The Pennsylvania State University

The Graduate School

John and Willie Leone Family Department of Energy and Mineral Engineering

EFFECT OF CHANGING INJECTION WATER SALINITY ON OIL RECOVERY FROM OIL-WET CARBONATE ROCKS

A Thesis in

Energy and Mineral Engineering

by

Ugur Pakoz

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

December 2015

The thesis of Ugur Pakoz was reviewed and approved* by the following:

Zuleima T. Karpyn
Associate Professor of Petroleum and Natural Gas Engineering
Thesis Advisor

Luis F. Ayala H.
Professor of Petroleum and Natural Gas Engineering
Associate Department Head for Graduate Education

Hamid Emami-Meybodi
Assistant Professor of Petroleum and Natural Gas Engineering

*Signatures are on file in the Graduate School

ABSTRACT

Experimental studies and some field applications have shown that tuning the salinity of the injected water can affect oil recovery from water flooding. Most of the available literature has dedicated efforts to investigate the effect of low salinity water injection, especially for sandstone. Further studies on carbonate rocks also proved that low salinity effect might be observed for carbonate rocks as well. The main mechanism for the improved oil recovery from low salinity water flooding has been attributed to wettability alteration. The purpose of this work is to further investigate the effect of water salinity on oil recovery from oil-wet carbonate rocks. A series of core flood experiments were performed in the laboratory to measure and compare oil recovery from increasing and decreasing salinity floods at room temperature. Selected carbonate cores were aged with synthetic oil at 100 $^{\circ}$C for 12 days prior to core flooding. Contact angles were measured on pre-aged and post-aged core slices to validate aging procedure and oil-wet conditions. Both, increasing and decreasing salinity floods showed measurable recovery gains in the secondary and tertiary modes compared with initial floods. In case of increasing water salinity, 1.3% and 0.6% additional recoveries were obtained while in the case of decreasing water salinity, additional recoveries were 0.6% and 0.7%, all in terms of original oil in place in the core. Results suggest that the system disturbance caused by the change in injection water salinity may have a greater influence on oil recovery than wettability alteration under the laboratory conditions tested.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

I would like to thank my advisor Dr. Zuleima T. Karpyn for motivating and supporting me throughout my thesis. Her friendship and kind personality helped me enjoy the hard process of getting a master degree. I am grateful to Turkish Petroleum Corporation (TPAO) for supporting me financially and making it possible for me to pursue my further education.

I am thankful to my committee members Dr. Luis F. Ayala and Dr. Hamid Emami-Meybodi for their valuable comments and contribution to my thesis. I am also thankful to Dr. Abdullah Alajmi and Dr. Meshal Algharaib for their help and advices during my experiments and throughout thesis writing process.

I would like to dedicate a special thanks to Dr. Turgay Ertekin, who helped me during the admission process and did not hesitate to help me whenever I needed during my entire education.

I also want to express my appreciation to our lab technician Tim Stecko and my lab friends for their valuable friendship and assistance. Thanks to them, I was able to solve some problems, which I was stuck and could not solve them by myself.

I dedicate this thesis to my family for their continuous support and love.

Ugur Pakoz

University Park, State College, Pennsylvania, 2015

Chapter 1 : Introduction

Carbonate rocks are crucial for petroleum industry for the amount of reserves that they contain. Their natural tendency to become oil wet causes quite low recoveries in the primary production. Wettability has been the main challenge in carbonate reservoirs for enhancing oil recovery (Alotaibi et al., 2010). Numerous investigations in recent years have focused on tuning the injected water salinity to enhance oil recovery from both carbonate and sandstone rocks in secondary and tertiary mode. Bernard (1967) was first to report that injecting fresh water in the presence of clay minerals may improve the recovery through clay swelling and additional pressure drop across the core compared with brine. This study was extended by Jadhunandan and Morrow (1995) where it was concluded that adjustment of brine may enhance production by wettability alteration. Continuous research on sandstone rocks proved that lowering the salinity of injected brine would improve the oil recovery by fine migration, increase in pH, mineral dissolution, salting-in , multi-ion exchange and overall wettability alteration (Yousef et al., 2011; Al-Harrasi, 2012). Morrow and Buckley (2011) suggested that clay existence, presence of connate water and exposure to crude oil was necessary conditions for the success of low salinity effect.

Carbonate rocks, on the other hand was first investigated by Bagci et al., (2001) for the possible effects of changing injection water salinity. Two possible reasons for the late interest would be the assumption that water flooding for carbonate rocks is less effective because of insufficient imbibition (Xie et al, 2005) and the speculations that clay content was a necessary condition for the process (Tang and Morrow, 1997; Lager et al., 2007). Further investigation on carbonate rocks showed that changing the salinity is also effective for carbonate rocks (Yousef et al, 2011; Shehata et al, 2014) and the presence of clay is not a necessary condition (Al-Aulaqi, 2013). Salinity effect for carbonate rocks were also attributed to wettability alteration through some additional mechanism such as electrical double layer expansion (Al-Shalabi et al, 2013), potential determining ions (Theweyo et al, 2006; Gomari et al, 2006; Mahani et al, 2015), and ion exchange processes (Bennetzen, 2014). On the other hand, it has recently been discovered that one possible proposed mechanism, mineral dissolution, is not very effective for carbonate rocks (Nasralla et al, 2014: Mahani et al, 2015). However, there is still a knowledge gap in carbonate rocks because of late interest regarding the salinity effect.

Although many possible mechanisms which explain the role of injected water salinity on oil recovery have been proposed, there is no consensus on which mechanism governs the process. The reason is that nature of crude oil-brine-rock interactions both for sandstone and carbonate rocks is complex. Therefore, there is a need to perform additional experiments in different conditions to have a better understanding of how salinity of injected water affects oil recovery.

The aim of this study is to gain further understanding the salinity effect on oil recovery from carbonate rocks by increasing and decreasing injection water salinity at room temperature. The experiments presented in this study utilize homogeneous non-fractured identical Indiana Limestone outcrop cores, synthetic paraffinic oil, sea water, 50% sea water and distilled water. Four water flooding experiments were performed. The first two aimed to compare the effect of aging, which is a very important step applied in almost all core flooding experiments. This work presents a quick way to justify if the aging applied is effective prior to actual brine injection experiments. The last two experiments were performed to investigate the effect of system disturbance created by changing the injection water salinity in the tertiary mode.

Our work will provide another point of view to the concept of salinity effect on oil recovery from carbonate rocks. The methodology we deploy to quantify the effect of salinity in increasing and decreasing order might be used with different oil-brine-rock combinations to enlarge the understanding of salinity effect on oil recovery. Likewise, our procedure to quantify the effect of aging might also be applied before starting water flooding experiments in order to ensure the aging process is efficient in converting the wettability to desired level.

Chapter 2 : Literature Review

2.1. Carbonate Rocks and Wettability

Carbonate rocks are sedimentary rocks composed primarily of carbonate minerals. The two most common carbonate rocks are dolostone and limestone; dolostone being composed of dolomite ($CaMg(CO_3)_2$) and limestone being composed of calcite or aragonite ($CaCO_3$). Carbonate rocks contain 60% of world oil and 40% of world natural gas reserves in terms conventional reservoirs. To better illustrate their importance, the richest region in terms of oil and gas reserves, Middle East, is dominated by different types of carbonate rocks by 70% in oil reserves and 90% in gas reserves (Schlumberger, 2015). The porosity, permeability and pore space distribution in carbonate rocks are related to both the depositional environment the diagenesis of the sediment. In carbonates, porosity and permeability are not well correlated with grain size or sorting. Porosity and permeability are controlled largely by the amount of fines and by diagenesis. Correlation of petro physical properties with rock type is very difficult. Uniformity of pore size, shape and distribution in carbonate rocks ranges from fairly uniform to extremely heterogeneous even within the same rock type (Peters, 2012).

Wettability of a rock is affected by many parameters. Mineralogy of the rock, the depositional environment, connate water content, properties of oil, pressure and temperature of the reservoir are the main factors determining the wetting phase of the rock over a long period of geological time. Initial wettability may be altered during the production period. Possible alterations in temperature, pressure and fluid content during the production may constantly change the wettability of the rock.

Table 2-1 shows the wettability state of some reservoir rocks (Treiber et al., 1972). Most carbonate rocks are preferentially mixed wet (intermediate wet) or oil wet as it can also be seen in the table. Recoveries in oil wet rocks are lower compared to water wet rocks. In shallow-shelf oil wet carbonate rocks, for example, recovery rates are less than 10% of the original oil in place, which means 90% of the oil remains in the reservoir after primary recovery (Xie et al, 2005). The most important reason for lower recovery in the primary production phase is that reservoir oil tends to spread over the reservoir rock and tends to stay on the rock surface. This phenomenon is illustrated by Abdallah et al. (2007) in Figure 2-1. The figure clearly shows that when the rock grains are oil wet, just like the majority of carbonate rocks, oil remains in the on the surface of grains, while in water wet grains, oil remains in the center of the pores. This figure justifies that recovering oil from carbonate rocks are harder and recovery rates are lower compared with mostly water wet or mixed wet sandstone rocks.

Wetting State	**Total Reservoirs**	**Carbonate Reservoirs**	**Silicic Reservoirs**
Water-Wet	27%	8%	43%
Intermediate-Wet	7%	8%	7%
Oil-Wet	66%	84%	50%

Table 2-1: Wettability Behavior of Some Reservoir Rocks (Treiber et al., 1972)

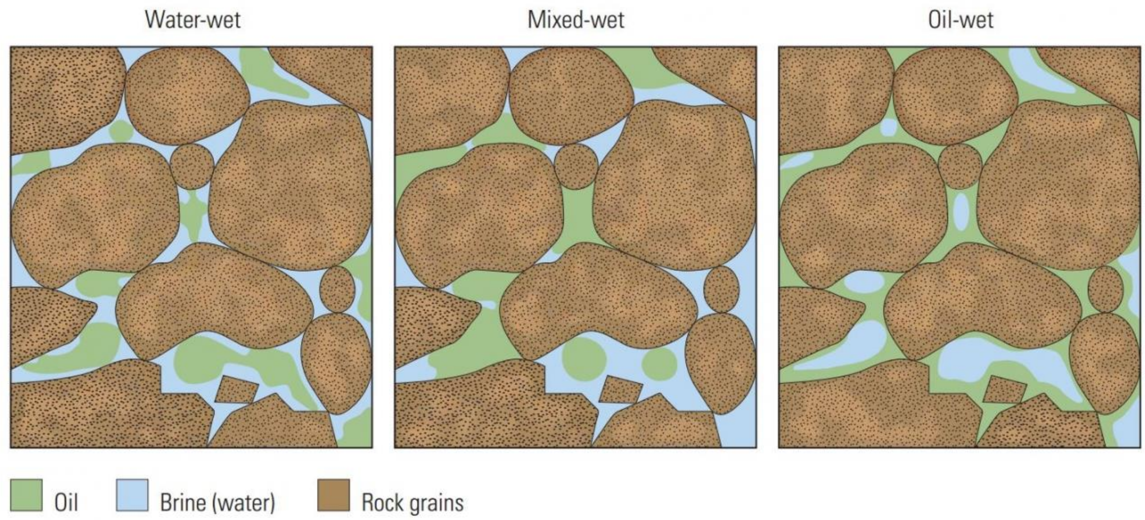

Figure 2-1: Fluid Distribution in Different Wetting Conditions. In water -wet case, oil places in the center of the pores while in oil-wet case, it stays on the surface of the rock grains (Abdallah et al, 2007)

To overcome the problem of low recovery, different enhanced oil recovery (EOR) and improved oil recovery (IOR) techniques have been applied to both mixed wet or oil wet carbonate reservoirs. Ultimate purposes of EOR and IOR applications for carbonate rocks are to provide pressure support (water and gas injection), to decrease viscosity (steam, chemical and bacterial injection) and ultimately to change the wettability (chemical injection, steam injection, low salinity waterflooding).

2.2. Waterflooding and the Role of Salinity

Waterflooding has been used as a secondary recovery method applied for more than 50 years to provide pressure support and improve sweep efficiency when the reservoir’s natural energy is not enough to push the oil toward producers, sometimes referred as initial depletion. Because water is readily available, cheap, easy to inject into oil bearing formations, effective in displacing light to medium oil and requires low capital investment, it has been one of the most successful, feasible and popular EOR method (Yousef et al, 2012, Sahikh and Sharifi, 2013). In the early stages of the process, the effect of waterflooding was attributed to improving the mobility ratio, which may in turn, improve the sweep efficiency and release the oil from the pores.

Despite its widespread use, it is possible that waterflooding may not yield significant recovery from oil wet carbonate rocks compared with sandstone rocks, because spontaneous imbibition of water does not occur in oil wet rocks. The spontaneous imbibition mechanism is effective in water wet reservoirs in which water penetrates into the rock matrix, expelling oil to the fractures and flushing it along the fractures toward the production wells (Xie et al, 2005) and plays a key role in waterflooding success. Therefore, the ultimate purpose of waterflooding should be to change the wettability of carbonate rocks so that the new wettability state allows successful waterflooding.

Bernard (1967) was first to report that injecting fresh water would yield higher recovery compared with injecting brine. He performed water flooding experiments on Berea Sandstone containing clay by injecting fresh water and brine containing NaCI with different concentrations. He concluded that injecting fresh water would cause a development of a relatively higher pressure drop due to swelling of clay minerals, thereby decreasing the pore space available for fluids. A second explanation he made was that the clay particles were dispersed by fresh water and those particles plug some of the flow channels which would cause new flow channels to be open. As a result, those flow channels would be flooded out, resulting in additional recovery. He also revealed that if fresh water does not develop a high pressure drop; no additional oil production is observed.

Jadhunandan and Morrow (1995) performed 50 slow rate laboratory water floods on Berea sandstone samples to evaluate the effect of wettability on oil recovery. They concluded that adjustment of injected brine composition may possibly increase oil/water production by wettability alteration. They suggested that wettability change caused by brine composition adjustment was less definitive than the effect of temperature and initial water saturation in their case. They urged that more investigation would help with optimizing the salinity of injected brine to increase water flood recoveries.

Shortly after, Tang and Morrow (1997) performed waterflooding and water imbibition experiments by utilizing 3 oil samples and 3 different brines on Berea Sandstone to investigate the effect of salinity, temperature and oil composition on oil recovery by waterflooding. They found out that in case of identical connate and injection water salinity, final oil recovery increased when the injection water salinity was lowered. Similar results were observed when they kept the same connate water but changed the injection water salinity. They also discovered that injection water salinity was sensitive to connate water salinity however the difference in final recoveries was much smaller.

Morrow and Buckley (2011) published a review paper related to low salinity effect (LSE) mostly from sandstone reservoirs. They investigated the reported results and analyze them under two categories: effect of low salinity in the secondary mode (Low salinity waterflooding (LSW) at initial water saturation) and in the tertiary mode (LSW at residual oil saturation). They idealized the low salinity effects in both mode as in Figure 2-2 and Figure 2-3. They summarized that in both categories, there are promising results;

however, there are some cases that no LSE was observed although the necessary conditions were met. They explained this contradiction as a possible result of the lack of a consistent mechanistic explanation and confusion caused by "the complexity of the minerals, crude oils, and aqueous phase compositions and their interactions".

