfacial Properties," Society of Petroleum Engineers, July 1986.

29. Hognose, E.J. and Austad, T. 2006; “Wettability Alteration of Carbonates-Effects of: Potential Determining Ions (Ca^{2+} and SO_4^{2-}) and Temperature,” *Colloids and Surfaces A: Physicochemical Engineering, Aspects* 275, 2006, pp.1-10.
30. Honarpur, M., Koederitz, L. and Harvey, A.H.: “Relative Permeability of Petroleum Reservoirs,” 1986.
31. Jabbar, M.Y., Al-Hashim, H.S. and Abdallah, W.,”Effect of Brine Composition on Wettability Alteration of Carbonate Rocks in the Presence of Polar Compounds,” SPE Saudi Arabia section Annual Technical Symposium and Exhibition, 19–22 May 2013.
32. Jadhunandan, P.P. and Morrow, N.R.: “Spontaneous Imbibition of Water by Crude Oil/Brine/Rock Systems,” *In Situ*, v.15 (1991), no.4, pp.319-45.
33. Jadhunandan, P.P., Morrow, N.R., 1995. “Effect of wettability on waterflood recovery for crude oil/brine /rock systems”. *SPE Reservoir Eng.* 10, 40–46.
34. Jens, H., Skule, S., Tor, A.:”Waterflooding of Preferential Oil-Wet Carbonates: Oil Recovery Related to Reservoir Temperature and Brine Composition,” SPE Europec/EAGE Annual Conference, Society of Petroleum Engineers, Madrid, Spain, 2005.
35. Karoussi, O. and Hamouda, A.A.:” Imbibition of sulfate and magnesium ions into carbonate rocks at elevated temperatures and their influence on wettability alteration and oil recovery, “*Energy & Fuels* 21 (2007) 2138-2146.
36. Lager, A., Webb, K.J., and Black, C.J.J. 2007. Impact of Brine Chemistry on Oil Recovery. Paper A24 presented at the 14 th European Symposium on IOR, Cairo, Egypt, 22-24 April.
37. Ligthelm, D.J., Gronsveld, J., Hofman, J.P., Brussee, N.J., Marcelis, F. and van der Linde, H.A.:” Novel Waterflooding Strategy by Manipulation of Injection Brine Composition,” Society of Petroleum Engineers, 2009.
38. McCaffery, F.G.: “Measurement of interfacial tension and contact angles at high temperature and pressure,” *Journal of Canadian Petroleum Technology*, Jul-Sep 1972: 26-32.
39. McGuire, P.L., Chatham, J.R., Paskvan, F.K., Sommer, D.M., Carini, F.H.:” Low Salinity Oil Recovery: An Exciting New EOR Opportunity for Alaska's North Slope”, SPE Western Regional Meeting, Society of Petroleum Engineers, Irvine, California, 2005.
40. Morrow N.R: “Wettability and Its Effect on Oil Recovery,” *JPT*, (Dec.1990), pp.1476-84.
41. Morrow, N.R., Tang, G., Valat, M. and Xie, X.: “Prospects of improved oil recovery related to Wettability and Brine Composition” *J. Pet. Sci. Eng.*, **20**, June 1998, 267-276.
42. Morrow, N., Buckley, j. 2011. Improved Oil Recovery by Low- Salinity Waterflooding. *Journal of Petroleum Technology* **63** (50): 106-112.