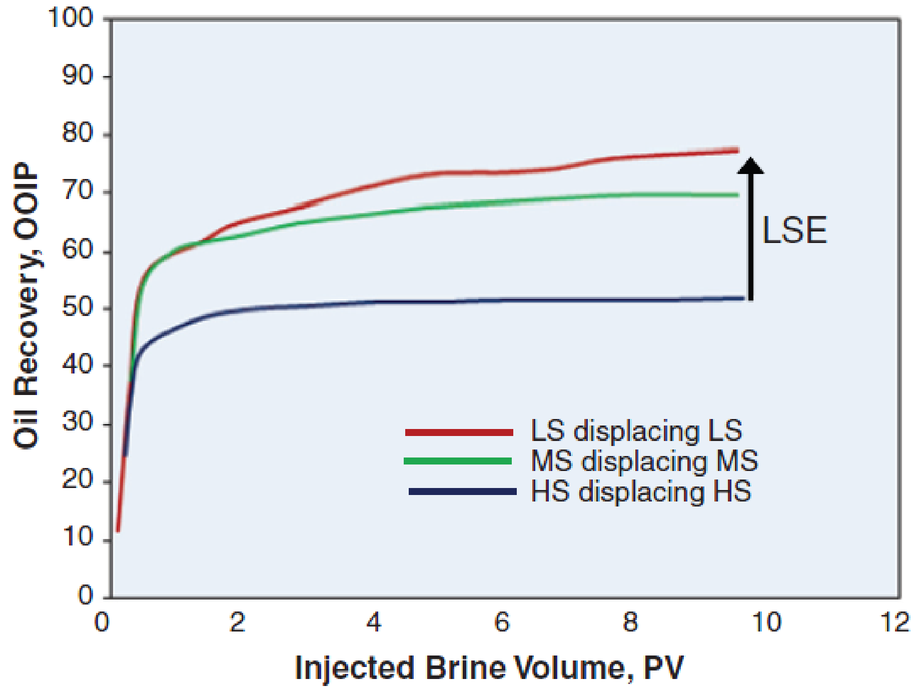

Figure 2-2: Waterflood Recovery vs. Pore Volume (PV) showing LSE for LSW at Swi. Connate and injected brines have identical concentrations. Experiments were conducted in matched Berea-sandstone core plugs. (LS: low salinity, MS: medium salinity, HS: high salinity) (Morrow and Buckley, 2011)

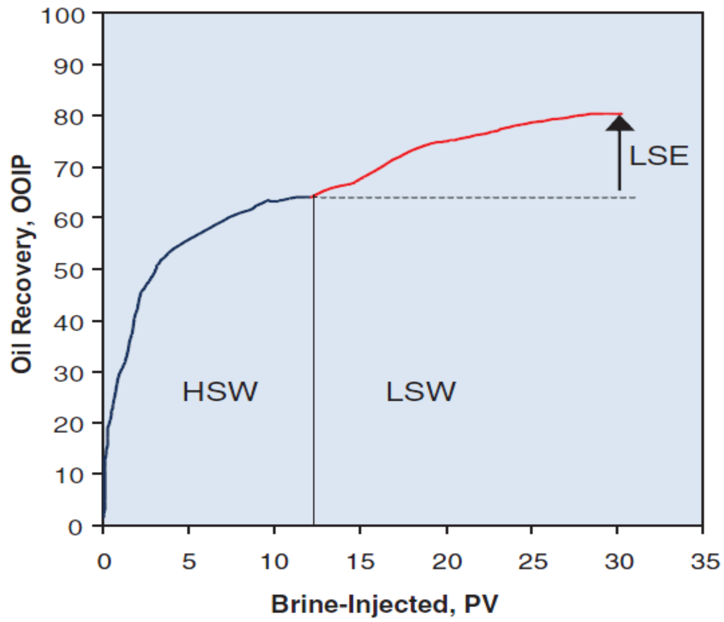

Figure 2-3: Waterflood Recovery Showing LSE for LSW at Sor with Reservoir core and fluids. (Morrow and Buckley, 2011)

Moreover, both experiments and field applications have shown that tuning of the composition of the injected brine may have a significant impact on oil recovery on sandstone (Aladasani et al., 2012; Al-Harrasi et al., 2013; Al-Shalabi et al., 2013). Aladasani et al (2012) reported 214 core flooding experiments for secondary recovery and 188 core flooding experiments for tertiary recovery for sandstone rock samples. Al-Harrasi et al (2012) summarized the mechanisms which are effective for low salinity water flooding for sandstone from the literature as fine migration, increase in pH/alkaline flooding, increase in pressure drop across the core, wettability alteration and mineral dissolution. In a very similar way, Al-Shalabi et al (2013) listed the effective mechanisms for LSE from sandstone reservoirs as fines migration, pH increase, multi-ion exchange, salting in and wettability alteration. However, how these mechanisms work and to what extent they contribute to additional recovery are still not very well understood.

When it comes to carbonate rocks, the research regarding the salinity effect on oil recovery is limited. Al-Shalabi et al. (2013) explained that the effect of low salinity waterflooding has not been investigated in carbonate rocks because of “the speculations of relating wettability to presence of clay”. Bagci et al. (2001) were first to investigate the effect of brine composition on oil recovery from carbonate rocks. In their work, they analyzed the effect of divalent and monovalent anions and cations by changing their concentrations. They performed water flooding experiments by using 10 different brine compositions, 3 brine mixtures and used limestone rock and crude oil from Garzan Field in Turkey. They concluded that the highest recovery was obtained when 2% KCl + 2% NaCI and it was 18.8% higher than distilled water injection, which is quite contradictory to the followed literature. Some of the experiments showed that decreasing the salinity of brine increased the oil recovery. They did not consider using sulfate and they have not performed IFT or contact angle measurements.

Hognesen et al. (2005) analyzed the effect of temperature and brine composition on carbonate rocks at 70 ºC. They specifically investigated the effect of sulfate concentration, one of the key potential determining ions, in the injected water. They concluded that spontaneous imbibition would increase with increase in temperature due to shift in wettability toward water-wetness and would occur only at elevated temperature. They observed that sulfate is a critical ion in altering wettability and “strong adsorption onto the chalk surface to facilitate desorption of the strongly adsorbed carboxylic material present in the crude oil is the key aspect. The authors concluded that the affinity of sulfate towards the carbonate surface would rise up with increasing temperature and increasing sulfate concentration would lead to higher recoveries at high temperatures. Zhang and Austad (2005) also concluded that the ability of sulfate to modify wettability is accelerated at higher temperatures and if the formation brine has significant calcium ion concentration, oil recovery would not be improved because of precipitation problems.

Theweyo et al. (2006) on the other hand, analyzed the effect of SO_4^{2-} and Ca^{2+} as potential determining ions for oil recovery from carbonate rocks. They performed their experiments at different temperatures with different ion concentrations. They concluded that sulfate is the main potential determining ion and it is more effective at higher temperatures in changing wettability. Similarly, calcium and magnesium are also effective in wettability alteration processes such that they lower the temperature characteristic needed for wettability alteration. Theweyo et al. (2006) observed that increasing the calcium concentration at 40 ^{o}C did not cause a significant improvement in oil recovery while the difference was quite obvious at higher temperatures.

Zhang et al. (2006) claimed that wettability alteration of carbonate rocks in the presence of high temperature takes place if the injection water contains the ion couples of calcium and sulfate or magnesium and sulfate. Gomari et al. (2006) also obtained the same result stating that sulfate could only be effective in the presence of magnesium or calcium at reservoir temperature.

Yousef et al. (2011) also analyzed how lowering the salinity of the injected brine would affect the recovery from a carbonate rock by performing water flooding experiments through diluting the injected water continuously and by using contact angle measurements at reservoir temperature and pressure. They also made NMR measurements to observe the alteration of the surface charges. After injecting sea water

(57,600 ppm) followed by 2 times diluted, 10 times diluted and 20 times diluted sea water, additional recoveries were 7-8.5%, 9-10% and 1-1.6% respectively. Contact angle measurements showed that the wettability was changed to be more water wet during dilution process. NMR results also confirmed injection of different salinity slugs of seawater altered the surface charges of the rock significantly. As a conclusion, they stressed that wettability change was responsible for additional recoveries, triggered by the altered surface charges of carbonate rocks.

Aladasani et al. (2012) performed simulation studies by using some of the available experimental data regarding salinity effect from the carbonate rocks. He concluded that the incremental recovery in case of intermediate wetting conditions is controlled by low capillary pressure. He also pointed out that when the rock's wettability is altered to become strongly water-wet, cations should be added to the injected brine to shift it back to intermediate wettability.

Al-Harrasi et al. (2012) stated that carbonate rock are still open to investigation for LSE. They performed four water imbibition tests and four water flooding experiments by using different diluted brines to investigate salinity effect on recovery at 70 $^{\circ}$C. It was argued that in cases where the rock is non-fractured, water imbibition tests may not be considered to evaluate the potential of LSE and this is why it is also important to perform water flooding experiments. Core flood experiments showed an LSE response of 3-5% additional recovery by lowering the injected water salinity, while water imbibition tests increased the recovery by 16-21% with lower salinity injection brine. The IFT values were measured between brines and oil and they suggested that the insignificant changes between IFT values for different brines imply that the main mechanism responsible for additional recovery from carbonate rock is wettability change.

Sharifi and Shaikh (2013) performed contact angle measurements between 27 different brine salinity combinations and calcite plate at high temperature and it was discovered that there is no direct relationship between the measured contact angle and salinity level of water. They stressed that using lower salinity brine does not necessarily cause higher recovery in the secondary mode, while a lower contact angle will guarantee a higher recovery. They also performed core flooding experiments on calcite cores at reservoir conditions and they concluded that there is an optimum level of purifying the brine after which no significant additional recovery could be achieved.

Al-Aulaqi et al. (2013) investigated the impact of brine salinity and temperature on wettability changes of sandstone and carbonate samples by NMR measurement and core flooding experiments. By performing experiments and measurements with different brine at 20, 40 and 60 ^{o}C, it was discovered that sandstone samples was more responsive to wettability changes through temperature change and low salinity brine injection and clay content was not a necessary condition for low salinity effect. They reported another interesting result that temperature window of 20 to 60 ^{o}C may not be enough to cause wettability alteration to impact the oil recovery.

Double layer expansion is another mechanism proposed by researchers and it is thickening the electrical double layers in rocks by changes in pH of the brine injected. In their work, Al-Shalabi et al. (2013) questioned if double layer expansion could potentially contribute to low salinity effect on oil recovery from carbonate rocks. They used experimental data introduced by Yousef at al. (2010) and performed simulations using UTCHEM^R simulator. It was concluded that wettability alteration had negligible effect on relative permeability of water. They claimed that negligible changes in water relative permeability curves might be contributed by double electrical layer expansion as "the immobile water film thickness increases and relative permeability remains constant".

Shehata et al. (2014) performed water flooding experiments on Indiana Limestone outcrops at 195^0F in order to investigate the overall effect of salinity and individual effect of some certain ions (Na^+, Ca^{2+}, Mg^{2+} and SO_4^{2-}) on oil recovery. The results of recoveries were compared in the secondary mode and additional recoveries in the tertiary mode as a result of injecting different brine compositions. The researchers found that distilled water injection provided 6% higher recovery in terms of original oil in place (OOIP) in the secondary mode. In the tertiary recovery mode, when the salinity of the injected brine was lower, an additional recovery of 2.4% OOIP was obtained. They were also first to observe that injection sea water in the tertiary mode after injecting distilled water in the secondary mode showed an increase of 4.5 % additional recovery. This result is contradictory to what might be thought in terms of LSE and they explained that "electrostatic interactions caused by sudden change in the salinity of the injected brine" was the reason for improved recovery.

Nasralla et al. (2014) made an extensive study on two different carbonate reservoirs to demonstrate the effect of salinity on oil recovery. They performed the experiments at reservoir temperature of 70 ºC and showed that lowering the salinity may improve the recovery by 3-5% in core flooding experiments. It was concluded that it is not only the total salinity that affects the recovery but also brine composition is also important. They also showed that calcite dissolution cannot be a dominant mechanism for LSE because there is no direct correlation between calcite dissolution and oil recovery.

Mahani et al. (2015) investigated if mineral dissolution is one of the primary mechanisms for LSE from carbonate rocks. They performed contact angle and zero potential measurements and utilized geochemical modeling for their work. They suggested that low salinity effect is still valid for carbonate rocks even without mineral dissolution. They claimed that the primary mechanism is driven by the composition dependency of electrostatic interactions between crude oil and rock and the extent to which it would be effective depends on the rock mineralogy. They also stressed that mineral dissolution is only relevant in a laboratory scale, not a field scale.

There have been a number of publications describing how overall salinity or ion changes in the injected brine would affect the oil recovery as summarized in Table 2-2. However, achieving a thorough understanding of the oil-brine-rock interactions in carbonate rocks that lead to maximum oil recovery is still in progress. Furthermore, a consistent mechanistic explanation regarding how wettability is changed through salinity change has not yet emerged (Dandekar, 2013). Another issue is that most of the research has focused on the wettability alterations and the cases where additional recovery is observed absent wettability alterations is yet to be studied. Therefore, it is clear that more research must be conducted on carbonate rocks in an effort to explain the effect of salinity. This includes performing more core flooding experiments using different rocks, oil and brine compositions to obtain a more general guideline for the issue.

In this thesis, effect of increasing and decreasing the overall salinity of brine on oil recovery from Indiana Limestone core is investigated at room temperature.

Authors, Year	Purpose of the Work	Rock Type	Temperature	Brine
Bernard, 1967	Effect of Overall Salinity	Sandstone	Ambient	Fresh Water and Brine of NaCI
Jadhunandan ad Morrow, 1999	Effect of Brine Composition on Oil Recovery	Sandstone	Ambient	Different Compositions of NACI and $CaCl_2$
Tang and Morrow, 1997	Effect of Wettability on Oil Recovery	Sandstone	22 ^oC – 75 ^oC	3 different brine compositions
Bagci et al., 2001	Effect of Overall Salinity	Carbonate	60 ^oC	10 different brine compositions
Hognesen et al., 2005	Effect of Temperature and Brine Composition on Oil Recovery	Carbonate	70 ^oC	5 different brine compositions
Theweyo et al., 2006	Effect of Potential Determining Ions on Oil Recovery	Carbonate	20 ^oC– 130 ^oC	12 different brine compositions
Yousef et al., 2011	Effect of Overall Salinity and Smart Water Flooding	Carbonate	Reservoir Temperature	Sea water and its diluted brines
Al-Aulaqi et al., 2013	Effect of Temperature and Salinity on Wettability	Carbonate and Sandstone	20 ^oC – 60 ^oC	Brine with NaCI and its dilutions
Sharifi and Shaikh, 2013	Effect of Wettability on Oil Recovery through Contact Angle Measurements	Carbonate	82 ^oC	27 different brine compositions
Al-Shalabi et al., 2013	Effect of Double Layer Expansion on Oil Recovery	Carbonate	Reservoir Temperature	Sea water and its diluted brines
Shehata et al., 2014	Effect of Overall Salinity and Brine Composition on Oil Recovery	Carbonate	91 ^oC	16 different types of brine
Mahani et al., 2015	Effect of Mineral Dissolution on Oil Recovery	Carbonate	Reservoir Temperature	4 different brine compositions

Table 2-2: Summary of the Early Literature on Sandstone and Recent Literature on Carbonate Rocks for the Salinity Effect Studies

2.3. A Detailed Analysis on Aging Process

Rock samples used for core flooding experiments should be treated first so that they could be representative of the reservoir in interest. To simplify the complexity and heterogeneity of the reservoir rocks itself, sometimes homogeneous outcrops might be used. In both case, the rock sample should be aged.

Aging is the process of changing wettability of core samples by fastening the geological time at high temperatures to stimulate the rock at reservoir conditions. Dandekar (2013) explains the steps of aging in his book. It is essentially removing all the available fluids by extraction and drying the sample, pre-saturating with formation brine, injecting oil until no more water is produced. It then involves keeping the core at reservoir temperature and pressure for a certain period of time to attempt to reestablish the wettability developed in the reservoir over a geological timescale. Some of the most dominant factors affecting aging process are pressure, aging time, temperature and fluid characteristics.

Pressure effect is negligible (Hjelmeland and Larondo, 1986; Saner et al, 1991; Wang and Gupta, 1995). The only exception to the pressure case is illustrated by Baldeo Singh (1991). He claimed that cores aged at lower pressures gave more oil wet behavior than cores aged at higher pressures.

To analyze the effect of time on aging and recovery, Tiab and Donaldson (2012) created a plot for injected water versus oil recovery for different aging times with a temperature range of 60-90 ^{o}C. They concluded that stable core wettability is obtained after aging at a high temperature at least for 100 hours. It is clear from Figure 2-4 that as aging time increases, oil recovery decreases. Since carbonate rocks are mostly oil wet, it can be interpreted that carbonate rocks become more oil wet as the aging time increases. This causes lower oil recovery due to reduced spontaneous imbibition.

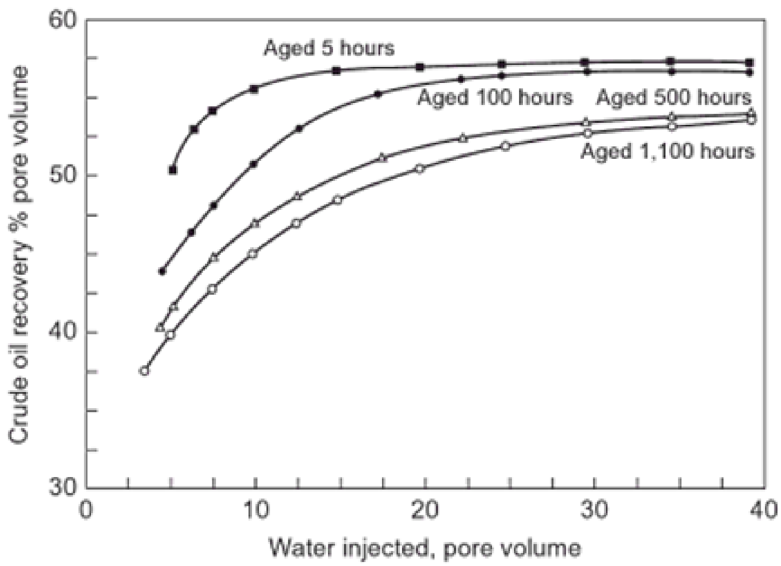

Figure 2-4: Effect of Aging of Oil-Water-Rock System on Oil Recovery Efficiency (Tiab and Donaldson, 2012)

However, as time is an important and valuable parameter in experiments, it is imperative to determine an optimum time for aging, after which wettability change will be negligible. Jadhunandan and Morrow (1995) concluded that for more than 50 different core samples of Berea sandstone, the average aging time was about 10 days at temperatures between 50 ^{o}C and 80 ^{o}C. They also investigated the effect of time on aging at time intervals of 20 to 40 days and they found out that no significant differences in wettability were observed from the extended time.

Graue et al. (1999) plotted imbibition rate and total recovery as a function of aging time (Figure 2-5). They found out that imbibition rate and total oil recovery decreased with increased aging time due to the fact that the rock samples became less water and more oil wet. They also noticed a very slight difference between the wettability of 14 days aged and 31 days aged core samples and they suggested that 2-3 weeks would be enough to see the maximum wettability change.

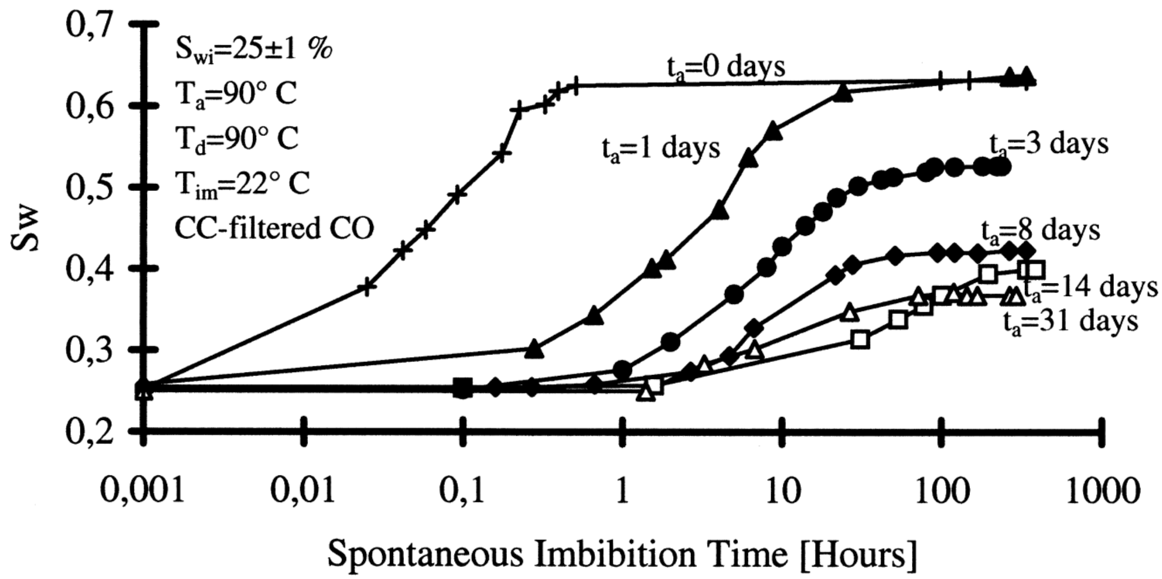

Figure 2-5: Effect of Aging Time in Crude Oil on the Recovery of Decane by Spontaneous imbibition in Rørdal chalk (Graue et al., 1999)

Temperature is another factor accumulating the aging period. Wettability alteration begins as soon as aging process starts and it occurs more rapidly at higher temperatures (Al-Mahrooqi et al, 2005). Heidari et al. (2014) found out that it takes 63 days for the reservoir rock they used to become intermediate wet at 25 °C in reservoir pressure condition while it takes only 10 days for intermediate wettability at 50 °C at the same reservoir pressure.

Oil in the core sample is another effective parameter in the aging process. It is widely accepted that the main mechanism altering the wettability during aging is the exposure of the rock to oil at high temperatures for a period of time. Oil composition and properties also affects carbonate rock wettability in aging process. According to Zhang and Austad (2005), the most important parameter in wettability change during aging is the acid content of the crude oil which is determined by the acid number of that oil. Quan et al. (2010) realized that the oil recovery from an oil wet volcanic reservoir increased as the acid number of oil decreased. Hognesen et al. (2005) claimed that carbonate reservoirs at high temperatures act like water wet contain crude oil with lower acid number. Therefore, oil with higher acid number has a higher tendency to make the rock more oil wet and lower the recovery. Fan and Buckley (2007) tested 255 different oil samples and found out that as oil becomes lighter, the acid number becomes lower (Figure 2-6). Thus, it is appropriate to expect that denser oil samples tend to make the rocks more oil wet compared with lighter oil at the same pressure, temperature and time.

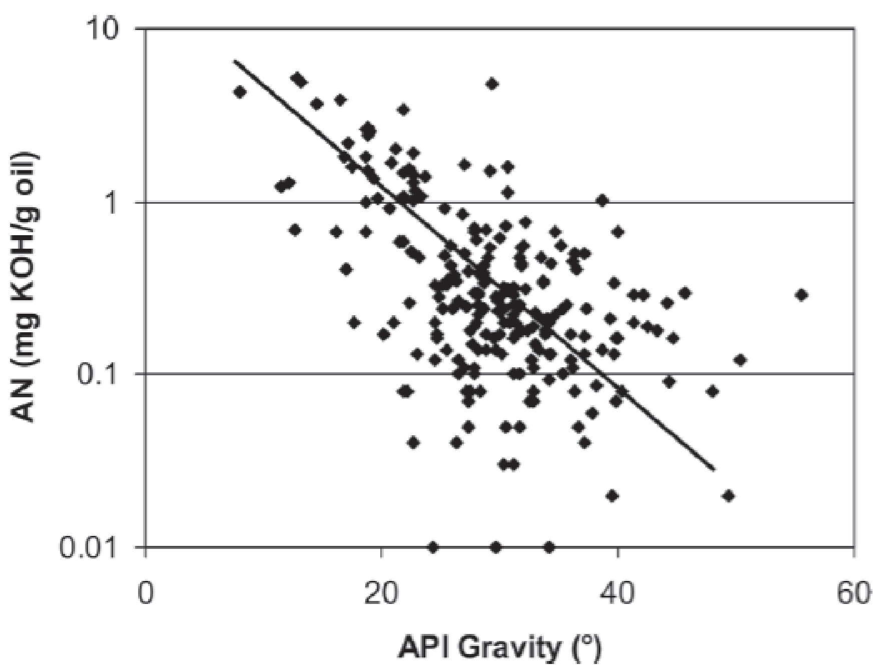

Figure 2-6: Acid Numbers of 255 Crude Oil Samples vs. API Gravity (Fan and Buckley, 2007)

Despite the fact that there is quite limited research regarding the effect of connate water salinity for wettability change in reservoirs rocks, it is also effective in the aging process. It is claimed that salinity of the connate water used may affect the residual oil saturations obtained from core flooding experiments for some crude oils (Filoco and Sharma, 1998). In their experimental studies, Chattopadhyay et al. (2002) suggested that both limestone and sandstone core samples become more likely to respond to wettability alteration during aging process as the salinity is increased. This conclusion implies that the carbonate rocks tend to become more oil wet as the connate water salinity is increased. However, there is no conducted study on carbonate rocks regarding the effect of connate water salinity on oil recovery.

As aging is the starting phase of most of the flooding experiments, it is vital to have an idea about the optimum time and temperature for the process. In addition to given case studies for the aging time and temperature, Hirasaki et al. (1990) aged their sandstone cores for 28 days at 65 ºC. Zhou et al. (1995) aged sandstone core samples at between room temperature and 80 ºC between 1 hour and 48 hours. Alotaibi et al. (2010) used only one day at 90 ºC to make a stimulated Middle East carbonate rock intermediate wet. Gupta et al. (2010) injected 5 pore volumes of oil into the brine saturated cores to reach residual water saturation. The oil saturated cores were aged for 60 days at 80 ºC to make them oil wet in case of the field oil and 20 days at room temperature in case of the model oil. Bennetzen et al. (2014) saturated carbonate rock sample with brine and injected dead oil until no more water was produced. Having established the initial water saturation, the cores were then placed in an oven and aged for 45 days at 90 ºC.

The Authors	Rock Type	Aging Time	Aging Temperature
Hirasaki et al. (1990)	Sandstone	28 days	65^0C
Zhou et al. (1995)	Sandstone	1 hour – 48 hours	80^0C
Alotaibi et al. (2010)	Carbonate	1 day	90^0C
Gupta et al. (2010)	Sandstone	60 days	100^0C
Bennetzen et al.	Carbonate	45 days	90^0C

Table 2-3: Some examples of aging time and temperature applied in the literature

As aging is a process depending on many parameters, there is no consensus on an ideal time and temperature as the complexity can be seen in Table 2-3. The complexity is increased further with different types of oil and connate water compositions. One of the best ways to achieve desired aging condition is to make wettability measurements on the rock/fluid system under observation. Another method to be employed to make sure that the core under investigation has been aged enough is to compare the oil recoveries before and after aging process. Aged core should yield lower recovery than the original core as shown in Figure 2-4.

In this thesis, we also attempted to quantify the effect of aging by performing both contact angle measurements and distilled water flooding experiments. The idea is to make sure that the pre-determined time and temperature is enough to cause a significant wettability change on the rock under investigation.

Chapter 3 : Problem Statement and Research Objectives

Tuning the injected water salinity has been popular in terms of secondary and tertiary recovery modes for both sandstone and carbonate rocks based on some encouraging experimental results and some field trials (Tang and Morrow, 1997; Yousef et al., 2011; Al-Shalabi et al., 2013; Nasralla et al., 2014; Mahani et al., 2015). Different mechanisms, such as changing wettability and fine migration have been proposed for the low salinity effect in different oil-brine-rock combinations. However, there is no consensus for both sandstone and carbonate rocks on how these mechanisms work. Besides, much of the attention regarding salinity effect was given to "decreasing the injected water salinity" in the tertiary mode and trying to see the "effect of lowering salinity". This effect has been referred as low salinity effect (LSE). Therefore, more experiments should be performed at different conditions and different rock-oil-brine combinations to have a better understanding of how salinity affects oil recovery.

In this study, we compare both increasing and decreasing salinity of injected water to further investigate their effect on oil recovery from oil-wet carbonate rocks at room temperature.

Chapter 4 : Materials and Methodology

This thesis attempted to analyze the effect of aging and injection water salinity on oil recovery from Indiana limestone rock samples through core flooding experiments at room temperature. To accomplish these purposes, two identical core slices and three identical limestone core samples were used in four water flooding experiments. This chapter gives detailed information about the properties of the materials employed and the methodology developed to perform the experiments.

4.1. Materials

This section gives information about the rock and fluid (brine and oil) properties as well as the core holder and other equipment (pumps, fluid collectors etc.) used in all experiments.

4.1.1. Rock and Fluid Properties

Homogeneous and non-fractured identical Indiana Limestone outcrop cores were used in all experiments to avoid reservoir complexities such as heterogeneity or fractures. The core samples were purchased from Kocurek Industries, Hard Rock Division. All the core samples were clear-cut and smooth in shape. Some basic parameters obtained from the company and confirmed by our measurements are shown in Table 4-1.

Lithology	Indiana Limestone
Diameter	2 inches
Length	12 inches
Brine Permeability	70 md
Effective Porosity	18-19%
Average Weight	1336 gr
Average Grain Density	2.7 g/cc

Table 4-1: Physical characteristics of Indiana Limestone from Kocurek Industries

Figure 4-1: Indiana Limestone Outcrop Cores used in Experiments

To have a better understanding of the core samples under investigation, some other detailed analysis was made. These detailed investigations include mineralogy, porosity and pore-size distribution.

Even though a reservoir might be called a carbonate reservoir, it is not necessarily composed of one type of carbonate mineral. It may include different types of carbonate minerals as well as other minerals such as quartz, silica, clays and sands. Quantifying different minerals present in the core sample under investigation is crucial to have a better understanding of the rock sample under investigation. Possible success of a waterflooding or any other EOR method strongly depends on the rock mineralogy. To illustrate, sandstone reservoirs respond better to waterflooding than carbonate rocks because of effective water imbibition as explained in Chapter 2. It was shown that the effect of low salinity is related to the presence of clay mineral (Tang and Morrow, 1997; Lager et al., 2007) and Yousef et al. (2011) claimed that the low salinity effect is the result of wettability alteration of clay minerals. Therefore, mineralogy of rock samples prior to waterflooding experiments should be analyzed and documented.

It is possible to determine different type of minerals present in the rock qualitatively or quantitatively through X-Ray Diffraction (XRD). X-ray Diffraction is a characterization technique in which X-rays are diffracted from different crystallographic planes in a material (Wonderling, 2015). The diffraction occurs when X-ray waves encounter an obstacle or crystalline material in this case. Diffraction occurrence mechanism is explained by Bragg's law. Each crystalline material has a unique atomic structure, thus it will diffract X-rays in a unique characteristic pattern (USGS, 2015). X-ray diffractometer is used for XRD analysis, which involves a source of monochromatic radiation and X-ray detector. Analysis of patterns at the end of XRD reveals the mineralogy of the rock sample. Qualitative analysis reveals the type of minerals that exists while quantitative analysis quantifies the amount of each existing minerals by percentage.

Representative samples were prepared by crushing and quartering to obtain an appropriate volume. This specimen was the ground in an agate mortar and pestle and prepared via the front load mount method in silicon zero background specimen support. It was ensured that the powder was representative of the whole rock sample by mixing rock pieces from different parts of the core. Figure 4-2 shows the powder prior to measurement.

Figure 4-2: Powdering the rock (left) and placing it in the X-Ray Diffractometer (right)

Data collection was performed on a PANalytical X'Pert Pro MPD theta-theta X-ray diffractometer using copper K-alpha radiation at 45 kV and 40 mA from 5-70 degree 2-theta. A PIXcel detector in scanning mode was utilized with a 3.34 degree active length and all 255 channels active. Figure 4-3 shows the diffractometer used in this study.

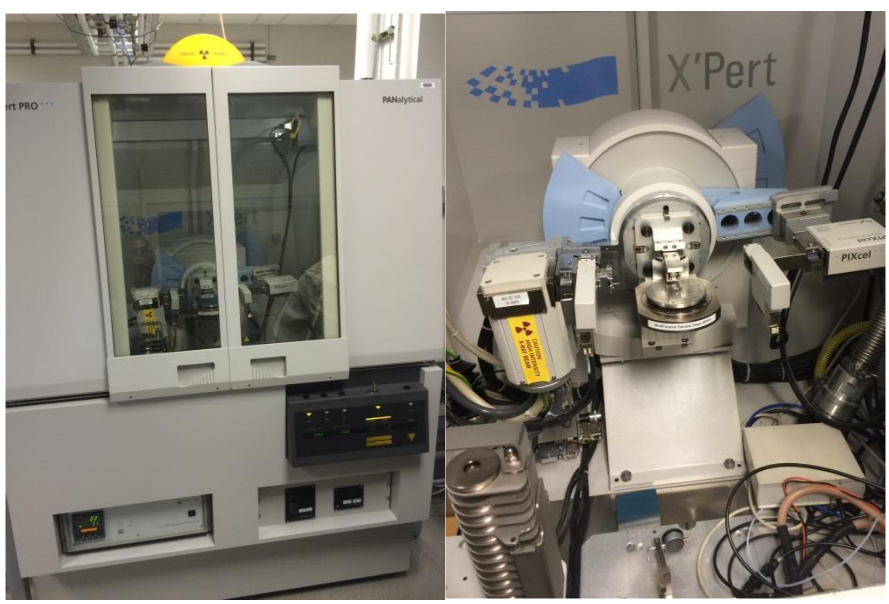

Figure 4-3: Outside of Diffractometer (left) and Inside of Diffractometer (right)

The data was collected using Data Collector Software and analyzed immediately after the measurements were complete. The data obtained was plotted by the program and analysis was made to obtain the best match. Figure 4-4 shows the XRD response plotted by the data obtained from the measurements while Figure 4-5 shows the mineralogy of the powder.