43. Muhammad. Z., “ Compositional Dependence of Reservoir Wettability”, Master thesis, The Craft and Hawkins Department of Petroleum Engineering, Louisiana State University, Baton Rouge, LA, May 2001.
44. Nanji, H., Havard Heldal, L., Kanwar, G.K., Kristoffer Andr, S., Jan Åge, S., Ole, T.:” Laboratory Investigation of Low Salinity Waterflooding on Reservoir Rock Samples from the Frøy Field”, SPE Middle East Oil and Gas Show and Conference, Society of Petroleum Engineers, Manama, Bahrain, 2011.
45. Peimao, Z., Tor, A. “Waterflooding in Chalk - Relationship between Oil Recovery, New Wettability Index, Brine Composition and Cationic Wettability Modifier,” SPE Europec/EAGE Annual Conference, Society of Petroleum Engineers, Madrid, Spain, 2005.
46. Pierre, A. et al. 1990. Calcium as Potential Determining Ion in Aqueous Calcite Suspensions. *Journal of Dispersion Science and Technology* **11**(6): 611-635.
47. Puntervold, T., Strand, S., Austad, T.:” Coinjection of Seawater and Produced Water to Improve Oil Recovery from Fractured North Sea Chalk Oil Reservoirs,” *Energy & fuels* **23** (2009) 2527-2536.
48. Rao, D.N., Girard, M., and Sayegh, S.G.: “Impact of miscible flooding on wettability, relative permeability, and oil recovery”, *SPE Reservoir Engineering*, May-1992, pp-204-212.
49. Rao, D. N. and Girard, M. G.: “A New Technique for Reservoir Wettability Characterization,” *Journal of Canadian Petroleum Technology*, 1996, Vol. 35, No.1:31- 39.
50. Rao, D. N.: “Wettability Effects in Thermal Recovery Operations,” *SPE Reservoir Evaluation & Engineering*, Vol. 2, No. 5, October 1999, 420-430.
51. Rao, D.N.: “Is there a correlation between wettability from corefloods and contact angles,” SPE 37234, Paper presented at the SPE International Symposium on Oil Field Chemistry held in Houston, TX, 18-21 February, 1997.
52. Rao, D. N.: “Correlation of Oil-Water Flow Behavior in Reservoir Rocks with Dynamic Contact Angles,” *Journal of Canadian Petroleum Technology*, July, 2002.
53. Rao, D.N., “Measurements of Dynamic Contact Angles in Solid- Liquid-Liquid Systems at Elevated Pressure and Temperatures”, *Colloids and Surface A*, **206** (2002) 203-216.
54. Rodriguez, K., and Araujo, M.:” Temperature and Pressure Effects on Zeta Potential Values of Reservoir Minerals,” *Journal of Colloid and Interface Science*, **300** (2), 2006, pp. 788-794.
55. Salathiel, R.A.: “Oil Recovery by Surface Film Drainage in Mixed-Wettability Rocks,” *JPT* (Oct. 1973).

56. Standnes, D.C. and Austad, T. 2000a." Wettability alteration in chalk 1. Preparations of Core Material and Oil Properties," J. of Petroleum Science and Engineering 28(3): 111-121. DOI: 10/1016/S0920-410500(000)83-8.
57. Strand, S., Standnes, D.C., and Austad, T. 2003. Spontaneous Imbibition of Aqueous Surfactant Solution into Neutral to Oil-wet Carbonate Cores: Effect of Brine Salinity and Composition. *Energy & Fuels* **17**: 1133-1144.
58. Strand, S. et al. 2008. "Smart Water" for Oil Recovery from Fractured Limestone: A Preliminary Study. *Energy & Fuels* **22**: 3126-3133.
59. Strand, S., and Austad, T. 2008. Effect of Temperature on Enhanced Oil Recovery from Mixed-wet Calk Cores by Spontaneous Imbibition and Forced Displacement using Seawater. *Energy & Fuels* **22**(5): 3222-3225.
60. Tang, G.Q. and Morrow, N.R. 1997." Salinity, Temperature, Oil Composition, and Oil Recovery by Waterflooding". *SPE Reservoir Engineering*, November: 269-276.
61. Tang, G., Morrow, N.R.:" Influence of Brine Composition and Fine Migration on Crude Oil/Brine/Rock Interactions and Oil recovery",*J.Pet. Sci &Eng.*, Vol.24, (Dec. 1999) 99-111.
62. Tang, G.Q. and Morrow, N.R. 2002. "Injection of Dilute Brine and Crude Oil/Brine/Rock Interactions". *Geophysical Monograph* 129: 171-179.
63. Vijapurapu, C. S., Rao, D. N. and Lian, K: "The Effect of Rock Surface Characteristics on Reservoir Wettability," paper SPE 75211, presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, 13-17 April 2002.
64. Vijapurapu, C. S. and Rao, D. N.: "Effect of Brine Dilution and Surfactant Concentration on Spreading and Wettability", Paper SPE 80273, the SPE international Symposium on Oilfield Chemistry held in Houston, Texas, USA, 5-7 February 2003.
65. Wang, W., and Gupta, A.:" Investigation of the effect of temperature and pressure on wettability using modified pendant drop method," SPE 30544, Paper presented at the SPE Annual Technical Conference and Exhibition, Dallas, TX, 22-25 October, 1995.
66. Webb, K.J., Black, C.J.J. and Jutland, G.: "A Laboratory Study Investigating Methods for Improving Oil Recovery in Carbonates," IPTC 10506, presented at the International Petroleum Technology Conference, Doha, Qatar, November 21-23, 2005.
67. Welge, H.J.: "A Simplified Method for Computing Recovery by Gas or Water Drive," *Trans. AIME*, 195, 91, 1952.
68. Xu, W., Ayirala, S.C., and Rao, D.N.: "Experimental investigation of oil compositional and surfactant effects on wettability at reservoir conditions," International Symposium of Society of Core Analysts held in Toronto, Canada, 2005.