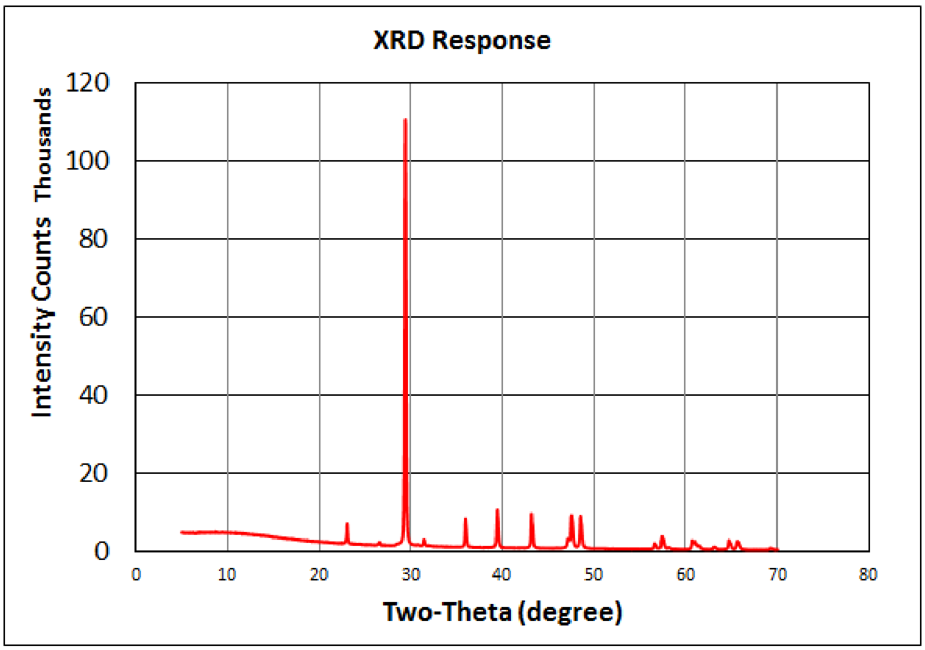

Figure 4-4: XRD Response of Indiana Limestone Powder

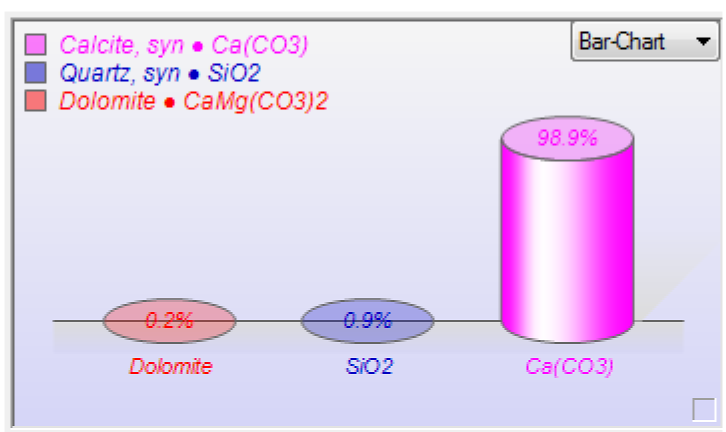

Figure 4-5: Mineralogy of Indiana Limestone Powder

The same measurement was performed on a different powder obtained by the same method from the same core sample to see if the core was homogeneous as suggested by the Kocurek Industries. The result from the second measurement was almost exactly the same and it completely overlapped on first powder XRD response plot. Figure 4-6 shows the overlapping plot of the two measurements while Figure 4-7, adjusted from the software, is used to show the responses in both cases.

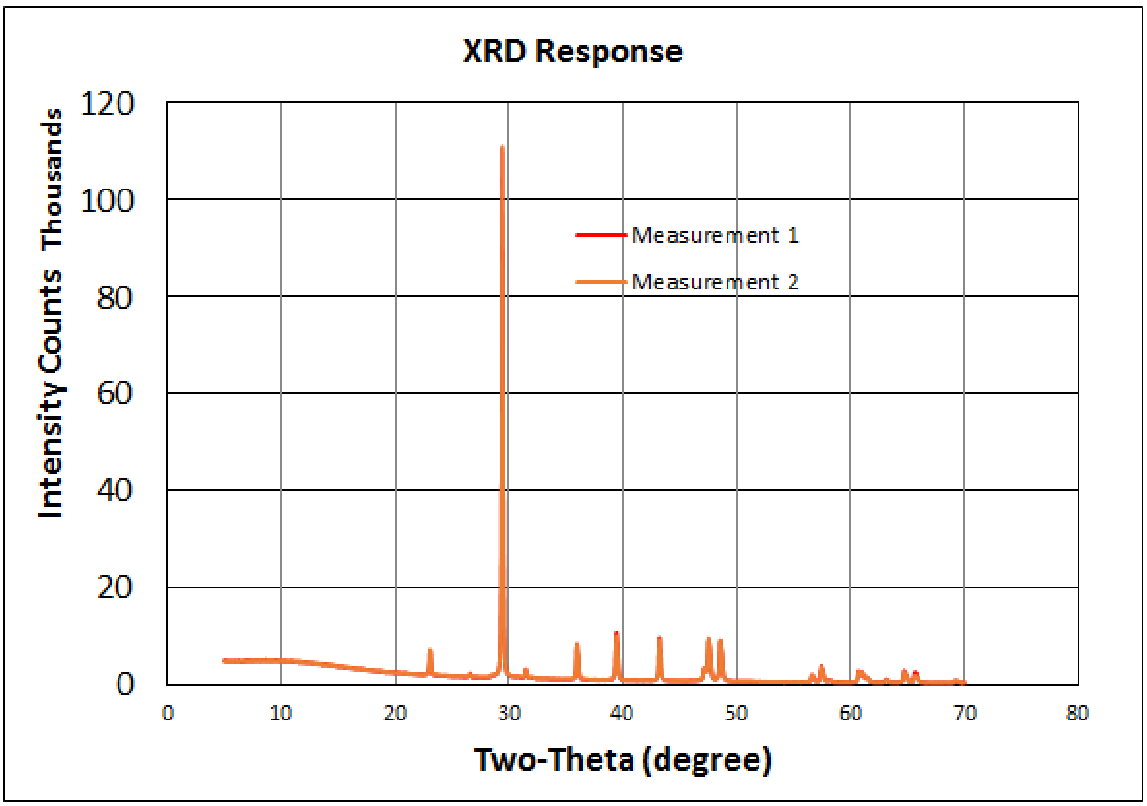

Figure 4-6: Comparison of the Results of Two Different Measurements

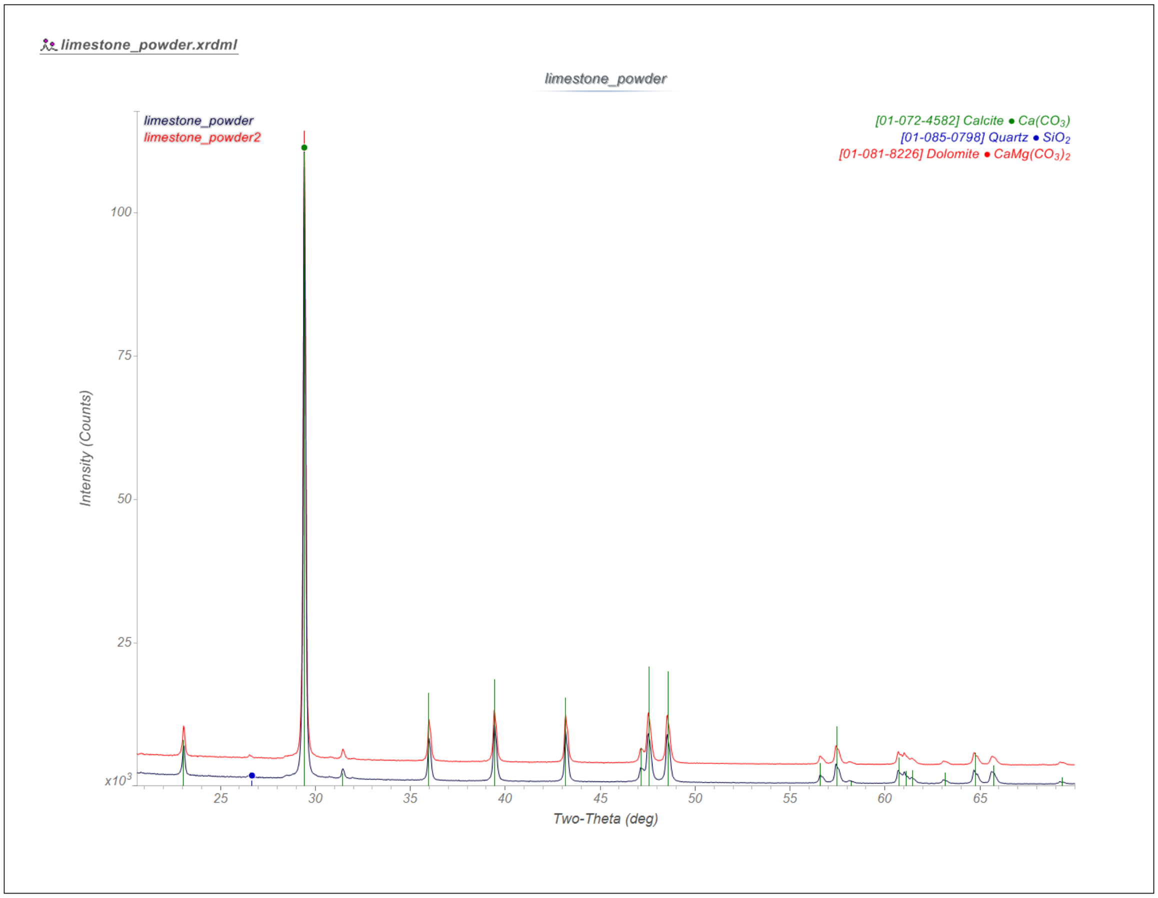

Figure 4-7: XRD Response in the First and Second Measurements

Therefore, it was proved that the rock sample was homogenous and it was limestone composed of 98.9% calcium carbonate ($CaCO_3$). No clay minerals were detected within the detection range of the X-ray diffractometer.

Porosity measurement was performed in Materials Research Institute at The Pennsylvania State University by mercury injection method up to 59,000 psi. A smaller core in a shape of triangular prism was used for the measurement. It was found that the porosity of the core was 18.4%, which is very close to the one given by the company. The average pore diameter was measured as 338.6 nm.

Commercial synthetic paraffinic oil from VWR Company was used in all experiment. Density and specific gravity measurements were performed by volumetric calculations using a graduated cylinder and precision advanced electronic weight. Viscosity was measured by recording the time for a volume of the oil to flow under gravity through a calibrated glass capillary viscometer. All measurements were performed at room temperature (25.5 ºC) and under atmospheric pressure. Acid number of the oil was found to be inversely proportional to the density of oil (Fan and Buckley. 2007). As we have a quite light oil, acid number is also in the low range. Table 4-2 summarizes the properties of the oil used in all experiments.

Type	Paraffin Oil
Color	Colorless
Density	0.822
Gravity	40 API
Viscosity	5.45 cp
Acid Number	Low

Table 4-2: Physical Properties of the Oil used in the Experiments

A commercial sea salt composition from Instant Ocean was used to prepare 3.5% and 1.75% brine solutions by weight. Distilled water was used to prepare the brine solutions. As a result, 3.5% and 1.75% brine solutions and distilled water were used as injection and connate water throughout the experiments. Density of the 1.75% and 3.5% brines were 1.0088 g/cc and 1.0221 g/cc, respectively while the viscosity of 1.75% and 3.5% brines were 1.026 cp and 1.074 cp as measured at atmospheric pressure and room temperature of 25.5 C. Throughout the report, 3.5% brine is referred as sea water while 1.75% brine is referred as 50% sea water.

Element	Category	mol/kg	MW, g/mol	gr/kg
Na	Cation	0.462	23	10.626
K	Cation	0.0094	39.1	0.368
Mg	Cation	0.052	24.3	1.264
Ca	Cation	0.0094	40.1	0.377
Sr	Cation	0.00019	87.6	0.017
Cl	Anion	0.521	35.5	18.496
SO4	Anion	0.023	32.1	0.738
TCO2	Anion	0.0019	12	0.02280
TB	Anion	0.00044	10.8	0.00475
Li	Trace	0.000054	6.9	0.00037
Si	Trace	0.000016	28.1	0.00045
Mo	Trace	0.0000018	95.9	0.00017
Ba	Trace	0.00000085	137	0.00012
V	Trace	0.0000029	50.9	0.00015
Ni	Trace	0.0000017	58.7	0.00010
Cr	Trace	0.0000075	52	0.00039
Al	Trace	0.00024	30	0.00720
Cu	Trace	0.0000018	63.5	0.00011
Zn	Trace	0.0000005	65.4	0.00003
Mn	Trace	0.0000012	54.9	0.00007
Fe	Trace	0.00000024	55.8	0.00001
Cd	Trace	0.00000024	112	0.00003
Pb	Trace	0.0000021	207	0.00043
Co	Trace	0.0000013	58.9	0.00008
Ag	Trace	0.0000023	108	0.00025
Ti	Trace	0.00000067	47.9	0.00003

Table 4-3: Elemental Composition of 29.65 ppt Instant Ocean Synthetic Sea Salt (Atkinson and Bingman, 1996)

4.1.2. Experimental Set-up and Tools

The experimental set-up for the vacuuming and pre-saturation process consists of a vacuum pump, a fluid reservoir (a tube) and the core holder containing the core completely sealed from the surroundings. The experimental set-up for the flooding experiments consists of an injector pump connected to and controlled by a computer, an air compressor for confining pressure, a fluid reservoir containing oil, distilled water or brine, core holder containing the core completely sealed from the surroundings and under confining pressure and fluid collectors. Figure 4-8 is the picture taken during the waterflooding experiment.

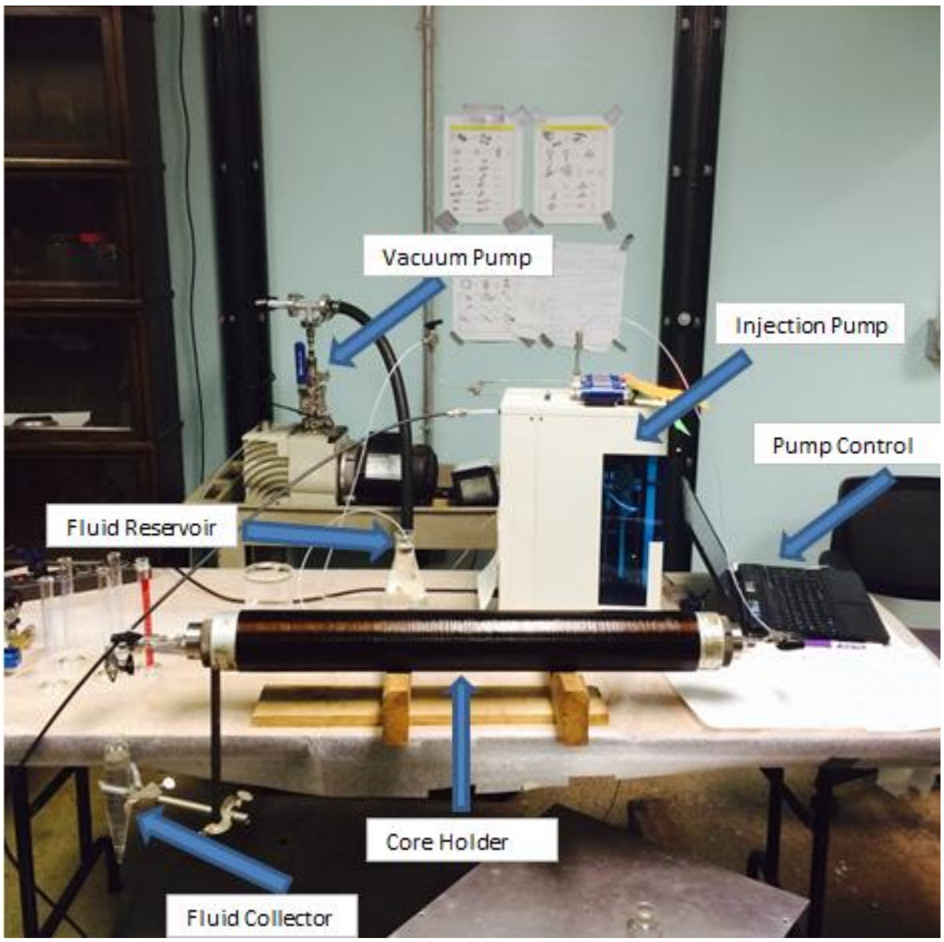

Figure 4-8: Experimental Set-up for Waterflooding

The core holder used in the experiments was an HCH-2.0 Standart Core Holder from Temco Company (now operating under Corelab Reservoir Optimization Company). The core holder can resist up to 3000 psi pressure and 300^0F (149^0C) temperature. It is compatible for scanning to run X-ray chromatography. Figure 4-9 shows the detailed sketch and properties of the core holder.

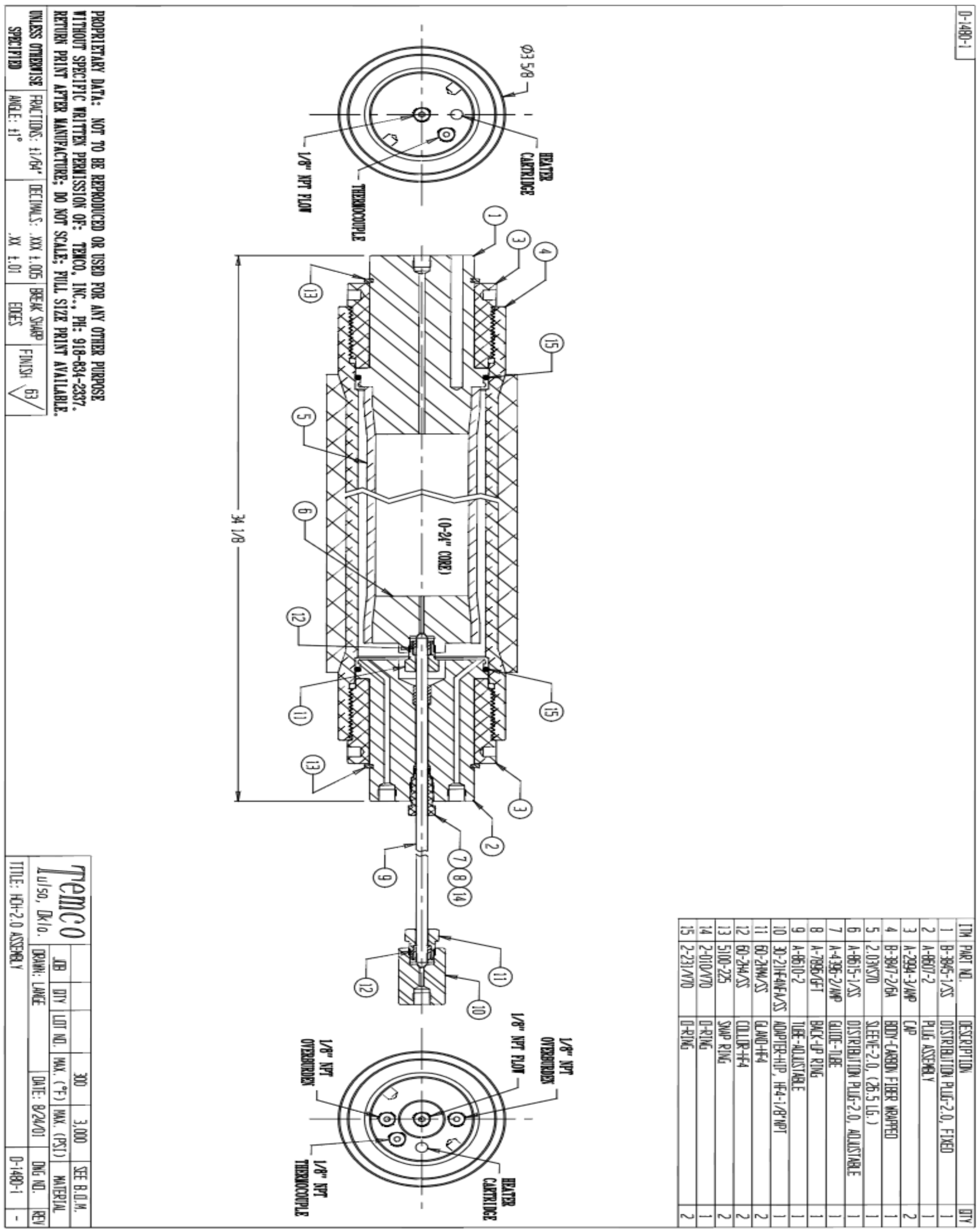

Figure 4-9: Top View of HCH 2.0 Standart Core Holder (Temco, 2001)

Considering the long time required for each series of experiment, the flow distributor at the outlet was modified in order to prevent a possible leakage problem during the experiments. The flow distributors were normally supposed to be attached to the sleeve and clamped with wire to prevent leakage. However, wiring itself might be the reason of leakage if it is not properly handled and especially when the duration of the experiment is long. Therefore, the layout of the original distribution pattern in a stainless steel cylinder was duplicated by increasing the length of the flow distributor to allow inclusion of the ribbed area. This way, it provided a function similar to that of a hose barb, which would double make sure sealing would be obtained throughout the experiment. The new flow distributor was built by the technicians of the Earth and Mineral Sciences (EMS) Machine Shop at The Pennsylvania State University.

Figure 4-10: Flow Distributor Built by EMS Machine Shop @ The Pennsylvania State University

Three types of pumps were used in the experiments. Vacuum pump from Marathon Electric Company was used to suck the air from the core prior to pre-saturation to make sure that the pores of the core samples were not occupied by air. An air compressor of 300 psi capacity from Kobalt Company was used to provide confining pressure during the flooding experiments. The injector pump was Quizix QX Series, which is able to perform under different specified conditions, such as constant flow rate or constant injection pressure by using single or double cylinders.

Fluid collectors were used to collect the fluid and measure the volume of oil and water during the experiments. The sensitivity of the fluid collector during the oil injection was as precise as +-0.05 cc/min, while the sensitivity during the water flooding was as precise as +-0.1 cc/min. The average pore volume was about 115 cc, therefore the accuracy of the fluid collectors was quite decent.

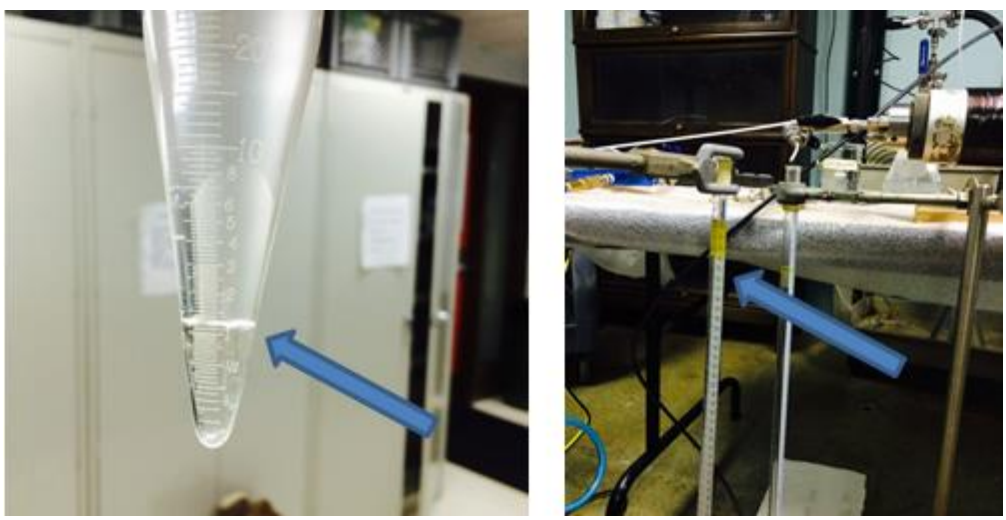

Figure 4-11: Flow Collectors for Oil Injection (left) and Waterflooding (right). Sensitivity of the tube used during oil injection was ±0.05 cc while it was ±0.1 cc during waterflooding.

4.2. Methodology

Four waterflooding experiments were performed on three Indiana limestone cores (cores 1, 2, and 3) with different connate water and injection water salinities. Distilled water and sea water were used as connate water while distilled water, 50% sea water and sea water was used as injection water. To quantify the effect of aging, one experiment was performed on a core prior to the aging process. Table 4-4 is a detailed description of each experiment regarding the type of connate water and injection water sequence used and the aging condition of the cores. It also includes the purpose of the experiments.

Flooding Sequence	Experiment Number	Connate Water		Aging Applied	Water Injected	Purpose of the Experiment
		Distilled Water	Sea Water			
I	1	√		√	Distilled Water	Effect of Aging
II	2	√			Distilled Water	
	3		√	√	Distilled Water, 50% Sea Water, Sea Water	Effect of Increasing Salinity
III	4		√	√	Sea Water, 50% Sea Water, Distilled Water	Effect of Decreasing Salinity

Table 4-4: Proposed Experiments, Initial Conditions in terms of Connate Water and Aging Condition, Injection Water Sequence and Purpose of Experiments

Figures 4-12 shows the flow charts and the steps followed to perform the flooding sequences on Core 1, Core 2 and Core 3.

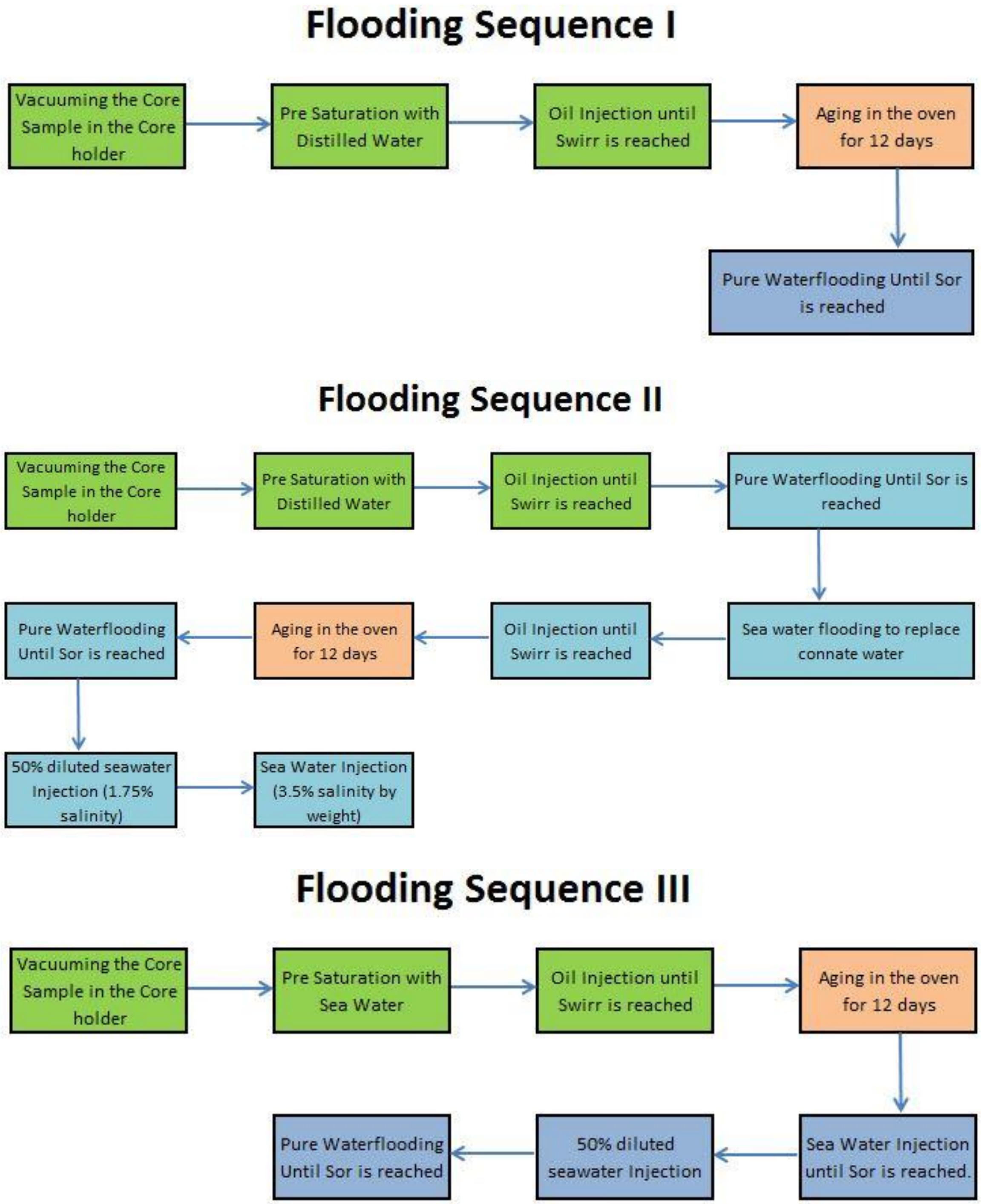

Figure 4-12: Flow Charts for Flooding Sequences I, II and III

In the flooding sequence I, after establishing initial oil and water saturations, aging was applied. After aging was complete after 12 days at 100 ^{o}C, distilled water flooding was performed in order to see the recovery after aging with distilled water. In the flooding sequence II, two experiments were performed. The first one was conducted on the core sample prior to aging. After establishing initial oil and water saturations with distilled water, waterflooding was performed with distilled water injection in order to compare the recoveries between aged and natural rock samples. After the experiment was complete, connate water was replaced with sea water and initial saturations are established once more. The second experiment in the second flooding sequence was performed after the core sample was aged. The aim was to see the effect of increasing injection water salinity, therefore the injection sequence started with distilled water and it was followed by 50% sea water and sea water. The effect of decreasing water salinity was analyzed in the final flooding sequence, where the injection sequence started with sea water and followed by 50% sea water and distilled water.

In all experiments, water flow rate was kept constant at 1 cc/min. The purpose of keeping the flow rate constant was to prevent a possible effect of flow rate on the recovery which may in turn affect the comparison of results of different experiments. Oil injection was started as low as 0.2 cc/min and completed as high as 1.5 cc/min depending on the pressure. The following part of this chapter explains each step of the methodology in details.

4.2.1. Vacuuming and Pre-Saturation

The core samples were placed in a black, 2” inner diameter viton plastic sleeve of 0.06” thickness. The sleeve used is resistant to many chemicals, oil and acids and it can perform up to 105 ^{o}C temperature. One end of the jacket was connected to the fixed end of the core holder where the core sample touches the flow distributor. An adjustable flow distributor with an attached flow line was put in the other end of the jacket until the flow distributor touched the core sample. This way it was made sure that there was not a gap between the ends of the core sample and the flow distributors. All the connections were tightened and checked for leakage. The jacket was put in to the core holder and all connections were assembled to isolate the annular space of the core holder and the core itself from surroundings.

After the core sample was completely sealed from the surroundings in and out of the core holder, the core had to be vacuumed until the air in the core is negligible. The purpose of vacuuming is also to make sure that all the pore spaces would be occupied by the connate water during the pre-saturation process. The core samples were vacuumed until the vacuum pump reached 90-140 micron. After desirable values were reached in the vacuum pump, the pre-saturation process was started for each core sample. Distilled water or brine, depending on connate water, was placed in a higher level than the core holder by attaching the beaker to a clamp system. This way, it was easier for the water to flow through the core thanks to the vacuum and the gravity. Connate water was allowed to flow until the water was seen at the outlet. At that moment, the outlet of the core holder was closed to make sure that no water will flow to vacuum line. A little more time was given to see if there would be additional flow from the tube to the core. When the liquid level is stabilized, volume of injected distilled water or brine was measured and the porosity was determined.

After the core samples were pre-saturated with their connate water, oil injection was performed by using pump until no more water was produced. In case the connate water was sea water, oil injection was started after one day of pre-saturation to establish the ionic equilibrium. The following table summarizes the results of the pre-saturation process for each core sample. It is important to note that we have two different data for Core-2 because we had to reestablish initial saturations after the waterflooding experiment prior to aging.

Core No	Diameter (in)	Length (in)	Porosity	Swirr	So
1	2	12	19.4%	31.7%	68.3%
2	2	12	18.7%	40.3%	59.7%
2	2	12	18.7%	41.7%	58.3%
3	2	12	18.3%	37.9%	62.1%

Table 4-5: Dimensions, Porosity and Initial Saturations of the Core Samples

After pre-saturation process, porosity values were quite close to the value given by Kocurek Industries and measured by helium injection method.

4.2.2. Aging

After the core samples were set to their initial irreducible water and oil saturations in each stage, pore pressure was kept at atmospheric pressure and the confining pressure was released. Then, the cores were moved to an oven at 100 ^{o}C in the sealed core holder and they were kept there for 12 days. In the first series, connate water was distilled water and in the second and third series, it was weight sea water. After the cores were aged at 100 ºC and atmospheric pressure for 12 days, it was cooled down to room temperature and the core holder was taken to the experiment room for the experiments.

Temperature was kept as high as possible depending on the equipment resistance limitation. As the jacket in use was able to resist up to 105 ºC, the core samples were aged at 100 ºC. The time in which the core sample wettability would have changed significantly was determined by contact angle measurement on aged core slice and natural core slice.

It was explained earlier that it is not easy to determine an exact temperature and time for aging process while it is known that pressure does not have a significant effect on the process. The reason is that wettability is affected by many factors such as the type of the rock, the oil and water used and the physics regarding wettability alteration is not well understood yet. To make sure the limestone core sample was more oil wet than water wet, wettability evaluation through contact angle measurement was performed. Contact angles were measured on two identical core slices of 1.5 millimeter thickness. One of the slices was dry and did not have any contact with distilled water or oil used. The other slice was immersed in the synthetic oil and kept in the oven for 12 days in total at a temperature of 100 ºC and then cleaned with alcohol and washed with water. The core sample was dried afterwards. Pictures of the core slices can be seen in the Figure 4-13.