69. Xu, W., Ayirala, S.C., and Rao, D.N.: "Compositional dependence of wetting and contact angles in solid-liquid-liquid systems under realistic environments," *The Canadian Journal of Chemical Engineering*, Vol. 84, February 2006, 44-51.
70. Yildiz, H.O., and Morrow, N.R. 1996. "Effect of brine composition on recovery of Moutray crude Oil by waterflooding. *J. Pet.Sci. Eng*, May, Vol. 14, No. 3/4: 159-168.
71. Yildiz, H.O., Valat, M., and Morrow, N.R. 1999. "Effect of brine composition on wettability and oil recovery of a Prudhoe Bay crude oil. "*J. Can. Pet. Tech*, Jan., Vol.38, No. 1:26-31.
72. Yousef, A.A., Al- Saleh, S.H., Al-Kaabi, A.O., and Al-Jawfi, M.S.: "laboratory Investigation of Novel Oil Recovery Method for Carbonate Reservoir," Paper CSUG/SPE 137634, the Canadian Unconventional Resources & International Petroleum Conference, Calgary, Alberta, Canada, 19-21 October 2010.
73. Yousef, A.A., Al- Saleh, S.H., and Al-Jawfi, M.S.: " New Recovery Method for Carbonate through Tuning the Injection Water Salinity: SmartWater Flooding," Paper SPE 143550, the SPE EUROPEC/EAGE Conference, and Exhibition held in Vienna, Austria, 23-26 May 2011 (a).
74. Yousef, A.A., Al- Saleh, S.H., and Al-Jawfi, M.S.: " Smart Water Flooding for Carbonate Reservoirs: Salinity and Role of Ions, "Paper SPE 141082, the SPE Middle East Oil and Gas Show and Conference held in Manama, Bahrain, 25-28 September 2011 (b).
75. Yousef, A.A., Al- Saleh, S.H., Al-Kaabi, A.O., and Al-Jawfi, M.S.: " laboratory Investigation of the impact of Injection Water Salinity and Ionic Content on Oil Recovery from Carbonate Reservoirs,"*SPE Reservoir Evaluation & Engineering Journal*, vol.14(5), pp. 578-593 October 2011 (c).
76. Yousef, A.A., Al- Saleh, S.H., Al-Kaabi, A.O.: "Improved/ Enhanced Oil Recovery from Carbonate Reservoirs by Tuning Injection Water Salinity and Ionic Content ". Paper SPE 154076 presented at the Eighteenth Improved Oil Symposium held in Tulsa, Oklahoma, USA, 14- 18 April 2012.
77. Yousef, A.A., Al- Saleh, S.H., and Al-Jawfi, M.S.: "The Impact of the Injection Water Chemistry on Oil Recovery from Carbonate Reservoirs," Paper SPE 154077 presented at the SPE EOR Conference at Oil and Gas West Asia held in Muscat, Oman, 16-18 April 2012.
78. Zekri, A.Y, Nasr, M., and Zaid, A.: "Effect of EOR technology on wettability and oil recovery of carbonate and sandstone formation (IPTC 14131): This paper was prepared for presentation at the International Petroleum held in Bangkok, Thailand, 7-9 February 2012.
79. Zhang, P., Austad, T." Waterflooding in Chalk: relationship Between Oil Recovery, New Wettability Index, Brine Composition and Cationic Wettability Modifier" SPE 94209, 2005.
80. Zhang, P., Austad, T.: "Wettability and Oil Recovery from Carbonates: Effects of Temperature and Potential Determining Ions," *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 279, 2006, pp. 179-187.

81. Zhang, P., Tweheyo, M.T. and Austad, T.: “Wettability Alteration and Improved Oil Recovery by Spontaneous Imbibition of Seawater into chalk; Impact of the Potential Determining Ions Ca^{2+} , Mg^{2+} and SO_4^{2-} ,” Colloids and Surfaces A: Physicochemical Engineering Aspects, 301,2007b, pp. 199-208.
82. Zhang, Y., Xie, X. and Morrow, N.R.: “ Waterflood Performance by Injection of Brine with Different Salinity for Reservoir Cores,” Paper SPE 109849, presented at the 2007 SPE Annual Technical Conference and Exhibition, Anaheim, California, November 11-14, 2007.
83. Zheng, Y., “Effect of Surfactants and Brine Salinity and Composition on Spreading, Wettability and Flow Behavior in Gas-Condensate Reservoirs,” Dissertaion, Department of Petroleum Engineering, 2012.

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