Figure 4-13: Core Slices Used for Contact Angle Measurement

Four different measurements were made to compare the aging effect on the slices. These measurements were: contact angles between oil/air/core slice on clean and aged limestone slices and contact angles between water/air/core slice on the same clean and aged limestone slices. As most of the limestone rocks tend to be oil wet, we expected the clean sample to have a smaller contact angle for oil, while this angle was expected to be even smaller for the aged slice due to the effect of aging. To measure contact angle, Drop Shape Analyzer – DSA 100 model instrument of Krüss Company was used (Figure 4-14). This device is able to capture images of a slice whenever a droplet starts to descend from an injection syringe to the core and when the droplet is spreading on the core. By using the Krüss Drop Shape Analysis System Software after capturing images of droplets, contact angle is calculated for each picture and the results are plotted.

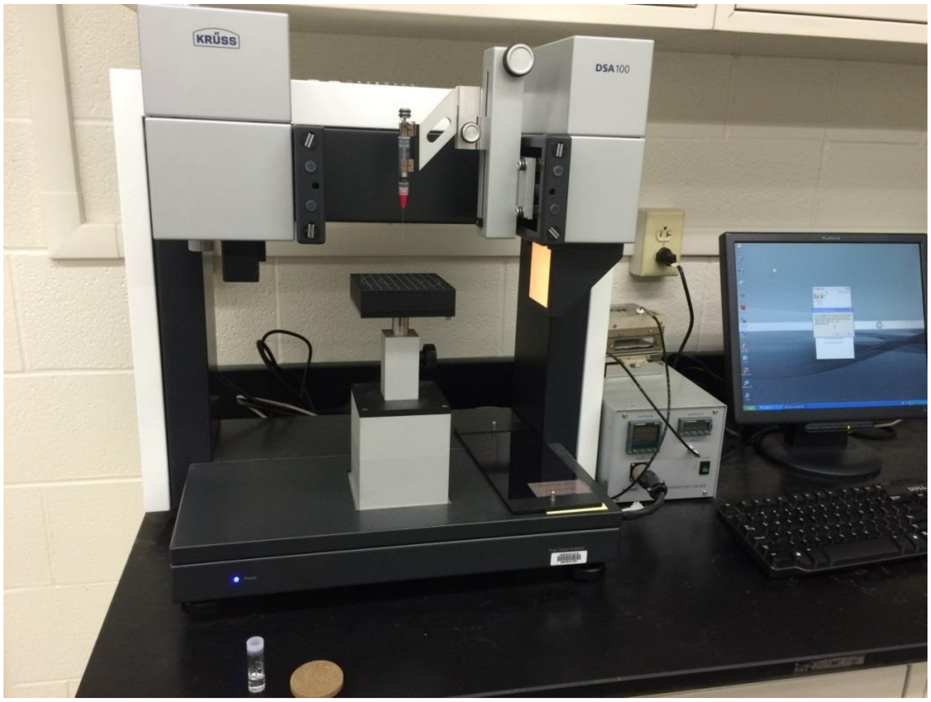

Figure 4-14: Drop Shape Analyzer – DSA 100

To further investigate the effect of aging in our case, recoveries from an aged rock sample (Core-1) and a natural rock (prior to aging) was also compared. It was important to perform the aging comparison before the increasing and decreasing injection water salinity experiments because the time and temperature to age the Core-2 and the Core-3 was determined by the results of aging comparison.

Chapter 5 : Results and Discussion

In this work, the purpose was to investigate the effect of changing injection water salinity of injected brine on oil recovery from carbonate rocks at low temperature. As aging is one of the most important parts in water flooding experiments to make carbonate rocks oil wet, effect of aging was also quantified before effect of changing salinity experiments. The methodology followed was to make sure that the pre-determined time and temperature was enough to make the aging process effective first and then to perform waterflooding experiments to analyze the effect of changing salinity of injected water.

Two core slices were used for contact angle measurements. They were cut from the homogeneous Indiana Limestone outcrop cores and one of them was aged for 12 days at 100 ºC in the oven in a container filled with oil. After 12 days, contact angle measurements were performed at room temperature by using Drop Shape Analyzer. It is very well known that wettability is the tendency of a rock sample to prefer one fluid in presence of another one. Therefore, if the aging process is successful, then there should be significant differences between contact angle measurements for synthetic oil used and distilled water droplets on core slices before and after aging.

The contact angle for water droplet on the pre-aged core slice was 50^0 while it was 71^0 on the post-aged core slice. The contact angle for oil droplet on the pre-aged core slice was 15^0 while it was measured as small as 10^0 on the post-aged core slice. The average error was 3% for the measurements. The measurements on pre-aged core slices show that Indiana limestone cores have tendency to be oil wet rather than water wet even without aging. Furthermore, the fact that the contact angle for water droplet increased significantly and the contact angle for the oil droplet decreased significantly is an indication that the core sample becomes more oil wet after aging. The changes in the contact angle values suggest that the wettability was changed toward oil-wet state during the aging. Figure 5-1 shows the images captured at the same time from the camera installed in Drop Shape Analyzer.

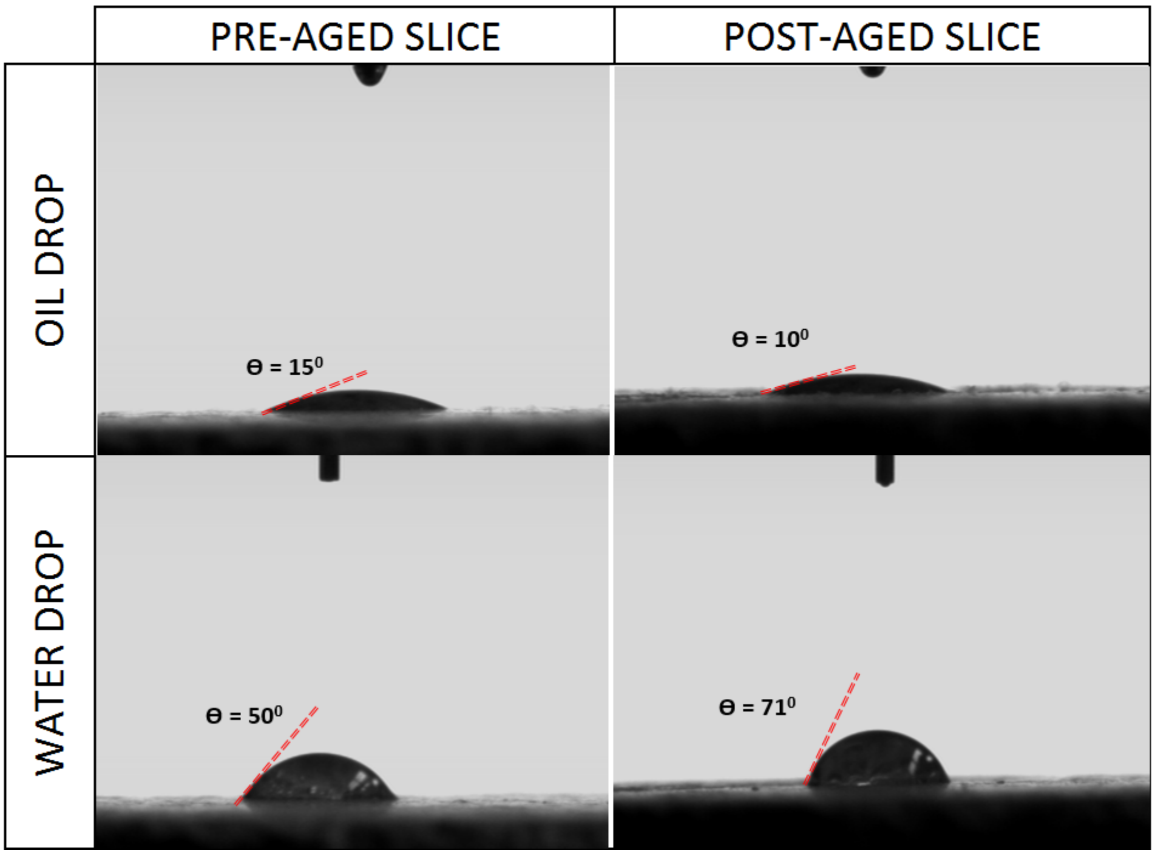

Figure 5-1: Oil and water drop images captured by the Drop Shape Analyzer during contact angle measurement on pre-aged and post-aged core slices.

Two water flooding experiments were performed in order to compare the recoveries of pre-aged and post-aged core samples through waterflooding. Distilled water was used as connate water for both Core-1 and Core-2. Core-1 was aged for 12 days at 100 ^oC in the oven and it was kept in the core holder in order to be completely isolated from the surroundings. Distilled water was injected in both waterflooding experiments. Confining pressure was kept constant at 100 psi and the injection rate was also kept constant at 1cc/min in order to prevent any possible effect due to rate change. Therefore, all the conditions were kept the same except that the Core-1 was post-aged core whereas Core-2 was pre-aged core.

Injecting 5 PV distilled water on Core-1 produced 30.5% OOIP and 0.6 PV distilled water was injected to make sure residual oil saturation was reached. The water breakthrough occurred after injecting only 0.1 PV distilled water. Core-2 on the other hand, produced most of the oil in the early stages of injection and the water breakthrough occurred later than it occurred in Core-1 (0.3 PV). After injecting 3 PV, oil production stopped and 1.6 PV more distilled water was injected to make sure residual oil saturation was reached. Total oil recovery was %43.2 in terms of OOIP and it was %12.7 more than the recovery from the post-aged rocks. The lower recovery in post-aged Core-1 is consistent with contact angle measurements. It associated with the fact that the core samples became more oil wet and its wettability changed significantly to cause such a high decrease in recovery. Figure 5-2 shows the oil recovery as a function of injected pore volume for both Core-1 and Core-2.

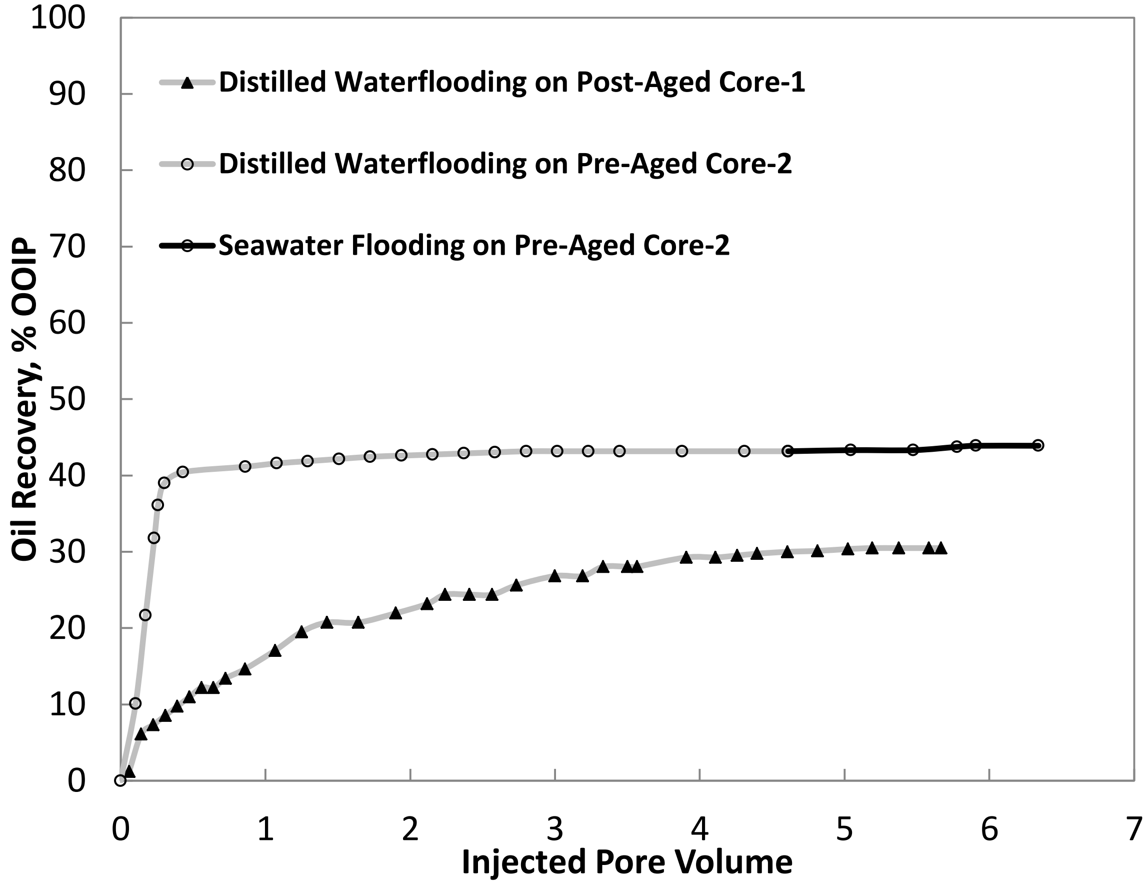

Figure 5-2: Oil Recoveries in terms of OOIP as a function of injected pore volume for Post- Aged Core-1 and Pre-Aged Core-2. After Sor is reached for Core-2, 1.7 PV sea water was injected in order to replace the connate water from distilled water to sea water.

As a result, both significant changes in contact angles of oil and water droplets on pre-aged and post-aged core slices and large difference in terms of oil recovery from pre-aged and post-ages cores clearly show that the aging process was successful in changing the wettability and making the rock more oil wet. For Core-2 and Core-3, the same temperature and same time, 100 ^{0}C and 12 days were used for aging.

Core-2 was flooded with 1.7 PV of sea water after the distilled water in order to replace the connate water. This was done to make sure that the connate water contains sea water as connate water, which is a more realistic scenario. During injection of sea water, additional pressure drop was observed as a result of injecting a more viscous fluid. The additional pressure drop was followed by an additional recovery of 0.7% OOIP. This was the first indication that increasing the salinity may somehow improve the oil recovery. It is appropriate to call this phenomenon as system disturbance. Figure 5-3 is the pressure differential across the core during distilled water and sea water flooding on pre-aged Core-2.

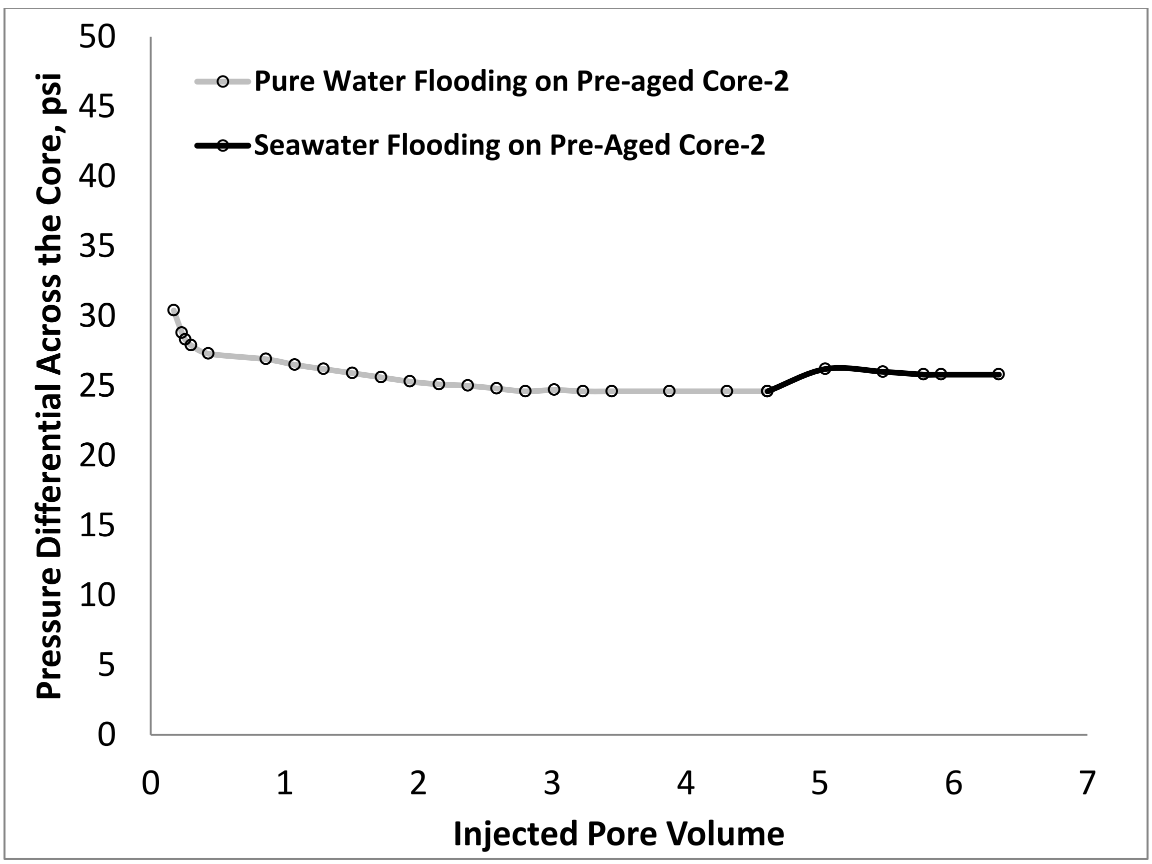

Figure 5-3: Pressure differential across the core during distilled water injection followed by sea water injection on pre-aged Core-2.

Two more water flooding experiments were performed in order to investigate the effect of increasing and decreasing water salinity on Indiana Limestone at room temperature. Pre-aged Core-2 was flooded with oil after connate water was replaced and it was kept in the oven for 12 days at 100 ºC. After aging process was complete, waterflooding experiments were performed by starting with distilled water followed by 50% sea water and sea water. Distilled water injection was able to produce 30.8% of OOIP. Injection of 50% sea water produced an additional 1.3% OOIP and then injection of sea water caused 0.6% additional recovery in OOIP. Figure 5-4 shows the oil recovery and oil cut vs pore volume injected.

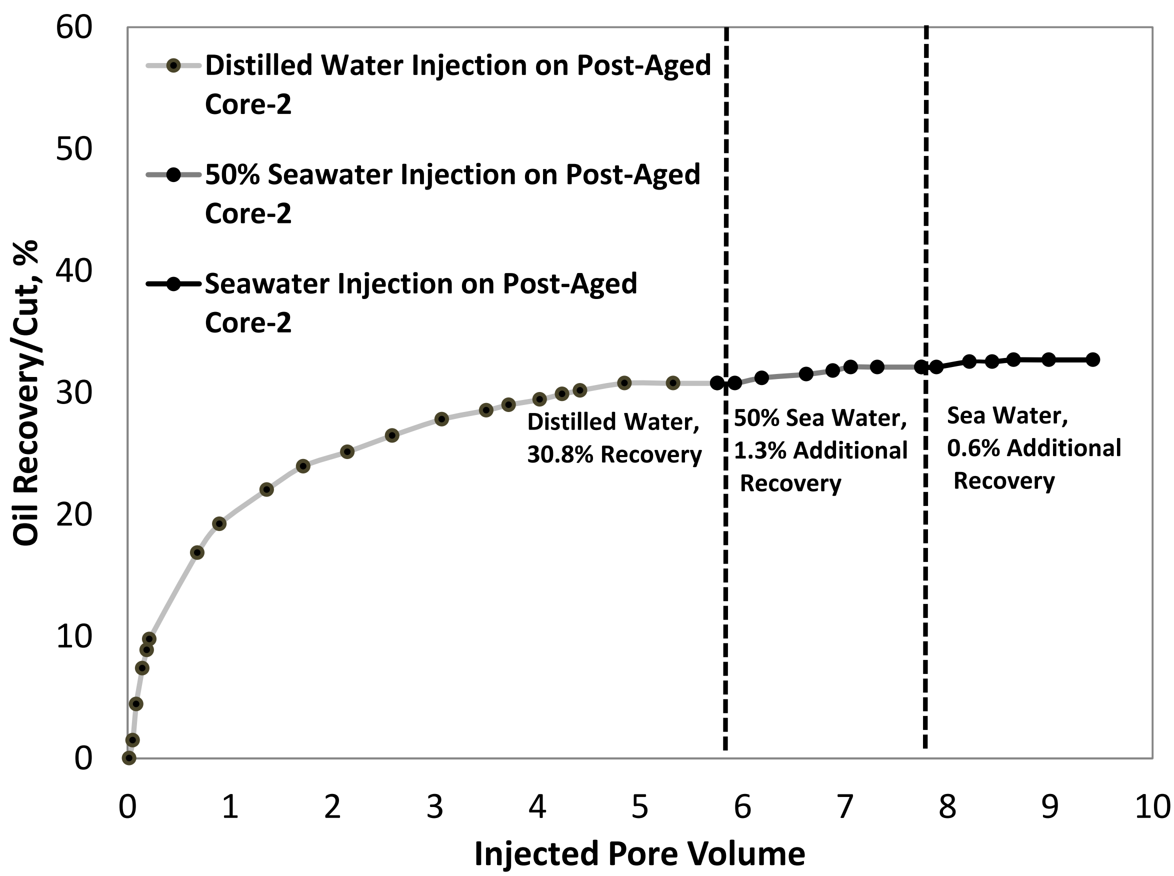

Figure 5-4: Oil Recovery and Oil Cut from the post-aged Core-2 vs pore volume injected. The injection started with distilled water followed by 50% sea water and sea water.

The results obtained in this work on Core-2 both pre-aged and post-aged cases are consistent that when the salinity of the injected brine was increased, it was accompanied by an additional pressure drop and production. Figure 5-5 is the pressure drop across the core for post-aged Core-2.

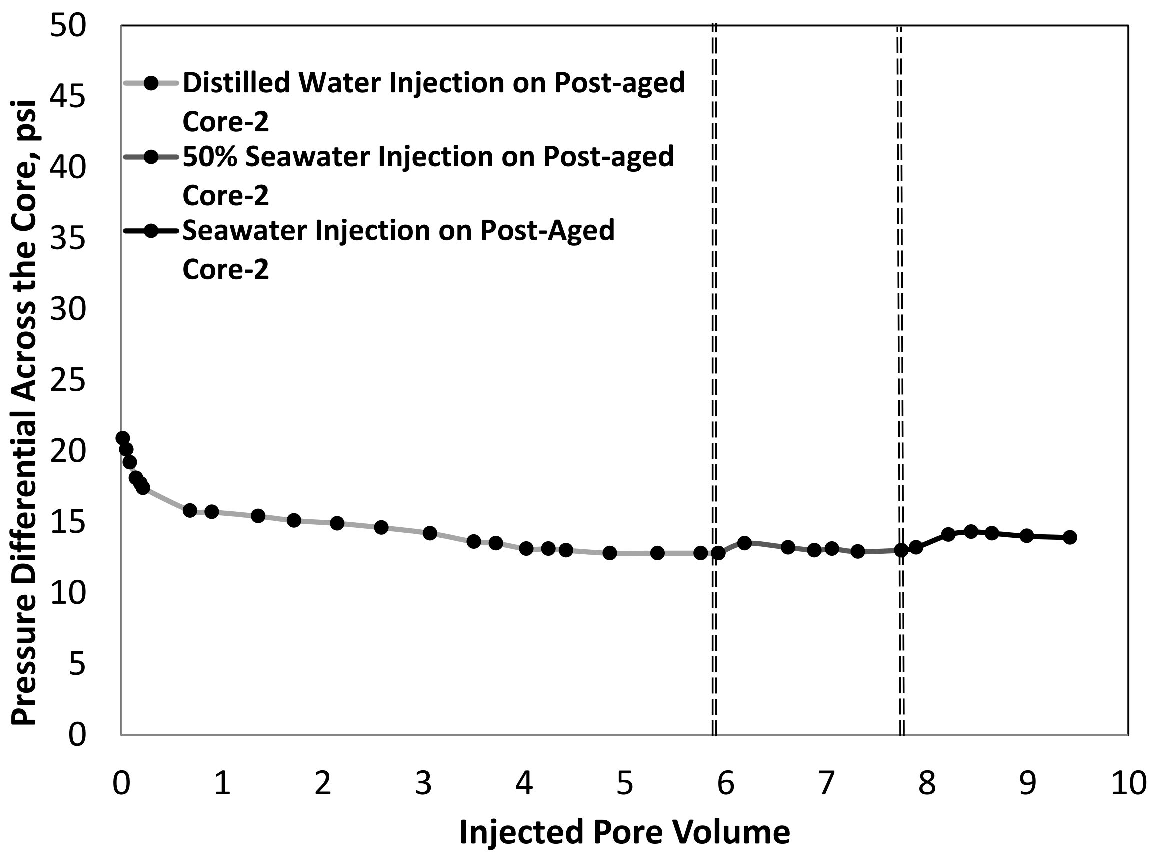

Figure 5-5: Pressure Differential across post-aged Core-2 vs pore volume injected. The injection started with distilled water followed by 50% sea water and sea water.

The very first idea of salinity effect was introduced by Bernard (1967) where he explained one possible mechanism as increased pressure drop due to swelling of clay minerals when fresh water was injected for Berea sandstone. Bernard (1967) also pointed out that dispersed clay particles by fresh water may plug some of the flow channels, directing the flow to the new channels to be flooded out. Besides, there was no additional recovery if no additional pressure drop was observed. Shehata et al. (2014) observed 4.5% additional recovery from Indiana Limestone when the injection water was changed to sea water in the tertiary mode from the distilled water in the secondary mode at 95 ^{0}C. They attributed this effect to electrostatic interactions caused by sudden change in the salinity of the injected brine, which would be expected to occur at high temperatures. Our results are also consistent with Shehata et al. (2014) where they observed a higher additional recovery at 95 ºC. However, this might be contradictory to what is known as low salinity effect, where additional recovery would be expected as a result of decreasing the salinity in the tertiary mode. The conventional point of view for the salinity effect is that lowering the injected water salinity at high temperatures would cause an additional recovery due to wettability changes through variety of different mechanisms. In this work, it was shown that system disturbance created by additional pressure drop when salinity of the injected brine increased also contributed to production.

Final experiments were conducted on post-aged Core-3. In this experiment, water injection started with sea water and then it was followed by 50% sea water and distilled water. Injection of 6.5 PV sea water produced 29.9% of OOIP. Injecting 2 PV 50% sea water caused 0.6% additional recovery and 2.2 PV distilled water injection resulted in 0.7% OOIP additional recovery. Therefore, decreasing the salinity in the tertiary mode was also accompanied by a measurable additional recovery. Figure 5-6 reveals the results of the final experiment in terms of oil recovery.

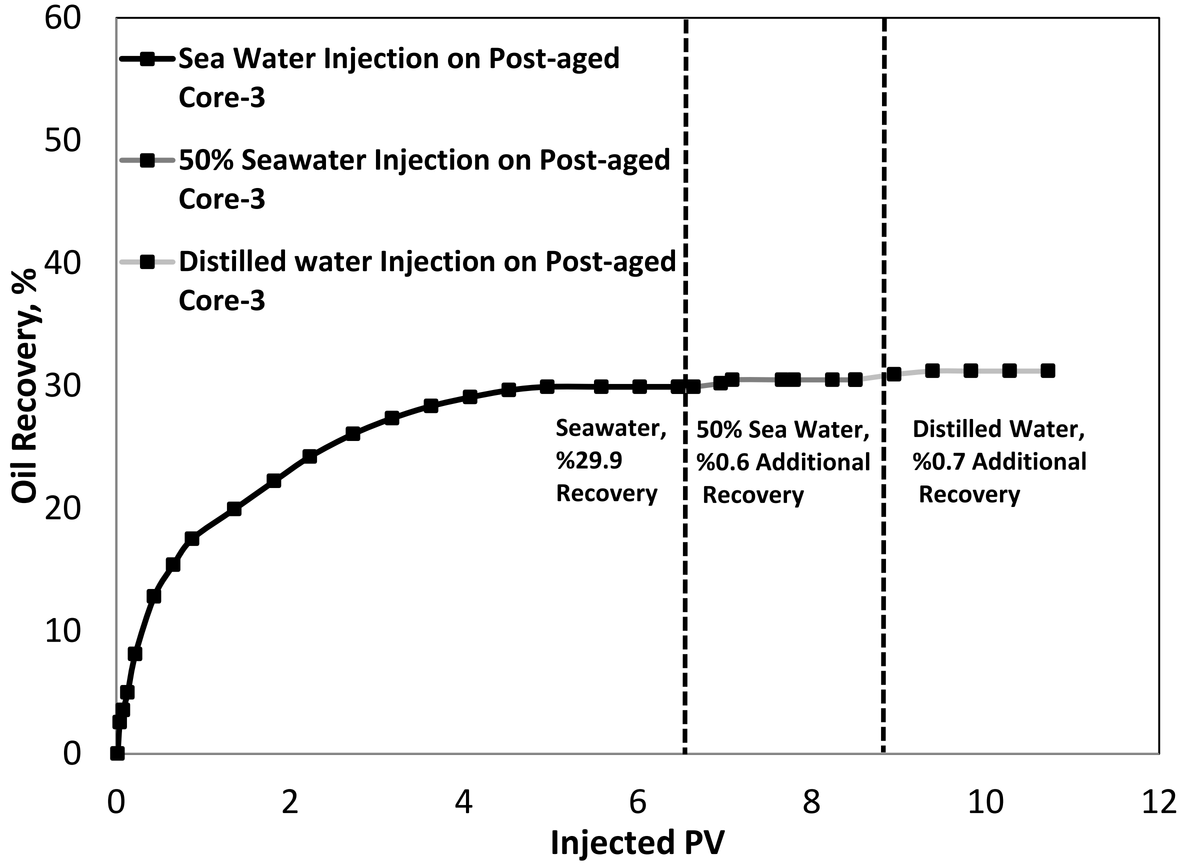

Figure 5-6: Oil Recovery and Oil Cut from the post-aged Core-3 vs pore volume Injected. The injection started with sea water followed by 50% sea water and distilled water.

Lowering the injection water salinity in two series resulted in decreasing the pressure drop as a result of increasing less viscous fluid (Figure 5-7). It was already documented that the wettability changing mechanisms such as double layer expansion, potential determining ions effect and ion exchange processes would be effective at high temperatures (Zhang, 2006; Theweyo et al., 2006; Gomari et al., 2006; Bennetzen, 2014). The XRD measurements also proved that Indiana limestone did not contain any clay content. Therefore, the measurable additional recovery is unlikely the result of wettability change. It might be possible that additional measureable recovery was also another result of system disturbance caused by the sudden pressure drop. Figure 5.7 is the pressure drop across post-aged Core-3.

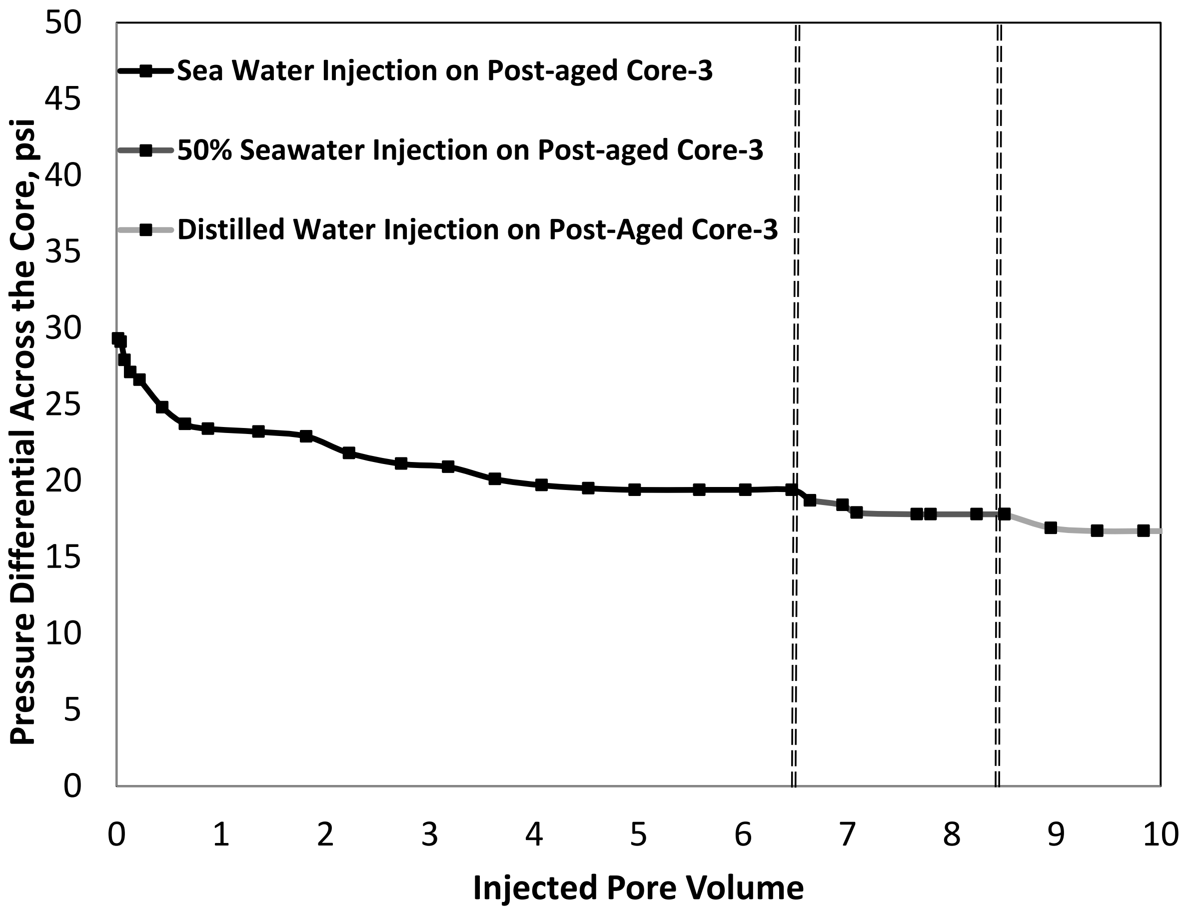

Figure 5-7: Pressure drop on post-aged Core-3 vs pore volume injected. The injection started with sea water followed by 50% sea water and distilled water.

As a result, some measurable additional recoveries were obtained as a result of increasing and decreasing the injected water salinity in tertiary mode. The results might be a supporting evidence for the illustrating the effect of system disturbance associated with changing pressure drop across the core and this is what was observed in this work. However, how system disturbance works is yet to be investigated. In case of increasing salinity of injected brine, one may argue that the additional recovery might be the result of slightly improved mobility ratio. However, this explanation will not be valid for decreasing injection water salinity where the pressure drop decreases as a result of injecting slight less viscous brine. Therefore, the way system disturbance works might be explained in two ways. The first is that the disturbance would have been created by sudden pressure changes in both cases and the distribution of oil and water phases might have been slightly changed causing some of the trapped oil to be mobile. The second option might be related to physical or chemical interactions between the salt content of the injected brine and the rock and oil. In order to have a better understanding of the phenomena, it might be better to perform more macro and micro model experiments, especially by scanning the core sample prior to, during and after injection sequences to see the oil and water distributions.

Chapter 6 : Conclusions

A series of core flood experiments were performed to investigate the effect of increasing and decreasing salinity floods on aged Indiana Limestone at room temperature. The effect of aging process was quantified by contact angle measurements and water flooding experiments on pre-aged and post-aged core slices and cores respectively prior to changing salinity experiments.

The main contribution of this work is the observation of relatively minor pressure disturbances with salinity change, which can affect the oil recovery curves to a larger extent than wettability alteration. This is especially noticeable in cases of low clay content and low temperature core floods, where wettability alteration effects are suppressed.

Increasing the salinity of the injected brine is associated with increase in pressure drop, which creates a system disturbance. This system disturbance may have caused additional recovery and this is consistent with Bernard (1967) and Shehata et al. (2014) findings. Likewise, decreasing the salinity of the injected brine also resulted in additional recovery where the wettability alteration was suppressed by no clay content and temperature conditions. Therefore, the system disturbance caused by sudden change in pressure drop may have also contributed to additional recovery. In the literature, the only mechanism that is responsible from additional recovery as a result of decreasing water salinity has been associated with wettability changes in the rock during injection process. It is important to note that there might be some additional recovery without changing the wettability but simply disturbing the system by changing the salinity of injected brine.

It should also be noted that additional recovery from carbonate rocks after S_{or} is reached may not be significant because of wetting nature of carbonate rocks. After S_{or} is reached, most of the oil remained in the core or the reservoir will most likely stay on the surface of the rocks. In order to recover more oil in such cases, changing wettability or causing a significant system disturbance might be needed. Even so, it is hard to predict how much additional recovery would be obtained because of the complex and heterogeneous nature of most carbonate rocks.

To conclude, the mechanisms under which the salinity of the injected brine affects oil recovery are still not well understood. In order to have a better understanding of how these mechanisms work and if these mechanisms would be responsible for additional recovery, more experiments should be performed for different oil-brine-rock combinations. If increasing water salinity which is also associated with increased pressure drop is proved to be successful in laboratory conditions, it might be useful to have some field trials as injecting higher salinity brine would cost less than purifying and injecting the low salinity brine. This way, it might be possible to both reduce the cost of the water flooding process and recover more oil when low salinity water injection reaches the residual oil saturation. It is also wise to keep in mind that injecting brine instead of fresh water may be also associated with corrosion problems depending on the concentration of brine and the equipment used. Therefore, careful planning is required before field trials.

Chapter 7 : Future Work and Recommendations

Our work can serve as a baseline for the future studies with a few recommendations to consider. During the aging process, we assumed that synthetic oil and crude oil would react to temperature in similar ways as there is not an exact differentiation between synthetic oil and crude oil in the literature. It might be true that the sensitivity of the crude oil to temperature might be higher because of the polar components they contain and temperature may not have the same impact for aging with synthetic oil. Therefore, it is recommended to age the core samples at different temperatures and measure the contact angles in order to compare the effect of temperature in case of synthetic oil. If temperature does not affect the aging process significantly, then there may not be a need to perform aging at a high temperature for synthetic oil.

Another suggestion is about the connate water replacement that we performed on Core-2. In our case, connate water content of post-aged Core-2 and post-aged Core-3 was not critical for the results as we did not compare the overall performances of Core-2 and Core-3. In cases where connate water salinity is critical, it is recommended to use another core instead of replacing the connate water as it may not be possible to replace the water content 100% (especially irreducible water saturation) and it may require a lot of extra time.

Our work can be extended to investigate how system disturbance may work through macro and micro scale experiments. Scanning the core sample before, during and after brine injections may help researches to see the fluid distributions or to make in depth measurements such as contact angle. There is still a lot to investigate how salinity of injected brine would improve the recovery in carbonate rocks considering the fact that there is not even a consistent mechanistic explanation for the most accepted mechanism, wettability change. Therefore, more experiments on carbonate rocks at different conditions should be performed.

References

Abdallah, W., J.S. Buckley, A. Carneige, J. Edwards, B. Herold, E. Fordham,, A. Graue, T. H., N. Seleznev, C. Signer, H. Hussain, B. Montaron, Ziauddin, M. 2007. Fundamentals of Wettability. Oilfield Review. www.SLB.com, Schlumberger.

Abhijit Y. Dandekar. (2010) Petroleum Reservoir Rock and Fluid Properties, Second Edition. Boca Raton, Florida, CRC Press. Page 143.

Al Harrasi, A., Al-maamari Rashid Salim, & Masalmeh, S. K. (2012, January 1). Laboratory Investigation of Low Salinity Waterflooding for Carbonate Reservoirs. Society of Petroleum Engineers. doi:10.2118/161468-MS

Al Shalabi, E. W., Sepehrnoori, K., & Delshad, M. (2013, April 19). Mechanisms Behind Low Salinity Water Flooding in Carbonate Reservoirs. Society of Petroleum Engineers. doi:10.2118/165339-MS

Al Shalabi, E., Delshad, M., & Sepehrnoori, K. (2013, September 16). Does the Double Layer Expansion Mechanism Contribute to the LSWI Effect on Hydrocarbon Recovery from Carbonate Rocks? Society of Petroleum Engineers. doi:10.2118/165974-MS

Al-adasani Ahmad, Bai, B., & Wu, Y.-S. (2012, January 1). Investigating Low Salinity Waterflooding Recovery Mechanisms in Carbonate Reservoirs. Society of Petroleum Engineers. doi:10.2118/155560-MS

Al-Aulaqi, T., Fisher, Q., Grattoni, C., & Al-Hinai, S. M. (2013, May 19). Wettability Alteration by Brine Salinity and Temperature in Reservoir Cores. Society of Petroleum Engineers. doi:10.2118/168652-MS

Al-Mahrooqi, S.H., Grattoni, C.A., Muggeridge A. H., Jing, X.D. (2005, August). Wettability Alteration During Aging: The Application of Nmr to Monitor Fluid Redistribution. Society of Core Analysts. Toronto, Canada.

Alotaibi, M. B., Azmy, R., & Nasr-El-Din, H. A. (2010, January 1). Wettability Challenges in Carbonate Reservoirs. Society of Petroleum Engineers. doi:10.2118/129972-MS

Arne Graue, Bjørn Gerry Viksund, Terje Eilertsen, Robert Moe, Systematic wettability alteration by aging sandstone and carbonate rock in crude oil, Journal of Petroleum Science and Engineering, Volume 24, Issues 2–4, December 1999, Pages 85-97, ISSN 0920-4105, http://dx.doi.org/10.1016/S0920-4105(99)00033-9.

Atkinson, M. J. and Bingman, C. (1996), Elemental Composition of Commercial Sea Salts. Journal of Aquariculture and Aquatic Sciences. Volume VIII, no 2. Pages 39-43.

Bennetzen, M. V., Mogensen, K., Frank, S., & Mohanty, K. (2014, January 19). Dilute Surfactant Flooding Studies in a Low-Permeability Oil-Wet Middle East Carbonate. International Petroleum Technology Conference. doi:10.2523/IPTC-17656-MS

Bernard, G. G. (1967, January 1). Effect of Floodwater Salinity on Recovery of Oil from Cores Containing Clays. Society of Petroleum Engineers. doi:10.2118/1725-MS

Chattopadhyay, S., Jain, V., & Sharma, M. M. (2002, January 1). Effect of Capillary Pressure, Salinity, and Aging on Wettability Alteration in Sandstones and Limestones. Society of Petroleum Engineers. doi:10.2118/75189-MS

Djebbar Tiab, Erle C. Donaldson. (2012) Petrophysics: Theory and Practice of Measuring Reservoir Rock and Fluid Transport Properties. Waltham, MA, Gulf Professional Publishing. Page 396

Fan, T., & Buckley, J. S. (2007, December 1). Acid Number Measurements Revisited. Society of Petroleum Engineers. doi:10.2118/99884-PA

Filoco, P. R., & Sharma, M. M. (1998, January 1). Effect of Brine Salinity and Crude Oil Properties on Relative Permeabilities and Residual Saturations. Society of Petroleum Engineers. doi:10.2118/49320-MS

Gupta, R., Adibhatla, B., & Mohanty, K. K. (2008, January 1). Parametric Study to Enhance Oil Recovery Rate from Fractured Oil Wet Carbonate Reservoirs. Society of Petroleum Engineers. doi:10.2118/116485-MS

Heidari, M. A., Habibi, A., Ayatollahi, S., Masihi, M., & Ashoorian, S. (2014, March 25). Effect of Time and Temperature on Crude Oil Aging to do a Right Surfactant Flooding with a New Approach. Offshore Technology Conference. doi:10.4043/24801-MS

Hirasaki, G. J., Rohan, J. A., Dubey, S. T., & Niko, H. (1990, January 1). Wettability Evaluation During Restored-State Core Analysis. Society of Petroleum Engineers. doi:10.2118/20506-MS

Hjelmeland, O. S., & Larrondo, L. E. (1986, July 1). Experimental Investigation of the Effects of Temperature, Pressure, and Crude Oil Composition on Interfacial Properties. Society of Petroleum Engineers. doi:10.2118/12124-PA

Hognesen, E. J., Strand, S., & Austad, T. (2005, January 1). Waterflooding of preferential oil-wet carbonates: Oil recovery related to reservoir temperature and brine composition. Society of Petroleum Engineers. doi:10.2118/94166-MS
http://pubs.usgs.gov/of/2001/of01-041/htmldocs/xrpd.htm

Jadhunandan, P. P., & Morrow, N. R. (1995, February 1). Effect of Wettability on Waterflood Recovery for Crude-Oil/Brine/Rock Systems. Society of Petroleum Engineers. doi:10.2118/22597-PA

Lager, A., Webb, K.J., Black, C.J.J. 2007. Impact of Brine Chemistry on Oil Recovery. Paper A24 presented at the 14th EAGE Symposium on Improved Oil Recovery, Cairo, 22

Mahani, H., Keya, A. L., Berg, S., Bartels, W.-B., Nasralla, R., & Rossen, W. (2015, June 1). Driving Mechanism of Low Salinity Flooding in Carbonate Rocks. Society of Petroleum Engineers. doi:10.2118/174300-MS

Morrow, N., & Buckley, J. (2011, May 1). Improved Oil Recovery by Low-Salinity Waterflooding. Society of Petroleum Engineers. doi:10.2118/129421-JPT

Nasralla, R. A., Sergienko, E., Masalmeh, S. K., van der Linde, H. A., Brussee, N. J., Mahani, H., … Alqarshubi, I. (2014, November 10). Demonstrating the Potential of Low-Salinity Waterflood to Improve Oil Recovery in Carbonate Reservoirs by Qualitative Coreflood. Society of Petroleum Engineers. doi:10.2118/172010-MS

P. Zhang, M. T. Tweheyo, and T. Austad, “Wettability alteration and improved oil recovery in chalk: the effect of calcium in the presence of sulfate,” Energy and Fuels, vol. 20, no. 5, pp. 2056–2062, 2006.

Peters, E.J. (2012), Advanced Petrophysics, Volume 1, Austin, TX, LiveOak Book Company, Chapter 1.

Quan, X., Shunli, H., Wanfeng, Pu. (2010). The Effects of temperature and acid number of crude oil on the wettability of acid volcanic reservoir rock from the Hailar Oilfield. China University of Petroleum (Beijing) and Springer-Verlag Berlin Heidelberg

Rezaei Gomari, K. A., Karoussi, O., & Hamouda, A. A. (2006, January 1). Mechanistic Study of Interaction between Water and Carbonate Rocks for Enhancing Oil Recovery. Society of Petroleum Engineers. doi:10.2118/99628-MS

S. Bagci, M. V. Kok, and U. Turksoy, “Effect of brine composition on oil recovery by waterflooding,” Petroleum Science and Technology, vol. 19, no. 3-4, pp. 359–372, 2001.

Saner, S. et al. 1991. Wettability Study of Saudi Arabian Carbonate Reservoir Core Samples. The Arabian Journal for Science & Engineering 16(3): 357-371.

Schlumberger, (2015), Services & Products, Technical Challenges, Carbonate Reservoirs, http://www.slb.com/services/technical_challenges/carbonates.aspx

Shaikh, M., & Sharifi, M. (2013, September 16). Investigation of Optimum Salinity of Injected Water in Carbonate Reservoirs using Wettability Measurement and Core Flooding. Society of Petroleum Engineers. doi:10.2118/165992-MS

Shehata, A. M., Alotaibi, M. B., & Nasr-El-Din, H. A. (2014, August 1). Waterflooding in Carbonate Reservoirs: Does the Salinity Matter? Society of Petroleum Engineers. doi:10.2118/170254-PA

Tang, G. Q., & Morrow, N. R. (1997, November 1). Salinity, Temperature, Oil Composition, and Oil Recovery by Waterflooding. Society of Petroleum Engineers. doi:10.2118/36680-PA

Treiber, L. E., & Owens, W. W. (1972, December 1). A Laboratory Evaluation of the Wettability of Fifty Oil-Producing Reservoirs. Society of Petroleum Engineers. doi:10.2118/3526-PA

Tweheyo, M. T., Zhang, P., & Austad, T. (2006, January 1). The Effects of Temperature and Potential Determining Ions Present in Seawater on Oil Recovery From Fractured Carbonates. Society of Petroleum Engineers. doi:10.2118/99438-MS

Wang, W., & Gupta, A. (1995, January 1). Investigation of the Effect of Temperature and Pressure on Wettability Using Modified Pendant Drop Method. Society of Petroleum Engineers. doi:10.2118/30544-MS

Wonderling, N.M. (2015, June). “Basics of X-Ray Diffraction”. Pennsylvania State University. Materials Characterization Lab. X-Ray Diffraction Facility.

Xie, X., Weiss, W. W., Tong, Z. J., & Morrow, N. R. (2005, September 1). Improved Oil Recovery from Carbonate Reservoirs by Chemical Stimulation. Society of Petroleum Engineers. doi:10.2118/89424-PA

Yousef, A. A., Al-Saleh, S., & Al-Jawfi, M. S. (2011, January 1). Smart WaterFlooding for Carbonate Reservoirs: Salinity and Role of Ions. Society of Petroleum Engineers. doi:10.2118/141082-MS

Yousef, A. A., Liu, J. S., Blanchard, G. W., Al-Saleh, S., Al-Zahrani, T., Al-zahrani Rashad Madees, … Al-mulhim Nayef. (2012, January 1). Smart Waterflooding: Industry. Society of Petroleum Engineers. doi:10.2118/159526-MS

Yousef, A., Al-Saleh, S., Al-Jawfi, M.S. (2012). The Impact of the Injection Water Chemistry on Oil Recovery from Carbonate Reservoirs. Presented at the SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman, 16-18 April. SPE-141082-MS. http://dx.doi.org/10.2118/154077-MS.

Zhang, P., & Austad, T. (2005, January 1). The Relative Effects of Acid Number and Temperature on Chalk Wettability. Society of Petroleum Engineers. doi:10.2118/92999-MS

Zhou, X., Torsaeter, O., Xie, X., & Morrow, N. R. (1995, December 1). The Effect of Crude-Oil Aging Time and Temperature on the Rate of Water Imbibition and Long-Term Recovery by Imbibition. Society of Petroleum Engineers. doi:10.2118/26674-PA